

# Deuterium excess reveals diurnal sources of water vapor in forest air

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**Abstract** An understanding of atmospheric water vapor content and its isotopic composition is important if we are to be able to model future water vapor dynamics and their potential feedback on future climate change. Here we present diurnal and vertical patterns of water isotope ratios in forest air ( $\delta^2\text{H}_v$  and  $\delta^{18}\text{O}_v$ ) not observed previously. Water vapor observed at three heights over 3 consecutive days in a coniferous forest in the Pacific Northwest of the United States, shows a stratified nocturnal structure of  $\delta^2\text{H}_v$  and  $\delta^{18}\text{O}_v$ , with the most positive values consistently observed above the canopy (60 m). Differences between 0.5 m and 60 m range between 2–6‰ for  $\delta^{18}\text{O}$  and 20–40‰ for  $\delta^2\text{H}$  at night. Using a box model, we simulated  $\text{H}_2\text{O}$  isotope fluxes and showed that the low to high  $\delta^2\text{H}_v$  and  $\delta^{18}\text{O}_v$  profiles can be explained by the vapor flux associated with evaporation from the forest floor and canopy transpiration. We used *d*-excess as a diagnostic tracer to identify processes that contribute to the diurnal variation in atmospheric moisture. Values of *d*-excess derived from water vapor measurements showed a repeated diel pattern, with the lowest values occurring in the early morning and the highest values occurring at midday. The isotopic composition of rain water, collected during a light rain event in the first morning of our experiment, suggested that considerable below-cloud secondary evaporation occurred

during the descent of raindrops. We conclude that atmospheric entrainment appears to drive the isotopic variation of water vapor in the early morning when the convective boundary layer rapidly develops, while evapotranspiration becomes more important in the mid-afternoon as a primary moisture source of water vapor in this forest. Our results demonstrate the interplay between the effects of vegetation and boundary layer mixing under the influence of rain evaporation, which has implications for larger-scale predictions of precipitation across the terrestrial landscape.

**Keywords** Water cycle · Atmospheric entrainment · Precipitation · Oxygen isotopes · Evapotranspiration · Land–atmosphere interaction

## Introduction

Atmospheric water vapor content is expected to increase due to climate change. This potent greenhouse gas exerts the largest feedback effect on surface warming (Hansen et al. 1984), and is the primary factor for the predicted increase in precipitation in mid- and high-latitudes (Dai 2006). Stable isotope analysis plays a crucial role in integrating regional-to-continental water cycles. For example, stable hydrogen ( $^2\text{H}/^1\text{H}$ ) and oxygen isotope ( $^{18}\text{O}/^{16}\text{O}$ ) ratio measurements in the tropical tropopause layer were useful in identifying ice particle size distribution—a key parameter in models of weather prediction and radiative transfer (Webster and Heysmsfield 2003). General circulation models (GCMs) that incorporate stable isotope tracers were developed to constrain predicted patterns of precipitation and water vapor transport (Joussaume et al. 1984; Hoffmann et al. 1998; Lee et al. 2007a, b; Brown et al. 2008). These isotope ratios are affected primarily by the

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fractionation occurring at phase changes—principally in the transition during surface evaporation or in-cloud condensation. Therefore, stable water isotope ratio measurements can be used as a diagnostic tracer to investigate hydrological cycles over many scales. An improved understanding of vapor isotope fractionation, both in the process of surface moisture exchange and cloud formation, is necessary if we are to fully exploit the power of stable isotopes in the water cycle.

Atmospheric water vapor contains a smaller amount of heavier water isotopes ( $^2\text{H}$  and  $^{18}\text{O}$ ) relative to the source water. This is primarily because, under the same temperature, saturation vapor pressure is lower for heavier isotopes than their lighter counterparts. A second effect that augments fractionation during evaporation is the kinetic difference between masses. Studies of atmospheric water isotopes have focused on processes that accompany evaporation from the oceans or large fresh water reservoirs (Gat et al. 1994, 2003). Using an isotopic approach, these authors showed that evaporation from lake water and sea-spray droplets may have contributed, respectively, up to 16 and 50% of added moisture to the overlying atmospheric moisture content. Using satellite infrared spectrometry measurements and a GCM, Worden et al. (2007) investigated sources of moisture in tropospheric water vapor over continents. They found that water vapor observed in continental troposphere was typically enriched in deuterium compared to observations over the ocean. The authors attributed the observation to the heavy water (HDO)-enriched vapor from evapotranspiration that was then lofted by thermal convection. These studies provide an example of how evapotranspiration may influence the isotopic composition of water vapor in the atmospheric boundary layer over continents without explicitly considering the role of vegetation.

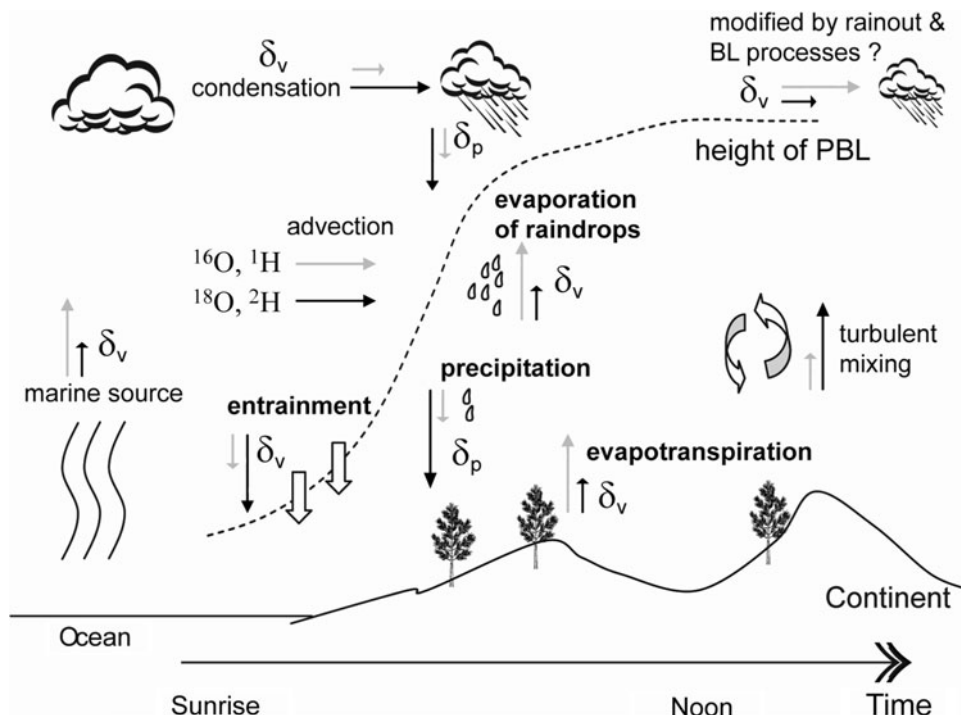
Very few studies have explicitly included the isotopic effects of vegetation in a global water isotope simulation (Cuntz et al. 2003). The isotope effect of vegetation has not been considered by most isotope-enabled GCMs perhaps because: (1) a general assumption that the isotopic composition of transpired water equals that of precipitation, (2) a lack of our prognostic ability to quantify the ratio of transpiration to evaporation, and (3) the scarcity of uninterrupted stable isotope ratio measurements in water vapor over actively transpiring vegetated landscapes. The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values in precipitation are measured routinely and archived by the International Atomic Energy Agency's Global Network for Isotopes in Precipitation (Rozanski et al. 1993; Araguas-Araguas et al. 2000). Only a handful of observations were made that reported both  $^2\text{H}$  and  $^{18}\text{O}$  isotope ratios in water vapor, including those measured over the sea surface (Craig and Gordon 1965; Gat et al. 2003), in the upper troposphere (Webster and Heymsfield

2003; Worden et al. 2007), in forests or woodlands (Moreira et al. 1997; Yopez et al. 2003), over rice crops (Brunel et al. 1992) and in an urban area (Wen et al. 2008). New laser techniques that offer near continuous measurements of water vapor isotopes are likely to overcome the scarcity of direct observations (Lee et al. 2005; Gupta et al. 2009; Wang et al. 2009), and are poised to provide new insights into factors that control vapor isotope variation. For example, a number of studies have used optical spectroscopy instruments to measure  $\text{H}_2^{18}\text{O}$  (Lee et al. 2007a, b; Welp et al. 2008) and HDO (Wen et al. 2008). Nevertheless, there remain very few studies that have focused on the influence of vegetation and boundary-layer dynamics on the isotope ratios in near-surface water vapor. Despite advances in sampling techniques, laser instruments will always be limited by the relatively large power requirement. The traditional analytical approach (physical trapping of water vapor coupled with mass spectrometer analysis) is likely to continue to be employed to complement the laser technique (Peters and Yakir 2010).

Figure 1 shows the major processes that influence hydrogen and oxygen isotope ratios in precipitation and water vapor above a coastal forest. The hydrogen ( $\delta^2\text{H}_v$ ) and oxygen ( $\delta^{18}\text{O}_v$ ) isotope ratios of water vapor in the upper atmosphere are generally more depleted in heavy isotopes compared to those near the continental surface. Dansgaard (1964) explained the low isotope values of water vapor in the upper atmosphere by the preferential removal of: (1) heavy isotopes in condensates in the cloud layer, and (2) lighter isotopes in raindrops that evaporate below the cloud base under low and moderate humidity conditions. The same effects result in high isotope values in precipitation reaching the surface. These interactions between precipitation and water vapor as raindrops fall through the air column were quantitatively evaluated by Lee and Fung (2007) in a modeling study. The isotope ratios of water vapor are determined primarily by the isotopic fractionation associated with in-cloud condensation and surface evaporation. Other boundary-layer processes, including evaporation of raindrops during their descent (Stewart 1975), entrainment (Lee and Fung 2007), and turbulent mixing (Lee et al. 2009), further modify the isotopic composition of water vapor and precipitation in a retrofit air mass that continues to move downstream.

Evaporation accounts for the most notable changes in the isotopic composition of water vapor near the surface. Variations in  $\delta^2\text{H}_v$  and  $\delta^{18}\text{O}_v$  within forest canopies generally reflect the combined effect of atmospheric entrainment from the upper atmosphere, transpiration and the evaporation from the forest floor under fair weather conditions, although the effect of atmospheric entrainment remains uncertain (Lai et al. 2006). Water fluxes from transpiring leaves, when integrated over hours to days

**Fig. 1** A schematic of processes that influence water isotope variations in the hydrosphere over coastal forested areas. The *arrows* of uneven length indicate isotopic fractionation. The superimposed *dashed curve* shows the growth of the planetary boundary layer (PBL) over land for a typical, dry summer day. Processes directly related to the current study are highlighted in *bold*



(Harwood et al. 1999), carry the same isotopic signature as that of the source water taken up by plants. Plants experiencing seasonal droughts tend to develop deep roots and rely on ground water to avoid cavitation. Following an ephemeral precipitation event, some plants may temporarily switch from deep water sources to shallower surface soil water (Ehleringer and Dawson 1992). To the best of our knowledge, no study to date has examined how this transient pattern of plant water use influences the isotope ratios of water vapor near a vegetative surface.

In this study, we investigate factors influencing near-surface hydrogen and oxygen isotope ratios in atmospheric water vapor based on observations made above and within an old-growth coniferous forest in the Pacific Northwest of the United States. Water vapor samples were collected every 3 h from three different heights above and within the canopy over 3 consecutive days in the summer of 2004, including daytime and nocturnal observations. We show an observed stratification of nocturnal  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  values in forest air that has not been reported previously. This vertical profile diminished as the convective mixing dominates during the day. We explain these observed patterns by using deuterium-excess derived from rainwater and vapor samples to indicate potential moisture sources. We then further support this interpretation with estimates from a canopy  $\text{H}_2\text{O}$  isotope balance model to quantitatively distinguish the relative contribution of various moisture sources.

## Materials and methods

### Atmospheric $\text{H}_2\text{O}$ and $\text{H}_2^{18}\text{O}$ (HDO) balance

Here we use  $^{18}\text{O}$  as an example to derive an isotope mass balance model in forest air. The same equations and the analytical solution can also be applied to  $^2\text{H}$ . Following Lai et al. (2006), atmospheric  $\text{H}_2\text{O}$  balance within a forest can be written by:

$$M_c \frac{dv_c}{dt} = F_+ - F_- + F_T + F_E \quad (1)$$

where  $M_c$  represents the number of moles of air in the column per unit ground area,  $v_c$  is the average mole fraction of water vapor in the column,  $F$  represents component fluxes;  $F_+$  is one-way flux of water vapor entering the canopy,  $F_-$  is the flux of water vapor leaving the top of the canopy, and  $F_T$  and  $F_E$  are fluxes of transpiration and evaporation, respectively. A mass balance equation can also be written for  $\text{H}_2^{18}\text{O}$ , given by:

$$M_c \frac{dR_c v_c}{dt} = R_+ F_+ - R_- F_- + R_T F_T + R_E F_E \quad (2)$$

where  $R_c$  is the average  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio within the column,  $R_+$  is the  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio of the atmosphere aloft,  $R_-$  is the  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio of air venting out of the column,  $R_T$  is the  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio associated with transpiration flux and  $R_E$  is the  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  ratio associated with evaporation flux.

Multiplying Eq. 1 by  $R_c$  and subtracting from Eq. 2, an 'isoflux' mass balance equation that describes the time evolution of the isotope composition of water vapor within plant canopies ( $d\delta_c/dt$ ) can be derived:

$$M_c v_c \frac{d\delta_c}{dt} = (\delta_+ - \delta_c)F_+ + (\delta_T - \delta_c)F_T + (\delta_E - \delta_c)F_E \quad (3)$$

The isoflux is therefore defined here as the product of a water flux and the deviation of its isotopic ratios from that of the canopy air. An analytical solution is provided here to solve for  $\delta_c$ , given by:

$$\delta_c = \delta_{c,t=0} \cdot e^{at} + (e^{at} - 1) \frac{b}{a} \quad (4)$$

where

$$a = -\frac{F_+ + F_T + F_E}{M_c v_c}; b = \frac{\delta_+ F_+ + \delta_T F_T + \delta_E F_E}{M_c v_c},$$

$t$  is time and  $\delta_{c,t=0}$  is the initial value of  $\delta_c$  at  $t = 0$ . Values of  $a$  and  $b$  were calculated either from direct measurements or model values using the approach described by Lai et al. (2006). Briefly, we used the Craig and Gordon (1965) model to predict values of  $\delta_T$  and  $\delta_E$ . We derived values of  $v_c$ ,  $F_T$ , and  $F_E$  from direct meteorological measurements of vapor concentration and water vapor fluxes. We estimated the one-way flux  $F_+$  by a relaxed eddy accumulation method (Lai et al. 2006). The isotope ratio of the one-way flux,  $\delta_+$ , was assumed equal to that measured at 60 m. Errors associated with this assumption were evaluated by a sensitivity test by arbitrarily altering  $\delta_+$  values by  $\pm 2\%$  for  $^{18}\text{O}$  and  $\pm 16\%$  for  $^2\text{H}$ . These values roughly equal one-half of the difference between surface air and the troposphere over the ocean. An initial value for  $\delta_c$  was set to the first average  $\delta_c$  value of  $-13.6\%$  for  $^{18}\text{O}$  and  $-114.8\%$  for  $^2\text{H}$  in the simulation.

### Isotopic enrichment of leaf water

The evaporative enrichment of leaf water was modeled using two approaches. First, we used a modified Craig-Gordon model that includes a boundary-layer effect between leaf surface and the surrounding air to predict  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of leaf water at steady state (Flanagan and Ehleringer 1991). Second, we used a transient model to predict  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of leaf water at non-steady state (Dongmann et al. 1974). In these models, we calculated equilibrium fractionation factors as a function of temperature using the formula given by Majoube (1971). We scaled values of kinetic fractionation factors (Merlivat 1978) to leaf stomatal and boundary resistance as suggested by Farquhar et al. (1989). The turnover time of leaf water was estimated using

sapflow and leaf water content measurements from needles of *Pseudotsuga menziesii* as described by Lai et al. (2006).

### Sample collection and analysis

Our study site is the Wind River Canopy Crane Research Facility (WRCCRF), which is located within an old-growth coniferous forest in southern Washington (45.8205°N 121.9519°W; elevation = 371 m). The long-term mean annual temperature is 8.7°C, and mean annual precipitation is 2,467 mm with <5% falling between June and August. The dominant overstory species include *Pseudotsuga menziesii* (Douglas-fir), *Tsuga heterophylla* (Western hemlock) and *Thuja plicata* (Western red cedar). Field sample collection began at 5:00 a.m. on 16 August and ended at 12:00 a.m. on 19 August 2004. Fair weather conditions were generally met except for a light rain event (0.25 mm), lasting 1.5 h (9:30–11:00 a.m.) on the first morning of our experiment. Water vapor samples were collected cryogenically from three heights. Air was pulled at a flow rate of 5 cc s<sup>-1</sup> through sampling glass tubes (Helliker et al. 2002) placed in a dewar of crushed dry ice to capture water vapor from two heights within the canopy (0.5, 10 m) and one above the canopy (60 m). Sampling time was pre-determined based on ambient temperature and relative humidity to obtain adequate volume for isotope determination (50 µl), and usually lasted between 15 and 20 min for this study. Lai et al. (2008) reported errors associated with the collection or storage of water vapor samples using this sampling protocol in a wet environment, but we did not encounter any problem in this experiment. Water vapor samples were immediately sealed and stored in a freezer until laboratory analysis.

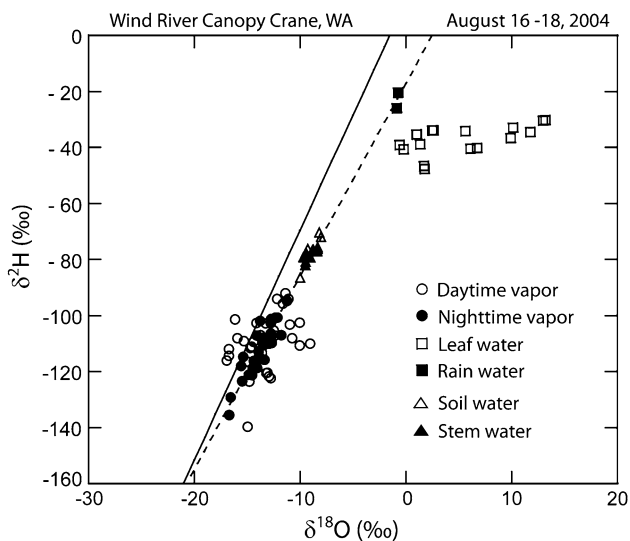
We collected stems from non-green tissues and leaves from the same branches under clear-sky conditions. Green leaves were collected from the three dominant species during each day of our experiment: at 05:00 on day 1, at 05:00, 09:30 and 13:30 on day 2 and at 05:00, 11:00 and 15:00 again on day 3. Soil samples were collected from the top 0.3 m. Samples were kept cold in the field and later frozen in the laboratory. Water was extracted from plant and soil samples using cryogenic vacuum distillation. Hydrogen and oxygen isotope ratios were determined using an online TCEA-IRMS process (Finnigan Delta Plus XL, Bremen, Germany). Average precision of our measurements was 1.3‰ for  $\delta^2\text{H}$  and 0.17‰ for  $\delta^{18}\text{O}$ . All observations are reported in the delta notation ( $\delta$ ) relative to Vienna Standard Mean Ocean water (Coplen 1996) by  $\delta = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1,000$ , where  $R$  is the molar ratio of heavy to light isotopes,  $R_{\text{standard}}$  (VSMOW) = 0.0020052 for  $^{18}\text{O}$  and 0.00015576 for  $^2\text{H}$ .

## Results

Relationship between  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in various water pools

Figure 2 shows measured isotopic composition of all the water samples in a  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  plot. The rain event encountered on 16 August registered a very small amount with an averaged  $\delta^{18}\text{O} = -0.8 \pm 0.1\text{‰}$  and  $\delta^2\text{H} = -23.2 \pm 3.9\text{‰}$  (Table 1). These values were substantially higher than the long-term averaged source water sampled in this forest:  $\delta^{18}\text{O} = -8.9 \pm 0.6\text{‰}$  and  $\delta^2\text{H} = -77.8 \pm 3.9\text{‰}$  (stem and soil water combined). Water vapor had the lowest values among all the waters with an averaged  $\delta^{18}\text{O} = -13.5 \pm 1.8\text{‰}$  and  $\delta^2\text{H} = -110.0 \pm 9.7\text{‰}$ . Waters derived from nocturnal atmospheric vapor, stem, soil and rainfall samples appeared to form a  $\delta^2\text{H}$ – $\delta^{18}\text{O}$  relationship with an equation  $\delta^2\text{H} = 6.9 \times \delta^{18}\text{O} - 17.2$ . This observation deviates from the local meteoric water line,  $\delta^2\text{H} = 8.2 \times \delta^{18}\text{O} + 12.39$  (see Fig. 3 in Kendall and Coplen 2001). Daytime water vapor appeared less organized and scattered on both sides of the mixing lines. Leaf water was highly enriched in heavier isotopes; even those collected in the early morning showed enrichment above source water with an averaged  $\delta^{18}\text{O} = 7.3 \pm 4.2\text{‰}$  and  $\delta^2\text{H} = -36.2 \pm 4.4\text{‰}$  (09:00–15:00,  $n = 14$ ).

Atmospheric water vapor showed the greatest variation in the observed  $\delta^2\text{H}$  values while leaf water showed the greatest variation in the observed  $\delta^{18}\text{O}$  values. Water vapor sampled above the canopy consistently showed the highest average  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values that decreased with height



**Fig. 2** Relationship between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of waters collected in the current study. The dashed line represents a linear regression ( $\delta^2\text{H} = 6.9 \times \delta^{18}\text{O} - 17.2$ ) that includes nocturnal vapor, stem, soil and rain waters. In comparison, the solid line shows the local meteoric water line with a slope of 8.2 (Kendall and Coplen 2001)

**Table 1** Averaged isotope ratios measured in the various water pools in the current study

Sample type	Mean $\delta^{18}\text{O}$ (‰)	Mean $\delta^2\text{H}$ (‰)	Number of samples
Rainwater	-0.8 (0.1)	-23.2 (3.9)	2
Water vapor at 0.5 m	-14.3 (1.2)	-116.6 (9.5)	23
Water vapor at 10 m	-13.6 (1.6)	-109.9 (6.8)	23
Water vapor at 60 m	-12.3 (1.9)	-103.5 (7.6)	21
Leaf water 05:00–15:00	5.5 (4.5)	-37.1 (4.5)	21
Stem water	-9.0 (0.5)	-78.5 (2.1)	9
Soil water	-8.8 (0.8)	-76.8 (5.8)	6

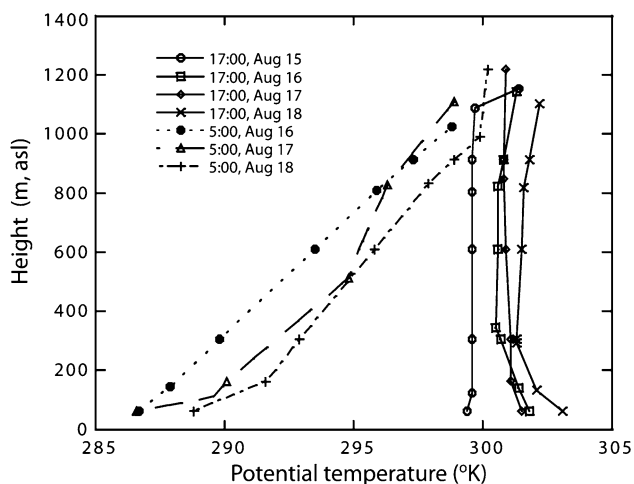
Rainwater samples were collected from a single, light (0.25 mm) rain event during our study period. Water vapor samples were collected cryogenically using a dry-ice trap. Bulk leaf water values represent the average combined from three different species. Stem samples were collected from the same branches where leaves were collected. Soil samples were collected from the top 0.3 m. Numbers in parenthesis are 1SD

(Table 1). To further investigate the spatial and temporal variation in the measured  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  values, we plotted diel variations and vertical profiles of absolute humidity,  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  values in Fig. 3.

Observed pattern in  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$ 

Figure 3 shows absolute humidity,  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  values observed at three heights for the study period. The highest atmospheric moisture content occurred in the first morning during the rain. The vapor pressure deficit of the air was low (<0.25 kPa) and did not exceed 1 kPa until 2:00 p.m. on the 1st day. In contrast, the vapor pressure deficit of the air began to increase above zero at 7:00 a.m., reaching 1 kPa by 10:00 a.m., and peaking at 2 kPa in the mid-afternoon in the last 2 days of our experiment—a typical pattern under fair weather conditions at this site. Atmospheric moisture content was consistently the highest near the ground during the day. By contrast, we observed the highest atmospheric moisture content near the top of the canopy at night. Measured  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  values showed a vertical stratification during the night, where the majority of the highest values were consistently observed above the canopy (60 m). The majority of the lowest values were often observed near the forest floor (0.5 m) and observed values at 10 m generally fell in between. We are not aware of any previous studies that have reported stratified nocturnal profiles of  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  within forests. These vertical profiles collapsed during mid-afternoon hours when convective turbulent mixing prevailed. Observed differences between 0.5 and 60 m ranged between 2–6‰ for  $\delta^{18}\text{O}$  and 20–40‰ for  $\delta^2\text{H}$  at night. These differences were consistently greater than values found during the day (<1.5‰ for  $\delta^{18}\text{O}$  and <7‰ for  $\delta^2\text{H}$ ). These diel changes in





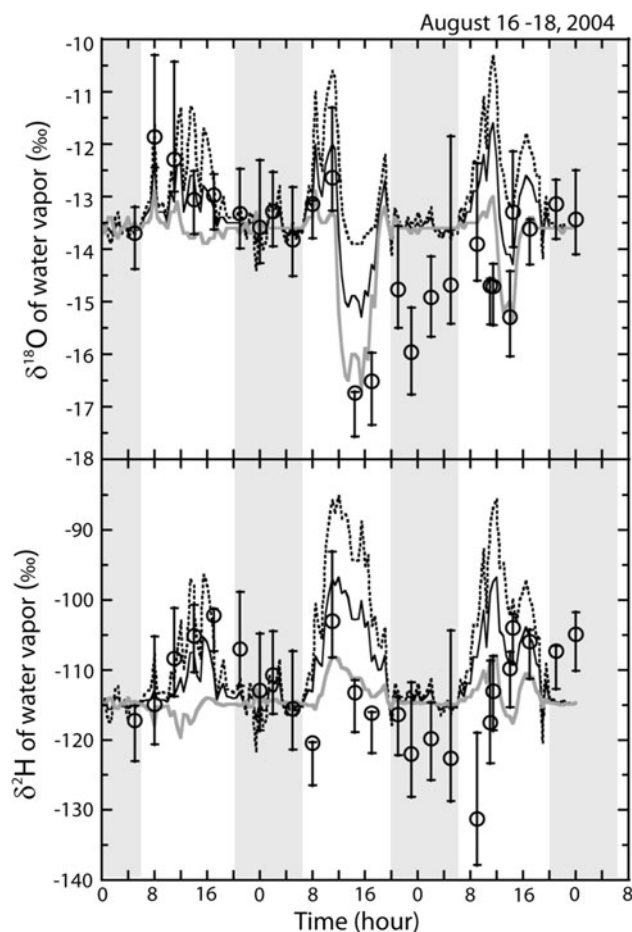
**Fig. 5** Upper air temperature profiles obtained from the sounding measurements near Salem, OR (44.91°N, 123.0°W, elevation = 61 m) operated by the Department of Atmospheric Science, University of Wyoming. *Broken lines* Profile observations at 5:00 a.m., *solid lines* profile observations at 5:00 p.m.

8:00 a.m. in the last 2 days of our study period. To further assess the relative importance of vapor fluxes from atmospheric entrainment, canopy transpiration and soil evaporation, we used a simple box model to simulate water isotope fluxes, height-averaged  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$ , and *d*-excess in this forest.

Comparison between measured and modeled  $\delta^{18}\text{O}_v$ ,  $\delta^2\text{H}_v$  and *d*-excess

Modeled *d* followed the observed diel variation very well, but underestimated the low values in the early morning hours (Fig. 4). Modeled *d* synchronized with the observed peaks in the mid-afternoon under fair weather conditions. The observed *d* values show similar patterns at all levels, suggesting that the canopy air was influenced by the same dominant processes. Isoflux analysis suggests that entrainment and evapotranspiration are the two potent processes controlling atmospheric moisture (explained below). The difference in absolute humidity between 0.5 and 60 m (Fig. 3a) was consistent with this interpretation.

Figure 6 shows the comparison between measured and modeled average  $\delta^2\text{H}_v$  and  $\delta^{18}\text{O}_v$ . The model did a poor job under nocturnal conditions when the vertical stratification was most pronounced. These discrepancies were expected because vapor measurements at 60 m were used as the boundary condition in the model (i.e.,  $\delta_+ = \delta_{60\text{m}}$ ) and were excluded in the average, whereas the model includes averages from the entire canopy height. During the day, the model agreed reasonably well with the observations, and was able to capture the principal features of the temporal variation in both  $\delta^2\text{H}_v$  and  $\delta^{18}\text{O}_v$ . Consistent with



**Fig. 6** Comparison between modeled and measured values of  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$ . Model calculations were performed by assuming  $\delta_+$ , the isotope composition of background atmosphere, equals that measured at 60 m (*solid line*). The *gray line* shows modeled values if the  $\delta_+$  value was altered by  $-2\text{‰}$  for  $\delta^{18}\text{O}$  and  $-16\text{‰}$  for  $\delta^2\text{H}$ . The *dotted line* shows modeled values if the  $\delta_+$  value was altered by  $+2\text{‰}$  for  $\delta^{18}\text{O}$  and  $+16\text{‰}$  for  $\delta^2\text{H}$ . For clarity, model calculations assumed steady-state leaf water enrichment

observations and modeling results shown by Lai et al. (2006), the average, within-canopy  $\delta^{18}\text{O}_v$  showed a midday depression under fair weather conditions. By contrast, modeled and measured  $\delta^2\text{H}_v$  values were elevated at midday hours. Given the consistency in these comparisons, we next utilized the model to simulate vapor isotope fluxes in order to provide a quantitative assessment of the observed  $\delta^2\text{H}_v$ ,  $\delta^{18}\text{O}_v$  and *d* variation.

Modeled water vapor isotope fluxes

Our model suggests that transpiration and evaporation from the forest floor have the opposite effect on the water vapor isotope ratios inside a forest canopy (Fig. 7). While transpiration tends to increase  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$ , evaporation from the forest floor tends to lower the isotopic composition of





$d$ -excess ( $\text{iso}F_d$ ) with respect to transpiration can be described as:

$$\text{iso}F_d = \text{iso}F_H - 8 \times \text{iso}F_o \quad (5)$$

where  $\text{iso}F_H$  and  $\text{iso}F_o$  are  $^2\text{H}$ -isoflux and  $^{18}\text{O}$ -isoflux of transpiration, respectively. Substitute the two isoflux terms on the RHS by their equivalents as defined in Eq. 3, we derive  $\text{iso}F_d$  as:

$$\begin{aligned} \text{iso}F_d &= (\delta^2H_T - \delta^2H_c) \cdot F_T - 8 \times (\delta^{18}O_T - \delta^{18}O_c) \cdot F_T \\ &= ((\delta^2H_T - 8 \times \delta^{18}O_T) - (\delta^2H_c - 8 \times \delta^{18}O_c)) \cdot F_T \\ &= (d_T - d_c) \cdot F_T \end{aligned}$$

The isoflux of  $d$ -excess therefore assumes a similar form as the isofluxes defined in Eq. 3. We reiterate that the balance of the isofluxes associated with the three water sources,  $F_+$ ,  $F_T$  and  $F_E$ , determines the  $d$ -excess value of canopy water vapor. Modeled  $\text{iso}F_d$  are shown in Fig. 7. According to our model, transpiration and evaporation consistently exerted positive isotope forcing on the  $d$ -excess of canopy vapor during the study period. Air entrainment consistently exerted negative isotope forcing on the  $d$ -excess of canopy vapor in the morning of each of the 3 days. These results suggest that entrainment was responsible for the observed low  $d$ -excess values during these hours. The isotope forcing associated with entrainment remained negative throughout the day during the 1st day of our study—likely a consequence of the rain and the low pressure system encountered. Entrainment imposed a positive isotope forcing in the afternoon during the last 2 days of our study. This is likely due to horizontal advection of surface air from the vicinity. Evaporation of raindrops during the small rainfall event results in very low  $d$ -excess values that can explain the pattern observed in the first morning. By contrast, the isotope forcing associated with entrainment were negative in the morning but became positive in the afternoon during the last 2 days of our study. There was no precipitation occurring in the vicinity of our study site based on the sounding measurements. Therefore, the low  $d$ -excess values observed during the last 2 days cannot be explained by precipitation. Model results suggest that a water reservoir of low  $d$ -excess (or a process that results in low  $d$ -excess) exists in the atmosphere aloft, which entrains the forest canopy in the morning as convective boundary layer rapidly grows. Our surface measurements do not provide enough information to explain the cause of this vapor source. In-cloud condensation, evaporation of raindrops below cloud bases, vertical mixing and horizontal advection from an upstream moisture source all possibly contribute to the variation observed near the surface. Future research must investigate possible mechanisms in the upper atmosphere including regional atmospheric circulation.

A seasonal cycle in the  $d$ -excess value was shown from near-surface water vapor samples collected in an Eastern Mediterranean location (Angert et al. 2008). To our best knowledge, diel variations in  $d$ -excess values derived from canopy water vapor have never been shown before. By definition,  $d = 10$  if water samples were to follow the meteoric relationship (Craig 1961). Values of  $d$  would gradually decrease, and can even fall below zero, if  $\delta^{18}\text{O}$  values increase at a rate faster than  $\delta^2\text{H}$  values. Stewart (1975) tested this kinetic fractionation effect in a laboratory experiment and showed that raindrops evaporating during descent were an example of this effect. Consequently, raindrops reaching the ground became enriched in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  compared to where they were formed. Our two rainwater samples collected on 16 August were likely subject to the evaporative effect, giving an average  $\delta^{18}\text{O} = -0.8\text{‰}$  and  $\delta^2\text{H} = -23.2\text{‰}$  (Table 1). These isotope ratios observed in a single, light rain event were at least 5‰ for  $\delta^{18}\text{O}$  and 20‰ for  $\delta^2\text{H}$  more enriched compared to long-term averages for this region (Welker 2000; Kendall and Coplen 2001). The  $d$  value derived from the two rainwater samples equals  $-16.9\text{‰}$ , which is similar to the intercepts from the  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  relationship for rainfalls of small amount ( $<2$  mm) observed in long-term precipitation studies (Peng et al. 2007). These authors attributed the low intercepts to the secondary evaporation of raindrops below the cloud base. This process, presumably if occurring repeatedly between cloud base and a height above ground such that moisture was recycled without reaching the ground, can substantially decrease  $d$ -excess to a level where  $d$  is no longer an ‘excess’. Alternatively, a large fraction of water would have evaporated during the descent of raindrops on 16 August 2004. According to Froehlich et al. (2008), the rate of change in  $d$ -excess resulting from this below-cloud effect is roughly 1‰ per 1% increase in the fraction of evaporation during rainfall. Their study was conducted in an area that has comparable temperature (mean annual temperature ranges between 1.3 and 11.9°C) to our study site. Assuming the same rate applies, and if the air at the cloud base represents that over the ocean, below-cloud evaporation would have accounted for  $>20\%$  of the water that precipitates from the cloud base on that day.

Similar to the isotopic effect in clouds that produce precipitation, the phase change of water associated with evaporation and condensation accounts for the most notable changes in the isotopic composition of water vapor in forests, with moisture influences from surface evapotranspiration and atmospheric entrainment from the air aloft. Atmospheric entrainment appears to drive the canopy  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  variation in early morning when the surface remains partially wet and the convective boundary layer develops rapidly. Vapor  $d$ -excess indicates that evapotranspiration becomes

more important in the mid-afternoon as a primary moisture source of vapor in this forest. These more positive  $d$ -excess values were consistent with those expected from the recycling of surface evapotranspiration (Gat et al. 1994, 2003).

Midday depletion of  $\delta^{18}\text{O}$  in atmospheric water has been observed in arid environments (Yakir 1998), temperate forests (Harwood et al. 1999; Lai et al. 2006; Lee et al. 2006), and a northern agricultural field (Welp et al. 2008). Observations in these studies contrast with the enriched pattern observed in rainforests (Moreira et al. 1997). In humid environment (tropical rainforests) where heavy rainfall occurs more frequently, the below-cloud secondary evaporation has a negligible effect on the isotopic composition of atmospheric moisture (Peng et al. 2007). Surface processes, such as evapotranspiration and the equilibrium fractionation between atmospheric moisture and leaf water, are two examples that influence the variation of  $\delta^{18}\text{O}_v$  and  $\delta^2\text{H}_v$  in Amazonian forests (Lai et al. 2008). These contrasting patterns call for the need to collect uninterrupted water vapor isotope measurements in a variety of ecosystem types across different climatic zones.

Water isotope analysis was shown to elucidate aspects of the shortcomings in the hydrological simulation at the scale of large basins (Henderson-Sellers et al. 2004). Our measured  $^2\text{H}$  and  $^{18}\text{O}$  isotope ratios in ecosystem waters perhaps provide an interesting dataset to address some of these shortcomings. The correlation equation derived from the waters collected in this forest (nocturnal atmospheric vapor, stem, soil and rain) was  $\delta^2\text{H} = 6.9 \times \delta^{18}\text{O} - 17.2$ . The slope and the intercept were similar to those found in small rainfalls (Peng et al. 2007) but lower than those in the local meteoric water line derived from river water (Kendall and Coplen 2001). Our isotope data are consistent with the results observed in a watershed in the Cascade Mountains, Oregon, in the United States, in which Brooks et al. (2009) showed a decoupling between the soil water used by vegetation and the water that flows into streams. Implied from the water isotope measurements, Brooks et al. suggested that soil waters are highly compartmentalized, with the longest residence time found in small pores that are removed by root water uptake but unaffected by winter storms. Isotope studies such as Brooks et al. (2009) provide field evidence that beg reconsideration of assumptions in subsurface flow models. Our data can be distinguished from those shown in Brooks et al. (2009) because we included isotope signatures in rainwater and water vapor. We cannot conclude whether our result is a coincidence resulting from a single rain event, or if it implies the existence of a discrete moisture cycle that may have been confined by local atmospheric circulation and the evapotranspiration process at the scale of a watershed. We hypothesize that the latter is a plausible explanation because the regression line consists of waters from pools

with various residence times, similar to the representation of a watershed. Continuous water vapor measurements using optical instruments will provide critical information to unravel these questions.

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