Journal of Hydrology (2008) **353**, 314–321

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journal homepage: www.elsevier.com/locate/jhydrol

Characteristics of water isotopes and hydrograph separation during the wet season in the Heishui River, China

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Received 31 December 2007; accepted 25 February 2008

KEYWORDS
Stable isotopes;
Spatial variations;
River water line;
Contribution

Summary Runoff generation and dynamics is an important issue in watershed and water resource management, but the mechanism in large scale is unclear and site-dependent. For this reason, spatial variations of δD and $\delta^{18}O$ of river water and their sources within large-area of the Heishui Valley of the upper Yangtze River in western China were investigated during the wet season. A total 117 river water samples were collected at 13 sampling sites located at the junction of the principal river course and its tributaries. The results showed no spatial variations of either δD or $\delta^{18}O$ values existed among tributary sampling sites A, B, E, F, H and I during the wet season, and significantly spatial variation occurred between tributary sampling sites A, B, E, F, H, I and site K; which indicated different proportions of rain entering river water should lead to spatial variation of water isotopes. The hydrograph separation analysis, based on the isotope data of river water, meltwater and rain water samples, showed the contribution of snow and glacier meltwater varied from 63.8% to 92.6%, and that of rain varied from 7.4% to 36.2%; which meant that snow and glacier meltwater was the main supplying water source of baseflow in the Heishui Valley. And the roles of glacier and snow meltwater should be significantly noticed in water resource management in this alpine valley at the rim of the Tibetan Plateau.

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0022-1694/$ - see front matter
doi:10.1016/j.jhydrol.2008.02.017

Introduction

The water shortage and low use efficiency make china thirsty, and the loss of glacier and wetland in the western plateau will exaggerate this thirst in the future (Wang et al., 2006), while the same situation happens in other places of the world (e.g. Mark, 2002). Therefore, it is important to understand the runoff generation mechanism when studying headwater and river water dynamics, especially the seasonal changes, sources and composition of the baseflow.

Leopoldo et al. (1987) reported that the runoff mainly came from surface flow along perennial streams in humid zones in Brazil. McDonnell et al. (1991) found that stream water in New Zealand was supplied partially by subsurface flow in the humid zone. Cooper et al. (1991) found that runoff derived mainly from meltwater, because a similarity in δ^{18}O existed between the stream water at peak flow and the pre-melt snow pack in the tundra of Northern Alaska. Geyh and Gu (1991) found that groundwater was recharged by high-intensity and sporadic rain (up to 100 mm/h) in the Gurinai grassland in Inner Mongolia. Thus, all the results show that components of river water may include surface flow, subsurface water, meltwater and ground water and their contribution is site-dependent.

The stable isotope ratios of hydrogen and oxygen of water samples can provide essential information about water dynamics within a given watershed (Ruck et al., 2007); it is useful to identify water sources by tracers of stable isotope hydrogen or oxygen, since different water sources are acting within a river at different seasons. In hydrograph separation analysis, the two-component model was widely used to compute the contributions of different components of river water. Mortathi et al. (1997) reported that the average surface runoff and baseflow (pre-event) contributions were 30.3% and 69.7%, respectively, in the Amazon River. Kendall (1993) believed that surface water and subsurface water contributions were 38% and 62%, respectively, in northeastern China, based on stable isotope oxygen data. Laudon and Slaymaker (1997) detected a much larger prestorm water fraction (60–90%) existent in the alpine basin of the coastal mountains of British Columbia, according to both stable isotope hydrogen and oxygen analyses of those waters. But, a little information was reported on the components and the generation mechanism of baseflow in a large watershed.

In this study, the identification of water sources, hydrograph separation analysis of different tributaries, and spatial variations of stable isotopes hydrogen and oxygen were conducted on large catchments of 7240 km^2. We attempted to: (1) compute the contribution of different water sources to baseflow during the wet season; and (2) clarify the causes of temporal and spatial variation of water isotopes. And we expected that the results will provide an insight for water resource and watershed management in a large-area.

Study areas

The Yangtze River, the longest river in China, has an upper course of 4511 km long and an upper catchment area of 1.0×10^6 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 is one of important tributaries in the upper course of Yangtze River and locates within the transition region between the Tibetan Plateau and the Sichuan Basin (Pu, 2000; Li et al., 2003). The Heishui River is the largest tributary of the Minjiang River and is 122 km long from the Maoergai Grassland to the Shaba village (Fig. 1).

According to the records of the Heishui precipitation station (32°03.00′N, 102°35.4′E; altitude of 2400 m above sea level (asl)), the average annual temperature is 9 °C and the average annual rain is 833 mm (Liu et al., 2008). The climate is 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).

Monthly precipitation data from 1971 to 2000 were provided by the Heishui precipitation station, and monthly runoff data from 1988 to 2002 were provided by the local hydrology stations which located in the catchment (Fig. 1). The precipitation fluctuates monthly between 3 mm and 155 mm (Fig. 2a), and there was a wet season (May–October) and a dry season (November–April). The similar variation existed for runoff (Fig. 2b). The trend of average monthly runoff was consistent with that of average monthly precipitation, which indicated that precipitation was the main reason of runoff variation; especially the rain was one of the main supplying sources of river water during the wet season. The amounts of precipitation and runoff in June were the highest among the twelve months. Shaba station collected more runoff than the Heishui, while the seasonal runoff dynamics are similar.

Methods

Field sampling

There were 13 sampling sites chosen within the junction of the river's principal course and its tributaries. The sampling sites were named C, D, G, L and M along the principal course, and A, B, E, F, H, I, J and K along the outlet of seven tributaries (Fig. 1). At each sampling site, water samples were collected at 8:00 a.m., 12:00 noon and 4:00 p.m. each day, and this regime was repeated for a total of three collection days. A total of 117 samples from the river were collected during the wet season. All water samples were collected by water collectors and stored in 250 ml non-reactive plastic bottles with rubber-seal caps. The sampling window ran from May 21rd through June 17th in 2004, technically during the wet season. The direct effects of floodwater on the river were avoided during the sampling time, according to curves of runoff provided by the hydrology station for Heishui County. Meanwhile, four rain samples were collected at June 2, 13, 14 and 15, respectively.

Measurement of δD and δ^{18}O

The measurement and analysis of water samples was completed using the Thermal Finnigan MAT DelTaplus XP. Accuracy of the measurements was ±3‰ for δD, and ±0.3‰ for

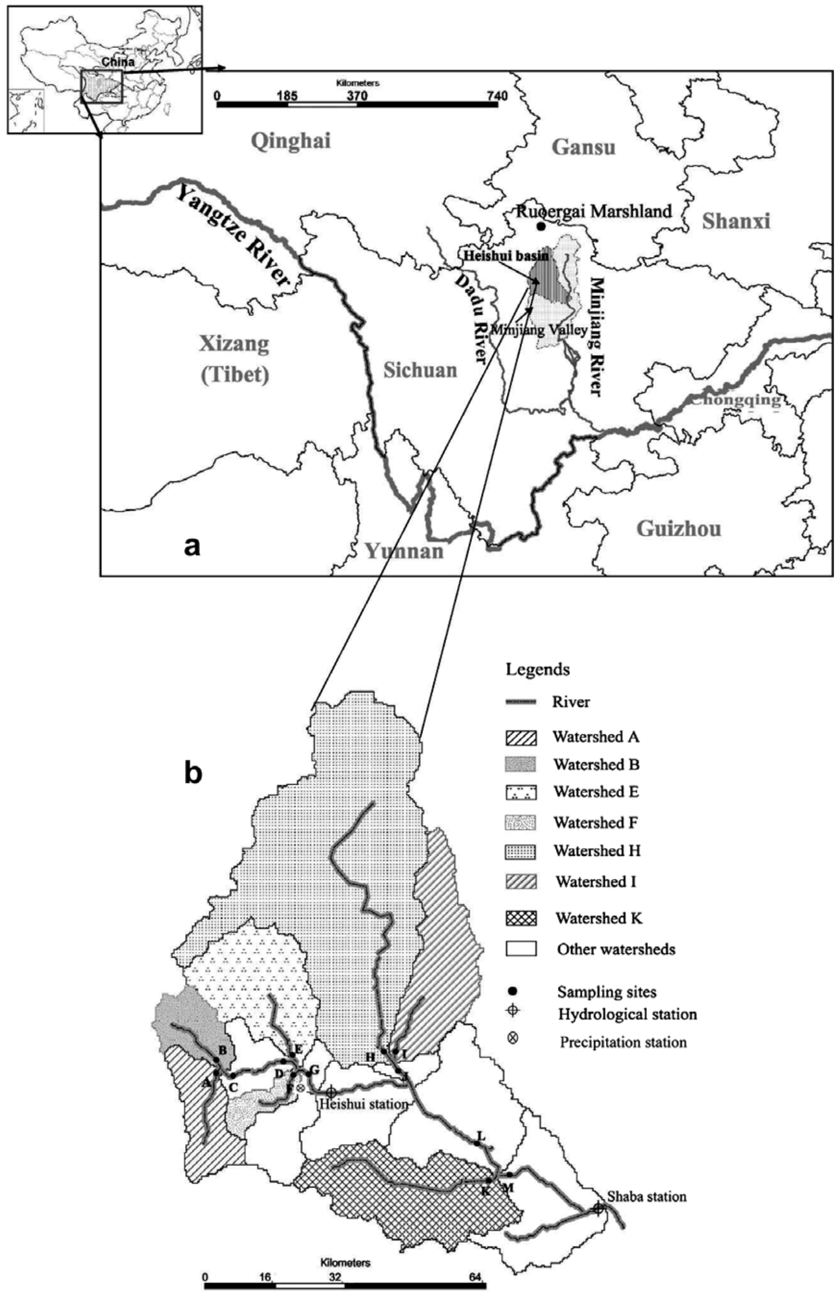

Figure 1 Map of the river course and the sampling sites. (a) The location of the Heishui Valley in western China; (b) The distribution of sampling sites in the Heishui Valley. Sampling sites C, D, G, L, and M were in the main stem river; sampling sites A, B, E, F, H, I and K were in tributaries. There were two hydrology stations and one climatic station in the Heishui Valley.

$\delta^{18}O$. The final results were expressed by the relative to the value over SMOW:

$$\delta^{18}O = [(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{SMOW}]/(^{18}O/^{16}O)_{SMOW} \times 10^3‰ \quad (1)$$

$$\delta D = [(D/H)_{sample} - (D/H)_{SMOW}]/(D/H)_{SMOW} \times 10^3‰ \quad (2)$$

Data analysis

A one-way analysis of variance (ANOVA) of the spatial variations of the waterborne isotopes was performed in order to test the significance of the variations. If the one-way ANOVA variation proved to be significantly different ($\alpha = 0.05$), MULTCOMPARE was then used to determine which variation was significantly different. The multiple-comparison was performed using Bonferroni's test at a 0.05 significance level (Learning, 2000) by Statistic Package for Social Science (SPSS). The spatial variations of water isotopes were displayed by BOX PLOT (Chen et al., 2000; Hager and Johnstone, 2003).

The relationship between river water and the local meteoric water line (LMWL) was displayed by bivariate plot of $\delta^{18}O$ versus δD. Since the local climatic factors affected the LMWL, comparing the different water samples with the LMWL was

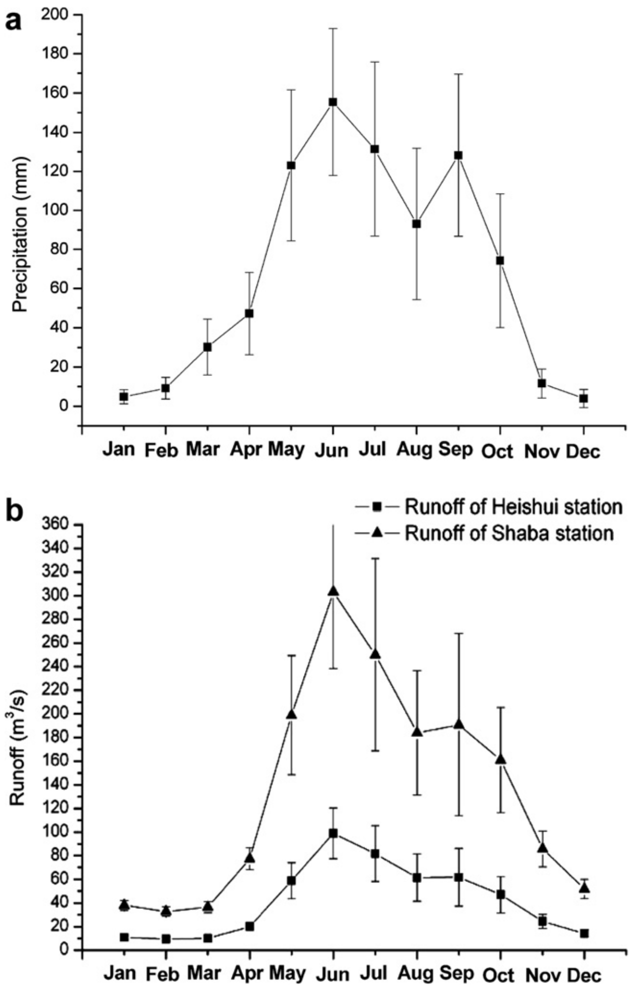

Figure 2 Monthly variations of precipitation (a) and runoff (b) in the Heishui valley. Data for precipitation is from 1971 to 2000 and data for runoff is from 1988 to 2000.

useful to test water source and isotopic fractionation for regional hydrology investigation (Clark and Fritz, 1997). LMWL was $\delta D = 9.3\delta^{18}O + 25.9$ and cited from previous report (Liu et al., 2008). Ground water values during the dry season were cited from previous report (Liu et al., 2008), too.

The measurement of mean contributions from different water sources within tributaries during the wet season was carried out by hydrograph separation analysis. In the hydrograph separation analysis, a two-component model, as described below, was used:

$$Q_t \times C_t = Q_s \times C_s + Q_p \times C_p; \tag{3}$$

$$Q_s + Q_p = Q_t \tag{4}$$

Q was the discharge, C was the concentration of the applicable tracer, and the subscripts t, s and p referred to total, event, and pre-event water components, respectively (Pinder and Jones, 1969). The value of river water during the wet season was used as the total, the average values of rain in each sub-watershed served as the event water, while the values of water samples collected from glacial and snow meltwater during the dry season was used as the pre-event water and cited from previous studies (Liu et al., 2008).

A method of volume weighted average value (VWA) was used to yield one constant isotopic input value of rain for hydrograph separation, which was described below (Mast et al., 1995; Laudon et al., 2002):

$$\mathrm{Ca} = \sum_{i=1}^{n} \mathrm{Cr}(i)M(i) / \sum_{i=1}^{n} M(i) \tag{5}$$

where Cave(Ca), Crain(i) (Cr(i)) and $M(i)$ expressed the average isotope values of rains, the isotope value of the rain and the rain volume during the sampling time, respectively. And the average δD or $\delta^{18}O$ of rain (Csub) in different sub-watersheds was obtained by using the average values of rains at the Heishui precipitation station (Cave) and isotopic variations with altitude and catchment parameters.

$$\mathrm{Csub} = \mathrm{Cave} \times (\mathrm{Hsub}/\mathrm{H_0}) \times \Delta\mathrm{C} \tag{6}$$

where Hsub was the average altitude of sub-watersheds and H_0 was the altitude of the Heishui precipitation station. ΔC was the decrease rate of $-0.2 \pm 0.04‰$ in $\delta^{18}O$ or $-1.9 \pm 0.2‰$ in δD with each 100 m in altitude (Liu et al., 2008).

The mean annual precipitation (P) distribution for seven watersheds was obtained from the spatial distribution of mean annual precipitation in the Minjiang valley (Jiang et al., 2004). The boundary lines of the Heishui Valley and their seven sub-watersheds were processed and overlapped on the spatial distribution by ArcGIS from environmental systems research institute (ESRI).

Results

Spatial variations of δD and $\delta^{18}O$ during the wet season

The one-way ANOVA results for the 13 sampling sites showed that the variations of δD or $\delta^{18}O$ values among sampling sites were significant during the wet season ($P < 0.05$). The multi-compare results of δD or $\delta^{18}O$ values showed that there was a significant difference existing between tributary K and tributaries A, B, E, F, H, I; while insignificant difference among tributaries A, B, E, F, H and I (Table 1). Meanwhile, significant tracer differences detected between the main stem river sites C, D, G, J and site L or M, and insignificant differences among the main stem river sites C, D, G and J for both $\delta^{18}O$ and δD values. Box plots of both δD and $\delta^{18}O$ values clearly displayed the spatial variations of δD and $\delta^{18}O$ values among all the sampling sites (Fig. 3). The spatial variations of δD or $\delta^{18}O$ values among the main stem river sites should be caused by spatial variations of water isotopes and different contribution of the tributaries.

Distribution of water stable isotope in the space of $\delta^{18}O$ versus δD

According to the distribution of river water in the space of $\delta^{18}O$ versus δD, most of the river water sample points were located above the local meteoric water line (LMWL) ($\delta D = 9.3\delta^{18}O + 25.9$), although some of them were more approaching the LMWL. It was obvious that the sample points of tributary K were isolated from those of others (Fig. 4), which indicated tributary K was significantly differ-

Table 1 Mean values of δD and $\delta^{18}O$ of river water during the wet season

Sampling sites	Sample number	$\delta^{18}O$ (‰)	δD (‰)	Longtitude(N)/Latitude (E)	Altitude (m)
A	9	−13.5 ± 0.4	−91.0 ± 3.1	102°45.89′/32°06.12′	2740
B	9	−13.6 ± 0.3	−91.3 ± 2.9	102°45.92′/32°06.17′	2740
C	9	−13.4 ± 0.3	−91.1 ± 4.6	102°48.49′/32°06.14′	2670
D	9	−13.5 ± 0.5	−89.4 ± 0.5	102°56.13′/32°07.16′	2400
E	9	−13.5 ± 0.3	−91.5 ± 3.6	102°55.62′/32°09.44′	2403
F	9	−13.2 ± 0.4	−88.5 ± 1.9	102°55.88′/32°06.38′	2380
G	9	−13.6 ± 0.3	−91.3 ± 2.5	102°58.26′/32°05.94′	2380
H	9	−13.3 ± 0.5	−89.6 ± 2.5	103°11.99′/32°06.26	2054
I	9	−13.1 ± 0.5	−86.7 ± 2.7	103°12.28′/32°06.41′	2040
J	9	−13.2 ± 0.4	−89.0 ± 3.2	103°12.74′/32°05.65′	2055
K	9	−12.0 ± 0.5	−78.4 ± 4.1	103°25.96′/31°53.8′	1799
L	9	−12.6 ± 0.6	−86.2 ± 2.7	103°25.46′/31°56.22′	1829
M	9	−12.4 ± 0.4	−12.4 ± 0.2	103°28.79′/31°54.98′	1769

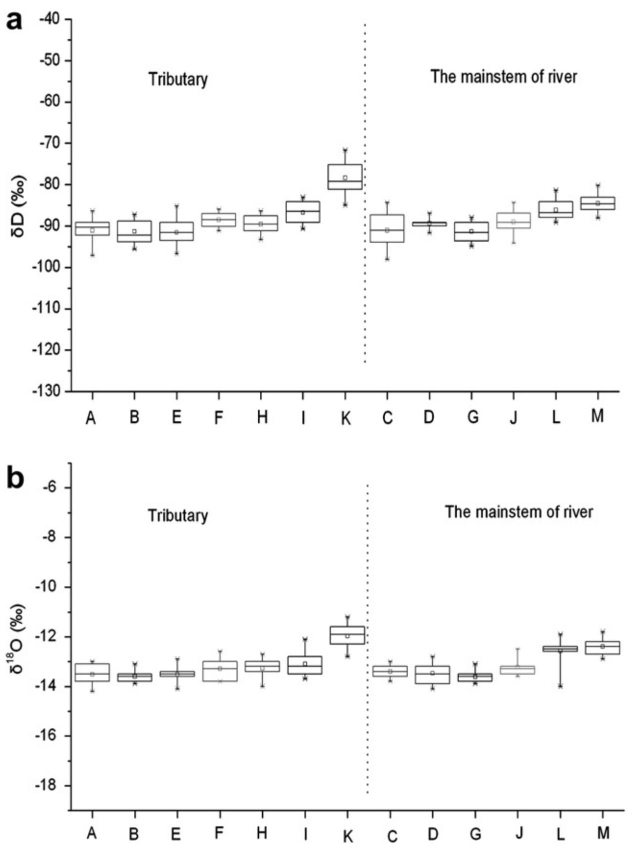

Figure 3 Box plots of spatial variations for δD (a) and $\delta^{18}O$ (b). Sampling sites C, D, G, L, and M were in the main stem river; sampling sites A, B, E, F, H, I, and K were in tributaries. Sampling site J was located at the junction of tributaries H and I. The box plot has lines at the lower 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 outliers of the box are data with values beyond the ends of the whiskers.

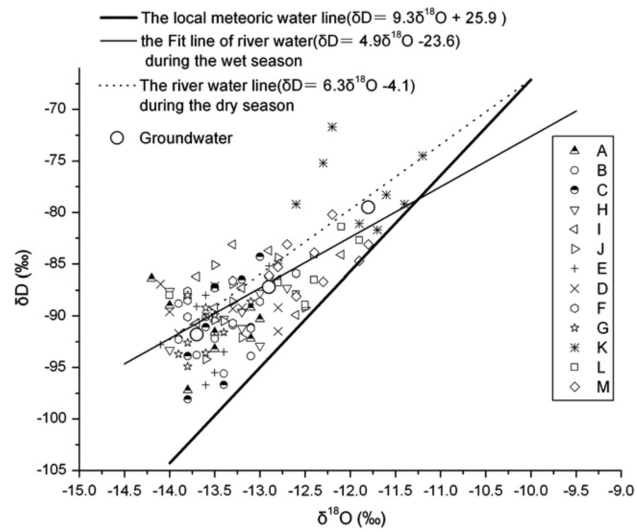

Figure 4 Distribution of river water data along the local meteoric water line (GMWL). The local Meteoric Water Line ($\delta D = 9.3\ \delta^{18}O + 25.9$) and the groundwater data during the dry season were cited from the report (Liu et al., 2008).

ent from other tributaries at water isotope values, and most points of other tributaries were overlapped, which displayed similarity in constitution of water sources. The fit line of river water samples for wet season was $\delta D = 4.9\delta^{18}O - 23.6$, which was different from the river water line ($\delta D = 6.3\delta^{18}O - 4.1$) during the dry season. This showed that river water during the wet season was different from that during the dry season. For sampling time belonged to the rainy season, it was possible for participation of rain. Groundwater samples distributed among the river water samples and were close to the river water line, which indicated that similarity existed among these water samples.

Mean contribution of different water sources in tributaries during the wet season

According to Eq. (5), the volume weighted average values of rain at the Heishui precipitation station was −81.5‰ in δD, −10.4‰ in $\delta^{18}O$ during the sampling period. The mean δD of rain in average altitude of seven sub-watersheds relatively to the precipitation station with an altitude of 2400 m were computed by Eq. (6), respectively (Table 2). For similarity of $\delta^{18}O$ existed between the two seasons, the δD was used to carry out hydrograph separation analysis. Based on Eqs. 3 and 4, the contribution of rain and the meltwater was computed with the hydrograph separation analysis. The contribution of glacial and snow meltwater varied from 63.8% to 92.6%, and that of rain varied from 7.4% to 36.2% within different sub-watersheds. This indicated that the river water during the wet season came mainly from snow and glacial meltwater. This result is different from the seasonal changes of precipitation and runoffs collected from the observatory stations (Fig. 2), which possibly meant that the main body of runoff was provided by snow and glacial melwater, while the rain provided the main part of the variation of the runoff.

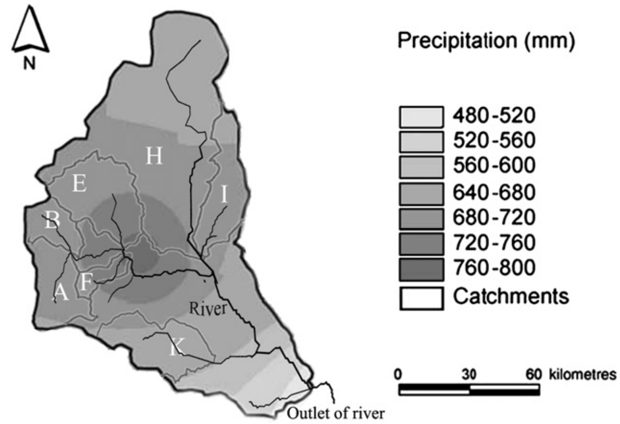

Figure 5 Spatial distribution of precipitation in the Heishui Valley. This figure was modified through ArcGIS from the report (Jiang et al., 2004). The boundary lines of the Heishui Valley and their seven sub-watersheds were overlapped on the spatial distribution of precipitation during the modification.

Discussion

Reasons of spatial and temporal variations of δD and $\delta^{18}O$ values of tributaries

Based on the results of spatial variations of δD and $\delta^{18}O$ within tributaries during the wet season, there were insignificant spatial variations of δD and $\delta^{18}O$ values among tributaries A, B, E, F, H, and I, but there were significant spatial variations between tributaries (A, B, E, F, H, I) and tributary K (Fig. 3). Why did this phenomenon occur? In general, the possible reasons included isotope fractionation by evaporation, altitude effects and different water sources they received (Leonitiadis and Nikolaou, 1999; Boronina et al., 2005; Liu et al., 2008). For the water samples distributing above the LMWL (Fig. 4), evaporation played unimportant role in the fractionation of water isotopes. Although altitude effects played a large role in isotopic variation in area with a large topographical range (Clark and Fritz, 1997; McKenzie et al., 2001), there was no obvious altitude effects displayed among tributaries A, B, E, F, H, and I. For rain season, the role of rain, as a supplying water source, was not ignored. The spatial distribution of rain was imbalance in the whole watershed, among which watershed K had relatively less precipitation amount (Fig. 5), which was proved by the lowest contribution of rain to watershed K, too (Table 2). This indicated that watershed K was affected slightly by the rain. And watershed K has the most heavy isotopes among the seven tributary (Table 1) caused by altitude effects. The similar isotopic values among tributaries A, B, E, F, H, and I were caused by participation of various proportion of rain. Therefore, patterns of rain and altitude effects would lead to difference in isotope values between tributaries (A, B, E, F, H, I) and tributary K.

At the same sites, Liu et al. (2008) discovered that there were significant spatial variations of δD and $\delta^{18}O$ among the tributaries A, B, E, F, H and I during the dry season, which were caused by altitude effect, but, there was insignificantly spatial variation among the tributaries A, B, E, F, H and I during the wet season in this study. During the dry season (November—April), snow and glacier meltwater was the main water source, while rain dominated the variation during the wet season (May—October) (Chen, 1995). In this study, both rain and snow and glacier meltwater have different proportions within baseflow (Table 2). This showed that mixed water sources could cause spatial differences among the tributaries A, B, E, F, H, I during the dry season to disappear during the wet season. By these analyses, we could find that isotope responses were often complex in

Table 2 Contribution of different water sources during the wet season

Watershed	Average watershed altitude	River water	Glacial and snow meltwater	Mean values of the rains	Contribution (%)	
	(m)	(D, ‰)	(D, ‰)	(D, ‰)	Meltwater	Rain
A	3800	−91.0 ± 3.1	−86.2 ± 7.9	−108.1 ± 2.8	78.1	21.9
B	3500	−91.3 ± 2.9	−88.8 ± 1.9	−102.4 ± 2.2	81.6	18.4
E	4000	−91.5 ± 3.6	−87.4 ± 1.8	−111.9 ± 3.2	83.2	16.7
F	3700	−88.5 ± 1.9	−82.6 ± 2.7	−106.2 ± 2.6	75.0	25.0
H	3800	−89.6 ± 2.5	−83.1 ± 4.3	−108.1 ± 2.8	74.0	26.0
I	3500	−86.7 ± 2.7	−78.7 ± 5.9	−102.4 ± 2.2	66.2	33.8
K	3500	−78.4 ± 4.1	−76.6 ± 3.1	−102.4 ± 2.2	93.0	6.9

The contribution was computed by the δD data River water is total, glacial and snow meltwater is the pre-event water, and the rain is event water. The mean values of the rain was modified by Eqs. 5 and 6, based on the rain samples collected in precipitation station. The isotope values of glacial and snow meltwater within tributary A, B, E, F, H, I, K during the dry season were cited from previous report (Liu et al., 2008).

large river, which reflected the cumulative influence of precipitation (e.g. water isotopic variation from dry to wet season) and included influence of different water sources and tributary mixing (Gibson et al., 2005).

At temporal scale, by *t*-test for pooled data at a 0.05 level of significance (Learning, 2000) between wet and the dry season, significant difference of δD existed at the most of tributary sampling sites except for K, and insignificant difference of $\delta^{18}O$ occurred at the most of tributary sampling sites except H and I between the dry and wet season. The most difference between the dry and wet season was that the numbers and amount of rain were increasing with time, and the isotopic values of rain became more negative in the wet season than that in the dry season (He et al., 2006). At the same site, comparison of electrical conductivity (EC) between the dry and wet season showed that the EC of the wet season became lower for participation of rain (Fan et al., 2006). As enrichment generally affected the δD values less than the $\delta^{18}O$ values (Boronina et al., 2005), the difference of δD was more obvious than that of $\delta^{18}O$ when rain entered into river water. As for those particular sampling sites including K, H and I, it was possible that the different proportions of rain mixed original river water.

Contributor to baseflow during the wet season

Stable isotopes D and ^{18}O have been successfully used to identify water sources (Sklash, 1990; Buttle, 1994) and separated hydrograph for computing the contributions of numerous water sources in a small spatial scale (e.g. Sklash, 1990; McDonnell et al., 1990; Kendall and McDonnell, 1998). In addition to small-scale catchment studies, the stable isotope of water have been applied in large river basin studies for partitioning relative contributions of flow derived from direct precipitation runoff, shallow and deep ground water and surface water (Gibson et al., 2005). In this study, hydrograph separation analysis showed successfully that glacier and snow meltwater of every estributary occupied more than 60% of its baseflow and runoff derived from rain contributed only 7% to 33% to the basflow of different tributaries during the sampling period at a large scale.

Some studies showed groundwater from lakes and wetland were significant contributors during the summer and fall in Mackenzie River basin, Canada (Natalie et al., 2005) and young groundwater was a major contributor to peak runoff in the western headwater portion of the Oldman river basin, Canada (Ruck et al., 2007). Usually, groundwater flow could control the baseflow through patterns of rock formations in catchments, and the discharge of groundwater could occur through faults that provided hydraulic connections to shallower aquifers or springs across the inter-bedded impermeable formations (Gonfiantini et al., 1998). Groundwater samples collected from the spring during the dry season distributed among the river water samples sampled from the wet season (Fig. 4), which indicated hydraulic connection and similar water sources existed between groundwater and river water. And these groundwater samples had similar isotopic characteristic to glacial and snow meltwater (Liu et al., 2008). Therefore, groundwater was a contributor to the baseflow and groundwater was possibly recharged by mixing of glacial and snow meltwater and rain, and discharged to the river by spring or faults in the alpine valley during the wet season.

Conclusions

The spatial difference of the stable isotopes of H and O within river water existed between tributary K and tributaries A, B, E, F, H, I in the Heishui Valley during the wet season at a large scale. This heterogeneity reflected complexity of isotopic response in the large river, which includes that the cumulative influence of precipitation from the dry to wet season, influence of different water sources and proportions of different tributary mixing. The contribution of glacial and snow meltwater to baseflow varied from 63.8% to 92.6%, and that of rain varied from 7.4% to 36.2%. Snow and glacier meltwater was still the main contributor to baseflow during the high flow period of the wet season, while the rain provided the main part of variation of the runoff in this area. And the roles of glacier and snow meltwater should be significantly noticed in water resource management in this alpine valley at the rim of the Tibetan Plateau.

Acknowledgements

This study was supported by The National Key Basic Research Special Funds (NKBRSF), PR China (No. 2002CB111504). Many thanks were to the employees of the Heishui Weather Bureau for supplying necessary meteorological data.

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