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Distribution of isotopes and chemicals in precipitation in Shule River Basin, northwestern China: an implication for water cycle and groundwater recharge

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Abstract: The distribution of stable isotopes and ions in precipitation in the Shule River Basin, northwestern China, were investigated to understand the regional water cycle and precipitation input to groundwater recharge. The study found that the mean annual concentrations of Ca^{2+}, Na^{+}, SO_4^{2-}, Cl^{-}, Mg^{2+}, NO_3^{-}, and K^{+} in the basin were lower than those in other arid areas of northwestern China. The average concentrations of ions in the lower reaches of the Shule River were higher than those in the upper reaches. The results showed that the main ionic concentrations decreased with the increase of precipitation amount, indicating that heavy precipitation cannot only wash crustal aerosols out of the atmosphere, but also create a dilution effect. Cl^{-} and Na^{+} in precipitation had a strong and positive correlation, suggesting a common origin for the two ions. However, the excess of Na^{+}, combined with non-marine SO_4^{2-} and NO_3^{-}, indicated that some ions were contributed by terrestrial origins. In the extremely arid regions of northwestern China, the evaporation process obviously changes the original relationship between δ^2H and $\delta^{18}O$ in precipitation, and leads to d-excess values <8‰. $\delta^{18}O$ and temperature were significantly correlated, suggested that temperature strongly affected the characteristics of isotopes in the study area. The $\delta^{18}O$ value indicates a dominant effect of westerly air masses and southwest monsoon in warm months, and the integrated influence of westerly and Siberian-Mongolian polar air masses in cold months. The d-excess values were generally lower in warm months than those in cold months, indicating that post-condensation processes played a significant role in the water cycle. The results provide reliable precipitation input information that can be used in future groundwater recharge calculations in the study area.

Keywords: precipitation; stable isotopes; ions; westerly air masses; Shule River Basin

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Isotopes are effective tracers in the studies of hydrologic cycles. Isotope hydrology (Dutton et al., 2005; Hren et al., 2009; Jeelani et al., 2013) is useful in investigating precipitation characteristics and air mass origins (Ulrich et al., 1998; Balestrini et al., 2000; Celle-Jeanton et al., 2008; Prathibha et al., 2010). The chemical components of precipitation have been used to identify the sources (i.e., natural inputs versus anthropogenic emissions) of rainwater chemistry (Kulshrestha et al., 2003; Demirak et al., 2006; Yamanaka et al., 2007). Because heavy isotopes are depleted rapidly than

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light isotopes in long-distance transport, the kinetic fractionation process results in differences between δ^2H and $\delta^{18}O$ in precipitation during water vapor transport (Siegenthaler et al and Osechger, 1980). Previous researches indicated that, above the sea surface, the d-excess in evaporated moisture increases with decreasing relative humidity and increasing temperature (Merlivat and Jouzel, 1979; Johnsen et al., 1989). Thus, the d-excess can indicate the source of the moisture (Feng et al., 2009). The chemistry of precipitation is useful in distinguishing the sources of natural inputs or anthropogenic emissions (Yamanaka et al., 2007), for example, precipitation with large amounts of Na^+ and Cl^- is generally of marine origins.

Precipitation strongly affects available water resources in arid basins. The precipitation cycle plays a significant role in the local water balance. In recent decades, population explosion in China caused the high demand for water which subsequently affected the hydrological cycle processes, particularly in the arid regions (Feng et al., 2004; Huang and Pang, 2012). The Shule River Basin is situated in northwestern China and is an endorheic basin in the Hexi Corridor. This area experienced severe water resource stresses because of the high evaporation and low precipitation (Jia et al., 2008). The Shule River is originated in the Qilian Mountains (Ma et al., 2005) and disappears in the Gobi desert near Dunhuang (Ma et al., 2009; Huang and Pang, 2010). Studies and investigations have been taken on the dynamics of precipitation in the Hexi Corridor region based on the patterns of various isotopes (Wu et al., 2010; Guo et al., 2014) and generated data on regional precipitation characteristics, such as the local meteoric water line (LMWL), the effects of temperature and the range of and changes in d-excess values. Ma et al. (2012) found that precipitation $\delta^{18}O$ increased significantly with increasing temperature and decreasing elevation in the Shiyang River Basin; and some ions in precipitation originated from terrestrial sources and were entrained the transport of air masses over land. Wu et al. (2010) and Zhao et al. (2011) found that the stable isotopes in precipitation were mainly controlled by different condensation mechanisms in the Heihe River Basin. Guo et al. (2014) studied the individual basins in the Hexi Corridor and provided a systematic overview of precipitation isotope characteristics throughout the region. However, there is no related, comprehensive research into the precipitation in the Shule River Basin.

The objectives of this study were to: (1) probe the precipitation chemistry seasonal variations and establish a quantitative relationship between $\delta^{18}O$ and δ^2H in precipitation; (2) determine the origins of the ions in precipitation; and (3) combine the re-analysis data of National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) to provide insights into the different sources of precipitation.

1 Study area

The Shule River Basin is located in the western Hexi Corridor, northwestern China and is the third largest interior river basin in China. The basin situated between the Mazong Mountains and the Qilian Mountains and is adjacent to the Lop Nur salt lake in the west and near Huahai city in the east (Fig. 1). This area, with a cultivated land of 838 km^2, is a historically, economically and ecologically important region in China (Ji et al., 2006) and is the home to more than 5.5×10^4 people. The sustainable management of water resources is particularly important here due to the high demand of water in the basin. There are three different geomorphological units in the basin, the Qilian Mountains in the south, the Beishan Mountains in the north and the plains between the mountains. The southern Qilian Mountains consist of a series of east-west trending hills with elevations higher than 2,000 m .The climate is typical continental monsoon and the annual mean temperature ranges from 6.9°C to 8.3°C. The annual mean precipitation is 63 mm with 70% in summer. The potential annual evapotranspiration is 3,042 mm.

The Changma Reservoir in the upper reaches and the Shuangta Reservoir in the middle reaches of the Shule River were established to manage the water allocation. The Danghe River was a tributary of the Shule River and continues to provide water for Dunhuang city while the Shule River is no longer directly supplied the city. The Shule and Danghe Rivers are perennial streams originated in the Qilian Mountains and are supplied by meltwater from glaciers and snow, as well

as by summer precipitation and water from springs (Gao et al., 2011). Precipitation samples were collected during individual precipitation events at four hydrometric stations in the Shule River Basin and its sub-watershed, the Danghe River Basin. The Changma and Shuangta sites are located along the Shule River between the upper reaches and the lower reaches. The Dangchengwan and Danghe sites are situated in the upper and lower reaches of the Danghe River.

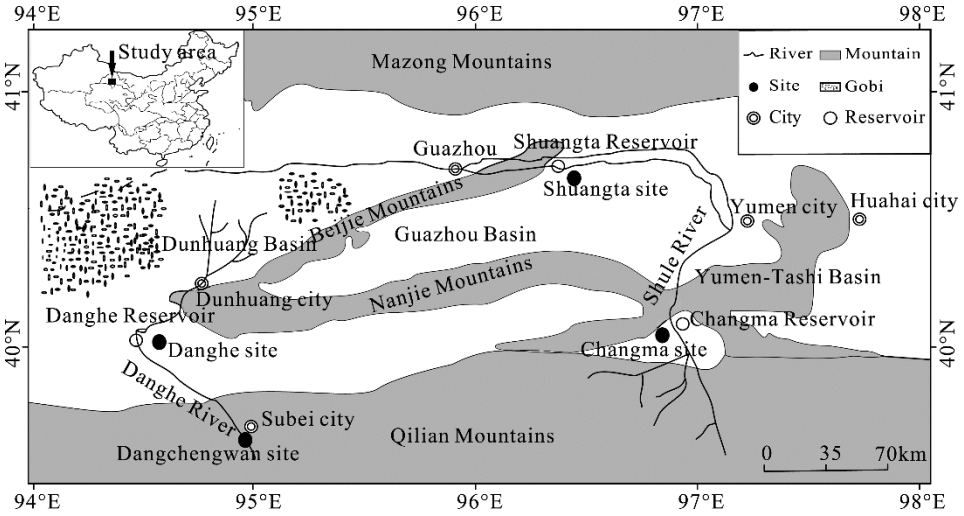

Fig. 1 The locations of the Shule River Basin and the four precipitation sampling sites

2 Methods

2.1 Data sources

The four sampling sites were selected at the different geomorphological locations: the Changma and Dangchengwan sites were at mountain areas; Shuangta site was at a vegetation-covered area; and the Dunhuang site was at a desert area. The four sites are long-term observation sites in the Shule River Basin with abundant, long-term hydrological data. A total of 126 samples, 28 snow samples and 98 rainwater samples, were collected between June 2013 and January 2015. Precipitation amount, atmospheric temperature, and atmospheric relative humidity were recorded during precipitation events. We collected the sample at the beginning of a precipitation event to ensure that the sample characteristics were not affected by subsequent dry deposition of atmospheric suspended particulates. All samples were collected by polythene bottles which were immediately sealed to prevent isotope fractionation. All samples were filtered with 0.45-μm membrane filter according to the instruments introduction of ionic and isotopic analysis. An aliquot of all samples were acidified with 1 mg/L HNO_3 for preservation for cation analysis. Unacidified samples were used for anionand stable isotope analyses. Software used for data analyses included MATLAB, SPSS and Sigmaplot.

2.2 Analysis

The $\delta^{18}O$ and $\delta^{2}H$ values were measured in laboratory using a liquid water isotope analyzer (Model DLT-100; Eq. 1).

$$\delta=\left[\left(R_{\text{sample}}-R_{\text{standard}}\right)/R_{\text{standard}}\right]\times 100\,. \tag{1}$$

Where R_{sample} and R_{standard} represent the isotope ratios ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) of the sample and the standard, respectively. The analytical error was 0.2‰ for $\delta^{18}O$ and 1.0‰ for $\delta^{2}H$.

The major cations (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) and anions (Cl^{-}, SO_4^{2-}, NO_3^{-}) were determined by ion chromatography (DX-2500; Freeze and Cherry, 1979; Eq. 2).

$$\%\ \text{Charge Balance}=\frac{\sum \mathrm{Z}\times m_c-\sum \mathrm{Z}\times m_a}{\sum \mathrm{Z}\times m_c+\sum \mathrm{Z}\times m_a}\times 100\ . \tag{2}$$

Where Z is the absolute value of the ionic valence; m_c is the molality of cationic species; and m_a is the molality of the anionic species. The charge balance error inferred from the balance between cations and anions was not more than ±5%, an acceptable error in the context of our analysis.

To identify the possible origins of ions in precipitation, previous researches introduced the concept of enrichment factor (EF) (Singer et al., 1993; Okay et al., 2002). In those methods, Ca^{2+} and Na^{+} are used as the standard for soil and marine sources (Taylor, 1964; Keene et al., 1986). The EF values are calculated as follows:

$$\mathrm{EF}_{\mathrm{soil}}=\left(X/Ca^{2+}\right)_{\mathrm{precipitation}}\Big/\left(X/Ca^{2+}\right)_{\mathrm{soil}}\ , \tag{3}$$

$$\mathrm{EF}_{\mathrm{marine}}=\left(X/Na^{+}\right)_{\mathrm{precipitation}}\Big/\left(X/Na^{+}\right)_{\mathrm{marine}}\ . \tag{4}$$

Where, X is the concentration of an ion, X/Ca^{2+} of soil sources is the ratio based on the crustal composition, and X/Na^{+} of marine sources is the ratio based on the seawater composition. In general, EF>>1 indicates enrichment compared with the reference source (i.e. suggesting that the water did not come from that source), EF<<1 indicates dilution (i.e. suggesting that the water came from that source) (Zhang et al., 2007).

Using the NCEP/NCAR re-analysis data, the average water vapor flux Q is calculated by Zhang et al. (2009) as

$$Q=-\frac{1}{\mathrm{g}}\int_{P_s}^{\mathrm{P_t}}(u,v)\times q\times \mathrm{dp}\ . \tag{5}$$

Where u is the meridional wind speed in m/s, v is the zonal wind speed in m/s，p is the pressure in hPa, p_s is surface pressure in hPa and p_t is 300 hPa, g is the acceleration of gravity in m/s^2, and q is specific humidity in g/kg.

3 Results and discussion

3.1 Chemical composition of the precipitation

Table 1 presented the characteristics of the main ion species in precipitation at the four sites and the basin as a whole. Generally, the mean ionic concentrations of the whole basin were higher than those in other arid areas of northwestern China (Wu et al., 2010; Ma et al., 2012). High ionic concentrations mostly occurred in spring and summer. This may be a result of increased transport of salty water or surface salt grain deposition from Lop Nur salt lake to the study sites by the dominant wind during this period. With increasing elevation, the average ion contents decreased from the lower reaches to the upper reaches. The volume weighted mean (VWMs) at the Changma and Dangchengwan sites were generally less than the values for the basin, whereas the values were higher at the Shuangta and Danghe sites. The differences can be explained by the frequent sandstorm activities in the Gobi desert areas of the middle and lower reaches. The ion concentration order was $Ca^{2+}>Na^{+}>SO_4^{2-}>Cl^{-}>Mg^{2+}>NO_3^{-}>K^{+}$ at the basin scale. A high concentration of Ca^{2+} depends mainly on a large number of calcium-containing compounds contributed by inland dust, whereas, for SO_4^{2-}, the influence of terrestrial sources is supplemented by anthropogenic pollution. The anion concentrations were ranked as $SO_4^{2-}>Cl^{-}>NO_3^{-}$, which differ from the standard rank in seawater ($Cl^{-}>SO_4^{2-}>NO_3^{-}$), suggesting that the anionic concentrations are controlled by terrestrial minerals and anthropogenic sources (Li et al., 2014).

The ionic concentrations in the precipitation showed some signs of seasonal variation (Demirak et al., 2006). The major ions presented similar seasonal trends. Cl^{-} is used as an example of major ions (Fig. 2) and its mean value during the warm months (March to August) was higher than the mean value during the cold months (September to February). The highest ionic concentrations were recorded in June to September and the values in the lower reaches were much higher than those in

the middle and upper reaches (Table 1). This may reflect seasonal fluctuations and spatial variations in the precipitation chemistry.

Table 1 Statistical parameters for the chemical and isotopic compositions of precipitation samples collected at the four sampling sites in the Shule River Basin

Location		$\delta^{18}O$	$\delta^{2}H$	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
							(μeq/L)			
Whole basin	Max	8.10	46.00	3,884.17	1,037.83	7,668.03	12,942.42	595.92	2,925.63	10,346.15
	Min	–26.10	–201.80	2.67	0.00	16.57	1.44	0.25	0.48	188.93
	VWM	–5.40	–39.40	555.35	121.35	1,092.28	1,470.69	76.66	264.38	1,746.15
	SD	7.31	54.15	776.43	163.20	1,353.92	2,377.73	120.26	461.91	1,523.67
Changma	Max	3.10	25.20	1,370.24	660.94	6,577.26	4,436.51	595.92	857.19	3,352.91
	Min	–23.80	–180.20	2.67	13.63	30.64	16.56	0.25	0.48	188.93
	VWM	–2.93	–20.64	264.56	96.96	663.84	732.62	49.37	66.44	1,176.16
	SD	6.76	49.75	341.94	116.62	1,204.42	992.84	117.06	164.20	787.98
Dangchengwan	Max	4.00	33.40	2,498.88	227.43	3,131.53	7,486.16	499.82	2,925.63	2,239.17
	Min	–20.50	–154.30	9.39	0.00	16.57	1.44	1.57	13.72	195.57
	VWM	–6.70	–46.60	256.03	50.66	454.29	853.11	55.38	206.79	1,036.21
	SD	6.09	48.73	500.04	55.29	668.46	1,360.70	90.73	722.97	513.76
Shuangta	Max	5.30	46.00	2,092.90	281.37	7,668.03	4,661.05	434.62	1,346.52	10,346.15
	Min	–23.70	–179.90	33.79	15.15	163.26	168.32	8.72	55.94	495.60
	VWM	–6.80	–50.20	713.57	102.92	1,840.38	1,604.46	95.53	349.04	3,151.38
	SD	6.95	51.97	510.46	84.53	1,512.54	1,138.30	94.63	257.69	2,015.47
Danghe	Max	8.10	39.20	3,884.17	1,037.83	4,778.53	12,942.42	495.03	589.46	7,632.71
	Min	–26.10	–201.80	9.39	0.00	91.40	47.90	6.26	39.46	617.07
	VWM	–4.50	–33.40	675.87	224.51	1,771.78	2,998.73	100.94	217.38	2,434.45
	SD	8.51	60.77	1,025.49	203.47	1,257.89	3,377.73	106.82	153.64	1,625.45

Note: Max, maximum; Min, minimum; VWM, volume weighted mean; SD, standard deviation.

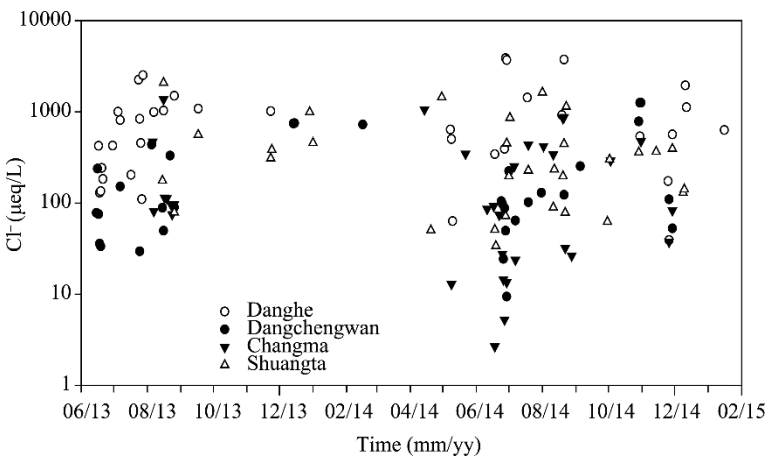

Fig. 2 Seasonal variations of Cl^- concentration in precipitation at the four sites in the Shule River Basin

During the warm months, the atmospheric precipitation chemistry exhibited elevated ionic concentrations and an increasing influence of pollutants (Li et al., 2014), and the amount of suspended particulates generally increases. The relationships between the ionic concentrations and the amount of precipitation for most ions were evident, such as Cl^- showed in Fig. 3.

During a precipitation event, the ionic concentrations decreased with the increasing amount of precipitation, suggesting that the ionic concentrations were diluted. However, we noted some anomalies, for example, the sample collected in a heavy precipitation at the Shuangta site on 22 August 2014 had a high Cl^- concentration. This was likely due to the strong sandstorm at the Shuangta meteorological station before the precipitation which would scour atmospheric aerosols from the air.

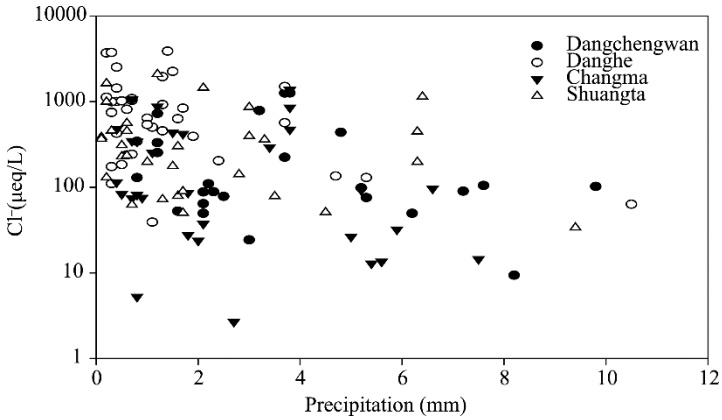

Fig. 3 The relationships between the amount of precipitation and the Cl^- concentration at the four sites

3.2 Correlations among different components

Table 2 shows that Na^+ and Cl^- had a significant and positive correlation, suggesting a common origin, most likely a marine source. NaCl is a significant soil component in desert areas and both Na^+ and Cl^- are likely sourced from dust aerosols with a halite component. The Lop Nur salt lake is located in the west of the study area which may be an important material source. There is also a strong positive correlation between K^+ and Ca^{2+}, suggesting a shared soil origin. SO_4^{2-} had a strong positive correlation with Cl^-, Ca^{2+} and K^+, but was not significantly correlated with NO_3^-. This suggested that most of the SO_4^{2-} is present as salt ($CaSO_4$) rather than as H_2SO_4.

Table 2 Pearson's Correlations among the ionic species in precipitation

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
Cl^-	1.00						
NO_3^-	0.48	1.00					
SO_4^{2-}	0.73*	0.53	1.00				
Na^+	0.91*	0.44	0.57	1.00			
K^+	0.46	0.34	0.60*	0.49	1.00		
Mg^{2+}	0.39	0.51	0.36	0.32	0.21	1.00	
Ca^{2+}	0.58	0.29	0.70*	0.55	0.67*	0.19	1.00

Note: * means significance level $P<0.05$.

Table 3 presented the EF results for the precipitation. Cl^- clearly exhibited a marine origin, K^+, Mg^{2+} and Ca^{2+}originated from terrestrial sources, which both contributed to Na^+. The EF values for NO_3^- and SO_4^{2-} were far above 1 for both terrestrial and marine sources. These high values indicated primary anthropogenic contributions.

Table 3 Enrichment factor values (EF) in precipitation

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
EF for marine source	0.21	910.25	2.86	1.00	1.42	1.48	29.62
EF for soil source	23.57	52.16	45.14	1.11	0.06	0.27	1.00

Note: EF, enrichment factor.

3.3 Stable isotopes

Figure 4 shows the relationship between δ^2H and $\delta^{18}O$ values of precipitation in the Shule River Basin. The precipitation data used to reconstruct the LMWL for the Shule River Basin provided a good fit ($\delta^2H=7.29\delta^{18}O+0.44$; $R^2=0.97$; $P<0.05$). The intercept and slope of the LMWL were less than those in the global meteoric water line (GMWL; $\delta^2H=8\delta^{18}O+10$; Craig, 1961). This suggests that atmospheric circulation patterns play an important role in isotopic signature of precipitation in the Shule River Basin. The kinetic fractionation of isotopes with re-evaporated water from the continent also influenced the isotopic values.

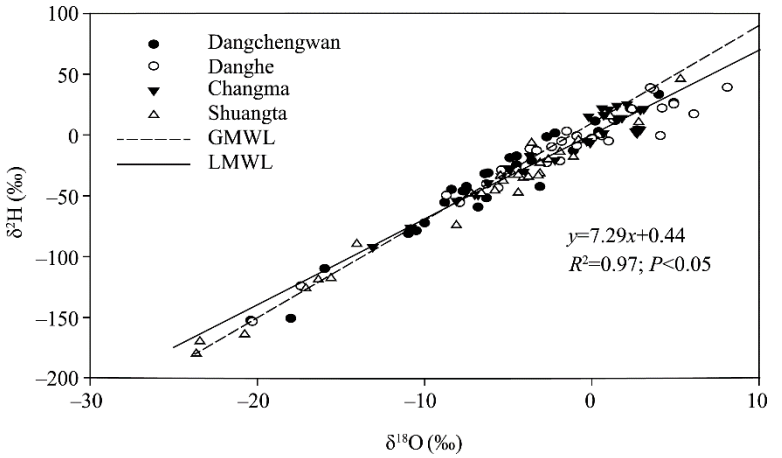

Fig. 4 δ^2H and $\delta^{18}O$ of the precipitation in the Shule River Basin, the local meteoric water line (LMWL) and the global meteoric water line (GMWL)

The isotope values measured in laboratory varied considerably (Fig. 5). For the whole basin, the $\delta^{18}O$ value ranged from –26.1‰ to 8.1‰ with a mean of –5.4‰ and δ^2H ranged from –201.8‰ to 46.0‰ with a mean of –39.4‰ (Table 1). Except at the Changma site, the mean values of the isotope were close to the mean value for the whole basin. In the upper reaches of the Shule River Basin, near Changma, an increase in the proportion of the heavy isotopes in the moisture supply would have caused the higher (less negative) isotope values.

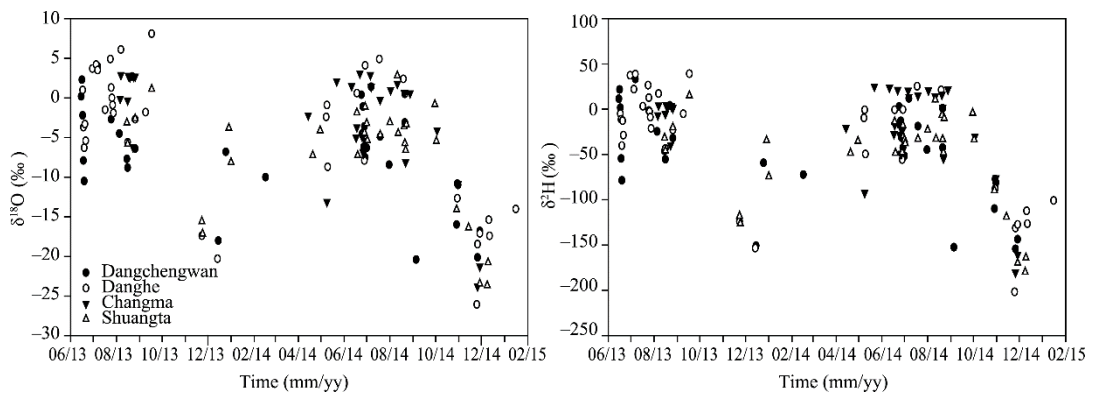

Fig. 5 Variations in $\delta^{18}O$ and δ^2H of the precipitation at the four sites from 2013 to 2015

Figure 5 shows that the $\delta^{18}O$ and δ^2H values exhibited similar variations in precipitation. The positive values most appeared in May to November and the average values for $\delta^{18}O$ and δ^2H were –1.7‰ and –15.4‰, respectively. Negative values occurred from November to February with average values for $\delta^{18}O$ and δ^2H of –12.3‰ and –98.7‰, respectively. The pattern may be caused by the differences in air temperature between the warm and cold months, which would have affected local evaporation, leading to dilution of heavy isotopes in the evaporated moisture. The variation

of moisture sources in the warm and cold months may also have important effects on isotopic signature. This was consistent with previous studies in northern China (Zhang et al., 2004; Zhou et al., 2007).

The precipitation $\delta^{18}O$ and $\delta^{2}H$ changed from positive to negative during continuous precipitation events. For instance, the values of $\delta^{18}O$ and $\delta^{2}H$ in precipitation gradually became negative from 15 June 2013 to 19 June 2013 at the Dangchengwan site, e.g. the $\delta^{2}H$ values decreased continuously from 2.3‰ to –10.5‰ for $\delta^{18}O$ and from 21.8‰ to –78.7‰ (Fig. 6). This because the moisture enriched the isotopes during a given precipitation event from the same air mass. When an event began, the precipitation would be generated from water vapor enriched in $\delta^{18}O$ and $\delta^{2}H$. As the precipitation continued, the $\delta^{18}O$ and $\delta^{2}H$ isotopes in precipitation became progressively exhausted. The effect of leaching and Rayleigh distillation depleted the $\delta^{18}O$ and $\delta^{2}H$ in the water during the precipitation (Clark and Fritz, 1997). However, some precipitation events may represent abnormal conditions where the isotope values can be much higher. This may be explained as a high heavier isotope mass from a new event mixed with the low heavier isotope mass from the previous event. For example, in the two precipitation events on 23 August at Changma, the $\delta^{18}O$ and $\delta^{2}H$ of the first precipitation event were –6.2‰ and –39.2‰, respectively at 07:50 and then the values increased to 2.7‰ and 3.3‰, respectively, at 14:00 in the second event.

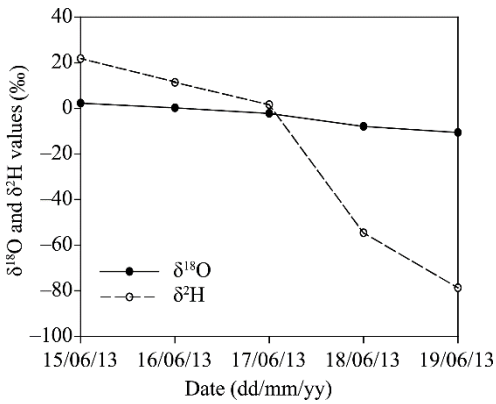

Fig. 6 Isotopic characteristics of a precipitation event during 15 to 19 June for Dangchengwan site

Figure 7 shows the regression relationships between $\delta^{18}O$ and the air temperature at the four sites, respectively. The goodness of fit in the $\delta^{18}O$-temperature relationship in the lower reaches is better than that in upper reaches, which may account for the local recycling due to the increase of moisture evaporation in the upper reaches (Pang et al., 2011). These relationships confirm that $\delta^{18}O$ in precipitation was generally controlled by the air temperature. In the upper reaches of the Danghe River, the correlation between $\delta^{18}O$ and air temperature was not as positive as that at the Dangchengwan study site. This is possibly a result of the complex topography around the site. In addition to the temperature, many factors could also affect the isotope composition, including variations in the moisture source, the precipitation amount, the elevation and the latitude. Some of these are caused by isotope fractionation during the condensation of atmospheric water vapor to produce precipitation. The amount of precipitation is another important factor that affects the isotopic values in precipitation (Fig. 8). With increasing precipitation, the precipitation $\delta^{18}O$ value decreases. That is, there is an inverse relationship between the two parameters (Yurtsever and Gat, 1981). The average precipitation amount decreased from the upper reaches to the lower reaches. However, the $\delta^{18}O$ values at the four study sites did not follow this trend. The goodness of fit for the regressions was close to zero at all four sites, which suggests that $\delta^{18}O$ was not significantly affected by the precipitation amount in a given event. This phenomenon can be explained by the low temperature, dilution of heavy isotopes and difficulty of evaporation of snowfall during the cold months. This is consistent with classic isotopic theory, indicating that the precipitation amount effect is not obvious in arid regions and confirms that the precipitation isotopes are strongly affected by temperature in the Shule River Basin.

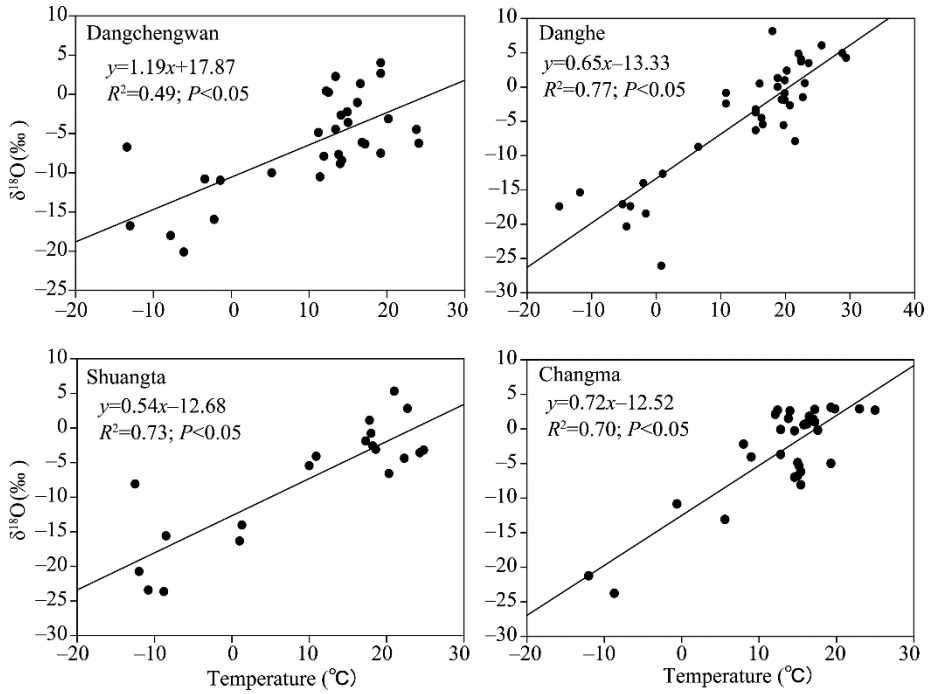

Fig. 7 The relationships between precipitation $\delta^{18}O$ and air temperature at the four sites

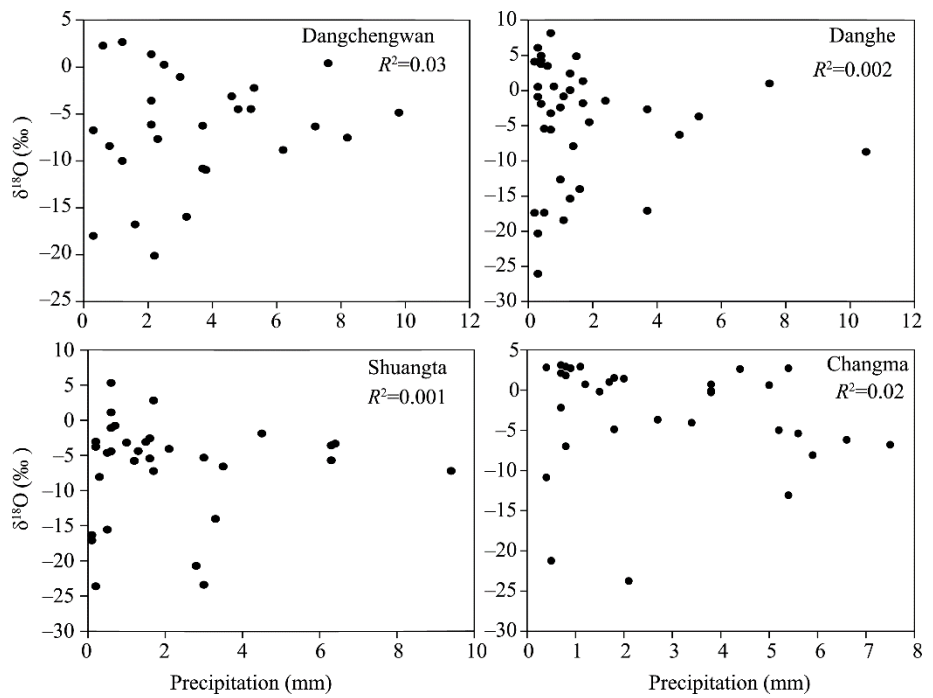

Fig. 8 Relationships between the precipitation $\delta^{18}O$ values and the amount of precipitation in given precipitation events at the four sites, respectively

The elevation effect is another possible factor that can affect isotope ratios, which gradually decrease with increasing elevation in other areas with complex topography (Huang et al., 2008). However, the elevation effect is not obvious in the study area. With the altitude from 1,170 m at

Shuangta to 2,160 m at Dangchengwan, the $\delta^{18}O$ values increased along a gradient of 0.22‰ per 100 m.

Compared with the GMWL, the precipitation isotope values in any area can be used to calculate a deuterium excess (d-excess) value, which is defined as follows:

$$\text{d-excess}=\delta^{2}H - \delta^{18}O. \quad (6)$$

Quantifying the precipitation d-excess value can help to reveal the moisture source and the spatial and temporal variations in moisture circulation patterns as well as the changes of the climate characteristics in headwater regions. Because the moisture source and other seasonal aspects of the water cycle vary temporally and spatially, the d-excess value in different areas could also reveal seasonal variations. In the Qinghai-Tibet Plateau region, a lower d-excess value reflects a strong monsoon precipitation and a weak westerly moisture transport period, whereas a higher d-excess value indicates a weak monsoon precipitation and a strong westerly moisture transport period (Tian et al., 2001). Figure 9 shows the changes in the mean monthly d-excess values at the four sites. The d-excess value varied significantly, ranging from –33.1‰ to 22.8‰. The mean d-excess values were lower in the warm months (1.57‰) than those in cold months (15.8‰).

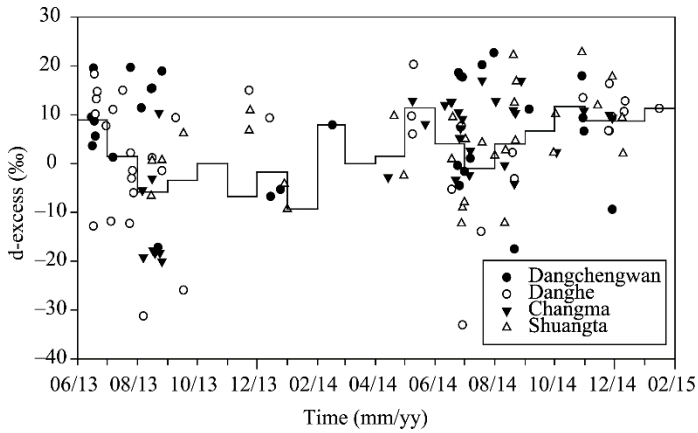

Fig. 9 Daily d-excess values at the four sites (the black line is the mean value in a given month)

The most of low d-excess values were found in the events with the precipitation amount <4 mm (Fig.10), which suggests that post-condensation processes played an important role in determining the isotopic characteristics in the study area (Froehlich et al., 2008). However, some samples indicated high d-excess values, which may result from re-evaporated water (Pang et al., 2011). The lowest d-excess values generally appeared at the Danghe site. This may be because Danghe site is located in a desert area with low vegetation cover. Some researchers found that evaporation from a bare soil can decrease the d-excess value (Yurtsever and Gat, 1981; Allison et al., 1983).

Combining the NCEP/NCAR re-analysis data, we could confirm the origin of precipitation. We used the NCEP/NCAR re-analysis datasets to calculate the wind fields in January and August 2014, which represent the moisture origins in the cold and warm periods, respectively. The origin of precipitation predominantly comes from the westerly air masses throughout the year. There is also an influence of Siberian-Mongolian polar air masses in the cold period. In the warm period, part of the precipitation events are affected by the southwest monsoon and local water vapor cycle. Although southwest monsoons occasionally arrived in the study area, their contributions to the precipitation cannot be ignored. This result is consistent with the results of $\delta^{18}O$ and d-excess.

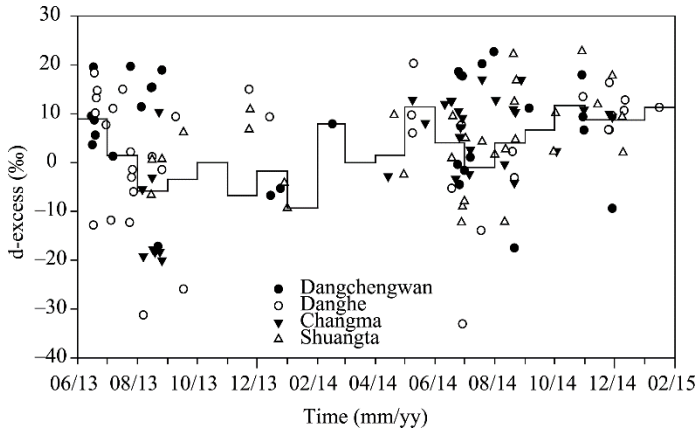

Fig. 10 Relationship between the daily d-excess values and the precipitation amount at the four sites

4 Conclusions

The ionic contents in precipitation gradually increased from the upper reaches to the lower reaches of the Shule River Basin. In addition, higher values tended to occur during the spring and summer. This may be a result of strong sandstorm activities during the warm months and the salinization in the middle and lower reaches. The ionic concentrations also decreased with increasing precipitation amounts. Na^+ and Cl^- had significant and positive correlations in the precipitation samples, which suggested a marine source, whereas Ca^{2+}, K^+ and Mg^{2+} had terrestrial origins. Anthropogenic sources may be responsible for NO_3^- and SO_4^{2-}.

The LMWL was similar to other arid areas and indicated a combination of intense mixing effects. The precipitation $\delta^{18}O$ values exhibited similar variations in precipitation at the four sites: more positive values from May to November and more negative values from November to February, which indicated that the source of moisture in precipitation was primarily westerly air masses during the warm months, whereas both westerly and polar air masses contributed to the precipitation during the cold months. There were significant correlations between $\delta^{18}O$ and temperature and their correlation coefficient showed increase from the upper to the lower reaches. There was no significant relationship between the $\delta^{18}O$ value and the precipitation amount, which suggests that the precipitation tended to be influenced by re-evaporation in the study area.

The d-excess values were lower in the warm months than those in the cold months, and most of lowest d-excess values appeared in the precipitation with the amount of proximately 4 mm, suggesting that post-condensation processes played an importantrole in determining the isotopic characteristics in the study area. By combining the NCEP/NCAR re-analysis data with our data, we determined that the origin of precipitation was predominantly from the westerly air masses throughout the year. There was also an influence of Siberian-Mongolian polar air masses in the cold period. In the warm period, part of the precipitation events was influenced by the southwest monsoon and local water vapor cycle.

The stable isotopes and chemistry of precipitation is important for the study of the water resources of the Shule River basin. These studies could be in help for tracing the local regional paleo hydrology and groundwater recharge.

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