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Stable Isotope Ratios in Tap Water of a Riverside City in a Semi-Arid Climate: An Application to Water Source Determination

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Abstract: Stable isotopes (e.g., δ^2H and δ^{18}O) in tap water are important tools to understand the local climate or environment background, water sources and the state of regional water supply. Based on 242 tap water samples, 35 precipitation samples and 24 surface water samples gathered in the urban area of Lanzhou, the basic spatiotemporal characteristics of isotopes in tap water, their connection with isotopes in other water bodies and change during the process from raw water to tap water are discussed in detail, combining the information of local tap water supply and water source. It can provide reliable help for understanding the isotope characteristics of local tap water, regional water supply management and determination of tap water source of in a small area. Except for the establishment of a new data set of isotopes in tap water with complete time series and uniform spatial distribution of sampling sites, other results show that: (1) The Local Tap Water Line (LTWL) of Lanzhou is δ^2H = (6.03 ± 0.57) δ^{18}O + (−8.63 ± 5.44) (r^2 = 0.41, p < 0.01). (2) For seasonal variations, δ^2H and δ^{18}O in tap water both are higher in autumn and lower in spring. The diurnal and daily variations of isotopes in tap water are not large. As for spatial variations, the monthly mean values of δ^2H and δ^{18}O in tap water at each sampling site show little difference. The isotopes in tap water collected from one single sampling site can be considered as a representative for isotopes in tap water in the area with a single tap water source. (3) Isotopes in tap water show weak connection with precipitation isotopes, but exhibit good connection (consistent seasonal variation, similar numerical range, small numerical difference and high correlation) with isotopes in surface water, which is the direct water source. Isotopes in water change little from raw water to tap water. Isotopic composition of tap water in Lanzhou can be used as a representative of isotopes in surface water.

Keywords: stable isotope; δ^2H and δ^{18}O; tap water; precipitation; surface water; Lanzhou; China

1. Introduction

Stable isotopes in water (e.g., δ^2H and δ^{18}O) are significant indicators of hydrological processes and ecological patterns [1–5], and they have been widely used as tracers in climatology, hydrology, ecology and forensic studies [6–8], e.g., tracking atmospheric sources [9,10], tracing water source of plants [11–13], identifying the origin of forensic samples [14–16] and so on [17,18]. Precipitation, surface water and groundwater are three main fresh water bodies. Stable isotopes in them contain abundant environmental information, which are important for climate and hydrology fields [9,10,19–21]. Tap water mainly comes from the three main natural water bodies, and meanwhile it is highly influenced by human activities [22]. Therefore, isotopes in tap water can reflect the comprehensive characteristics of regional hydrological processes and human activities [23,24].

In recent years, except for being widely used to understand and monitor the hydrological cycle in the natural environment [25–29], stable isotopes in water have been increasingly used in urban water supply system research [30–36]; especially isotopes in tap water [24,37,38]. The isotopes of tap water in the United States were analyzed by Bowen et al. [39] and Landwehr et al. [40] successively. The spatial and temporal variations of stable isotopes in tap water were presented in detail, and the applicability of isotopic data to forensic identification of human tissues was evaluated [39,40]. Stable isotopes in tap water, the water supply system and adjustments during a major drought in the San Francisco Bay Area were explored by Tipple et al. [37]. Based on 612 tap water samples, Good et al. [41] analyzed isotopes in tap water and the utilization patterns of water resources in the western United States. West et al. [23] presented the first tap water and ground water isoscapes in South Africa and compared the isotopic characteristics between the two water resources. Jameel et al. [24] revealed the temporal and spatial patterns of isotopes in tap water collected from Salt Lake Valley in northern Utah, USA, and discussed the water source regions and the management of regional water resource. Zhao et al. [38] presented the spatiotemporal variations of δ^2H and δ^{18}O in tap water in China and analyzed the relationship between isotopes in tap water and topographic and meteorological factors. Wang et al. [42] analyzed the connection between monthly stable isotopes in tap water and precipitation based on a new nationwide network of tap water isotope data across China, and found that the diagnostic patterns of isotopes in tap water were associated with water resource use. As a whole, studies on isotopes in tap water are of great significance for enriching the understanding of tap water isotopes characteristics, environmental effect elements and water sources [23,24,39]. Stable isotopes (e.g., δ^2H and δ^{18}O) in tap water come to be important tools to understand the climate and environment characteristics in local area and water resources, monitor complex hydrological systems impacted by human activities, and reflect the state of regional water supply [24,43,44].

For domestic studies in China, there are only studies on the isotope characteristics of tap water and its relationship with precipitation isotopes in the whole country, based on relatively sparse sampling sites [38,42]. However, research on the detailed characteristics of isotopes and water sources of tap water in some small areas of China is scarce. For Lanzhou, the only provincial capital city that the Yellow River passes through in China, with semi-arid climate in the urban area, planning and maintaining a sustainable drinking water resource show great importance for the continuous development of the city. To isotopes in tap water in the urban area of Lanzhou, the basic spatiotemporal characteristics, connection with isotopes in other water bodies and change during the process from raw water to tap water are not yet clear, at present. It is necessary to establish a data set of isotopes in tap water with a complete time series and uniform spatial distribution of sampling sites, in order to analyze these problems. Studying these problems and combining the information of local tap water supply or water source can provide reliable help for understanding the isotope characteristics of local tap water, regional water supply management and determination of tap water source in a small area. In this study, stable isotopes (δ^2H and δ^{18}O) in 242 tap water samples gathered at 7 sampling sites, 35 precipitation samples and 24 surface water samples collected in the urban area of Lanzhou were discussed around these issues.

2. Data and Method

2.1. Sample Acquisition

The samples of tap water, precipitation and surface water were collected in the urban area of Lanzhou, mainly concentrating in the valley area. Water samples were gathered in 50 mL high density polyethylene (HDPE) bottles with parafilm. Cold tap water samples were obtained through running the tap for 10 s before filling into the bottles [45]. Tap water samples were gathered at the 7 sampling sites in Lanzhou, including Xiguan (T-1), Tanjianzi (T-2), Xizhan (T-3), Qiujiawan (T-4), Shijiawan (T-5), Jincheng (T-6) and Sunjiazhuang (T-7). Sampling sites of tap water show a relatively complete geographic coverage in the urban area of Lanzhou. Tap water samples at the site of Qiujiawan (T-4) were collected once a month from August 2014 to February 2018. Tap water samples from the other 6 sampling sites were gathered once a month from March 2016 and February 2018. The daily tap water samples were collected at the site of Qiujiawan (T-4) between 1 March 2018 and 31 March 2018, and the hourly tap water samples were gathered at the same site on 11 March 2018. The total number of tap water samples from the 7 sampling sites is 242. There were 35 precipitation samples collected from 35 precipitation events at the site of Qiujiawan from April 2016 to October 2016. Surface water samples were gathered at the site of Zhongshan Bridge in the Yellow River located in Lanzhou. They were collected monthly between March 2016 and February 2018, and the total number is 24. The spatial distribution and detailed information of sampling sites of tap water, precipitation and surface water are showed in Figure 1 and Table 1.

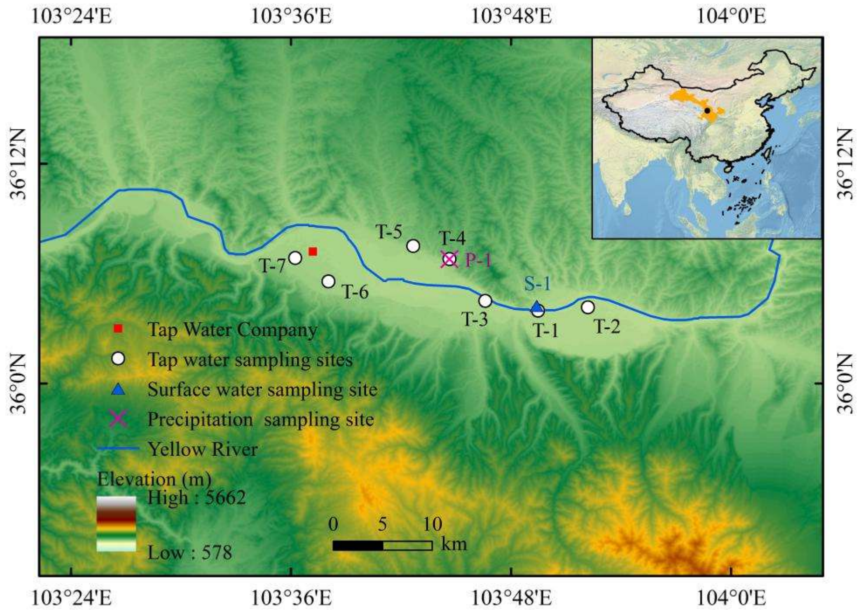

Figure 1. Spatial distribution of sampling sites of tap water, precipitation and surface water in Lanzhou.

Table 1. Information of sample sites of tap water, precipitation and surface water in Lanzhou.

Type	Code	Name of Sampling Sites	Longitude (°)	Latitude (°)	Elevation (m)	Sampling Period	Number of Samples (n)
Tap water sampling sites	T-1	Xiguan	103.825	36.066	1533	March 2016–February 2018	24
	T-2	Tanjianzi	103.870	36.069	1517	March 2016–February 2018	24
	T-3	Xizhan	103.777	36.075	1543	March 2016–February 2018	24
	T-4	Qiujiawan	103.744	36.113	1545	August 2014–February 2018 1 March 2018–31 March 2018 11 March 2018, 00:30–23:30	98
	T-5	Shijiawan	103.711	36.125	1550	March 2016–February 2018	24
	T-6	Jincheng	103.634	36.093	1586	March 2016–February 2018	24
	T-7	Sunjiazhuang	103.604	36.114	1542	March 2016–February 2018	24
Precipitation sampling site	P-1	Qiujiawan	103.744	36.113	1545	April 2016–October 2016	35
Surface water sampling site	S-1	Zhongshan Bridge	103.823	36.071	1551	March 2016–February 2018	24

2.2. Isotope Analysis

All the samples of tap water, precipitation and surface water were analyzed for δ^2H and δ^{18}O used the DLT-100 liquid water isotope analyzer (developed by the Los Gatos Research company, San Jose, CA, the United States) at the Stable Isotope Laboratory in College of Geography and Environmental Science, Northwest Normal University. Normally, all the samples were stored in the freezer to prevent the fractionation of isotopes, and they were taken out to thaw at room temperature before analysis. During the test process, every test group includes 3 standard samples and 6 unknown samples. Every sample (including standard sample and unknown sample) is measured for 6 injections. The first and second needles are abandoned in consideration of the memory effect of isotopes, and the test values of the latter 4 needles are calculated as the final result [46,47]. The measurement uncertainties in this study for δ^2H and δ^{18}O are ±0.6‰ and ±0.2‰, respectively. The test results are expressed relative to the Vienna Standard Mean Ocean Water (VSMOW).

$$\delta_{\text{sample}} = \frac{\left(R_{\text{sample}} - R_{\text{standard}}\right)}{R_{\text{standard}}} \times 1000‰ \tag{1}$$

In the formula, R_{sample} is the ratio of $^{18}O/^{16}O$ ($^2H/^1H$) in the water sample, and R_{standard} is the ratio of $^{18}O/^{16}O$ ($^2H/^1H$) in the VSMOW.

2.3. Other Data

The observational precipitation isotope data of long time series used in this paper are from the Global Network of Isotopes in Precipitation [48] (GNIP). The monthly mean values of δ^2H and δ^{18}O in precipitation at the site of Lanzhou were selected. They were calculated based on 84 precipitation samples from 1985 to 1999, and the monthly mean values of δ^2H and δ^{18}O in February were absent [48]. Deuterium and oxygen-18 in precipitation samples were determined by traditional isotope ratio mass spectrometry or laser absorption spectrometry. The test results were also expressed relative to the VSMOW [49,50]. At one standard deviation, the long-term precision of δ^2H and δ^{18}O reported in GNIP were about ±0.8‰ and ±0.1‰, respectively.

3. Result

3.1. Basic Characteristics of Isotopes in Tap Water

3.1.1. Local Tap Water Line

The relationship between δ^2H and δ^{18}O in tap water in Lanzhou is presented in Figure 2. The Local Tap Water Line (LTWL) in Lanzhou based on 168 tap water samples is $\delta^2H = (6.03 \pm 0.57)\ \delta^{18}O + (-8.63 \pm 5.44)$ ($r^2 = 0.41$, $p < 0.01$). The Global Meteoric Water Line (GMWL) fitted by Craig [19] is $\delta^2H = 8\delta^{18}O + 10$. The slope in the equation of tap water is lower than that in GMWL, which may be a reflection of the difference of evaporation intensity in the water source area [51]. Compared with the Chinese Tap Water Line $\delta^2H = 7.72\ \delta^{18}O + 6.57$ [38], the LTWL in Lanzhou presents a lower slope. The reason may be the relatively arid climate, and the evaporation in the water source area is more obvious. Compared with other countries or regions, the slope of the LTWL in Lanzhou is lower than those of Tap Water Lines in the USA (in February: $\delta^2H_{\text{February}} = 8.12\ \delta^{18}O_{\text{February}} + 4.94$, in August: $\delta^2H_{\text{August}} = 8.02\ \delta^{18}O_{\text{August}} + 8.21$) [40] and the San Francisco Bay Area [37] ($\delta^2H = 7.6\ \delta^{18}O + 2.3$). The slopes of the LTWL in South Africa [23] ($\delta^2H = 5.6\ \delta^{18}O + 0.91$) and the Salt Lake Valley of northern Utah, USA [24] (slopes range between 4.9 and 5.3 in 6 spring or autumn sampling sessions) are both lower than that of the LTWL in Lanzhou. Different slope values in Tap Water Lines in different countries or regions may be a result of different water sources and evaporation rates [51].

Moreover, the Local Meteoric Water Line (LMWL) in Lanzhou based on 35 precipitation samples presents as $\delta^2H = (7.08 \pm 0.34)\ \delta^{18}O + (5.12 \pm 1.90)$ ($r^2 = 0.93$, $p < 0.01$) (Figure S2 in Supplementary Materials). The LMWL in Lanzhou based on monthly δ^2H and δ^{18}O in precipitation from the Global Network of Isotopes in Precipitation (GNIP) is $\delta^2H = (6.62 \pm 0.22)\ \delta^{18}O + (-2.62 \pm 2.27)$ ($r^2 = 0.99$, $p < 0.01$) (Figure S3 in Supplementary Materials). The slope and intercept are both lower than those in GMWL, which may be as a result of more intense evaporation in Lanzhou. In addition, the Local Surface Water Line (LSWL) in Lanzhou based on 24 surface water samples collected monthly from March 2016 and February 2018 is $\delta^2H = (8.80 \pm 1.40)\ \delta^{18}O + (18.34 \pm 13.45)$ ($r^2 = 0.64$, $p < 0.01$) (Figure S2 in Supplementary Materials).

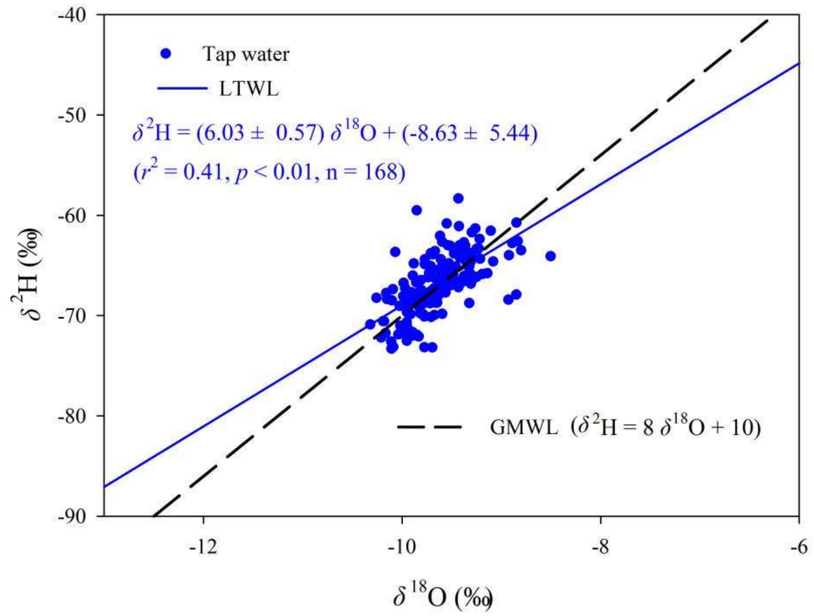

Figure 2. Relationship between δ^2H and $\delta^{18}O$ in tap water in Lanzhou. There were 168 tap water samples used in this chart, which were collected monthly at the seven sites from March 2016 to February 2018. (GMWL: Global Meteoric Water Line, LTWL: Local Tap Water Line).

3.1.2. Temporal Variations of Isotopes in Tap Water

Figure 3 shows the seasonal variations of stable isotope ratios in tap water at each sampling site in Lanzhou from March 2016 to February 2018. Seasonal and annual mean values of stable isotope ratios in tap water at all sampling sites and their standard deviations (SD) in Lanzhou from March 2016 to February 2018 are presented in Table 2. On the whole, there is a relatively small range for δ^2H and $\delta^{18}O$ in tap water samples in Lanzhou compared to those in samples collected throughout the country [38]. The seasonal mean values of δ^2H at each sampling site vary from −70.2 ± 3.0‰ to −64.1 ± 3.8‰, with a difference of 6.1‰ (Figure 3a). Those of $\delta^{18}O$ at each sampling site range from −9.9 ± 0.3‰ to −9.3 ± 0.4‰, with a difference of 0.6‰ (Figure 3b). From the aspect of seasonal variations, the δ^2H and $\delta^{18}O$ in tap water both show higher values in autumn and lower values in spring as a whole (Figure 3). For all the tap water sampling sites, the highest seasonal mean values of δ^2H and $\delta^{18}O$ both appear in autumn and they are −64.8 ± 0.5‰ and −9.5 ± 0.1‰, respectively (Table 2). And the lowest seasonal mean values of δ^2H and $\delta^{18}O$ both appear in spring (Table 2). The annual mean values of δ^2H and $\delta^{18}O$ are −66.7 ± 0.26‰ and −9.6 ± 0.06‰, respectively (Table 2).

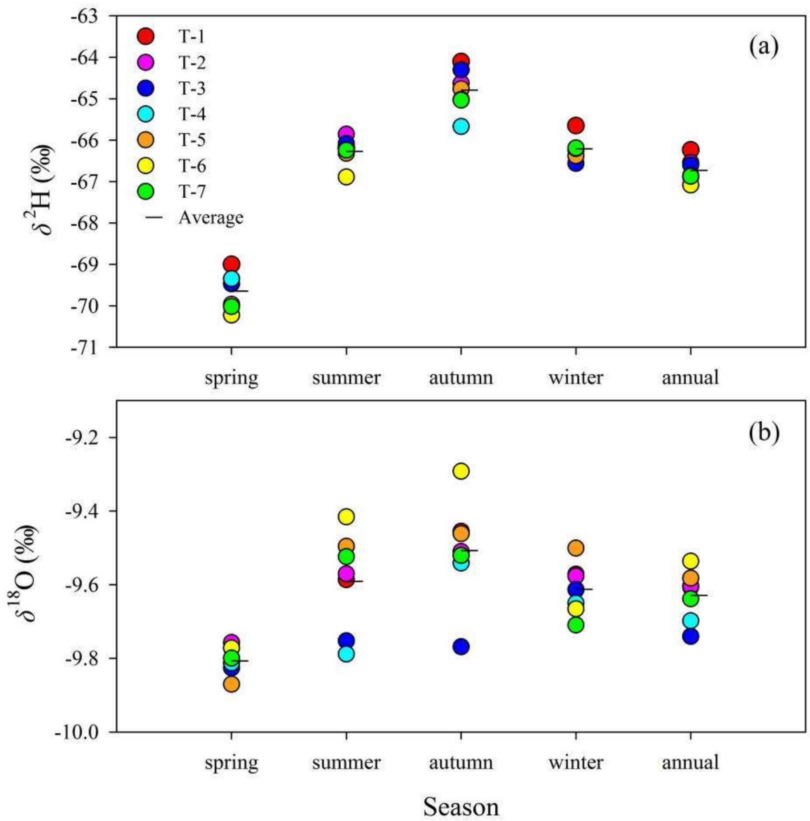

Figure 3. Seasonal variations of δ^2H and δ^{18}O in tap water at each sampling site in Lanzhou from March 2016 to February 2018. (**a**) δ^2H, (**b**) δ^{18}O.

Table 2. Seasonal and annual mean values of δ^2H and δ^{18}O in tap water at all sampling sites and their standard deviations (SD) in Lanzhou from March 2016 to February 2018.

Isotope and SD	Spring	Summer	Autumn	Winter	Annual
δ^2H (‰)	−69.6	−66.3	−64.8	−66.2	−66.7
SD for δ^2H (‰)	0.4	0.3	0.5	0.3	0.3 [1]
δ^{18}O (‰)	−9.8	−9.6	−9.5	−9.6	−9.6
SD for δ^{18}O (‰)	0.03	0.1	0.1	0.1	0.1 [1]

[1] Annual standard deviations are calculated based on the 4 seasonal mean isotope values.

The sampling period at the sampling site of Qiujiawan is longer than that of other sites and more temporal features can be analyzed. Figure 4 shows the interannual variations of stable isotope ratios in tap water at the sampling site of Qiujiawan (T-4) in Lanzhou from August 2014 to February 2018. The seasonal values of δ^2H in tap water samples collected in 2017 (purple symbols in Figure 4a) are higher than those of δ^2H in tap water samples collected in other years. The highest annual mean values of δ^2H and δ^{18}O both appear in 2017, and they are −65.9 ± 2.4‰ and −9.7 ± 0.3‰, respectively. The lowest annual mean values of δ^2H and δ^{18}O both present in 2015.

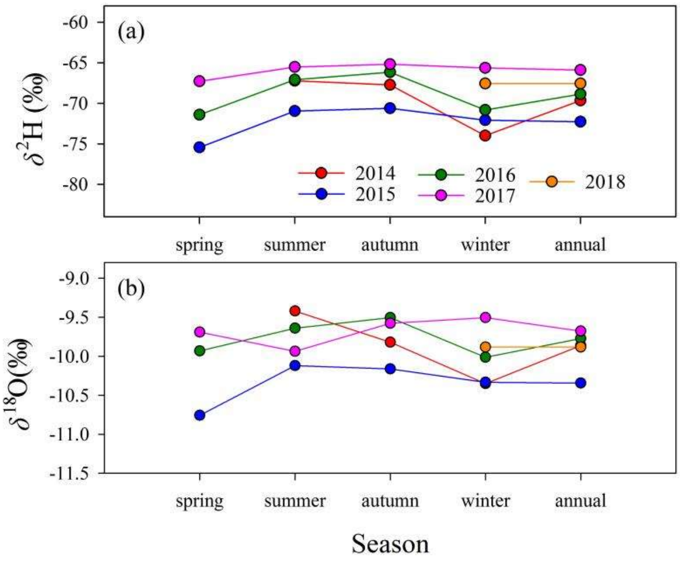

Figure 4. Interannual variations of stable isotope ratios in tap water at the sampling site of Qiujiawan (T-4) in Lanzhou from August 2014 to February 2018. (**a**) δ^2H, (**b**) δ^{18}O.

Figure 5 exhibits the daily variations of stable isotope ratios in tap water at the sampling site of Qiujiawan (T-4) in Lanzhou from 1 March 2018 to 31 March 2018. The ranges of daily values of δ^2H and δ^{18}O at Qiujiawan in March 2018 are small, from −73.2‰ to −67.6‰ and from −10.6‰ to −9.2‰, respectively. The standard deviations for daily δ^2H and δ^{18}O are 1.6‰ and 0.3‰, respectively. The highest value of δ^2H at Qiujiawan appears on 8 March 2018 and the lowest value presents on 31 March 2018 (Figure 5a). The highest and lowest values of δ^{18}O can be seen on 3 March 2018 and 27 March 2018, respectively (Figure 5b).

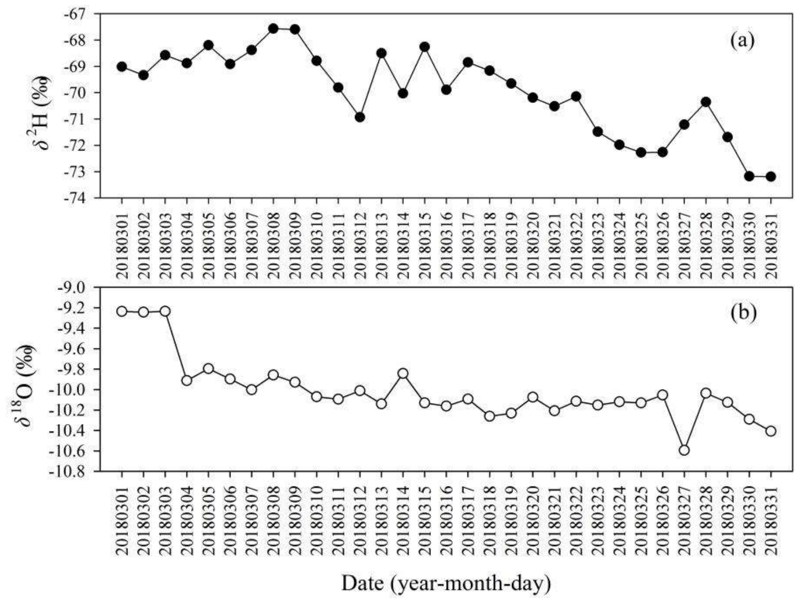

Figure 5. Daily variations of stable isotope ratios in tap water at the sampling site of Qiujiawan (T-4) in Lanzhou from March 1, 2018 to March 31, 2018. (**a**) δ^2H, (**b**) δ^{18}O.

Figure 6 shows the diurnal variations of stable isotope ratios in tap water at the sampling site of Qiujiawan (T−4) in Lanzhou on 11 March 2018. As a whole, the daily values of stable isotope ratios in tap water at Qiujiawan vary within a small range. The hourly values of δ^2H at Qiujiawan vary from −71.0‰ to −67.6‰ (Figure 6a). The highest and lowest values of δ^2H appear at 23:30 and 18:30, respectively (Figure 6a). The highest and lowest values of δ^{18}O present at 12:30 and 23:30, and they are −9.8‰ and −10.4‰, respectively (Figure 6b). The differences between the average isotopes (δ^2H: −69.5‰, δ^{18}O: −10.0‰) in tap water during the day time (8:00–20:00) and those (δ^2H: −68.8‰, δ^{18}O: −10.1‰) at night are small. The standard deviations for hourly δ^2H and δ^{18}O are 0.8‰ and 0.2‰, respectively.

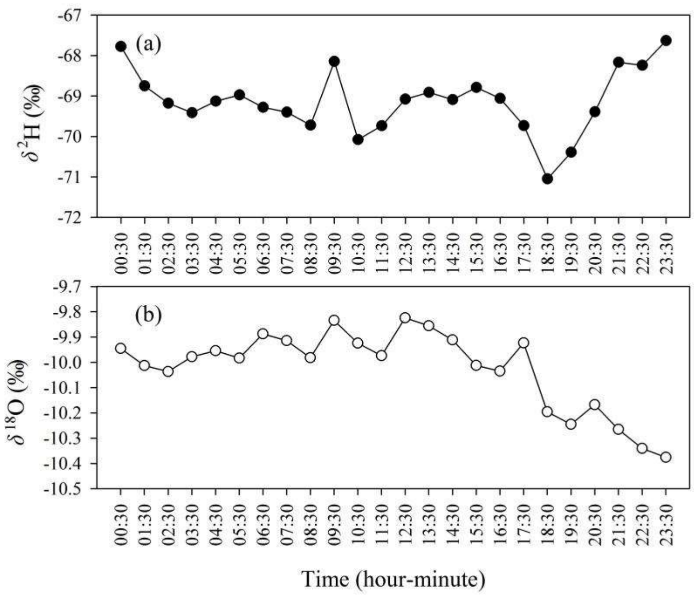

Figure 6. Diurnal variations of stable isotope ratios in tap water at the sampling site of Qiujiawan (T-4) in Lanzhou on March 11, 2018. (**a**) δ^2H, (**b**) δ^{18}O.

3.1.3. Differences of Isotopes in Tap Water at Each Sampling Site

In order to analyze the differences among all the tap water sampling sites, the monthly anomaly values of stable isotope ratios in tap water are presented in Figure 7. In general, the monthly anomaly values of δ^2H and δ^{18}O in tap water among the 7 sampling sites are relatively small. Those for δ^2H and δ^{18}O mostly concentrate from −1‰ to 1‰ and between −0.2‰ and 0.2‰, respectively. Stable isotopes in tap water exhibit small differences among the 7 sampling sites.

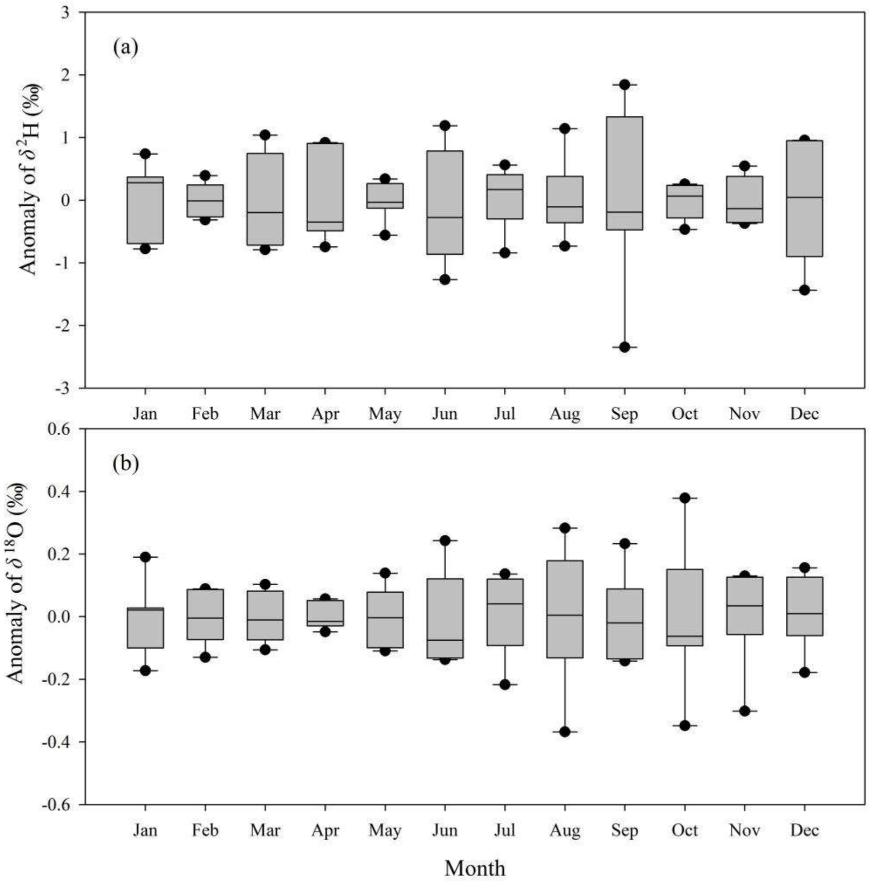

Figure 7. Monthly anomaly values of stable isotope ratios in tap water in Lanzhou. (**a**) monthly anomaly of δ^2H, (**b**) monthly anomaly of δ^{18}O. The anomaly value of one sampling site means the difference between the monthly value at this sampling site and the mean value at all sampling sites in the same month. The bottom and top of the box indicate the 25th and 75th percentiles, the line in the box marks the 50th percentile (median), whiskers exhibit the 10th and 90th percentiles; points below and above the whiskers show the 5th and 95th percentiles, respectively.

3.2. Comparison of Isotopes in Tap Water with Those in Precipitation and Surface Water

Figures 8 and 9 present the comparison of temporal variations of isotopes in tap water with those in precipitation and surface water, respectively. Table 3 exhibits the seasonal and annual mean values of δ^2H and δ^{18}O in precipitation and surface water and their standard deviations (SD). Generally speaking, the temporal changes of δ^2H and δ^{18}O in tap water and collected precipitation present inconsistent characteristics (Figure 8a,c). The highest median of δ^2H in collected precipitation appears in June and the lowest median presents in April (Figure 8a). Within the same sampling period, the highest median of δ^2H in tap water can be found in September and the lowest median can be seen in May (Figure 8a). The highest and lowest medians of δ^{18}O in collected precipitation appear in October and April (Figure 8c). Those of δ^{18}O in tap water can be found in August and June (Figure 8c). The seasonal mean values of δ^2H and δ^{18}O in collected precipitation are the highest in autumn and the lowest in spring (Table 3). In addition, the range of isotope values in tap water is smaller than those in collected precipitation in Lanzhou (Figure 8). From April 2016 to October 2016, the values of δ^2H in collected precipitation range between −90.5‰ and 34.8‰, and for tap water, the range is from −73.2‰ to−58.3‰ (Figure 8a). As for δ^{18}O, the values in collected precipitation range from −12.5‰ to 4.4‰, and those in tap water are from −10.3‰ to −8.5‰ (Figure 8c).

Figure 8a,c showed the comparison of δ^2H and δ^{18}O in tap water with those in collected precipitation gathered within a shorter period of time. To explore whether there are some different conclusions for the precipitation isotope data of longer time series, the monthly mean values of δ^2H and δ^{18}O in tap water and GNIP precipitation were compared in Figure 8b,d. They present different seasonal variations (Figure 8b,d). For example, the monthly mean values of δ^2H and δ^{18}O in tap water present lower spring and higher autumn values, and GNIP precipitation data show a typical behaviour for the Northern Hemisphere stations, with lower winter and higher summer values (Figure 8b,d). The numerical differences of δ^2H and δ^{18}O between tap water and GNIP precipitation are relatively large (Figure 8b,d). The GNIP precipitation isotope data for Lanzhou are from 1985 to 1999, which is about 20 years ago, and the present precipitation isotope data (isotope in collected precipitation) may differ from the older ones due to current global climate change (i.e., global temperature increase). The results show that the relations between the isotopes in tap water and those in the present and older precipitation are both weak.

On the contrary, δ^2H and δ^{18}O in surface water and tap water show consistent seasonal variations in general, which exhibit higher values in autumn and lower values in spring (Figure 9). The seasonal mean values of δ^2H and δ^{18}O in surface water in autumn are both the highest in the four seasons and they are −64.1 ± 3.0‰ and −9.5 ± 0.2‰, respectively (Table 3). The lowest seasonal mean values of δ^2H and δ^{18}O both appear in spring and they are −70.0 ± 0.4‰ and −9.9 ± 0.1‰, respectively (Table 3). The highest and lowest seasonal mean values of δ^2H and δ^{18}O in tap water also can be found in autumn and spring, respectively (Table 2). Besides, the range of isotope values in surface water in Lanzhou is similar to those in tap water. The 12 monthly mean values of δ^2H between surface water and tap water are similar (Figure 9a). The annual mean values of δ^2H in surface water and tap water are −66.5 ± 1.2‰ (Table 3) and −66.7 ± 0.3‰ (Table 2), respectively. Those of δ^{18}O in surface water and tap water are −9.6 ± 0.2‰ (Table 3) and −9.6 ± 0.1‰ (Table 2), respectively.

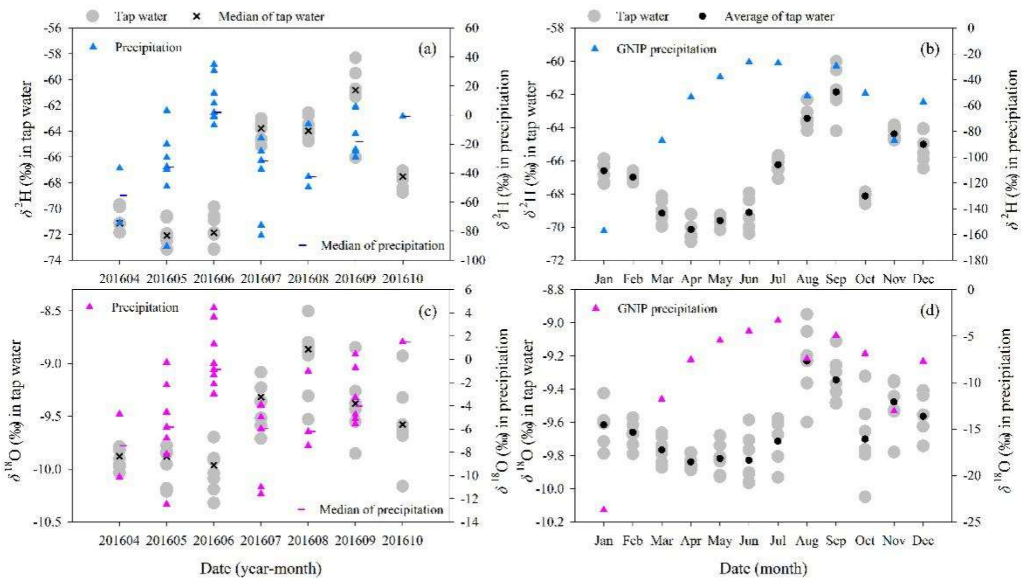

Figure 8. Comparison of temporal variations of δ^2H and δ^{18}O in tap water with those in collected precipitation (**a**,**c**) and those in precipitation from GNIP [48] (Global Network of Isotopes in Precipitation) (**b**,**d**). (**a**,**c**) The data of δ^2H and δ^{18}O in collected precipitation at the site of Qiujiawan (P-1) are from April 2016 to October 2016. The monthly data of δ^2H and δ^{18}O in tap water at 7 sampling sites are from April 2016 to October 2016. (**b**,**d**) The monthly mean values of δ^2H and δ^{18}O in GNIP precipitation at the site of Lanzhou are from 1985 to 1999 (the monthly mean values of δ^2H and δ^{18}O in February are absent). The monthly data of δ^2H and δ^{18}O in tap water at 7 sampling sites are between March 2016 and February 2018.

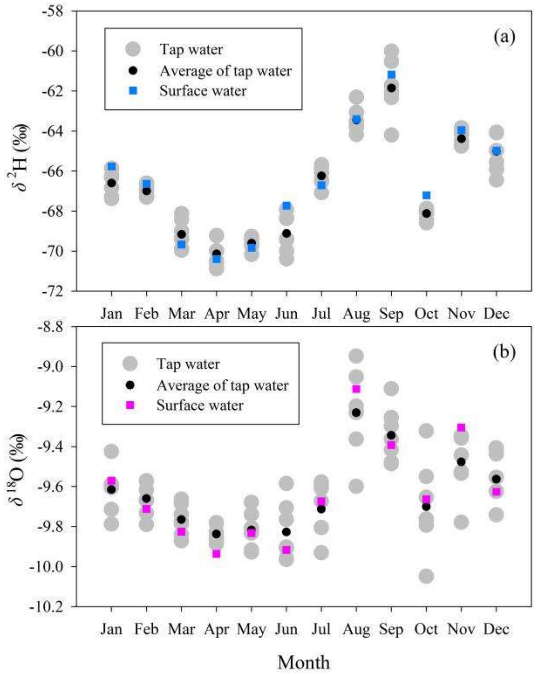

Figure 9. Comparison of temporal variations of δ^2H (**a**) and δ^{18}O (**b**) in tap water with those in surface water. The monthly data of δ^2H and δ^{18}O in tap water at 7 sampling sites and those in surface water at the site of Zhongshan Bridge (S-1) are both between March 2016 and February 2018.

Table 3. Seasonal and annual mean values of δ^2H and δ^{18}O in precipitation and surface water and their standard deviations (SD) in Lanzhou.

Type of Water	Seasonal or Annual Mean Value	δ^2H (‰)	SD for δ^2H (‰)	δ^{18}O (‰)	SD for δ^{18}O (‰)
Precipitation	spring	−46.2	13.1	−6.6	1.1
	summer	−22.2	27.4	−3.9	3.6
	autumn	−7.1	8.7	−0.8	3.3
Surface water	spring	−70.0	0.4	−9.9	0.1
	summer	−65.9	2.3	−9.6	0.4
	autumn	−64.1	3.0	−9.5	0.2
	winter	−65.8	0.8	−9.6	0.1
	annual	−66.5	1.2 [1]	−9.6	0.2 [1]

[1] Annual standard deviations are calculated based on the 4 seasonal mean isotope values.

Figure 10 shows the differences between δ^2H and δ^{18}O in tap water and those in collected precipitation and surface water. Obviously, the values of δ^2H and δ^{18}O in tap water are much closer to those in surface water rather than to those in collected precipitation. The absolute values of differences for δ^2H between tap water and surface water in the four seasons are all < 1‰. Those for δ^2H between tap water and collected precipitation in spring, summer and autumn are all > 20‰ (Figure 10a). The absolute values of differences for δ^{18}O between tap water and surface water in each season are all < 0.1‰. Those for δ^{18}O between tap water and collected precipitation in spring, summer and autumn are all > 3‰ (Figure 10b).

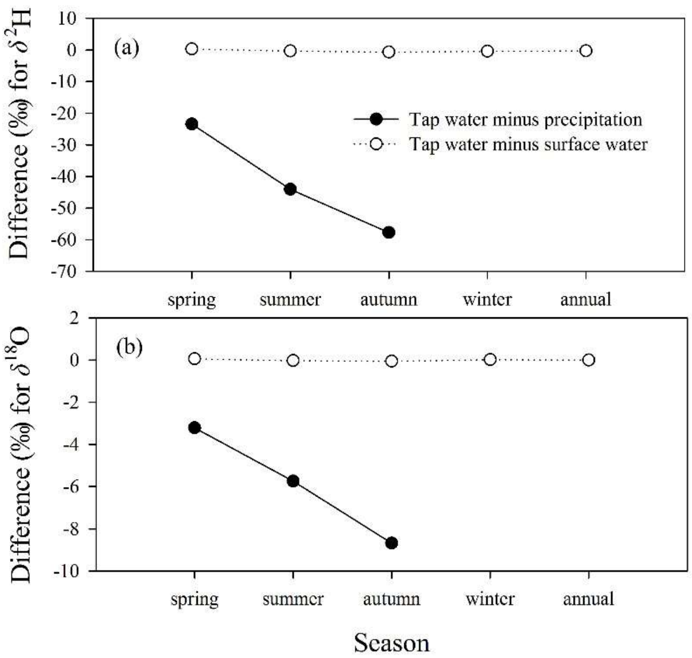

Figure 10. Differences between δ^2H (**a**) and $\delta^{18}O$ (**b**) in tap water and those in collected precipitation and surface water.

Figure 11 exhibits the relationships of δ^2H and $\delta^{18}O$ in surface water, GNIP precipitation and collected precipitation with those in tap water in Lanzhou. Solid circles and error bars show the arithmetic average and standard deviation, respectively. Generally speaking, stable isotope ratios in tap water show better correlation with those in surface water than with those in GNIP precipitation and collected precipitation. The isotope values in tap water and surface water show good positive correlation (all R values for $\delta^2H > 0.8$, all R values for $\delta^{18}O > 0.5$, and p values < 0.01, shown in Figure S3 in Supplementary Materials), while there is no correlation between isotope values in tap water and either GNIP and collected precipitation (all R values < 0.3, and p values > 0.05, shown in Figure S3 in Supplementary Materials).

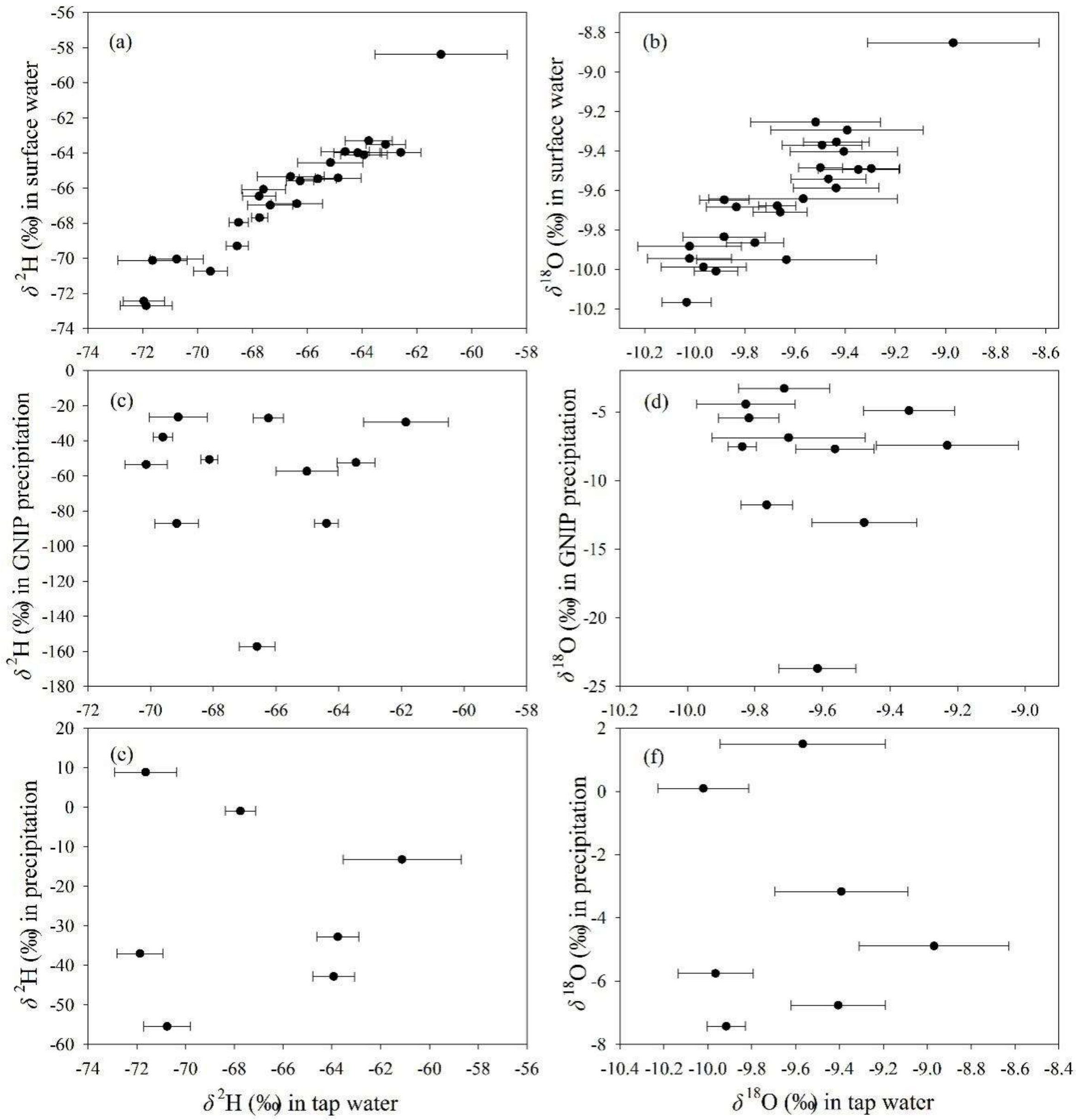

Figure 11. Relationship of δ^2H and δ^{18}O in surface water (**a**,**b**), GNIP precipitation (**c**,**d**) and collected precipitation (**e**,**f**) with those in tap water in Lanzhou. Solid circles and error bars show the arithmetic average and standard deviation, respectively. The monthly data of δ^2H and δ^{18}O in surface water and tap water at 7 sampling sites from March 2016 to February 2018 were used in (**a**) and (**b**). The monthly mean values of δ^2H and δ^{18}O in GNIP precipitation at the site of Lanzhou from 1985 to 1999 (the monthly mean values of δ^2H and δ^{18}O in February were absent) and those in tap water at 7 sampling sites from March 2016 to February 2018 were used in (**c**) and (**d**). The data of δ^2H and δ^{18}O in collected precipitation at the site of Qiujiawan and tap water at 7 sampling sites from April 2016 to October 2016 were applied in (**e**) and (**f**).

4. Discussion

4.1. Representation of Isotope Data at a Single Sampling Site

In the analysis of anomaly values (Figure 7), the monthly anomaly values of δ^2H and δ^{18}O in tap water at all sampling sites are relatively small. Those for δ^2H mainly range from −1‰ to 1‰ and those for δ^{18}O mostly vary between −0.2‰ and 0.2‰. This shows that the isotope data in tap water samples collected from a single sampling site have a good representation for the tap water isotope composition in the region with same water source.

4.2. Determination of Tap Water Source Based on Isotope Data

As shown in the comparison of isotopes among different water bodies (Tables 2 and 3, Figures 8–11, Figure S1), isotopes in tap water and precipitation exhibit large differences at the aspects of seasonal variation, numerical range and numerical value. In contrast, isotopes in tap water and surface water exhibit consistent seasonal variation, similar numerical range, small numerical difference and high correlation. According to the water source information in the Water Resources Bulletin of Gansu Province [52] and investigation data from tap water supplier (Figure 1) in Lanzhou, the main source of tap water is the Yellow River water (surface water). Therefore, tap water isotope composition is a good indicator for the direct water source, and the connection of isotopes between tap water and non-direct source water is weak for small regions (e.g., a city).

In the existing tap water isotope studies [23,42] on large scales, it has been proved that isotopes in tap water mainly supplied by surface water show good correlation with precipitation isotopes [42]. Our conclusion supplements the analysis of tap water source based on the isotopes method at different spatial scales. It provides a basis for the identification of direct tap water source in small, centralized or non-centralized water supply areas.

4.3. Change of Isotopes from Raw Water to Tap Water

In this study, consistent seasonal patterns and similar numerical values of isotopes between tap water and source water (Tables 2 and 3, Figures 9 and 10) indicate that the production processes of tap water in tap water company have little effect on isotopes in water, and the database of tap water isotope composition in the urban area of Lanzhou can be used as a proxy for isotopes in surface water.

5. Conclusions

The stable isotope composition of tap water is useful for the studies of climate, urban water management, water source, health, ecology and forensic science. A new urban tap water isotope composition dataset with complete time series and uniform spatial distribution of sampling sites was established in this study. The spatiotemporal characteristics of isotopes in tap water, their connection with isotopes in other water bodies and change during the process from raw water to tap water are discussed in detail, combining the information of local tap water supply and water source. Results show that: the Local Tap Water Line (LTWL) of Lanzhou is $\delta^2H = (6.03 \pm 0.57)\ \delta^{18}O + (-8.63 \pm 5.44)$ ($r^2 = 0.41$, $p < 0.01$). About seasonal variations, δ^2H and $\delta^{18}O$ in tap water both show higher values in autumn and lower values in spring. The diurnal and daily changes of δ^2H and $\delta^{18}O$ in tap water are relatively small. From the perspective of spatial differences, the monthly mean values of δ^2H and $\delta^{18}O$ in tap water at each sampling site show little difference. The isotopic composition of tap water from one single sampling site can be considered as a representative for isotopes in tap water in the area with a single tap water source. Isotopes in tap water show weak connection with precipitation isotopes, but exhibit good connection with isotopes in surface water which is direct water source, showing consistent seasonal variation, similar numerical range, small numerical difference and high correlation. Tap water isotope composition is a good indicator for the direct water source. Isotopes in water change little from raw water to tap water. The isotopic composition of tap water in Lanzhou can be used as a proxy for that of surface water.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/11/7/1441/s1, Figure S1. Relationship between δ^2H and δ^{18}O in collected precipitation and surface water in Lanzhou. 35 precipitation samples were gathered from 35 precipitation events at the site of Qiujiawan from April 2016 and October 2016. 24 surface water samples were monthly collected at the site of Zhongshan Bridge in the Yellow River located in Lanzhou between March 2016 and February 2018. (GMWL: Global Meteoric Water Line, LMWL: Local Meteoric Water Line, LSWL: Local Surface Water Line), Figure S2. Relationship between δ^2H and δ^{18}O in precipitation of Lanzhou from the Global Network of Isotopes in Precipitation (GNIP). The monthly mean values of δ^2H and δ^{18}O in precipitation at the site of Lanzhou from 1985 to 1999 were used, and the monthly mean values of δ^2H and δ^{18}O in February were absent. (GMWL: Global Meteoric Water Line, LMWL: Local Meteoric Water Line). Figure S3. Correlation coefficients of stable isotope ratios in tap water with those in collected precipitation and surface water at all sampling sites. (a) correlation coefficient (*R*) of δ^{18}O, (b) correlation coefficient (*R*) of δ^2H.

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