Spatio-temporal variation of stable isotopes of river waters, water source identification and water security in the Heishui Valley (China) during the dry-season

Yuhong Liu · Shuqing An · Zhen Xu · Ningjiang Fan · Jun Cui · Zhongsheng Wang · Shirong Liu · Jiayong Pan · Guanghui Lin

Abstract Spatial variations of δD and $\delta^{18}O$ among seven tributaries and their water sources were investigated in the Heishui Valley of the Yangtze River, China during the dry-season in 2004. A one-way ANOVA (analysis of variation) test showed that both δD ($p<0.01$) and $\delta^{18}O$ ($p=0.045$) spatially varied among the seven tributaries. The plot of $\delta^{18}O$ versus δD for the river water collected at different locations showed that isotopic fractionation occurred during the snow and glacial melting process. The depleted $\delta^{18}O$ and δD in the tributary waters distributed above the local meteoric water line (LMWL) suggested that the glacial and early snowpack meltwater largely recharged these streams during the early spring. The meltwater was isotopically distinguishable from the precipitation and river water, which had been evaporated during warmer and drier times. If glaciers and snow accumulation diminish with future climate warming, the recharge of these tributaries' baseflow will decline and the security of the water resource in this watershed will be threatened.

Résumé Les variations spatiales de δD et $\delta^{18}O$ le long de sept affluents et de leurs sources ont été étudiées dans la Vallée de Heishui de la Rivière Yangtze, en Chine, durant la saison sèche de 2004. Un test ANOVA (analyse de la variance) à un facteur a montré que δD ($p<0.01$) et $\delta^{18}O$ ($p=0.045$) sont tous les deux spatialement variables le long des sept affluents. Le graphique $\delta^{18}O$ versus δD de l'eau de la rivière récoltée en différents endroits montre que le fractionnement isotopique apparaît durant la fonte de la neige et des glaces. Les $\delta^{18}O$ et δD appauvris dans les affluents distribués au dessus de la ligne météoritique locale (LMWL en anglais), suggèrent que les eaux de la fonte des neiges précoces et des glaciers ont largement rechargé les cours d'eau au début du printemps. L'eau de la fonte a été isotopiquement distinguée des précipitations et de l'eau de la rivière, qui été évaporée durant les périodes plus chaudes et plus sèches. Si les glaciers et l'accumulation de la neige diminuent avec les futurs changements climatiques, la recharge de l'écoulement de base de ces affluents diminuera et la sécurité de la ressource en eau de ce bassin versant sera menacée.

Resumen Las variaciones espaciales de δD y $\delta^{18}O$ entre siete tributarios y sus fuentes de agua fueron investigadas en el Heishui Valley del Yangtze River, China durante la estación seca de 2004. Una prueba ANOVA de una vía (análisis de variación) mostró que ambos δD ($p<0.01$) y $\delta^{18}O$ ($p=0.045$) variaron espacialmente entre los siete tributarios. La gráfica de δD versus $\delta^{18}O$ para el agua del río muestreada en diferentes localidades mostró que el fraccionamiento isotópico ocurrió durante el proceso de derretimiento de nieve y glaciar. La reducción de $\delta^{18}O$ y δD en el agua de los tributarios distribuida sobre la línea de agua meteórica local (LMWL) sugirió que el glaciar y deshielo temprano de la nieve compactada recargó fuertemente estos arroyos durante el comienzo de la primavera. El agua resultado del deshielo fue isotopica-

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mente distinguible del agua precipitada y del agua del río, la cual ha sido evaporada durante épocas más calientes y secas. Si la acumulación de glaciares y nieve disminuye con un futuro calentamiento climático, la recarga de los flujos base de estos tributarios disminuirá y la seguridad de recursos del agua en esta cuenca estará amenazada.

Key words China · Climate change · Snow and glacial meltwater · Stable isotopes · Water-resource conservation

Introduction

Variations in the stable isotopic composition of water can be used as useful tracers in studying hydrological cycles (Buttle 1998) where there may be potentially different sources of water. For example, river runoff can be derived from different sources including surface flow, meltwater, rainfall and groundwater (Leopoldo et al. 1987; Cooper et al. 1991; McDonnel et al. 1991; Neal et al. 1997). Similarly, groundwater may be recharged by different water sources, including lakes and other surface water bodies as well as precipitation (Jacobson et al. 1991; Geyh and Gu 1991; Tantawi et al. 1998).

Identifying and tracing the source of different waters in mixtures can be done if it can be assumed that the isotopic composition of the water has not changed once mixing has occurred. For example, evaporation enriches the isotopic composition of surface water bodies. This isotopic signal of evaporation can then be identified and traced as the water subsequently moves down rivers or within groundwater systems (Fontes et al. 1979a, 1979b; Simpson and Herczeg 1991; Friedman et al. 1992; McKenna et al. 1992; Martinelli et al. 1996). Alternatively, the isotopically depleted composition of melting snow and ice, originally formed under colder times of precipitation, also can be used to trace water if the water is not subsequently fractionated by evaporation along flow paths (Obradovic and Sklash 1986; Gibson et al. 1993; Cooper et al. 1993).

Glacial recession caused by global warming may potentially compromise water supplies in some places, particularly rivers (Thompson 2000; Whitfield 2001; Mark et al. 2002), and in these places, the stable isotopes of water can be used to determine the extent to which glacial meltwater is a water source. In China, the water-supply problem has become acute (Liu and Diamond 2005). Of the water resources, Yangtze River provides one third of the nation's water (Varis and Vakkilainen 2001), and is critical to eastern and middle Chinese economic growth. The headwaters of the Yangtze River are located in the Tibetan Plateau, where glacial meltwater provides baseflow water during winter and early spring when there is little rainfall (Wang et al. 2006). However, due to the enhanced greenhouse effect, global warming may diminish the extent to which this critical baseflow can be sustained to the Yangtze River (Thompson 2000).

This study presents the research results on the isotopic composition, spatial and temporal variation and water-source characteristics of surface waters in the Heishui Valley, one of the upper large catchments in the Yangtze River, located at the southeast rim of the Tibetan Plateau. The goal of this study was to determine the extent to which snow and glacial meltwater contributes to baseflow during the dry season, and thereby provide critical background information on the water security from which future management decisions of the Yangtze River can be made.

Study area

The Yangtze River, the longest river in China, has an upper course 4,511 km long and an upper catchment area of 10^6 km^2 or so from the Geladandong snow-covered mountain in the Tibetan Plateau to the Yichang City in the Hubei Province (Chen 2000). The Minjiang River, which originates on Gonggang Mountain, is an important tributary in the upper course of Yangtze River and occupies the transition region between the Tibetan Plateau and the Sichuan Basin (Pu 2000; Li et al. 2003). The upper course of the Minjiang River is 340 km long and 24,000 km^2 in area. The Heishui River captures water originating from the Yanggong Mountain and is the largest tributary of the Minjiang River's course in western Sichuan Province. The Heishui Valley covers 7,240 km^2 and includes about 30% of the total area of the upper Minjiang River. The main tributary of the Heishui River is 122 km long with a 1,048-m drop in elevation from the Maoergai Grassland to Shaba village. In the Heishui Valley, there are 19 modern glaciers (Wang 2003). The average annual runoff of the Heishui River is 4.4×10^9 m^3/year.

Based on the records of the Heishui precipitation station—32°03.00′N, 102°35.4′E; altitude of 2,400 m above sea level (asl)—the average annual temperature is 9°C and the average annual rainfall is 833 mm in the Heishui Valley. The climate is best described as a monsoon climate, affected by two atmospheric circulations. Western dry circulation from the Atlantic Ocean prevails during winter, and wet southwesterly monsoons enter from the Indian Ocean during summer (Zhang et al. 2002). There is a clear wet-season (May to October) and a dry-season (November to April; Chen 1995). Because of this seasonality, it should be possible to test the hypothesis that glacial meltwater in the river system should be isotopically distinguishable from precipitation and water that may have been subsequently evaporated during warmer and drier times.

Methods

Field sampling

Locations where surface waters were collected during 19–30 March, 31 March to 2 April and 5–8 April 2004 are shown in Fig. 1. Seven sample sites were chosen at the

Fig. 1 Location and topography of the study area. **a** Location of the Heishui Valley in Sichuan Province, central China, **b** the location of Minjiang River in the upper course of Yangtze River, and Heishui Valley in the upper course of the Minjiang River catchment, and **c** the topography of Heishui Valley, river courses and the sampling sites. (Modification from Liu et al. 2006) ▶

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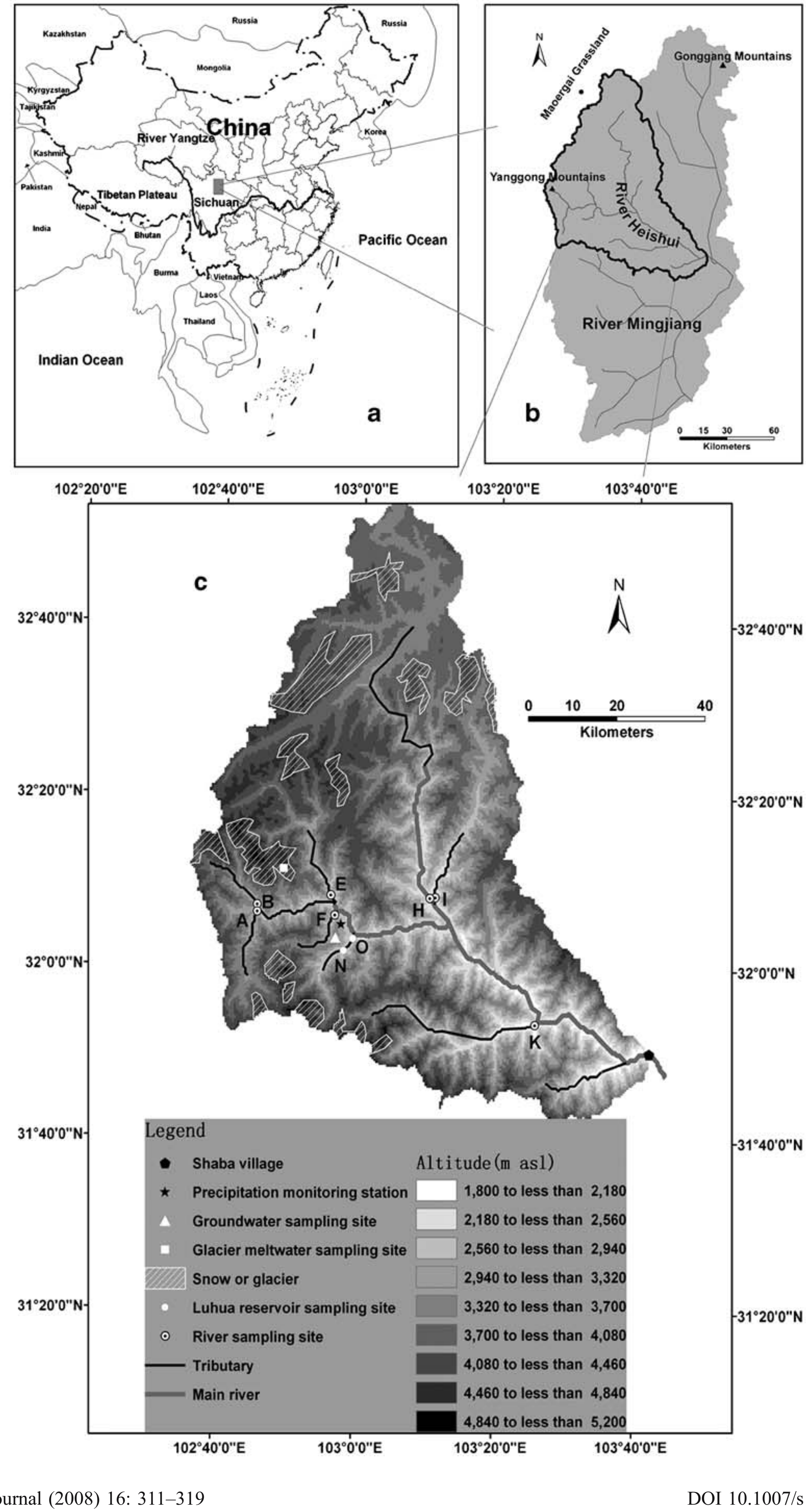

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outlet of the tributaries. The sampling sites were named A, B, E, F, H, I, K for the tributaries, respectively. Water samples were collected three times per day, at 8:00 am, 12:00 pm and 4:00 pm, respectively, for three days. At sites E, H, water samples were collected at depths of 0.1 and 0.5 m. Where the stream depth was less than 0.2 m, water samples from sites A, B, F, I and K were collected only at the depth of 0.1 m. At inlet "N" and outlet "O", sites of the Luhua reservoir formed naturally in 2000 with acreage of 15 km^2, one water sample was collected each day at 6:00 pm for three days. There were 87 surface water samples collected totally. The stable isotope values of every water sample were measured separately.

Meanwhile, groundwater was sampled from three springs at an altitude of about 2,500 m (32°04.11′N, 102°56.57′E) near the Heishui precipitation station on 25 March 2004. Glacier meltwater was sampled at the Sandagu Glacier at an altitude of 4,800 m (32°12.28′N, 102°48.79′E) on 3 April 2004 (Fig. 1). Thirty-three precipitation samples were also collected at the Heishui precipitation station (32°03.00′N, 102°35.4′E; altitude of 2400 m). These samples included two rain samples during March–April in 2004, 19 rain samples during May–June in 2004, 10 rain samples during September–October in 2004, and two snow samples in December in 2004 and January in 2005.

Measurement of δD and δ^{18}O

Water samples were measured by Thermal Finnigan MAT DelTaplus XP with a precision of 3‰ for δ D and 0.5‰ for δ ^{18}O. The final results were expressed in relation to the value for Standard Mean Ocean Water (SMOW):

$$\delta^{18}\mathrm{O} = \left\{ \left[\left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{\mathrm{sample}} - \left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{\mathrm{standard}} \right] \Big/ \left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{\mathrm{standard}} \right\} \times 10^3 \left(^0\!/_{00}\right)$$

$$\delta\mathrm{D} = \left\{ \left[(\mathrm{D/H})_{\mathrm{sample}} - \mathrm{DH}_{\mathrm{standard}} \right] \Big/ (\mathrm{D/H})_{\mathrm{standard}} \right\} \times 10^3 \left(^0\!/_{00}\right)$$

Where, oxygen and hydrogen isotope ratios are expressed by δ^{18}O and δD, respectively. $(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{sample}}$ or $(\mathrm{D/H})_{\mathrm{sample}}$ is the isotope ratio in the sampled water, $(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{standard}}$ or $\mathrm{D/H}_{\mathrm{standard}}$ is isotope ratio in standard mean ocean water.

Data analysis

A one-way ANOVA (analysis of variance) of river water isotopes among seven sampling sites was done using Statistical Package for Social Science (SPSS) to test the significant difference among the mean of multiple samples of each site. The concept of d excess (d=δD–8δ^{18}O) was proposed by Dansgaard (1964) and this was used to characterize the deuterium excess in global precipitation. In the current study, the d excess was used to describe the characteristics of river water at various altitudes.

The variations of δ^{18}O and δD of the seven sampling sites are displayed by using box plots (following the guidance of Learning 2000; Chen et al. 2000; Hager and Johnstone 2003). Bivariate plot of δ^{18}O versus δD is used to analyze the relationship between river water and the local precipitation. The local meteoric water line (LMWL) is controlled by local climatic factors. For regional or local investigation, it is important to compare surface water and groundwater with the LMWL (Clark and Fritz 1997).

The average altitude of each catchment was used in analysis of altitude effects because the river water of each tributary was derived from its own whole watershed, and computed by a digital elevation model (Hall 1998) and Hydro model of ArcGIS from Environmental Systems Research Institute (ESRI).

Results

Spatial variations of δD and δ^{18}O

The one-way ANOVA for river water of sampling sites from seven tributaries (A, B, E, F, H, I, K) showed that the variations in δD among sampling sites were most significant ($p<0.01$), whereas the variations of δ^{18}O were significant, but the test value ($p=0.045$) was close to the test criterion ($p=0.05$; Table 1). These results showed that a spatial variation existed among these tributaries (Fig. 2). From tributary A to K, mean river water δD varied from −86.2 to −76.6‰ (Fig. 2a) and mean river water δ^{18}O showed a steady increase from −13.4 to −12.1‰ (Fig. 2b).

Temporal variations of deuterium (d) excess and δ^{18}O

Figure 3a showed d excess within the seven tributaries during the spring melting period (from March 21 to April

Table 1 One-way ANOVA comparison of the stable isotope values of seven tributaries

Sites	Longtitude/latitude	Altitude (m asl)	Number of samples	δ^{18}O (‰) Average±SD	δD (‰) Average±SD
Tributary water A	102°45.89′E/32°06.12′N	2,740	9	−86.27.9	−12.91.9
Tributary water B	102°45.92′E/32°06.17′N	2,740	9	−88.87.9	−13.40.5
Tributary water E	102°55.62′E/32°09.44′N	2,400	18	−87.31.8	−13.10.6
Tributary water F	102°55.88′E/32°06.38′N	2,380	9	−82.62.7	−12.70.6
Tributary water H	103°11.99′E/32°06.26N	2,050	18	−83.14.3	−12.60.4
Tributary water I	103°12.28′E/32°06.41N	2,040	9	−78.15.9	−12.20.3
Tributary water K	103°25.96′E/31°53.8′N	1,800	9	−76.62.4	−12.10.1
ANOVA test				$p=0.045$	$p<0.01$

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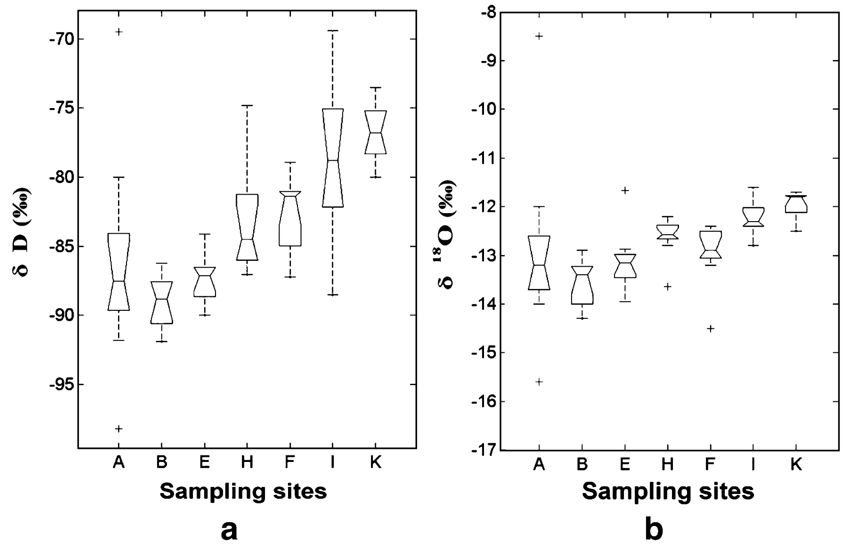

Fig. 2 Box plots of spatial variation of δD and $\delta^{18}O$ at different sampling sites. **a** Box plot of δD; **b** box plot of $\delta^{18}O$. Sampling sites A, B, E, F, H, I and K were in the outlets of their tributaries. The box plot has lines at the lower quartile, median, and upper quartile values. The *whiskers* of the box are lines extending from each end of the box to show the extent of the rest of the data. The *small crosses* (+) of the box are data with values beyond the ends of the whiskers

10). Most of d excess values of tributaries A, B, E, F, H, I, K distributed above 10‰, while three points of tributaries A and E distributing below the line (d excess = 10‰). According to the relationship between d excess and humidity, in which the higher d excess exists in relatively lower humidity, the d excess data showed every tributary was under the condition of lower humidity during the research period.

The $\delta^{18}O$ values of tributary B, F, H, I, K varied insignificantly or remained steady with time (Fig. 3b), while there were three water samples associated with sampling points A and E that showed significant variation. These are highlighted by ellipses in Fig. 3b and correspond to the three points below the line in Fig. 3a.

These results showed that temporal variability of isotopic composition within tributary B, F, H, I, K was insignificant, which indicated that water sources supplying the rivers were, on the whole, stable during the short sampling period. The exception was the significant variability found in tributaries A and E.

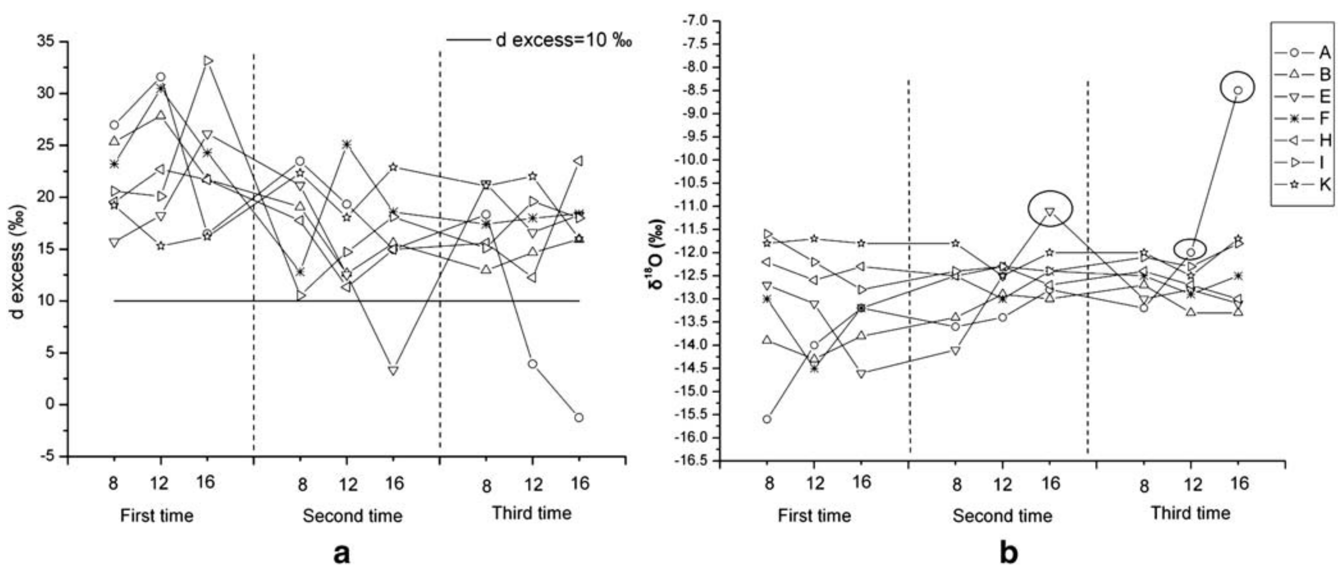

Fig. 3 Temporal variation of the stable isotopes at tributary sampling sites (A, B, E, F, H, I and K) during the spring melting period (March–April). **a** temporal variation of d excess; **b** temporal variation of $\delta^{18}O$. On the *x*-axis of each figure, 8, 12 and 16 denote sampling time each day (i.e. 8:00 am, 12:00 noon, 4:00 pm). Three water samples associated with sampling points A and E (showing significant variation) are highlighted by ellipses in **b** and correspond to the three points below the line in **a**, which means some rainwater mixing with early snowmelt water or later snowmelt water entering tributaries A and E on a large scale

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Identification of water sources

Based on a least square regression of the 33 precipitation samples, the LMWL was δD=9.3δ^{18}O + 25.9 (R=0.99; p=0.00; Fig. 4a). Most of the river-water samples fell above the LMWL and the regression line of these river waters (the 'river water line') was δD=6.3δ^{18}O–4.1(R= 0.73, p=0.00; Fig. 4b). Because the water exiting from the snowpack first during snowmelt was highly depleted isotopically, most of the river waters plotted above the LMWL were from early meltwater of snowpack, and they had depleted isotope values owing to the fractionation effect playing an important role during the melting process. In addition, there were four water samples that fell below the LMWL in Fig. 4b, which corresponded to the samples of tributaries A and E in the Fig. 3b. A possible reason for this is that there was occasionally some rainwater mixing with early snowmelt water or later snowmelt water entering the river during the sampling period on a large scale.

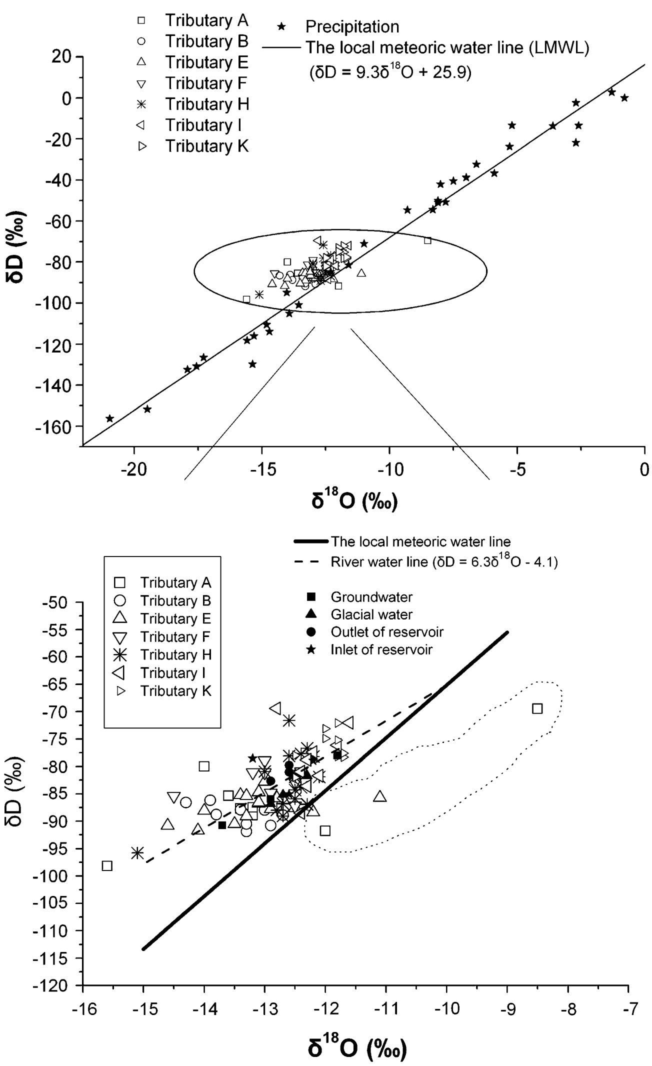

Fig. 4 Relationship between tributary waters, groundwater and glacial meltwater and the local meteoric water line (LMWL). Note: δD=9.3δ^{18}O+25.9 (R=0.97) is the local meteoric water line and computed by 31 rain and two snow samples from the precipitation station in 2004–2005

Glacial waters, reservoir waters and groundwaters distributed among the river waters above the LMWL and there were major overlaps among all these waters in this cluster. Glacial waters, reservoir waters and groundwaters most likely fall on a river water line (δD=6.3δ^{18}O–4.1). These also indicated that river waters, reservoir waters and groundwaters were very similar to glacier meltwaters that were sampled above an altitude of 4,800 m. Therefore, reservoir waters, groundwaters and river waters were mainly supplied with earlier meltwater from snowpack and glaciers during the spring melting period.

Discussions

Reasons for spatial and temporal variation of δD and δ^{18}O in the Heishui Valley

Most stable isotopic studies of river catchments focus on the smaller catchments (<100 km^2; Buttle 1994), under the assumption of spatial and/or temporal homogeneity of the water isotope signature (Buttle 1998; Rodhe 1998). The work in Heishui Valley was carried out at a large spatial scale (7,240 km^2), and clearly showed the significant difference in mean values of both δD and δ^{18}O among seven sites. The possible reasons for the spatial variation include different isotope fractionation through physical and chemical processes along different water-flow paths and different water sources from which the flows were derived.

Fractionation always occurs during evaporation and may contribute to the variations of δD and δ^{18}O in surface water (Merlivat 1978; Jouzel 1986). In the Heishui Valley, mean air temperature is 8°C, mean water temperature is 10° C, and mean humidity is 57% during the dry-season (Zhang 2002; Jiang et al. 2004; Yoshimura 2004). Roles of evaporation from water under snowpack may be negligible due to low temperature and lack of turbulent exchange with the atmosphere during the spring melting period (Rodhe 1998; Stichler and Schotterer 2000). The results of water samples collected from the seven tributaries and from the inlet and outlet of the Luhua natural reservoir showed that evaporation had insignificant effects on both δD and δ^{18}O values of flowing water and even relatively stagnant water, because these waters were from early snowmelt water and distributed above the LMWL.

In most low-temperature environments, stable hydrogen and oxygen isotopes behave conservatively because any interactions with oxygen and hydrogen in the organic and geologic materials in the catchments will have a negligible effect on the ratios of isotopes of the water molecule when they move through the catchments (Kendll and Caldwell 1998). So these kinds of interactions probably are not important in variations of δD and δ^{18}O values when runoff moves through the river catchments.

Altitude is an important factor related to isotopic fractionation in areas with a large topographical range (Clark and Fritz 1997; McKenzie et al. 2001); higher

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altitude correlates to lower values of both δD and $\delta^{18}O$ (Craig 1961; Stichler and Schotterer 2000). Spatial variation of δD and $\delta^{18}O$ values of tributary sites in Heishui Valley should be controlled by different altitudes at which local precipitation occurs. The relationship between the values of δD and $\delta^{18}O$ and the average altitude of the catchments is shown in Fig. 5. δD and $\delta^{18}O$ become more negative with increasing altitude. The decrease of −0.2±0.04‰ in $\delta^{18}O$ and −1.9±0.2‰ in δD with each 100 m in altitude computed by the slope of regression equation in this study are similar to other research results, which include general altitude gradients in precipitation of −1.7±1.9‰/100 m for δD and −0.27± 0.26‰/100 m for $\delta^{18}O$ in the Kouris catchment, Cyprus (Boronina et al. 2005) and approximately −0.2‰/100 m in $\delta^{18}O$ in the Swiss Alps (Stichler and Schotterer 2000). Therefore, altitude is possibly a major reason why the isotopic composition of water in the tributaries varies spatially.

In addition, this study also showed that there were insignificantly temporal variations of $\delta^{18}O$ in tributaries B, F, H, I, K, while temporal variation of tributaries A and E was intense. This was because other water sources, which were different from the earlier snow and glacier meltwater, supplied tributary A and E at sampling time. For d excess as a function of humidity (Merlivat and Jouzel 1979; Clark and Fritz 1997), temporal variation of d excess reflected the fractionation during the snow melting process that occurred under conditions of lower humidity.

Water source and water security in the Heishui Valley

The southeast Tibetan Plateau is influenced by southwest monsoons from the Indian Ocean (Tian et al. 2001; Yang et al. 2006), and rainwater has lower values of δD and $\delta^{18}O$ because of its distance from the ocean and rain at higher elevation (Ingraham and Taylor 1991). In the Heishui Valley, the monsoon water vapor moves from northwest to southeast and, as it moves, the land altitude decreases, temperature increases, and evaporation is enhanced. This process may enrich residual monsoon water vapor from northwest to southeast, which should cause spatial variation of snowpack isotope content at different altitudes.

The results of this work show that the isotopic composition of some samples within the tributary water and groundwater (between 1,700 m and 2,700 m) was similar to that of glacial meltwater (above 4,800 m) above the LMWL (Fig. 4), and suggested that river waters at lower altitude may originally have come from earlier meltwater at higher altitudes. These meltwaters were highly depleted in δD and $\delta^{18}O$ and plotted above the LMWL; the meltwaters were isotopically distinguished from precipitation and water that may have been subsequently evaporated during warmer and drier times. The earlier low δD and $\delta^{18}O$ snowmelt should provide sufficiently distinct isotopic inputs for a useful interpretation of catchment flow processes (Unnikrishna et al. 2002).

In the Heishui Valley, present glaciers and permanent snow are currently distributed only on the peaks of high mountains (Zhang et al. 2002). Water resources in the Tibetan Plateau have decreased with shrinking glaciers and permanent snow snowpack (Shi and Li 1994; Kang 2005). With increasing temperatures as a result of climate change, relatively lower altitude melting water sources could decrease and eventually disappear. Therefore, water security is a vital challenge for this alpine valley during future dry seasons, especially in spring melting periods of the future.

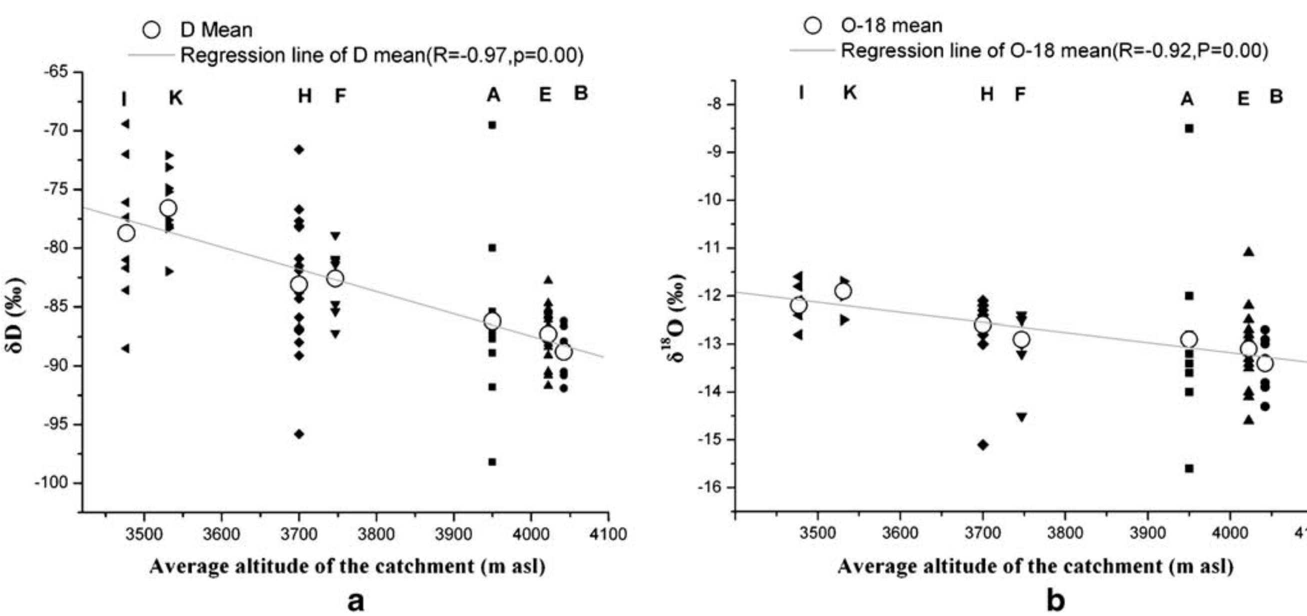

Fig. 5 Relationship between δD and $\delta^{18}O$ of different tributary sampling sites and average altitude of the catchments A, B, E, F, G, H, I and K. **a** Relationship between δD and average altitude of the catchments; **b** relationship between $\delta^{18}O$ and average altitude of the catchments

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Conclusions

In the Heishui Valley, the spatial variation of the stable hydrogen and oxygen isotopes from different tributaries was correlated with changes in altitude. According to the distribution of water samples in δD versus $\delta^{18}O$ space, most water samples plotted above the LMWL and were depleted in δD and $\delta^{18}O$, which indicated that the river waters and groundwaters were from the early snow meltwater and glaciers. If glaciers and snow accumulation at specific altitudes (above 4,800 m asl) diminish with future climate warming, the recharge of these tributaries' baseflow would be threatened during the dry season.

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