



Run-off analyses using isotopes and hydrochemistry in Yushugou River basin, eastern Tianshan Mountains

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Yushugou River basin of East Tianshan Mountains receives water from melting glaciers. In recent years, the glaciers retreated strongly due to global warming which intensified the water cycle in the river basin. For this reason, the relation of water bodies based on hydrochemistry and isotope in the summer flood was carried out. Hydrochemistry research showed that there was frequent hydraulic interaction between river water and groundwater. Studying the isotopes and Cl^- of river water, glacier meltwater, groundwater and precipitation, indicated that Yushugou River was recharged by the glacier meltwater, groundwater and precipitation during the summer flood period. The analysis result based on the three-component mixing model showed that Yushugou River was recharged by 54.9% of glacier meltwater, 37.6% of the run-off came from groundwater, while less than 8% was contributed by precipitation. The study suggests that the role of glacier meltwater and groundwater, especially glacier meltwater, should be specially concerned in water resource protection and reasonable utilization, and the injection of glacier meltwater is the main reason for run-off variation in this alpine basin during the summer flood period.

Keywords. Stable isotopes; run-off composition; hydrograph separation; Yushugou River basin.

1. Introduction

Water resource is the important material, base of human survival and development, especially in the arid inland areas. Located in the Eurasian hinterland, northwest China, arid areas are far away from the water supply source, with less average annual rainfall and more intense evaporation. Mountain glaciers are considered as natural reservoirs of solid water. The impact of climate change on run-off process has aroused great attention in global change studies. In the process of run-off response to climate change, the response of snow run-off is the most sensitive (Watson *et al.* 1995;

Chen *et al.* 2012). Affected by global warming, glaciers retreat in western China and water cycle reinforce in alpine region will further aggravate ecological environment deterioration in arid areas.

The chemical composition in natural water is a representative research part in regional and global ecological environment problem research (Stallard and Edmond 1983; Gaillardet *et al.* 1999). The chemicals (Ca^{2+} , Na^+ , Mg^{2+} , K^+ , HCO_3^- , SO_4^{2-} , Cl^- and NO_3^-) in surface water and groundwater are mainly controlled by the rock, climate, soil, precipitation, and human activities of the study area (Berner and Berner 1987; Roy *et al.* 1999). The small watershed located in the alpine region

is rarely affected by man-made factors directly (Zhang and Dong 1990). As a result, the main ion in water body can basically reveal the hydrogeological conditions of the region.

The isotope tracer method has been widely used in tracing water formation, circulation and transformation process (Kendall and McDonnell 1998; Kattan 2008; Sun *et al.* 2016). Due to different hydrogen and oxygen isotopic composition in different water sources, it can be used to research the source of the water. One of the more valuable tools for investigating hydrological processes is isotopic stream hydrograph separation using oxygen-18 (^{18}O). Isotopic and geochemical tracers can offer powerful information and data which can study the origin of stream flow components and run-off processes. Also, it can help identify hydrological source areas or flow paths under different flow conditions (Dmitry *et al.* 2007; Stump *et al.* 2009; Catherine *et al.* 2010). In alpine catchment, there are glacier and snow cover, so the recharge sources of river water are precipitation, ice-snow melting water and groundwater in these areas (Kong and Pang 2010; Zhou *et al.* 2015). Over the past century, especially over the past 20~30 years, the climate system of the earth is experiencing warming which is the main characteristic of the significant changes (Qin 2008). Temperature rise will inevitably lead to increased amount of snow and ice melting, and then result in the increase of the alpine mountain watershed run-off. Hydrograph separation is used to research different water source and its composition ratio (Cooper *et al.* 1991; Qu *et al.* 2006; Liu *et al.* 2008; Yang *et al.* 2012; Michael *et al.* 2016).

The Yushugou River is one of the important water sources for industrial and agricultural production and city life. Due to the effect of arid and semi-arid climate, water resource shortage has become a serious restriction factor for the sustainable development of the region. Affected by global warming, glaciers in high-mountain in Yushugou River basin have been generally shrunk, an intense retreat since the 1980s (Ruozihan and Luo 2013). The decline of glacier area will lead to some changes, such as regional hydrological processes and river water balance, which have a significant impact on regional water resources and ecological environment. From May to September, the high temperature in the basin, intensely melting glaciers, and increasing precipitation, make the volume of run-off increase largely which accounts for

87.7% of the annual run-off (Luo *et al.* 2002). Many studies have reported the precipitation, moisture source, run-off, and floods in this area (Luo *et al.* 2002; Ma and Luo 2009; Zhang and Liu 2011; Wang *et al.* 2014, 2015a, b). But, considering the reasonable development and utilization of water resources, the achieved results do not provide a comprehensive data support for the reasonable development and utilization of water resources. Therefore, it is necessary to deeply research water resources in Yushugou River basin and quantitatively assess the glacier contribution to the regional water resources.

In order to research the recharge sources of river water in summer flood period, we sampled river water, groundwater, glacier meltwater and precipitation, and measured the stable isotope and chemical composition of water bodies. In this paper, it aims to: (1) determine the evolution process of the water bodies by hydrogeochemical research; and (2) quantitatively estimate influence and contribution of the high altitude snow and ice resources to water resources in this area. Also, it not only has practical significance for sustainable utilization of the basin water resources and ecological environment construction, but also has reference and guiding significance for other similar basins in the northwest region to carry out the research.

2. Study area

Yushugou River basin is located in Eastern Tianshan Mountains in China, with longitudes $93^{\circ}57'\sim 94^{\circ}19'E$ and latitudes $43^{\circ}02'\sim 43^{\circ}11'N$ (Luo *et al.* 2002). The maximum altitude of the basin is 4886 m, and altitude of mountain-pass is 1300 m (Ma and Luo 2009). 15 km above the mountain-pass of the river basin, there is Yushugou Hydrological Station (altitude 1670 m, $93^{\circ}57'E$, $43^{\circ}05'N$) which is the only hydrologic monitor station (Zhang and Liu 2011). River length above the monitor station is 34 km, with 308 km² catchment area and 3091 m mean height. Above altitude 4050 m of the basin is permanent snow cover and modern glaciation area (Ma and Luo 2009; Zhang and Liu 2011). There are nine glaciers. Glacier terminus altitude is between 4360 and 3500 m. The total area and ice volume is about 22.85 km² (four glaciers area > 4.0 km²) and 1.59 km³, respectively. Two glacier lakes are at the ice tongue bottom which is with area of about 1.01 km² (Luo *et al.*

2002). The geological structure in Yushugou River basin is mainly constituted by variscan granite and limestone, while soil is composed by alpine and subalpine meadow, chestnut soil and limestone weathering soil (Luo *et al.* 2002). Overall, the study area is mostly bare mountain. Due to the influence of cold and wind, the mountain denudation and wind erosion is very obvious. The fountains densely cover the area. Fissure water and pore water gave priority to groundwater in the study area. The hydraulic relationship between shallow groundwater and river water is very close (Wang *et al.* 2015a).

The water vapour source of atmosphere precipitation in the study area is mainly from the Atlantic air flow brought by west wind circulation. The more dry Arctic Ocean air flow also affects this area, but the water vapour content is very low. In addition, the area is far away from the ocean and belongs to the mountain arid climate. Therefore, insufficient water vapour condition, hot summer and cold winter, and more windy than rainy are the main climate characteristics of the region. According to the hydrologic data of Yushugou Hydrological Station, over the years, the annual average temperature has been 5.9°C, and the extreme high temperature and extreme low temperature is 34.2°C and -25.8°C, respectively (Zhang and Liu 2011). In the summer half year, the precipitation is mainly controlled by west wind circulation. The precipitation mainly concentrates between May and September, accounting for 79.6% of annual precipitation. The years of average precipitation is 149 mm. The average annual run-off observed from Yushugou Hydrological Station is $5.2 \times 10^4 \text{ km}^3$ (Luo *et al.* 2002).

3. Sampling and measurement

In this paper, all the water samples including glacier meltwater, groundwater, precipitation, and river water were collected in the river basin from July to August in 2013 (the northern hemisphere's summer). The sampling sites are displayed in figure 1. According to the hydrological characteristics of the basin, detailed sampling is as follows:

Forty samples of river water were collected at the Yushugou Hydrological Station from July 29 to August 5 and from August 23 to August 27.

Two glacier meltwater samples were collected at the tongue of glacier in headwater region.

Groundwater: Six groundwater samples were collected from a spring near the Yushugou Hydrological Station.

Precipitation samples: In Yushugou Hydrometric Station, 13 precipitation samples were collected.

The samples were measured in Tianshan Glaciological Station, Cold and Arid Regions Environment and Engineering Research Institute, Chinese Academy of Sciences. The $\delta^{18}\text{O}$ and δD data were determined by liquid hydrogen and oxygen stable isotope analyzer (LGR DLT-100 LWIA). The isotope international standard sample is Vienna Standard Mean Ocean (V-SMOW) (Craig 1961). The measurement error was $\pm 0.5\text{‰}$ and $\pm 0.2\text{‰}$ for δD and $\delta^{18}\text{O}$, respectively. Electrical ductivity (EC), pH and total dissolved solids (TDS) were measured in the field. Cations are analyzed by a Dionex-320 Ion Chromatograph and anions with ICS-1500 Ion Chromatograph. Results are shown in table 1. By experimental conditions, the concentrations of HCO_3^- - CO_3^{2-} were not determined directly but were calculated from ion balances

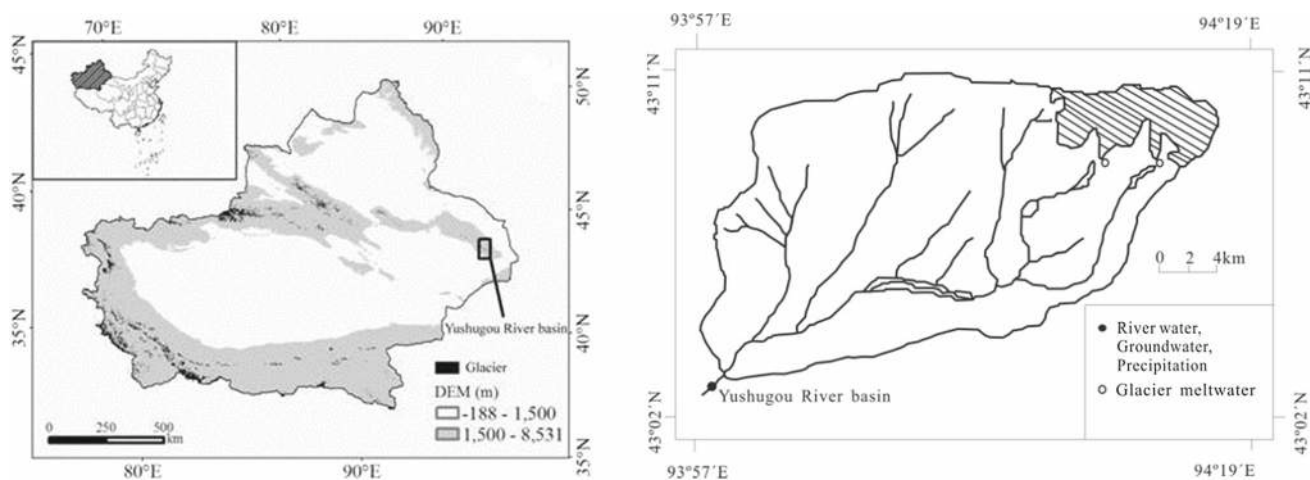


Figure 1. Location of Yushugou River basin and sampling sites.

Table 1. Values of pH, EC ($\mu\text{S} \cdot \text{cm}^{-1}$), TDS ($\text{mg} \cdot \text{L}^{-1}$), inorganic ions ($\text{mg} \cdot \text{L}^{-1}$) and isotopic composition (‰) of different water types in the study area.

Samples	River water			Ground water			Glacier-melt water			Precipitation		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean
pH	7.2	8.55	7.66	7.43	8.06	7.82	7.3	7.33	7.17	5.97	7.59	6.76
EC	74.8	140.2	106.74	187.7	237	206.12	46.9	60.6	53.75	5.46	239	73.86
TDS	35.9	67.2	51.4	90.1	114	99	22.5	29	25.75	2.62	115	35.47
Ca ²⁺	8.93	21.23	14.74	27.57	34.49	31.98	5.76	7.46	6.61	0.53	7.4	2.46
Mg ²⁺	1.46	3.27	2.34	4.31	4.68	4.53	0.63	0.99	0.81	0.01	1.12	0.28
Na ⁺	2.06	5.38	3.42	9.52	11.12	10.27	1.44	1.82	1.63	0.02	17.53	1.68
K ⁺	0.51	0.87	0.67	0.84	0.9	0.86	0.68	0.74	0.71	0.11	6.91	0.77
SO ₄ ²⁻	3.86	9.2	6.41	12.11	14.26	12.89	2.78	4.02	3.4	0.27	14.72	3.78
NO ₃ ⁻	0.8	2.03	1.37	0.2	0.77	0.48	1.62	2.19	1.9	0.16	8.15	1.92
Cl ⁻	1.42	3.6	2.26	3.18	3.94	3.63	1.08	1.45	1.26	0.21	19.09	2.71
HCO ₃ ⁻	34.18	77.78	53.60	123.88	134.22	126.06	18.66	24.01	21.33	-	-	-
$\delta^{18}\text{O}$	-12.38	-10.7	-11.67	-11.98	-11.6	-11.78	-12.54	-12.14	-12.34	-12.32	0.52	-6.23
δD	-79.14	-70.59	-74.77	-79.47	-75.8	-77.36	-83.43	-77.23	-80.33	-82.88	1.84	-41.21

(Mitamura *et al.* 2003; Murakami *et al.* 2007). In weak acid environment, CO_3^{2-} can be basically ignored (Hopkinson and English 2001; Liu *et al.* 2004). Laboratory tests found that organic acid content was very low. It was sure that HCO_3^- was balanced by the excess cation.

The meteorological data and hydrological data were measured when the samples collected.

4. Data analysis

The Gibbs diagram, Piper trilinear nomograph, and molar ratios among main ions can be used to determine the ion source and distinguish the water-rock intersections (Gibbs 1970; Xu *et al.* 2010).

In hydrological process, physical properties of hydrogen and oxygen isotope are affected by the change of the evaporation and condensation. Hydrogen and oxygen isotope characteristics of different water bodies are markedly different, and the influence of different water mixture is not obvious. Therefore, hydrogen and oxygen isotope can be used to trace components of the run-off. Due to the relatively stable and lack of input sources in the subsurface environment, Cl^- is frequently used as a tracer along generate flow paths. Because of the conservative characteristic, Cl^- can also be used to assist ^{18}O for hydrograph separation. So, in this paper, we select Cl^- and ^{18}O as complementary tracer to carry out hydrograph separation analysis. And a three-component mixing model was used to calculate the contribution rate of different water sources for river water. The three-component hydrograph separation method expression is described below (Ogunkoya and Jenkins 1993; Jenkins *et al.* 1994);

$$Q_t = Q_p + Q_s + Q_g, \quad (1)$$

$$\delta_t Q_t = \delta_p Q_p + \delta_s Q_s + \delta_g Q_g, \quad (2)$$

$$C_t Q_t = C_p Q_p + C_s Q_s + C_g Q_g, \quad (3)$$

where Q_t is total river run-off discharge; Q_p , Q_s , Q_g are the discharge of components p , s , g ; C_t , C_p , C_s , C_g are the respective concentrations of Cl^- for t , p , s , g ; δ_t , δ_p , δ_s , δ_g are the respective concentrations of ^{18}O for t , p , s , g ; and t , p , s , g refer to the three components (precipitation, groundwater, and glacier meltwater).

Equations (1–3) can be solved for the mixing fractions in terms of the eight measured tracer concentrations:

$$f_p = \frac{\delta_t C_s - \delta_t C_g + \delta_s C_g - \delta_s C_t + \delta_g C_t - \delta_g C_s}{\delta_p C_s - \delta_p C_g + \delta_s C_g - \delta_s C_p + \delta_g C_p - \delta_g C_s} \quad (4)$$

$$f_s = \frac{\delta_t C_g - \delta_t C_p + \delta_p C_t - \delta_p C_g + \delta_g C_p - \delta_g C_t}{\delta_p C_s - \delta_p C_g + \delta_s C_g - \delta_s C_p + \delta_g C_p - \delta_g C_s} \quad (5)$$

$$f_g = \frac{\delta_t C_p - \delta_t C_s + \delta_p C_s - \delta_p C_t + \delta_s C_t - \delta_s C_p}{\delta_p C_s - \delta_p C_g + \delta_s C_g - \delta_s C_p + \delta_g C_p - \delta_g C_s} \quad (6)$$

The application of these equations is based on the following assumptions (Sklash and Farvolden 1979; Butte 2006; Zhang *et al.* 2009):

- Groundwater is the same as the base flow, and isotopic composition is constant;
- Precipitation isotope is spatial-temporal uniform, or the change can be characterized;
- There is a large difference between rainfall and run-off isotope compositions;
- Contribution from soil water to the run-off can be ignored, or soil water isotopic composition is the same as groundwater;
- The surface water volume contribution to hydrograph can be ignored.

The uncertainty associated with the calculated mixing fractions was evaluated using the technique described by Genereux (1998):

$$W_f = \sqrt{\left(\frac{\partial f}{\partial x_1} W_{x_1}\right)^2 + \left(\frac{\partial f}{\partial x_2} W_{x_2}\right)^2 + \dots + \left(\frac{\partial f}{\partial x_n} W_{x_n}\right)^2} \quad (7)$$

where W is the uncertainty, x is the tracer concentration, and f is the mixing fraction.

In order to reduce errors for hydrograph separation, volume weighted average value (VWA) was used to calculate the isotopic value for precipitation, and glacier meltwater (Laudon *et al.* 2002). For example, when we take ^{18}O , the expression becomes:

$$\delta^{18}\text{O}_e = \frac{\sum_{i=1}^N M_i \delta^{18}\text{O}_{m,i}}{\sum_{i=1}^N M_i} \quad (8)$$

where $\delta^{18}\text{O}_e$ and $\delta^{18}\text{O}_{m,i}$ represent per mil deviation values of the calculative and actual measure, respectively. M_i is the rain volume during the sampling time. N in equation (8) refers to the number of samples.

5. Results and discussion

5.1 Characteristics of hydrogeochemistry

5.1.1 Chemical composition

As shown in table 1, there was no significant difference for pH among river water, groundwater, and glacier meltwater. The pH value of the water bodies was alkaline (<8.0). The EC value order was groundwater ($206.12 \mu\text{S}\cdot\text{cm}^{-1}$) $>$ river water ($106.74 \mu\text{S}\cdot\text{cm}^{-1}$) $>$ glacier meltwater ($53.75 \mu\text{S}\cdot\text{cm}^{-1}$). There were same results with TDS and the ion concentration. The TDS values of river water and groundwater were all below $500 \text{ mg}\cdot\text{L}^{-1}$, which belong to the weak water salinity. This agrees with the result of Cai (2012) that interannual variability of salinity was from 141 to $209 \text{ mg}\cdot\text{L}^{-1}$. Due to the close relationship between evolution of groundwater solute component and groundwater flow paths and water-rock interaction (the latter two have great relation to residence time of groundwater) (Edmunds 2009; Yang *et al.* 2009). Therefore, low salinity of groundwater characteristics is considered to be strong evidence which only participate in underground shallow circulation and residence time is short.

Table 1 shows the geochemical ions analyses of surface and ground waters in this study. The result confirmed that groundwater had the highest ionic compositions among all water types. In ground water, the concentration of Ca^{2+} ($31.98 \text{ mg}\cdot\text{L}^{-1}$) was the dominant, which accounted for 67.07% of cations, followed by Na^+ , Mg^{2+} and K^+ . The concentration of HCO_3^- ($126.06 \text{ mg}\cdot\text{L}^{-1}$) accounted for 88.12% far more than others. Comparing groundwater with river water samples, though the ion concentration of river water was lower than that of groundwater, the cations in the samples (river and spring) were in a same order of $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, while the order of anions is $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. It indicated that there was rapid transfer and frequent intersection between groundwater and river water. The maximum value of NO_3^- in groundwater and river water were 0.77 and $2.03 \text{ mg}\cdot\text{L}^{-1}$, which suggested that water quality of water supply area was rarely affected by human activities (such as agricultural production) and its water chemical characteristics basically reflects the hydrogeological conditions of the area. Moreover, it also has a great relation with the position of sample point located in the mountains. The hydrochemical type of groundwater and river water

was HCO_3^- - Ca^{2+} which contributed nearly 85% to the total ionic concentration. The value of TDS, EC and ionic concentration were higher than that of river water in the same period. It illustrated that groundwater experienced more intense water-rock action in the process of the flow.

5.1.2 Ionic sources

The concentration ratios of $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ of groundwater and river water samples in this research were plotted in Gibbs figure (figure 2), to evaluate the relative importance of each source. The $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio is lower than 0.5 concentrated in the range of about 0.2. All

samples were located in the water-rock dominant field, suggesting that the major process controlling the river water and groundwater ionic composition was rock weathering.

In order to further study the influence of rock weathering on the main ionic composition in waters, the triangular diagrams of anions and cations were employed to determine the rock weathering type (figure 3). The samples fell near the HCO_3^- field and in the Ca^{2+} field, indicating that the chemical composition was mainly controlled by carbonate rock weathering. The geological structure in Yushugou River basin is mainly constituted by variscan granite and limestone, while soil is composed by alpine and subalpine

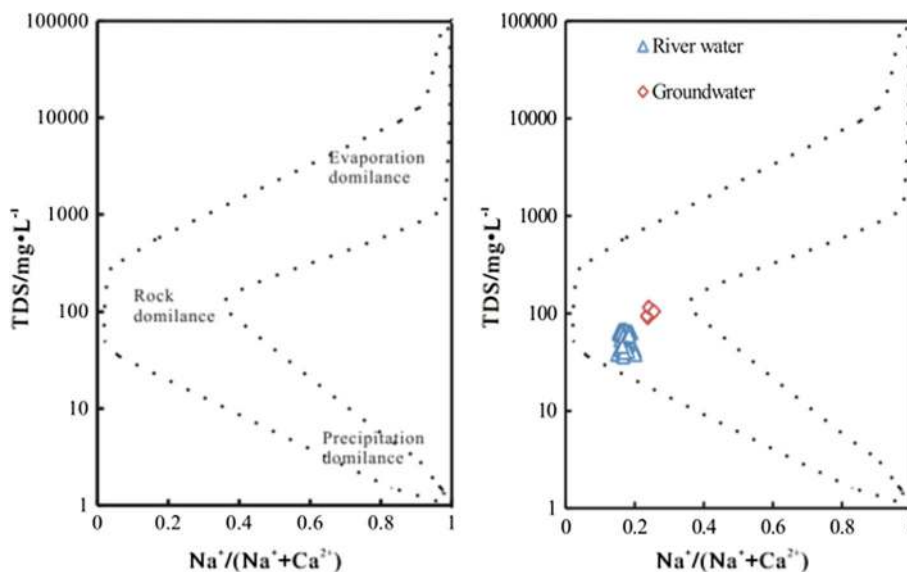


Figure 2. Gibbs-type TDS vs. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ diagram.

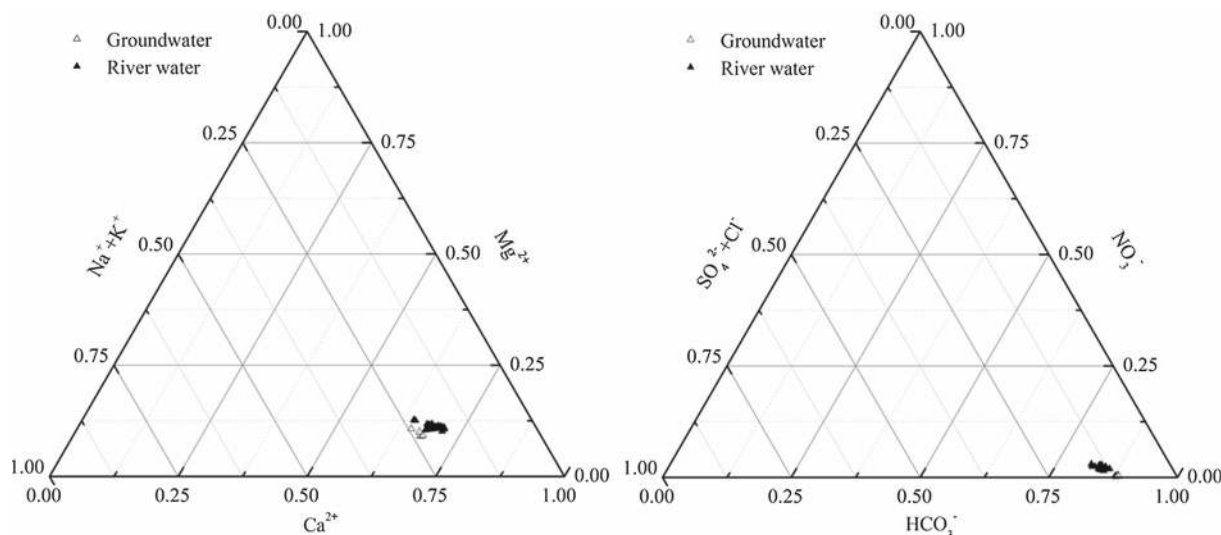


Figure 3. The piper trilinear nomograph for cations and anions of river water and groundwater.

meadow and chestnut soil and limestone weathering soil (Luo *et al.* 2002). Calcium carbonate in the rock and soil can resolve down into the water from meltwater erosion. It further illustrated that the chemical composition was mainly influenced by carbonate rock weathering in Yushugou River basin.

Molar ratio can reflect the evolution process of rock weathering and hydrogeological condition in the basin (Hussein 2004; Su *et al.* 2009). Generally speaking, Cl^- in precipitation mainly origins from sea salt ions and is relatively stable in the

water cycle (Meybeck 1983). In addition, Na^+ and Cl^- are difficult to generate sediments and be adsorbed by colloid. Molar Na^+/Cl^- ratio in precipitation derived from seawater is about 0.86 (Stallard and Edmond 1983). Therefore, molar Na^+/Cl^- ratio can used to research the influence of atmospheric transportation on surface hydrochemistry. The variation range of molar Na^+/Cl^- ratio in river water was 2.17~2.54 (figure 4a; table 2), far more than 0.86, indicating that the hydrochemical composition was less influenced by precipitation and mainly affected by water–rock interaction.

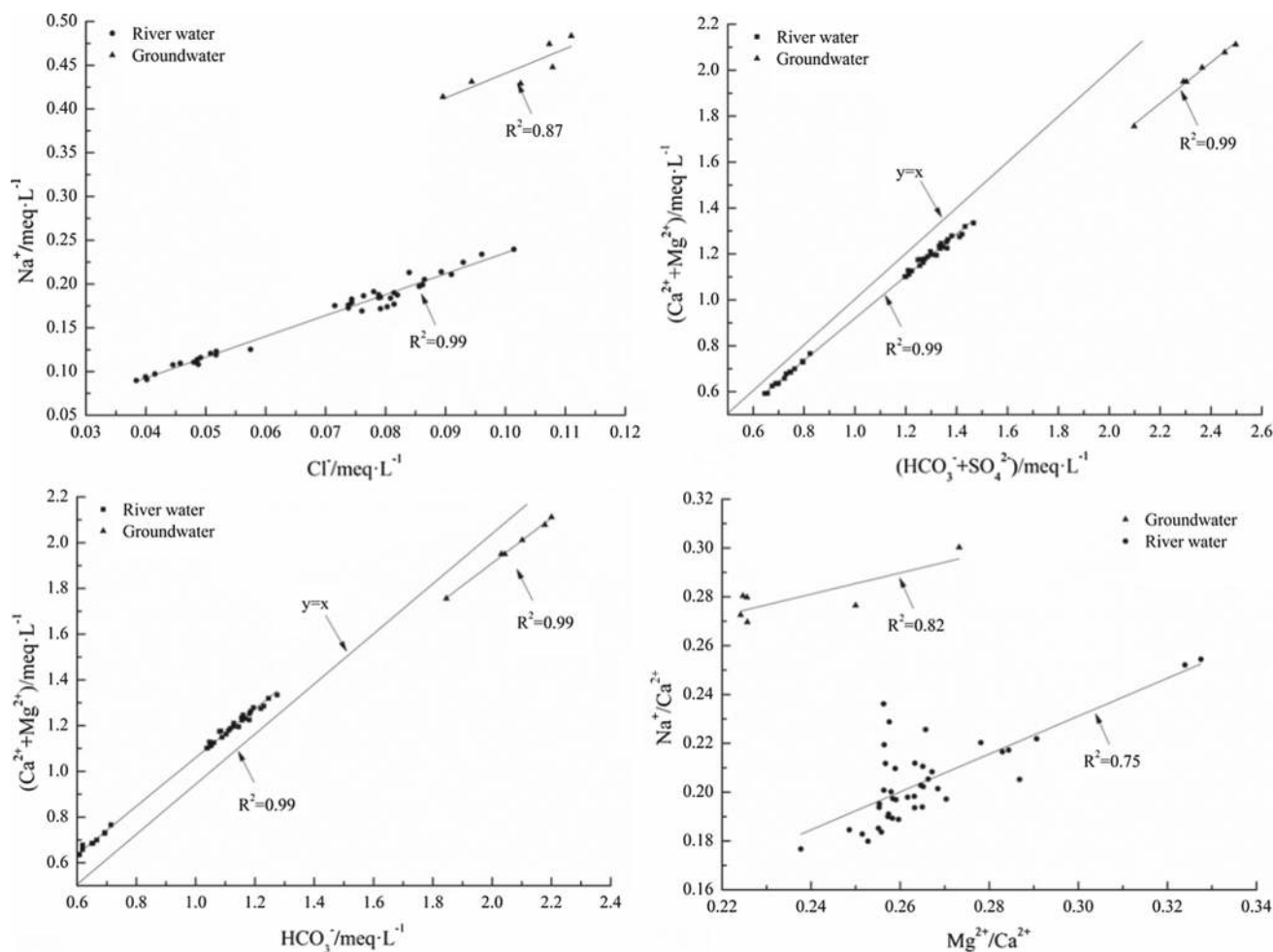


Figure 4. Equivalent concentration proportions of major ions in river water and groundwater.

Table 2. Mean molar concentration ratio of major ions in river water and groundwater.

Molar ratio	River water	Groundwater
$\text{Mg}^{2+}/\text{Ca}^{2+}$	0.27	0.24
$\text{Na}^+/\text{Ca}^{2+}$	0.2	0.28
$(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^-$	1.06	0.96
$(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$	0.92	0.85

The correlation coefficient of Na^+ and Cl^- in river water and groundwater ($R^2 = 0.99, 0.87$) were very remarkable which may be due to the water supply source and strong evaporation. At the same time, the increase of Na^+/Cl^- is disproportionate. It means that dissolution of silicon rock and albite weathering and other mineralizer (such as MgCl_2) affects Na^+/Cl^- equilibrium relation.

The molar $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^- + \text{SO}_4^{2-}]$ ratio was shown in figure 4(b). All the samples were below the line of $y=x$. The ratio value of groundwater and river water is 0.85 and 0.92 (table 2), respectively. The nearly 1 value showed that the main formation function of water chemistry was carbonate and sulfate minerals dissolution. Ca^{2+} and Mg^{2+} were not enough to balance HCO_3^- and SO_4^{2-} , meanwhile it needed a small quantity of Na^+ and K^+ to maintain the balance. The molar $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$ ratio in river water was just 1.06, indicating that the carbonate weathering was mainly controlled by H_2CO_3 , with a little impact of H_2SO_4 . The molar $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$ ratio in groundwater was 0.96 (table 2), a little less than 1. It illustrated that the primary formation process of groundwater chemistry was carbonate weathering, accompanied with very little silicate rocks dissolution.

In figure 4(d), the $\text{Mg}^{2+}/\text{Ca}^{2+}$, $\text{Na}^+/\text{Ca}^{2+}$ values in groundwater and river water were far less than 1 (about 0.2, table 2) and it revealed that carbonate weathering was mainly composited of calcite mineral dissolution in this basin. This was consistent with the result of hydrochemical type analysis. In other words, the hydrochemical type ($\text{Ca}^{2+}-\text{HCO}_3^-$) was associated with local lithology.

5.2 Characteristics of water stable isotopes

As an important link of water cycle, river water is a bond of conversion between different water bodies. The research of river water isotopes in arid areas is crucial to understanding isotope hydrological cycle (Torgersen 1979). Therefore, the study of river water isotope is not only beneficial to the understanding of the water cycle process, but can also provide a reliable evidence for the reasonable utilization of water resources.

During the summer flood period in the study area, the daily variation of river water isotope values is relatively small (table 1). The variation range is from -12.23‰ to -10.7‰ for $\delta^{18}\text{O}$

and from -79.14‰ to -70.59‰ for δD . The precipitation isotopic values ranged from -12.32‰ to 0.52‰ for $\delta^{18}\text{O}$ and from -82.88‰ to -3.19‰ for δD . For, groundwater, the variation range of $\delta^{18}\text{O}$ is -11.98‰ to -11.6‰ , with average value -11.78‰ . With an average of -77.36‰ , δD values range from -79.47‰ to -75.8‰ . The groundwater environment is relatively stable judging from the little variation of groundwater isotopic values. The river water isotopic values change relatively larger. The characteristic difference of isotopes can reflect the supply relationship between groundwater and river water. In general, river water $\delta^{18}\text{O}$ and δD are relatively stable when it mainly recharges by groundwater (Su *et al.* 2009). During the summer flood period in Yushugou River basin, relative to the greater fluctuation in the atmospheric precipitation isotope values, the fluctuation of δD and $\delta^{18}\text{O}$ in river water were relatively small. It indicated that the river water was supplied by other water sources with the exception of precipitation supply in this time. According to the characters of river basin, under the greater influence of groundwater and glacier meltwater, the river water δD and $\delta^{18}\text{O}$ values were less affected by the precipitation change.

5.2.1 $\delta^{18}\text{O}$ variation in river water

Throughout the observation period, the $\delta^{18}\text{O}$ of river water presents daily periodicity variation in figure 5. We can also see that the variation trend was opposite between $\delta^{18}\text{O}$ and run-off when there was no precipitation. The daily periodicity variation was due to daily change of glacier meltwater affected by temperature and insolation. In these days, the river flow was dominated by glacier meltwater. When the glacier meltwater outflow, the run-off increases gradually. At the same time, river water $\delta^{18}\text{O}$ value was decreased. When the glacier meltwater outflow decreased, the contribution ratio of groundwater in river water began to increase. The greater contribution of groundwater increased the $\delta^{18}\text{O}$ value in river water, and also reduced the daily variability. From samples 1–15 (2013.7.29/19:00–2013.8.2/07:30) and samples 37–39 (2013.8.26/17:30–2013.8.27/07:40), the corresponding inverse correlation between river water $\delta^{18}\text{O}$ and run-off was not obvious. This may be because of the precipitation on July 29 and August 26–27. In addition, in high mountains rainfall event may happen.

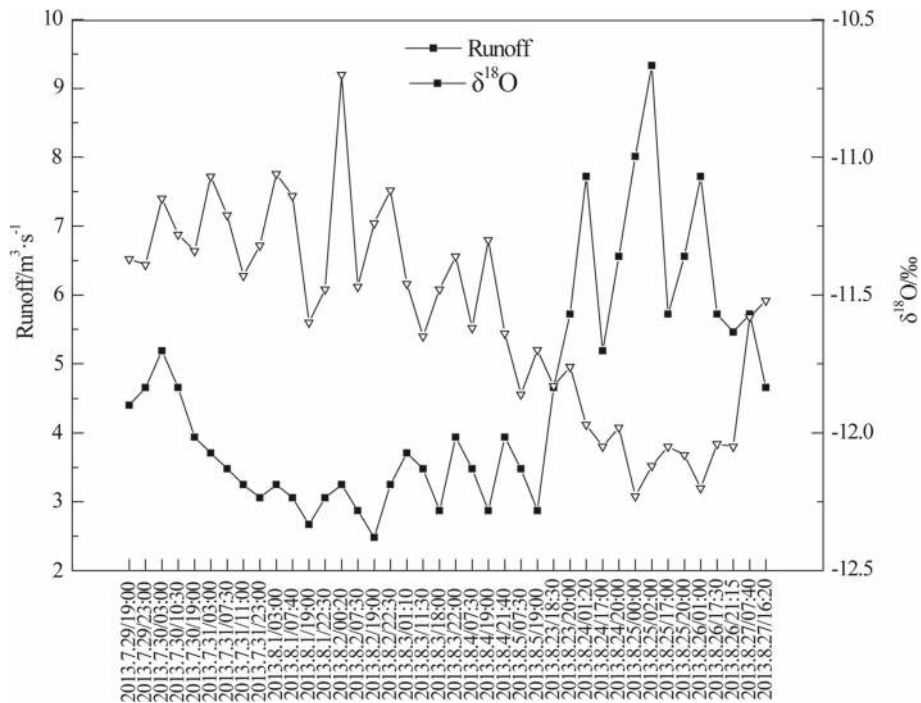


Figure 5. Variation of river water $\delta^{18}\text{O}$ and run-off in summer flood period.

5.2.2 Correlations of $\delta^{18}\text{O}$ and δD for water bodies

Distribution of all the samples of $\delta^{18}\text{O}$ and δD compared with Local Meteoric Water Line (LMWL) is shown in figure 6. Samples of river, glacier meltwater and groundwater lie above LMWL, and all plots distribute in a concentrated way nearly to LMWL (figure 6; table 1). In summer half year, precipitation and glacier meltwater

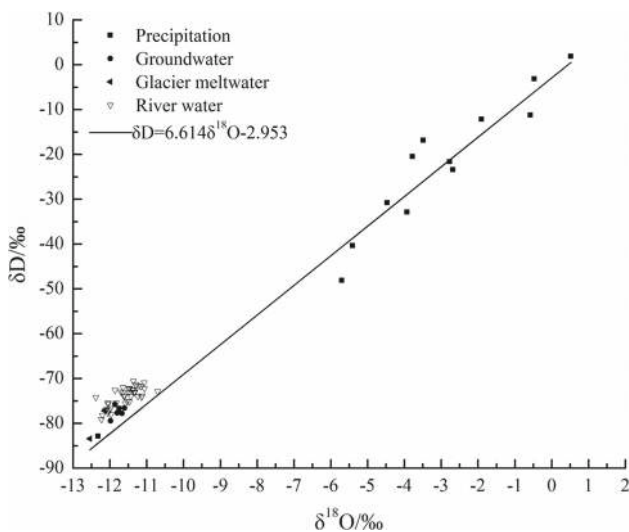


Figure 6. Relation between $\delta^{18}\text{O}$ and δD of all water bodies and LMWL. LMWL was $\delta D = 6.614\delta^{18}\text{O} - 2.953$, $R^2 = 0.98$ cited from previous study (Wang *et al.* 2014).

infiltrate and form groundwater, so the isotopes of groundwater samples just lie between precipitation and glacier meltwater. Similar isotopes and Cl^- in groundwater with vicinal river showed almost no evaporation process of groundwater. Isotopes of the river are enriched than groundwater and glacier meltwater, showing that the river water had other resource besides groundwater and glacier meltwater. Precipitation isotopes values are the most enriched at the right end, while the isotopes values of glacier meltwater are most depleted at the left end. The isotopes values of river water just lie among that of glacier meltwater, groundwater and precipitation. Thus, by analysis of the isotopic and hydrochemical data above, it can be deduced that Yushugou River water is recharged by glacier meltwater, groundwater and precipitation during the summer flood period.

From figure 6, we can also find that the isotopic values of groundwater partially overlapped with that of river water. This fully embodies the close hydraulic relationship between river water and groundwater. As the research area is located in the mountain area, groundwater recharges the river water directly. During the summer flood period, the river was mainly recharged by groundwater before the discharge of glacier meltwater. So the isotopic value of river water is more close to groundwater.

When glacier meltwater heavily recharges the river, the proportion of the groundwater in river water decreases; accordingly, the hydrogen and oxygen isotope of river water is depleted. At this time, the distribution points of river water incline to the glacier meltwater. The hydrogen and oxygen isotope distribution points of precipitation are far apart from that of river water, which suggests that river water is a little recharged by precipitation during the summer flood period.

5.3 Hydrograph separation

5.3.1 The condition judgment of the separation model

Before carrying out the three-component hydrograph separation, we need to discuss the requirement for the model. Based on the assumptions in section 4, the relation between $\delta^{18}\text{O}$ and δD of all water bodies and LMWL can be made which is shown in figure 6. The hydrogen and oxygen isotope values in different water bodies are quite different and all generally distribute near the LMWL. It shows that the samples are less affected by the imbalance of evaporation fractionation. Only the precipitation samples lie in the upper end of the LMWL, indicating the great effect by imbalance of fractionation. The glacier melt water is located in the left section, and precipitation distributes in the upper right. The isotope values of river water just lie among that of glacier meltwater, groundwater and precipitation. The water supply is obvious, that is to say the river water consists of the three kinds of water supplies. Therefore, three-component isotope hydrograph separation in Yushugou River during the summer flood season is reasonable.

As in the above paper, three-component isotope hydrograph separation can be used for the Yushugou River. But after adding Cl^- , the linear relationship between different tracers may cause the separation infeasible. For this reason, it is necessary to further analyze the condition of separation by Cl^- and $\delta^{18}\text{O}$ and discuss the feasibility of three-component hydrograph separation. The concentration of Cl^- as the abscissa, $\delta^{18}\text{O}$ as the ordinate, the relational graph of Cl^- and $\delta^{18}\text{O}$ for river water, glacier meltwater, groundwater and precipitation was made (figure 7). Connecting mean value point of glacier meltwater, groundwater and precipitation, a closed triangle was made up with three water tracer values as vertices.

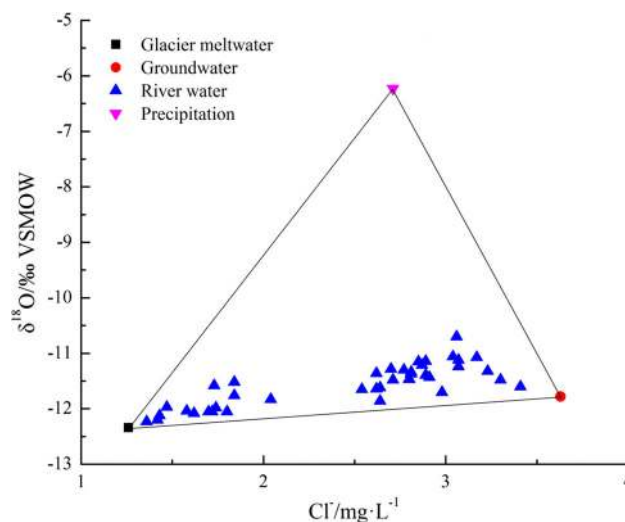


Figure 7. Relations of Cl^- – $\delta^{18}\text{O}$ of water bodies in Yushugou River basin during summer flood period.

In figure 7, the river water was trapped in the closed triangle area which was formed by glacier meltwater, groundwater and precipitation. The river water is clear and no contact with the trilateral of the triangle, that is, the river water is mixed by the three waters. It further proves that three-component hydrograph separation using Cl^- and $\delta^{18}\text{O}$ is feasible in Yushugou River basin during summer flood period.

5.3.2 Results of hydrograph separation

Using three-component hydrograph separation, we got the contributions of glacier meltwater, groundwater and precipitation, which are shown in table 3. 54.9% of the Yushugou River water originated from glacier meltwater, 37.6% from groundwater, and precipitation about 7.5% during the 2013 summer flood period. This result indicated that Yushugou River water was mainly recharged by glacier meltwater and groundwater. Although summer is the concentrating period of precipitation in this river basin, the amount of precipitation was very small in July and August (only 24.4 mm). Part of the precipitation directly produces surface run-off supplying to the river, and the other part of the rainfall infiltrates into groundwater, eventually recharging to the river. Therefore, only a very little river water was recharged by direct precipitation. The glaciers area in headwaters is 22.85 km² (the glacier coverage up to 6%), and the ice volume 1.59 km³. In summer, the glacier strongly melt as a result of the continuous high temperature and a wide range or strong rainfall scouring effect. Since 1980s, affected by global climate change, the

Table 3. Contributions of different water sources during the summer flood period as a result of hydrograph separation.

Water type	$\delta^{18}\text{O}$	$\text{Cl}^- (\text{mg} \cdot \text{L}^{-1})$	Mixing fraction/%
Groundwater	-11.78	3.63	37.6
Precipitation	-6.23	2.71	7.5
Glacier meltwater	-12.34	1.26	54.9
River water	-11.67	2.26	

Table 4. The necessary tracer data used in computing mixing fractions and their uncertainties.

Water type	Concentration ^a	Mean ^b	σ^c	n^d	$t/70\%^e$	$W/70\%^f$
Glacier meltwater	δ_g	-12.34	0.28	2	1.963	0.55
	Cl_g^-	1.26	0.26	2	1.963	0.51
Groundwater	δ_s	-11.78	0.14	6	1.156	0.16
	Cl_s^-	3.63	0.30	6	1.156	0.35
Precipitation	δ_p	-6.23	3.23	13	1.083	3.50
	Cl_p^-	2.71	5.19	13	1.083	5.62
River water	δ_t	-11.67	0.37	40	1.050	0.39
	Cl_t^-	2.26	0.63	40	1.050	0.66

^a Tracer concentration.

^b Mean tracer concentration, relative to SMOW for ^{18}O , and mg/l for Cl.

^c The standard deviation of the mean values for samples.

^d The number of samples used to compute the mean.

^e The appropriate t value in t -distribution statistic for 70% confidence.

^f The propagated uncertainty, equal to the t statistic for 70% confidence multiplied by the standard deviation of the tracer concentration.

glacier has retreated severely, thinning in thickness and decreasing in area (Li *et al.* 2010; Xie and Jiang 2014). Thus, glacier meltwater recharge of river water was on the rise, and became one of the main sources for river water in summer. Fissure water and pore water gave priority to groundwater in the study area. During summertime, the temperature rising strengthened the melting degree of frozen soil, even completely melting. In this case, rainfall infiltration capacity enhanced and the groundwater level increased. More groundwater was discharged into the river. As a result, this promoted the deep groundwater contribution to the river run-off amount.

5.3.3 Uncertainty in three-component separation

The method of uncertainty analysis described in section 4 was carried out using chloride and ^{18}O data for Yushugou River basin during summer flood period, in order to illustrate the application of three-component hydrograph separation method, and to demonstrate the construction of an “uncertainty budget” which can be used to quantify the different sources of uncertainty.

In table 4, tracer concentrations and uncertainties were used to evaluate the partial derivatives of (4–6) and compute the mixing fractions (equations 4–6) and their uncertainties (equation 1). The t values chosen were those for 70% confidence. The asymptotic t value at 70% confidence (1.050) was used for the river water solute concentrations, because the uncertainty in these values was taken to be the laboratory precision of the analyses determined from a large number of laboratory replicates (Genereux 1998).

Moreover, the individual terms on the right-hand side of equation (7) were used to quantitatively assess the significance of uncertainty in each computed mixing fraction of the eight different sources. Concentration Cl_t^- (the Cl^- concentration of river water) accounts for the majority of uncertainty in f_g (60.64%) and f_s (60.00%), but a much smaller proportion of the uncertainty in f_p (6.82%; table 4). While the uncertainty value of Cl_t^- is very small compared to others (0.66; table 5, second column from the left), the significance of the uncertainty in f_g and f_s is surprising, because $\partial f_g / \partial \text{Cl}_t^-$ and $\partial f_s / \partial \text{Cl}_t^-$ are much larger than others. Uncertainty in δ_t is much more important for f_p than

Table 5. Percentage of the total uncertainty in each f value arising from the uncertainties in eight tracer concentrations.

Tracer concentration ^a	$W/70\%$ ^b	Uncertainty in f_x due to each tracer concentration ^c (%)		
		f_g	f_s	f_p
δ_g	0.55	0.34	0.69	25.23
Cl_g^-	0.51	10.90	10.83	1.21
δ_s	0.16	0.02	0.03	0.93
Cl_s^-	0.35	2.45	2.41	0.28
δ_p	3.50	0.25	0.54	19.63
Cl_p^-	5.62	24.83	24.59	2.8
δ_t	0.39	0.59	1.17	42.99
Cl_t^-	0.66	60.64	60.00	6.82

^a Tracer concentration.

^b $W/70\%$ is the uncertainty in each concentration at the 70% confidence level, as given in table 3.

^c The 'error budget' in the three right columns is presented for the 70% confidence level.

Table 6. Separation and model uncertainty results for water bodies.

Component	Mixing fraction (%)	Uncertainty	
		U_v	U_m
Glacier meltwater	54.9	± 0.34	± 0.20
Groundwater precipitation	37.6	± 0.38	± 0.22
	7.5	± 0.10	± 0.09

U_v is uncertainty of hydrograph separation from the spatial and temporal variation of tracer concentrations.

U_m is uncertainty of hydrograph separation from laboratory analytical error.

for f_g and f_s . Nearly half of the uncertainty in f_p is due to the variation of tracer concentrations in δ_g and δ_p , while the other half is due to uncertainty in δ_t (the third smallest of the eight contributing uncertainties). Uncertainty in Cl_p^- is much less important for f_p than for f_g and f_s . Though uncertainty in Cl_p^- is the largest of the eight uncertainty values, it is insignificant for f_p , f_g and f_s , especially for f_p . Uncertainty in δ_s is the smallest of the eight contributing uncertainties, and also it is insignificant for f_p , f_g and f_s .

The estimated uncertainties and mixing fractions of f_g , f_s and f_p are shown in table 6. The results show that the temporal and spatial variations uncertainty (± 0.34 , ± 0.38 , ± 0.10) has greater influence than the uncertainty in the tracer concentration from the measurement method (± 0.20 , ± 0.22 , ± 0.09). The uncertainty terms for the glacier meltwater and groundwater are larger than precipitation. In Yushugou River basin, carrying out three-component separation for flood water in summer is reasonable and feasible, because the

difference values between the tracer concentrations are far larger than the uncertainty of the model (Genereux 1998).

6. Conclusions

In Yushugou River basin, the hydrochemical type for surface water and groundwater was $HCO_3^- - Ca^{2+}$. The hydrochemical composition mainly came from carbonate rocks weathering. The similar composition of river water and groundwater suggests that the rapid transfer and frequent interaction existed. The low content of NO_3^- and SO_4^{2-} in groundwater and river water confirmed that the basin was rarely affected by human activities. In other words, the chemical characteristics basically reflects the hydrogeological conditions of the area.

According to the characteristics comparison of the water stable isotopes and chemistry in Yushugou River basin, the river water is greater influenced by groundwater and glacier meltwater,

but there is little effect of the precipitate change. Comparing $\delta^{18}\text{O}$ and δD values of basin waters with the LMWL, we can conclude that Yushugou River is recharged by the glacier meltwater, groundwater and precipitation during the summer flood period. Using three-component mixing model, we find that glacier meltwater and groundwater are the main contributors to Yushugou River in summer flood period, and the glacier meltwater provides the main part of variation in the run-off. In Yushugou River, the glacier meltwater and groundwater account for 54.9% and 37.6%, respectively, while precipitation accounts for less than 8%. The variations of the glacier meltwater and groundwater $\delta^{18}\text{O}$ account for the majority of uncertainty for this hydrograph separation model. Glacier meltwater is vital to Yushugou River during summer flood period. The importance of glacier meltwater should draw enough attention in the river basin.

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