

Article

# Stable Isotope Composition in Surface Water in the Upper Yellow River in Northwest China

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Received: 14 March 2019; Accepted: 6 May 2019; Published: 8 May 2019



**Abstract:** Although stable isotopes of hydrogen and oxygen in surface waters (especially in river waters) are useful tools to understand regional hydrological processes, relevant information at some upper reaches of large rivers in western China is still limited. During 2016–2017, we focused on the Liujiaxia Reservoir along the upper Yellow River, where we collected surface water samples at two locations, above and below the dam (identified as “lake water” and “river water”). The results show that the heavy isotopes in lake and river waters are enriched during the warm months, when the river discharge is large, and depleted during the cold months. The slopes of the water line ( $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$ ) for both the lake and river waters were lower than that of the global mean, due to evaporation. The different  $d$  values of the lake and river water reflect the regional evaporation and water sources.

**Keywords:** stable isotope; surface water; river water; Yellow River

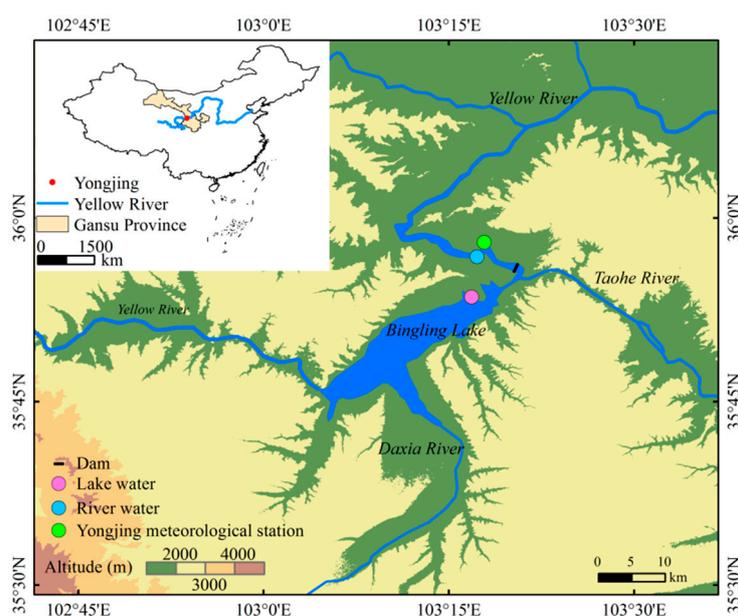
## 1. Introduction

Stable isotopes of hydrogen and oxygen are important in understanding hydrological processes [1–5]. Surface runoff is a vital component of the terrestrial water cycle, and the interactions between surface water and other hydrological components (especially precipitation and groundwater) can be investigated using stable isotopes of water [6–10]. For example, simultaneous in-situ monitoring of the isotopic composition of surface water provides a basis to investigate the regional water budget [11–14], water interaction [15–17], and paleoclimate reconstruction [18,19]. In most cases, the stable isotope ratios of surface water reflect a seasonal variation, which is associated with the isotope signature of water from which it is derived (e.g., stream water, precipitation, and groundwater) and the climate [20–24]. According to the isotopic assessment of nationwide river water in the United States (U.S.), heavy isotopes of river water are more depleted in southeastern to northwestern (except for the East Coast of the U.S.) United States, due to evaporation and water vapor sources [25]. Generally, water isotopes experience kinetic fractionation depending on the climate conditions. Dansgaard [26] demonstrated that temperature and precipitation amount are important meteorological factors controlling stable isotope composition in precipitation, which is commonly known as temperature effect and precipitation effect, respectively. Light isotopes evaporate preferentially to heavy isotopes, so heavy isotopes of evaporated (condensed) water are more depleted

(enriched) than those of residual water. Hence, in some open water bodies (especially lakes), the heavy isotopes were more enriched, relative to precipitation, due to strong evaporation [23,27,28].

The Yellow River (Huanghe River), the second longest river in China, originates from the high-elevation Qinghai–Tibet Plateau and flows to the Bohai Sea in eastern China. The isotopic signature of river water at many sites along the Yellow River has been analyzed and has provided useful information to understand the regional water cycle [29–33]. According to these studies, in this drainage basin, with different climate conditions and hydrological regimes, the isotope values of water are spatially dependent [29]. The downstream reaches are greatly affected by the East Asia monsoon. This may be reflected by the seasonal variations of stable isotope composition. Water in the middle reaches is enriched in heavy isotopes due to evaporation and complex moisture sources at the monsoon margin. The heavy isotope values of river water are lower in the upper reaches because the isotopes of precipitation and surface water are more depleted in high elevation inland areas, although the arid background may also affect the signature of isotopes [29]. Consequently, the isotopic composition of river water can be applied to understand the climatic and hydrological conditions.

Among these studies [29–33], very few were conducted in the high-altitude upper reaches of the Yellow River [33], especially at the eastern Tibetan Plateau and the western Loess Plateau, where the climate is mostly arid and semi-arid, and surface water is for agriculture and domestic use [34]. The Liujiaxia Reservoir (Figure 1), a famous reservoir in western China, is located at the upper Yellow River. The water level of the wide bay behind the dam (also called the Bingling Lake) is approximately at 1700 m above sea level. The lake occupies an area of approximately 130 km<sup>2</sup>, with a capacity of  $39 \times 10^8$  m<sup>3</sup> [35]. The annual average air temperature in the Yongjing Meteorological Station (35°58' N, 103°18' E) from 1 January 2016 to 31 December 2017 was 10.1 °C, and the annual average precipitation amount was 280.7 mm. This reservoir plays a very important role in irrigation and flood control across the region and will serve as the main water source of the nearby Lanzhou city (the capital city of Gansu Province) in future years. During 2016–2017, the monthly average storage capacity of the Bingling Lake was  $35.68 \times 10^8$  m<sup>3</sup>. However, the existing knowledge of the isotopic signature in surface water around the dam is still limited, even though isotope techniques have been widely applied to detect the hydrological process worldwide.



**Figure 1.** Map showing the sampling sites of lake water and river water in this study. The Yellow River, the Daxia River, and the Taohe River flow into the Bingling Lake and flow out through the dam.

During the period of 2016–2017, we established monitoring sites near the Liujiaxia Reservoir and collected surface water samples at two sites, above and below the dam. The purpose of the present study is to improve the knowledge of stable isotopes at the upper reaches of the Yellow River and to investigate the isotope signature of surface water in this region. Moreover, the influence of the dam on the isotopic signature in the surface water will be considered. The sampling network around the Liujiaxia Reservoir could be useful to understand the hydrogen and oxygen isotopes in the regional water cycle.

## 2. Data and Methods

Surface water samples were collected twice a month at a depth of 20 cm from the river downstream the Liujiaxia dam (35°57' N, 103°17' E, 1646 m; hereafter referred to as river water), from January 2016 to August 2017, and the Bingling Lake (35°53' N, 103°18' E, 1731 m; hereafter termed to as lake water), from January 2016 to March 2017. The climate parameters (including air temperature, precipitation amount, wind speed, and relative humidity) come from the National Meteorological Information Center, China (NMIC). The storage of the Bingling Lake during 2016–2017, based on the daily gauge-based records, was provided by the local water resources administration [36]. The water samples were stored in 50-mL narrow-mouth HDPE bottles with an inner cap and waterproof tape. All samples were analyzed by the Stable Isotope Laboratory, College of Geography and Environmental Science, Northwest Normal University, Lanzhou, China, using a liquid water isotope analyzer (DLT-100, Los Gatos Research, San Jose, CA, USA). Both the sample and isotopic standard were injected six times. In order to eliminate any memory effect, we used the average value of the last four measurements as the final result. The stable isotope ratio is expressed relatively to the Vienna Standard Mean Ocean Water (V-SMOW):

$$\delta = \left( R_{\text{sample}} / R_{\text{standard}} - 1 \right) \times 1000\text{‰} \quad (1)$$

where  $R_{\text{sample}}$  is the  $^{18}\text{O}/^{16}\text{O}$  (or  $^2\text{H}/^1\text{H}$ ) ratio of the analyzed sample and  $R_{\text{standard}}$  is the ratio of the V-SMOW. The analytic precision was better than  $\pm 0.2\text{‰}$  for the  $\delta^{18}\text{O}$  and  $\pm 0.6\text{‰}$  for the  $\delta^2\text{H}$ , respectively. This same protocol has also been applied in previous studies [4,37]. The characteristics of the surface water isotopes are shown in Supplementary Table S1.

## 3. Results and Discussion

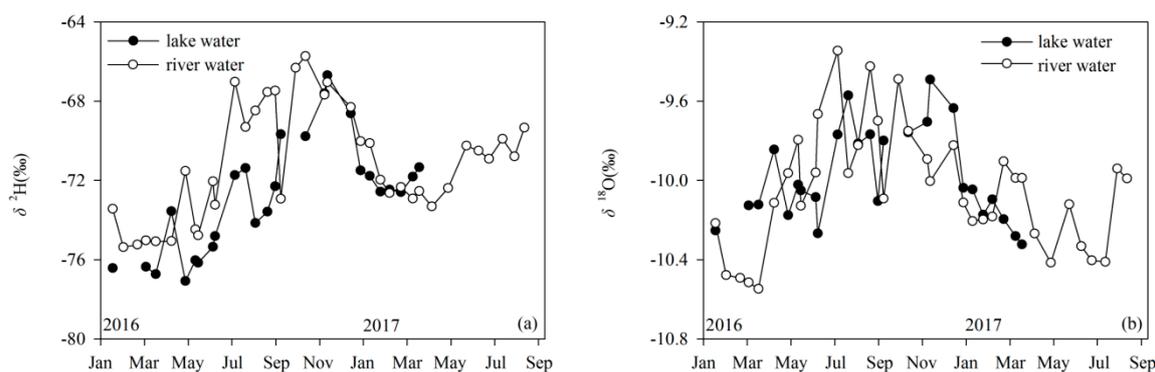
### 3.1. Stable Isotopes in Surface Water

The stable isotope ratios ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) in the lake and river waters are provided in Table 1 and illustrated in Figure 2. The maximum and minimum values of  $\delta^{18}\text{O}$  in the lake water were  $-9.49\text{‰}$  and  $-10.32\text{‰}$ , and those of  $\delta^2\text{H}$  were  $-66.69\text{‰}$  and  $-77.07\text{‰}$ , respectively. For the river water, the  $\delta^{18}\text{O}$  value ranges from  $-9.35\text{‰}$  to  $-10.55\text{‰}$ , while the  $\delta^2\text{H}$  ranges between  $-65.72\text{‰}$  and  $-75.37\text{‰}$ . The stable isotope composition of the lake and river waters exhibits a seasonal variability. In general, the isotopes values of surface water are enriched during the warm months (defined in this study as the period from April to October) and depleted during the cold months (from November to March). The range of the isotope values of the river water is close to that of the lake water.

**Table 1.** Descriptive statistics of isotopes in the lake and river water from 2016 to 2017.

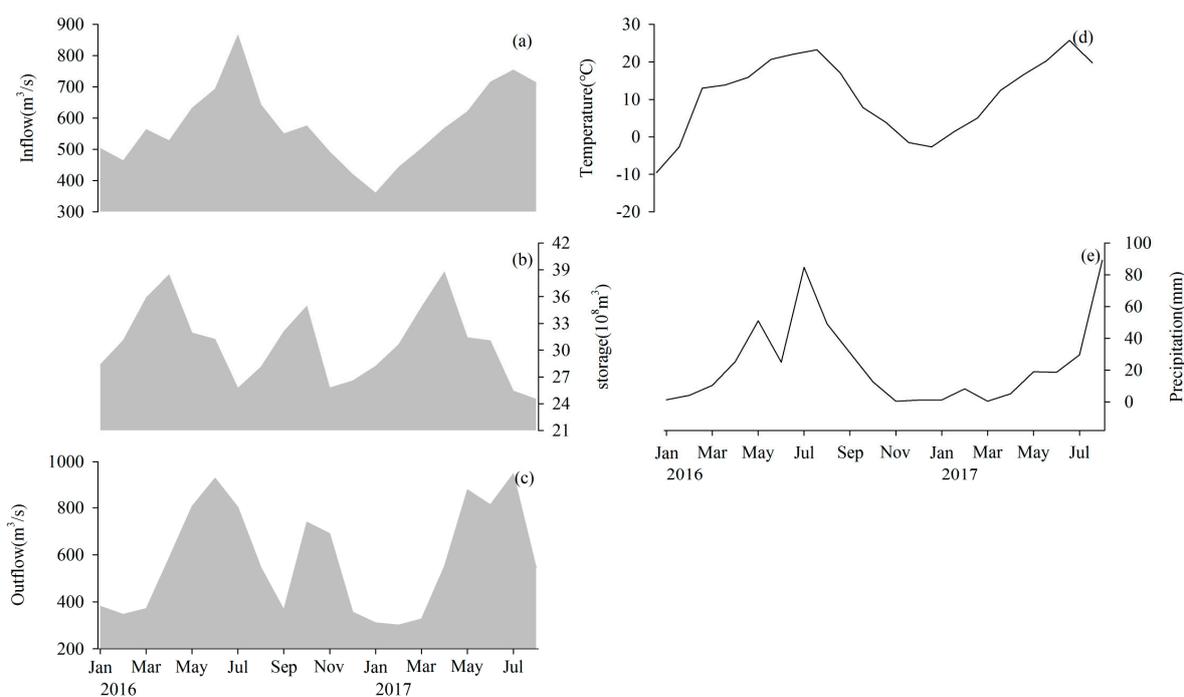
| Sample      | $\delta$ Value        | Mean (‰) | SD (‰) | Max (‰) | Min (‰) | <i>n</i> | Period                   |
|-------------|-----------------------|----------|--------|---------|---------|----------|--------------------------|
| Lake water  | $\delta^{18}\text{O}$ | -10.0    | 0.2    | -9.49   | -10.32  | 26       | January 2016–April 2017  |
|             | $\delta^2\text{H}$    | -73      | 3.0    | -66.69  | -77.07  |          |                          |
| River water | $\delta^{18}\text{O}$ | -10.0    | 0.3    | -9.35   | -10.55  | 37       | January 2016–August 2017 |
|             | $\delta^2\text{H}$    | -71      | 3.0    | -65.72  | -75.37  |          |                          |

SD: Standard deviation; *n*: Number of samples.



**Figure 2.** Seasonal variations of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in (a) the lake water and (b) the river water from 2016 to 2017.

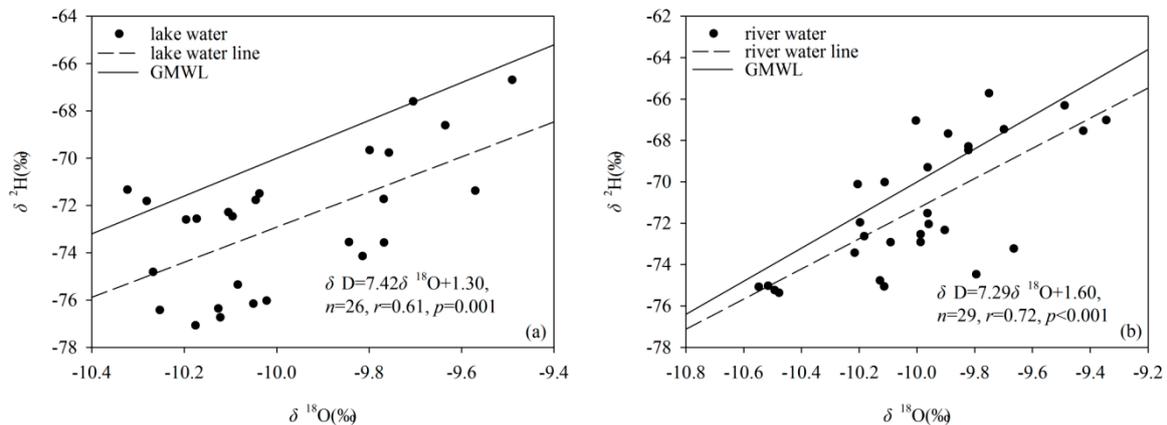
Figure 3 shows the seasonal variation of inflow, storage, outflow, and the corresponding meteorological parameters. The flow of water reaches its maximum during the warm months, which corresponds to the seasonality of precipitation and air temperature. The local precipitation usually concentrates in summer, leading to an increase of water supply during the warm months.



**Figure 3.** Seasonal variation of (a) inflow, (b) storage, (c) outflow, (d) air temperature, and (e) precipitation amount from January 2016 to August 2017.

The linear regression between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in surface waters reflects, to some extent, the local evaporation conditions [38]. The slope reflects the relationship between fractionation rates of  $^2\text{H}$  and  $^{18}\text{O}$ , and the intercept represents the degree of deviation of  $^2\text{H}$  from the equilibrium. Figure 4 shows the correlation between the stable hydrogen and oxygen isotopes in the lake water, the river water, and the global meteoric water line (GMWL:  $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$  [39]). The same time series of the lake water and river water samples was selected for comparison (Figure 4). The lake water and river water samples are almost distributed on the right-hand lower side of the GMWL, and the slopes of the lake water line (7.42) and river water line (7.29) are much lower than that of the GMWL. Low slopes of lake and river water are commonly associated with low humidity and with evaporation due to non-equilibrium evaporation [1,40]. In western China, where precipitation is limited, the strong evaporation may lead

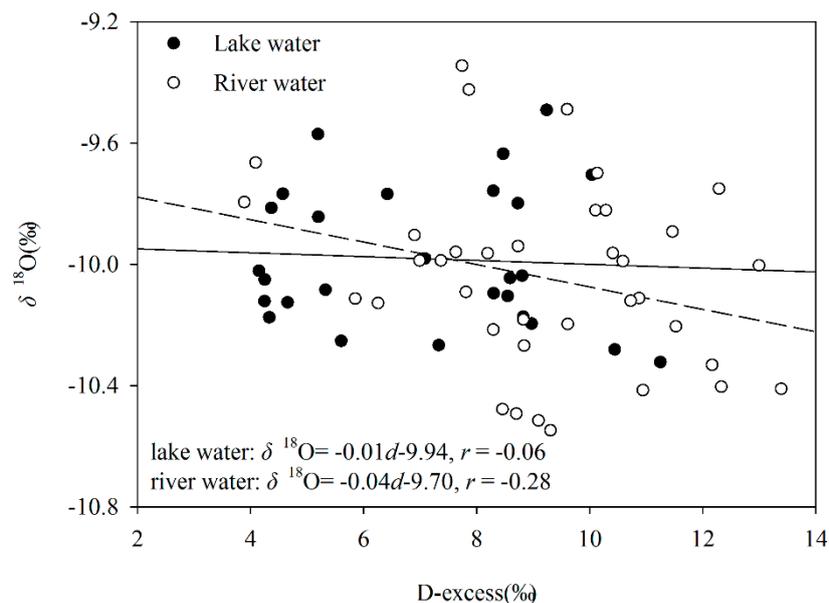
to an enrichment of heavy isotopes in surface water [41,42]. In addition, the water in the Bingling Lake originates from higher elevations, where it is relatively cold, and the value of the slope of surface water close to eight may also imply an altitude effect. However, some river water samples are distributed on the left side of the GMWL, showing a weak evaporation, which may be associated with the flow and water source. In addition, the river water is actually mixed with the Bingling Lake water and the Taohe River water, which may affect the relationship of isotopes in the sampled water.



**Figure 4.** The relationship between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  in (a) lake water and (b) river water from January 2016 to March 2017. The global meteoric water line (GMWL) is based on Craig [38].

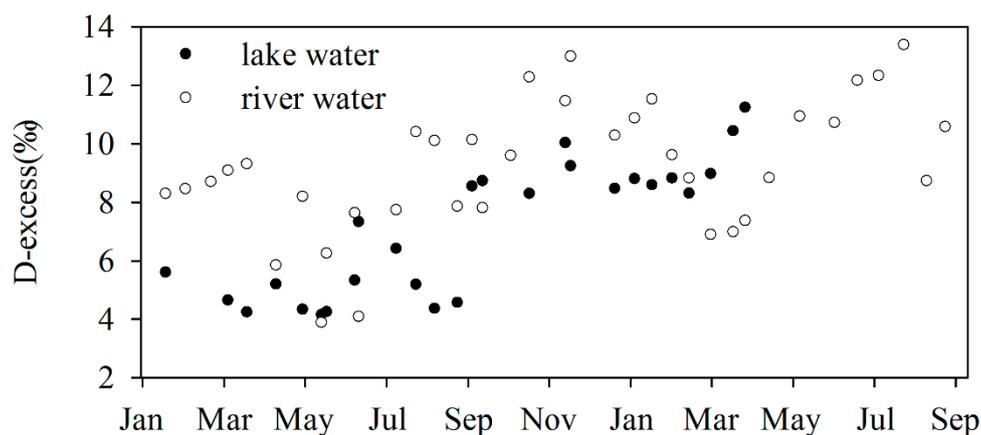
### 3.2. Deuterium-Excess in Surface Water

Deuterium excess ( $d$ , defined as  $d = \delta^2\text{H} - 8\delta^{18}\text{O}$ ) values of water can be used to identify vapor source regions and below-cloud evaporation [23,27,41,43–46]. The  $d$  value is the intercept value of  $\delta^2\text{H}$  while maintaining a slope equal to eight. D-excess is usually associated with climate parameters such as air temperature, wind speed, and relative humidity in the water vapor source area [25,45–49]. The  $d$  value in precipitation is usually high in western China ( $d = 8 - 12$ ) and low in eastern China ( $d = 4 - 12$ ) [47]. In the study area, the actual evaporation is high, which corresponds to a high temperature and low precipitation amount [50]. Consequently, the  $d$  value in the surface water is influenced by the local climate condition. Figure 5 shows that  $d$  value weakly correlates with  $\delta^{18}\text{O}$  in the river water ( $r = -0.28$ ), indicating that the high  $\delta^{18}\text{O}$  usually corresponds to a low  $d$  value.



**Figure 5.** Correlation between D-excess and  $\delta^{18}\text{O}$  in the lake and river waters. The dashed line denotes the linear fit of lake water and the solid line denotes the linear fit of the river water.

During the study period,  $d$  values of the lake water varied from 4.15‰ to 11.25‰ and from 3.89‰ to 13.39‰ for the river water (Figure 6). The  $d$  values of the lake water were lower from March to August (except for June) in 2016 and were higher from September 2016 to March 2017. The  $d$  values of the river water were lower from April to September (except for August) in 2016 and were higher from October 2016 to February 2017. Generally, the warm months, with high solar radiation, air temperature and flow, correspond to relatively strong surface evaporation. However, contrary to 2016, the  $d$  values of river water were higher from May to August in 2017. This indicates that the evaporation condition is not the only factor influencing D-excess, and other factors such as river recharge sources and river inputs may also play an important role [51]. Moreover, it looks like the lake water  $d$  values may have a long-term positive linear trend that may need to be removed before the values can be compared between the river and lake water. According to the detrended plot (Figure S1 in the Supplementary Material), the low values of  $d$  in spring and summer can be more easily seen.

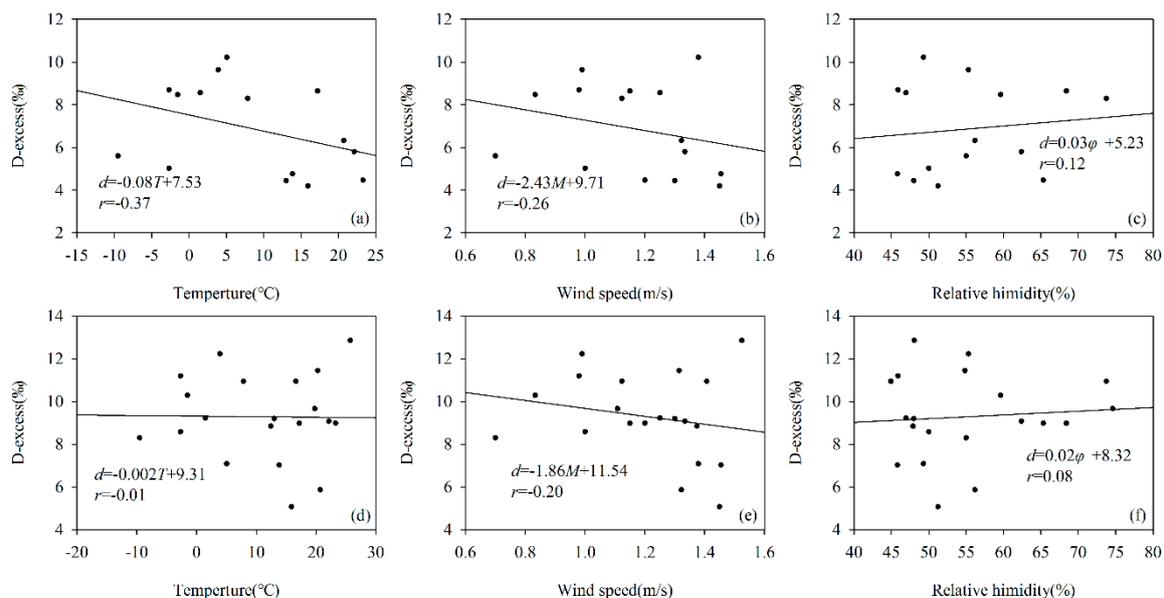


**Figure 6.** Variation of the D-excess value in (a) lake water from January 2016 to March 2017 and (b) river water from January 2016 to August 2017.

The mean  $d$  value in the lake water (7.08‰) was found to be lower than that of the river water (9.19‰). If the lake and river water have the exactly same water source, this difference in isotope signature is usually considered to reflect the evaporation of lake water being higher than that of the

river water. Because of the interception of the dam, the lake water in this study may be mixed in a relatively long residence time. However, another river stream, the Taohe River, contributes to the lake above the dam and does influence this hydrological process. The river water sampled was collected below the dam, which was mixed with the lake water in the study, as well as the Taohe River water. In this study, the surface water of the Taohe River was not directly collected, which may impact the explanations of the relationship of the stable isotope signature in the sampled river and lake waters. Although the proportional contribution of the Taohe River to the stream of the Yellow River is not very large [35], these integrated effects make the stable isotope signature of the river water more complex.

The regression equations between  $d$  value and air temperature are  $d = -0.08 T + 7.53$  ( $r = -0.37$ ) for the lake water and  $d = -0.002 T + 9.31$  ( $r = -0.01$ ) for the river water, respectively (Figure 7a,d). There is no correlation between  $d$  and temperature in the river water. The mixture process, considering the Taohe River, may weaken the temperature effect of surface water. There are negative correlations between  $d$  value and wind speed, and the regression lines were  $d = -2.43 M + 9.71$  ( $r = -0.26$ ) for lake water and  $d = -1.86 M + 11.54$  ( $r = -0.20$ ) for river water, respectively (Figure 7b,e). In addition, the correlation between  $d$  value and relative humidity is very weak. The regression equations are  $d = 0.03 \phi + 5.23$  ( $r = 0.12$ ) for the lake water and  $d = 0.02 \phi + 8.32$  ( $r = 0.08$ ) for the river water, respectively (Figure 7c,f). The above-mentioned correlation coefficients for the lake water were generally larger than those for the river water. Further conclusions require an improved sampling network, including more sites along this river, at least at the Taohe River mouth.



**Figure 7.** Correlation between meteorological parameters (surface air temperature, wind speed, and relative humidity) and D-excess in the lake (a, b and c) and the river water (d, e and f).

#### 4. Conclusion

In this work, we provide recent measurements of the stable isotope composition of lake water and river water at the upper reaches of the Yellow River. The isotopic values of the lake and river waters exhibit a seasonal variation. The heavy isotopes of surface water were more enriched during the warm months and depleted during the cold months. Moreover, a high precipitation amount would increase the water supply, resulting in an increase in river flow along the flow pathways during the warm months. The slopes of the lake water and river water lines are lower than that of the GMWL due to evaporation. Low  $d$  values correspond to positive  $\delta^{18}\text{O}$  values in the lake and river waters. Moreover, the  $d$  values of the lake water are higher than those of the river water. The river water samples were

collected at the lower part of the dam, where the lake water and Taohe River water is mixed. Thus, the isotopic signature of the collected river water is a result of the integrated effects.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4441/11/5/967/s1>, Figure S1: The variation of original and detrended D-excess in (a) the lake water and (b) the river water, Table S1: Inventory of surface water isotopes in the Liujiaxia Reservoir from 2016 to 2017.

**Author Contributions:** Conceptualization, S.W. and M.Z.; Software, M.S.; Validation, M.S.; Formal analysis, M.S.; Investigation, M.S.; Methodology, S.W., R.J., and Y.Z.; Resources, R.G. and S.Z.; Data curation, J.K.; Writing—original draft preparation, M.S.; Writing—review and editing, M.S., S.W., and A.A.A.; Supervision, X.Q.; Funding acquisition, S.W. and M.Z.

**Funding:** The study was supported by the National Natural Science Foundation of China Nos. 41701028 and 41771035, the Scientific Research Program of Higher Education Institutions of Gansu Province Nos. 2016B-019 and 2018C-02, and the Foundation of Key Laboratory for Ecology and Environment of River Wetlands of the Shaanxi Province No. SXSD201703.

**Acknowledgments:** The authors greatly thank the colleagues in the Northwest Normal University for their help in the laboratory analysis. Thanks also to J. E. Saylor (University of Houston) for the constructive suggestions.

**Conflicts of Interest:** The authors have declared no conflict of interest. The work described here has not been submitted elsewhere for publication, in whole or in part, and all the authors listed have approved the manuscript that is enclosed.

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