

# The O and H isotope characteristics of water from major rivers in China

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**Abstract** Isotopic compositions of the water sources and evapotranspiration in large rivers of China are not well explored. In this investigation,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of water from major large rivers of China are integrated to understand the spatial and temporal variations in the isotopes of water and *d*-excess. River water samples were collected from the channels and tributaries of the Changjiang, Yellow, Songhua, and Liao Rivers in China. Water from upstream was generally enriched with light isotopes relative to that from downstream areas. Water from the Songhua River and upper reach of the Changjiang River has relatively negative isotopic values, impacted by latitude and altitude effects, respectively. The spatial pattern showed that  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values in rivers mainly ranged from  $-9$  to  $-7$  ‰ in most of China based on roughly mapped contours, and rivers enriched in light isotopes were primarily located in the Tibetan Plateau and northeast China. The slopes of linear regression from the Yellow and Liao Rivers suggested that the loss of water by direct evaporation shifted the isotopes of water, especially in some small tributaries. Additionally, there was a narrow range of low  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values from the main channel of rivers during the low-flow season relative to the high-flow season due to influence of the monsoon climate. No distinct spatial variation of *d*-excess values was found in the rivers of China. However, water samples in some rivers with low *d*-excess values had high  $\delta^{18}\text{O}$  values, indicating that evaporation in the tributaries has led to significant water loss, especially in tributaries of the Yellow and Liao Rivers.

**Keywords** Stable isotopes · Spatial variation · *d*-Excess · Major rivers · China

## 1 Introduction

River water originates from alpine snow/ice melting, recent precipitation, and groundwater in the basin, and serves as the major water source for cities and ecological systems located alongside the rivers. Therefore, it is important to understand the sources and evapotranspiration of water to improve the effects of best management practices on such resources. Isotopes are ideal tracers for investigation of hydrological processes such as transport and mixing because they provide a conservative fingerprint that is intrinsic to the water molecules (Gat 1996; Clark and Fritz 1997; Criss 1999). The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of water in rivers and streams are commonly used to estimate water sources, through examination of proportions among different reservoirs and evaporation processes within catchments (Dalai et al. 2002; Lambs et al. 2009; Bowen et al. 2011). Accordingly, spatial isotopic data can be used to reconstruct continental palaeoclimate and palaeohydrology since climatic signals controlling the isotopic composition of precipitation samples have been preserved in river samples (Hren et al. 2009; Bershaw et al. 2012). Additionally, the isotopic fingerprint of water samples can help evaluate aspects of biogeochemical cycling of nutrient and microbial production that are dependent on the water cycle, such as the formation of nitrate, sulfate, and phosphate via oxidation processes (Michener and Lajtha 2007).

The isotopic compositions of water from different areas are affected by meteorological processes, which provide a characteristic fingerprint of their origin (Clark and Fritz 1997). The isotopic values of river water decrease northward roughly parallel to latitude in the eastern United

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States, while they decrease eastward from the Pacific Ocean to the top of the Rocky Mountains and then increase eastward along the eastern flanks of the Rockies in the western United States (Kendall and Coplen 2001). The waters of major Indian rivers are enriched with light isotopes in Himalayan rivers and with heavy isotopes in peninsular rivers in a northwest-southeast gradient (Lambs et al. 2005). The isotope signature of precipitation was found to be reasonably well preserved in both monsoon and non-monsoon seasons according to the regression analysis of  $\delta D$ - $\delta^{18}O$  data describing the Yamuna River (Dalai et al. 2002). Moreover, isotope balance calculations in the Indus River basin indicated that up to 72 % of the Indus discharge close to its mouth might be derived from the Mediterranean end-member (Karim and Veizer 2002).

Many studies have investigated the isotopic composition of precipitation and controlling factors in China, especially in the Himalayas and western China (Ding et al. 2009; Tian et al. 2001, 2007; Yao et al. 2009; Wen et al. 2012; Zhao et al. 2011, 2012). However, a few data are available for individual rivers such as the Yellow River (Su et al. 2003), Changjiang (Li et al. 2010; Ding et al. 2013), and other small rivers in western China (Liu et al. 2009; Yu et al. 2010). Moreover, the spatial isotopic compositions of

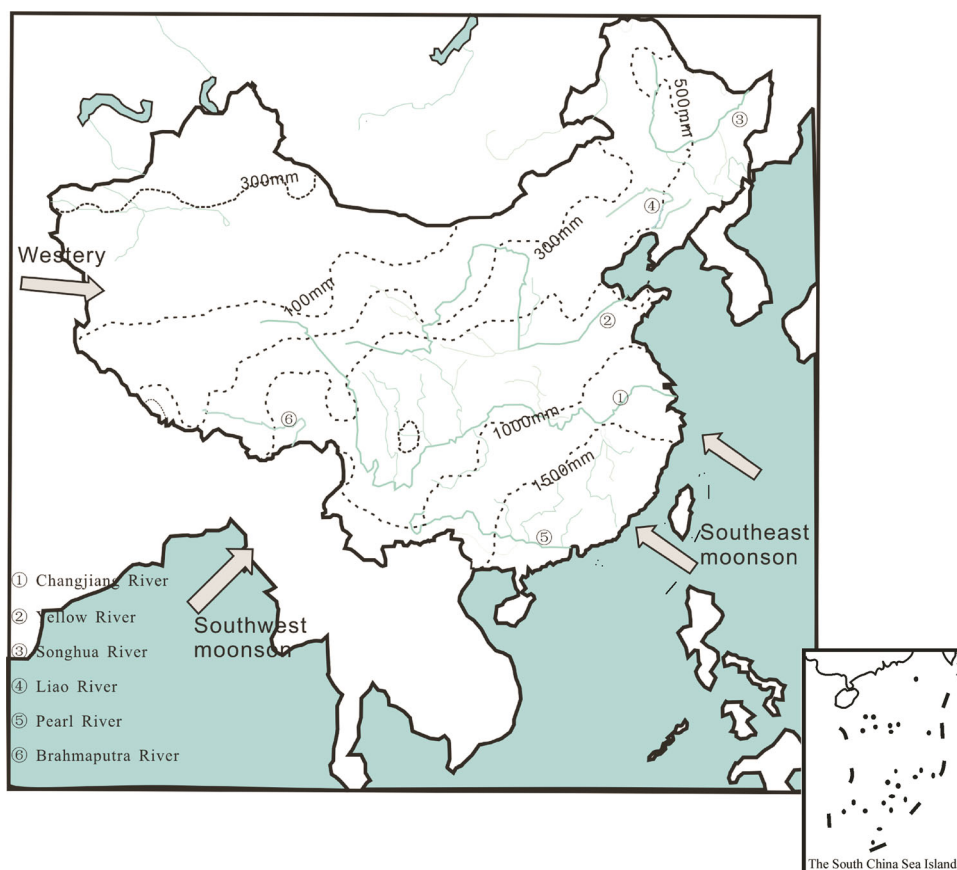
rivers have not been explored well in China. Therefore, in this study, data from our studies and other studies of major rivers of China are integrated to enable a better understanding of spatial and temporal variations in isotopes of water as well as *d*-excess.

## 2 Materials and methods

### 2.1 Characteristics of the major rivers in China

The major rivers in China are shown in Fig. 1. The two largest rivers (the Changjiang River and the Yellow River) originate from the Tibetan Plateau, and the basin area drained by these two rivers is approximately 25 % of the total area of mainland China. The Changjiang and Yellow Rivers are the two longest rivers in China. Both rivers originate in the eastern Tibetan Plateau at an elevation higher than 4,000 m. The Changjiang River has a basin area of  $180 \times 10^4 \text{ km}^2$  with a mainstream river length of over 6,300 km, while the Yellow River has a basin area of  $75.2 \times 10^4 \text{ km}^2$  with a mainstream river length of over 5,460 km (Table 1; Zhu 2007). The Songhua River Basin and Liao River Basin are located in northeast China. The

**Fig. 1** Major rivers, spatial variation of annual rainfall (dashed line) and moisture masses in China



**Table 1** The characteristics of major rivers in China (Zhu 2007)

	Length ( $\times 10^3$ km)	Discharge ( $\times 10^3$ m <sup>3</sup> /s)	Area ( $\times 10^4$ km <sup>2</sup> )	Annual average precipitation (mm)
Changjiang River	6.3	30.48	180	1,100
Yellow River	5.46	1.77	75.2	450
Pearl River	2.21	10.65	44.2	1,500
Songhua River	2.03	2.53	54.6	500
Liao River	1.39	0.18	20.6	400

Songhua River Basin is bounded by the Changbai Mountains in the east, Daxingan Mountains in the west, Xiaoxingan Mountains in the north, and Songliao watershed divide in the south; the Songhua drains an area of  $54.6 \times 10^4$  km<sup>2</sup> and has a length of 2,030 km. The Liao River has an area of  $2.3 \times 10^5$  km<sup>2</sup> and a length of 1,430 km. The Pearl River originates in Maxiong Mountain of the Yunnan-Guizhou Plateau at above 2,000 m and has a basin area  $44.2 \times 10^4$  km<sup>2</sup> and a mainstream river length of 2,214 km that runs through southern China; it has second greatest discharge of all the rivers in China.

Southern and eastern China are impacted by a southeast monsoon from the Pacific Ocean and a southwest monsoon from the Indian Ocean, which bring high rainfall in summer (Fig. 1). Additionally, the westerly and minor polar air mass in winter provide moisture for northern and western China (Tian et al. 2007). The majority of the Changjiang and Pearl River Basins are located in a humid subtropical zone subject to a typical monsoon climate, with precipitation that generally ranges from 800 to 2,000 mm/a. The Yellow River flows across the dry Loess Plateau of northern China, where precipitation is relatively low (approximately 500 mm/a). The Songhua and the Liao Rivers belong to the temperate continental monsoon climate zone, with some areas belonging to the cold temperate climate zone, which receives precipitation of 400 mm/a in the west and 800 mm/a in the east.

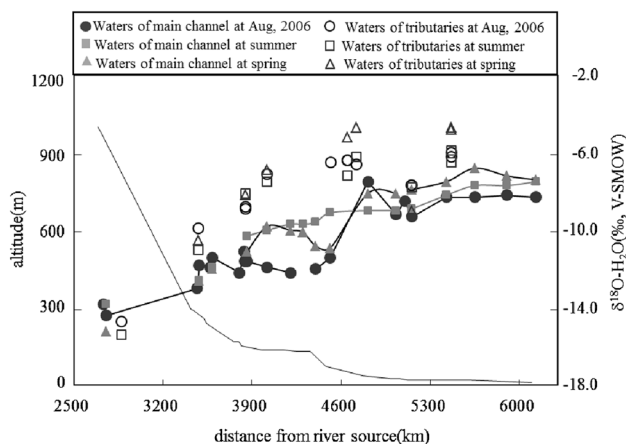
## 2.2 Sampling and analysis method

Water samples were collected by us from the main channel and the major tributaries of the Changjiang (Li et al. 2010), Liao (Yue et al. 2013), Yellow, and Songhua Rivers (Yue et al. 2014). One sampling campaign was carried out for the Changjiang during August, 2006. For other rivers, water samples were collected during the high flow season of 2010 and the low flow season of 2010, respectively. The  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of water were measured using a Micromass IsoPrime mass spectrometer coupled to an automated line after equilibration between O-water and CO<sub>2</sub> gas ( $\delta^{18}\text{O}$ ), and between H-water and H<sub>2</sub> gas with a Pt catalyst ( $\delta\text{D}$ ). The analytical precision of the  $\delta^{18}\text{O}$ -H<sub>2</sub>O was generally better than 0.2 ‰.  $\delta\text{D}$ -H<sub>2</sub>O has a precision of 3 ‰ for

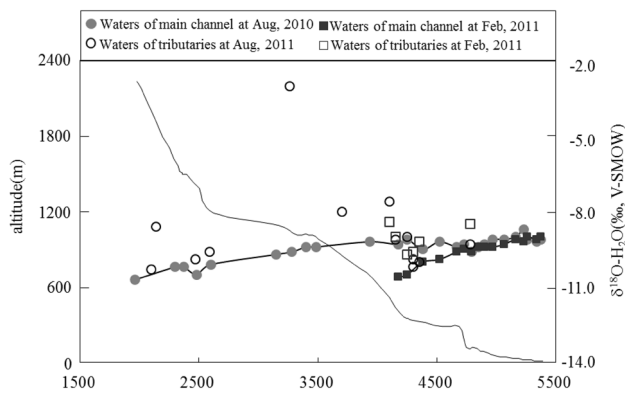
water samples in the Changjiang River (Li et al. 2010) and 2 ‰ for other rivers.

## 3 Results

There was wide variation in isotopic values from  $-14.7$  to  $-3.0$  ‰ for  $\delta^{18}\text{O}$  and  $-102.4$  to  $-32.2$  ‰ for  $\delta\text{D}$  in the rivers. The  $\delta^{18}\text{O}$ -H<sub>2</sub>O ranged from  $-14.7$  to  $-6.0$  ‰ with a mean value of  $-9.7$  ‰, while the  $\delta\text{D}$ -H<sub>2</sub>O ranged from  $-101.2$  to  $-32.2$  ‰ with a mean value of  $-72.4$  ‰ in the Changjiang River. Water from upstream was generally enriched with light isotopes relative to water from downstream in the Changjiang. The  $\delta^{18}\text{O}$  of water increased from  $-13.8$  to  $-8.3$  ‰ along the main channel of the Changjiang River due to the high isotopic values of water from tributaries (Fig. 2). The  $\delta^{18}\text{O}$  and  $\delta\text{D}$ -H<sub>2</sub>O were found to range from  $-10.7$  to  $-3.0$  ‰ and  $-74.7$  to  $-35.8$  ‰ in the Yellow River, with mean values of  $-9.3$  and  $-64.9$  ‰, respectively. An increasing trend in light  $\delta^{18}\text{O}$ -H<sub>2</sub>O was observed in the main channel of the Yellow River during the high flow season (Fig. 3), similar to that of the Changjiang River. During the low flow season, the water had



**Fig. 2** Oxygen isotopic compositions and altitude as functions of the distance from the source of the Changjiang River. Circles represents data from Li et al. (2010), squares and triangles represent data between 2003 and 2007 from Ding et al. (2013)



**Fig. 3** Oxygen isotopic compositions and altitude as functions of the distance from the source of the Yellow River

slight negative values of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  relative to the high flow season in the Yellow River.

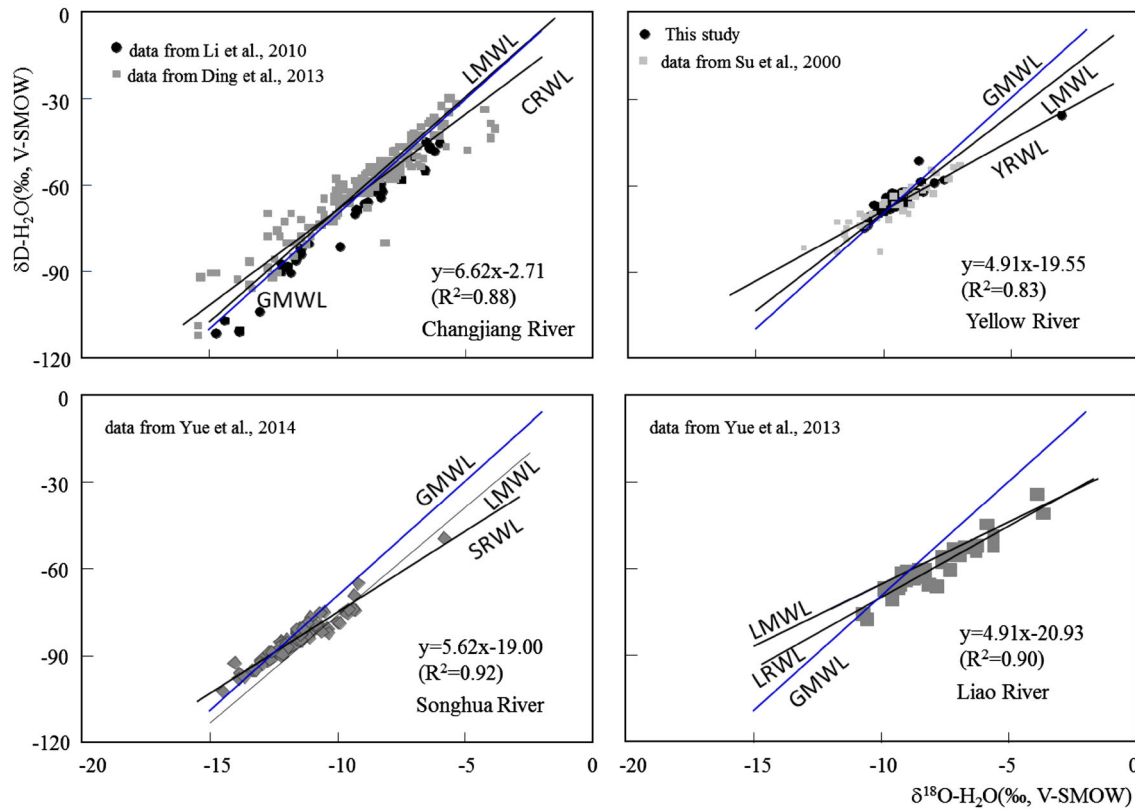
In the Songhua River, the river water contained stable hydrogen and oxygen isotope ratios ranging from  $-102.4$  to  $-49.5$  ‰ with a mean value of  $-83.8$  ‰ and from  $-14.5$  to  $-5.8$  ‰ with a mean value of  $-11.5$  ‰, respectively. The water with low  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values was located at tributaries and headwaters originating from the mountain. There was a narrow range of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values in water collected during low flow season from the Songhua River main channel, with water samples having  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values between  $-11.6$  and  $-9.9$  ‰. The water samples were generally enriched with heavy isotopes of water from the Liao River when compared with water from Songhua River, which had  $\delta^{18}\text{O}$ - and  $\delta\text{D}\text{-H}_2\text{O}$  values ranging from  $-10.7$  to  $-3.7$  ‰ with a mean value of  $-8.0$  ‰ and from  $-77.6$  to  $-34.6$  ‰ with a mean value of  $-60.4$  ‰, respectively.

## 4 Discussion

### 4.1 Comparison of isotopes of river water and precipitation in different basins

Stable isotope ratios in precipitation found to form the Global Meteoric Water Line (GMWL) were defined as  $\delta\text{D} = 8\delta^{18}\text{O} + 10$  on a global scale (Craig 1961). The more accurate GMWL of  $\delta\text{D} = 8.17\delta^{18}\text{O} + 10.35$  was then given based on the large database from Global Network of Isotope in Precipitation (GNIP) sites located worldwide (Rozanski et al. 1993). Local precipitation should be a major source of water for rivers, while evaporation would increase the oxygen and hydrogen isotope ratios of the residual fraction and the residual surface water to produce systematic linear deviations from the local meteoric water line (LMWL), which can be used to track the source of water and as tracers of hydrogeological processes (Clark and Fritz 1997; Wassenaar et al. 2011).

LMWLs in different basins were generated from the database of GNIP sites (IAEA 2006) based on locations in China (Fig. 4). A significant difference between LMWL and GMWL in different basins was observed except LMWL of the Changjiang Basin, which showed local water sources were impacted by different air masses and evaporation processes. The  $\delta\text{D}\text{-}\delta^{18}\text{O}$  plots of the data from different rivers are shown in Fig. 4. The Changjiang River water line produced by data from previous studies (Li et al. 2010; Ding et al. 2013) is  $\delta\text{D} = 6.62\delta^{18}\text{O} - 2.71$  ( $R^2 = 0.88$ ,  $p < 0.005$ ), which differed from that of the Chanjiang Basin somewhat, with an LMWL of  $\delta\text{D} = 7.83\delta^{18}\text{O} + 9.65$  ( $R^2 = 0.92$ ) being present in the Changjiang Basin. These findings suggest that multi water sources in the upper reach and evaporation in some tributaries or lakes in the middle and lower reaches resulted in the difference. Linear regression of the Yellow River water line results in the equation of  $\delta\text{D} = 4.91\delta^{18}\text{O} - 19.55$  ( $R^2 = 0.83$ ,  $p < 0.005$ ), which has a slope lower than that from the LMWL of  $\delta\text{D} = 6.86\delta^{18}\text{O} - 0.95$  ( $R^2 = 0.93$ ) in the Yellow Basin. The river water lines of the Songhua and Liao Rivers generated from water isotopic analyses were  $\delta\text{D} = 5.62\delta^{18}\text{O} - 19.00$  ( $R^2 = 0.92$ ,  $p < 0.001$ ) and  $\delta\text{D} = 4.91\delta^{18}\text{O} - 20.93$  ( $R^2 = 0.90$ ,  $p < 0.001$ ), respectively. The local meteoric water lines of the Songhua and Liao Basins were  $\delta\text{D} = 7.48\delta^{18}\text{O} - 0.98$  ( $R^2 = 0.97$ ) and  $\delta\text{D} = 4.28\delta^{18}\text{O} - 22.57$  ( $R^2 = 0.84$ ), respectively. In western China, evaporation was the major reason for the shift in isotopes of water due to limited precipitation and high evapotranspiration rates, which lead to residual surface water being enriched with heavy isotopes (Su et al. 2003; Zhao et al. 2011). Indeed, LMWL slopes of less than five have been reported in the Great Basin and other arid parts of the western United States (Kendall and Coplen 2001). The slopes of linear regression from the Yellow River and the Songhua River are lower than those of the LMWL, which suggests that significant loss of water by direct evaporation shifts the isotopes of water, especially in some individual tributaries. Another possible explanation for the difference between the river water line and LMWL in the Songhua Basin might be the limited data describing precipitation from just two cities in GNIP sites. Similar slopes of regression analysis of  $\delta\text{D}\text{-}\delta^{18}\text{O}$  data between river water and precipitation were observed at New Delhi during the same period (Dalai et al. 2002). It showed that there was little evaporation from river surfaces or soils in the hydrological continuum with surface water based on similar slopes of the linear regression between the river water line and LMWL in the Indus River (Karim and Veizer 2002). The slopes of the Liao River Water Line and the LMWL were generally less than five, and there was no significant difference in slopes between the Liao River Water Line and the LMWL. The pattern of slope might indicate that evaporation processes from surface water did not play a major role in formation of



**Fig. 4** Scatter plots of  $\delta^{18}O$  and  $\delta D$  in different rivers of China. The slopes of regression in the Changjiang River and Yellow River are generated by all plots in the figure

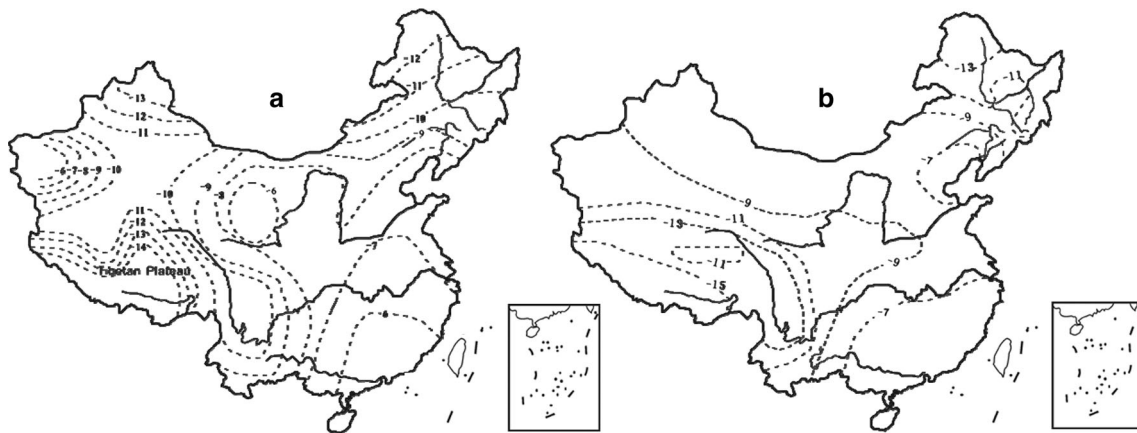
isotopic compositions in the Liao River during the sampling periods.

#### 4.2 Spatial variation of $\delta^{18}O-H_2O$ in major rivers of China and controlling factors

The isotopic compositions of precipitation are influenced by temperature, altitude, continental effects, latitude, and amount and source of vapor (Dansgaard 1964; Rozanski et al. 1993; Clark and Fritz 1997), which should be responsible for distribution of isotopes in river water being mainly derived from modern precipitation. The moisture for precipitation in China mainly included the southwest monsoon from the Indian Ocean, the southeast monsoon from the Pacific Ocean, and moisture from the westerlies (Numaguti 1999). The moisture from the westerlies would produce precipitation with relatively heavy oxygen in northwest China due to significant local moisture recycling (Tian et al. 2001) when compared with precipitation from monsoons, especially the southwest monsoon. As indicated by Fig. 5, the  $\delta^{18}O$  value of weighted precipitation is generally between  $-9$  and  $-6$  ‰ in most areas located in the south, east, southwest, and northwest of China. Meteoric water in the Tibetan Plateau and mountain areas of

northeast and western China generally has  $\delta^{18}O$  values lower than  $-10$  ‰ (Luo et al. 2008; Zhang and Yao 1998; Zhao et al. 2012). Specifically, the lowest  $\delta^{18}O$  values were observed in rivers in the southern Tibetan Plateau due to movement of water vapor from the southeast monsoon along the southern boundary of the Asian Continent and the southern slope of the Himalayas (Bershaw et al. 2012; Yao et al. 2009).

Water enriched in light isotopes in the upper reaches of the Changjiang and Yellow Rivers originated from the Tibetan Plateau. The  $\delta^{18}O$  value of the first sample from the main channel of the Changjiang River was  $-13.8$  ‰, which was lower than that of other water samples from the main channel due to the river originating from a mountain area. During most months, the  $\delta^{18}O$  value of precipitation weighted monthly for Yushu station located on the upper tributary of Changjiang River had values lower than  $-12$  ‰ (Tian et al. 2007). The isotopic pattern of these water samples suggested that alpine precipitation and snowmelt were the major source for the upper reach of the Changjiang River during summer, mainly reflecting the altitude effect. The increasing trend was observed from different sampling periods (Fig. 2) due to water contribution from tributaries with relatively high  $\delta^{18}O$  values,



**Fig. 5** The contour of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values (‰) in mainland of China. **a** precipitation, modified from studies (Zhang and Yao 1998; Luo et al. 2008); **b** river waters based on data during summer mentioned in the text

which is similar to the results of other studies (Dalai et al. 2002; Karim and Veizer 2002; Lambs et al. 2009). There were two distinct increases in  $\delta^{18}\text{O}$  values in the main channel of the Changjiang River. The first was due to water from other tributaries in the Sichuan Basin, such as Minjiang River ( $-9.9$  ‰), Jialinjiang River ( $-8.8$  ‰), and Wujiang River ( $-7.1$  ‰). The latter increase was due to water from Dongting Lake and nearby tributaries, which have a large discharge in the middle reach and generally show  $\delta^{18}\text{O}$  values near  $-6.5$  ‰. In the lower reach, the  $\delta^{18}\text{O}$  values of water in the main channel of the Changjiang River were stable due to there being few large tributaries.

The  $\delta^{18}\text{O}$  value of the first sample from the main channel of the Yellow River was near  $-11$  ‰, which was lower than those of water samples from the main channel (Fig. 3), and similar to the trend observed in the Changjiang River. The headwater in the Yellow River has higher  $\delta^{18}\text{O}$  values than that from the Changjiang River, and there is a significantly negative relationship between precipitation  $\delta^{18}\text{O}$  and altitude in the northern Tibetan Plateau (Luo et al. 2008; Zhao et al. 2012). During summer, the moisture at the south of the Tibetan Plateau is affected by the southwest monsoon, while the mid-latitude westerlies provide moisture for the northern part of west China. The pattern of precipitation influenced by altitude and mixing of airmasses should be responsible for the distribution of isotopic compositions in the Tibetan Plateau (Tian et al. 2007; Bershaw et al. 2012), which lead to water in the northern Tibetan Plateau being enriched with heavy isotopes. Collectively, these effects of different  $\delta^{18}\text{O}$  of precipitation at different places might be responsible for the higher  $\delta^{18}\text{O}$  values in headwater of the Yellow River than that in the Changjiang River. The  $\delta^{18}\text{O}$  values have a relatively narrow range between  $-10.7$  and  $-9.0$  ‰ in the main channel of the Yellow River when compared with the Changjiang River. However, there was a wide variance of

$\delta^{18}\text{O}$  values in water samples collected from tributaries ranging from  $-10.3$  to  $-3.0$  ‰, which indicated that evaporation leads to large water loss in some tributaries due to the arid climate in northwest China.

There is an increasing trend of  $\delta^{18}\text{O}$  values with a range from  $-9.5$  to  $-6.2$  ‰ in the main channel of the Liao River. The river water that originated in the mountains in the east of the Liao Basin had lower  $\delta^{18}\text{O}$  values than that from the west of the Liao Basin owing to the impact of the westerlies. Evaporation was likely another reason for the high  $\delta^{18}\text{O}$  values above  $-6$  ‰ observed in several tributaries that have low discharge of water in the river channel when sampling. However, only a slight increasing trend was observed in  $\delta^{18}\text{O}$  values in the main channel of the Songhua River during the sampling period. The water from tributaries originating in the Daxingan Mountains in the west had low  $\delta^{18}\text{O}$  values that primarily ranged from  $-14$  to  $-12$  ‰, while water from the tributaries originating from the Changbai Mountains in the east had  $\delta^{18}\text{O}$  values primarily ranging from  $-13$  to  $-11$  ‰ in the Songhua Basin. The distribution of  $\delta^{18}\text{O}$  values in these two rivers is in accordance with the difference in weighted  $\delta^{18}\text{O}$  values in precipitation based on the database for these basins (IAEA 2006), which showed that the weighted  $\delta^{18}\text{O}$  values of precipitation were  $-8.3$  ‰ for Liao Basin and  $-10.2$  ‰ for the Songhua Basin. The relatively high annual precipitation contents in the Songhua Basin were likely responsible for this pattern due to the basin being more strongly influenced by monsoons than that in the Liao Basin.

There are few  $\delta^{18}\text{O}\text{-H}_2\text{O}$  data available for the Pearl River. The water from several small streams flowing into Pearl River has  $\delta^{18}\text{O}$  values ranging from  $-9$  to  $-6$  ‰ in the southern Guizhou Plateau (Li et al. 2013), while the majority ranged from  $-7$  to  $-6$  ‰ for river water flowing into Pearl River. The  $\delta^{18}\text{O}$  values from underground river water in Guilin in the Pearl River basin ranged from  $-6.6$

to  $-5.8\text{‰}$  (Huang et al. 2013), while the weighted precipitation  $\delta^{18}\text{O}$  values were close to  $-6\text{‰}$  at Guilin ( $-6.3\text{‰}$ ), Liuzhou ( $-6.4\text{‰}$ ), and Guangzhou ( $-5.9\text{‰}$ ) in the Pearl River basin (IAEA 2006). These data suggested that the  $\delta^{18}\text{O}$  values in the Pearl River might be close to  $-6\text{‰}$ , especially for water in the middle and lower reaches. Many studies based on dual isotopes of water have been conducted in rivers of southern Tibet for paleoelevation reconstruction and to determine methods of controlling factors for patterns of distribution of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  (Ding et al. 2009; Hren et al. 2009). The results of these studies have suggested that the unique pattern of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values in Tibetan rivers was mainly influenced by elevation and mixing between the southwest monsoon from the Indian Ocean and westerly moisture sources from central Asia. The Brahmaputra River originates in the Himalayas and flows across southern Tibet into India. The river has a basin area of  $24.1 \times 10^4 \text{ km}^2$  with a mainstream river length of over 2,210 km in China. The isotopic compositions of water in the upper Brahmaputra have depleted  $\delta^{18}\text{O}$  values ranging from  $-20$  to  $-15\text{‰}$  in southern Tibet (Ding et al. 2009; Hren et al. 2009). An increasing trend of  $\delta^{18}\text{O}$  values from south to north were observed with increasing altitude and  $\delta^{18}\text{O}$  values of the river water in the north of the Tibetan Plateau primarily ranged from  $-12$  to  $-8\text{‰}$  (Ding et al. 2009) due to isotopic characteristics of different air masses in Tibet. In Xinjiang Province of west China, the  $\delta^{18}\text{O}$  value was found to be close to  $-9\text{‰}$  in the Kaidu River in the south of Xinjiang Province (Liu et al. 2009), while the headwater of the Urumqi River had a  $\delta^{18}\text{O}$  value of about  $-10\text{‰}$  in the middle of Xinjiang Province (Zhang et al. 2003). It has been reported that the mean value of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  was  $-6.3\text{‰}$  in surface water of Beijing in northern China (Zhai et al. 2011), while water from the mouth of Minjiang River in southern China has a  $\delta^{18}\text{O}$  value of  $-6.5\text{‰}$  (Zhang et al. 2012). Based on the above discussion, the contour of  $\delta^{18}\text{O}\text{-H}_2\text{O}$  for river water in summer could be roughly mapped (Fig. 5). This map was generated using data collected from rivers across in China, excluding data from the main channels of large rivers. The spatial variation in  $\delta^{18}\text{O}$  values for river water fit the distribution pattern of  $\delta^{18}\text{O}$  of the meteoric water well regardless of limited data sources and lack of a monitoring network. In most areas of China,  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values in rivers mainly ranged from  $-9$  to  $-7\text{‰}$ . The river waters enriched with light isotopes were mainly located in the Tibetan Plateau and northeast China. Water with more positive values above  $-7\text{‰}$  in rivers was found in southern China and in the Bohai Sea surrounding northern China. However, the headwaters of the large river might be influenced by snowmelt and lake recharge water with long term evaporation (Ding et al. 2013), which would produce a slight deviation for  $\delta^{18}\text{O}\text{-H}_2\text{O}$ , especially for streams

derived from the Tibetan Plateau. Another possible deviation was caused by over evaporation in small tributaries in northern and western China due to the arid and semiarid climate. Of course, contouring the spatial distribution of the isotopic composition of river water would present a number of challenges (Kendall and Coplen 2001) due to possible temporal variation and different size basins, different extent of evaporation, as well as unweighted data in the large area. More studies and data sources are needed to understand spatial variation of water isotopes and sources.

#### 4.3 Seasonal variation of isotopic composition of river water

In southern and eastern China, the precipitation generally has more negative  $\delta^{18}\text{O}$  values in summer than winter due to the summer monsoon (Zhao et al. 2012). There were no significant differences in the isotopic values found in river water from Changjiang rivers between spring and summer throughout the five-year sampling period (Ding et al. 2013). The lowest  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values were found in August in Chongqing station of the upper reaches based on semi-monthly sampling in the Changjiang River (Lu et al. 2012), which might have been due to the contribution of water from snowmelt and precipitation in Tibet during summer. Poor seasonal correspondence of  $\delta^{18}\text{O}$  values has been reported for many sites in the United States (Kendall and Coplen 2001). The average  $\delta^{18}\text{O}$  values of  $-11.4\text{‰}$  and  $\delta\text{D}\text{-H}_2\text{O}$  values of  $-82.2\text{‰}$  in the dry season were similar to those for  $\delta^{18}\text{O}$  of  $-11.5\text{‰}$  and  $\delta\text{D}\text{-H}_2\text{O}$  of  $-82.6\text{‰}$  during the wet season based on a comparison of data from the same sampling sites in the Songhua River. A possible reason for this seasonal pattern is that monsoon precipitation is the major river water supply in the monsoon domain, which could account for up to 80 % of the total river water supplied annually (Yao et al. 2009). In general, the low amount of precipitation should contribute less water to rivers during the dry season. This pattern differs from that observed in other studies showing that heavy isotopes in the Tien and Hau rivers were enriched during the dry season (November to April), indicating seasonal variation in the Mekong River Basin of Southeast Asia (Nguyen et al. 2012). However, slightly depleted  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values were observed in the middle reaches of the Yellow River (Fig. 3), which might have been due to evaporation in summer and to that portion of the river having a different water source. In the Yellow River, the mean values of  $\delta^{18}\text{O}$  and  $\delta\text{D}\text{-H}_2\text{O}$  in the dry season ranged from  $-9.4$  to  $-66.1\text{‰}$ , respectively, slightly lower than the values of  $\delta^{18}\text{O}$  and  $\delta\text{D}\text{-H}_2\text{O}$  of  $-9.2$  and  $-63.7\text{‰}$ , respectively, during the wet season based on data from the same sampling sites. These results are similar to those of previous study (Su et al. 2003) in which no distinct

seasonal variation of isotopic compositions in water from the Yellow River were observed.

The  $\delta^{18}\text{O}$  values of precipitation in winter were lower than those in summer throughout the west and most of the North China due to precipitation being influenced by the polar air mass in winter (Tian et al. 2001; Zhao et al. 2012). It has been reported that the values of  $\delta^{18}\text{O}$  in April to June are lower due to snowmelt, while they are higher at the end of summer due to local rainfall in the Garonne River (Lambs et al. 2009). The alpine river water in Lulang in southeast Tibet was found to have more negative  $\delta^{18}\text{O}$  values between August and November, indicating that monsoon precipitation was the major source of water to this stream (Yang et al. 2009). These findings revealed that moisture entering the headwaters of the Heihe River Basin was derived predominantly from the westerly and polar air masses, leading to the more depleted  $\delta^{18}\text{O}$  values during the dry season (Zhao et al. 2011). Additionally, evaporation will lead to residual waters being enriched with heavy isotopes under high temperature conditions during the wet season (Clark and Fritz 1997). During the dry season, the water had mean  $\delta^{18}\text{O}$  and  $\delta\text{D-H}_2\text{O}$  values of  $-8.7$  and  $-61.6$  ‰, respectively, which were lower than the mean values of  $\delta^{18}\text{O}$  and  $\delta\text{D-H}_2\text{O}$  of  $-7.7$  and  $-58.9$  ‰, respectively, that were observed during the wet season at the same sampling sites. The seasonal pattern of dual isotopes of river water samples might suggest that evaporation and different water mass influenced the isotopic composition in the Liao River, with the former being responsible for the small difference in  $\delta\text{D}$  values between seasons. Moreover, long term monitoring should be conducted to enable a better understanding of temporal variations in water sources based on isotopic analysis of rivers in China.

#### 4.4 The variation of $d$ -excess in river water

The deuterium excess ( $d$ -excess) in precipitation is defined as the y-intercept when the slope = 8, expressed by  $d = \delta\text{D} - 8 \times \delta^{18}\text{O}$  (Dansgaard 1964). This equation could reflect differences in humidity between vapor source and evaporation (Clark and Fritz 1997; Rozanski et al. 1993) although the analyzed precision of  $\delta^{18}\text{O}$  and  $\delta\text{D-H}_2\text{O}$  would introduce uncertainties of the calculation of  $d$ -excess values. The  $d$ -excess values in water from Changjiang River ranged from  $-2.2$  to  $10$  ‰ with a mean value of  $4.5$  ‰, which is different from the mean of  $10.6$  ‰ determined based on the isotopic data obtained from multiple sampling campaigns (Ding et al. 2013), suggesting the influence by hydrological condition under different sampling campaigns. The water in the Yellow River was found to have  $d$ -excess values ranging from  $-11.8$  to  $17.3$  ‰ with a mean value of  $9.6$  ‰, which is similar to the range

of  $-2.9$  to  $19.7$  ‰ with a mean value of  $8.5$  ‰ observed for the Songhua River. The lowest mean value of  $3.8$  ‰ for  $d$ -excess values was found in Liao River waters, where they ranged from  $-11.9$  to  $12.1$  ‰. More negative  $d$ -excess values might suggest that evapotranspiration is impacting the water isotopic compositions. The high  $d$ -excess and low slope of the  $\delta^{18}\text{O}$ - $\delta\text{D}$  regression line ( $<8$ ) in precipitation suggest that kinetic evapotranspiration influenced the isotopic shift in the source region under low humidity conditions (Clark and Fritz 1997). The  $d$ -excess values were higher than the long-term average value of the Indian monsoon ( $8$  ‰), which reflected contributions from water vapor originating in the Mediterranean ( $22$  ‰) or other inland seas (Karim and Veizer 2002). Several water samples from the tributaries of the Yellow River, the Songhua River, and the Liao River had  $d$ -excess values higher than  $15$ , which was far above the mean value of the rivers. These findings may indicate that the water in these regions was partly derived from vapor recycling due to a portion of these basins being impacted by semi-arid and arid climates.

As indicated in Fig. 6, there were significant negative relationships between  $d$ -excess and  $\delta^{18}\text{O}$  values in the Yellow River ( $d = -3.1\delta^{18}\text{O} - 19.4$ ,  $R^2 = 0.73$ ,  $p < 0.001$ ), the Songhua River ( $d = -2.3\delta^{18}\text{O} - 19.0$ ,  $R^2 = 0.68$ ,  $p < 0.001$ ), and the Liao River ( $d = -3.1\delta^{18}\text{O} - 20.9$ ,  $R^2 = 0.78$ ,  $p < 0.001$ ). The significant inverse trend between  $\delta^{18}\text{O}$  values and  $d$ -excess in the Yamuna River system suggests different mixing proportions of snow/glacial melt and precipitation (Dalai et al. 2002). In this study, water samples with  $d$ -excess values below  $0$  generally had high  $\delta^{18}\text{O}$  values, and samples with these values were only collected from small tributaries or tributaries discharged from lake systems. This pattern suggests that the evaporation of surface water leads to water loss and shifting isotopic compositions in these rivers. However, the relationship between  $d$ -excess and  $\delta^{18}\text{O}$  values in the Changjiang River did not show a similar

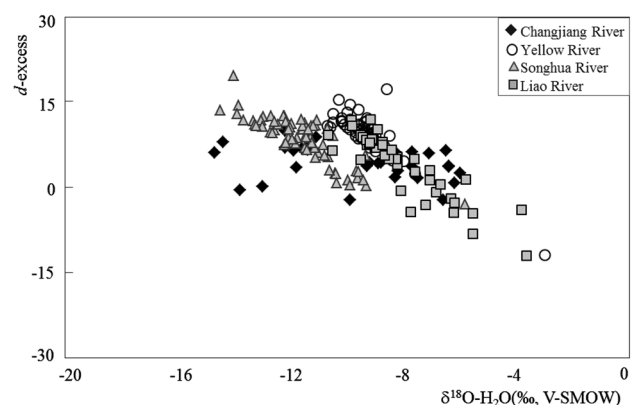


Fig. 6  $\delta^{18}\text{O}$  and  $d$ -excess values in different rivers of China



pattern ( $d = -0.4\delta^{18}\text{O} + 0.87$ ,  $R^2 = 0.10$ ). A slight negative trend was found based on data from another study (Ding et al. 2013), in which  $d = -1.8\delta^{18}\text{O} - 5.3$  ( $R^2 = 0.39$ ). These results suggest that multiple factors influenced isotopic compositions of river water in the Changjiang Basin, such as mixing between glacial melt and different water masses from tributaries and local precipitation, as well as evaporation effects. Meanwhile, the high precision of  $\delta\text{D}$  analysis by laser spectroscopy analyzer (Wassenaar et al. 2011) would be better to understand the variations of  $d$ -excess values and the controlling factors. Moreover, there was no clear relationship between  $d$ -excess and  $\delta^{18}\text{O}$  values for the entire dataset, which is similar to earlier results (Kendall and Coplen 2001).

There was no significant spatial pattern of  $d$ -excess values for precipitation based on data at GNIP sites in China (IAEA 2006). The monsoonal precipitation in summer at the Tibetan Plateau has low  $d$ -excess and dual isotopic values when compared with precipitation in winter due to westerly effects (Yao et al. 2009). In stream water in the southern Tibetan Plateau, the deuterium excess values are characterized by  $d$  values above +10 ‰ in water from below 4 km and a wide range of values from -7 to +15 ‰ (Hren et al. 2009). The  $d$ -excess values ranged from 6.9 to 14.5 ‰ with a mean value of 10.2 ‰ in the Lasha River in the southern Tibetan Plateau (Yu et al. 2010). Most stream water was found to have  $d$ -excess values close to 8 ‰ based on the data from southern Guizhou province in the Pearl River Basin (Li et al. 2013). Based on this rough assessment, river water generally has  $d$ -excess values below 10 ‰ in southern and eastern China and a wide range of values in western and northern China due to evapotranspiration of air masses and evaporation from the water surface under the arid/semi-arid conditions of the region.

## 5 Conclusions

Water was sampled from the Changjiang, Yellow, Songhua, and Liao Rivers to evaluate spatial and temporal variation of isotopes of water as well as  $d$ -excess in rivers of China. There is a wide range of isotopic values in water in major rivers of China. Within a river, the altitude effect influences the isotopic characteristics significantly, showing water from upstream was generally enriched with light isotopes. The slopes of equations describing river water values were generally slightly lower than the LMWL generated by data from GNIP sites. In the four investigated rivers, the evaporation process remains limited in the Changjiang and Songhua Rivers, and the Yellow and Liao Rivers present relatively high evaporation as deduced from the slope close to 5. The rough contour of  $\delta^{18}\text{O}$  values in summer for river water fits the distribution pattern of  $\delta^{18}\text{O}$

of the meteoric water in China regardless of limited data sources and lack of a monitoring network. The spatial pattern has showed that  $\delta^{18}\text{O}\text{-H}_2\text{O}$  values in rivers mainly range from -9 to -7 ‰ for most of China, but samples from the Tibetan Plateau and northeast China have lower values. The  $\delta^{18}\text{O}$  values in the middle and lower reaches of the Pearl River and other rivers in southern China might be enriched in heavy isotopes due to relatively high isotopic values in the rain water. Meanwhile, some rivers in northern and northwest China have relative high  $\delta^{18}\text{O}$  values due to the evaporation effect. In general, there is a wide variation of isotopic values of river waters in the summer compared with those in the winter. However, the slight distinct seasonal variation of isotopic compositions found in these rivers (aside from the Songhua) might be caused by river water mainly derived from summer monsoons across the majority of China. River water with relatively low  $d$ -excess values has more positive  $\delta^{18}\text{O}$  values in rivers of northern and western China, indicating that the evaporation in the tributaries of large rivers leads to water loss. Furthermore, long-term monitoring networks should be established and more samples should be evaluated to enable a better understanding of the water source and circulation at a regional scale, which could improve the management of water resources in major rivers of China.

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