

Article

Characteristics of Water Isotopes and Water Source Identification During the Wet Season in Naqu River Basin, Qinghai–Tibet Plateau

Xi Chen ¹, Guoli Wang ¹, Fuqiang Wang ^{2,3,*}, Denghua Yan ⁴ and Heng Zhao ^{2,3}

¹ School of Hydraulic Engineering, Dalian University of Technology, Dalian 116024, China; chenxi218@mail.dlut.edu.cn (X.C.); wanggl@dlut.edu.cn (G.W.)

² Department of Water Conservancy Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450046, China; zhaoheng@ncwu.edu.cn

³ Collaborative Innovation Center of Water Resources Efficient Utilization and Support Engineering, Zhengzhou 450046, China

⁴ Water Resources Department, China Institute of Water Resources and Hydropower Research, Beijing 100038, China; yandh@iwhr.com

* Correspondence: wangfuqiang@ncwu.edu.cn; Tel.: +86-137-0371-4661

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Abstract: Climate change is affecting the discharge of headstreams from mountainous areas on the Qinghai–Tibet Plateau. To constrain future changes in discharge, it is important to understand the present-day formation mechanism and components of runoff in the basin. Here we explore the sources of runoff and spatial variations in discharge through measurements of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in the Naqu River, at the source of the Nu River, on the Qinghai–Tibet plateau, during the month of August from 2016 to 2018. We established thirteen sampling sites on the main stream and tributaries, and collected 39 samples from the river. We examined all the water samples and analyzed them for isotopes. We find a significant spatial variation trend based on one-way analysis of variance (ANOVA) ($p < 0.05$) between Main stream-2 and tributaries. The local meteoric water-line (LMWL) can be described as: $\delta^2\text{H} = 7.9\delta^{18}\text{O} + 6.29$. Isotopic evaporative fractionation in water and mixing of different water sources are responsible for the spatial difference in isotopic values between Main stream-2 and tributaries. Based on isotopic hydrograph separation, the proportion of snowmelt in runoff components ranges from 15% to 47%, and the proportion of rainwater ranges from 3% to 35%. Thus, the main components of runoff in the Naqu River are snowmelt and groundwater.

Keywords: stable isotopes; spatial variations; hydrograph separation; Naqu River basin; Qinghai–Tibet Plateau

1. Introduction

The gradual trend of global warming will affect the discharge of headstreams to plateau rivers, including on the Qinghai–Tibet Plateau [1–4]. Therefore, it is important to explore the formation mechanism and identify the components of runoff on the Qinghai–Tibet Plateau [5,6].

The Naqu River basin is sensitive to environmental change due to its high altitude. Studying its water cycle is not straightforward due to the lack of hydrological data and harsh natural conditions. Meanwhile, little is known about the water source contribution and the mechanism of the runoff. To constrain future changes in discharge, it is important to understand the present-day formation mechanism and components of runoff in the basin.

There are many methods to identify runoff components [7–13]. Recent studies have shown that hydrograph separation based on stable isotopes is an effective way to study the runoff

mechanism [14–16]. In general, river components can be divided into precipitation, groundwater, soil water, and snowmelt based on isotope hydrological separation [17–25]. For example, based on the isotopic values of river waters, significant spatial and temporal variations of the Xijiang River were investigated [26]; Kong et al. found that the snowmelt water accounted for more than 57% of runoff of the Kumalak River [1], and more than 53% during the wet season [6]. Based on isotopes and geochemical tracers, streams in plateau regions are mainly replenished by snowmelt and groundwater [27–38]. There has been relatively little research on the composition and mechanism of water sources on the Qinghai–Tibet Plateau. The advantages of isotope techniques in the hydrologic cycle are obvious and water samples can be obtained easily in the plateau region due to the lack of hydrological and meteorological data [18].

In this study, we analyze the spatial variation of isotopes in the runoff and compute the proportions of runoff components in the month of August based on hydrograph separation. We hope that the research results of this paper will provide a relevant theoretical basis for the formation mechanism of runoff on the Qinghai–Tibet Plateau.

2. Study Areas

The Naqu River basin is the source of the Nu River in southwest China (Figure 1). The Naqu River has several main tributaries, such as the Najinqu, Sangqu, Bazongqu, Mumuqu, Chengqu, Zongqungqu, Mugequ, and Gongqu Rivers. There are many seasonal streams and mountain streams flowing into the Naqu River. The average annual temperature in this area is $-0.6\text{ }^{\circ}\text{C}$. The drainage area of the Naqu River basin is $16,350\text{ km}^2$, at a high altitude of 4600 m above sea level [39].

Annual precipitation is 531 mm. From May to October, precipitation accounts for about 82% of the total annual rainfall, with less precipitation from November to April. Although there is not a significant amount of snowfall throughout the whole year, snowmelt has a strong replenishment effect on the runoff in the flood season. The climate is affected by Indian Ocean southwest monsoon in summer. The water vapor of precipitation comes from water vapor that evaporated under wetter conditions. This is consistent with summer southwest monsoon precipitation in the region coming directly from the Bay of Bengal. The d-excess value in the precipitation directly from the Bay of Bengal is lower due to the high relative humidity of the sea surface [37–42]. For this reason, the precipitation is coincident with the annual peak of snowmelt during the wet season. And they become the main components of runoff in the Naqu River basin.

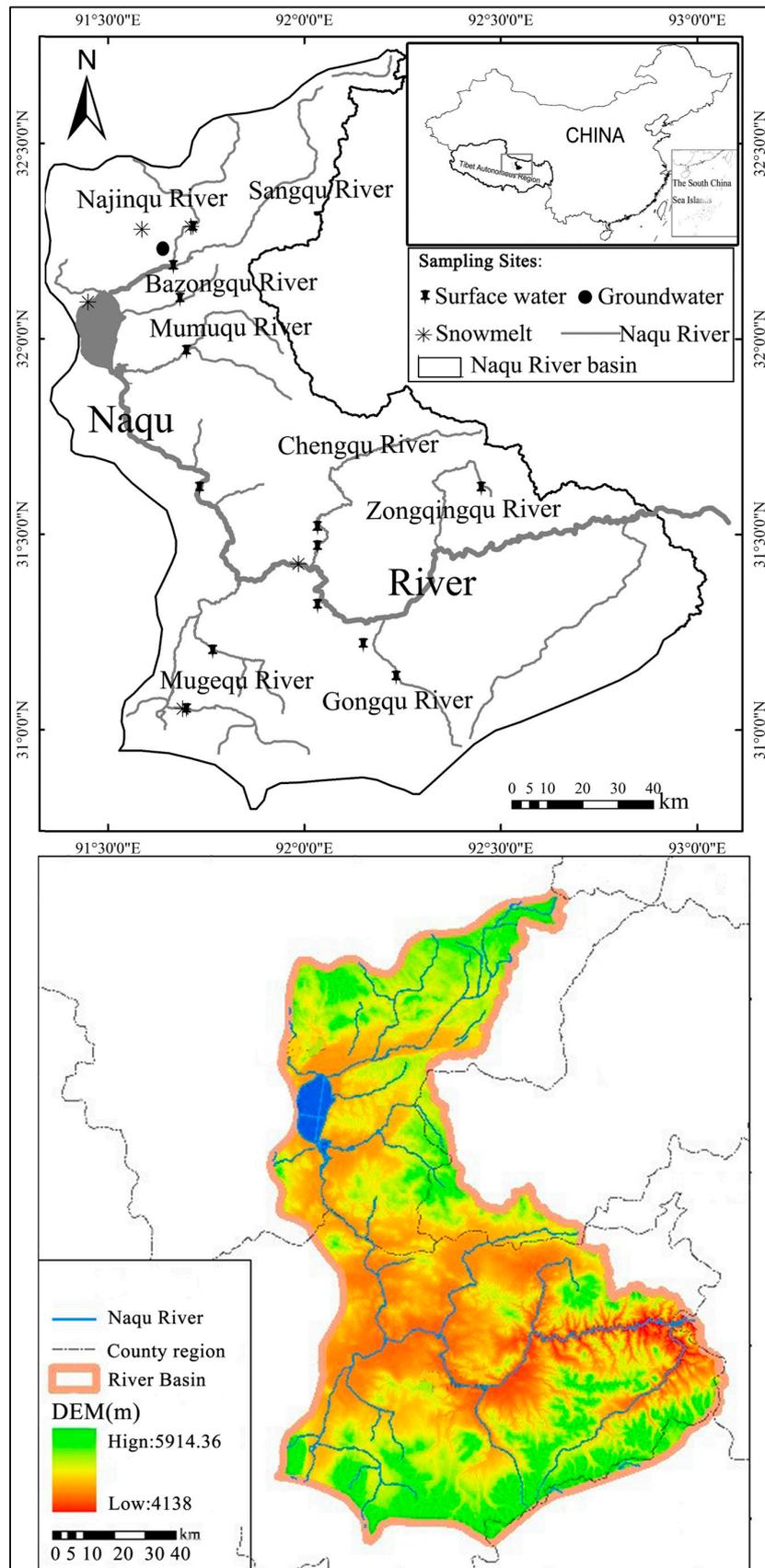


Figure 1. Research area and geographic location.

3. Materials and Methods

3.1. Field Sampling

We installed thirteen sampling sites on the main stream and tributaries of the Naqu River, with the sampling sites of Main stream-1 and Main stream-2 along the main channel, and Najinqu, Sangqu, Bazongqu, Mumuqu, Chengqu, Zongqungqu, Mugequ, and Gongqu on eight tributaries (Figure 1). We collected a total of 39 samples from the river in the month of August from 2016 to 2018.

In general, water samples included 39 runoff samples, two groundwater samples, two rain samples, and five snowmelt samples during the wet season from 2016 to 2018. We collected two rain samples on 13 August 2018.

3.2. Measurement

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis: Wavelength-scanned cavity ring down spectroscopy (WS-CRDS) (Picarro L1115-I, Picarro, Santa Clara, CA, USA) was used to measure water isotope composition, which were corrected using the Vienna Standard Mean Ocean Water (VSMOW, $\delta^2\text{H} = 0\text{‰}$, $\delta^{18}\text{O} = 0\text{‰}$) and Standard Light Antarctic Precipitation ($\delta^2\text{H} = -428\text{‰}$, $\delta^{18}\text{O} = -55.5\text{‰}$). The analytical precision was generally 0.5‰ for $\delta^2\text{H}$ and 0.1‰ for $\delta^{18}\text{O}$ [39]. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are expressed as follows:

$$\delta^2\text{H}_{\text{V-SMOW}} = \left(\frac{{}^2\text{H}/{}^1\text{H}_{\text{sample}}}{{}^2\text{H}/{}^1\text{H}_{\text{standard}}} - 1 \right) \times 1000(\text{‰}) \quad (1)$$

$$\delta^{18}\text{O}_{\text{V-SMOW}} = \left(\frac{{}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}}}{{}^{18}\text{O}/{}^{16}\text{O}_{\text{standard}}} - 1 \right) \times 1000(\text{‰}) \quad (2)$$

EC analysis: Electrical conductivity (EC) was measured in situ with a conductivity meter. EC was measured concurrently with stream sampling using a standard conductivity cell (WTW Cond 340iTM). The standard conductivity cell was calibrated to correct for water temperature to $25\text{ }^\circ\text{C}$.

D-excess calculation: The deuterium excess (d-excess) was used to measure the isotopic variability [19] and is defined as:

$$\text{d-excess} = \delta^2\text{H} - 8 \times \delta^{18}\text{O} \quad (3)$$

3.3. Data Analysis

We explored the spatial characteristics of the isotopes based on one-way analysis of variance (ANOVA) by using SPSS 17.0. Isotopic contents in water bodies of different main stream tributaries are expressed by box plot. ArcGIS of ESRI is applied to display spatial features of the Naqu River basin based on inverse distance weighting (IDW).

We analyzed samples for the two tracers collected from snowmelt, rain, stream water, and groundwater. Respecting the water and tracer mass conservation, electrical conductivity was measured in situ with a conductivity meter. The percentage of different components in the total runoff was determined using isotope hydrologic separation. If we suppose the objective percentage of n components are evaluated based on n parts and $n - 1$ measuring factors t_1, t_2, \dots, t_{n-1} , there are n linear mixing equations. These are defined as follows:

$$Q_T = Q_1 + Q_2 + \dots + Q_n \quad (4)$$

$$C_T^{t_i} Q_T = C_1^{t_i} Q_1 + C_2^{t_i} Q_2 + \dots + C_n^{t_i} Q_n \quad (5)$$

where Q_T is the total flow of the river; Q_1, Q_2, \dots, Q_n represent the flows of different water sources of runoff, and $C_1^{t_1}, C_2^{t_2}, \dots, C_i^{t_i}$ represent the concentrations of relevant observed tracer t_i .

When the runoff contains only two sources of water, the percentages of different components of the runoff can be expressed as follows:

$$Q_1/Q_s = (C_2 - C_s)/(C_2 - C_1) \quad (6)$$

$$Q_2/Q_s = (C_s - C_1)/(C_2 - C_1) \quad (7)$$

where Q is the runoff of each component, C is the concentrations of relevant observed tracer, and s is the total flow.

When the runoff contains only three sources of water, groundwater, snowmelt, and precipitation are the main components of runoff in August in the Naqu River basin. Hydrograph separation is used to calculate the various composition of the runoff based on two tracers ($\delta^2\text{H}$ and EC). Supposing the river flow is a function of snowmelt, groundwater, and precipitation, then the three-component sources model can be defined as follows:

$$f_p + f_g + f_m = 1 \quad (8)$$

$$f_p Q_p + f_g Q_g + f_m Q_m = Q_r \quad (9)$$

$$f_p E_p + f_g E_g + f_m E_m = E_r \quad (10)$$

where f_p, f_g, f_m represent the shares of the individual components in the total runoff, and Q and E represent the concentrations of tracers.

4. Results

4.1. Spatial Characteristics of $\delta^{18}\text{O}$ and $\delta^2\text{H}$

In August 2017, $\delta^{18}\text{O}$ values of runoff vary from -15.6‰ to -10.5‰ with a mean of -15.49‰ . The $\delta^{18}\text{O}$ values of snowmelt water range from -15.0‰ and -7.6‰ with an average of -11.4‰ . The $\delta^{18}\text{O}$ values of runoff vary from -15.49‰ to -14.27‰ (Table 1). For groundwater, the $\delta^{18}\text{O}$ values are relatively stable, ranging from -19.03‰ to -17.66‰ , which indicated that the surrounding environment had little influence on groundwater and the recharge source of groundwater was relatively stable (Table 1).

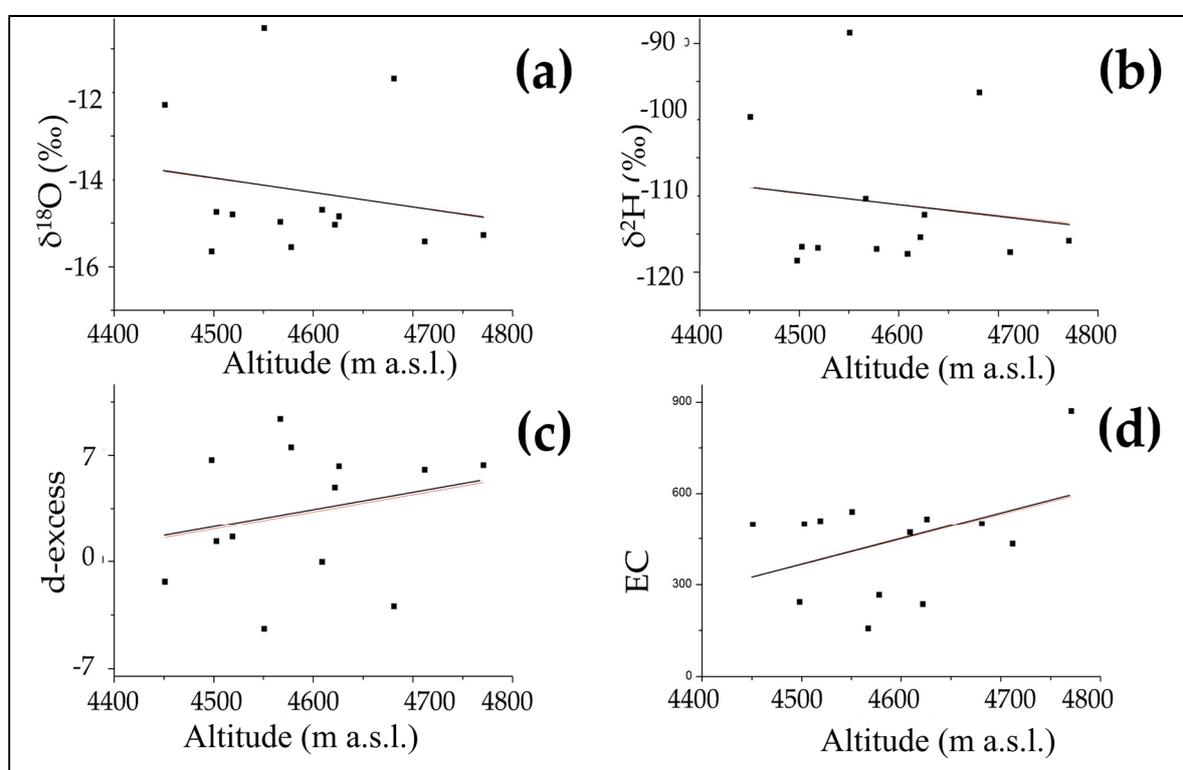
Table 1. Oxygen isotope composition of different types of water in the Naqu River basin.

Water type		2016.8	2017.8	2018.8
Stream water	Sample number	13	13	13
	Mean of $\delta^{18}\text{O}$ (‰)	-14.27	-15.49	-14.83
Water type		2016–2018		
Snowmelt water	Sample number	5		
	Mean of $\delta^{18}\text{O}$ (‰)	-11.37		
Groundwater	Sample number	2		
	Mean of $\delta^{18}\text{O}$ (‰)	-18.51		
Rain	Sample number	2		
	Mean of $\delta^{18}\text{O}$ (‰)	-18.35		

The results of elevation effect analysis on the collected rivers (Table 2) show that the isotopes in runoff do not change with elevation (Figure 2). All values are plotted against altitude. We hypothesize that the water body experienced intense evaporative fractionation due to the slow river flow rate in the Naqu River basin.

Table 2. Average values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of main streams and tributaries.

Location	Sampling Sites	Sample Number	$\delta^{18}\text{O}$ (‰)	$\delta^2\text{H}$ (‰)	Longitude (E)	Latitude (N)	Altitude (m a.s.l.)
Main stream-1	4	3	-15.68	-118.58	92°02'38.7"	31°19'52"	4451
Main stream-2	8	3	-15.48	-116.32	91°44'17.7"	31°37'15.2"	4551
Bazongqu	9	3	-16.88	-124.93	91°42'51.9"	31°58'40.2"	4622
Chengqu	3	3	-16.37	-124.20	92°03'34.9"	31°29'44.7"	4503
	13	3	-17.03	-127.50	92°02'19.3"	31°31'39.5"	4519
Gongqu	5	3	-15.83	-119.46	92°09'30.5"	31°13'32.5"	4498
	6	3	-16.21	-121.16	92°14'23.2"	31°08'21.8"	4578
Mugequ	2	3	-15.17	-113.81	91°41'23.3"	31°3'17.9"	4681
	14	3	-15.26	-115.65	91°46'33.3"	31°11'56"	4591
Mumuqu	10	3	-14.97	-113.63	91°41'23.4"	32°06'5.1"	4712
Najinqu	12	3	-14.81	-111.99	91°42'38.5"	32°22'30.3"	4771
Sangqu	11	3	-14.57	-111.32	91°40'44.3"	32°11'22"	4626
Zongqingqu	7	3	-13.18	-103.02	92°25'42.2"	31°41'12.6"	4567

**Figure 2.** (a) $\delta^{18}\text{O}$ altitude, (b) $\delta^2\text{H}$ altitude, (c) d-excess altitude, and (d) electrical conductivity (EC) altitude relationship.

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are shown in box plots for all the sampling sites (Figure 3).

Our analysis showed a significant spatial trend based on one-way ANOVA ($p < 0.05$) at 13 sampling sites between Main stream-2 and tributaries (Najinqu, Sangqu, Bazongqu, Mumuqu, Chengqu, Zongqingqu, Mugequ, and Gongqu). We speculate that isotopic evaporative fractionation in water and mixing of different water sources are the reasons for the spatial difference in isotopic values between Main stream-2 and tributaries.

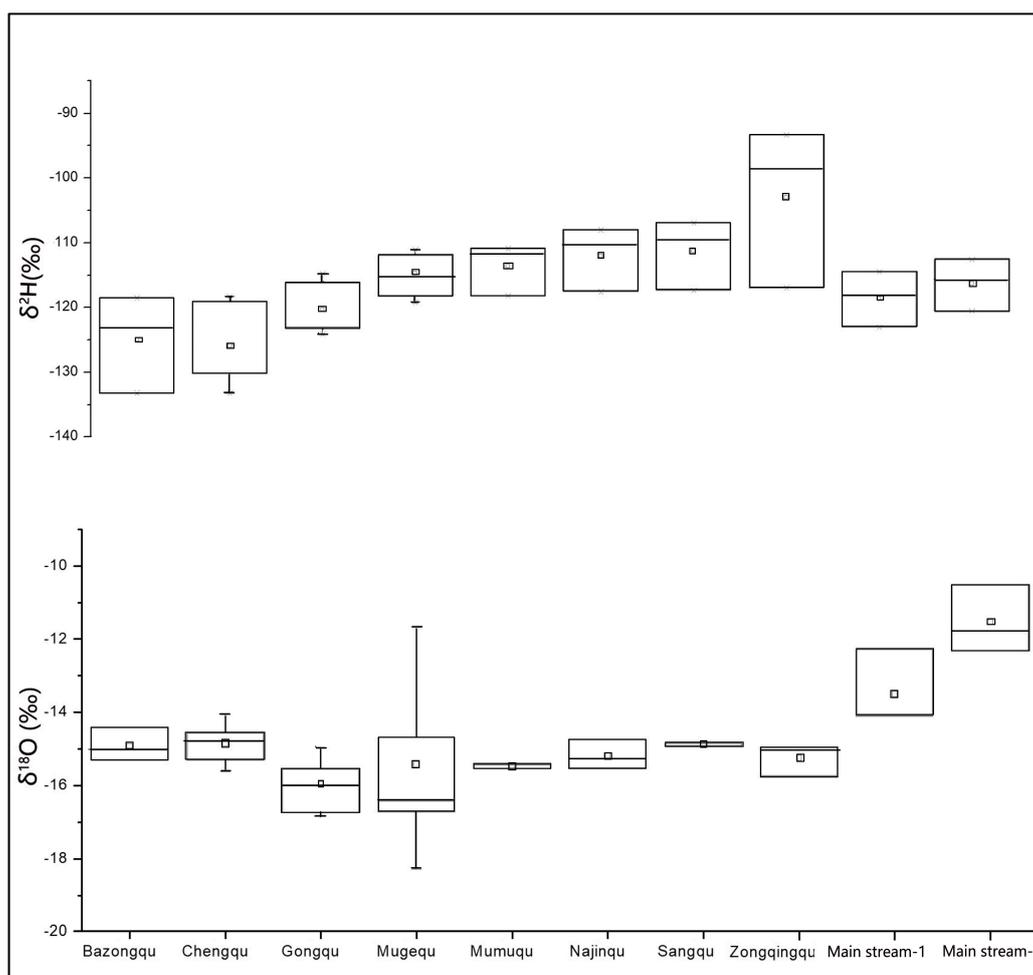


Figure 3. Box plots for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of runoff.

4.2. Isotopic Characterization of River

Craig [12] found that stable isotope ratios of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation correlate at a global scale in a linear relationship known as the global meteoric water line (GMWL). A linear relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ was established for average local meteoric waters as the local meteoric water line (LMWL). Important information about the water sources of precipitation can be revealed based on the deviation between LMWL and GMWL. By the location characteristics of different water samples, the water sources of rivers and the isotopic evaporative fractionation can be analyzed. In this paper, the LMWL of Lhasa region is adopted to replace the LMWL of the Naqu River basin. The LMWL can be described as: $\delta^2\text{H} = 7.9\delta^{18}\text{O} + 6.29$ [43]. Compared to the LMWL, some sets of isotopic data with high $\delta^{18}\text{O}$ values are below the LMWL, which signifies the effect of intensive evaporation processes.

By comparing different water samples with the LMWL, the water sources of the river and the isotopic evaporative fractionation can be analyzed. Most of the river sampling sites are close to LMWL ($\delta^2\text{H} = 7.9\delta^{18}\text{O} + 6.29$) (Figure 4). At the same time, many samples are close to each other, indicating that the water sources of these tributaries are relatively similar. The river water line is $\delta^2\text{H} = 5.75\delta^{18}\text{O} - 27.98$. The groundwater and snowmelt samples are distributed around the river samples, indicating that the water is originated from local rainfall and runoff is recharged by groundwater, snowmelt, and precipitation.

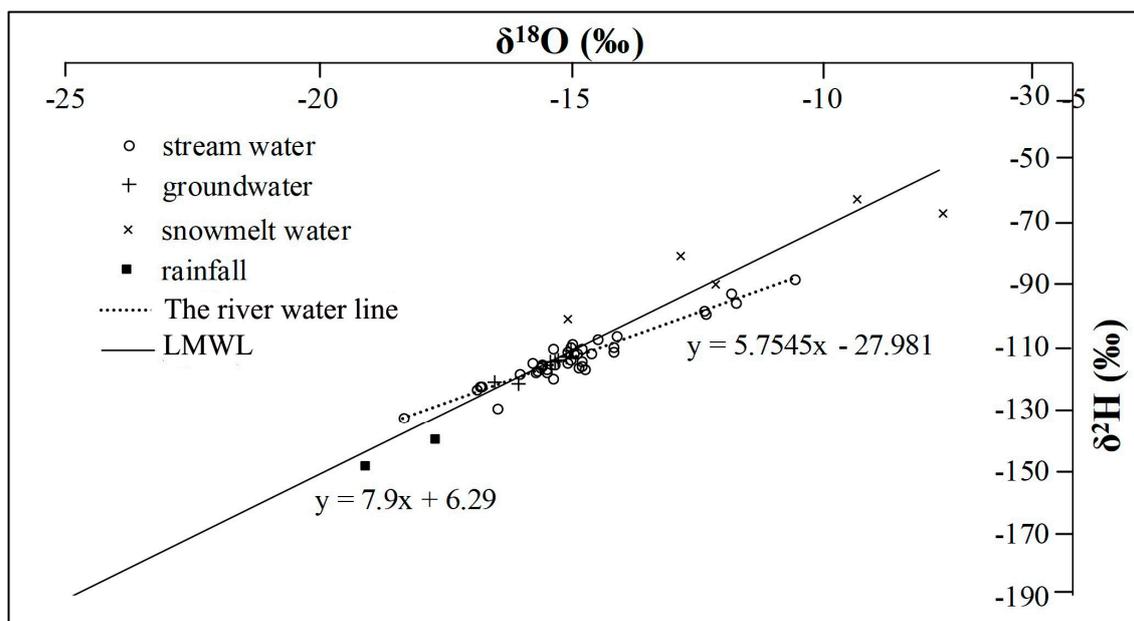


Figure 4. Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ for different water sources.

The isotopic values of river water samples are closer to groundwater than those of snowmelt, indicating the frequent interaction between groundwater and runoff (Figure 4). Meanwhile, the slope and intercept are both smaller than that of LMWL, indicating that the water body in the Naqu River basin have experienced an obvious evaporation process.

The isotopes of snowmelt in winter appear to be the most enriched compared with other water sources, which is due to evaporation. When the snow begins to melt, the influence of evaporative fractionation increases, and the content of heavy isotopes in the meltwater increases.

4.3. Hydrograph Separation

Based on the formulas provided above, we calculated the contributions of rain, groundwater, and snowmelt by isotopic hydrograph separation in 2018 (Table 3, Figure 5). The proportion of snowmelt in runoff components ranges from 15% to 47%, and the proportion of rainwater ranges from 3% to 35%. The main components of runoff in the Naqu River are snowmelt and groundwater.

Table 3. Contribution of different water sources (^2H , ‰; EC, ms/cm).

Tributary	Mean Elevation (m a.s.l.)	River Water		Snowmelt		Groundwater		Rainfall		Contribution (%)		
		D	EC	D	EC	D	EC	D	EC	Snowmelt	Groundwater	Rainfall
Bazongqu	4622	-112	0.21	-87	0.12	-122	0.50	-144	0.01	45%	30%	24%
Chengqu	4519	-115	0.31	-87	0.12	-122	0.50	-144	0.01	29%	56%	16%
Gongqu	4578	-119	0.22	-87	0.12	-122	0.50	-144	0.01	29%	36%	35%
Mugequ	4609	-121	0.31	-87	0.12	-122	0.50	-144	0.01	18%	58%	24%
Mumuqu	4712	-117	0.43	-87	0.12	-122	0.50	-144	0.01	15%	82%	3%
Najinqu	4771	-114	0.21	-87	0.12	-122	0.50	-144	0.01	40%	32%	29%
Sangqu	4626	-112	0.21	-87	0.12	-122	0.50	-144	0.01	45%	30%	25%
Zongqingqu	4567	-113	0.17	-87	0.12	-122	0.50	-144	0.01	46%	23%	31%

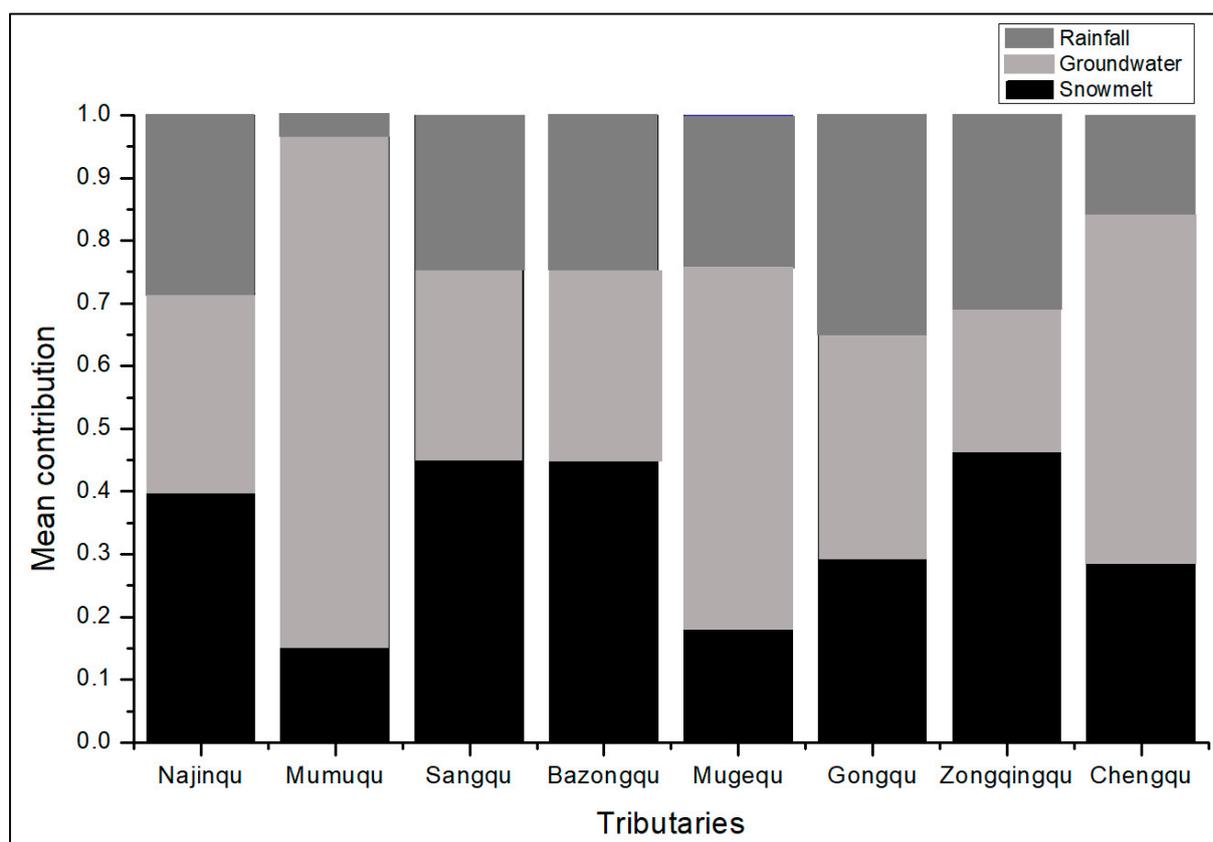


Figure 5. Contribution of different water sources.

5. Discussion

5.1. Analysis of Spatial Variations of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ Values of the River

Our analysis showed an insignificant spatial trend of either $\delta^2\text{H}$ or $\delta^{18}\text{O}$ among tributaries Najinqu, Sangqu, Bazongqu, Mumuqu, Chengqu, Zongqingqu, Mugequ, and Gongqu in August. However, there is a significant spatial variation trend based on one-way ANOVA between Main stream-2 and tributaries (Najinqu, Sangqu, Bazongqu, Mumuqu, Chengqu, Zongqingqu, Mugequ, and Gongqu) (Figure 3). Although elevation effects play an important role in isotopic variation in large topographic area, there was no obvious elevation effects between Main stream-2 and tributaries (Figure 2). Surface and groundwater samples are often below the LMWL and GMWL under intense evaporative fractionation and low humidity. In the Naqu River, some water samples deviate from the LMWL, and the waters experience intense evaporative fractionation due to the slow river flow rate.

For groundwater, the $\delta^{18}\text{O}$ values were relatively stable, ranging from -19.03‰ to -17.66‰ , indicating that the surrounding environment has little influence on groundwater and the recharge source of groundwater is relatively stable (Table 1). The groundwater was recharged by old water stored in the basin previously.

5.2. Estimation of Different Water Sources Contribution to the River Flow

Based on the analysis of runoff components, runoff of the Naqu River can be divided into three water sources by isotopic hydrograph separation: Groundwater, rain, and snowmelt. The calculation results show that snowmelt of most tributaries contributed more than 30% to the runoff, while the proportion of rain ranges from 3% to 35% in the Naqu River basin. The results of hydrologic separation show that during the wet season, the river sources are mainly meltwater, and groundwater, with groundwater accounting for the largest proportion (more than 50%). Groundwater and snowmelt

account for a greater proportion of runoff composition in the Naqu River basin. Such results are different from the runoff data collected at the hydrological station (Figure 6). In the past, we believed that the changing trend of runoff was completely controlled by precipitation. We speculate that the main components of runoff are snowmelt water and groundwater, while rain affects the change of runoff in the Naqu River.

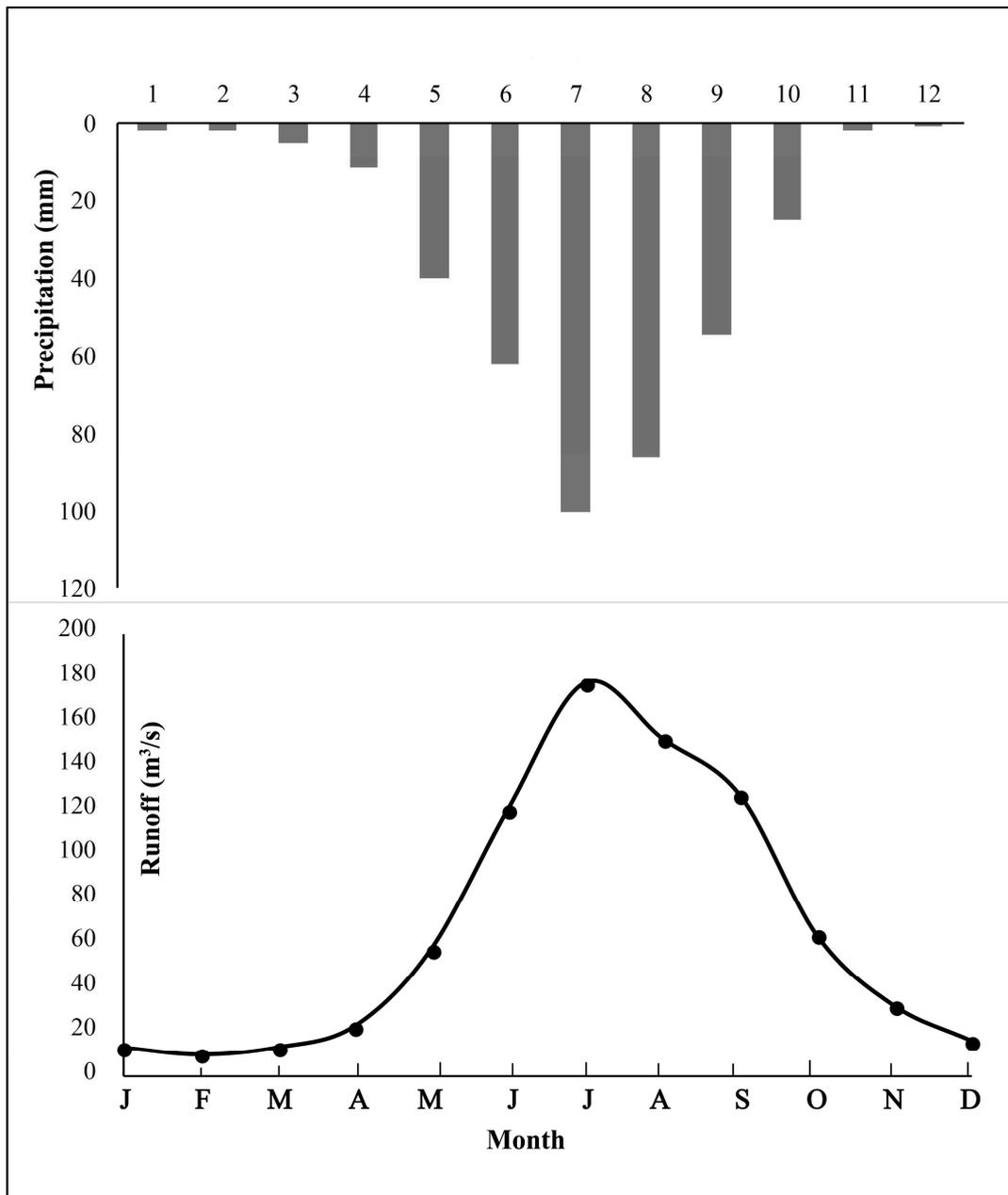


Figure 6. Monthly variations of precipitation and runoff in the Naqu River basin.

As shown in Figure 7, the contributions of groundwater of Mumuqu, Mugequ, and Chengqu are bigger than those of other tributaries. The contributions of snowmelt of Najinqu, Sangqu, Bazongqu, and Zongqingqu Rivers are bigger than those of other tributaries. We speculate that this phenomenon is related to the elevation characteristics of the Naqu River basin (Figure 1). At lower altitudes to the south, the recharge of groundwater in the river is stronger. The loose structure of the rocks, large areas of grassland, and abundant melt-water make the area relatively permeable. At higher altitudes in the north and east, the recharge of snowmelt to the river is stronger. The results of elevation effect

analysis on the collected samples of the main stream and tributaries showed that isotopes in runoff do not change with elevation. There is a certain correlation between runoff composition and elevation, particularly related to the proportion of groundwater and snowmelt. Groundwater contributes more to the river in the central and western regions. Spatially, in the Naqu River, meltwater contributes more than 30% to runoff in the north, east, and south. Our results show that the groundwater and snowmelt water have different dominant effects on runoff composition from the upper to the lower reaches in the Naqu River. And the results can be referred to for near-future assessments of changes in discharge in the basin.

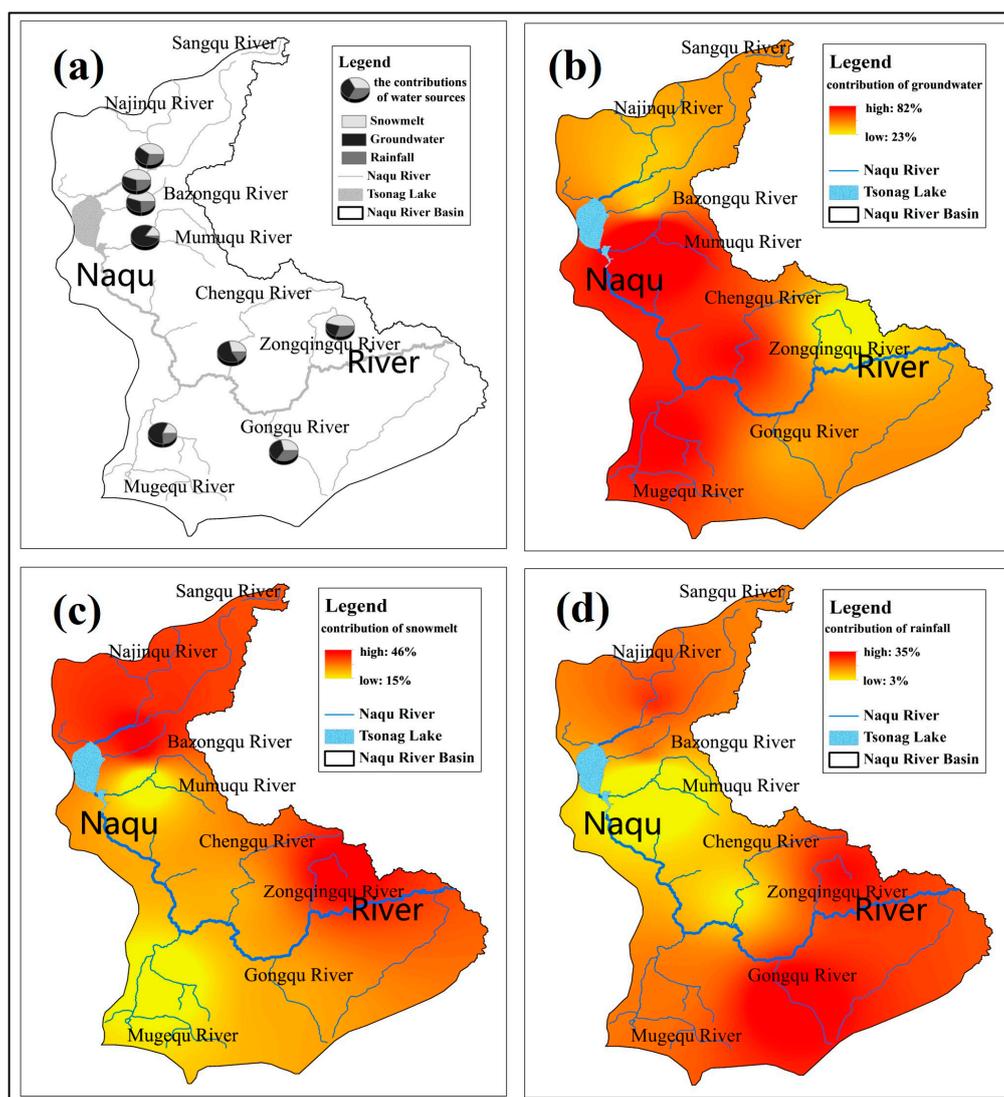


Figure 7. Spatial variation of contributions of numerous water sources in the Naqu River basin: (a) numerous water sources (b) groundwater, (c) snowmelt, and (d) rainfall.

6. Conclusions

We analyze the spatial variations of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ with influencing factors and the sources of runoff in August, 2016–2018, for the Naqu River at the source of the Nu River on the Qinghai–Tibet. Our analysis showed an insignificant spatial trend of either $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values among the tributaries Najinju, Sangqu, Bazongqu, Mumuqu, Chengqu, Zongqungqu, Mugequ, and Gongqu in August. However, there is a significant spatial variation trend based on one-way ANOVA at 13 sampling sites between Main stream-2 and tributaries (Najinju, Sangqu, Bazongqu, Mumuqu, Chengqu, Zongqungqu,

Mugequ, and Gongqu). Isotopic evaporative fractionation in water and mixing of different water sources are the reasons for the spatial difference of isotopic values between Main stream-2 and tributaries. Runoff of the Naqu River can be divided into three water sources: Groundwater, rainwater, and snowmelt. The proportion of snowmelt in runoff components ranges from 15% to 47%, and the proportion of rainwater ranges from 3% to 35%. Thus, the main components of runoff are snowmelt and groundwater, while rain affects the change of runoff.

Author Contributions: X.C. and F.W. conceived, designed, and drafted the manuscript; X.C., G.W., D.Y. and H.Z. planned and designed the methodology; X.C. revised the manuscript; F.W. guided and supervised the whole process; and all authors read and approved the final manuscript.

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