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Title

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Permalink

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Journal

Ecohydrology, 7(3)

ISSN

1936-0584

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Publication Date

2014

DOI

10.1002/eco.1420

Peer reviewed

Vegetation induced changes in the stable isotope composition of near surface humidity

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ABSTRACT

Obtaining the *d*-excess parameter from oxygen and hydrogen stable isotope composition of meteoric waters has the potential power to reconstruct changes in atmospheric water pools (e.g. sources, origins and overall balance) and the climatic conditions that prevail during surface evaporation. Recently, plant and ecosystem scientists turned their attention using *d*-excess information to inform questions at these scales. Here, we use the *d*-excess parameter to evaluate the influence of forest canopies on atmospheric humidity within a mixed evergreen forest in coastal California. We found that during the day, when transpiration was at a maximum, the *d*-excess of atmospheric water vapour exceeded model predictions for the background atmosphere into which the ecosystem evapotranspiration mixes. At night when transpiration was minor, the *d*-excess of atmospheric water vapour was on average less than model predictions for an ocean derived water vapour source. The observed diurnal fluctuations around the *d*-excess of the modelled background water vapour provided a strong evidence that during the day as the land surface warms and the boundary layer grows plants alter the isotope composition of atmospheric humidity via non-steady state isotope effects. In contrast, at night equilibrium isotope effects dominate as the atmosphere stabilizes. These day and nighttime fluctuations around the *d*-excess of ocean derived water vapour highlight the importance of plant transpiration for the isotope hydrology of near surface humidity and subsequently for the isotope composition of condensate like dew, an important water input to this ecosystem. Copyright © 2013 John Wiley & Sons, Ltd.

KEY WORDS *d*-excess; water isotopes; transpiration; water cycling

Received 28 January 2013; Revised 16 July 2013; Accepted 18 July 2013

INTRODUCTION

Most climate models predict dramatic changes in atmospheric humidity and in the distribution and abundance of precipitation in a future warmer climate (Bates *et al.*, 2008). Although temperature-induced changes to the Earth's water cycle seem quite certain, other aspects of how water will cycle on Earth remain uncertain (Roderick and Farquhar, 2002; Huntington, 2006; Bowen, 2011). Part of this uncertainty comes from an incomplete understanding of the relative contributions of plant transpiration, surface evaporation (e.g. soils and lakes) and oceanic sources to atmospheric humidity over land, and by extension, to terrestrial precipitation (Araguas-Araguas *et al.*, 2000; Gerten *et al.* 2005; Lawrence *et al.* 2007; Worden *et al.*, 2007; Jasechko *et al.* 2013). Globally, the vast majority of atmospheric water

vapour is ocean derived (Trenberth *et al.*, 2007) such that variation in the stable O and H isotope composition of water vapour and subsequent condensation events (e.g. rain, dew, fog and snow) are largely the result of changes in ocean surface conditions, for example, sea surface temperature and relative humidity (Merlivat and Jouzel, 1979; Uemura *et al.*, 2008). However, variation in the stable isotope composition of terrestrial precipitation often deviates from the Raleigh distillation model predictions for ocean-derived air masses providing strong evidence that terrestrial water sources can cycle, perhaps several times, between the liquid and vapour phase before returning to the ocean. As such, terrestrial ecosystems may exert a greater influence on atmospheric humidity than previously thought (e.g. Salati *et al.*, 1979; Ingraham and Taylor, 1991; Gerten *et al.* 2005), and recent estimates suggest that they are dominated (>80%) by plant transpiration (Jasechko *et al.* 2013). In this context, the extent to which plants contribute to terrestrial water recycling (not just as a one-way flux from transpiration; Jasechko *et al.* 2013) is perhaps the most poorly understood dimension of the terrestrial water cycle (Lawrence *et al.* 2007; Bonan, 2008).

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Although plants are known to play a major role in terrestrial hydrology, our ability to quantify the relative contribution of plant transpiration to atmospheric humidity and the influence of this water flux on future condensation events remains limited (Bonan, 2008). Characterizing the relative contribution of plant transpiration to atmospheric humidity over daily, seasonal and annual time scales is essential for understanding how naturally configured and human reconfigured land surfaces interact with climate and ultimately the water balance of the landscape and the atmosphere. Previous research suggests that vegetated landscapes directly influence atmospheric humidity, and therefore, the chemical (isotope) composition of water vapour most strongly during the day, when leaf surface conductance and water flux from leaf to atmosphere (i.e. transpiration) are the greatest (e.g. Lai *et al.* 2006; Jasechko *et al.* 2013). Yet, the fact that many plants do not completely close their stomata at night (e.g. Dawson *et al.*, 2007) has potentially important consequences for the water balance of the landscape (e.g. Fisher *et al.*, 2007) and the H and O isotope composition near surface water vapour.

Knowing and using the stable isotope composition of water has long been considered a powerful tool for enhancing our understanding of the processes that drive variation in atmospheric water balance and terrestrial water cycling (Gat, 1996). Furthermore, modelling the stable isotope composition of water in the Earth's hydrologic cycle is an important diagnostic component of atmosphere general circulation models (Noone and Simmonds, 2002; Schmidt *et al.*, 2005; Risi *et al.*, 2010). This is because the isotopic composition of water varies predictably during phase changes between solid, liquid and vapour. Once water is elevated into the atmosphere as vapour, it is transported horizontally and vertically without any fractionation effects as long as no cloud processes occur, that is liquid–vapour phase changes (Bony *et al.*, 2008). As such, any changes in the isotope composition of water vapour can be used to infer changes in the climatic conditions that occur during evaporation or condensation. In particular, the *d*-excess parameter, originally defined by Dansgaard, is considered a valuable tool for evaluating changes in atmospheric water balance and the climatic conditions that prevailed during evaporation and condensation (Craig, 1961; Dansgaard, 1964; Merlivat and Jouzel, 1979). Here, we use the *d*-excess parameter and associated theory to characterize the influence of a coastal mixed evergreen forest canopy on the isotope composition of near surface water vapour, during the day and at night.

Theory – d-excess and the physical processes regulating the distribution of O and H stable isotopes in water

Globally, the stable isotope ratios of oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) of precipitation show a strong linear

relationship described by the general equation, $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$ with the y-intercept generally referred to as the *d*-excess (i.e. *d*-excess = $\delta\text{D} - 8 \times \delta^{18}\text{O}$; Dansgaard, 1964). This strong covariation between the $\delta^{18}\text{O}$ and δD within precipitation is ultimately controlled by two mass-dependent isotope effects: (1) the equilibrium fractionation effect (α_{equil}) as a result of temperature-dependent differences in the saturation vapour pressure of the 'heavy' and 'light' stable isotopes in water and (2) the kinetic fractionation effect (α_{diff}) as a result of differences in the molecular diffusivity of the heavy and light isotopes moving in air. Isotope fractionation during the process of evaporation (α_{evap}) involves both equilibrium and kinetic isotope effects (Gat, 1996; Criss, 1999). At the air–water interface, equilibrium processes dominate, such that $\alpha_{\text{evap}} = \alpha_{\text{equil}} = R_{\text{L}}/R_{\text{V}}$, where R_{L} and R_{V} are the heavy to light isotope ratio (i.e. D/H , $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$) of liquid and vapour at the air–water interface. The isotope composition of the water vapour transported away from the air–water interface into the surrounding of unsaturated air is largely determined by the relative humidity (*h*) of the air mass and α_{diff} . Subsequent fractionation during condensation (α_{cond}), in the form of rain and/or dew events, are associated with equilibrium isotope effects where $\alpha_{\text{cond}} = \alpha_{\text{equil}} = R_{\text{L}}/R_{\text{V}}$ (Merlivat and Jouzel, 1979; Criss, 1999). The α_{equil} is approximately eight to ten times greater for H_2^{18}O than H_2^{16}O , depending on the surface temperature at the liquid–vapour interface, with $\alpha_{\text{equil}}^{\text{D}}/\alpha_{\text{equil}}^{\text{O}}$ increasing as surface temperature decreases (Majoube, 1971). In contrast, the kinetic isotope effect is greater for H_2^{16}O than H_2^{18}O , with the ratio of the α_{diff} less than one (Merlivat, 1978; Cappa *et al.*, 2003; Luz *et al.*, 2009). Taken together, these two fractionation events result in *d*-excess values for water vapour and precipitation that are largely a function of the temperature and humidity during evaporation and condensation (Figure 1).

We use the theoretical framework described in Figure 1 to evaluate the influence of forest canopy water vapour exchange on the isotope composition of near surface humidity. The physical processes determining α_{evap} , originally described for open bodies of water (Craig and Gordon, 1965), can also be used to describe fractionation during transpiration (α_{trans}):

$$\alpha_{\text{trans}} = \frac{R_{\text{liq}}}{R_{\text{trans}}} = \alpha_{\text{equil}} \left[a_{\text{diff}} \left(1 - \frac{w_{\text{a}}}{w_{\text{i}}} \right) + \frac{w_{\text{a}}}{w_{\text{i}}} \frac{R_{\text{atm}}}{R_{\text{trans}}} \right] \quad (1)$$

where R_{trans} , R_{liq} and R_{atm} are the heavy to light isotope ratio of transpired water vapour, liquid water at the site of evaporation and atmospheric water vapour; w_{a} and w_{i} are the molar concentrations of water (mol mol^{-1}) in the atmosphere and the leaf (Dongmann, 1974; Flanagan *et al.*, 1991; Farquhar and Cernusak, 2005). Because the water volume of a leaf is relatively small in relation to the daily transpiration flux, R_{trans} is often assumed to be equal to the isotope composition of water taken up by roots, that is, R_{trans} occurs

Figure 1. Climatic processes determining the covariation between ^{18}O and D in vapour (open symbols) and liquid water (closed symbols) via (1) equilibrium (blue arrows) and (2) kinetic fractionation (red arrow) events. Water vapour at the air-seawater interface (open triangle) is in isotopic equilibrium with surface water; with a d -excess determined by the temperature-dependent α_{equil} (blue dashed line). The d -excess of water vapour transported away from the air-seawater interface (red dashed line) is inversely related to relative humidity (h). The isotopic composition of subsequent precipitation depends on the temperature-dependent α_{equil} .

at isotopic steady state where R_{trans} is equal to the isotope composition of xylem water (R_{xylem}). Thus, Equation (1) was originally used to predict R_{liq} by substituting R_{xylem} for R_{trans} (Flanagan *et al.*, 1991; Farquhar and Cernusak, 2005). However, under naturally varying environmental conditions isotopic steady state transpiration is often not a valid assumption (Harwood *et al.*, 1998; Harwood *et al.*, 1999; Simonin *et al.* 2013), and therefore, we opt to use non-steady state conditions for the work we present here. If transpiration does not occur at isotopic steady state than we can use Equation (1) and the d -excess model described in Figure 1 to evaluate the influence of climate variability, specifically temperature and humidity, on the d -excess of the transpiration water (isoflux) for a given R_{atm} and R_{liq} as:

$$d\text{-excess} \approx \left[\frac{R_{\text{liq}} - a_{\text{equil}}^{\text{D}} R_{\text{atm}} \frac{w_a}{w_i}}{a_{\text{equil}}^{\text{D}} a_{\text{diff}}^{\text{D}} \left(1 - \frac{w_a}{w_i} \right)} \right] - 8 \cdot \left[\frac{R_{\text{liq}} - a_{\text{equil}}^{18\text{O}} R_{\text{atm}} \frac{w_a}{w_i}}{a_{\text{equil}}^{18\text{O}} a_{\text{diff}}^{18\text{O}} \left(1 - \frac{w_a}{w_i} \right)} \right] \quad (2)$$

A model sensitivity analysis of Equation (2) predicts that for a given w_a/w_i , or as depicted in Figure 1, h normalized to

the temperature of the evaporating surface, as temperature increases the d -excess of the transpiration isoflux is predicted to increase because of the temperature dependence of $\alpha_{\text{equil}}^{\text{D}}/\alpha_{\text{equil}}^{18\text{O}}$ (Figure 1, dashed blue line; Figure 2A). The opposite is true for humidity. If temperature is constant, as w_a/w_i increases, the d -excess of the transpiration isoflux is predicted to decrease (Figure 1, dashed red line; Figure 2B). Using Equation (2) to describe the isotope effects that occur during non-steady state transpiration, we predict that during the day as w_a/w_i decreases the d -excess of the transpiration isoflux should increase and have a positive forcing on the d -excess of near surface humidity (e.g. analogous to surface evaporation shown in Figure 1). Similarly, at night during a stable atmosphere, we predict that if average canopy leaf temperature approaches dew point temperature (i.e. w_a/w_i approaches 1) the canopy isoflux will approach equilibrium isotope exchange (Figure 1). Under this scenario, the

Figure 2. Results for the sensitivity analyses using a d -excess version of the Craig and Gordon evaporation model (Equation 2 in Theory section; δ_e is the ^{18}O and D in liquid water at the site of evaporation, δ_E is the ^{18}O and D in vapour). Leaf temperature and relative humidity, normalised to leaf temperature (i.e. w_a/w_i in equation 2), were varied independently, whereas other parameters were held constant; (A) Leaf temperatures varied by $\pm 25\%$ and $\pm 50\%$ from 18°C (i.e. 12, 18, 24, 30 and 36°C) values in parentheses represent the ratio of equilibrium fractionation factors for D and ^{18}O , i.e. $(\alpha_{\text{equil}}^{\text{D}} - 1)/(\alpha_{\text{equil}}^{18\text{O}} - 1)$, (B) w_a/w_i varied by $\pm 25\%$ and $\pm 50\%$ from 0.5 (i.e. 0.25, 0.375, 0.5, 0.625 and 0.75).

d -excess of the canopy isoflux will approach the d -excess of source water, analogous to equilibrium isotope exchange in Figure 1. How quickly the canopy isoflux approaches the d -excess of source water is dependent upon the leaf water residence time (Dongmann *et al.*, 1974; Farquhar and Cernusak, 2005):

$$\tau = \frac{W a_{\text{equil}} a_{\text{diff}}}{g w_i} \quad (3)$$

where W is leaf water content (mol m^{-2}), and g is total leaf surface conductance ($\text{mol m}^{-2} \text{s}^{-1}$). During this process of nighttime equilibration between leaves and the atmosphere, we predict that canopy water vapour exchange with the atmosphere will have a negative forcing on the d -excess of near surface humidity.

METHODS

Site description

The focus of this study was a mixed evergreen forest on a steep hillslope in coastal Mendocino County, in northern California where an intensive monitoring programme has been underway since 2007 (Salve *et al.* 2012). The site, referred to as Rivendell, is located in the Angelo Coast Range Reserve, on a north-facing, ~32 degree, unchanneled

slope ~12 km from the Pacific coast (Figure 3). The unchanneled slope drains a surface watershed area that is about 125 m long, with a maximum width of 40 m. The site extends from Elder Creek (at 392 masl) to 470 masl, close to the ridge-top. Across the Rivendell hillslope a thin-soil layer (up to ~0.50 m) blankets nearly vertically dipping argillite and a sandstone interbed along the eastern divide. The hillslope is forested and has a limited understory. There are more than 30 Douglas fir (*Pseudotsuga menziesii*) trees that are >25 m tall within or adjacent to the surface drainage area delineated in Figure 3, with some older trees >50 m tall. These mature conifers represent the majority of the leaf area on this hillslope and are separated by a variety of lower canopy trees [e.g. interior live oak (*Quercus wislizeni*), tanbark oak (*Notholithocarpus densiflorus*), madrone (*Arbutus menziesii*) and California bay laurel (*Umbellularia californica*)], creating a relatively densely vegetated hillslope. Some relatively young redwood trees (*Sequoia sempervirens*) are also present.

The Angelo Coast Range Reserve has a Mediterranean-type climate characterized by warm dry summers and cool wet winters. It receives on average 1900 mm of rain annually with little snow, and there is significant variability in total annual precipitation. The bulk of annual precipitation is restricted to a 5–6 month period beginning in October. Typically, in early October, daily average temperatures at

Figure 3. (A) Laser altimetry map of Elder Creek watershed derived from data collected by the National Centre for Airborne Laser Mapping. Vegetation within the watershed is coloured by canopy height (light green is brush and hardwoods, dark green is the taller conifers). Elsewhere, vegetation is filtered to reveal bare earth topography. Inset shows location of Elder Creek watershed within Northern California (B) Image of Elder Creek and (C) Rivendell Field Site. (D) Study site showing elevation contours (1 and 5 m intervals), the location of meteorological instruments (air temperature and relative humidity, surface soil temperature) and W1, W2, W3, W5, W6, W7, W10, W12, W13, W14, W15 and W16 are identifiers for the 12 wells. Level 1 corresponds with wells W1, W12 and W13; level 2 corresponds with wells W2, W3 and W13; level 3 corresponds with W10.

the site fluctuate around $\sim 10^{\circ}\text{C}$ and then decrease close to zero by the end of December, before increasing to $\sim 20^{\circ}\text{C}$ in early August. Daily fluctuations in temperature are much larger during the warm summer months than in the winter (Figure 4).

Forest Meteorology

Three microclimate stations were installed along the hillslope to monitor precipitation (TE525, Campbell Sci., Inc.), soil temperature (PST-55, Campbell Sci., Inc.), air temperature and relative humidity (Vaisala HMP45C-L, Campbell Sci., Inc.). An additional rain gauge was installed in an open meadow across from the site. The average annual rainfall among the three sites that monitored continuously throughout the 2010 water year (Meadow, Level 1 and Level 3) was 1729 mm. For the 2010 water year, interception at the forested sites along the hillslope likely caused average rainfall to be 26% less than was received at the meadow (Salve *et al.*, 2012). During dry periods, diurnal relative humidity fluctuations often exceeded 60% with the largest fluctuations occurring during the hotter summer months. At Level 1, which experienced the highest mean annual relative humidity of 82%, dew point temperature exceeded the measured air temperature for 2% of the 2010 water year (Figure 4). Shallow (0.05 m) soil temperatures tracked air temperatures closely (Figure 4) but were limited to smaller amplitude fluctuations.

Tree water use

Variation in tree water use was characterized by measuring xylem sap velocity by way of the heat ratio method (Burgess *et al.*, 2001). Sap velocity was measured at 1 m above the ground in the trunks of 26 trees at two radial depths in the sapwood (1.25 and 2.75 cm). The heat ratio sensors measure heat pulse velocity, which is subsequently converted to sap velocity by measuring the wood density and water content of the sapwood at the two radial depths where heat pulse velocity is measured (Burgess *et al.*, 2001). Additionally, we corrected sap velocity for variation in probe spacing by assuming zero sap flow during periods of low-wind speed, when relative humidity was between 92 and 95%, 3 h prior to sunrise and during periods of no rain between January and March when soil moisture was near the annual maximum using the method described in Burgess *et al.* (2001).

Water vapour stable isotopes

Diurnal variation in the H and O isotope composition of atmospheric water vapour was evaluated at three different locations in our field site using an isotope ratio infrared spectroscopy (IRIS) instrument (model L1102-i, Picarro Inc., Sunnyvale, CA, USA). Air was sampled continuously over a 24-hour-period at 21 min^{-1} from one, 10 and 50 m above the forest floor and solenoids were used to switch

Figure 4. Variation in site meteorology from October 2009 to January 2011. Relative humidity (%), air temperature ($^{\circ}\text{C}$), soil temperature ($^{\circ}\text{C}$) and the time when air temperatures reached dew point temperature. Meteorological variables were measured at three different locations (A) level 1 (B) level 2 and (C) level 3 (D) Precipitation. See Figure 3 for a description of levels 1–3.

between each sample inlet every 20 min. For all 20 min measurement periods, we discarded the first 5 min of sampling at each location to allow for flushing of the previous sample through the optical cell and tubing and to allow for dissipation of transient pressure variation because of switching between sampling locations. The IRIS instrument makes a measurement every 5–10 s, which we then converted to 1 min averages.

The IRIS instrument calculates the $\delta^{18}\text{O}$ and δD of water vapour from spectral absorbance in specific wavelengths. All measurements are expressed in per mil (‰) as:

$$\delta X = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \quad (4)$$

where X is either D or ^{18}O , R is the ratio of the heavy to light isotope (e.g. D/H or $^{18}\text{O}/^{16}\text{O}$) of the sample (R_{sample}) and standard [R_{standard} ; in this case vienna standard mean ocean water (V-SMOW)]. Two calibration standards bracketing the range of measured values were used to calibrate each instrument and to express the measured delta values relative to V-SMOW. The calibration standards were sent to the IRIS using a custom built standard delivery device described by Simonin *et al.* (2013). Additionally, measurements of $\delta^{18}\text{O}$ and δD by the IRIS show a concentration dependence that is instrument-specific. We used the standard delivery device to characterize the dependence of $\delta^{18}\text{O}$ and δD measurements on the concentration of water vapour across the range of concentrations observed during the measurement periods. To correct for concentration dependencies, we first linearly regressed the actual isotope ratios against the measured isotope ratios (determined by mass spectrometry) at a fixed concentration of 10 000–10 200 ppmv, and applied this calibration factor to all the data resulting in a partially corrected value. We then plotted the residual isotope error (actual minus partially corrected measured) against water vapour concentration, and we fit a polynomial to this relationship for each standard. We used these fitted equations (actual vs measured delta value and residual delta error vs concentration) to correct the sample measurements made during the evaluation.

In order to estimate the isotope composition of the overlying background air, we used a back trajectory analysis to identify the source area and climatic conditions at 20 m above the ocean from which the air masses entering our site originated. STILT, the Stochastic Time-Inverted Lagrangian Transport Model, uses an ensemble of back trajectories to estimate the source area of the air mass reaching the study site (Lin *et al.*, 2003). Back trajectories were run for a 72-hour period based on Trenberth (1998). These trajectories are computed using wind fields from the Eta Data Assimilation System (EDAS40) (Rogers *et al.* 1996). We constructed an empirical d -excess condition

over the source area using temperature and relative humidity data from North American Regional Reanalysis (Mesinger *et al.*, 2006) and the empirical model of Uemura *et al.* (2008). The range of d -excess values sampled by the ensemble of trajectories provides an estimate of uncertainty in the model prediction.

Liquid water stable isotope analyses

We evaluated diurnal variation in leaf and stem water for the tree species occurring at our site by collecting samples three times per day (morning, midday and afternoon), rapidly sealing them in water-tight vials and storing them in a cool, dark location until water could be extracted from each sample. We removed the water via cryogenic water distillation (Ehleringer *et al.*, 2000) and then subsequently analyzed each sample for its H and O isotope composition using an isotope ratio mass spectrometer (IRMS). We avoided analyzing any of our plant water samples on the IRIS instrument because many plants are known to possess secondary metabolites that, if distilled into the water sample, can cause spectral interferences that invalidate the isotope ratio data (see West *et al.*, 2010 and 2011 for a complete discussion). Soil and saprolite (see Salve *et al.*, 2012 for description of subsurface materials) water samples were taken around midday along a transect that started near the stream and ended on the south facing slope. Samples were taken at eight locations on the north-facing slope and four locations on the south-facing slope (Figure 3D). In May, subsurface water was sampled at 2 and 10 cm depths and then at one site a deeper core was drilled to 145 cm and samples collected about every 15 cm. In August, samples were collected to a depth of 100 cm, at about 8–10 cm intervals. At one location, a deeper core was taken to 110 cm and between 65 and 110 cm samples were collected about every 9 cm. As with the leaf samples, samples were placed in water-tight vials and stored in a cool, dark location until water could be extracted from each sample via cryogenic water distillation. All soil and saprolite water samples were analyzed for their H and O isotope composition on the IRIS instrument. A subset of these samples was analyzed on the IRMS for $\delta^{18}\text{O}$ to test for any interference from secondary compounds. Differences between the IRIS and IRMS ranged from 0.1–0.4‰.

Well water was sampled on the morning of 7 May and 25 August. Water samples were taken from well 1, 3 and 6 (Figure 3D). Samples were kept in water-tight vials and stored in a cool, dark location until analysis.

RESULTS

In May (spring) and August (summer), the d -excess of water in the unsaturated zone (i.e. bulk subsurface water, representing a combination of loosely bound and mobile

water pools extracted from the soil and saprolite – See methods section) was less than the d -excess of winter precipitation and ground water. Overall, the isotopic composition of water in the unsaturated zone fell to the right of the local meteoric water line, with the greatest difference between water in the unsaturated zone and precipitation occurring in August (Figure 5 and 6). The vertical structure in the d -excess of water in the unsaturated zone provides strong evidence that the evaporation affect detected in the isotope composition and d -excess is not limited to near surface water but can also influence the isotope composition of water at depth; in this case, the uppermost 50 cm of the soil profile. The isotope composition of water in the uppermost soil layers (averaged across 0–5 cm) was strongly coupled to topographic position. In May, the d -excess of the near surface soil water increased from the north slope near the stream, to the south slope, to the north slope near the ridge top (Figure 5A). Contrary to May, in August, near surface soil water on the south slope and the north slope near the ridge top showed the most negative d -excess values.

The stable isotope composition of xylem water fell within the range of δD and $\delta^{18}O$ values for precipitation at our site (Figure 6A and B). However, the d -excess of tree

Figure 5. Variation in the d -excess of water in the unsaturated zone at depth (cm) for (A) 6 May 2010 and (C) 24 August 2010. The average y -intercept of the local meteoric water line $\pm$ or -1 SD is shown by the solid and dotted lines. The d -excess of water at the soil surface as related to position in the watershed for (B) 6 May 2010 and (D) 24 August 2010 (Means $\pm$ SE).

Figure 6. The δD and $\delta^{18}O$ of precipitation, atmospheric water vapour, water in the unsaturated zone, tree xylem water, well water and modelled leaf water in equilibrium with atmospheric water vapour prior to dawn for 6 May 2010 (A) and 24 August 2010 (B). The solid line represents the local meteoric water line and the dashed line is the leaf-water evaporation line. The figure inserts are a close-up of the covariation between the δD and $\delta^{18}O$ of tree xylem water, water in the unsaturated zone and well water; the triangles represent the potential range of values that can occur through mixing of well water and water in the unsaturated zone.

xylem water was less than the d -excess of both precipitation and well water (Figure 7A and C) such that tree xylem water fell to the right of the local meteoric water line (Figure 6). Additionally, in both May and August the isotope composition of tree xylem water was bounded by the isotope composition of water in the unsaturated zone (which extends into the underlying saprolite), precipitation and well water (Figure 6 inserts), with the majority of the samples falling along an evaporation line between deeper rock moisture (*sensu* Salve, *et al.*, 2012) of the saprolite and the shallow evaporatively enriched soil moisture. Based on samples collected during this study, the observed pattern is consistent with isotope mass balance if subsurface water sources are the primary sources of plant water (Dawson and Simonin, 2011), and all reservoirs contributing to a tree's isotopic signature are accurately measured during the study period. The data therefore suggests that trees at our site rely upon a mixture of subsurface water sources. The d -excess of xylem water varied between the angiosperm trees (*A. menziesii*, *L. densiflorus*, *Q. agrifolia* and *U. californica*) and the

Figure 7. The d -excess of tree xylem water on (A, B) 6 May 2010 and (C, D) 24 August 2010 as related to position in the watershed (Means $\pm$ SD). The solid and dashed lines represent the d -excess of well water and the y -intercept of the local meteoric water line.

gymnosperm trees (both mature and sapling *P. menziesii*) in May with much less variation between individual trees during the August campaign. In May, two species hardwoods on the south-facing side had xylem water d -excess lower than the xylem water d -excess of trees located on the north-facing slope near the stream (Figure 7B). This small topographic pattern in the d -excess of tree xylem water suggests that, in May, trees on the south-facing slope relied to a greater degree on water sources that were more enriched in D and ^{18}O brought about by evaporation in the near surface soils layers than trees near the stream. In contrast to May, by August the d -excess of tree xylem water was not significantly different between the stream-side trees and those located on the south-facing slope (Figure 7D). Trees located near the ridge-top on the north-facing slope possessed a slightly lower xylem water d -excess than trees on the south-facing slope but were not different from trees nearest the stream (Figure 7D).

Not unlike tree xylem water and water in the unsaturated zone, the isotope composition of leaf water was enriched in δD and $\delta^{18}\text{O}$ relative to precipitation. Leaf water showed the lowest d -excess values of any water reservoir at our site falling much further off the local meteoric water line (LMWL) than tree xylem water and water in the unsaturated zone (Figure 6). The covariation between δD

and $\delta^{18}\text{O}$ of leaf water showed a linear pattern in enrichment along its own evaporation line, a pattern that has been observed for many other plant species (e.g. Cernusak *et al.*, 2002; Twining *et al.*, 2006)

Diurnal variation in the d -excess of atmospheric water vapour tracked diurnal variation in tree water use, air temperature and relative humidity during the May and August 2010 campaigns (Figure 8A and B). On 6 May, diurnal variation in the d -excess of atmospheric water vapour spanned $\sim 50\text{‰}$ range, air temperature varied between 1 and 20 $^{\circ}\text{C}$, and relative humidity between 12 and 91%. At sunrise, the d -excess of atmospheric water vapour was near 0‰ at both the 1 and 10 m heights (Figure 8A). Then, as transpiration and air temperature increased, and relative humidity decreased, the d -excess of atmospheric water vapour increased to an average midday maximum of 35‰ across all of the heights (Figure 8A, C and E). After midday, as transpiration and air temperature decreased, and relative humidity increased, the d -excess of atmospheric water decreased to a minimum of -10‰ at 1 and 10 m and -6 at 50 m, measured at 0342 h (Figure 8B). Across all three heights, $\delta^{18}\text{O}$ varied between a morning high of -12‰ and a midday low of -26‰ , whereas δD varied between a morning high of -90‰ and a midday low of -170‰ (Figure 9A and C). If we assume leaf temperature is approximately equal to air temperature (and for the dominant tree with needle leaves, *P. menziesii*, this would be true), then $(\alpha_{\text{equil}}^{\text{D}} - 1) / (\alpha_{\text{equil}}^{18\text{O}} - 1)$ varied between 9.5, when temperature was at its minimum, and 8.6 (Figure 8G), when temperature was at its maximum.

The diurnal pattern in air temperature, relative humidity and the isotope composition of atmospheric water vapour observed on the 24 August 2010 was similar to the 6 May 2010. However, air temperatures were greater in August (10–34 $^{\circ}\text{C}$) than May, and the d -excess of atmospheric water vapour at midday was approximately 50% lower than that observed during the 6th of May. Additionally, δD and $\delta^{18}\text{O}$ of atmospheric water vapour was higher at midday and varied over a narrower range in August than in May (Figure 9). Prior to dawn on the 24 August 2010, the d -excess of atmospheric water vapour at the 50 m height was higher (-2‰) than the d -excess at 1 m (-13‰) and 10 m (-14‰ ; Figure 6B). As transpiration and air temperature increased, and relative humidity decreased, the d -excess of atmospheric water vapour increased to an average midday maximum of 13‰ at 1 and 50 m, and 18‰ at 10 m (Figure 8B, D and F). After midday, as transpiration and air temperature decreased, and relative humidity increased, the d -excess of atmospheric water decreased to a minimum of -6.5‰ at 50 m and -17‰ at 1 and 10 m (Fig 8B, D and F). Again, assuming leaf temperature is approximately equal to air temperature the $(\alpha_{\text{equil}}^{\text{D}} - 1) / (\alpha_{\text{equil}}^{18\text{O}} - 1)$ varied from 9, when temperature was at its minimum, to 8 (Figure 6G), when temperature was at its maximum. Across all three

Figure 8. Diurnal variation in tree water use (Means $\pm$ SD), the d -excess of atmospheric humidity, air temperature, relative humidity (%) and the equilibrium fractionation factor ($\alpha_{\text{equil}} - 1$) expressed as the ratio of D to ^{18}O measured at 1, 10, and 50 m above the soil surface (white, dark grey and black circles) on the 6–7 May 2010 (A, C, E and G) and the 24–25 August 2010 (B, D, F and H). The dark grey bars in A and B represent time when water vapour standards were sent to the isotope ratio infrared spectroscopy.

Figure 9. Diurnal variation in the δD and $\delta^{18}\text{O}$ of forest humidity measured at 1, 10 and 50 m above the soil surface (white, dark grey and black circles) on the 6–7 May 2010 (A, C) and the 24–25 August 2010 (B, D). The dark grey represent time when water vapour standards were sent to the isotope ratio infrared spectroscopy.

heights, $\delta^{18}\text{O}$ varied between a morning high of -12‰ and a midday low of -19‰ , whereas δD varied between a morning high of -118‰ and a midday low of -140‰ (Figure 9A and C).

The empirical model of Uemura *et al.* (2008) in combination with STILT showed large differences in the d -excess of ocean derived water vapour. The calculated d -excess of the background, ocean derived, near surface

water vapour differed between May (spring) and August (summer) campaigns and was different than the average d -excess observed for precipitation annually. On the 6–7 May, the average relative humidity at 20 m above the ocean surface was $74.6\% \pm 4.6$ with an average d -excess of $7.8\% \pm 3.9$. During the spring campaign, the model predicted d -excess of the near surface, ocean derived, water vapour was lower than the d -excess of precipitation averaged over 2008–2010 ($11.3\% \pm 3.6$). On average, the bulk of precipitation at our site occurs between October and March with relatively infrequent, minor, rain events occurring in April and May. In 2010, there were a few small rain events in May (105.6 mm total) with an average d -excess of $7.6\% \pm 2.4$. On the 24–25 August the average relative humidity at 20 m above the ocean surface was greater than May at $90.9\% \pm 0.62$ with an average d -excess of $-0.59\% \pm 2.5$. During the summer campaign, the model predicted d -excess of the near surface, ocean derived and water vapour was lower than the spring campaign and much lower than the annual average d -excess of precipitation ($-0.59\% \pm 2.5$; $7.8\% \pm 3.9$ and $11.3\% \pm 3.6$, respectively).

DISCUSSION

In coastal areas dominated by ocean-to-continental air mass trajectories, it is often assumed that during non-rainy periods the d -excess of atmospheric water vapour will be very close or equal to the average d -excess of ocean born storms unless: (1) there are drastic changes in ocean surface conditions between rainy and non-rainy periods, that is, temperature and relative humidity, as shown in Figure 1 or (2) there is a significant contribution of evapotranspiration to the isotope composition of atmospheric humidity (Gat, 2000; Lai and Ehleringer, 2011; Welp *et al.*, 2012). For the present investigation, we propose that unraveling the underlying reasons for the isotope patterns we observed requires that both mechanisms be evaluated as potential explanations for this mixed evergreen forest in the north coast of California.

In order to understand the relative influence of evapotranspiration on the isotope composition of near surface humidity, it is necessary to identify all the potential sources of moisture to the atmosphere. To accomplish this, we first used back trajectory analysis (i.e. STILT see methods) and the empirical model of Uemura *et al.* (2008) to estimate the d -excess of the background atmospheric water vapour (i.e. ocean derived vapour) into which terrestrial evapotranspiration mixes. The lower d -excess values of the background, ocean derived, near surface water vapour during the 24–25 August relative to the 6–7 May were associated with an increase in relative humidity above the ocean from $74.6\% \pm 4.6$ on 6–7 May to $90.9\% \pm 0.62$ on 24–25 August. The strong seasonal change in the d -excess of atmospheric water vapour

between the spring and summer sample periods suggests that in environments with distinct rainy and non-rainy seasons it cannot be assumed that the d -excess of water vapour is equal to the d -excess of precipitation especially during non-rainy periods. Additionally, the d -excess of atmospheric water vapour measured within and below the forest canopy was different from model predicted values for the near surface, ocean-derived water vapour. We, therefore, interpret the observed differences between the d -excess of water vapour within and below the forest canopy and the d -excess of ocean derived water vapour as providing strong evidence for non-isotopic steady state transpiration during the day, and equilibrium isotope effects between leaf water and ambient humidity at night, as the mechanisms driving variation in the isotope composition of near surface humidity at our site.

During spring and summer campaign, the d -excess showed a distinct diurnal pattern, increasing from pre-dawn to midday. In the early morning hours, as near surface temperatures increase due to an increase in incoming solar radiation, buoyant convection in combination with mechanical turbulence will result in a mixing of the background atmosphere into the forest canopy air (i.e. entrainment). This early morning mixing, that occurs as both transpiration and evaporation are at a minimum, is expected to cause a shift in the isotope composition of forest water vapour towards the isotope composition of the background water vapour. As predicted, the rapid increase in the d -excess of water vapour within and below the forest canopy towards the model predicted d -excess of the overlying air provides strong evidence for entrainment as one of the mechanism for changes in the d -excess of forest water vapour during these early morning hours. As the day progresses from late morning to midday, the d -excess of atmospheric water vapour within and below the forest canopy continued to increase as forest evapotranspiration increased. According to isotope mass balance, this further increase in the d -excess of water vapour cannot be explained by entrainment because the d -excess of forest water vapour exceeds the d -excess of the background, overlying ocean-derived air. Because forest water vapour is ultimately a mixture of water evaporated from both ocean and terrestrial water sources any increases above the d -excess of ocean derived water vapour must be associated with a greater contribution of terrestrial water sources, in this case transpiration and soil evaporation.

Previous research aimed at describing the influence of terrestrial evaporation on the isotope hydrologic cycle generally start with the assumption that transpiration, unlike soil evaporation and surface evaporation from open bodies of water, occurs at isotopic steady state (e.g. Williams *et al.* 2004; Jasechko *et al.* 2013). At isotopic steady state, the isotope composition of transpiration is equal to the isotope composition of xylem water (Gat, 1996; Gat, 2000). However, recent lab-based and field-based evaluations of

the isotope composition of transpiration at the leaf level suggest that under naturally occurring conditions the rate of change in abiotic and biotic fractionation events that occur during transpiration (e.g. Equation 2) are likely greater than leaf water residence times and thus preclude isotopic steady state transpiration (Wang and Yakir, 1995; Harwood *et al.*, 1998, 1999; Simonin *et al.*, 2013). Our observations of tree water use (as measured by sapflow) and the isotope composition of both near surface ocean derived water vapour and humidity within the forest canopy provide further evidence that transpiration is generally not at isotopic steady state. If transpiration did occur at isotopic steady state, then the d -excess of atmospheric water vapour should move in the direction of the d -excess of tree xylem water as the relative contribution of transpiration to atmospheric humidity increases from early morning to midday.

Because the d -excess of tree xylem water at our site was less than the average d -excess of precipitation (i.e. fell to the right of the LMWL; Figure 6), isotopic steady state transpiration should result in a negative relationship between solar radiation, atmospheric demand and the d -excess of atmospheric water vapour over a diurnal cycle, such that during the day atmospheric water vapour would lie to the right of the LMWL. In other words, isotopic steady state transpiration would have a negative forcing on the d -excess of near surface humidity with the d -excess of forest water vapour at its minimum when transpiration is at its maximum. Clearly, this pattern of variation in the d -excess of atmospheric water vapour was not observed at our site (Figure 8). Instead, we found that the d -excess of atmospheric water vapour during the day was greater than the average d -excess of precipitation, with the maximum d -excess of atmospheric water vapour occurring when transpiration was at its maximum, and the minimum d -excess occurring when transpiration was at its minimum (Figure 8). The observed correlation between the d -excess of near surface humidity and tree water use suggest that day-time transpiration is rarely at isotopic steady state at the ecosystem scale, when measured at high-temporal frequencies. Previous research evaluating changes in the isotope composition of forest water vapour integrated over longer time scales (e.g. 15–20 min) also suggests forest transpiration is generally not occurring at isotopic steady state (Lai *et al.*, 2006; Lai and Ehleringer, 2011). That said, when integrated over even longer periods, the isotope composition of water leaving the forest canopy should equal the isotope composition of water taken up by roots. The question that remains to be adequately answered is what that time-frame is. Our data do not allow us to answer this question.

If transpiration does not occur at isotopic steady state then the d -excess of transpiration should be negatively related to relative humidity as predicted by Equation (2) (Figure 2B). For both May and August campaigns, the d -excess of atmospheric water vapour was positively

correlated with variation in air temperature and negatively correlated with variation in relative humidity (Figure 8); a pattern observed previously in other terrestrial ecosystems (Welp *et al.*, 2012). According to the Craig and Gordon model for evaporation (2) increasing temperature should increase the d -excess of the evaporative flux because of a decrease in $(\alpha_{\text{equil}}^D - 1) / (\alpha_{\text{equil}}^{18\text{O}} - 1)$. However, variation in temperature is expected to have a relatively minor effect on the d -excess of the evaporation flux when compared with relative humidity (e.g. Figure 2A and B). Instead, the large diurnal variation in d -excess was likely more closely associated with changes in relative humidity than temperature.

Despite a similar range of magnitude in transpiration and relative humidity, the d -excess of forest water vapour was higher in May than August. This was likely a result of two different factors. Firstly, absolute humidity was lower in May than August as shown by the lower air temperature for a given relative humidity, resulting in a higher mixing ratio of transpiration with background air. Secondly, the d -excess of the background ocean derived water vapour was lower in August than May. It's also important to note that transpiration is not the only terrestrial source of water vapour at our site. As such, an alternative hypothesis for the positive relationship between d -excess, air temperature and relative humidity could be that soil evaporation contributes more to forest evapotranspiration than tree transpiration. However, because of the large amount of leaf area and the north-facing aspect, we do not believe this is a likely scenario at our site. A large amount of leaf area and a north-facing aspect will greatly reduce the amount of solar radiation reaching the soil surface resulting in a decrease in potential evaporation from soils.

In addition to the daytime processes discussed previously, we propose that the nighttime variation in the isotope composition of atmospheric humidity was largely a function of equilibrium isotope interactions between the forest canopy and the atmosphere that dominate during periods of high-relative humidity when there is little to no transpiration. When considering the nighttime contribution of plants to atmospheric humidity, it is important to note that mass flux and isoflux are not the same. At night when the atmosphere stabilizes, if the average canopy leaf temperature approaches T_{dew} , the vapour pressure difference between the leaf and the atmosphere (i.e. the driving force for transpiration) approaches zero resulting in no net loss of water vapour from the canopy. However, differences between the isotope compositions of water vapour inside the leaf and the atmospheric vapour may still exist, which would result in equilibrium isotope exchange between leaf water and atmospheric humidity, if nighttime stomatal conductance is >0 . In other words, there can be a net flow of different water isotopologues even if there is no measureable (net) flow of total water molecules from canopy to atmosphere.

If nighttime equilibration between forest canopy leaf water and atmospheric humidity is occurring, then we can predict the isotope composition of leaf water using the equilibrium fractionation factor and the measured isotopic composition of vapour. On 6 May and 24 August, the nighttime air temperatures approached T_{dew} , a requirement for equilibration between the canopy leaf water and the atmosphere. Assuming the average canopy leaf temperature is also near T_{dew} prior to dawn then, we can model the isotope composition of leaf water from the isotope composition of atmospheric humidity (i.e. R_V) as $\alpha_{\text{equil}} = R_{\text{leaf}}/R_V$. If nighttime stomatal conductance and the duration of equilibrium isotope exchange results in the complete turnover of leaf water (Kim and Lee, 2011; Lai and Ehleringer, 2011) then the predicted R_{leaf} should lie on the leaf water enrichment line as the minimum leaf water enrichment achieved over a 24-hour period (Landais *et al.*, 2006). As shown in Figure 6A and B, the α_{equil} -predicted leaf water lies very close to the leaf water enrichment line. Therefore, the α_{equil} -predicted leaf water provides strong evidence that the changes in the $\delta^{18}\text{O}$, δD and the d -excess of atmospheric water vapour that occur as the atmosphere stabilizes and subsides are the result of nighttime equilibration between leaves and atmosphere. Previous research using artificially induced conditions has provided strong evidence for nighttime equilibration between leaf water and water vapour (Kim and Lee, 2011). Here, we show under naturally occurring conditions that nighttime equilibration between leaf water and atmospheric water vapour can occur at the canopy and perhaps even the ecosystem scale. These observed nighttime effects of forest canopies on the isotope composition of atmospheric water vapour, when relative humidities approach 100%, will directly influence the water isotope composition of dew and/or radiation fog and by extension the isotope composition of near surface soil water. For example, on the north-facing slope close to the stream the near surface soil water, in May, was as isotopically enriched in $\delta^{18}\text{O}$ and δD as surface soils on the south-facing slope (Figure 7). Because south-facing slopes in the northern hemisphere receive more energy to drive soil evaporation than north-facing slopes do, isotope theory predicts that all else being equal the surface soil water on the south slope should be more isotopically enriched in ^{18}O and D than surface soils on the north-facing slope, in response to greater soil evaporation. However, if nighttime stomatal conductance is >0 and leaf temperature approaches dew point temperature, then the daytime evaporatively enriched leaf water signal could enter the surface soil water reservoir as dew drip from leaf surfaces during the process of equilibrium isotope exchange as leaf water turns over. Air temperatures on the north-facing slope near the stream reached dew point temperature on a regular basis during the early spring, whereas other areas in the watershed remained above dew point (Figure 4). Thus, we propose that the enrichment of

^{18}O , D and the d -excess of surface soil water near the stream was the result of dew formation that occurred as leaf water and atmospheric water vapour were equilibrating. Because nighttime stomatal conductance is relatively common among woody plants (Dawson *et al.*, 2007), nighttime equilibration between leaf water and atmospheric water vapour may be a common phenomenon across woody ecosystems. Nighttime equilibration followed by the formation of dew and/or radiation fog may represent another pathway by which water is redistributed in any ecosystem other than just via root systems (e.g. hydraulic redistribution; see Prieto *et al.*, 2012 and Neumann and Cardon, 2012 for recent reviews).

CONCLUSION

Stable isotopes have proven to be a powerful tool for monitoring changes in terrestrial water cycling across large spatial and temporal scales. Here, we highlight the utility of the d -excess parameter for characterizing the influence of forest canopies on the isotope composition of near surface water vapour. Our data provides strong evidence that during the day forest canopies significantly alter the isotope composition of atmospheric humidity via non-steady state isotope effects (i.e. isotopic non-steady state transpiration). Additionally, our data provides strong evidence that nighttime variation in the isotope composition of atmospheric humidity is strongly influenced by equilibrium isotope interactions between the forest canopy and the atmosphere that occur during periods of high relative humidity when there is little to no transpiration. These observed daytime and nighttime effects of forest canopies on the isotopic composition of atmospheric water vapour may have profound effects on the isotope composition of future condensation events.

ACKNOWLEDGEMENTS

This work was supported by a grant from the Keck Foundation (HydroWatch), the National Centre for Earth-Surface Dynamics and the UC Berkeley Centre for Stable Isotope Biogeochemistry. The topographic map was derived from data provided to Mary Power (University of California, Berkeley) by the National Centre for Airborne Laser Mapping. Daniella Rempe was supported in part by the Department of Energy Office of Science Graduate Fellowship Program (DOE SCGF), made possible in part by the American Recovery and Reinvestment Act of 2009 administered by ORISE-ORAU under contract DE-AC05-06OR23100. Jasper Oshun was supported by National Science Foundation CMG Collaborative Research project. Much of the monitoring infrastructure was installed by Rohit Salve.

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