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Climatic and environmental controls on stable isotopes in atmospheric water vapor near the surface observed in Changsha, China

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Abstract

Continuous measurements were made of isotopic compositions in atmospheric water vapor (δv) and in atmospheric precipitation (δp) near the surface in the subtropical monsoon region (Changsha, China) from October 2014 to March 2017 to investigate the change characteristics of vapor isotopes and their interactions with precipitation isotopes. On a diurnal time scale, the δ18Ov values were more negative in the daytime and more positive at night, and the change in dv was reversed during non-rainy days; however, the δ18Ov values were more positive in the daytime and more negative at night, and the variation in dv was not significant during rainy days. On a seasonal time scale, affected by distinctive moisture sources, the vapor isotopes had obvious seasonal variations, with higher δ18Ov and dv values occurring in cold seasons than in warm seasons. There were generally consistent and significant negative linear relationships of dv with temperature and absolute humidity, but the linear relationships between δ18Ov and meteorological factors were variable on the different time scales, which is closely associated with the local weather conditions on the short time scales from diurnal to intra-seasonal and movements of air masses with distinct thermodynamic properties on seasonal and sometimes intra-seasonal time scales. Although the change trend of daily δ18Ov closely approximated that of δ18Op, δ18Op experienced significant relative enrichment compared to δ18Ov, with an average enrichment of 9.18 ‰. Overall, the isotopic compositions of atmospheric water vapor were in equilibrium with those of precipitation while rainfall events occurred, except for those in the cold season in 2014, and when tracing short-duration weather events, δ18Ov provided more details and information related to weather processes than δ18Op.

Keywords: Changsha; atmospheric water vapor; precipitation; stable isotopes; isotope effect
1. Introduction

Stable isotopes in precipitation (e.g., $^2$H and $^{18}$O) are useful environmental tracers that are used to investigate climate change and hydrological processes. Since the investigation of the stable isotopic compositions of precipitation in the early 1950s, the change characteristics of stable precipitation isotopes on different temporal and spatial scales and their applications have been widely reported, and a great deal of meaningful information has been obtained (Araguás, Froehlich, & Rozanski, 1998; Dansgaard, 1964; Wu, Zhang, Li, Li, & Huang, 2015; Yao et al., 2013; Yoshimura, 2015), such as the mechanisms controlling natural stable isotopic fractionation (Dansgaard, 1953, 1964; Jouzel, 1986; Stewart, 1975; Zhang, Guan, Zhang, & Yao, 2016), the relationships between stable isotopes and meteorological variables (known as the “isotope effect”; Bowen & Wilkinson, 2002; Dansgaard, 1964), and the interpretation of the paleoclimate from stable isotopes records in tree cellulose, ice cores, and carbonates (Cheng et al., 2016; Johnsen et al., 2001; Sidorova et al., 2013; Thompson et al., 2000; Yao et al., 1996).

Precipitation, however, only represents the terminal unit of the processes of evaporation, mixing, and subsequent condensation, and it exhibits large spatiotemporal variability. Accordingly, there are certain roles-constrained for stable precipitation isotopes in tracing the water cycle process in a specific region and examining the patterns of atmospheric circulation (Frankenberg et al., 2009; Zhang, Zhang, Guan, Huang, & Wu, 2012). Water vapor is one of the most active atmospheric components. Compared with precipitation, water vapor not only has a continuous spatial-temporal distribution but also responds more sensitively to changes in atmospheric conditions. As a consequence, studies of stable vapor isotopes can complement the deficiency of understanding caused by discrete and brief precipitation observations.

The systematic sampling survey of stable isotopes in atmospheric water vapor dates back to the late 1960s, when Talor (1968) reported measurements of deuterium, the water vapor mixing ratio, and
temperature in the atmosphere at altitudes between 0.5 and 5000 m from June 1967 to June 1968 and
delineated 20 average vertical profiles of $\delta^2$H, in Heidelberg. After that, in order to evaluate the influences
of thermonuclear explosions on tritium content in the atmosphere and investigate the characteristics of
variations of stable vapor isotopes, the monitoring programs of vapor isotopes were carried out
successively by several countries. For example, the National Center for Atmospheric Research in the
United States investigated the vertical distributions of deuterium, tritium, temperature, and humidity from
the surface to an altitude of 9.2 km in Scottsbluff, Santa Barbara, Palestine, and Death Valley, United
States, from November 1965 to September 1973, using aircraft and radiosondes (Ehhalt, 1974). In
addition, a comprehensive sampling program of $^2$H, $^{18}$O, and $^3$H in atmospheric water vapor near the
surface in Heidelberg, Paris, Hannover, Krakow, and Miami was sponsored by Germany in June 1980
(Schoch-Fischer et al., 1984). All of these abovementioned observations have provided rather valuable
data for the studies of vapor isotopes. However, due to instrumental and technical limitations, there are
just a few stations for observations of vapor isotopes around the world.

In recent years, fortunately, with advances in spectral technology, various vapor isotope
spectrometers have emerged. Using these instruments, we can monitor the stable isotopic compositions in
the atmospheric water vapor of different layers over the ground with automatic, high-frequency, and
continuous sampling. The previous studies show that the change characteristics and influencing factors of
vapor isotopes near the surface may vary geographically. Lee, Smith, & Williams (2006) studied vapor
isotopes in New Haven using a 1-year record observed by a tunable diode laser (TDL) trace gas analyser
and found that the changes of vapor isotopes were in good agreement with the variations in the water
vapor mixing ratio and temperature, with higher values occurring in warm seasons (May to October) and
lower values occurring in cold seasons (November to April). On a short time scale, such as that of a
weather process, affected by the distinct moisture origins and degree of condensation of an advection air
mass, the scatter of $\delta$ versus the water vapor mixing ratio showed an interesting looping. Tremoy et al. (2012) used the high-temporal-resolution measurements of stable vapor isotopes near the ground to
investigate seasonal and diurnal vapor isotopic variations in Niamey. They found that on a seasonal time
scale, the change of $\delta^{18}$O$_v$ showed a W-shape, affected by the regional convective activity during the
monsoon season and large-scale subsidence north of Niamey during the dry season. However, the
pronounced diurnal variation of $\delta^{18}$O$_v$ recorded the propagation of density currents related to mesoscale
convective systems during the monsoon season and a mixing process between the boundary layer and the
free atmosphere during the dry season. Laskar et al. (2014) showed, on a seasonal time scale, the
variations of $\delta^{18}$O in atmospheric water vapor and precipitation were not consistent, but they found that
the vapor and precipitation were nearly in isotopic equilibrium during a typhoon in the case study.

In mainland China, most stable vapor isotope observation campaigns are in the Qinghai-Tibet area
(Cui, Tian, Liu, & Wen, 2014; Hu et al., 2009; Yin et al., 2008; Yu, Tian, Ma, Xu, & Qu, 2015; Yu, Yao,
Tian, Wang, & Yin, 2005) and North China (Wen et al., 2008; Wen, Zhang, Sun, Yu, & Lee, 2010; Yuan,
example, in the Qinghai-Tibet area, Yin et al. (2008) sampled atmospheric water vapor near the surface in
Delingha with a cold trap. They noted that distinct moisture origins had significant impacts on the vapor
isotopes. Overall, higher $\delta^{18}$O$_v$ values were associated with water vapor transported by the westerlies, and
lower $\delta^{18}$O$_v$ values were associated with that transported by the southwest monsoon. Wen et al. (2010)
measured the in situ $\delta^2$H and $\delta^{18}$O of atmospheric water vapor in surface air with a TDL from December
2006 to December 2007, and in their observations, much fewer daily and diurnal variations of vapor
isotopes were recorded during the summer monsoon season than during other times of the year;
additionally, during the non-monsoon season, the δ²H, and δ¹⁸O, values showed a positive log-linear
dependence on the water vapor mixing ratio, and the deuterium excess (d_v), as calculated by the stable
oxygen and hydrogen isotopic compositions of atmospheric water vapor (d_v = δ²H_v – 8δ¹⁸O_v), revealed a
remarkable negative correlation with relative humidity.

Comparatively speaking, because it is difficult to capture atmospheric water vapor, the related
studies to date are deficient, and the observations of vapor isotopes are limited in specific regions,
especially in the subtropical and tropical monsoon regions. Consequently, the change patterns of vapor
isotopes in these regions are uncertain. To fill this gap, we carried out a field experiment to collect
real-time isotope data in atmospheric water vapor and in-event precipitation near the surface from
October 2014 to March 2017 in Changsha, a subtropical monsoon region. In the present work, our
objectives are to analyse the influences of moisture sources and local meteorological variables on
variations in vapor isotopes on diurnal, a few days, seasonal, and intra-seasonal time scales and to detect
the interactions between falling raindrops and surrounding water vapor during rainfall events. This will
enhance our understanding of the characteristics of stable isotopic compositions in atmospheric water
vapor and precipitation near the surface in the subtropical monsoon region and provide insights into
distinct moisture sources and local atmospheric and hydrological processes. Furthermore, the results will
also have important implications for validation of the isotopic observations of the satellite, as well as the
analyses of paleoclimate reconstructions and atmospheric circulation patterns.

2. Methodology

2.1. Study area

Changsha (27.68° - 28.85° N and 111.88° - 114.25° E; Fig. 1) is located in the northeastern Hunan
Province of China, i.e., in the lower reach of the Xiangjiang River and western Changsha-Liuyang Basin.
The elevation of Changsha varies greatly, with the Mufu-Luoxiao Mountains to the northeast and Xuefeng Mountains to the northwest. And Changsha is situated in the transition zone from the Changsha-Hengyang Hills to Lake Dongting Plain, with the elevation generally decreasing from the south to the north of the study area.

This sampling program was performed at the meteorological observation station (28.19° N, 112.94° E) on the Hunan Normal University campus, which is situated in Changsha City. The study area is in a typical subtropical monsoon moist climate, with a cold and dry winter influenced primarily by air masses from the north, and a warm and wet summer influenced mainly by air masses from the south. Overall, the mean annual temperature and mean annual total precipitation in Changsha are about 17.4 °C and 1428.1 mm, respectively, based on the meteorological data between 1981 and 2010 provided by the China Meteorological Administration. The mean annual temperature and mean annual total precipitation are approximately 6.5 °C and 215.7 mm, respectively, in winter (December to February), and 27.8 °C and 473.3 mm, respectively, in summer (June to August). Soil types are characterized by red soil and yellow-brown soil, with loose soil texture and sufficient soil water content. Vegetation is dominated by

Fig. 1. The map showing the location of sampling point in Changsha, China.
subtropical evergreen tree species, such as broad-leaf tree species *Cinnamomum camphora*, *Osmanthus fragrans*, and *Ulmus pumila* L. The shrubs are *Rhododendron simsii* Planch and *Loropetalum chinense* var. rubrum.

### 2.2. Measurements and data

The stable isotopic compositions of atmospheric water vapor, at approximately 10 m above the ground, were measured every ~10 s from October 2014 to March 2017 using an infrared laser spectrometer (Model 35EP, Los Gatos Research, Inc., USA) with off-axis integrated cavity output spectroscopy. The spectrometer consists of two subsystems, namely, a standard water vapor generator and a water isotope analyser. The former is used to generate the calibration standard gases at different concentrations with known stable isotope values, and the latter is used to determine the concentrations of calibration standard gases and ambient air samples, as well as their stable isotopic compositions. The two subsystems operate in an alternating fashion in a measurement cycle, which is 1 h in the standard water vapor generator and 1.5 h in the water isotope analyser. Due to the significant concentration dependence on stable isotopic compositions, we are required to make a correction for the initial ambient vapor isotope measurements based on the relationships between the isotope measurements of calibration standard gases and their concentrations. Additionally, memory effects often occur due to residual water vapor that cannot be completely pumped out from the pipeline before the next measurement. Therefore, we excluded the data observed during the first one minute of each measurement.

Along with regular water vapor sampling, precipitation (greater than or equal to 0.1 mm) samples were collected at 08:00 A.M. and 20:00 P.M. (China Standard Time, hereafter CST) on rainy days. A total of 435 precipitation samples were obtained during the whole period. The stable isotopic compositions of all precipitation samples were measured using the LGR 35EP.
The isotopic compositions of atmospheric water vapor (or precipitation) were expressed using the conventional delta notation:

$$\delta_v (\text{or } \delta_p) = \left( \frac{R_{\text{sample}}}{R_{\text{V-SMOW}}} - 1 \right) \times 1000 \text{‰},$$  \hspace{1cm} (1)

where $R_{\text{sample}}$ and $R_{\text{V-SMOW}}$ are the isotope molar ratios of the heavy to the light isotope (e.g., $\delta^2\text{H}/\delta^1\text{H}$, $\delta^{18}\text{O}/\delta^{16}\text{O}$) in samples and in Vienna Standard Mean Ocean Water (V-SMOW), respectively. The measurement accuracies of $\delta^2\text{H}_v$ and $\delta^{18}\text{O}_v$ are better than 1.2 ‰ and 0.4 ‰, respectively. The measurement accuracies for $\delta^2\text{H}_p$ and $\delta^{18}\text{O}_p$ are better than 0.6 ‰ and 0.2 ‰, respectively.

Some meteorological elements, including surface air temperature ($T$), precipitation ($P$), and humidity ($Q$), were measured using automatic weather survey equipment (Model Weather Hawk-232, USA) at a 30-min interval. Additionally, the atmospheric precipitable water ($PW$) was obtained from the ERA-Interim dataset provided by the European Centre for Medium-Range Weather Forecasts (ECMWF), with a spatial resolution of 1.5º × 1.5º.

It should be noted that the calculations of the mean isotopic compositions in atmospheric water vapor and in precipitation were different in a given period. The arithmetic mean value was calculated for the vapor isotopes and the amount-weighted mean value was calculated for the precipitation isotopes. To analyse the relationships between the stable isotopic compositions in atmospheric water vapor and in precipitation, the stable isotopic ratio $\delta_e$ (defined as the predicted value and assumed to be in an equilibrium state with that of precipitation near the surface) was calculated using the classic Rayleigh distillation equation (Saxena, & Eriksson, 1985):

$$\delta_e = \left( 1 + \delta_p / \alpha \right) / \alpha - 1,$$ \hspace{1cm} (2)

where $\alpha$ is a temperature-dependent equilibrium fractionation factor (Majoube, 1971) and $\delta_p$ is the isotopic ratio in precipitation. Based on the criterion of surface meteorological observations, all daily data
in this study were calculated for the daily period of 8:00 A.M. to 8:00 A.M. on the next day.

3. Results and discussion

3.1. Overall variations of vapor isotopic compositions

Fig. 2 shows the daily variations in $\delta^{18}$O, $d_v$, temperature, absolute humidity ($Q$), and precipitation observed during the whole study period. In addition, the frequency distributions of $\delta^{18}$O and $d_v$ are shown in Fig. 3.

![Variations of daily mean $\delta^{18}$O, $d_v$, temperature, and absolute humidity, as well as daily total precipitation near the surface during the whole sampling period in Changsha.](image)

Fig. 2. Variations of daily mean $\delta^{18}$O, $d_v$, temperature, and absolute humidity, as well as daily total precipitation near the surface during the whole sampling period in Changsha.

![The frequency distributions of daily mean $\delta^{18}$O (a) and $d_v$ (b) near the surface during the whole sampling period in Changsha. The sum of the frequency of the slashed bar is greater than 0.8.](image)

Fig. 3. The frequency distributions of daily mean $\delta^{18}$O (a) and $d_v$ (b) near the surface during the whole sampling period in Changsha. The sum of the frequency of the slashed bar is greater than 0.8.
As shown in Figs. 2 and 3, the δ\textsuperscript{18}O\textsubscript{v} values varied from -28.15 ‰ to -1.18 ‰, with a mean value of -13.94 ‰, and 80 % of the values were distributed in the range from -20 ‰ to -10 ‰ in the whole survey period in Changsha. Comparatively, the mean annual δ\textsuperscript{18}O\textsubscript{v} value was more positive than the yearly average of -20.7 ‰ reported in Beijing at 40°00' N and 116°23’ E (Wen et al., 2010) and the 1-year average of -17.1 ‰ observed in Tsukuba at 36°03' N and 140°02’ E (Wei et al., 2016), but it is very similar to the yearly average of -14.4 ‰ recorded in Taipei at 25°1’ N and 121°30’ E (Laskar et al., 2014).

Considering the similar climatic characteristics of four stations, the difference between the four, in a sense, reflects the impact of the latitudinal effect in precipitation isotopes, which refers to that precipitation δ\textsuperscript{18}O in low latitudes is greater than in high latitudes. The \textit{d} values varied from -17.47 ‰ to 52.49 ‰, with a mean value of 18.18 ‰, and 80 % of the values were distributed in the range from 10 ‰ to 25 ‰. By comparison, the mean \textit{d} value was also more positive than that observed in Beijing, where the mean annual value was 11.8 ‰, but very close to those observed in Tsukuba and Taipei, with mean values of 19.28 ‰ and 19.69 ‰, respectively.

We defined the warm season as the months from April to September and the cold season as the months from October to March based on the seasonal distribution patterns of precipitation and temperature in the study area (Fig. 2). In general, accompanying the remarkable seasonal variations, in the warm season, the δ\textsuperscript{18}O\textsubscript{v} values varied from -22.45 ‰ to -2.72 ‰, with a mean value of -14.14 ‰, and the \textit{d} values ranged from -5.02 ‰ to 30.56 ‰, with a mean value of 15.30 ‰; in the cold season, the δ\textsuperscript{18}O\textsubscript{v} values varied from -28.15 ‰ to -1.18 ‰, with a mean value of -13.70 ‰, and the \textit{d} values varied from -17.47 ‰ to 47.91 ‰, with a mean value of 19.72 ‰. The seasonality patterns of vapor isotopes are connected with the difference of moisture sources between the warm season and the cold season, as well as with the air masses controlling this area (Srivastava, Ramesh, Gandhi, Jani, & Singh, 2015; Strong,
Sharp, & Gutzler, 2007; Yu et al., 2005). Generally, the $\delta^{18}O_p$ and $d_p$ in Changsha were more negative in the warm season, controlled by warm and wet marine air mass transported by the southwest and southeast monsoon, and thus the $\delta^{18}O_v$ and $d_v$ were also lower, impacted by the recycling of precipitation and under the evaporation fractionation of surface water with relatively negative isotope values; however, the $\delta^{18}O_p$ and $d_p$ in Changsha were more positive in the cold season, controlled by the cold and dry continental air mass transported by westerly circulation, and thus the $\delta^{18}O_v$ and $d_v$ were also more positive, impacted by the recycling of precipitation and under the evaporation fractionation of surface water with relatively positive isotope values (Zhang, Yang, Niu, & Wang, 2009). For the most positive $\delta^{18}O_v$ in the period from December 2014 to April 2015, the large positive deviation is probably related to the abnormally continuous drought over East Asia since the summer of 2014. Using the study area as an example, the total precipitation in autumn and winter of 2014 was much less than the normal precipitation for the climatological period 1961 - 2014; it was only 181.6 mm. Due to limited time series of vapor isotope observations, further study is needed for this inference.

3.2. The relationships between the vapor isotopes and meteorological factors on different time scales

3.2.1. Diurnal variations of vapor isotopic compositions

Generally, the movements of air masses with different thermodynamic properties have minimum effects on stable isotopic compositions in atmospheric water vapor on a diurnal time scale. The variations in vapor isotopes are predominantly controlled by short-term weather processes. The full data set was divided into non-rainy and rainy days, with the latter day total precipitation greater than or equal to 0.1 mm. By averaging hourly mean $\delta^{18}O_v$ and $d_v$, as well as the related meteorological factors for period of non-rainy days and rainy days, the ensemble mean diurnal variations of these variables were obtained (Fig. 4).
Fig. 4. Ensemble mean diurnal variations of $\delta^{18}O$, $d_v$, temperature and absolute humidity near the surface on non-rainy days (a) and rainy days (b) in Changsha.

During non-rainy days, the mean value of $\delta^{18}O$ was -13.94 ‰, the mean value of $d_v$ was 18.73 ‰, the mean temperature was 18.07 °C, and the mean absolute humidity was 9.69 g kg$^{-1}$. All of these values were higher than the mean values for the whole sampling period. In response to the diurnal variations of temperature and atmospheric humidity, both $\delta^{18}O$ and $d_v$ had notable diurnal cycles, but with the opposite trends: the maximum $\delta^{18}O$ value was recorded when the minimum $d_v$ value was observed therein (Fig. 4a). This diurnal variation in the stable isotopic composition of atmospheric water vapor was likely associated with near-surface atmospheric turbulence (Lai, Ehleringer, Bond, & Paw, 2006; Welp et al., 2008; Zhang et al., 2011). The intensity of turbulence is closely related to the temperature (Monin & Obukhov, 1954), has a direct impact on the variations of atmospheric humidity (McBean, 1971), and thereby affects the stable isotopic compositions of the atmospheric water vapor. Atmospheric turbulence strengthened gradually in the morning due to the increasing near-surface temperature, and the water vapor exchange between the upper and lower ground layers was enhanced in the morning. This resulted in
decreased atmospheric humidity near the surface and correspondingly depleted stable isotopic signatures in atmospheric water vapor; in particular, the $\delta^{18}$O, value reduced by about 0.53 ‰ from sunrise to noon. In contrast, atmospheric turbulence gradually weakened with decreasing temperature in the afternoon and was accompanied by the decreased water vapor exchange between the upper and lower ground layers. The increased near-surface atmospheric humidity resulted in enriched stable isotopic signatures. At night, however, the atmospheric lamination was relatively stable and humidity was less variable, with correspondingly negligible variations in the stable isotopic compositions of atmospheric water vapor being recorded. Despite the fact that the diurnal amplitude of air temperature can reach up to 6.37 °C, the low potential evaporation only resulted in variabilities of absolute humidity and $\delta^{18}$O, of 0.35 g kg$^{-1}$ and 0.71 ‰, respectively. In comparison, $d_v$ varied notably, exhibiting daily variability of up to 3.99 ‰. The diurnal variations of $d_v$ and $\delta^{18}$O, had opposite trends because both atmospheric turbulence and evapotranspiration have a positive impact on $d_v$ (Welp et al., 2012). Comparatively, the diurnal patterns of $\delta^{18}$O, and $d_v$ are in line with the Welp et al. (2012) meta-study on six sites in mid-latitudes, all of which support the concept that robust diurnal patterns of vapor isotopes may result from the combined effects of local atmospheric turbulence and evapotranspiration on non-rainy days.

During rainy days, the mean value of $\delta^{18}$O in atmospheric water vapor was -14.66 ‰, the mean value of $d_v$ was 17.16 ‰, the mean temperature was 16.35 °C, and the mean absolute humidity was 10.52 g kg$^{-1}$. The mean values of all the above-mentioned variables, except for absolute humidity, were lower than the mean values of those when pooling all the data together during the whole sampling period. Compared with the results on non-rainy days, the stable isotopic signatures on rainy days were notably depleted. The atmospheric humidity was largely controlled by the air temperature, given that the underlying surface had enough water for evapotranspiration. Therefore, diurnal variations in the
temperature, atmospheric humidity, and stable isotopic signatures in atmospheric water vapor exhibited similar trends (Fig. 4b). During the daytime, the atmospheric humidity remained at a high level because of the high temperature and strong underlying surface evapotranspiration, and thereby producing enriched stable isotopic signatures in atmospheric water vapor. At night, however, the atmospheric humidity continuously declined as a result of the low temperature and decreased underlying evapotranspiration, thereby resulting in the continuous depletion of stable isotopic signatures. Since the underlying surface evapotranspiration has no impact on the stable isotopic fractionation, the $d_v$ within a day varied minimally.

3.2.2. Seasonal and intraseasonal variations of daily vapor isotopic compositions

The above analyses indicated that $\delta^{18}O_v$ was proportional to the absolute humidity regardless of whether it was rainy or not. This suggests that the water vapor derived from underlying surface evapotranspiration will probably result in the enrichment of stable isotopic signatures during its diurnal variation. The relationship between the stable isotopic signatures in atmospheric water vapor and the atmospheric humidity was unchanged, although rainfall generally depleted the stable vapor isotopic signatures. Correspondingly, $d_v$ had a negative correlation with atmospheric humidity on both non-rainy days and rainy days. However, the relationships between $\delta^{18}O_v$ and temperature, as well as those between $d_v$ and temperature, showed differences between non-rainy days and rainy days. From Fig. 2, seasonally, the variations of vapor isotopes displayed opposite trends with temperature, precipitation, and absolute humidity. In the warm and rainy summer, vapor isotopic signatures were notably depleted; however, in the cold and dry winter, vapor isotopic signatures were notably enriched. Our results showed that $\delta^{18}O_v$ had significant ($p < 0.01$, similarly hereinafter) negative relationships with temperature, precipitation, and absolute humidity during the whole sampling period (Table 1). Significant negative relationships were
observed between \( d_v \) and temperature and between \( d_v \) and absolute humidity; the negative relationship between \( d_v \) and precipitation was not significant (\( p > 0.01 \), similarly hereinafter) and could be explained by the effect of evapotranspiration during rainfall events (Zhang, Liu, Nakawo, & Xie, 2009).

**Table 1** The linear relationships between daily mean \( \delta^{18}O_v \), \( d_v \) and temperature, precipitation and absolute humidity near the surface in Changsha.

<table>
<thead>
<tr>
<th>Period</th>
<th>Relationships</th>
<th>( \delta^{18}O_v/T )</th>
<th>( \delta^{18}O_v/P )</th>
<th>( \delta^{18}O_v/Q )</th>
<th>( d_v/T )</th>
<th>( d_v/P )</th>
<th>( d_v/Q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>The whole period</td>
<td></td>
<td>-0.09*(880)</td>
<td>-0.18*(340)</td>
<td>-0.17*(865)</td>
<td>-0.42*(880)</td>
<td>-0.13(340)</td>
<td>-0.46*(865)</td>
</tr>
<tr>
<td>2014/10-2017/03</td>
<td>Non-rainy days</td>
<td>-0.09(540)</td>
<td>—</td>
<td>-0.16*(533)</td>
<td>-0.44*(540)</td>
<td>—</td>
<td>-0.47*(533)</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>-0.11(340)</td>
<td>-0.18*(340)</td>
<td>-0.19*(332)</td>
<td>-0.42*(340)</td>
<td>-0.13(340)</td>
<td>-0.44*(332)</td>
</tr>
</tbody>
</table>

*Note.* The number in parentheses represents the sample size; asterisk indicates \( p < 0.01 \), the same below.

The negative correlations between \( \delta^{18}O_v \) and temperature, absolute humidity, as well as those of between \( d_v \) and temperature, absolute humidity, did not notably change between non-rainy days and rainy days, as shown in Table 1. This result indicates that air masses with distinct thermodynamic properties and their interactions are the most predominant factors controlling the seasonal variations of vapor isotopic signatures. On a seasonal time scale, the variations of stable isotopes in atmospheric water vapor depended largely on moisture sources.

Intra-seasonal analyses are mainly used to investigate the linear relationships of vapor isotopes with temperature, precipitation, and absolute humidity in spring (March to May), summer (June to August), autumn (September to November) and winter (December to February), during the whole period, for non-rainy days and rainy days (see Fig. 5). Under the three circumstances, the stable negative relationship between \( \delta^{18}O_v \) and precipitation was observed in Changsha, although it did not reach the confidence level of 0.01. Significant positive linear relationships of \( \delta^{18}O_v \) with temperature and absolute humidity were recorded, which were especially pronounced in fall and winter primarily controlled by westerly winds.

However, due to the frequent interactions between cold and warm air masses in the middle and lower
reaches of the Yangtze River in spring and in the “plum rains” season (June to July), the relationships between $\delta^{18}O_v$ and temperature and between $\delta^{18}O_v$ and absolute humidity varied greatly. For instance, significant positive linear relationships in the spring of 2016, significant negative linear relationships in the spring of 2015, and no significant relationships in the summer of 2015 were recorded between $\delta^{18}O_v$ and temperature and between $\delta^{18}O_v$ and absolute humidity.

![Graph showing comparisons of linear relationships between daily mean $\delta^{18}O_v$ and temperature, precipitation, absolute humidity near the surface in different seasons in Changsha.](image)

**Fig. 5.** Comparisons of linear relationships between daily mean $\delta^{18}O_v$ and temperature, precipitation, absolute humidity near the surface in different seasons in Changsha (a). Same as (a) but for $d_v$ (b). Asterisk indicates $p < 0.01$, the same below.

As shown in Figs. 2, 4 and 5, on the three time scales, including diurnal, intra-seasonal and seasonal time scales, $d_v$ was mostly inversely proportional to temperature and absolute humidity, and showed no significant relationship with precipitation. In addition, precipitation always depleted atmospheric water vapor in $^{18}O$. By comparison, the relationships of $\delta^{18}O_v$ with temperature and absolute humidity were various on different time scales.

On the short time scales, including diurnal and intra-seasonal time scales, the positive correlations of
\[ \delta^{18}O_v \] with temperature and absolute humidity reflected the relationship between the stable isotopes and
temperature of the same air mass. Increased atmospheric humidity induced by elevated temperature and
enhanced evaporation led to the enrichment of stable isotopic signatures in atmospheric water vapor; on
the contrary, decreased atmospheric humidity induced by a declining temperature and evaporation led to
the depletion of stable isotopic signatures in atmospheric water vapor.

On seasonal and sometimes on intra-seasonal time scales, the negative correlations of \( \delta^{18}O_v \) with
temperature and absolute humidity reflected the interactions across different air masses. In the cold
season, continental air masses resulted in a low mean temperature, atmospheric humidity, and enriched
stable vapor isotopic signatures. In the warm season, however, marine air masses resulted in a high mean
temperature, atmospheric humidity, and depleted stable vapor isotopic signatures. Consequently, changes
in vapor isotopes showed markedly negative correlations with those of temperature and atmospheric
humidity. Further analysis of the relationships between vapor isotopic compositions and temperature and
atmospheric humidity showed that on different time scales, the effects of temperature and atmospheric
humidity on vapor isotopes were differential, and sometimes opposite relationships could be recorded.

For example, significant positive correlations were recorded between \( \delta^{18}O_v \) and temperature and between
\( \delta^{18}O_v \), and absolute humidity in the fall and winter of 2014 (Fig. 6). However, during the whole period
from October 2014 to February 2015, significant negative relationships were observed between \( \delta^{18}O_v \) and
temperature and between \( \delta^{18}O_v \), and absolute humidity. These results illustrate the strong influence of
water vapor sources on vapor isotopic compositions on an intra-seasonal time scale. But it can be noted
that the correlation patterns between \( \delta^{18}O_v \) and temperature and absolute humidity discussed above do not
always exist, suggesting there are more influencing factors besides water vapor sources, which needs
further investigation.
Fig. 6. The linear relationships between daily mean δ\textsubscript{18}O\textsubscript{v} and temperature (a), absolute humidity (b) near the surface in fall and winter, 2014. Linear regression lines and correlation coefficient $r$ are also shown.

3.3. Comparisons between isotopic compositions in vapor and precipitation

3.3.1. Comparisons of temporal variations

It is of great significance to understand the interactions between precipitation and water vapor during the descent process of each precipitation event and thus to explain the mechanisms of the variations of stable isotopic compositions in atmospheric water vapor and precipitation (Dansgaard, 1964; Zhang, Xie, & Yao, 1998). Fig. 7 shows the daily variations of δ\textsuperscript{18}O and $d$ in atmospheric water vapor and precipitation, as well as the δ\textsuperscript{18}O predicted from the equilibrium theory during the whole sampling period in Changsha.
Fig. 7. Comparisons of the temporal variations of daily mean $\delta^{18}O$ (a) and $d$ (b) in atmospheric water vapor and in precipitation near the surface in Changsha. The subscript e identifies the daily mean stable isotopic compositions in atmospheric water vapor in equilibrium with those in precipitation.

During the whole survey period, the $\delta^{18}O_v$ values varied from -28.15 ‰ to -1.18 ‰, with the mean value of -13.94 ‰, and the $d_v$ values varied from -17.47 ‰ to 52.49 ‰, with the mean value of 18.18 ‰. By contrast, the $\delta^{18}O_p$ values varied from -17.52 ‰ to 6.73 ‰, with the amount-weighted mean value of -4.90 ‰, and the $d_p$ values varied from -8.82 ‰ to 33.32 ‰, with the amount-weighted mean value of 14.25 ‰. More negative $\delta^{18}O$ values were observed in atmospheric water vapor compared to those in precipitation. The difference between $\delta^{18}O$ in precipitation and in atmospheric water vapor ($\Delta \delta$) varied from 1.24 ‰ to 20.13 ‰ with the mean value of 9.18 ‰ on rainy days. The low $\Delta \delta$ values mainly occurred during the winter of 2014 (Fig. 7a). The more depleted stable isotopic signatures in atmospheric water vapor were closely associated with the evaporative processes of new rainfall reaching the ground and of raindrops during their descent. In general, raindrops that fell in the unsaturated atmospheric environment with low humidity would experience strong evaporative processes. These processes caused
the heavy isotopic water molecules (e.g., $^{1}$H$_2^{18}$O and $^{1}$H$^{2}$H$^{16}$O) in raindrops to become enriched and their counterparts in atmospheric water vapor to gradually become depleted. Saxena and Eriksson (1985) have identified the evaporated strength of falling raindrops below the cloud according to the magnitude of difference between predicted-δ$^{18}$O$_e$ and δ$^{18}$O$_v$, showing that smaller difference indicated the greater evaporative enrichment of stable isotopic signatures in raindrops below the cloud and vice versa. Following Saxena’s inference, the weaker evaporative enrichment of stable isotopic signatures in raindrops below the cloud appeared during the winter of 2014, whereas there was stronger evaporative enrichment during other periods. The $d$ was higher in atmospheric water vapor than that in precipitation because the light isotopic water molecules were preferentially lost from raindrops during the evaporative processes. The average ∆$d$ value of 3.43 ‰ was found during rainy days. The trends of seasonal variations of both δ$^{18}$O and $d$ in atmospheric water vapor and precipitation were generally consistent, suggesting that these variations were influenced by large-scale climate systems and the interactions between local precipitation and water vapor.

3.3.2. Comparisons of the relationships between δ$^{2}$H and δ$^{18}$O in vapor and precipitation

The linear correlation between δ$^{2}$H and δ$^{18}$O in atmospheric water vapor here was described as the Meteoric Vapor Line (MVL), similar to the definition of the Meteoric Water Line (MWL; Craig, 1961). Both MVL and MWL are powerful tools and are widely applied in isotope hydrology. The MVL and MWL in Changsha calculated from daily stable isotope data for the whole sampling period were expressed as Equations (3) and (4), respectively.

\[
\delta^{2}H_v = 7.59\delta^{18}O_v + 12.43 \quad (n=868, \ r=0.98)
\]

\[
\delta^{2}H_p = 8.28\delta^{18}O_p + 15.98 \quad (n=352, \ r=0.98),
\]

The slope of the MVL was lower than 8, while that of the MWL was greater than 8, although the
intercepts of both the MVL and MWL were greater than 10 therein. Numerous previous studies have demonstrated that the slope of MWL and the corresponding linear correlation coefficient between $\delta^2$H and $\delta^{18}$O in precipitation may be considered as an important indicator to identify the degree of isotopic enrichment of raindrops below the cloud (Crawford, Hollins, Meredith, & Hughes, 2017; Dansgaard, 1964; Peng, Mayer, Harris, & Krouse, 2007; Salamalikis, Argiriou, & Dotsika, 2016). In general, greater slopes of the MWLs and more significant linear correlations indicate the weaker secondary evaporative effect on the stable isotopic compositions of raindrops below the cloud and vice versa. The slopes of the MWLs and $\delta^2$H/$\delta^{18}$O$_p$ correlations in different seasons were analysed in Changsha (Table 2). As shown in Table 2, the lowest slope (7.64) and a relatively non-significant linear correlation ($r = 0.95$) occurred in the cold season of 2014, suggesting that the stable isotopic signatures in raindrops experienced great evaporative enrichment below the cloud; by contrast, the higher slopes and more significant linear correlations were recorded during other periods, indicating that the stable isotopic signatures in raindrops experienced relatively weak evaporative enrichment below the cloud. This result contrasts with the results derived from the difference between $\delta^{18}$O$_e$ and $\delta^{18}$O$_v$.

From the seasonal variations of $\delta^{18}$O$_v$, the stable isotopic signatures in the atmospheric water vapor tend to be depleted with the occurrence of rainfall, probably resulting from the evaporation of new rainfall and raindrops below the cloud. By comparing the values between the MVLs on non-rainy and rainy days in the same period (Table 2), it can be found that the contribution of rainfall events caused the increases of the slope and intercept of the MVL, supplemented by evaporated vapor. In classic isotope fractionation theory (Clark & Fritz, 1997; Dansgaard, 1964), the evaporation of raindrops will result in the decreases of the slope and intercept of the $\delta^2$H-$\delta^{18}$O linear relationship in falling raindrops but the increases of the slope and intercept of the $\delta^2$H-$\delta^{18}$O linear relationship in the evaporated vapor. Affected by the evaporated
vapor, which has a higher slope and intercept, the slope and intercept of the MVL will increase. Because the secondary evaporation of raindrops is a continuous process from cloud to ground, its effect on atmospheric water vapor near the surface is lighter than the evaporation from the underlying surface on rainy days.

Table 2 Comparisons of the relationships between daily mean $\delta^2$H and $\delta^{18}$O in atmospheric water vapor and precipitation in different seasons in Changsha.

<table>
<thead>
<tr>
<th>Timescale</th>
<th>Period</th>
<th>Slope</th>
<th>Intercept (‰)</th>
<th>$\delta^2$H/$\delta^{18}$O</th>
<th>Slope</th>
<th>Intercept (‰)</th>
<th>$\delta^2$H/$\delta^{18}$O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Warm season</td>
<td>Whole period</td>
<td>7.83</td>
<td>12.92</td>
<td>0.98*</td>
<td>8.46</td>
<td>13.96</td>
<td>0.99*</td>
</tr>
<tr>
<td></td>
<td>Non-rainy days</td>
<td>7.73</td>
<td>11.36</td>
<td>0.98*</td>
<td>8.46</td>
<td>13.96</td>
<td>0.99*</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>8.01</td>
<td>15.60</td>
<td>0.98*</td>
<td>8.46</td>
<td>13.96</td>
<td>0.99*</td>
</tr>
<tr>
<td>Cold season</td>
<td>Whole period</td>
<td>7.54</td>
<td>13.48</td>
<td>0.99*</td>
<td>7.96</td>
<td>16.13</td>
<td>0.97*</td>
</tr>
<tr>
<td></td>
<td>Non-rainy days</td>
<td>7.47</td>
<td>12.91</td>
<td>0.98*</td>
<td>7.96</td>
<td>16.13</td>
<td>0.97*</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>7.66</td>
<td>14.26</td>
<td>0.99*</td>
<td>7.96</td>
<td>16.13</td>
<td>0.97*</td>
</tr>
<tr>
<td>Cold season in 2014</td>
<td>Whole period</td>
<td>7.21</td>
<td>11.78</td>
<td>0.98*</td>
<td>7.64</td>
<td>14.01</td>
<td>0.95*</td>
</tr>
<tr>
<td></td>
<td>Non-rainy days</td>
<td>7.22</td>
<td>11.93</td>
<td>0.97*</td>
<td>7.64</td>
<td>14.01</td>
<td>0.95*</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>7.33</td>
<td>12.99</td>
<td>0.98*</td>
<td>7.64</td>
<td>14.01</td>
<td>0.95*</td>
</tr>
<tr>
<td>Warm season in 2015</td>
<td>Whole period</td>
<td>8.00</td>
<td>14.57</td>
<td>0.98*</td>
<td>8.53</td>
<td>14.19</td>
<td>0.99*</td>
</tr>
<tr>
<td></td>
<td>Non-rainy days</td>
<td>7.99</td>
<td>13.69</td>
<td>0.98*</td>
<td>8.53</td>
<td>14.19</td>
<td>0.99*</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>8.10</td>
<td>17.20</td>
<td>0.99*</td>
<td>8.53</td>
<td>14.19</td>
<td>0.99*</td>
</tr>
<tr>
<td>Cold season in 2015</td>
<td>Whole period</td>
<td>7.19</td>
<td>8.24</td>
<td>0.97*</td>
<td>8.32</td>
<td>19.34</td>
<td>0.98*</td>
</tr>
<tr>
<td></td>
<td>Non-rainy days</td>
<td>6.98</td>
<td>5.08</td>
<td>0.97*</td>
<td>8.32</td>
<td>19.34</td>
<td>0.98*</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>7.48</td>
<td>12.46</td>
<td>0.96*</td>
<td>8.32</td>
<td>19.34</td>
<td>0.98*</td>
</tr>
<tr>
<td>Warm season in 2016</td>
<td>Whole period</td>
<td>7.61</td>
<td>10.39</td>
<td>0.98*</td>
<td>8.40</td>
<td>13.72</td>
<td>0.99*</td>
</tr>
<tr>
<td></td>
<td>Non-rainy days</td>
<td>7.49</td>
<td>8.99</td>
<td>0.98*</td>
<td>8.40</td>
<td>13.72</td>
<td>0.99*</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>7.80</td>
<td>12.11</td>
<td>0.98*</td>
<td>8.40</td>
<td>13.72</td>
<td>0.99*</td>
</tr>
<tr>
<td>Cold season in 2016</td>
<td>Whole period</td>
<td>7.67</td>
<td>15.31</td>
<td>0.98*</td>
<td>7.76</td>
<td>16.15</td>
<td>0.97*</td>
</tr>
<tr>
<td></td>
<td>Non-rainy days</td>
<td>7.62</td>
<td>15.37</td>
<td>0.97*</td>
<td>7.76</td>
<td>16.15</td>
<td>0.97*</td>
</tr>
<tr>
<td></td>
<td>Rainy days</td>
<td>7.82</td>
<td>16.31</td>
<td>0.98*</td>
<td>7.76</td>
<td>16.15</td>
<td>0.97*</td>
</tr>
</tbody>
</table>

According to the aforementioned analyses, on average, the strong evaporative enrichment in falling raindrops, but weak evaporation from the underlying surface, as well as a great difference between predicted-$\delta^{18}$O and $\delta^{18}$O near the surface, appeared in the cold season of 2014, suggesting that the isotopic compositions in atmospheric water vapor and precipitation were in a non-equilibrium state. Under the action of weak surface evaporation, the slope and intercept of the MVL increased by only 0.11 and 1.06 ‰ on rainy days, respectively, compared with those on non-rainy days (the increment is
calculated as arithmetic difference between the both). By contrast, the weak evaporative enrichment in falling raindrops but the strong evaporation from the underlying surface, as well as the small difference between the predicted-$\delta^{18}$Oe and $\delta^{18}$Ov near the surface, happened in other periods, indicating that the isotopic compositions of atmospheric water vapor and precipitation were in or near an equilibrium state.

Under the action of strong surface evaporation, compared with those on non-rainy days, the slope and intercept of the MVL increased by 0.11 and 3.51 ‰ in the warm season of 2015, respectively; by 0.5 and 7.38 ‰ in the cold season of 2015, respectively; by 0.31 and 3.12 ‰ in the warm season of 2016, respectively; and by 0.20 and 0.54 ‰ in the cold season of 2016, respectively. For the whole survey period, the evaporation of new rainfall and falling raindrops induced the increases of the slope and intercept of the MVL by 0.2 and 1.98 ‰ on rainy days, respectively, compared with those on non-rainy days.

3.4. Variations of stable water isotopes during typical weather patterns

3.4.1. Variations of vapor isotopes during continuous non-rainy days

Under the influence of the seasonal movement of the subtropical high over the western Pacific, the climate exhibits a dry and hot weather pattern from July to September of every year in Changsha. For example, there was not any precipitation from September 12 to September 27 of 2016 in Changsha. During this period, the temperature varied from 19.24 to 34.90 °C, with a mean value of 26.15 °C; the absolute humidity varied from 7.51 to 18.58 g kg$^{-1}$, with a mean value of 13.75 g kg$^{-1}$; and the $\delta^{18}$Ov values varied from -24.48 ‰ to -12.77 ‰, with a mean value of -17.04 ‰. Interestingly, all these statistics were lower than the mean values of corresponding variables in September except for the air temperature. The heavy isotopes in different water bodies of the underlying surface and thus those in atmospheric water vapor near the surface were successively enriched because no rainfall event happened.
throughout this process. From Fig. 8, the isotopes in atmospheric water vapor exhibited a positive trend from September 12 to September 27 but showed a negative trend from September 15 to September 18. It can be found that, after analysing simultaneous synoptic charts, super typhoon Morandi landed in Xiamen, China on September 15. The daily minimum temperature and atmospheric precipitable water dropped to 22.28 °C and 32.84 mm on September 18 from 24.73 °C and 54.92 mm on September 15, respectively, influenced by the peripheral cloud system of the super typhoon. Simultaneously, $d_v$ also showed obvious fluctuations. The changes in $\delta^{18}O_v$ and $d_v$ during the passage of typhoon Morandi are similar to the results reported by Fudeyasu et al. (2008), which showed the water vapor was isotopically depleted due to the rainout effect. This synoptic process indicates that the effects of a weather system can still be detected by tracers of the vapor isotopes, even though no rainfall occurs.

**Fig. 8.** Variations of the hourly mean $\delta^{18}O_v$ (a), $d_v$ (b), temperature, and absolute humidity (c) near the surface, as well as the hourly mean precipitable water (d) from September 12 to September 27 of 2016 in Changsha.
3.4.2. Variations of stable water isotopes during continuous rainy days

In the Yangtze River Basin and Huai River Basin of China, the period from middle June to early July of every year is called the “plum rains” season (Tao, Zhao, & Chen, 1958; Zhang, Kuang, Guo, & Zhou, 2006). The precipitation has the characteristics of continuity and high intensity during this season. As an example, Fig. 9 shows the hourly variations in $\delta^{18}O$ and $d$ in atmospheric water vapor and in precipitation, precipitation, air temperature, and absolute humidity near the surface, as well as the precipitable water during a continuous rainfall process in the plum rains season of 2016 in Changsha. From June 30 to July 6, the accumulated precipitation reached 226.59 mm, accounting for 20.35% of the warm season of 2016; the mean temperature was 26.0 °C and the mean absolute humidity was 18.22 g kg$^{-1}$ (Table 3). Based on the temporal patterns of precipitation variations in this period, the variation of $\delta^{18}O_v$ is divided into three stages. In the first stage, from 00:00 on June 30 to 19:00 on July 2, $\delta^{18}O_v$ was generally maintained at a relatively high level with less precipitation, high mean temperature, and absolute humidity; in the second stage, from 20:00 on July 2 to 16:00 on July 4, $\delta^{18}O_v$ fluctuated significantly and $^{18}O_v$ was depleted averagely relative to that in the first stage, with the accumulated precipitation of 197.13 mm, accounting for 87.0% of total precipitation in this period, as well as reduced mean temperature and absolute humidity; in the third stage, from 17:00 on July 4 to 00:00 on July 7, $^{18}O_v$ was gradually depleted, with less precipitation, low mean temperature, and absolute humidity.
Fig. 9. Variations of the hourly mean $\delta^{18}O$ (a), $d$ (b) in atmospheric water vapor and in precipitation, precipitation, temperature, and absolute humidity (c) near the surface, as well as the hourly mean precipitable water (d) from June 30 to July 6 of 2016 in Changsha.

Table 3 Comparisons of the mean $\delta^{18}O$, precipitation, mean temperature and absolute humidity near the surface at different stages of continuous rainfall in Changsha.

<table>
<thead>
<tr>
<th>Period</th>
<th>$\delta^{18}O$ (%)</th>
<th>$P$ (mm)</th>
<th>Mean $T$ (°C)</th>
<th>Mean $Q$ (g kg$^{-1}$)</th>
<th>Relationships</th>
<th>$\delta^{18}O/T$</th>
<th>$\delta^{18}O/P$</th>
<th>$\delta^{18}O/Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole period</td>
<td>-18.89(2.55)</td>
<td>226.59</td>
<td>26.00</td>
<td>18.22</td>
<td></td>
<td>0.64*</td>
<td>-0.21</td>
<td>0.78*</td>
</tr>
<tr>
<td>First stage</td>
<td>-16.67(0.92)</td>
<td>11.43</td>
<td>27.46</td>
<td>18.89</td>
<td>-0.13</td>
<td>-0.17</td>
<td>0.39*</td>
<td></td>
</tr>
<tr>
<td>Second stage</td>
<td>-19.35(2.13)</td>
<td>197.13</td>
<td>24.89</td>
<td>18.31</td>
<td>0.68*</td>
<td>-0.09</td>
<td>0.72*</td>
<td></td>
</tr>
<tr>
<td>Third stage</td>
<td>-21.27(1.80)</td>
<td>18.04</td>
<td>25.11</td>
<td>17.32</td>
<td>0.79*</td>
<td>-0.30</td>
<td>0.84*</td>
<td></td>
</tr>
</tbody>
</table>

Note. The number in the parentheses represents the standard deviation.

From the statistics in Table 3, the $\delta^{18}O$ values of every stage displayed significant positive correlations with absolute humidity, which were consistent with their relationships on a diurnal time scale. However, the correlations of $\delta^{18}O$ with temperature varied in different stages. Specifically, $\delta^{18}O$ showed an insignificant negative correlation with temperature in the first stage, but it did show significant positive
correlations with temperature in the last two stages, with an increase in temperature and more positive \( \delta^{18}\text{O} \), (Fig. 9). Although rainfall always depleted vapor isotopes, the negative correlations between them were not significant, especially in the second stage. It can be seen that \( ^{18}\text{O} \) was not significantly depleted in the second stage, which had the most precipitation, compared to that in the first stage, which had the least precipitation. In addition, by analysing the variation of the precipitable water in the second stage, a steady input of ambient water vapor might compensate for the loss of water vapor due to condensation and offset the depletion effect of precipitation on vapor isotopes; thus, the decrease of \( \delta^{18}\text{O} \) was not obvious in the second stage. The small fluctuation in \( d \), also supports this hypothesis to some extent. With the decrease of water vapor input and change of water vapor transport type (Li et al., 2015; Munksgaard, Wurster, Bass, & Bird, 2012), as well as the contribution from surface evapotranspiration, the precipitable water and precipitation tended to decrease, but \( \delta^{18}\text{O} \) began to rise steadily in the third stage. Although the variations of precipitation isotopes can partly reflect the characteristics of weather conditions and water vapor transports in different stages, the vapor isotopes provided details about the continuous variations of relevant elements.

3.4.3. Variations of stable water isotopes during a strong cold wave

The cold wave and cold air moving down southward are the main weather systems in winter in East Asia. In the period from January 20 to January 25, 2016, the whole of East Asia had experienced a wide range of cooling, heavy rain and snow, and gale weather from north to south. Under the influence of strong cold air from Central Siberian and East Siberian, the air temperatures of 179 weather stations over North China, Huang Huai Basin, south of the Yangtze River, Southern China, and the Southwest fell below the historical minimum in January since the establishments of these stations and those of 82 cities and counties in Shandong, Jiangsu, Fujian, Sichuan, and other 19 provinces in China fell below the
historical extreme values of minimum temperature (Jiang, Ma, & Wang, 2016). Fig. 10 exhibits the temporal variations of vapor isotopes, precipitation isotopes, and related meteorological factors before and after this strong cold wave passed through Changsha.

![Fig. 10](image)

**Fig. 10.** Variations of the hourly mean $\delta^{18}O$ (a), $d$ (b) in atmospheric water vapor and in precipitation, precipitation, temperature, and absolute humidity (c) near the surface, as well as the hourly mean precipitable water (d) from January 17 to January 28 of 2016 in Changsha.

From Fig. 10, the temperature and absolute humidity with mean values of 7.20 °C and 4.12 g kg$^{-1}$, respectively, showed great fluctuations, but $\delta^{18}O_v$ with a mean value of -15.94 ‰ varied smoothly from 00:00 on January 17 to 04:00 on January 20. Since the cold front arrived on January 20, the Changsha area had begun an obvious precipitation and cooling process. The main rainfall processes occurred from 14:00 on January 20 to 07:00 on January 21 with 20.06 mm of precipitation and from 23:00 on January 21 to 09:00 on January 22 with 6.35 mm of precipitation. The daily mean temperature decreased from 6.62 °C on January 19 to 1.80 °C on January 22 with the lowest temperature of 0.88 °C; the absolute
humidity, with a mean value of 3.60 g kg$^{-1}$, decreased slightly; $\delta^{18}$O$_v$ showed a small fluctuation and was almost equivalent with those in the period from 00:00 on January 17 to 04:00 on January 20, which were unaffected by the cold front. After the cold front passed through Changsha, the $\delta^{18}$O$_v$ and absolute humidity decreased sharply, from -17.30 ‰ to -24.45 ‰ and from 2.88 to 1.60 g kg$^{-1}$, respectively, from 00:00 to 13:00 on January 23. They were all maintained at low levels until 00:00 on January 25. With the end of the cold wave process, the temperature, absolute humidity, and $\delta^{18}$O$_v$ all began to rise and basically returned to their former levels on January 26. During the strong cold wave, only 7 precipitation samples were collected. All water samples, except one collected at 08:00 on January 27, showed small differences in $\delta^{18}$O$_v$ and $d_v$.

During the cold wave, there was a close relationship between $\delta^{18}$O$_v$ and absolute humidity, with a correlation coefficient of 0.85 ($p < 0.01$). Because absolute humidity was primarily controlled by the precipitable water, and the latter was dependent on the transportation of total water vapor during the invasion of the cold wave, it can be inferred that the variation of $\delta^{18}$O$_v$ was mainly caused by that of the cold wave. Indeed, the variation of $\delta^{18}$O$_v$ well indicates the activities of the cold wave.

The analyses above indicate that the short-term weather processes can be reflected in the temporal evolutions of vapor isotopes. In addition, atmospheric humidity is a good predictor for vapor isotope on the time scales from diurnal to a few days, which is similar to the finding by Lee et al. (2006).

4. Conclusions

Long-term and continuous measurements of stable isotopic compositions in atmospheric water vapor near the surface show the obvious multi time scale variation characteristics of vapor isotopes. On a diurnal time scale, the $\delta^{18}$O$_v$ values were more negative in the daytime and more positive at night, and the variation of $d_v$ was the opposite on non-rainy days; however, the $\delta^{18}$O$_v$ values were more positive in the
daytime and more negative at night, and the variation of $d_v$ was not significant on rainy days; on a
seasonal time scale, affected by air masses with distinct thermodynamic properties, the $\delta^{18}$O and $d$ values
in atmospheric water vapor were more negative in the warm season than in the cold season.

On different time scales, including diurnal, a few days, intra-seasonal and seasonal time scales, $d_v$
was generally inversely proportional to temperature and absolute humidity, and had no significant
relationship with precipitation; moreover, $\delta^{18}$O$_v$ had a stable negative linear relationship with precipitation,
although sometimes the relationship was statistically insignificant. However, the relationships of $\delta^{18}$O$_v$
with temperature and absolute humidity were obviously different on different time scales. Overall, $\delta^{18}$O$_v$
had very significantly positive linear relations with temperature and absolute humidity on short time
scales, including diurnal, a few days, and intra-seasonal time scales, which indicated the relationship
between the stable isotopes and the temperature of the same air mass. The negative linear relationships
between $\delta^{18}$O$_v$ and temperature and absolute humidity reflected the interactions between different air
masses on seasonal and sometimes intra-seasonal timescales.

The change patterns of $\delta^{18}$O and $d$ in atmospheric water vapor and precipitation were highly
consistent, but affected by below-cloud secondary evaporation, there was an average $^{18}$O$_v$ depletion of
9.18 ‰ relative to $^{18}$O$_p$ and an average $d_v$ enrichment of 3.43 ‰ relative to $d_p$ on rainy days. For the
whole sampling period, the local Meteoric Water Line in Changsha was $\delta$H$_p$ = 8.28$\delta^{18}$O$_p$ + 15.98, the
Meteoric Vapor Line was $\delta$H$_v$ = 7.59$\delta^{18}$O$_v$ + 12.43. Under the influence of the evaporation of falling
raindrops and the underlying surface, the slopes and intercepts of the MVLs on rainy days all increased,
with average increases of 0.2 and 1.98 ‰, respectively, relative to those on non-rainy days. Generally, the
isotopic compositions of atmospheric water vapor were in equilibrium with those of precipitation during
each rainfall event, except for those in the cold season in 2014. And further analysis suggested that
compared with precipitation isotopes, the vapor isotopes can provide details about weather processes due to the time-space continuity of water vapor.

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Highlights:

1. Rare high resolution vapor isotopic data in the subtropical monsoon region.
2. Environmental controls on vapor isotopes on different time scales are discussed.
3. Isotopic compositions of atmospheric water vapor and precipitation are compared.
4. Detection of short-duration weather processes using vapor isotopes appears possible.