Influence of Sub-Cloud Secondary Evaporation and Moisture Sources on Stable Isotopes of Precipitation in Shiyang River Basin, Northwest China

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Abstract: Fractionation of stable isotopes in precipitation runs through the water cycle, and deuterium excess is a second-order parameter linking water-stable oxygen and hydrogen isotopes. It is strongly influenced by under-cloud evaporation in unsaturated air, especially in arid climates. Based on the improved Stewart model, this study used 670 precipitation stable isotope data and measured meteorological element data from 11 sampling points from January 2018 to September 2019 to verify the existence of sub-cloud secondary evaporation in the Shiyang river basin and quantitatively calculate the intensity of sub-cloud secondary evaporation and its influence on precipitation stable isotopes. The study used the vapor flux and the improved Lagrangian model to track the moisture source of precipitation and analyze the influence of the moisture source of different paths on the stable isotopes of precipitation. Therefore, this study is helpful to understand the evapotranspiration loss mechanism and recharge mechanism of moisture in the watershed. The results showed that there is sub-cloud secondary evaporation in the Shiyang River Basin, and from the seasonal scale, the sub-cloud secondary evaporation is stronger in spring and summer, but weaker in autumn and winter, which makes heavy isotopes enriched in spring and summer and depleted in autumn and winter. From the perspective of spatial distribution, the sub-cloud secondary evaporation is stronger in the midstream and downstream of the Shiyang river, resulting in more enrichment of heavy isotopes. In the vertical direction, the sub-cloud secondary evaporation at 850–700 hPa is the strongest, which enriches the heavy isotope in this layer and reduces the deuterium excess. In addition, the main moisture source of precipitation in the Shiyang River Basin is the westerly air mass, and the mid and high-latitude land sources contribute more moisture to the precipitation. However, the supply of the sea source is very limited, which makes the deuterium excess of precipitation higher and does not show regional consistency and seasonality well.

Keywords: Shiyang River Basin; precipitation; stable isotope; sub-cloud secondary evaporation; moisture sources

1. Introduction

Hydrogen and oxygen stable isotopes are the main substances that constitute water molecules. In the process of evaporation, condensation, moisture transport, and precipitation, they are usually accompanied by thermodynamic equilibrium fractionation and dynamic non-equilibrium fractionation, which can reflect the phase transition history of water, record important information in the water body and reflect the development and changes of climate and environment [1] Therefore, $^2$H and $^{18}$O have become an important tracer and are widely used in researching different forms and scales of ecological hydrological processes [2,3]. In addition, the recharge of terrestrial water resources mainly depends on atmospheric precipitation to a certain extent, which is a key link in the water cycle process. The analysis and research of precipitation stable isotopes are crucial for a
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The stable isotopic composition of hydrogen and oxygen in the residual water that has
precipitation, which will enrich heavy isotopes and reduce
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the liquid phase to form vapor and then enter the atmosphere, making the light isotopes
H and 18O) evaporation first, heavy isotopes (2H and 18O) enrich, the slopes and intercepts of the LMWL deviate from the GMWL (to some extent), and deuterium excess reduces. It has been proved that the sub-cloud secondary evaporation is an important factor for this phenomenon [11] but it is not the only factor, and the d-excess can reflect the changes in the composition of 2H and 18O in the precipitation process and used to indicate the degree of imbalance in the evaporation process [12]. Some studies have pointed out that analyzing the slope and intercept of LMWL and the changes in d-excess under different environmental conditions can qualitatively assess the existence and intensity of sub-cloud secondary evaporation [13–15]. In the actual water evaporation process, since light water molecules are more active, they are the first to separate from the liquid phase to form vapor and then enter the atmosphere, making the light isotopes (H and 16O) preferentially evaporate and concentrate in the moisture, while the remaining water heavy isotopes (2H and 18O) usually have stronger binding energy and lower diffusion rate, making it difficult to evaporate, and thus are enriched in the liquid phase. The stable isotopic composition of hydrogen and oxygen in the residual water that has undergone the evaporation process and the newly formed moisture are different from the isotopic composition of the original water. Heavy isotopes in precipitation are gradually depleted with increasing altitude and humidity, and enriched with increasing temperature and recirculated moisture. The non-equilibrium kinetic fractionation caused by sub-cloud secondary evaporation has an important effect on the composition of stable isotopes in precipitation, which will enrich heavy isotopes and reduce d-excess [16] [Kress et al., 2010]. Although the ratio of hydrogen and oxygen isotope changes linearly, this linear relationship also has a deviation from the equilibrium state, which is manifested as a change of d-excess in precipitation [17]. Moisture recirculation will deplete heavy isotopes in precipitation and increase the d-excess, while sub-cloud secondary evaporation will enrich heavy isotopes in precipitation and reduce the d-excess [18–21]. Therefore, analyzing the effects of sub-cloud secondary evaporation and moisture sources on precipitation stable isotopes is an indispensable part of the research area’s atmospheric water cycle.

The quantitative study of sub-cloud secondary evaporation begins with Stewart [22] used experimental methods to calculate the effect of evaporation on stable isotopes in raindrops under different ambient gases and meteorological conditions. Froehlich et al. [23,24] simulated and established a raindrop evaporation model to study the effect of sub-cloud secondary evaporation. After that, some studies have proposed different methods to improve the raindrop evaporation model. Using several standard isobaric surfaces as the dividing line in the falling process of raindrops, Guan et al. [25] divided the atmosphere into several homogeneous horizon combinations to calculate the sub-cloud secondary evaporation, which can more accurately characterize the evaporation experienced during the fall of
raindrops. Wang et al. [26] improved the input parameters of the Stewart model, using the precipitation intensity to calculate the diameter of the raindrops, and using the lifting condensation level (LCL) as the precipitation height (cloud base height), that is, setting the precipitation height and raindrop diameter as variables, replacing the fixed parameters in the Stewart model. However, the Stewart model has some limitations in its basic assumptions. It proposes to take the atmosphere experienced by raindrops as a homogeneous body and use ground-measured meteorological data instead of upper-air meteorological data as the input parameters of the model for calculation and analysis (that is, the homogeneous assumption). At present, most studies on sub-cloud secondary evaporation are based on the homogeneous assumption, but the atmospheric parameters are neither homogeneous nor uniform from upper air to the ground. Therefore, Crawford et al. [27] based on the Stewart raindrop evaporation model used vertical temperature and humidity profiles, subdivided the raindrop falling process into six vertical layers, and calculated the raindrop falling process hierarchically, that is, the hierarchical assumption. It mainly divides the atmosphere experienced by raindrops in the process of falling into several homogeneous horizon combinations according to several standard isobaric surfaces. This method takes into account the changes in temperature and humidity in the vertical direction, reduces the error of the calculation results, and can more accurately describe the sub-cloud secondary evaporation. This method has been applied in Xinjiang [28] and Australia [15].

There are many research methods for precipitation moisture sources, such as Hysplit and Flexpart models, isotope analysis, and Euler methods [29,30]. The analysis method of the Hysplit backward trajectory based on the Lagrangian model is widely used, since the overall spatial minimum variance cluster analysis method proposed by Draxler et al. [31]. The number of trajectories in the channel is used to trace the moisture source of the precipitation, and can simulate the main source direction and proportion of the air mass at the observation point in a certain period of time, providing a better technical approach for studying the moisture. Sodemann et al. [32] and Crawford et al. [27] improved the traditional Lagrangian approach (i.e., using the back trajectory), which considered the meteorological elements on the model trajectory, and used the specific humidity to correct the backward trajectory of moisture, that is to judge the source of moisture from the perspective of moisture supply intensity on the trajectory. For the calculated multiple sources, the continuous increase of specific humidity and the maximum position of the sum of continuous changes is used as the moisture source. This method has been applied to Greenland [32], Australia [33], and the moisture source analysis of short-duration rainstorms in Xinjiang [34].

The Shiyang River Basin is deep in the hinterland of the Eurasian continent, where the formation and transformation of water resources and the hydrological cycle process are complex [35]. As one of three major inland river basins in Gansu Province, the water supply mainly comes from mountain precipitation and meltwater. Due to global climate warming that led to the decrease of glacier reserves and precipitation, coupled with the increase of population and rapid development of economy and society, the over-extraction of groundwater is serious in the basin. The decline of water conservation capacity was caused by the destruction of vegetation in the upper Qilian Mountains and the increase of irrigation water in the midstream oasis, leading to the amount of surface water decreasing in the downstream oasis. Since the contradiction between the supply and demand of water has become increasingly prominent, the problem of desertification is very serious [36,37]. Therefore, changes in hydrological processes caused by precipitation and snowmelt are related to the redistribution of regional water resources and water security. Based on the measured meteorological data and the hydrogen and oxygen stable isotope data obtained from the precipitation samples in the Shiyang River Basin, the improved Stewart model was used to quantitatively calculate the proportion of the remaining mass of raindrops after evaporation during falling and the change of stable isotopes in precipitation. The process of sub-cloud secondary evaporation is difficult to observe by traditional meteorological methods. It can be analyzed based on the change characteristics of hydrogen and oxygen stable isotopes in the process of precipitation, which can reveal the evaporation loss mecha-
nism in the process of raindrops falling. Traceback to the moisture source of precipitation was performed to reveal the moisture driving mechanism of the seasonal variation of precipitation in the basin. In addition, this study further analyzed the effects of sub-cloud secondary evaporation and moisture sources on the stable isotopes of precipitation, which also provides a theoretical basis for the study of the regional eco-hydrological processes.

2. Data and Methods

2.1. Study Area

The Shiyang River Basin is located in the eastern part of Hexi Corridor in Gansu Province and the northern slope of the Qilian Mountains (101°41′–104°16′ E, 36°29′–39°27′ N). The basin area is $4.16 \times 10^4$ km² and the altitude is 1254–5125 m. The terrain is higher in the south than the north, and it slopes from southwest to northeast. The natural environment in the Shiyang River Basin is quite different, it can be divided into four major geomorphological units from south to north: the Qilian Mountains, the corridor plain, the northern low hills and the desert [38]. The Shiyang River Basin is located in the transitional area between the monsoon area and the arid area, with short and hot summer, long and cold winter, large temperature difference, small precipitation, strong evaporation, and dry air [39]. From south to north, it can be divided into three climate zones: the alpine semi-arid and semi-humid area in the southern Qilian Mountains, with an average annual temperature of 2–6 °C, annual precipitation of more than 300 mm, and annual evaporation of 700–1200 mm; the cool and arid area in the central corridor plain, with the annual average temperature of 6–8 °C, the annual precipitation of 150–300 mm, and the annual evaporation of 1200–2000 mm; the warmer and arid area in the north, with the annual average temperature of more than 8 °C, the annual precipitation of less than 150 mm, and the annual evaporation of more than 2000 mm [40,41]. Shiyang River originates from Daxue Mountain on the north side of Lenglongling in the eastern section of the Qilian Mountains, with an average annual runoff of 15.6 × 10^8 m³ [42]. It is supplied mainly by precipitation (91.2%) and also contains alpine meltwater (3.6%) [43], which is concentrated mainly in summer and autumn [44]. After going northward, it flows through the corridor plain and Minqin Oasis and disappears gradually in the desert on the northern margin of the basin (Figure 1).

![Figure 1](image-url)
it is divided into three sections, which are labeled as upstream: Lenglongling (S1), Hulinzhan (S2), Hujianxiang (S3), Xiyingwugou (S4), midstream: Xiyingzhen (S5), Yangxiaba (S6), Dengjiazhuang (S7), Jiuquntan (S8), and downstream: Xuebaizhen (S9) Hongqigu (S10), Datanxiang (S11). Note: This map is made based on the standard map with the approval number GS (2020) 4619 downloaded from the standard map service website of the State Bureau of Surveying and Mapping, and the base map has not been modified.

2.2. Sample Collection and Data Sources

2.2.1. Collection and Processing of Precipitation Sample

As shown in Figure 1, this study selected 11 collection points of precipitation samples in the Shiyang River Basin, and the sampling period is from January 2018 to September 2019. The collection of all precipitation samples was carried out according to the definition of precipitation events stipulated by meteorological observations (that is, all precipitation from 20:00 on the current day to 20:00 on the next day was defined as a precipitation event, and a sample was collected). The sample was collected using the SM1 rain and snow gauge (stainless steel), which comes with a 5 L polyethylene collection bottle and a 26 cm polyethylene funnel, is an instrument used in meteorological observatories (stations), agriculture, forestry and other units to determine the amount of precipitation and snowfall in the atmosphere. The measures to limit evaporation have been taken, and a ping-pong is placed on the funnel mouth to prevent evaporation of the samples. These measures were placed in an open area away from the sampling points of soil and plant about 700 m. Using the automatic weather observation instruments, the data of temperature, dew point, relative humidity, and atmospheric pressure were also recorded. A total of 670 precipitation samples were transported to the isotope laboratory of the College of Geography and Environmental Sciences of Northwest Normal University for testing and analysis. The testing instrument is the DLT-100 liquid water isotope analyzer developed by Los Gatos Research in the United States. The test error of $\delta D$ value does not exceed $\pm 0.6\%$, and the test error of $\delta^{18}O$ value does not exceed $\pm 0.2\%$, and the measurement result is expressed by the difference between the test sample isotope ratio and the standard sample ratio ($\%$):

$$\delta^{18}O (\text{or} \delta D) = \left( \frac{R_s}{R_{V-SMOW}} - 1 \right) \times 1000$$  \hspace{1cm} (1)

where $R_s$ is the ratio of $^{18}O/^{16}O$ in the precipitation sample, and $R_{V-SMOW}$ is the ratio of $^{18}O/^{16}O$ in the Vienna Standard Mean Ocean Water.

2.2.2. Other Data Sources

As shown in Figure 1, this study selected the meteorological data of 11 upper-air stations near the Shiyang River Basin (Minqin, Yuzhong, Kongtong, Hezuo, Jiuquan, Dunhuang, Mazongshan, Xining, Dulan, Yinchnan, Ejinaqi) (https://www.ncdc.noaa.gov accessed on 10 November 2020), and used Inverse Distance Weighting (IDW) to interpolate the high-altitude data of the sounding station to the locations of the weather stations on the ground. The reanalyzing data comes from NCEP/NCAR ($2.5^\circ \times 2.5^\circ$) of Physical Sciences Laboratory of the National Ocean and Atmospheric Administration of the United States (NOAA) (https://www.psl.noaa.gov accessed on 15 December 2020). The backward trajectory data comes from the Global Data Assimilation System (GDAS) (ftp://arlitftp.arlhq.noaa.gov accessed on 15 December 2020) operated by the National Environmental Forecast Center of the United States.
2.3. Method

2.3.1. Local Meteoric Water Line

The method of ordinary least squares [45] is used to calculate the local meteoric water line (LMWL), and the slope ($a$) and intercept ($b$) are, respectively:

$$a = \frac{\sum_{i=1}^{n} xy - (1/n) \sum_{i=1}^{n} x \sum_{i=1}^{n} y}{\sum_{i=1}^{n} x^2 - (1/n) \left( \sum_{i=1}^{n} x \right)^2}$$  \hspace{1cm} (2)

$$b = \frac{1}{n} \sum_{i=1}^{n} y - (a/n) \sum_{i=1}^{n} x$$  \hspace{1cm} (3)

where $n$ is the number of samples, $x$ is the $\delta^{18}O$, and $y$ is the $\delta^D$.

The theoretical slope ($S_T$) of the LMWL is calculated based on the condensation temperature [46]:

$$S_T = \frac{\left(2^\alpha - 1\right)(1000 + \delta^D)}{\left(18^\alpha - 1\right)(1000 + \delta^{18}O)}$$  \hspace{1cm} (4)

where $2^\alpha$ and $18^\alpha$ are the equilibrium fractionation coefficients of hydrogen and oxygen isotopes between water and gas, respectively [47].

2.3.2. Raindrop Evaporation Model of Improved STEWART

Due to the sub-cloud secondary evaporation, there are some differences in the isotopes between the raindrops at the cloud bottom and the raindrops falling on the ground ($\Delta d$). The formula as follows:

$$\Delta d = \left(1 - \frac{2^\gamma}{2^\alpha}\right)\left(f^\beta - 1\right) - 8\left(1 - \frac{18^\gamma}{18^\alpha}\right)\left(f^{18\beta} - 1\right)$$  \hspace{1cm} (5)

where $2^\gamma$, $18^\gamma$, $2^\beta$, and $18^\beta$ are defined by Stewart [22]; $2^\alpha$ and $18^\alpha$ are the same as Formula (4); $f$ is the proportion of the remaining mass of raindrops after evaporation during falling [26]. The $f$ can be calculated as:

$$f = \frac{m_{end}}{m_{end} + m_{ev}}$$  \hspace{1cm} (6)

where $m_{end}$ is the mass of the raindrop touching the ground and is defined as:

$$m_{end} = \frac{4}{3} \pi r_{end}^3 \rho$$  \hspace{1cm} (7)

where $r_{end}$ is radius of raindrops falling to the ground, $\rho$ is the density of water. $m_{ev}$ is the mass lost by evaporation. $m_{ev}$ can be expressed by the raindrop evaporation rate ($r_{ev}$) multiply the raindrop landing time ($t$), where the $t$ is used the cloud base height ($H$) and the terminal velocity of raindrops ($v_{end}$) to calculate. The $H$ is calculated by the Laplace pressure formula [48]:

$$H = 18,400(1 + T_{mean}/273)\log(P/P_{LCL})$$  \hspace{1cm} (8)

where $T_{mean}$ is the average temperature between the lifting condensation level (LCL) and the ground (°C). $P$ and $P_{LCL}$ are the pressure (hPa) at the ground and the LCL, respectively. According to Kinzer et al. [49], the $r_{ev}$ can be calculated as:

$$r_{ev} = Q_1 Q_2$$  \hspace{1cm} (9)

where $Q_1$ is a function (cm) of temperature ($T$) and raindrop diameter ($D$); $Q_2$ is a function (g·cm$^{-1}$·s$^{-1}$) of $T$ and relative humidity ($RH$). The raindrop diameter is based on the empirical formula of global rainfall raindrop diameter distribution proposed by Best [50] (1950).
and is obtained after calculating the rain intensity based on the measured precipitation data at sampling points in the basin. The $D$ can be calculated as:

$$1 - F = e^{-\left(\frac{D}{AI}\right)\cdot n}$$  \hspace{1cm} (10)

where $e$ is a natural constant; $D$ is the raindrop diameter; $I$ is the precipitation intensity (mm·h$^{-1}$); $F$ is fraction of liquid water in the air composed of raindrops with diameter less than $D$.

The $D_c$ in the stratification hypothesis is based on the raindrop diameter of the ground to calculate the raindrop diameter of the cloud base through the iterative calculation:

$$D_c = \sqrt[3]{\frac{6(m_{end} + m_{ev})}{\pi \rho}}$$  \hspace{1cm} (11)

where $D_c$ is the diameter of raindrops at cloud base; $m_{end}$ is the mass of the raindrop touching the ground, $m_{ev}$ is the mass lost by evaporation; $\rho$ is the density of water.

2.3.3. Calculation of Atmospheric Vapor Flux and Contribution Rate of Water Vapor Transportation

Atmospheric water vapor content is also called atmospheric precipitable amount, that is, the amount of liquid water vapor that can be obtained when the moisture in the column of air is condensed [51]. The formula is as follows:

$$W(\lambda, \varphi, t) = \frac{1}{g} \int_{p_s}^{p} q dp$$  \hspace{1cm} (12)

where $W$ is the total water vapor content of the entire layer of the atmosphere over a unit area; $q$ is the specific humidity of each layer, $p$ and $p_s$ are the atmospheric top and ground pressures, respectively. Sufficient moisture is required to produce precipitation, while the water vapor content above 300 hPa is low, and the water vapor data is not accurate above this point. Therefore, this study take 300 hPa is the top layer.

In the $p$ coordinate, the calculation formula for the latitude and longitude of the water vapor transport flux vector $Q$ (vertically integrated water vapor flux) per unit length through the bottom side perpendicular to the wind direction and the height of the entire atmospheric column area for [51,52]

$$Q_v = \frac{1}{g} \int_{p_s}^{p} v q dp$$

$$Q_u = \frac{1}{g} \int_{p_s}^{p} u q dp$$  \hspace{1cm} (13)

where $q$ is the specific humidity of each layer; $p_s$ and $p$ are surface pressure and atmospheric top pressure, respectively, $u$ and $v$ are the wind speed vectors of each layer of the atmosphere in the unit column of longitude and latitude, and the units of $Q_u$ and $Q_v$ are kg·m$^{-1}$·s$^{-1}$.

The calculation method of the contribution rate of the water vapor transportation of each water vapor channel is [53]:

$$Q_S = \frac{\sum_{i=1}^{n} q_{last}}{\sum_{i=1}^{n} q_{last}} \times 100\%$$  \hspace{1cm} (14)

where $Q_S$ is the channel water vapor transport contribution rate, $q_{last}$ represents the specific humidity of the final position on the channel, $m$ represents the number of trajectories contained in the channel, and $n$ represents the total number of all trajectories.

2.3.4. Backward Trajectory Adjusted Using Specific Humidity

The Backward Trajectory used the United States National Ocean and Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) developed by the Atmospheric Resources Laboratory of the NOAA to track moisture sources. HYSPLIT is a complete system for
computing simple air parcel trajectories, as well as complex transport, dispersion, chemical transformation, and deposition simulations. The version used in this study is HYSPLIT 5.

The number of trajectories in the channel is used to trace the moisture source of the precipitation using the HYSPLIT backward trajectory model, and the overall spatial minimum variance cluster analysis method proposed by Draxler et al. [31]. That is, assuming that there are certain number of tracks, the spatial variance of each cluster is defined as the sum of the squares of the distances between each track in the cluster and the corresponding point of the average track of the cluster. The spatial variance of each track is zero at the starting time, and each is an independent cluster; The spatial variance of all possible combinations of two clusters, any two clusters are merged into a new cluster, so that the sum of the spatial variances (TVS) of all clusters after merging is the smallest increase compared with before merging, until all trajectories are merged into one cluster. The results of the cluster analysis have good reliability, and can simulate the main source direction and proportion of the air mass at the observation point in a certain period of time.

The residence time of moisture is generally about 10 days in the stratosphere, but the replenishment of moisture does not necessarily occur before 10 days. Therefore, this study refers to the studies of Sodemann et al. [32] and Crawford et al. [33], the meteorological elements on the Lagrangian trajectory are also taken into consideration, that is, the moisture source is judged from the perspective of the moisture supply intensity on the trajectory. Specifically, in the process of backtracking, when the specific humidity at an earlier time (every 6 h) is higher than that at a later time by more than 0.1 g/kg and the simulated height of the air mass trajectory is below the planetary boundary layer, which is judged as the moisture source. For the multiple sources calculated, the maximum position where the specific humidity increases continuously and the sum of the continuous changes is used as the moisture source. If the specific humidity on the backward trajectory is less than 0.05 g/kg, it is considered that there is no more moisture replenishment before, that is, do not backtracking the moisture source. The starting height of the backward trajectory is the height at which precipitation occurs. In this study, the lifting condensation level is used as the starting height, which the specific algorithm refers to Equation (8).

3. Results

3.1. Local Meteoric Water Line

Table 1 reflects the mean of $\delta$D and $\delta^{18}$O at different sampling points during the research period, as well as the slope and intercept of the LMWL, which can be judged the existence and intensity of the sub-cloud secondary evaporation.

<table>
<thead>
<tr>
<th>Station</th>
<th>Longitude (E)</th>
<th>Latitude (N)</th>
<th>Altitude (m)</th>
<th>Number of Samples</th>
<th>Research Period</th>
<th>Mean $\delta$D (%)</th>
<th>Mean $\delta^{18}$O (%)</th>
<th>Intercept (%)</th>
<th>Slope</th>
<th>$r^2$</th>
<th>Theoretical Slope</th>
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<tbody>
<tr>
<td>Lenglongling</td>
<td>101.86°</td>
<td>37.56°</td>
<td>3653</td>
<td>188</td>
<td>January 2018–August 2019</td>
<td>$-68.19$</td>
<td>$-10.26$</td>
<td>$12.70$</td>
<td>$7.88$</td>
<td>0.98</td>
<td>8.87</td>
</tr>
<tr>
<td>Hulinzhuan</td>
<td>101.86°</td>
<td>37.69°</td>
<td>2720</td>
<td>65</td>
<td>March 2018–August 2019</td>
<td>$-43.62$</td>
<td>$-7.16$</td>
<td>$11.65$</td>
<td>$7.69$</td>
<td>0.97</td>
<td>8.78</td>
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<tr>
<td>Huaiyuanxiang</td>
<td>102.01°</td>
<td>37.84°</td>
<td>2324</td>
<td>150</td>
<td>January 2018–September 2019</td>
<td>$-52.54$</td>
<td>$-7.80$</td>
<td>$7.70$</td>
<td>$7.22$</td>
<td>0.99</td>
<td>8.61</td>
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<tr>
<td>Xiyingwugou</td>
<td>102.18°</td>
<td>37.89°</td>
<td>2096</td>
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<td>January 2018–October 2019</td>
<td>$-78.40$</td>
<td>$-11.29$</td>
<td>$7.93$</td>
<td>$7.93$</td>
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<tr>
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<td>37.97°</td>
<td>1748</td>
<td>43</td>
<td>May 2018–April 2019</td>
<td>$-46.30$</td>
<td>$-6.77$</td>
<td>$3.64$</td>
<td>$7.38$</td>
<td>0.98</td>
<td>8.52</td>
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<td>38.03°</td>
<td>1489</td>
<td>23</td>
<td>May 2018–January 2019</td>
<td>$-29.57$</td>
<td>$-4.49$</td>
<td>$1.10$</td>
<td>$6.82$</td>
<td>0.97</td>
<td>8.41</td>
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<td>38.10°</td>
<td>1468</td>
<td>15</td>
<td>July 2019–October 2019</td>
<td>$-60.15$</td>
<td>$-8.89$</td>
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<td>May 2018–September 2019</td>
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<td>1348</td>
<td>57</td>
<td>April 2018–September 2019</td>
<td>$-47.08$</td>
<td>$-7.03$</td>
<td>$4.22$</td>
<td>$7.29$</td>
<td>0.96</td>
<td>8.19</td>
</tr>
</tbody>
</table>

By comparing the mean of $\delta$D and $\delta^{18}$O at each sampling point, it can be seen that the $\delta$D and $\delta^{18}$O of the Shiyang River Basin generally show a decreasing trend with altitude increase. Although the altitude of Xiyingwugou is lower than other sampling points of the upstream, the mean of $\delta$D and $\delta^{18}$O are the lowest. This may be due to the fact that the sampling point is close to the reservoir and is affected by the combined influence of moisture recirculation intensity, relative humidity, and temperature, which masks the elevation effect
of the stable isotope. The slopes and intercepts of the LMWL at sampling plots in the Shiyang River Basin deviate to a certain extent from the GMWL ($\delta D = 8\delta^{18}O + 10$). Except for Dengjiazhuang, the slopes of the LMWL of other sampling points are all less than 8. Compared with the slope, the intercept change of the LMWL is more complicated, which is related to the degree to which $\delta D$ deviates from equilibrium due to fractionation. Except for Lenglongling, Hulinzhan, Xiyangwugou, and Dengjiazhuang, the intercepts of the LMWL at other sampling points are much lower than the GMWL. At the same time, the $S_T$ of each sampling point is greater than 8 and greater than the slope of the LMWL, indicating that the precipitation process occurs under non-Rayleigh conditions, which also shows that there exists sub-cloud secondary evaporation. Besides, the slopes of most sampling points in the midstream and downstream are lower than those in the upstream, indicating that the sub-cloud secondary evaporation is stronger in the midstream and downstream than in the upstream.

3.2. Sub-Cloud Secondary Evaporation

3.2.1. The Sub-Cloud Secondary Evaporation Based on Homogeneous Assumptions

Based on the measured meteorological elements of 11 sampling points, these data are averages over the study periods, assumed the atmosphere of raindrops falling from the cloud base to the ground as a homogeneous form, and used the measured meteorological data of ground sampling points as input parameters, the sub-cloud secondary evaporation was calculated at different sampling points (Table 2). Therefore, this study focuses on the environmental factors during precipitation to clarify their impact on the sub-cloud secondary evaporation.

<table>
<thead>
<tr>
<th>Station</th>
<th>$T$ (°C)</th>
<th>RH (%)</th>
<th>$D$ (mm)</th>
<th>$H$ (m)</th>
<th>$F$ (%)</th>
<th>$\Delta d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lenglongling</td>
<td>3.23</td>
<td>71.77</td>
<td>0.85</td>
<td>577.77</td>
<td>76.97</td>
<td>$-$3.03</td>
</tr>
<tr>
<td>Hulinzhan</td>
<td>10.12</td>
<td>73.74</td>
<td>0.94</td>
<td>568.88</td>
<td>78.72</td>
<td>$-$2.39</td>
</tr>
<tr>
<td>Huajianxiang</td>
<td>12.22</td>
<td>60.07</td>
<td>1.11</td>
<td>968.38</td>
<td>68.71</td>
<td>$-$4.14</td>
</tr>
<tr>
<td>Xiyangwugou</td>
<td>7.81</td>
<td>69.88</td>
<td>0.94</td>
<td>649.54</td>
<td>73.74</td>
<td>$-$3.69</td>
</tr>
<tr>
<td>Xiyingzhen</td>
<td>15.3</td>
<td>60.73</td>
<td>0.84</td>
<td>980.65</td>
<td>51.36</td>
<td>$-$12.39</td>
</tr>
<tr>
<td>Yangxiaba</td>
<td>16.07</td>
<td>58.71</td>
<td>0.93</td>
<td>1038.14</td>
<td>53.33</td>
<td>$-$9.89</td>
</tr>
<tr>
<td>Dengjiazhuang</td>
<td>19.27</td>
<td>69.57</td>
<td>1.26</td>
<td>719.94</td>
<td>79.12</td>
<td>$-$1.73</td>
</tr>
<tr>
<td>Jiuduntan</td>
<td>21.34</td>
<td>69.71</td>
<td>1.18</td>
<td>762.26</td>
<td>72.12</td>
<td>$-$2.83</td>
</tr>
<tr>
<td>Xuebaizhen</td>
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<td>69.19</td>
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<td>773.20</td>
<td>67.00</td>
<td>$-$4.71</td>
</tr>
<tr>
<td>Hongqigu</td>
<td>20.02</td>
<td>62.6</td>
<td>1.32</td>
<td>1006.48</td>
<td>70.42</td>
<td>$-$3.88</td>
</tr>
<tr>
<td>Datanxiang</td>
<td>23.36</td>
<td>68.44</td>
<td>0.94</td>
<td>818.85</td>
<td>60.82</td>
<td>$-$4.21</td>
</tr>
</tbody>
</table>

Note: Environmental factors including air temperature ($T$), relative humidity (RH), raindrop diameter ($D$), and the height of the cloud base (precipitation height) ($H$). 11 sampling points are presented in the same order as in Table 1.

From the results in Table 2, it can be seen that, except for Hongqigu, Dengjiazhuang, and Jiuduntan, the change trends of $f$ and $\Delta d$ are basically the same for most of the other sampling points, and the $f$ of most sampling points in the midstream and downstream is smaller than that in the upstream. This indicates that the sub-cloud secondary evaporation in the midstream and downstream is stronger than that in the upstream, which is consistent with the results of the LMWL. Comparing the environmental elements in Table 2, it can be shown that the temperature in the midstream and downstream is higher than that in the upstream. This is mainly due to the fact that the underlying surface causes temperature differences and the upstream is mountainous (whereas the downstream is desert). Although the average raindrop diameter of most sampling points in the midstream and downstream is larger than that in the upstream, the lower altitudes, long time for raindrops to fall, temperature and precipitation conditions are favorable for evaporation, so the sub-cloud secondary evaporation of the former is stronger than that in the latter. The $f$ in Hongqigu is relatively larger compared with other midstream and downstream sampling points. This is due to the fact that the nearby Hongyashan Reservoir has a large water area, which makes the water vapor content in this area higher than other midstream and downstream sampling points, and the raindrops diameter is larger, which restricts the production of
evaporation to a certain extent. The \( f \) of Dengjiazhuang and Jiuduntan is also relatively larger. The reason is that the precipitation samples are mostly concentrated in summer with abundant precipitation, and the larger raindrop diameters, the higher relative humidity, the lower height of raindrops, and the short time for raindrops make the sub-cloud secondary evaporation weaker than other sampling plots in the midstream and downstream.

3.2.2. The Sub-Cloud Secondary Evaporation Based on Stratification Assumption

Due to the non-uniform variation of atmospheric elements from high altitudes to the ground, the sub-cloud secondary evaporation will also vary in the vertical direction. In this study, according to the altitudes and pressure of the sampling point, the raindrop falling process is calculated in sections, three atmospheric pressure layers of 850 hPa (approximately 1500 m), 700 hPa (approximately 3000 m), and 500 hPa (approximately 5500 m) are selected as the dividing line from the ground to the high altitude, and the atmosphere is divided correspondingly into several homogeneous layer combinations. Based on the homogeneous assumption, the input parameters required for each layer are calculated by iterative calculations, and the evaporation of raindrops falling from the cloud base to the ground is calculated. Since the large differences in the geomorphology of the sampling points in the study area, the altitude of them and the atmospheric pressure during the precipitation period are considered comprehensively when using the stratification assumption. When the height between the cloud base and the ground is less than the height of the isobaric surface, the height difference between the isobaric surface and the ground is used as the height of the raindrop landing. The sampling points are divided into three groups for calculation: ① The altitude of the sampling point > 3000 m (Sampling point air pressure < 700 hPa); ② 1500 m < sampling point altitude < 3000 m (700 hPa < sampling point air pressure < 800 hPa); ③ Sampling point altitude < 1500 m (sampling point air pressure > 850 hPa).

According to the calculation results of the stratification assumption in Table 3, it can be seen that the \( f \) values and the \( d \)-excess of the first group (Lenglongling) are relatively low, which indicates the sub-cloud secondary evaporation is strong. This may be related to the raindrop diameter that is the smallest among all sampling points, which is conducive to evaporation. For the sampling points of the secondary group, the \( f \) values at 700–500 hPa reach the maximum, which indicates the sub-cloud secondary evaporation is weaker. The \( f \) value at ground–700 hPa is lower than that at 700–500 hPa at Huilinzhan, Huajianxiang, Xiyinwugou, and Xiyin2zhen, indicating that heavy isotope enriches and light isotope deplete, and they further make the \( d \)-excess decrease. Comparing the environmental factors, although the relative humidity of 700–500 hpa is lower than that of the ground–700 hpa, the temperature of the ground–700 hPa is higher, the height of the raindrops is larger, the raindrops fall for a long time, and the diameter of the raindrops is also smaller, which provides a favorable environment condition for the sub-cloud secondary evaporation, while 700–500 hpa is the opposite, so the sub-cloud secondary evaporation effect is weaker. The changing trends of the \( f \) of each sampling point are the same in the third group, that all of them are ground–850 hPa > 700–500 hPa > 850–700 hPa. Comparing environmental factors, it can be seen that this phenomenon is related closely to temperature, raindrop landing height, and raindrop diameter. At ground–850 hPa, the temperature is the highest among the three levels, and the raindrop diameter is the smallest, this creates good conditions for evaporation. However, the landing height of raindrops is the lowest, so the raindrop landing time is the shortest and the sub-cloud secondary evaporation effect is weaker. At 700–500 hPa, the landing height of raindrops is the highest among the three levels and the raindrop landing time is the longest, but the temperature is the lowest and the raindrop diameter is the largest, which is not conducive to evaporation and the sub-cloud secondary evaporation is weaker relatively. At 850–700 hPa, not only temperature is higher, but also the landing height of raindrops is higher, and the raindrops diameter has not reached the maximum, so the sub-cloud secondary evaporation effect is the strongest.
Table 3. Sub-cloud secondary evaporation and environmental factors based on stratification assumption.

<table>
<thead>
<tr>
<th>Group</th>
<th>Station</th>
<th>Stratification</th>
<th>$T$ ($^{\circ}$C)</th>
<th>RH (%)</th>
<th>$H$ (m)</th>
<th>$D$ (mm)</th>
<th>$f$ (%)</th>
<th>$\Delta^{18}O$ (%)</th>
<th>$\Delta^{2}H$ (%)</th>
<th>$\Delta d$ (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>①</td>
<td>Lenglongling</td>
<td>Ground–500 hPa</td>
<td>1.14</td>
<td>69.58</td>
<td>576.47</td>
<td>0.81</td>
<td>76.47</td>
<td>5.94</td>
<td>25.31</td>
<td>−22.18</td>
</tr>
<tr>
<td></td>
<td>Hulinzhan</td>
<td>Ground–700 hPa</td>
<td>8.65</td>
<td>68.47</td>
<td>306.21</td>
<td>0.93</td>
<td>84.42</td>
<td>3.36</td>
<td>13.06</td>
<td>−13.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700–500 hPa</td>
<td>5.92</td>
<td>63.94</td>
<td>369.68</td>
<td>0.99</td>
<td>85.37</td>
<td>2.71</td>
<td>10.79</td>
<td>−10.92</td>
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<td>②</td>
<td>Huajianxiang</td>
<td>Ground–700 hPa</td>
<td>9.19</td>
<td>60.12</td>
<td>670.57</td>
<td>0.81</td>
<td>62.32</td>
<td>9.66</td>
<td>38.64</td>
<td>−38.65</td>
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<tr>
<td></td>
<td></td>
<td>700–500 hPa</td>
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<td>53.34</td>
<td>469.49</td>
<td>0.96</td>
<td>85.57</td>
<td>4.09</td>
<td>16.91</td>
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<td>Ground–700 hPa</td>
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<td>601.64</td>
<td>0.77</td>
<td>69.79</td>
<td>7.16</td>
<td>29.05</td>
<td>−28.20</td>
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<td></td>
<td></td>
<td>700–500 hPa</td>
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<td>49.52</td>
<td>344.94</td>
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<td>86.49</td>
<td>3.92</td>
<td>15.49</td>
<td>−15.84</td>
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<td>③</td>
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<td>11.52</td>
<td>62.32</td>
<td>902.58</td>
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<td>55.32</td>
<td>11.2</td>
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<td></td>
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<td>335.70</td>
<td>1.10</td>
<td>92.46</td>
<td>2.03</td>
<td>7.80</td>
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<td>15.85</td>
<td>58.84</td>
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<td>94.38</td>
<td>1.55</td>
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<td>49.04</td>
<td>84.55</td>
<td>1.28</td>
<td>98.31</td>
<td>0.46</td>
<td>1.78</td>
<td>−1.90</td>
</tr>
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<td>69.96</td>
<td>36.86</td>
<td>0.79</td>
<td>94.30</td>
<td>1.46</td>
<td>5.38</td>
<td>−6.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850 hPa–700 hPa</td>
<td>14.62</td>
<td>60.26</td>
<td>701.51</td>
<td>0.83</td>
<td>57.95</td>
<td>10.64</td>
<td>40.53</td>
<td>−44.58</td>
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<td></td>
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<td>49.04</td>
<td>84.55</td>
<td>1.28</td>
<td>98.31</td>
<td>0.46</td>
<td>1.78</td>
<td>−1.90</td>
</tr>
<tr>
<td></td>
<td>Jiuduntan</td>
<td>Ground–850 hPa</td>
<td>21.52</td>
<td>71.72</td>
<td>23.59</td>
<td>0.88</td>
<td>98.48</td>
<td>0.40</td>
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<td>1.76</td>
<td>6.01</td>
<td>−7.50</td>
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<td>92.64</td>
<td>1.89</td>
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<td>81.88</td>
<td>5.17</td>
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<td>−21.30</td>
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<tr>
<td></td>
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<td>66.73</td>
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<td>89.61</td>
<td>2.60</td>
<td>8.10</td>
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<td></td>
<td></td>
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<td>17.05</td>
<td>64.67</td>
<td>701.88</td>
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<td>7.49</td>
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<td>50.88</td>
<td>434.34</td>
<td>1.04</td>
<td>90.74</td>
<td>2.47</td>
<td>9.28</td>
<td>−10.46</td>
</tr>
</tbody>
</table>

Since the meteorological elements at different levels and the height of the cloud base are quite different, which makes the sub-cloud secondary evaporation is different, further makes the stable isotopes of precipitation change in the vertical direction. The third group of sampling points is stratified in detail, so the difference of sub-cloud secondary evaporation is more obvious. At the 850–700hPa, the sub-cloud secondary evaporation is the strongest, indicating that the heavy isotopes of precipitation are most concentrated in this layer. At the 700–500 hPa, the sub-cloud secondary evaporation is larger, but the evaporation is restricted by the lower temperature, so the stable isotope of precipitation is gradually depleted as the altitude rises and the temperature drops. At the ground–850 hPa, the $f$ reaches more than 90%, indicating that the sub-cloud secondary evaporation near the ground is weaker. At the same time, the $\Delta d$ of each sampling point at this layer is greater than $−1$‰, indicating that the isotope composition of precipitation is less affected by environmental conditions and the change of it is not obvious.

3.3. Temporal and Spatial Changes of d-Excess

The change of $d$-excess indicates the relative humidity of the moisture source to a certain extent and provides a basis for inferring the source of precipitation moisture. Therefore, this study divides the $d$-excess by time and region and further analyzes its change characteristics (Figure 2).
Figure 2. Temporal and spatial changes of d-excess in Shiyang River Basin.

As shown in Figure 2, the d-excess has no obvious seasonal variation in the Shiyang River Basin, and the overall trend is bimodal fluctuations. The specific manifestation is that the d-excess increases gradually from February to May and July to October, and decreases gradually from May to July and after October. The d-excess is relatively stable in winter half-year, and fluctuates greatly in summer half-year, indicating that the source of precipitation is more complicated in summer half-year. Besides, the d-excess in the midstream and downstream is lower than that in the upstream every month. From February to May, due to the temperature rise and less precipitation, the dry moisture causes the d-excess increase. From May to July, the summer monsoon causes the relatively humid moisture increase, the temperature is higher and the sub-cloud secondary evaporation is stronger, which makes the d-excess decrease. From July to October, owing to the precipitation increase the δD and δ18O continue to deplete, and the d-excess increases gradually. After October, precipitation is scarce in the midstream and downstream, even there is no precipitation in December, February, and March, while it is dominated by solid precipitation in the upstream. The solid precipitation falling from the cloud base to the ground does not change the isotope ratio [54] (Rozanski, 1993), and the small liquid precipitation is still facing the exchange of moisture [55,56], so the d-excess is relatively low in winter. Besides, the low d-excess of the study area in winter may also be related to the moisture source of precipitation.

3.4. The Influence of Moisture Source on Stable Isotope of Precipitation

3.4.1. Analysis of the Moisture Source Based on Wind Field and Vapor Flux

This study used the reanalysis data to analyze the geopotential height and wind field at 500 hPa and 700 hPa (Figures 3 and 4), the vapor flux fields, and the atmospheric precipitation from the ground to 500 hPa (Figure 5) during the research period.
This study used the reanalysis data to analyze the geopotential height and wind field at 500 hPa and 700 hPa (Figures 3 and 4), the vapor flux fields, and the atmospheric precipitation from the ground to 500 hPa (Figure 5) during the research period.

### Figure 3
Geopotential height in geopotential meters (gpm) and wind in m/s at 500 hPa in different seasons: (a) Spring geopotential height and wind; (b) Summer geopotential height and wind; (c) Autumn geopotential height and wind; (d) Winter geopotential height and wind. Red dashed frames for each subfigure mark the study region.

### Figure 4
Geopotential height in geopotential meters (gpm) and wind in m/s at 700 hPa in different seasons: (a) Spring geopotential height and wind; (b) Summer geopotential height and wind; (c) Autumn geopotential height and wind; (d) Winter geopotential height and wind. Red dashed frames for each subfigure mark the study region.
Figure 5. Vapor flux streamline and atmospheric precipitation from surface to 500 hPa based on NCEP/NCAR data: (a) Spring vapor flux streamline and atmospheric precipitation; (b) Summer vapor flux streamline and atmospheric precipitation; (c) Autumn vapor flux streamline and atmospheric precipitation; (d) Winter vapor flux streamline and atmospheric precipitation. Red dashed frames for each subfigure mark the study region.

From Figures 3 and 4, at 500 hPa (Figure 3), the geological height contours and wind direction are parallel basically with latitude (except for the summer), and the wind speed has obvious seasonal changes. The wind speed is the largest in winter (40 m/s), and is the smallest in summer (10 m/s). At 700 hPa, the wind fields are similar relatively in spring, autumn, and winter, and all of which are dominated by westerly winds. The wind speed is highest in winter (20 m/s), and it is weaker in spring, summer, and autumn (10 m/s). Compared with 500 hPa, the geopotential height and wind field at 700 hPa are more complicated, the geopotential height is no longer parallel to the latitude, and even a large closed circulation of low-pressure is formed near the study area in summer, which changes the wind direction. This is mainly affected by the influence of the topography of the Qinghai-Tibet Plateau. The moisture from the Indian Ocean in summer is blocked and enters the study area along the edge of the Qinghai-Tibet Plateau, which increases the moisture of relatively humid from the south.

It can be seen from Figure 5 that the Shiyang River Basin is affected by westerly moisture throughout the year. The atmospheric precipitation and vapor flux from the ground to 500 hPa have similar seasonal changes. The moisture transport is stronger in summer and the atmospheric precipitation is the largest. From the perspective of sea and land sources, natural water bodies such as the Atlantic Ocean, Arctic Ocean, Caspian Sea, and the Black Sea located in the upwind of moisture can be used as potential sources of moisture. However, it can be seen from Figure 5 that the amount of atmospheric precipitation in these areas is relatively scarce. The Shiyang River Basin is located in the hinterland of Eurasia, and the ocean moisture carried by the westerly undergoes long-distance transportation, so the supply of precipitation is very limited. As far as the lower part of the atmosphere is concerned, the moisture channel of the westerly in the northern part of the Shiyang River Basin is more unobstructed, but the moisture transport in the southern area is affected by the mountain topography is weak. However, compared with the southern mountains, the humidity degree of moisture transport is lower in the northern, and the amount of atmospheric precipitation is smaller. Therefore, the difference in moisture transport between them leads to the heavy isotopes of precipitation in the south being more depleted generally than that in the north.
3.4.2. Analysis of the Moisture Source Based on the Lagrangian Model with the Correction of Specific Humidity

To further clarify the precipitation source of sampling points at different altitudes, this study used Hysplit backward trajectory model to analyze the air masses that affect precipitation in the study area. The spatial resolution of the GDAS data is 1° × 1°. Considering the altitude and terrain of the sampling points as well as the distance between them, three sampling points of Lenglongling, Jiuduntan, and Datanxiang in the upstream, midstream, and downstream, respectively, are selected for air mass track (Figure 6).

Figure 6. Cluster analysis of moisture sources in different seasons in the Shiyang River Basin based on the adjusted back trajectories: (a–c) Spring trajectory of moisture source: Lenglongling (upstream), Jiuduntan (midstream), Datanxiang (downstream); (d–f) Summer trajectory of moisture source: Lenglongling (d), Jiuduntan (e), Datanxiang (f); (g–i) Autumn trajectory of moisture source: Lenglongling (g), Jiuduntan (h), Datanxiang (i); (j–l) Winter trajectory of moisture source: Lenglongling (j), Jiuduntan (k), Datanxiang (l).
As shown in Figure 6, the adjusted back trajectories of the air masses is shortened significantly and the backtracking time has temporal and spatial differences. The backtracking time is shorter in summer and autumn than that in winter and spring. The backtracking time of air mass of Lenglongling is the smallest (3.8 d in spring, 3.3 d in summer, 3.2 d in autumn, and 5.6 d in winter), followed by Jiuduntan (4.5 d in spring, 3.9 d in summer, 3.7 d in autumn and 5.7 d in winter), but that of Datangxiang is the longest (5 d in spring, 4 d in summer, 4.7 d in autumn and 6.1 d in winter), which is affected mainly by the topographical factor of the sampling point. Lenglongling is located in the Qilian Mountains, the transportation of moisture is prevented by the mountains and is slow relatively. While the terrain of the midstream and downstream is flat, and the transportation of moisture is fast relatively.

There are certain differences in the moisture sources in different seasons and at different heights. Overall, the analysis results of moisture source direction and vapor flux have high consistency, that the westward air mass and air mass of mid-high latitude land influence on the Shiyang River Basin, which leads to the changes of stable isotopes in precipitation. According to the source direction and weight ratio of the main air masses in different seasons in Figure 6, it can be seen that the westerly airflow accounts for a large proportion in each season. The vapor flux shows that natural water bodies such as the Atlantic Ocean, Arctic Ocean, Caspian Sea, and the Black Sea are all potential sources of moisture, but it is found that the moisture of the Atlantic and the Black Sea cannot be transported to the study area after correcting the backward trajectory. In addition, the moisture of the Caspian Sea and the Arctic Ocean has seasonal and accounts for a small proportion of the moisture transport. Therefore, the moisture transport from the sea source has a limited impact on the precipitation in the study area. From Figure 6, it can be seen that West Asia, Central Asia, and Europe are all in the upwind direction of moisture. The precipitation in the Shiyang River Basin may be supplemented by moisture from the land surface in these areas.

By comparing the moisture sources of precipitation at three selected sampling points in different seasons, it is found that the moisture sources of Jiuduntan and Datangxiang have high similarities, while that of Lenglongling is different from the others. In spring, at the height of 500–2000 m, Lenglongling is not only affected by the same air masses of mid-high latitude continental in the northwest as Jiuduntan and Datangxiang but also affected by air masses from Lake Baikal in the northeast (6%). At a height above 2000 m, the air masses in Jiuduntan and Datangxiang come mainly from the Caspian Sea, high-latitude land, and polar oceans, that they are transported from the northwest to the Shiyang River Basin. In summer, the moisture sources are more diverse, but inland air masses from mid-high latitudes still account for a larger proportion. Besides, there are relatively humid air masses from the southeast monsoon and evaporative supply from inland lakes. The moisture of 2% in Lenglongling comes from Lake Balkhash, and Jiuduntan and Datangxiang have moisture from Lake Baikal, which increases the relative humidity in the study area and decreases the d-excess. In autumn, the air mass sources of sampling points have high similarities, especially the height below 3000 m, which they come mainly from the mid-high latitude continental in the northwest and make the d-excess higher. In winter, the air masses are still dominated by the mid-high latitude continents to the west, but the transport path of moisture of Lenglongling increases significantly. The water vapor of long-distance transport makes δD more deplete than δ¹⁸O and results in d-excess lower. In addition, the moisture of 1% in Jiuduntan comes from the remote Arctic Ocean, which has a small proportion and long transport distance and has little impact on precipitation.

4. Discussion

Evaporation and condensation are the processes of hydrogen and oxygen stable isotope fractionation in atmospheric precipitation and are also an important reason for the differences in isotopic compositions of different water bodies. The isotopic composition of atmospheric precipitation varies greatly and the isotopic composition of precipitation in the same area at different times will vary greatly, but the relationship between D and ¹⁸O is
very regular since the fractionation of $^2$H/H is about 8 times that of $^{18}$O/$^{16}$O at equilibrium. The global meteoric water line (GMWL) reflects the average value of the meteoric water line in many parts of the world, and the local meteoric water line (LMWL) in different regions is controlled by local climatic factors, including the moisture source of precipitation, the secondary evaporation in precipitation (the sub-cloud secondary evaporation) and seasonal changes in precipitation. These factors affect the slope of the meteoric water line and deuterium excess ($d$-excess), especially the kinetic effects during evaporation, evaporation after condensation will affect the slope of the meteoric water line, making the stable isotope deviate from the precipitation line, even eliminating the linear relationship between $\delta^2$H and $\delta^{18}$O. However, the intercept of LMWL is more complex and is related to the degree of fractionation. The factors affecting fractionation include humidity, temperature, and wind speed. Generally, high temperature and low relative humidity cause the isotopes of precipitation to deviate more from the equilibrium state, which results in the intercept of LMWL decrease [57,58]. In this study, two methods of homogeneity assumption and stratification assumption are used to quantitatively calculate the evaporation loss during the falling process of raindrops and the isotopic composition change of raindrops at the cloud base and raindrops falling to the ground. Although the calculation results of the two methods are different, the conclusions are consistent, that is, the sub-cloud secondary evaporation in spring and summer is stronger than that in autumn and winter, and it is stronger in the midstream and downstream than in the upstream. Therefore, heavy isotopes in precipitation are enriched in spring and summer and in the midstream and downstream. In the vertical direction, the natural environment of each sampling point is quite different, and there are differences in the sub-cloud secondary evaporation at different precipitation heights. However, the overall law is basically the same.

The $d$-excess reflects the hydrogen and oxygen isotopic composition of the precipitation process, which is affected by the sub-cloud secondary evaporation, sea surface temperature, wind speed, and relative humidity in the moisture source region [12,59], which contains important information about the source area of the formation of warm humid air masses related to precipitation, including the equilibrium or non-equilibrium of the entire evaporation process and the speed of the evaporation rate [60]. The factors affecting the deuterium excess are very complex, and its variation depends entirely on the actual conditions of isotopic fractionation during evaporation and condensation. The evaporation is always carried out under unbalanced conditions, so there is a kinetic isotope fractionation effect. In addition, the change of $d$-excess can indicate the relative humidity of the moisture source to a certain extent, and provide a basis for predicting the source of atmospheric precipitation and moisture. The $d$-excess is relatively stable in the winter half year in the Shiyang River Basin and has a large variation in the summer half year, which shows that the stable isotope of precipitation in the study area is affected by various factors in the summer half year, the sub-cloud secondary evaporation is stronger in the summer half year in the study area, which reduces the $d$-excess.

In order to further analyze other factors that affect the $d$-excess, the moisture source analysis is carried out in the study area. Through the analysis of the wind field, it can be found that although the higher wind speed is conducive to the sub-cloud secondary evaporation, the study area is deep inland, and the winter is dominated by dry and cold air from the northwest. Therefore, except for the upper mountainous, the precipitation of the winter half-year is sparse and mainly solid precipitation, which causes the sub-cloud secondary evaporation to be generally weaker. The seasonal characteristics of heavy isotopes in precipitation enriched in summer and depleted in winter are considered widely to reflect the dominance of westerly moisture [30]. This understanding is also supported by reanalysis data. Considering the relative humidity of moisture that forms precipitation, the lower $d$-excess corresponds to the season when moisture is replenished in large quantities in the Shiyang River Basin. That is, $d$-excess is lower in summer and higher in winter. However, the increase of recirculated moisture of inland from local evaporation will lead to the $d$-excess increase, which causes the change of $d$-excess to have no obvious seasonality.
This further shows that the stable isotopes of precipitation are affected deeply by the sub-cloud secondary evaporation and the moisture source.

According to the reanalysis data, it can be seen that the westward moisture plays a leading role in the Shiyang River Basin, which is consistent with previous studies [61,62]. However, the method of identifying the moisture source has limitations by a wide range of vapor flux, which ignores the contribution of evaporation moisture of local land to precipitation. Relevant studies have shown that the moisture source of precipitation not only comes from transport moisture and large surface water bodies but also includes a large proportion of local recirculated moisture, especially in inland arid areas. Local recirculated moisture is very important for the replenishment of precipitation [63]. Therefore, the study used the Hysplit backward trajectory model to analyze the air masses that affect the precipitation of the sampling points in the study area. From the perspective of the backward trajectory of moisture, there is no air mass from the southwest that transports to the Shiyang River Basin. However, based on the analysis of the wind field and vapor flux, it can be seen that the moisture of the Bay of Bengal can affect the study area in summer. The reason why it is not reflected in the backward trajectory is that the Qinghai-Tibet Plateau prevents the moisture of the Indian Ocean from moving northward. However, when the summer monsoon is stronger, the moisture from the Indian Ocean moves to the northeast along the edge of the Qinghai-Tibet Plateau and enters the Shiyang River Basin from the southeast with the monsoon, which can bring moist moisture to the study area and make the $d$-excess lower.

In summary, from the perspective of the influence of the sub-cloud secondary evaporation on the stable isotopes of precipitation, the sub-cloud secondary evaporation is stronger in spring and summer, which enriches heavy isotopes in precipitation, while the opposite in autumn and winter. The sub-cloud secondary evaporation in mid-downstream is stronger than that in the upstream, and the heavy isotope in the precipitation is more enriched in the mid-downstream, and depleted in the upstream. Viewed from the vertical direction, the sub-cloud secondary evaporation at 850–700 hPa is stronger, and the heavy isotopes in the precipitation are enriched in this layer. From the perspective of the influence of moisture sources on precipitation stable isotopes, the moisture source of precipitation in the Shiyang River Basin is mainly from the land surface evaporation of mid-high latitudes, and the ocean moisture has little impact on the study area. The moisture supplied by mid-latitude inland dryness, short transportation distance, low relative humidity, and strong evaporation makes the $d$-excess in precipitation higher. Except for summer, the study area is affected greatly by the cold and dry air of high-latitude, which makes the moisture with lower temperature and relative humidity but higher $d$-excess. Therefore, the supply of relatively humid moisture increases in the Shiyang River Basin, the sub-cloud secondary evaporation is stronger. When the sub-cloud evaporation process occurs, the composition of heavy isotopes in moisture is lower, but it is higher in the liquid phase [64] (Galewsky et al., 2016), which causes the $d$-excess in precipitation to be lower in summer. Additionally, the moisture transport path from the polar ocean is long, and the long-distance moisture transport makes $\delta^{18}O$ gradually depleted under the influence of leaching and the strong convective activity. In short, the stable isotopes of precipitation in the Shiyang River Basin are affected by the sub-cloud secondary evaporation and the moisture source, which makes the $d$-excess show temporal and spatial differences.

5. Conclusions

Based on the improved Stewart model, this study uses the methods of homogeneity assumption and stratification assumption to quantitatively calculate the intensity of the sub-cloud secondary evaporation and the variation of precipitation stable isotopes during the raindrops falling at 11 sampling points in the Shiyang River Basin. The moisture source of precipitation was corrected by the specific humidity, and the influence of the moisture source on stable isotopes in precipitation was analyzed. The main conclusions are as follows:
The intensity of sub-cloud secondary evaporation at different sites is different in the Shiyang River Basin, resulting in different degrees of changes in the stable isotopes in the precipitation at different sampling points. The sub-cloud secondary evaporation intensity is generally stronger in spring and summer and weaker in autumn and winter and stronger in the mid-downstream than that in upstream, which makes the heavy isotopes of precipitation in upstream more depleted than those in the mid-downstream. In the vertical direction, the intensity of sub-cloud secondary evaporation at different heights is also different, which makes the stable isotope continuously change during the process of raindrops falling to the ground. Specifically, the sub-cloud secondary evaporation is the strongest at 850 hPa–700 hPa, and $\delta^{18}$O is enriched at this layer. When the altitude exceeds 3000 m, the stable isotopes of precipitation are continuously depleted.

The $d$-excess in precipitation does not show seasonal and regional consistency well. The variation trend of $d$-excess in precipitation is relatively stable in the winter half year, but fluctuates greatly in the summer half year. The monthly $d$-excess in the mid-downstream is lower than that in the upstream, which is related to the stronger sub-cloud secondary evaporation and different moisture sources in the mid-downstream.

The moisture source of precipitation in the Shiyang River Basin has temporal and special differences, but it comes mainly from westward air masse. After correction based on specific humidity, the backward trajectory path of the air mass is shortened, the backtracking time is short in summer and autumn but longer in winter and spring, and it is longer in the mid-downstream than that in the upstream. Additionally, the moisture source of precipitation in the Shiyang River Basin is affected mainly by inland air masses from mid-high latitudes, while the moisture from the ocean has little impact on precipitation, which makes the $d$-excess of precipitation larger.

**Author Contributions:** H.X. analyzed the data and wrote the original draft. W.J. revised the original draft. G.Z. conceived the idea of the study. Y.S. and Z.Z. collected the samples. L.Y., M.Z. and F.Z. participated in the experiment. All authors have read and agreed to the published version of the manuscript.

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