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Water vapor and precipitation isotope ratios in Beijing, China

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[1] The objective of this study is to investigate the characteristics of δD, δ^{18}O, and deuterium excess (*d*) of precipitation and water vapor in surface air in Beijing, China. The δD, δ^{18}O, and *d* of atmospheric water vapor in surface air were measured continuously with an in situ technique. Much less day-to-day and diurnal variations in the vapor isotopic contents were observed in the summer monsoon season (June–August) than in the rest of the year. Outside the monsoon season, the vapor δD and δ^{18}O showed a log linear dependence on the vapor mixing ratio, and *d* showed a negative correlation with the local relative humidity (RH). Both relationships were statistically significant. The vapor mixing ratio and RH were poor predictors of the vapor isotopic temporal variability during the peak summer monsoon activities. In addition, an analysis was presented of the interaction of the isotopic exchange between the vapor and the condensed phase. The δD and δ^{18}O departure from the equilibrium state was positively correlated with RH, and the *d* departure from the equilibrium state was negatively correlated with RH.

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1. Introduction

[2] Measurements of δD, δ^{18}O, and deuterium excess (*d*) in atmospheric water provide insights into the hydrologic cycle, ecological processes, and paleoclimate [e.g., *Gat*, 1996; *Yakir and Sternberg*, 2000; *Jouzel et al.*, 2000]. These measurements are important tools used to calibrate atmospheric models of the water cycle at the global and regional scales [*Joussaume et al.*, 1984; *Jouzel et al.*, 1994; *Hoffmann and Heimann*, 1997; *Hoffmann et al.*, 1998; *Cuntz et al.*, 2003; *Sturm et al.*, 2005; *Vuille et al.*, 2005; *Angert et al.*, 2008]. To date, there are extensive data on the isotope content of the condensed phases. For example, the spatial and temporal variations of δD and δ^{18}O in precipitation at the global scale are presented from the analysis of the data set from the Global Network of Isotopes in Precipitation (GNIP) [e.g., *Rozanski et al.*, 1993; *Johnson and Ingram*, 2004]. A limited number of long-term observations of δD and δ^{18}O in the vapor phase have been reported [e.g., *Jacob and Sonntag*, 1991; *Angert et al.*, 2008]. They reveal that the vapor phase measurements provide us new information on the mechanisms of the atmospheric transport process of water vapor and the subsequent phase changes in the atmosphere.

[3] Few water isotopic studies exist for China, a country under the influence of the Asian monsoon climate. Most parts of China have a clear division between seasons [e.g., *Huang et al.*, 2003; *Liu et al.*, 2008]. In the winter, the weather is cold and dry because of northerly winds from high-latitude areas. In the summer, it is warm and moist because east and southeast airflow transports moisture from the southern Pacific Ocean and the Indian Ocean. The isotopes in precipitation are strongly affected by these circulation patterns. *Yamanaka et al.* [2004] showed that the isotopic contents in precipitation in the North China Plain are lower in the summer monsoon than in the rest of the year. *Hoffmann and Heimann* [1997] analyzed the water isotope in the Asian monsoon region by implementing a water isotopic component in the hydrological cycle of the atmospheric general circulation model (AGCM) under the boundary conditions of the Last Glacial Maximum. *Johnson and Ingram* [2004] investigated the links between δ^{18}O in precipitation and meteorological and geographic factors based on 10 GNIP sites in China. They found that at any given site, the links are closely related to the strength of the summer monsoon activity. *Vuille et al.* [2005] investigated δ^{18}O in precipitation using the AGCM that is validated with the GNIP δ^{18}O data and reanalysis data. *Liu et al.* [2008] reported the precipitation δ^{18}O pattern over the entire country of China based on a data set collected at 55 sites. In the only study on δ^{18}O of atmospheric water vapor that we are aware of, *Yu et al.* [2005] reported a 3 month observation of δ^{18}O of atmospheric water vapor on the Tibetan Plateau. They found that the transport of moisture by the southwest monsoon causes a reduction in the vapor δ^{18}O.

[4] In this paper, we investigate the meteorological mechanisms that influence δD, δ^{18}O, and *d* of precipitation and water vapor in surface air in Beijing, China, under the influence of the Asian monsoon climate. We want to characterize the temporal variations in δD, δ^{18}O, and *d* of atmospheric water vapor on seasonal, diurnal, and rain shower time scales and discuss the mechanisms that contribute to these variations. The vapor data were obtained at

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hourly intervals using an in situ measurement technique from December 2006 to December 2007 [*Wen et al.*, 2008]. Such continuous measurement of the isotopic composition of atmospheric water vapor provides an improved understanding of the mechanisms of evaporation and transpiration at the surface of the Earth and the subsequent transport and phase changes in the atmosphere [e.g., *Gat*, 1996, 2000]. The full data set is available at http://pantheon.yale.edu/~xhlee/data.htm.

[5] One focus of our study is the temporal variations of d of atmospheric water vapor. Quantification of both δD and δ^{18}O of atmospheric water vapor can provide insights into the atmospheric water cycle that would otherwise be difficult by studying either δD or δ^{18}O separately [*Dansgaard*, 1964; *Merlivat and Jouzel*, 1979]. Here d is a measure of the deviation of a given data point from the global meteoric water line (GMWL) with a slope of 8 going through Vienna SMOW. The GMWL defines the isotopic relationship of continental precipitation that has not experienced evaporation [*Gat*, 1996]. The d of precipitation provides information on the climatic conditions at distant evaporative sources but can be modified by the vapor evaporated in continental basins [*Merlivat and Jouzel*, 1979; *Araguás-Araguás et al.*, 2000]. Values of d lower than 10‰ may be indicative of secondary evaporation processes, and values of d higher than 10‰ are found in the vapor generated under low relative humidity (RH) conditions in the source region [*Merlivat and Jouzel*, 1979]. Direct measurement of d in the vapor phase may also offer constraints on how to separate local evaporative contribution to the atmospheric water vapor from lateral transport [*Gat*, 1996; *Araguás-Araguás et al.*, 2000], and on the interaction of different air masses [*Araguás-Araguás et al.*, 2000]. In an 8 year study, *Jacob and Sonntag* [1991] found that the mean value of the d of atmospheric water vapor is significantly higher than that of precipitation. *Angert et al.* [2008] showed that the d observation offers additional information when the variations in δD and δ^{18}O are not linearly correlated. To our best knowledge, our study appears to be the first to analyze d of atmospheric water vapor at hourly temporal resolution.

[6] Our detailed, point measurement contributes to a small but growing literature on the temporal dynamics of the vapor isotopic content in the atmosphere [e.g., *Jacob and Sonntag*, 1991; *Lee et al.*, 2006; *Welp et al.*, 2008a; *Angert et al.*, 2008; *Wang et al.*, 2009]. It also complements the studies of *Yamanaka et al.* [2004] and others [*Yu et al.*, 2005; *Liu et al.*, 2008] on the spatial variations of the precipitation isotopic content in the region of the Asian monsoon climate. The simultaneous measurement of the condensed and vapor phases reveals how the two phases interact isotopically near the ground. That the measurement was made at a high temporal resolution allows us to examine how local factors influence δD, δ^{18}O, and d of precipitation and water vapor in surface air.

2. Experimental Method

[7] The measurement of δD and δ^{18}O of atmospheric water vapor in surface air was made in Beijing (40°00′N, 116°23′E, elevation 45 m above mean sea level), China, with a tunable diode laser (TDL) trace gas analyzer (model TGA100A, Campbell Scientific Inc., Logan, Utah), from December 2006 to December 2007. The schematic diagram of the analyzer, its principle of operation, and its calibration procedure were described in detail by *Wen et al.* [2008]. In brief, ambient air was drawn through one sample intake from the outside of our laboratory in Beijing, at ~10 m above the ground, into the TDL analyzer. Gain calibration was made in situ with a dripper that consisted of a syringe pump and an evaporating flask. The TDL zero was checked against a dry airstream made from a dry air generator (model MDH1-FLE, Twin Tower Engineering, Broomfield, Colorado) and further scrubbed by a molecular sieve (model RGF-250-200, Labclear Inc., Oakland, California). The TDL signals were recorded at 1 Hz by a data logger (model CR1000, Campbell Scientific Inc.) and block averaged over 25 s intervals for analysis and archiving. The data reported in this study were block averaged to hourly intervals. Our laboratory tests showed that the 1 h precision (one standard deviation) of δD and δ^{18}O was 1.1‰ and 0.07‰ at dewpoint temperature 15°C and 2.0‰ and 0.12‰ at dewpoint temperature 1°C, respectively.

[8] Auxiliary data (air temperature, relative humidity, precipitation time, and amount) were obtained with a Davis weather station (model Vantage Pro, Davis Instruments Inc., Hayard, California) mounted on the rooftop of our laboratory building, at ~20 m above the ground. Precipitation water was also collected at the rooftop. All precipitation samples were analyzed for their isotope ratios by pyrolysis with a continuous flow method on a mass spectrometer (MAT 253, Thermo Fisher Scientific, Inc., Waltham, Massachusetts). The precision of the analysis was better than 2‰ for δD and 0.3‰ for δ^{18}O.

[9] The reader should be aware of two potential measurement artifacts. First, the length of the TDL sampling tube was kept short to minimize water absorption on the tube wall. This resulted in a 10 m difference between the heights of the TDL intake and the auxiliary observations. Such a difference should be inconsequential in the daytime but could cause a slight error in the nighttime when air was stably stratified. Second, the measurement took place in an urban environment. The extent of anthropogenic influence on the vapor isotopic signal is not known, although that local precipitation water was the source of the municipal use implies that the anthropogenic signal may be indistinguishable from the natural evapotranspiration process.

[10] The conventional delta notation is used to report the isotopic data,

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

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 of atmospheric water vapor and precipitation is defined as [*Dansgaard*, 1964; *Merlivat and Jouzel*, 1979]

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

[11] We used the equilibrium theory to understand the relationship of the isotopic ratios between precipitation and

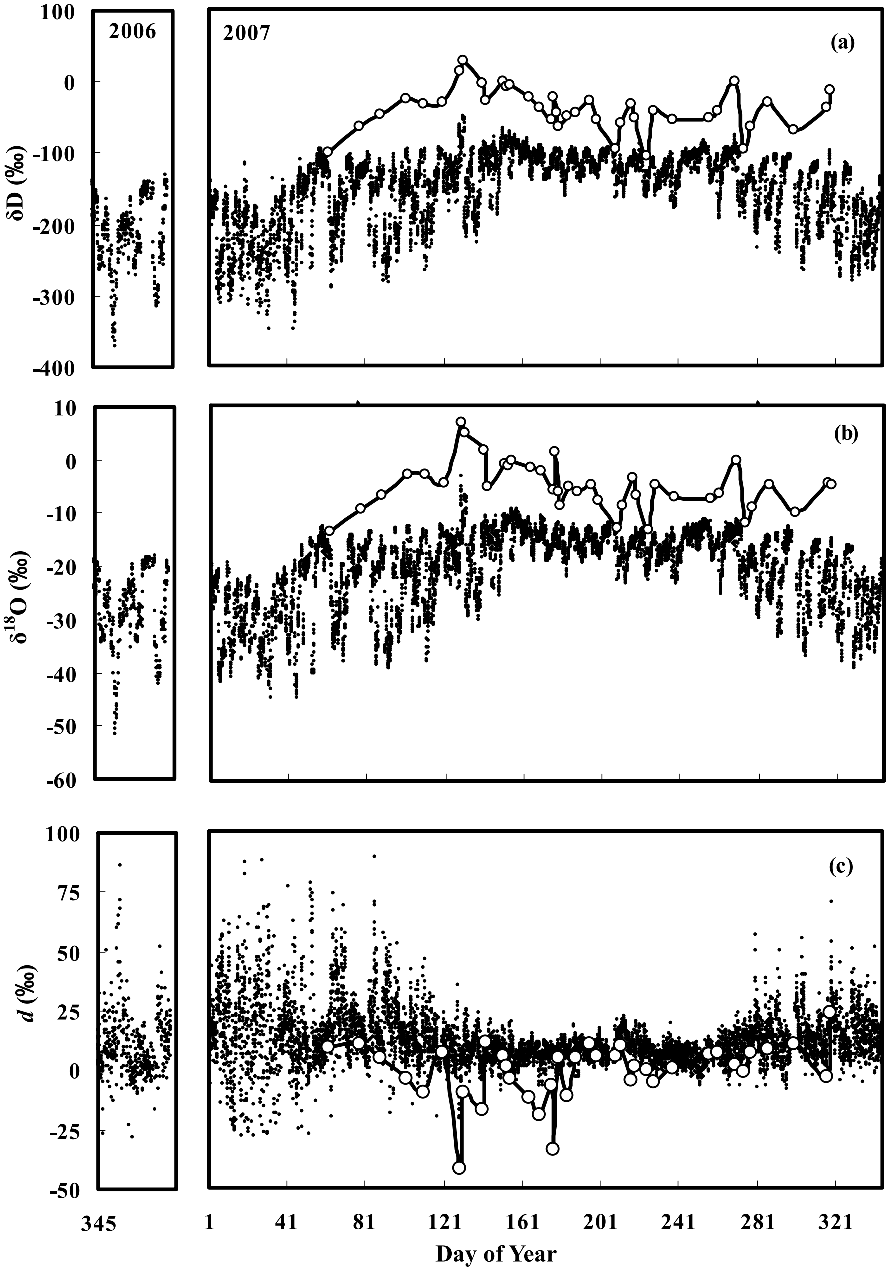

Figure 1. Hourly values of (a) δD, (b) δ^{18}O, and (c) deuterium excess (d) of atmospheric water vapor (dots) and precipitation (circles) from December 2006 to December 2007 in Beijing, China.

water vapor. In saturated air, thermodynamic equilibrium is expected as

$$R_v = \frac{R_l}{\alpha}, \tag{3}$$

where R_v is the water vapor isotope ratio of D/H or ^{18}O/^{16}O, R_l is the isotope ratio in precipitation, and α is a temperature-dependent equilibrium fractionation factor. In the case of precipitation events, the equilibrium δD and δ^{18}O values were evaluated from the isotope ratio of the rainwater collected over the full event and the surface temperature averaged during the event. They were then compared with the event-based mean δD and δ^{18}O of atmospheric water vapor, computed from the hourly observations, and weighted by the hourly precipitation amount. In the case of monthly statistics, the equilibrium values were computed from the monthly mean precipitation isotope ratio and monthly surface temperature.

3. Results and Discussion

3.1. Temporal Patterns

3.1.1. Seasonal Variations

[12] Figure 1 presents the time series of the hourly observations of δD, δ^{18}O, and d of atmospheric water vapor and event-based precipitation data. Table 1 summarizes monthly mean values of precipitation and water vapor δD, δ^{18}O, and d and standard deviation of vapor values. There was considerably less variability in the vapor δD, δ^{18}O, and

Table 1. Summary of Monthly Mean Values of Data Used in This Study[a]

					Vapor									Precipitation (‰)			Vapor in Equilibrium (‰)		
					δD (‰)		δ^{18}O (‰)		d (‰)										
Date	w (mmol mol^{-1})	T (°C)	RH (%)	P (mm)	Mean	SD	Mean	SD	Mean	SD	r_w, D	r_w, ^{18}O	r_{RH}, d	δD	δ^{18}O	d	δD	δ^{18}O	d
Dec 2006	2.3	−1.0	45.2	-	−212	44	−27.9	6.3	11.8	12.2	0.81	0.80	−0.35	-	-	-	-	-	-
Jan 2007	1.3	−2.0	41.1	-	−224	45	−30.4	5.8	18.8	19.9	0.76	0.81	−0.19	-	-	-	-	-	-
Feb 2007	3.0	3.6	40.5	-	−181	55	−24.3	7.7	13.8	15.5	0.83	0.83	−0.42	-	-	-	-	-	-
Mar 2007	4.6	6.1	49.5	31.4	−159	42	−22.3	6.4	19.6	13.5	0.77	0.81	−0.59	−94	−12.8	8.6	−183	−24.0	9.3
Apr 2007	5.3	14.7	32.4	7.0	−171	44	−23.3	6.6	15.3	11.1	0.78	0.78	−0.54	−29	−3.7	0.6	−112	−14.0	−0.2
May 2007	8.5	22.5	34.4	42.7	−129	37	−17.1	5.1	7.4	6.6	0.70	0.68	−0.34	−26	−4.4	9.4	−104	−14.2	9.8
Jun 2007	17.8	26.1	54.4	26.3	−106	16	−14.0	2.3	5.7	4.1	0.14	0.20	−0.34	−58	−7.6	2.4	−129	−16.9	6.5
Jul 2007	23.5	26.5	68.9	69.8	−118	15	−15.8	2.1	8.1	3.9	−0.22	−0.15	−0.15	−63	−9.0	8.6	−132	−18.2	13.4
Aug 2007	21.7	26.6	63.1	56.1	−129	19	−17.1	2.4	7.8	4.6	0.29	0.29	−0.09	−58	−7.3	1.0	−128	−16.6	5.2
Sep 2007	15.4	22.1	59.8	42.5	−115	22	−15.2	3.0	6.5	4.5	0.41	0.46	−0.35	−44	−6.4	6.6	−121	−16.1	8.3
Oct 2007	8.5	13.5	53.3	56.9	−154	36	−20.9	5.3	13.6	9.2	0.62	0.62	−0.49	−70	−9.7	7.3	−148	−19.8	9.8
Nov 2007	4.2	4.6	46.6	2.0	−175	45	−23.7	6.3	15.0	9.5	0.86	0.88	−0.52	−17	−4.6	19.8	−111	−15.7	14.7

[a] Parameters are as follows: water vapor mixing ratio (w); surface air temperature (T); relative humidity (RH); total precipitation (P); isotope ratios of atmospheric water vapor, precipitation, and the vapor in equilibrium with precipitation (δD, δ^{18}O, and d); standard deviation of δD, δ^{18}O, and d; linear correlation coefficients of the vapor δD and δ ^{18}O with w (r_w, D and r_w, ^{18}O); and the correlation of the vapor d with RH (r_{RH}, d). The monthly δD, δ^{18}O, and d in precipitation were computed as the precipitation weighted mean values.

d in the summer season (June–August) than in the rest of the year. In the cold season, the day-to-day variations could exceed 200‰, 25‰, and 50‰ for δD, δ^{18}O, and d, respectively. In the summer, the variations were usually less than 100‰, 10‰, and 25‰ for δD, δ^{18}O, and d, respectively. The months of June–August mark the peak activity of the monsoon in eastern China [*Wang and Gaffen*, 2001]. In comparison, in the humid continental climate in New England, where precipitation is evenly distributed throughout the year, equal day-to-day variability is seen in both the cold and warm seasons [*Lee et al.*, 2006].

[13] The seasonal variations of δD and δ^{18}O in precipitation were positively correlated with the vapor values. The event-based d of precipitation was highly variable, ranging from −42‰ to 24‰, and reached its lowest value on day of year (DOY) 128–129 (8–9 May). On these days, the δ^{18}O in precipitation reached its highest value. The δD in precipitation reached its highest value on DOY 131 and decreased slowly through the summer season, a pattern similar to the results of *Yamanaka et al.* [2004] for the North China Plain.

[14] The hourly maximum and minimum were approximately −51‰ and −370‰ for the vapor δD and −3‰ and −52‰ for the vapor δ^{18}O. In comparison, the observed maximum and minimum hourly δ^{18}O values of atmospheric water vapor in New Haven, Connecticut, are approximately −10‰ and −38‰, respectively [*Lee et al.*, 2006]. The hourly d of atmospheric vapor generally fluctuated between −40‰ and 89‰, mostly in the winter months. The maximum vapor δD and δ^{18}O occurred on DOY 131 and DOY 128, respectively. These maximum values were in approximate equilibrium with precipitation water. On DOY 128–129, a short rain shower produced 0.5 mm rain with the highest δ^{18}O of 6.9‰ of the year. On DOY 131, a short rain shower produced 1.8 mm rain with the highest δD of 28‰ of the year. Positive δD and δ^{18}O values in precipitation have also been reported by a number of studies in China and tend to occur in small rain showers [e.g., *Yamanaka et al.*, 2004; *Yu et al.*, 2006; *Liu et al.*, 2007; *Tian et al.*, 2008]. They are likely caused by the evaporation from falling raindrops under the cloud.

[15] According to Table 1, in general, δD and δ^{18}O of atmospheric water vapor were higher in the warm season than in the cold season. The highest monthly mean values of the vapor δD (−106‰) and δ^{18}O (−14.0‰) occurred in June 2007, and the lowest values (−224‰ and −30.4‰) occurred in January 2007. In comparison, the highest monthly mean value of the vapor δ^{18}O in southern New England occurs in May (−15.1%), and the lowest value occurs in January (−29.4‰) [*Lee et al.*, 2006]. The seasonal course of the monthly mean vapor d was not in phase with those of δD and δ^{18}O. The highest monthly mean value (19.6‰) occurred in March 2007, and the lowest value (5.7‰) occurred in June 2007.

[16] The annual mean values of the vapor δD, δ^{18}O, and d were −154‰, −20.7‰, and 11.8‰, respectively. Our δD and δ^{18}O values were lower than the 7 year average of −140‰ and −18.9‰ reported for Heidelberg, Germany [*Jacob and Sonntag*, 1991]. Our d value was almost identical to the 7 year average of 11.5‰ of the same data set. Our δ^{18}O value was similar to the annual mean of −20.8‰ for New Haven [*Lee et al.*, 2006]. Weighted by precipitation amount, the annual mean values of δD, δ^{18}O, and d in precipitation were −58‰, −8.0‰, and 6.2‰, respectively. Our annual δ^{18}O value in precipitation was higher than another annual mean of −8.8‰ in Beijing, China, in 1979–1980 [*Wei and Lin*, 1994] and was in the range of −20.4‰ to −5.4‰ over the entire country of China based on a 55-site data set [*Liu et al.*, 2008]. That the d in precipitation was significantly lower than the vapor d may be indicative of partial evaporation of raindrops beneath the cloud base level, which decreases the d in precipitation and increases the vapor d [*Jacob and Sonntag*, 1991].

3.1.2. Diurnal Variations

[17] Figure 2 shows the 24 h ensemble average values of the vapor δD, δ^{18}O, and d. In Figure 2, the full data set was broken into the winter (December–February), spring (March–May), summer (June–August), and autumn (September–November) seasons. The peak-to-peak variation of the vapor δD was 23‰, 14‰, 4‰, and 16‰ in the winter, spring, summer, and autumn seasons, respectively. The peak-to-peak variation of the vapor δ^{18}O was 3.4‰,

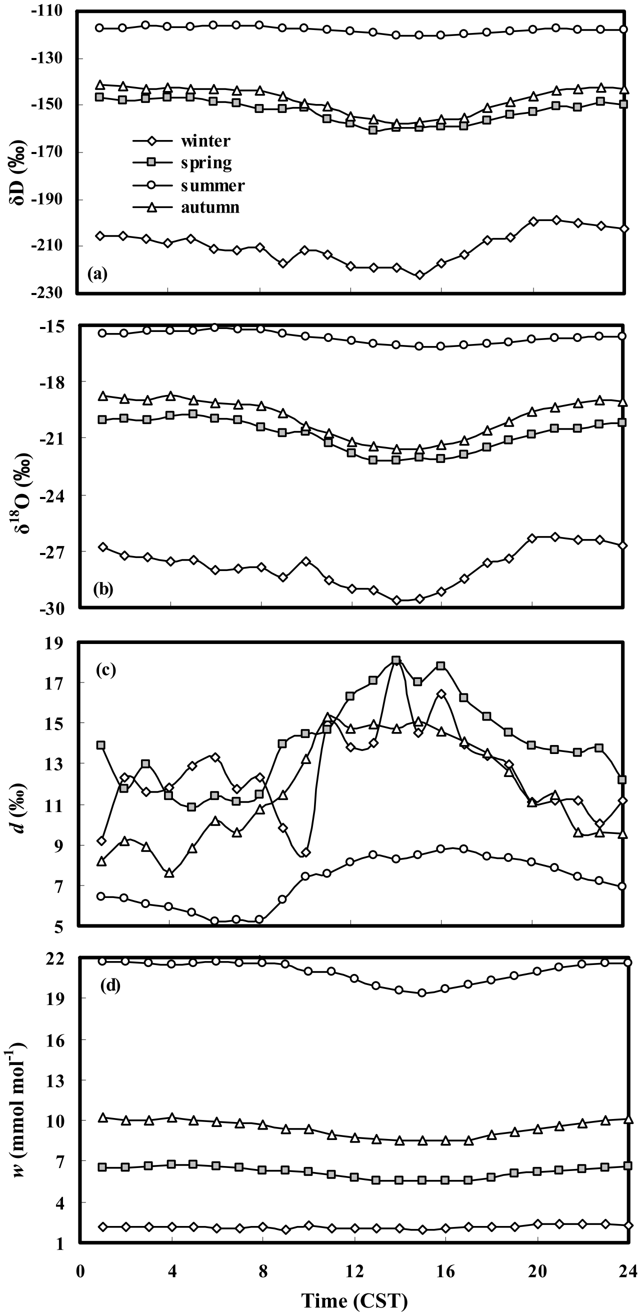

Figure 2. Twenty-four hour ensemble average values of (a) δD, (b) δ^{18}O, (c) d, and (d) water vapor mixing ratio (w) of atmospheric water vapor for winter (December–February; diamonds), spring (March–May; squares), summer (June–August; circles), and autumn (September–November; triangles).

2.5‰, 1.0‰, and 2.8‰, respectively. The minimum δD and δ^{18}O occurred in the early afternoon hours (1200 to 1600 CST), and the maximum δD and δ^{18}O occurred around midnight. These diurnal variations seemed to be in phase with the variations in the vapor mixing ratio. *Welp et al.* [2008a] suggested that lower δ^{18}O values in midday than at midnight may be related to the entrainment of the lighter vapor from the free atmosphere into the convective boundary layer. In the present study, the small diurnal amplitude in the summer may indicate a weak entrainment flux at the top of the boundary layer in the peak monsoon season.

[18] To our best knowledge, Figure 2c represents the first data showing the diurnal change in the vapor d. Its peak-to-peak variation was 9.4‰, 7.3‰, 3.5‰, and 7.7‰ in the winter, spring, summer, and autumn seasons, respectively. The diurnal pattern of d was in opposite phase with those of the vapor δD and δ^{18}O. The mixing of air between the free atmosphere and the boundary layer may have played a role in the diurnal variations in d, although to date, no researcher has made comparative measurement of the vapor d in these two air layers.

3.2. Statistical Relationships

3.2.1. Relationship Between Water Vapor and Precipitation Isotope Ratios

[19] Figure 3 presents a scatterplot of the monthly vapor isotope composition against the values the vapor would have were it in the state of equilibrium with the precipitation water. In comparison, several published monthly data sets are also shown. In this study, the monthly vapor δD and δ^{18}O were in reasonable agreement with the equilibrium prediction, with two exceptions (Figures 3a and 3b). Similarly good agreement was also reported by *Jacob and Sonntag* [1991], *Lee et al.* [2006], and *Welp et al.* [2008a]. With the exclusion of the two outliers, the relationship was quite robust for δ^{18}O (R^2 = 0.56, p < 0.001) and δD (R^2 = 0.50, p < 0.001). *Jacob and Sonntag* [1991] showed that it is possible to derive the isotope composition of atmospheric water vapor based on that of the monthly precipitation. Our data are broadly consistent with their work but also raise two important issues. First, this relationship was not applicable in the cold months when no precipitation was recorded. Second, in months with low precipitation, the relationship could largely be in error. The two outliers in Figure 3 occurred in April and November when less than 10 mm of precipitation was recorded, with the equilibrium value biased high by 8‰ for δ^{18}O and 59‰ for δD. We postulate that in arid and semiarid climates, the equilibrium method cannot accurately predict the isotope composition of the vapor near the ground.

[20] During the experimental period, no obvious relationship was observed on the monthly vapor d and the equilibrium d values, consistent with the data reported by *Jacob and Sonntag* [1991] (Figure 3c). The equilibrium d was computed as $d_e = \delta D_e - 8\delta^{18}O_e$, where δD_e and $\delta^{18}O_e$ are the vapor isotope composition in the state of equilibrium with precipitation.

[21] Figure 4 presents a comparison of the vapor isotopic measurement with the equilibrium prediction during precipitation events. Each data point represents one precipitation event. The relationship was more robust for δD (R^2 = 0.88, p < 0.001) than δ^{18}O (R^2 = 0.82, p < 0.001) when the linear regression was considered and the intercept was forced to zero. In both cases, the equilibrium prediction was more accurate than the results at the monthly scale (Figures 3a and 3b). As for d, a statistically significant relationship was also observed on the event-based values (R^2 = 0.31, p < 0.001), although the equilibrium value was systematically biased low.

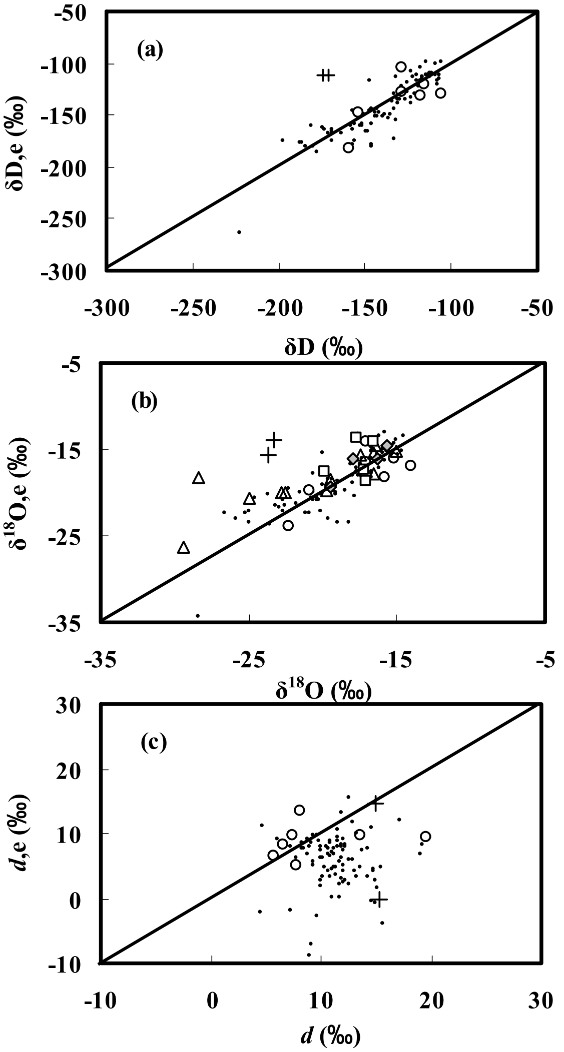

Figure 3. A comparison of the monthly vapor isotopic contents with the values in equilibrium with monthly precipitation at local temperature. The data in this study are given by circles except for the months of April and November, which are marked by crosses. Also shown are monthly data found in the published literature (dots, Heidelberg, *Jacob and Sonntag* [1991]; triangles, New Haven, *Lee et al.* [2006]; squares, Great Mountain, *Lee et al.* [2006]; diamonds, Minnesota, *Welp et al.* [2008a]).

[22] To further understand the scatters in Figure 4, in Figure 5 we illustrate the dependence of the difference between the observed and predicted δD, δ^{18}O, and d on the local RH during the precipitation event. The residuals should vanish in the saturation condition at least for a prolonged rain event because of the equilibrium state. If RH is less than 100%, the kinetic fractionation effects should cause the vapor isotopic ratio to be lower than the equilibrium ratio, and the difference should increase with decreasing RH. This expectation is confirmed by our observations. Similar dependence is also seen in the data obtained in the midwestern United States (Figure 5b) [*Welp et al.*, 2008a]. That the kinetic fractionation is stronger for the oxygen isotopes than for the hydrogen isotopes may explain why the relationship of the linear regression in Figure 5 was more robust for δ^{18}O (R^2 = 0.44, $p < 0.001$) than δD (R^2 = 0.18, $p < 0.001$) and why there is more scatter in the 1:1 plot for δ^{18}O than for δD (Figure 4).

[23] The d departure from the equilibrium state was negatively correlated with RH (Figure 5c). The correlation was statistically significant (R^2 = 0.49, $p < 0.001$). Figure 5c is strong experimental evidence supporting the notion that low RH should increase the vapor phase d. This relationship is consistent with the fact that kinetic fractionation affects the vapor-liquid phase interactions more for δ^{18}O than for δD. *Merlivat* [1978] showed that the kinetic effect is ~50% stronger on δ^{18}O than on δD. As RH decreases, the vapor δ^{18}O should depart more from the equilibrium value than the vapor δD. The net result is that d should be higher than its equilibrium vapor according to the definition of d.

[24] Figure 6 is a scatterplot of the hourly vapor δD against δ^{18}O in all weather conditions, together with the event-by-event precipitation data. The GMWL is given by δD = 8δ^{18}O + 10. Most of the precipitation data points fell below this line, indicating that the precipitation d in Beijing was generally less than 10‰. The vapor data points

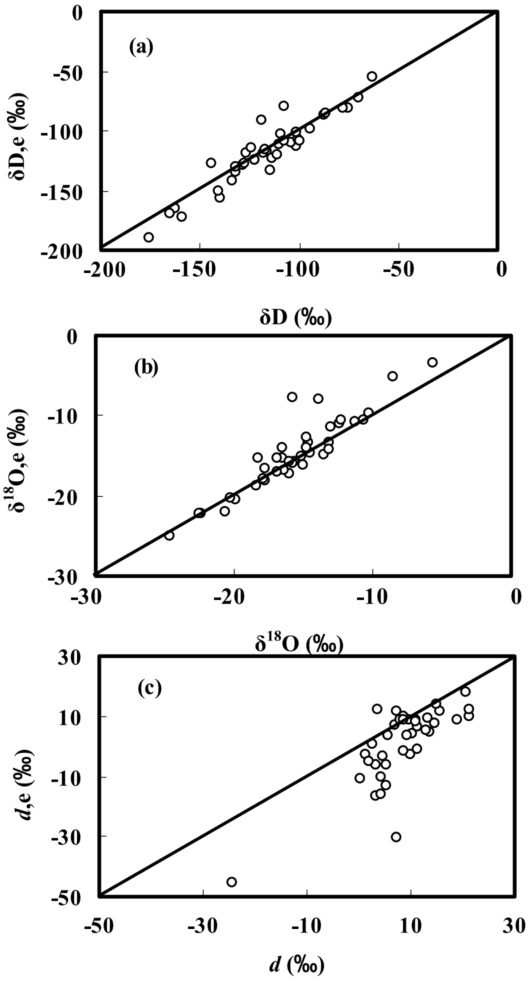

Figure 4. A comparison of the measured water vapor isotope ratios δD, δ^{18}O, and d and the isotope ratios of water vapor in equilibrium with the precipitation (a) δD_e, (b) $\delta^{18}O_e$, and (c) d_e during precipitation events.

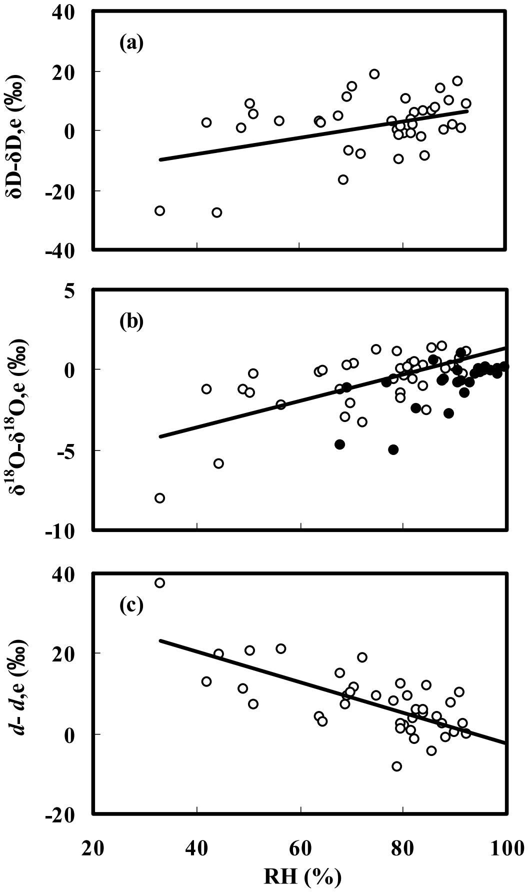

Figure 5. Relationship between the difference of the measured and equilibrium water vapor isotope ratios and relative humidity (RH, %) during precipitation events. The determination coefficient of line regression is (a) R^2 = 0.18, (b) R^2 = 0.44, and (c) R^2 = 0.49. The data reported by *Welp et al.* [2008a] are shown for comparison (solid circles in Figure 5b).

generally fell below the GMWL (indicating $d < 10‰$) in the warm season when δ^{18}O was greater than −17‰ and stayed above the line ($d > 10‰$) in the cold season (Table 1). The regression fit to the vapor data yields an equation with a slope of 7.0 ($\delta D = 7.0\delta^{18}O + 8.1$, $R^2 = 0.97$, $p < 0.001$; number of observations is 8128). In other words, the vapor phase of atmospheric water did not follow the GMWL. *He and Smith* [1999] reported that the vapor phase isotope ratios have a slope less than 8 in the convective boundary layer. In comparison, the two equilibrium lines for vapor are given by $\delta D = 7.3\delta^{18}O - 7.2$ and $\delta D = 7.4\delta^{18}O + 0.6$ for temperatures of 1°C and 15°C, respectively. These equilibrium lines define the δD-δ^{18}O relationship that the vapor would have if it was in full equilibrium with the rainwater that follows exactly the GMWL. They provide a slightly better match with the observations than the standard GMWL.

3.2.2. Dependence on Weather Variables

[25] In the past, researchers have linked the temporal variations in the vapor isotopic ratios to air temperature and atmospheric humidity [e.g., *Jacob and Sonntag*, 1991; *Yu et al.*, 2005; *Lee et al.*, 2006]. *Jacob and Sonntag* [1991] showed that the monthly mean δD and δ^{18}O are linearly correlated with the monthly mean temperature, with linear correlation coefficients of 0.87 and 0.88, respectively. *Lee et al.* [2006] found that on time scales shorter than a few weeks, atmospheric humidity is a better predictor for the δ^{18}O variations than air temperature. In a related study, *Lawrence and Gedzelman* [2003] found a poor correlation between vapor mixing ratio and δ^{18}O values in the tropical region. In the present study, the coefficients of linear correlation with air temperature for the hourly observations varied from month to month in the range of −0.30 to 0.24 and −0.33 to 0.19 for δD and δ^{18}O, respectively. The coefficients of correlation with water vapor mixing ratio varied from −0.22 to 0.86 and −0.15 to 0.88 for δD and δ^{18}O, respectively, with a stronger correlation found in the cold seasons and a much weaker correlation found in the summer (Table 1).

[26] Figure 7 shows the dependence of the δD and δ^{18}O of atmospheric water vapor against the water vapor molar mixing ratio over the full year of observation. There are two distinct groups of data. In the first group for DOY 345–170, 269–272, and 280–344, the correlations of the water vapor molar mixing ratio with δD and δ^{18}O were log linear. The least squares regression equations captured 78% and 79% (R^2 = 0.78 and R^2 = 0.79, $p < 0.001$) of the observed variations in the vapor δD and δ^{18}O, respectively. The log linear dependence on the water vapor mixing ratio can be partially explained by the principle of Rayleigh distillation for air mass advection [*Lee et al.*, 2006; *Welp et al.*, 2008a]. In the second group, for DOY 171–269 and 272–280 during the summer monsoon, the mixing ratio was a poor predictor of the water vapor isotopes, consistent with the correlation data in Table 1. It appears that in the monsoon season, Rayleigh distillation was not the main mechanism explaining the temporal variations in the vapor isotope ratios.

[27] Figure 8 shows the dependence of the hourly values of *d* of atmospheric water vapor on the local relative humidity over the full year of observations. In principle, *d* of precipitation is mainly controlled by the relative humidity

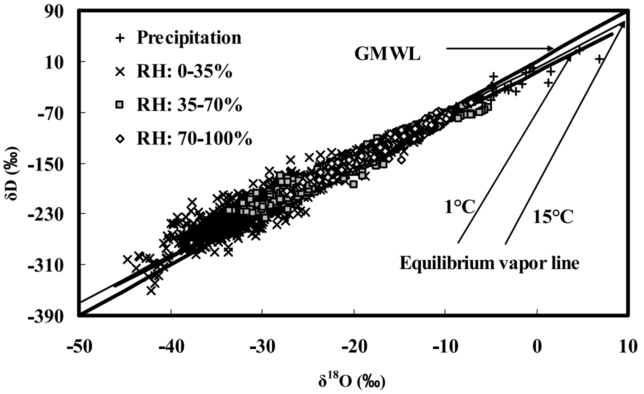

Figure 6. Relationship between the measured δD and δ^{18}O of ambient water vapor (crosses, squares, and diamonds) and precipitation (pluses). For comparison, also shown are the standard GMWL and the equilibrium water vapor lines for vapor at 1°C and 15°C.

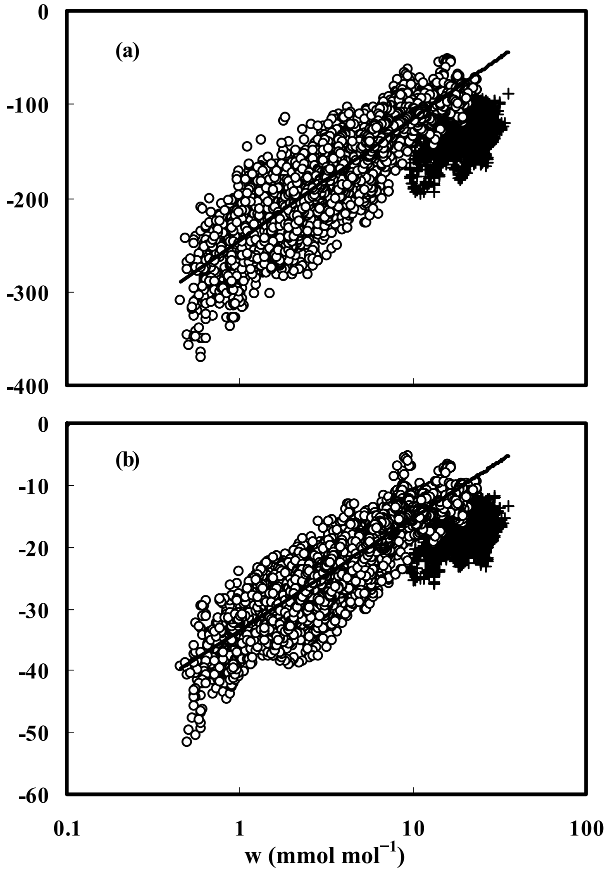

Figure 7. Log linear plots of the vapor (a) δD and (b) δ^{18}O against the vapor molar mixing ratio (w). Open circles, days of year 345–170, 269–272, and 280–344; crosses, days of year 171–269 and 272–280. The least squares regression of the data marked by the open circles is given by the solid line (δD = 56.4 ln(w) − 245.1, R^2 = 0.78; δ^{18}O = 7.91 ln(w) − 33.52, R^2 = 0.79).

at distant evaporative sources but can be modified by vapor evaporated in continental basins [*Merlivat and Jouzel*, 1979; *Araguás-Araguás et al.*, 2000]. Figure 8 shows that d in the vapor phase was negatively correlated with the local relative humidity. Part of the negative correlation was linked to the diurnal pattern in d, where d was higher in daylight hours when humidity was lower than at night (Figure 2c). The very large values (d > 20‰) seen in Figure 8 mostly occurred in the cold season when relative humidity was low (Table 1). Using the monthly data, d was negatively correlated with RH, with a linear correlation coefficient of −0.47. However, the negative relationship was not statistically significant. The RH dependence in Figure 8 that includes all the data from the entire experiment can be described by a modified Misterlich equation (Figure 8). This regression equation captured 23% (R^2 = 0.23, $p < 0.001$) of the observed variation at the hourly intervals. When the local relative humidity approached 100%, the limit of the d equaled 6.4‰. In other words, the d value of the vapor in saturated air was 1.6‰ lower than the standard precipitation d value of 8‰. In comparison, the annual precipitation-weighted mean d value that the vapor would have in equilibrium with the local precipitation was 9.1‰ (Table 1). In section 3.1.1, we suggested that during rain events, reevaporation of the falling raindrops should result in a negative correlation between d and RH (Figure 5c). That the negative correlation existed in fair weather indicates that other unknown local processes may have changed the vapor δD and δ^{18}O values differently.

[28] The predicting power of the modified Misterlich equation was different for the two subgroups of data as Figures 8a and 8b. It was able to explain 19% of the observation variation for DOY 345–170, 269–272, and 280–344 but captured little (R^2 = 0.03) of the variation for DOY 171–269 and 272–280 during the summer monsoon. In other words, RH was not a good predictor of d during the peak monsoon activities.

[29] The negative correlation between d and local RH seems to be a common phenomenon in midlatitudes. For example, we also observed a negative correlation of d and local RH in a crop field 200 km outside Beijing, from 1 April to 13 September 2008 (X. Wen et al., unpublished data, 2008). In a parallel experiment at a coastal site in Connecticut, *Welp et al.* [2008b] found that midday vapor d is negatively corrected with midday RH. Similar results were also reported by *Uemura et al.* [2008] and *Pfahl and Wernli* [2008].

4. Conclusions

[30] In this paper, the characteristics of the δD, δ^{18}O, and d of precipitation and atmospheric water vapor were investigated using the data collected in Beijing from December

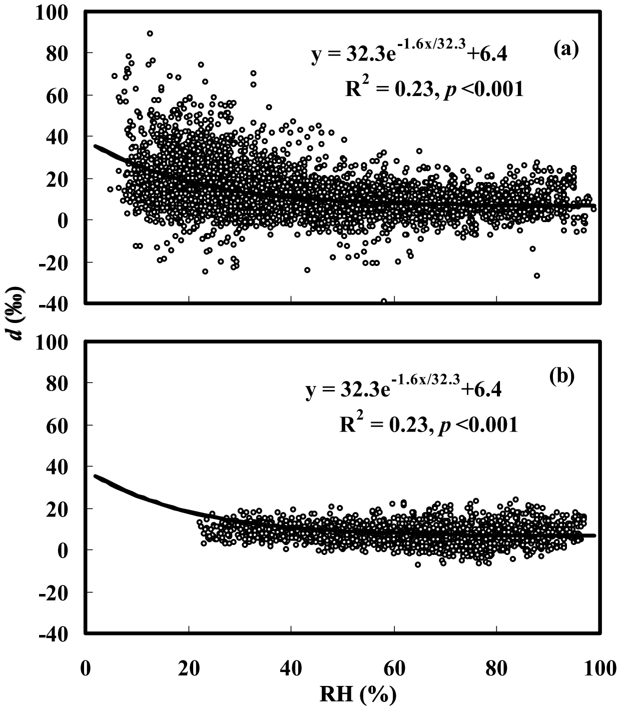

Figure 8. The dependence of hourly values of d (dots) of atmospheric water vapor on the local relative humidity (RH). (a) Days of year 345–170, 269–272, and 280–344; (b) days of year 171–269 and 272–280. The nonlinear regression is shown by the solid line, which is based on all the data from the entire experiment.

2006 to December 2007. The main findings are summarized as follows.

[31] 1. There was much less day-to-day variability in the vapor δD, δ^{18}O, and *d* in the summer monsoon season (June–August) than in the rest of the year. The diurnal amplitudes of variations of the vapor δD and δ^{18}O were roughly half of those in the winter months (December–February).

[32] 2. The monthly vapor δD and δ^{18}O were in reasonable agreement with the equilibrium prediction. An improved agreement was obtained if the analysis was restricted to individual precipitation events. During precipitation events, the δD and δ^{18}O departure from the equilibrium state was positively correlated with RH, and the *d* departure from the equilibrium state was negatively correlated with RH, as a result of the kinetic effects on the D and ^{18}O exchanges between the liquid and the vapor phase.

[33] 3. Outside the monsoon season, the vapor δD and δ^{18}O showed a log linear dependence on the vapor mixing ratio, and *d* showed a negative correlation with the local RH. Both relationships were statistically significant. The vapor mixing ratio and RH were poor predictors of the vapor isotopic temporal variability during the peak summer monsoon activities.

[34] In future work, we will continue to explore this data set in conjunction with other meteorological data, including surface, balloon, and satellite observations and data reconstructed by reanalysis models, using a method similar to that of *Lawrence et al.* [2004]. We hope that the combined data use can generate new insights into how the monsoon and other meteorological events modify the recycling of water in the atmosphere.

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