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Short-term variations of vapor isotope ratios reveal the influence of atmospheric processes

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Abstract: Stable isotopes of atmospheric water vapor reveal rich information on water movement and phase changes in the atmosphere. Here we presented two nearly continuous time-series of δD and δ^{18}O of atmospheric water vapor (δ_v) measured at hourly intervals in surface air in Beijing and above a winter wheat canopy in Shijiazhuang using in-situ measurement technique. During the precipitation events, the δ_v values in both Beijing and Shijiazhuang were in the state of equilibrium with precipitation water, revealing the influence of precipitation processes. However, the δ_v departures from the equilibrium state were positively correlated with local relative humidity. Note that the δ_v tended to enrich in Beijing, but deplete in Shijiazhuang during the precipitation events, which mainly resulted from the influence of transpiration processes that enriched the δ_v in Shijiazhuang. On seasonal time-scale, the δ_v values were log-linear functions of water vapor mixing ratios in both Beijing and Shijiazhuang. The water vapor mixing ratio was an excellent predictor of the δ_v by the Rayleigh distillation mechanisms, indicating that air mass advection could also play an important role in determining the δ_v. On a diurnal time-scale, the δ_v reached the minimum in the early afternoon hours in Beijing which was closely related to the atmospheric processes of boundary layer entrainment. During the peak of growing season of winter wheat, however, the δ_v reached the minimum in the early morning, and increased gradually through the daytime, and reached the maximum in the late afternoon, which was responsible by the interaction between boundary layer entrainment and the local atmospheric processes, such as transpiration and dew formation. This study has the implications for the important role of vegetation in determining the surface δ_v and highlights the need to conduct δ_v measurement on short-term (e.g. diurnal) time scales.

Keywords: stables isotopes; atmospheric water vapor; precipitation; TDLAS

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1 Introduction

The stable isotopes of atmospheric water vapor, HDO, $H_2{}^{18}O$ and $H_2{}^{16}O$, are excellent tracers for water movement and phase changes in the atmosphere (Gat, 1996; Lee *et al*., 2006). The δD and $\delta^{18}O$ values of atmospheric water vapor (δ_v) bear rich information on hydrological, ecological and climatological processes, and have proven to be an efficient tool in studies on sources and mixing of atmospheric moisture (Dansgaard, 1964; Yamanaka *et al*., 2007), water recycling (Vallet-Coulomb *et al*., 2008), partitioning of evapotranspiration (ET) into evaporation and transpiration (Moreira *et al*., 1997; Yepez *et al*., 2005) and leaf water enrichment (Welp *et al*., 2008). It is suggested that δ_v can be estimated based on the monthly or event-based precipitation because δ_v can potentially reach equilibrium with the isotopic composition of the falling rain droplets during rainy periods (Stewart, 1975; Jacob *et al*., 1991). However, the equilibrium method for predicting δ_v in surface air may suffer large errors in arid and semiarid climates, and even fail during the non-rainy periods (Wen *et al*., 2010).

The temporal variations of δ_v near the surface are related to the atmospheric processes on various time-scales such as air mass advection, precipitation, ET and entrainment from the free atmosphere (Lai *et al*., 2006; Lee *et al*., 2006; Wen *et al*., 2010). Most of the seasonal variability in δ_v can be understood through the Rayleigh distillation mechanisms (Gat, 1996). The temperature and more importantly, the water content of an air mass are indicators of its rainout history (Jacob *et al*., 1991; Lee *et al*., 2006). Seasonal variations of δ_v are attributed to the entrainment at the top of the planetary boundary layer (Angert *et al*., 2008), the intensity of monsoon activities (Yu *et al*., 2005; Wen *et al*., 2010), and synoptic events, such as precipitation events(Lee *et al*., 2006), passage of fronts (Wen *et al*., 2010) and tropical depression (Fudeyasu *et al*., 2008). The factors that contribute to the diurnal variations of δ_v may be different geographically. It may be local ET, diurnally variable entrainment in the boundary layer, sea breeze, or a combination of these processes that drives the diurnal cycles of δ_v (Lai *et al*., 2006; Lee *et al*., 2006; Welp *et al*., 2008; Wen *et al*., 2010).

To date, most of the published studies on δ_v are limited to brief campaign and discrete sampling due to instrumental and technical limitations (Helliker *et al*., 2002). Only a limited number of long-term observations have been reported. For example, Jacob and Sonntag (1991) have reported an 8-year record of the δ_v at Heidelberg, Germany. Angert *et al*. (2008) reported a 9-year observation of the δ_v in the Eastern Mediterranean. However, the measurements of δ_v are limited to coarse temporal resolutions ranging from 24 hours to several days by the traditional cold-trap/mass spectrometry methods (e.g. Jacob and Sonntag, 1991; Angert *et al*., 2008). Therefore, it is difficult to discern the atmospheric processes contributing to the short-term variations of δ_v and the associated mechanisms.

Recent advances in tunable diode laser absorption spectrometer (TDLAS) have made it possible to make high temporal resolution measurements of δ_v (Lee *et al*., 2005; Wen *et al*., 2008). Such kinds of measurements offer us new opportunities to investigate the temporal variations of δ_v and gain insights into the mechanisms involved. For example, using a tunable diode laser (TDL), Lee *et al*. (2006) investigated the temporal variations of the vapor $\delta^{18}O$ in surface air in New England and suggested that water vapor mixing ratio (w) was a better predictor for the vapor $\delta^{18}O$ than the air temperature on time-scale shorter than a few

days. In contrast, Wen *et al*. (2010) found that w was a poor predictor of the temporal variability of the δ_v during the peak summer monsoon activities in Beijing. Lee *et al*. (2007) reported the continuous measurements of $\delta^{18}O$ of atmospheric water vapor and ET over a temperate forest, and observed a diurnal variation of 60‰ or more of the $\delta^{18}O$ flux ratio on some days. Welp *et al*. (2008) presented the observations of the $\delta^{18}O$ of atmospheric water vapor and ET above a soybean canopy, and suggested that the temporal variations of the vapor $\delta^{18}O$ were driven by a variety of processes, such as Rayleigh distillation, vertical atmospheric mixing and local ET. On the other hand, advances in off-axis integrated cavity output spectroscopy (Lis *et al*., 2008; Wang *et al*., 2009) and wavelength-scanned cavity ring down spectroscopy (Crosson, 2008; Gupta *et al*., 2009) have also made it possible to make continuous measurements of δ_v.

A central part of this study was two nearly continuous time-series of the δ_v measured at hourly intervals in surface air during day of year (DOY) 95-170 in 2007 in Beijing and above a winter wheat canopy during DOY 95-170 in 2008 in Shijiazhuang using in-situ tunable diode laser technique. In this paper, the two high temporal resolution datasets provide us an opportunity to characterize how the atmospheric processes, such as air mass advection, evapotranspiration (including transpiration and evaporation) and entrainment from the free atmosphere other than precipitation, influenced the surface δ_v on various time-scales including event-based precipitation, seasonal and diurnal scales. Especially, the effect of vegetation, namely transpiration, was elucidated by comparing the δ_v in Beijing and Shijiazhuang under the similar climate conditions.

2 Materials and methods

2.1 Study sites

Beijing (40°00′N, 116°23′E), the capital city of China, lies on the northern edge of the North China Plain. It is located on the eastern rim of the Eurasian land mass and belongs to the West Wind Belt. The city is surrounded by mountains in its west, north and northeast; its southeast is plain extending to the seashore of the Bohai Sea. The annual average temperature is 11.5℃, with an average precipitation of 554.5 mm, about 80% of which is concentrated in June–September period (Sun *et al*., 2007). Beijing has a typical monsoon-influenced climate, characterized by hot, humid summers due to the East Asian monsoon, and generally cold, windy, dry winters due to the vast Siberian anticyclone. The mesurement of δ_v in this study was conducted in the plain and urbanized area, with an elevation of about 45 m above the sea level.

Shijiazhuang (37.53′N, 114.40′E), the capital city of Hebei Province, North China, is located at 270 km southwest from Beijing and lies on the western edge of the North China Plain. It is located at the base of Mt. Taihang. The annual average temperature is 12.3℃. The average annual precipitation is 482 mm with 70% falling in summer (from June to September) (Chen *et al*., 2010). In this study, the δ_v measurement was made above a winter wheat canopy in Luancheng, an agricultural ecosystem experimental site in Shijiazhuang, with an elevation of about 50 m above the sea level. Rotation of winter wheat and summer maize dominates agricultural activities at this site. Only δ_v data in the winter wheat growth period

were reported here.

2.2 In situ measurement of water vapor isotope ratios

The δ_v in surface air in Beijing and above a winter wheat canopy in Shijiazhuang were measured using a tunable diode laser (TDL) trace gas analyzer (Model TGA100A, Campbell Scientific Inc., Logan, UT, USA), respectively. The schematic diagram of the analyzer, its principle of operation, and calibration procedure were described in detail in Wen *et al*. (2008; 2010). The analyzer was configured with a six-intake manifold, with three air sample intakes and three calibration gas intakes. The air samples and calibration gases were pumped through the sample cell in an alternating fashion, with 25s in Beijing and 20s in Shijiazhuang spent on each port in a measurement cycle. The TDL signals were recorded at 1 Hz by a datalogger (Model CR1000, Campbell Scientific Inc., Logan, UT, USA) and then block-averaged over 25s intervals in Beijing and 20s intervals in Shijiazhuang for analysis and archiving. The data reported in this study were block-averaged to hourly intervals. The 1-h precision (one standard deviation) of δD and δ^{18}O was 1.1‰ and 0.07‰ at dewpoint temperature 15℃, and 2.0‰ and 0.12‰ at dewpoint temperature 1℃, respectively (Wen *et al*., 2008).

In Beijing, ambient air was drawn through one sample intake from the outside of our laboratory, at approximately 10 m above the ground, into the TDL analyzer. Further information was given in Wen *et al*. (2010). The sub-dataset during April 5 and June 19, 2007 (DOY 95-170) was used for comparison.

In the spring of 2008, the TDL system was moved to Luancheng site in Shijiazhuang. Ambient air was drawn through two sample intakes above the winter wheat and summer maize canopy, since April 4 in 2008 with the returning green of winter wheat. The heights of the two intakes increased over the season from 0.6 and 1.6 m at the beginning to 1.1 and 2.1 m by the end of the growing season of winter wheat, and to 3.2 and 4.2 m by the end of the growing season of summer maize to adjust for canopy growth. The harvesting of winter wheat was completed on June 18, 2008. The summer maize was planted on June 13. The experiment was ended up on September 14. Only the dataset of the upper intake was reported here. The sub-dataset during April 4 and June 18, 2008 (DOY 95-170) was used for comparison.

The isotopic data is expressed using the conventional delta notation,

$$\delta=(R/R_{\text{vsmow}}-1)\times 1000‰ \quad (1)$$

where R_{vsmow}= 0.00015576 for D/H and 0.0020052 for ^{18}O/^{16}O, and R is the isotope molar ratio. The deuterium excess (d) of atmospheric water vapor and precipitation is calculated as (Dansgaard, 1964; Merlivat *et al*., 1979),

$$d=\delta\text{D}-8\delta^{18}\text{O} \quad (2)$$

2.3 Auxiliary measurement

In Beijing, auxiliary variables (air temperature, relative humidity, precipitation time and amount) were measured with a Davis weather station (Model Vantage Pro, Davis Instruments Inc., USA) mounted on the rooftop of our laboratory building, at approximately 20 m above the ground (Wen *et al*., 2010). In Shijiazhuang, air temperature and humidity were measured with HMP45C sensors (Model HMP45C, Campbell Scientific Inc., Logan, UT,

USA). To get the information of background moisture, an HMP45C sensor was mounted on a nearby observation tower, at about 30 m above the ground. Precipitation time and amount were recorded with a rain gauge (Model 52203, RM Young, Inc., Michigan, USA). Leaf area index (LAI) was measured every 7–10 days.

Precipitation waters were collected after each rain event, in both Bejing and Shijiazhuang. Their isotope ratios were analyzed by pyrolysis with a continuous flow method using a mass spectrometer (MAT253, Finnigan Inc.). The precision of the analysis was better than 2‰ for δD and 0.3‰ for δ^{18}O.

3 Results and discussion

3.1 Temporal variations of the vapor δD, δ^{18}O and d

Figure 1 illustrates the temporal variations of all valid hourly observations of the δD, δ^{18}O and d of atmospheric water vapor and event-based precipitation from April 5 to June 19, 2007 (DOY 95-170) in Beijing, and Figure 2 from April 4 to June 18, 2008 (DOY 95-170) in Shijiazhuang. In both Beijing and Shijiazhuang, the δD and δ^{18}O of atmospheric water vapor covaried with those of precipitation, reflecting the influence of precipitation processes (also

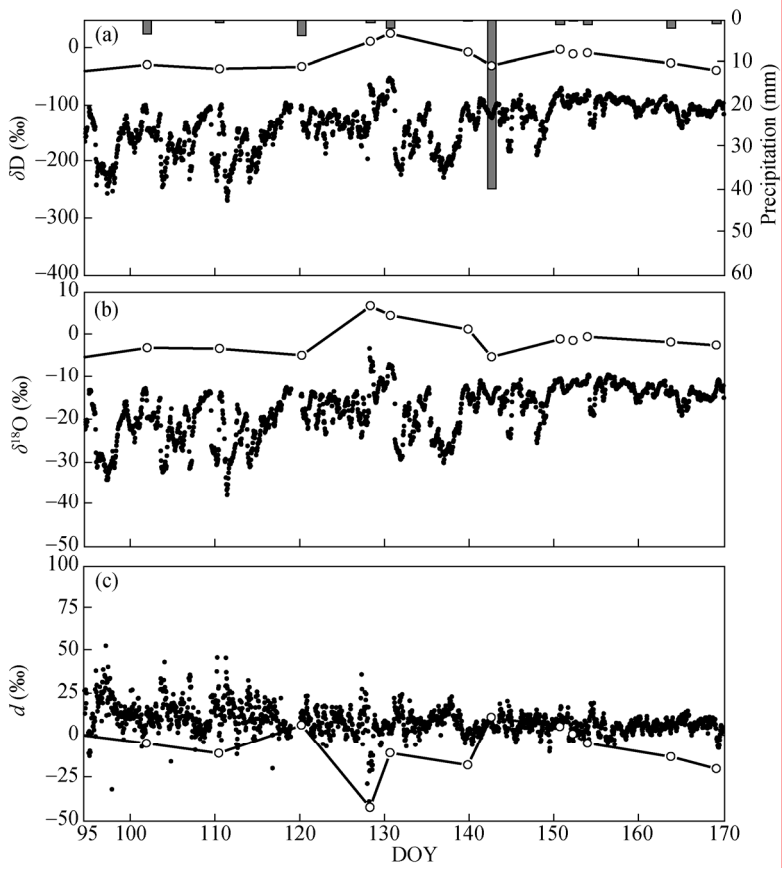

Figure 1 Hourly values of δD, δ^{18}O and d of atmospheric water vapor (dots) and precipitation (circles) from April 5 to June 19 2007 (DOY 95-170) in Beijing, China. Also shown are the precipitation amounts (colomn).

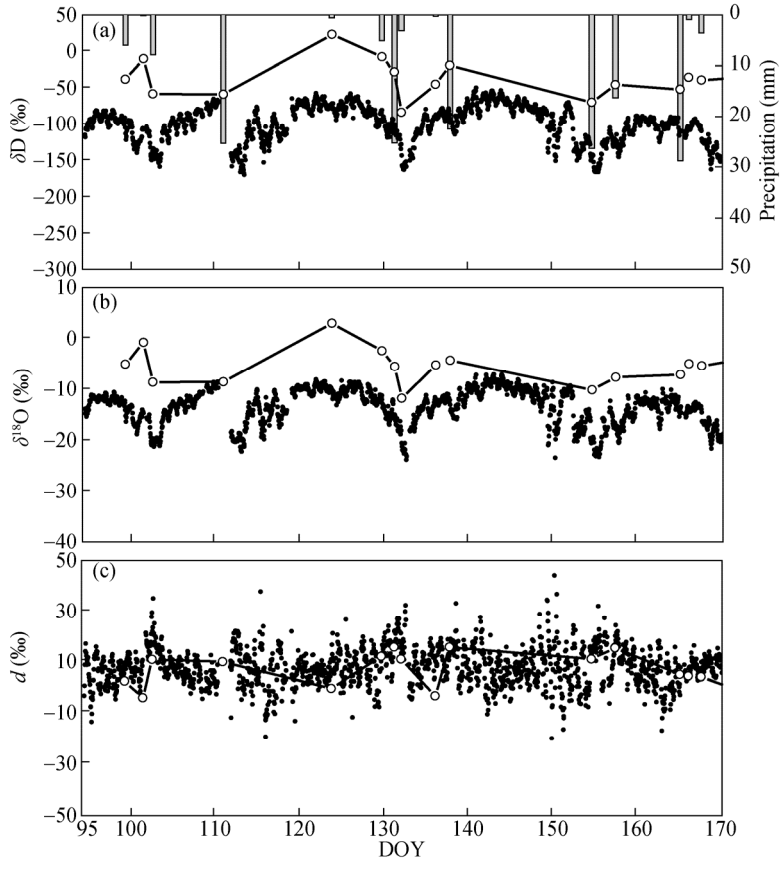

Figure 2 Hourly values of δD, δ^{18}O and d of atmospheric water vapor (dots) and precipitation (circles) from April 4 to June 18 2008 (DOY 95-170) in Shijiazhuang, China. Also shown are the precipitation amounts (colomn).

see Section 3.2). On time-scale of a few days at both sites, considerable variations of the δD, δ^{18}O and d in vapor phase were observed, sometimes exceeding 100‰, 10‰ and 20‰, respectively, but the magnitudes of temporal variations in Shijiazhuang were less than those in Beijing.

Table 1 summarizes the maximum and minimum of the hourly δD, δ^{18}O and d of atmospheric water vapor and event-based precipitation in Beijing and Shijiazhuang. The observed hourly maximum and minimum in Beijing were approximately –50.7‰ and –267.0‰ for δD, –3.08‰ and –37.82‰ for δ^{18}O, and 52.9‰ and –38.6‰ for d, respectively. In comparison, the observed hourly maximum and minimum in Shijiazhuang were approximately –49.8‰ and –169.5‰ for δD, –7.06‰ and –23.85‰ for δ^{18}O, and 44.1‰ and –20.1‰ for d, respectively.

The precipitation δD and δ^{18}O in Beijing reached their maximum values of 27.5‰ and 6.90‰ during two small rain showers on DOY 131 and DOY 128, respectively, and, on these days, the event-based d of precipitation reached its lowest value of –42.0‰. Similarly, in Shijiazhuang, a small shower on DOY 124 produced 0.5 mm rainfall with the highest values of 23.7‰ for δD and 3.02‰ for δ^{18}O, while a 0.1 mm rainfall on DOY 102 resulted in the lowest d value of –4.0‰ in precipitation. The observed maximum values of δD and δ^{18}O of atmospheric water vapor in Beijing were caused by their respective maximum values of

Table 1 Statistics of the measrued meterological factors and isotopic compositions of the atmospheric water vapor and precipitation in Beijing (BJ) and Shijiazhuang (SJZ) during the observational periods

Sites	Statistical Parameters	T (℃)	w (mmol mol^{-1})	RH (%)	LAI (m^{2}m^{-2})	Vapor			Precipitation			Equilibrium vapor		
						δD	δ^{18}O	d	δD	δ^{18}O	d	δD	δ^{18}O	d
						(‰)			(‰)			(‰)		
BJ	Max	37.0	23.7	98.0	—	–50.7	–3.08	52.9	27.5	6.90	11.1	–55.0	–3.41	11.7
	Min	7.2	1.4	7.5	—	–267.0	–37.82	–38.6	–100.7	–13.67	–42.0	–189.8	–24.94	–45.4
	Mean	21.6	9.5	38.2	—	–133.0	–17.73	8.8	–25.9	–4.09	6.8	–104.2	–13.92	7.2
	SD	6.0	5.5	20.6	—	41.4	5.87	8.1	31.7	5.14	14.4	34.4	5.53	14.8
SJZ	Max	33.2	28.9	100.0	4.5	–49.8	–7.06	44.1	23.7	3.02	15.7	–58.0	–6.82	16.5
	Min	3.2	3.3	14.7	0.1	–169.5	–23.85	–20.1	–83.2	–11.79	–4.0	–164.7	–22.24	–8.7
	Mean	18.0	15.3	69.3	2.9	–99.6	–13.44	7.9	–45.5	–7.07	11.1	–126.1	–17.21	11.6
	SD	5.8	5.1	20.0	—	25.0	3.43	7.5	26.9	3.71	6.7	25.7	3.76	7.4

Max is maximum, Min is minimum, SD is standard deviation, T is surface air temperature, w is water vapor mixing ratio, RH is relative humidity, and LAI is leaf area index. The event-based δD, δ^{18}O and d values in precipitation were computed as the precipitation weighted mean values. The equilibrium vapor δD, δ^{18}O and d values were evaluated at the surface air temperature from the isotope ratios of precipitation. The δD, δ^{18}O and d values in vapor, as well as T, w and RH, were calculated from the hourly measurements.

δD and δ^{18}O in precipitation, but they were not the case in Shijiazhuang.

That the highest δD and δ^{18}O and lowest d values of precipitation at both sites occurred in spring season prior to summertime monsoon activities was consistent with previous observations made in Beijing (Wei *et al*., 1982), Shijiazhuang (Yamanaka *et al*., 2004) and the south of the Tibetan Plateau (Liu *et al*., 2007), indicating the influence of secondary evaporation of raindrops between the cloud base and ground in the warm and dry spring season.

Table 1 also summarizes the averages of δD, δ^{18}O and d of atmospheric water vapor and precipitation for the whole observation period in Beijing and Shijiazhuang. In Beijing, the mean values of the vapor δD, δ^{18}O and d were −133.0‰, −17.73‰ and 8.8‰, respectively. The precipitation amount weighted mean values of the δD, δ^{18}O and d in precipitation were –25.9‰, –4.09‰ and 6.8‰, respectively. The low precipitation d values less than 10‰ may indicate a secondary evaporation process of the falling raindrops under the cloud base (Stewart, 1975; Gat, 2005). In Shijiazhuang, the averaged vapor δD, δ^{18}O and d were –99.6‰, –13.44‰ and 7.9‰, respectively. The precipitation amount weighted values of the δD, δ^{18}O and d in precipitation were –45.5‰, –7.07‰ and 11.1‰, respectively. In contrast with Beijing, where the air humidity was lower, the rain water in Shijiazhuang was characterized with a d value usually higher than 10‰, which may indicate the contribution of moisture from surface evaporation (Gat *et al*., 1994), or the non-equilibrium evaporation conditions in the remote water source region (Merlivat *et al*., 1979).

3.2 Effects of precipitation on the vapor δD, δ^{18}O and d

Figure 3 presents a comparison of the vapor δD, δ^{18}O and d measurements with the equilibrium predictions during precipitation events. Each data point represents one precipitation event. The event-based averages of δD and δ^{18}O of atmospheric water vapor were computed from the hourly observations and weighted by hourly precipitation amount. The equilibrium δD and δ^{18}O values were evaluated at the surface temperature from the isotope ratios of the

rain water collected over the full events. Note that, as expected, the vapor δD, δ^{18}O and d agreed well with equilibrium predictions at both sites. Such relationships are also observed by other studies (Lee *et al*., 2006; Welp *et al*., 2008; Wen *et al*., 2010). They were the basis of the equilibrium method for estimating isotope ratios of atmospheric water vapor from those of precipitation, and vice versa. On the other hand, the event-based vapor δD, δ^{18}O in Shijiazhuang appeared to be slightly higher than the equilibrium predictions, consistent with the statistical results of all the data in the experimental period (Table 1). In contrast, the mean δD and δ^{18}O values of vapor in the whole observation period in Beijing were lower than the equilibrium predictions (Table 1). We postulated that the canopy transpiration in Shijiazhuang might be responsible for the more enriched δD and δ^{18}O of the observations than the equilibrium predictions.

Figure 4 illustrates the departures of the vapor δD, δ^{18}O and d from the equilibrium predictions against local relative humidity (RH) during the precipitation events. The departures of the vapor δD and δ^{18}O were positively correlated with RH, and the departure of the vapor d was negatively correlated with RH, confirming our expectations that as RH decreased, the kinetic fractionation effects should cause the vapor isotope ratios to depart far away from the equilibrium state. However, such relationships were more robust in Beijing than in Shijiazhuang. The reader should be aware of two potential reasons. First, this was likely caused by the different magnitudes of the changing RH between Beijing (RH=44%–86%) and Shijiazhuang (RH=72%–94%). Second, the discrepancy of ET, including evaporation and transpiration between Beijing and Shijiazhuang might also be responsible.

The negative relationships between the vapor d and RH have been reported in several recent studies. By observation on a ship in Southern Ocean, Uemura *et al*. (2008) reported a negative correlation of the vapor d with RH normalized to the sea surface temperature. Using air parcel trajectory analysis method, Pfahl and Wernli (2008) also found a strong negative correlation (r= –0.82) between normalized RH in the source regions and measured vapor d. Wen *et al*. (2010) showed that the observed vapor d negatively correlated with local RH under both rainy and clear weather conditions.

During rainy periods, the δD and δ^{18}O of atmospheric water vapor were in the state of equilibrium with precipitation water. However, the vapor δD and δ^{18}O tended to enrich during the precipitation events in Beijing, but tended to deplete in Shijiazhuang (Figures 1 and 2). In Beijing, precipitation events usually brought the vapor δD and δ^{18}O to higher values than those in the periods just before and after the rainfall. For example, as mentioned above, during the rainfall on DOY 128 and 131, the vapor δD and δ^{18}O reached their maximum values of −50.7‰ and −3.08‰, respectively. In Shijiazhuang, however, the vapor δD and δ^{18}O depleted dramatically during most of the precipitation events. For instance, the rain shower (3 mm) on the night of DOY 132 produced the lowest precipitation δD and δ^{18}O values of –83.2‰ and –11.79‰, resulting in the pretty low δD and δ^{18}O values of –162.7‰ and –23.85‰ in vapor comparing with those in the periods before and after the rainfall.

Further, when the data were grouped into periods with and without rain, statistical analysis revealed that the δD and δ^{18}O values of atmospheric water vapor during the rainy periods were significantly (p<0.001) higher than those during the no-rain periods in Beijing. In comparison, statistical analysis also revealed that the vapor δD and δ^{18}O during the rainy periods were significantly (p<0.001) lower than those during the no-rain periods in Shijiazhuang.

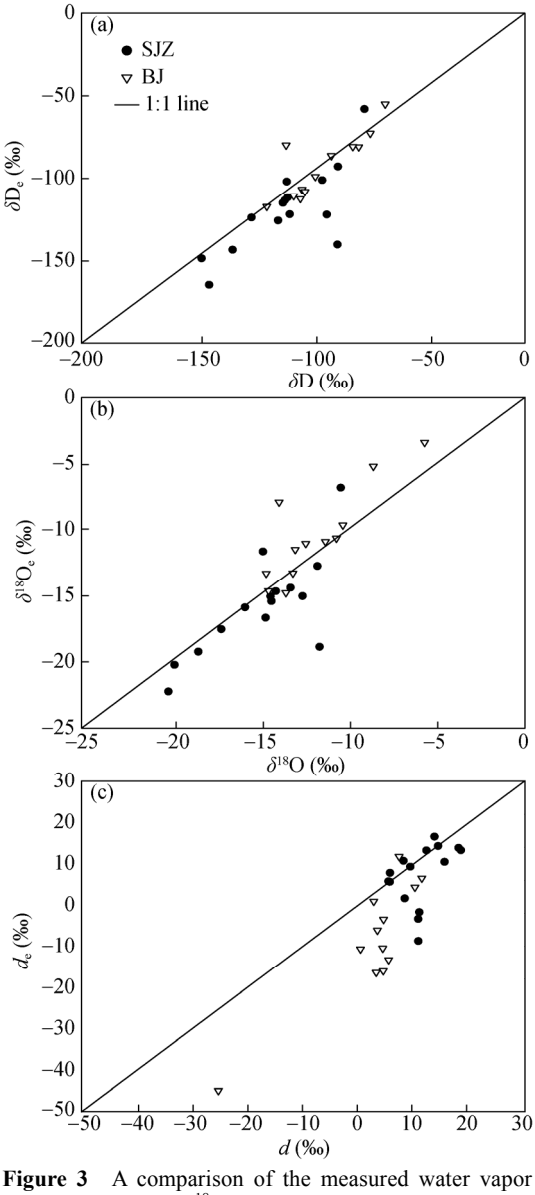

Figure 3 A comparison of the measured water vapor isotope ratios, δD, δ^{18}O and d, and the isotope ratios of water vapor in equilibrium with the precipitation, δD_e, $\delta^{18}O_e$ and d_e during precipitation events in Beijing (BJ) and Shijiazhuang (SJZ). The δD, δ^{18}O and d values in precipitation and vapor were computed as the precipitation weighted mean values. The equilibrium vapor δD, δ^{18}O and d values were evaluated at the surface air temperature from the isotope ratios of precipitation. Least-squares regression of the data for BJ is (a) $\delta D_e = 1.0\delta D - 3.3$, $R^2=0.71$ (n=12, $p<0.001$); (b) $\delta^{18}O_e = 1.13\delta^{18}O + 2.75$, $R^2 = 0.71$ (n=12, $p<0.001$); (c) $d_e = 1.4d - 12.1$, $R^2 = 0.77$ (n=12, $p<0.001$), and for SJZ is (a) $\delta D_e = 0.9\delta D - 20.1$, $R^2 = 0.59$ (n=15, $p<0.001$); (b) $\delta^{18}O_e = 0.97\delta^{18}O - 1.31$, $R^2 = 0.58$ (n=15, $p<0.01$); (c) $d_e = 0.7d - 0.9$, $R^2 = 0.18$ (n=15, $p=0.120$).

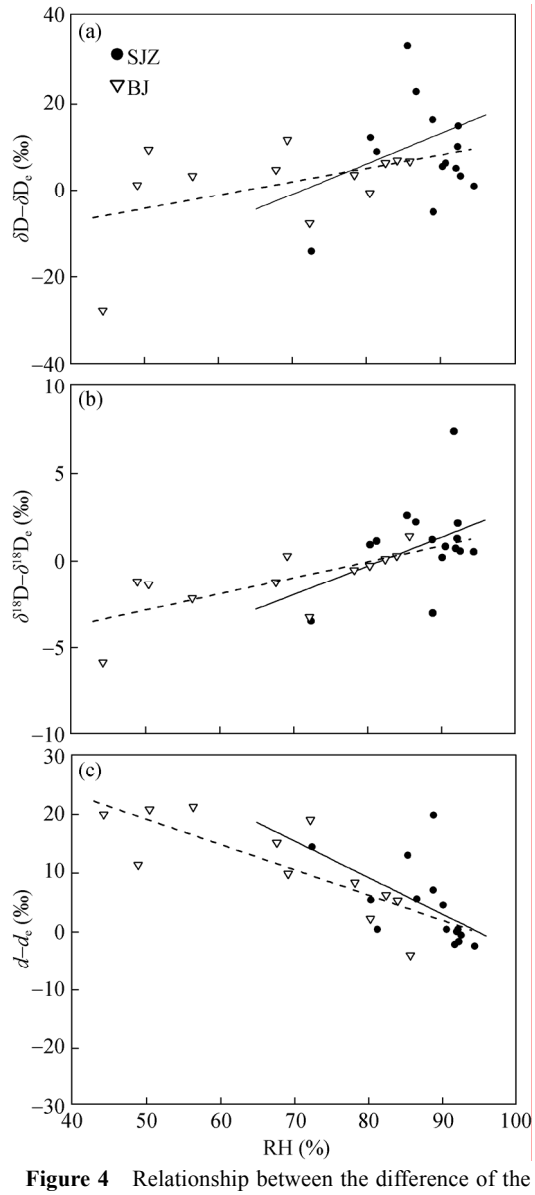

Figure 4 Relationship between the difference of the measured and equilibrium water vapor isotope ratios and relative humidity (RH, %) during precipitation events in Beijing (BJ) and Shijiazhuang (SJZ). The determination coefficient of linear regression for BJ is (a) $R^2=0.20$ (n=12, $p=0.15$), (b) $R^2=0.51$ (n=12, $p<0.01$); (c) $R^2=0.62$ (n=12, $p<0.01$); and for SJZ is (a) $R^2=0.06$ (n=15, $p=0.366$), (b) $R^2=0.16$ (n=15, $p=0.136$); (c) $R^2=0.30$ (n=15, $p=0.035$).

That the vapor δD and δ^{18}O were significantly influenced by precipitation events, and variations of the vapor δD and δ^{18}O on seasonal and diurnal scales outside rainy periods were observed, were strong pieces of experimental evidence supporting the notion that the δD and δ^{18}O of the atmospheric water vapor were controlled by not only precipitation process, but also other atmospheric processes.

The effects of vegetation should play differently important roles in determining the δD and δ^{18}O of atmospheric water vapor in Beijing and Shijiazhuang. There was no vegetation effects on the vapor δD and δ^{18}O in Beijing (Wen *et al*., 2010). Since transpiration always acts to enrich the surface air with ^{18}O and D (Lee *et al*., 2007), admixture of transpired water from winter wheat canopy in Shijiazhuang under clear weather conditions should enrich the vapor δD and δ^{18}O. Consequently, the vapor δD and δ^{18}O exhibited a downward trend during the precipitation events, when a precipitation air mass dominated the surface air.

3.3 Dependence on water vapor mixing ratios

Figure 5 presents a scatter plot of all the hourly vapor isotope composition against atmospheric water vapor mixing ratios (w). It is known that temporal variations of isotopic com-

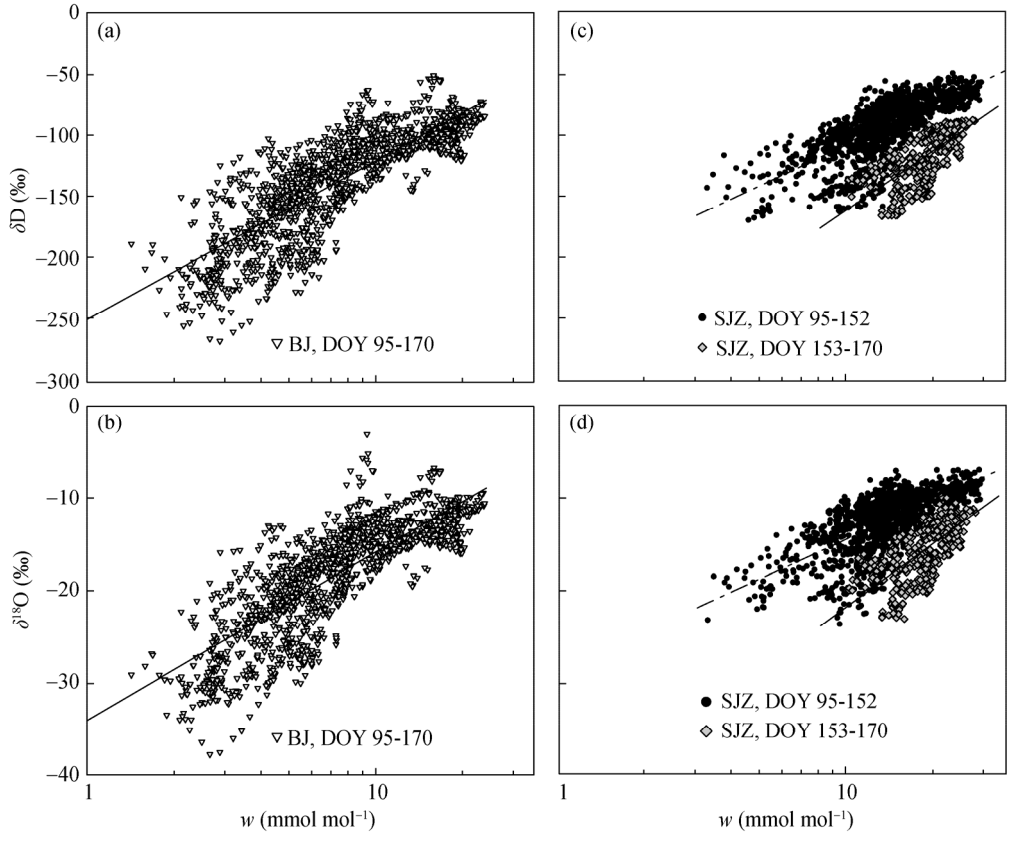

Figure 5 Log-linear plots of the vapor δD and δ^{18}O against the vapor molar mixing ratio(w) in Beijing (BJ) and Shijiazhuang (SJZ). Least-squares regression of the data for BJ is (a) δD= –249.4 +56.2ln$w$, R^2=0.70 (n=1777, p<0.001); (b) δ^{18}O= –34.18+7.95ln$w$, R^2=0.70 (n=1777, p<0.001); and for SJZ is (c) δD= –218.3 +48.0ln$w$, R^2=0.54 (n=1316, p<0.001, DOY 95-152) and δD= –321.1 +69.8ln$w$, R^2=0.50 (n=407, p<0.001, DOY 153-170); (d) δ^{18}O= –28.93+6.24ln$w$, R^2=0.48 (n=1316, p<0.001, DOY 95-152); and δ^{18}O= –44.76 +9.96ln$w$, R^2=0.46 (n=407, p<0.001, DOY 153-170).

position of precipitation are dominated by the temperature effect in mid-high latitudes on seasonal scale (Zhang *et al*., 2004). However, it is suggested that w is a good predictor for variations of δD and δ^{18}O in the vapor phase (Lee *et al*., 2006; Wen *et al*., 2010). In this study, least-squares regressions showed that the δD and δ^{18}O of atmospheric water vapor in Beijing and Shijiazhuang exhibited a significant (p<0.001) log-linear dependence on w, suggesting the dominating effect of Rayleigh distillation accompanying with advection of an air mass. Wen *et al*. (2010) also found that w was not a good predictor for variations of δD and δ^{18}O in the vapor phase during the peak of summer monsoon season. Therefore the robust relationships here would suggest that the surface air in Beijing and Shijiazhuang had not been affected significantly by the summer monsoon activities.

The capability of w in predicting the variability of δD and δ^{18}O of atmospheric water vapor was different for Beijing and Shijiazhuang (Figure 5). In Beijing, the least-squares log-linear equations captured 70% (R^2=0.70, p<0.001) of the observed variations of the hourly δD and δ^{18}O (Figures 5a and 5b), respectively. However, in Shijiazhuang, two distinct groups of data existed (Figures 5c and 5d) with one group in the peak of growth of winter wheat (DOY 95-152) with LAI increasing from 2.3 to 4.5, and the other group in the wither period (DOY 153-170) with LAI decreasing from 2.3 to nearly zero. In the first group, the regression equations captured 54% (R^2=0.54, p<0.001) and 48% (R^2=0.48, p<0.001) of the observed variability in the vapor δD and δ^{18}O, respectively. In the second group, the regression equations captured 50% (R^2=0.50, p<0.001) and 46% (R^2=0.46, p<0.001) of the observed variability in the vapor δD and δ^{18}O, respectively. In fact, the predicting power of w in Shijiazhuang was lower than that in Beijing, implying that other processes would also play important roles in the observed variability of the vapor δD and δ^{18}O in Shijiazhuang.

One might assume that the lower vapor isotopic composition during the withering period should be mainly caused by the decreased contribution of enriched water from the canopy transpiration. On the other hand, we were also aware of the fact that the vapor δD and δ^{18}O in the entire summer maize season (data not shown) approximated to the values in the withering period of winter wheat, instead of returning to high values similar to those in the peak period of winter wheat. The Rayleigh distillation model did not work well for the summer maize season, which might indicate that summer monsoon dominated their activities (Wen *et al*., 2010). Smith *et al*. (2006) have shown that w is not a good predictor of the vapor δD and δ^{18}O if the changes in δD and δ^{18}O of vapor are associated with deep convective activities. During the peak of summer monsoon season, occurrence of deep convection might have acted to dilute the vapor δD and δ^{18}O above the summer maize canopy in the warm season.

3.4 Effects of local ET, dew formation and entrainment

To further understand atmospheric processes that influence the temporal variations of isotope ratios in vapor phase, Figure 6 illustrates the 24-h diurnal ensemble mean values of the vapor δD, δ^{18}O and d for three groups of data: the whole observation period (DOY 95-170) in Beijing, the peak (DOY 95-152) and withering (DOY 153-170) growing period of winter wheat in Shijiazhuang. Small fluctuations for periods less than 24-h and the time-trend associated with weather cycles are smoothed out by the calculation of ensemble averages (Lee *et al*., 2006). For convenience of comparison, the averaged value of each group was removed from the ensemble mean values. In Beijing, the peak-to-peak variations were 14.5‰, 2.37‰

and 6.1‰ for the vapor δD, δ^{18}O and d, respectively. The vapor δD and δ^{18}O exhibited a diurnal pattern, with maximum in the early morning, and minimum in the early afternoon. They decreased gradually from 6:00 to 16:00 and increased steadily from 16:00 to 6:00. The diurnal variation was determined by the interaction between local ET and entrainment at the top of the boundary layer (Lee *et al*., 2006; Wen *et al*., 2010). Through turbulent diffusion, the continuous exchange of vapor between the drier free atmosphere above the boundary layer and the more moist boundary layer can be taken as entrainment (Lee *et al*., 2006). The local ET, especially transpiration, tended to enrich the vapor δD and δ^{18}O, but the entrainment tended to deplete them. In Beijing, the entrainment at the top of the boundary layer dominated the diurnal cycle during the daytime.

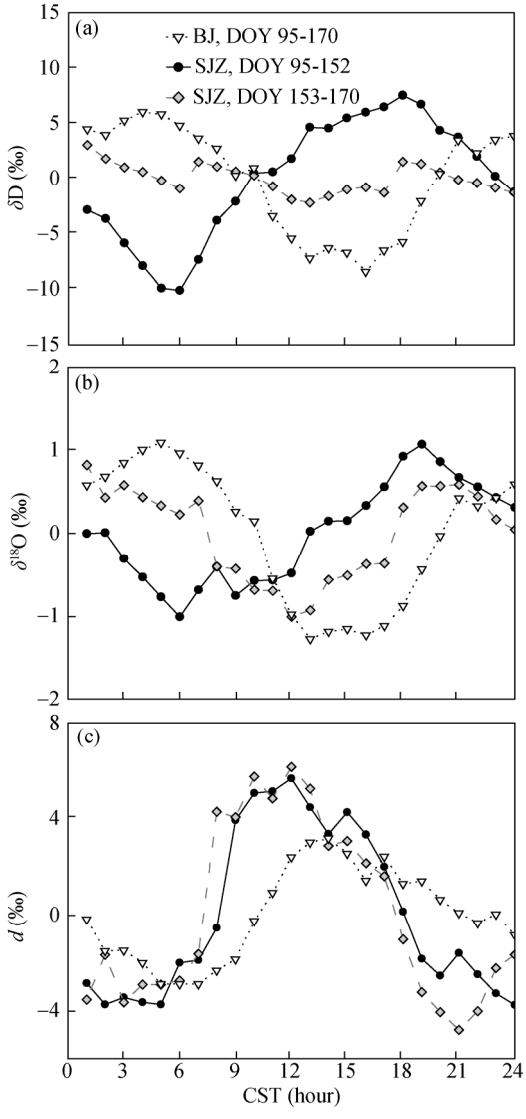

Figure 6 Twenty-four hour ensemble average values of δD, δ^{18}O, d of atmospheric water vapor in Beijing (BJ) and Shijiazhuang (SJZ). CST, Chinese Standard Time.

However, in Shijiazhuang, distinct diurnal patterns were observed between the peak and withering growing periods of winter wheat. During the peak growing period, the peak-to-peak variations were 17.6‰, 2.08‰ and 9.4‰ for the vapor δD, δ^{18}O and d, respectively. The diurnal changes of the vapor δD and δ^{18}O during the peak growing period in Shijiazhuang showed a different pattern compared with that in Beijing: they decreased gradually from 18:00 to 6:00, but increased steadily from 6:00 to 18:00. The maximum δD and δ^{18}O values were obtained during the sunset transition, when the mixed layer usually collapsed but transpiration still acted to enrich the vapor. We postulated that the diurnal cycle was driven by processes such as local ET and entrainment, but the effect of local ET gradually overrode that of entrainment, and dominated the diurnal cycle during the daytime with the intensive transpiration.

During the withering period, however, the diurnal cycle of δD and δ^{18}O in vapor phase showed intermediate patterns between that in Beijing and that during the peak growing period in Shijiazhuang, with minimum values occuring at early afternoon hours. The diurnal amplitudes were 5.2‰, 1.83‰ and 11.0‰ for the vapor δD, δ^{18}O and d, respectively. The diurnal changes of the vapor δD and δ^{18}O were less than those in Beijing and during the

peak growing period in Shijiazhuang. In comparison, Welp *et al*. (2008) observed persistent diurnal patterns of midday depression in the vapor $\delta^{18}O$ over a soybean canopy for the whole growing season.

Figure 6 also shows that there were small peaks in the diurnal cycle of δD, $\delta^{18}O$ and d during the early morning in Shijiazhuang. We postulated that the dew formation should be responsible. Dew formation at night was a frequent event over the observational period in Shijiazhuang. At low air temperatures at night, dew water was formed from air moisture condensed out, leaving the vapor with relatively negative δD and $\delta^{18}O$ values. Consequently the vapor δD and $\delta^{18}O$ reached minimum values just before sunrise, as expected, when the dew formation was most likely to occur. After sunrise, the evaporation of dew water as well as the increasing canopy transpiration should increase the δD and $\delta^{18}O$ values, but the signal was presumably overwhelmed by the opposing effects of atmospheric vertical mixing in the meantime.

Strong diurnal cycles in the vapor d were observed in both Beijing and Shijiazhuang (Figure 6c), indicating that the variations of the vapor δD were not in phase with the vapor $\delta^{18}O$. The maximum d occurred in midday hours and minimum at night. In addition, the diurnal centroid of the vapor d in Shijiazhuang seemed to be several hours earlier than that in Beijing, which might reflect the time difference of the dominant turbulent/diffusion exchange processes of water vapor. It is known that the kinetic fractionation is stronger for the oxygen isotopes than for the hydrogen isotopes (Cappa *et al*., 2003). Lee *et al*. (2009) suggests that it is important to consider the canopy-scale kinetic isotope fractionation effects of $H_2{}^{18}O$ in isotopic gaseous exchange studies, especially for ecosystems with lower canopies. In the current study, we hypothesized that the difference between HDO and $H_2{}^{18}O$ in kinetic fractionation effects associated with turbulent/diffusion transportation of vapor (e.g. ET and entrainment) in surface air might have played a role in the diurnal cycle of the vapor d.

There was also other evidence of vegetation effect on the δD, $\delta^{18}O$ and d of atmospheric water vapor. In Figure 7, we illustrate the ensemble diurnal means of the difference of water vapor mixing ratios measured above the winter wheat (w) and on the observation tower at 30 m height (w_{30}). The vertical gradient of water vapor mixing ratio between the two heights

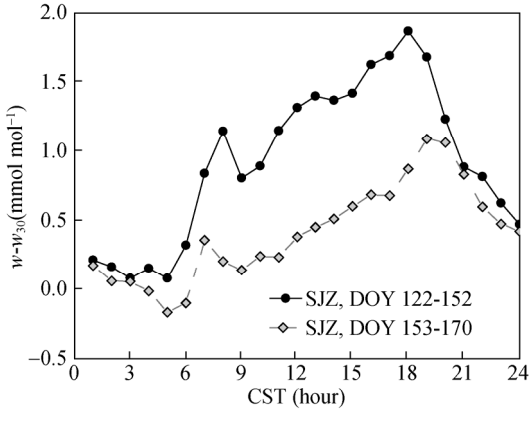

Figure 7 Twenty-four hour ensemble average values of the difference between water vapor mixing ratios above the winter wheat canopy (w) and at the height of 30 m (w_{30}), w–w_{30}, in Shijiazhuang (SJZ). CST, Chinese Standard Time

could be regarded as a representation of the contribution from local ET. There were two obvious peaks in the $w–w_{30}$ gradient with one main peak in the late afternoon, which was indicative of the influence of local ET and a secondary peak in the morning, which was probably caused by the evaporation of dew water. In the peak of growing season, the values of $w–w_{30}$ were in the range of 0.08 to 1.87 mmol mol^{-1}. The value of $w–w_{30}$ was positive for every hour of the day, and was exactly synchronous with the diurnal cycle of the vapor δD (Figure 6a) and especially the vapor δ^{18}O (Figure 6b), supporting our speculation that the transpiration flux, which dominated local ET, might have played an important role in the δD and ^{18}O budgets in the vapor phase. During the withering period, $w–w_{30}$ showed a remarkable decrease, indicating a decreased contribution of local ET from canopy.

4 Conclusions

Using in-situ measurement technique, two nearly continuous time-series of δD and δ^{18}O of atmospheric water vapor were measured at hourly intervals in surface air in Beijing and above a winter wheat canopy in Shijiazhuang. In this study, the influences of atmospheric processes on δD and δ^{18}O in the vapor phase on various time-scales including precipitation events, seasonal scale and diurnal cycles were investigated.

In both Beijing and Shijiazhuang, the δD and δ^{18}O of atmospheric water vapor covaried with those of precipitation. During precipitation events, the δD and δ^{18}O of atmospheric water vapor were in equilibrium state with precipitation (R^2>0.50) at both sites, but the departures of δD and δ^{18}O from the equilibrium state were positively correlated with local relative humidity. Note that the vapor δD and δ^{18}O tended to enrich in Beijing, but deplete in Shijiazhuang during the precipitation events, which should be responsible by the contribution of isotopically heavier transpiration moisture from the winter wheat canopy in Shijiazhuang.

On seasonal time scale, considerable variations of the vapor δD, δ^{18}O and d, sometimes exceeding 100‰, 10‰ and 20‰ respectively, were observed over just a few days at both sites, but the magnitudes of seasonal variations in Shijiazhuang were less than those in Beijing. Water vapor mixing ratio was a good predictor for variations of δD and δ^{18}O in the vapor phase in Beijing and Shijiazhuang, and the log-linear equations captured much (R^2>0.40) of the observed variability of the hourly δD and δ^{18}O, which could be largely explained by the Rayleigh distillation mechanisms, indicating the important role of air mass advection.

On a diurnal time scale, the peak-to-peak variations of vapor δD, δ^{18}O and d were respectively 14.5‰, 2.37‰ and 6.1‰ in Beijing, and, in Shijiazhuang, 17.6‰, 2.08‰ and 9.4‰ for the peak growing period and 5.2‰, 1.83‰ and 11.0‰ for the withering period of winter wheat, respectively. The diurnal patterns in Beijing and Shijiazhuang were determined by the interaction between local ET and entrainment at the top of the boundary layer. In Beijing, the entrainment process dominated the diurnal cycle of the vapor δD and δ^{18}O. During the peak growing period of winter wheat in Shijiazhuang, the local ET, especially transpiration and dew formation played an important role in determining the δD and δ^{18}O. In the withering period of winter wheat, the vapor δD and δ^{18}O showed an intermediate diurnal pattern. The vapor d reached maximum during the midday hours in Beijing and Shijiazhuang, but the diurnal centroid showed several hours earlier in Shijiazhuang than in Beijing.

In summary, we have shown that the δD and δ^{18}O of water vapor in surface air in both

Beijing and Shijiazhuang exhibited considerable variations on varying time-scales including diurnal and seasonal scales and precipitation events. The results revealed that atmospheric processes such as local ET, dew formation and entrainment other than precipitation could play important roles in determining the vapor δD and δ^{18}O. We propose that continuous measurements of δD and δ^{18}O of atmospheric water vapor are useful in understanding the mechanisms underlying the variations of the vapor δD and δ^{18}O and may open new window for hydrological and ecological applications.

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