

# Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the $\delta^{18}\text{O}$ of water vapour in Pacific Northwest coniferous forests

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## ABSTRACT

Changes in the  $^2\text{H}$  and  $^{18}\text{O}$  of atmospheric water vapour provide information for integrating aspects of gas exchange within forest canopies. In this study, we show that diurnal fluctuations in the oxygen isotope ratio ( $\delta^{18}\text{O}$ ) as high as 4‰ were observed for water vapour ( $\delta^{18}\text{O}_{\text{vp}}$ ) above and within an old-growth coniferous forest in the Pacific Northwest region of the United States. Values of  $\delta^{18}\text{O}_{\text{vp}}$  decreased in the morning, reached a minimum at midday, and recovered to early-morning values in the late afternoon, creating a nearly symmetrical diurnal pattern for two consecutive summer days. A mass balance budget was derived and assessed for the  $^{18}\text{O}$  of canopy water vapour over a 2-d period by considering the  $^{18}\text{O}$ -isoflux of canopy transpiration, soil evaporation and the air entering the canopy column. The budget was used to address two questions: (1) do  $\delta^{18}\text{O}$  values of canopy water vapour reflect the biospheric influence, or are such signals swamped by atmospheric mixing? and (2) what mechanisms drive temporal variations of  $\delta^{18}\text{O}_{\text{vp}}$ ? Model calculations show that the entry of air into the canopy column resulted in an isotopically depleted  $^{18}\text{O}$ -isoflux in the morning of day 1, causing values of  $\delta^{18}\text{O}_{\text{vp}}$  to decrease. An isotopically enriched  $^{18}\text{O}$ -isoflux resulting from transpiration then offset this decreased  $\delta^{18}\text{O}_{\text{vp}}$  later during the day. Contributions of  $^{18}\text{O}$ -isoflux from soil evaporation were relatively small on day 1 but were more significant on day 2, despite the small  $\text{H}_2^{16}\text{O}$  fluxes. From measurements of leaf water volume and sapflux, we determined the turnover time of leaf water in the needles of Douglas-fir trees as  $\approx 11$  h at midday. Such an extended turnover time suggests that transpiration may not have occurred at the commonly assumed isotopic steady state. We tested a non-steady state model for predicting  $\delta^{18}\text{O}$  of leaf water. Our model calculations show that assuming isotopic steady state increased isoflux of transpiration. The impact of this increase on the modelled  $\delta^{18}\text{O}_{\text{vp}}$  was clearly detectable, suggesting the importance of considering isoto-

pic non-steady state of transpiration in studies of forest  $^{18}\text{O}$  water balance.

*Key-words:* biosphere–atmosphere exchange; canopy water budget; Craig–Gordon enrichment; eddy covariance; evapotranspiration; isoflux; oxygen isotopes.

## INTRODUCTION

Carbon dioxide and water vapour exchange of coniferous forests in the Pacific Northwest are affected by ecosystem water balance in two ways: (1) stomatal limitation of photosynthesis and transpiration (Anthoni, Law & Unsworth 1999; Bauerle *et al.* 1999; Chen *et al.* 2002; Irvine *et al.* 2002; Fessenden & Ehleringer 2003; Unsworth *et al.* 2004) and (2) soil moisture constraints on below-ground respiration (Law, Baldocchi & Anthoni 1999; Law, Ryan & Anthoni 1999; Irvine *et al.* 2002). Stomatal conductances are sensitive to increasing vapour pressure deficit (VPD) in Pacific Northwest forests, regardless of stand age (Chen *et al.* 2002; B. Bond, unpublished data). Given that the regional climates of much of the Pacific Northwest are characterized by a summer drought period, limited moisture availability may significantly reduce forest productivity. Although hydraulic redistribution of soil moisture has been suggested to at least partially offset the limitation on overstorey gas exchange caused by drought in some of these forest ecosystems (Brooks *et al.* 2002), its impact on total transpiration is small. An improved knowledge of soil–plant water transfer is therefore important to advance our understanding of carbon assimilation and storage within these forest ecosystems.

Oxygen isotopes ( $^{18}\text{O}/^{16}\text{O}$ ) at natural abundance levels are useful tracers for studying carbon and water transport within terrestrial ecosystems because of the distinct isotopic signatures presented by water in the soil and overstorey foliage (Yakir & Sternberg 2000). Figure 1 shows a schematic illustration of the oxygen isotope ratio ( $\delta^{18}\text{O}$ ) of major water pools within a forest. While there is no fractionation against  $^{18}\text{O}$  during plant water uptake (Ehleringer & Dawson 1992), the light isotope ( $^{16}\text{O}$ ) is more readily transpired through stomatal apertures. Consequently,  $\delta^{18}\text{O}$

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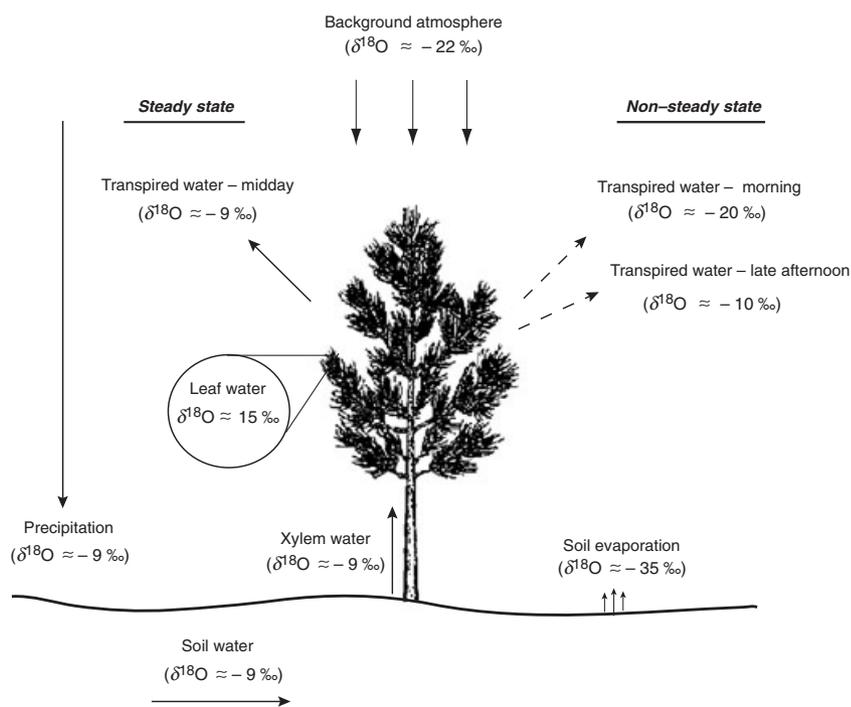
in leaf water become  $^{18}\text{O}$  enriched relative to xylem (soil) water (Dongmann *et al.* 1974; Flanagan, Comstock & Ehleringer 1991). Distinction in the  $\delta^{18}\text{O}$  of water fluxes from foliage and soil water establishes the basis for using  $\delta^{18}\text{O}$  to partition canopy fluxes for net ecosystem exchange (Yakir & Wang 1996) and above- and below-ground fluxes (Mortazavi & Chanton 2002; Bowling *et al.* 2003).  $\delta^{18}\text{O}$  is also widely used for studying plant-water relations and water transfer within terrestrial ecosystems (Farquhar, Ehleringer & Hubick 1989; Flanagan *et al.* 1991). Typically a simple two-part mixing model has been applied to determine plant water sources when distinct sources are isotopically identifiable (e.g. precipitation versus ground water, fog versus surface water) (Ehleringer *et al.* 1991; Dawson 1993; Ehleringer, Schwinning & Gebauer 1999; Williams & Ehleringer 2000).

Of the water pools within an ecosystem,  $\delta^{18}\text{O}$  in water vapour is perhaps the least investigated. Atmospheric water vapour is expected to be depleted of  $^{18}\text{O}$  relative to the source water. Two possible fractionation processes contribute to this difference: (1) an equilibrium fractionation between liquid and vapour water under saturation conditions and (2) a kinetic fractionation resulting from the diffusional difference between  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{16}\text{O}$ . The oxygen isotope ratio of water vapour ( $\delta^{18}\text{O}_{\text{vp}}$ ) measured in the canopy boundary layer should represent an integration of both surface evapotranspiration (ET) and background water vapour in the regional air mass (Fig. 1). Using measurements over an irrigated rice crop, Brunel *et al.* (1992) showed that observed oxygen and hydrogen isotope composition of water vapour were controlled by both regional air circulation and local evapotranspiration. In tall closed forests where transpiration dominates ET, values of  $\delta^{18}\text{O}_{\text{vp}}$

are expected to reflect primarily a balance between transpired water and the air entering the canopy column from the atmosphere above (Moreira *et al.* 1997).

Measurements of  $\delta^{18}\text{O}_{\text{vp}}$  are critical to the prediction of evaporative enrichment of surface water pools (i.e. lakes, leaf and soil surface water) (Craig & Gordon 1965; Flanagan *et al.* 1991; Yakir *et al.* 1994; Roden & Ehleringer 1999). In addition, diurnal variations in the observed  $\delta^{18}\text{O}_{\text{vp}}$  within forest canopies may provide insight into the effect of biospheric  $\text{H}_2\text{O}$  fluxes on the atmosphere. For instance, using  $\delta^{18}\text{O}$  measurements of canopy vapour, previous studies found that plant transpiration dominated isotope ratios of local evapotranspiration (Moreira *et al.* 1997; Harwood *et al.* 1999; Yepez *et al.* 2003; Williams *et al.* 2004).

Oxygen isotopes have been used to partition evapotranspiration fluxes into component contributions from plant transpiration and soil evaporation in humid (Moreira *et al.* 1997) and semiarid (Yepez *et al.* 2003; Williams *et al.* 2004) environments. Three isotopic approaches have been developed to partition ET by using  $^{18}\text{O}$  as a tracer: gradient, isotopic mass balance and steady state/mixing. Yakir & Wang (1996) estimated transpiration rate in a wheat field by measuring the gradients in the concentration and the  $\delta^{18}\text{O}_{\text{vp}}$  (also see Wang & Yakir 2000). Hsieh *et al.* (1998) showed that measurements of  $\delta^{18}\text{O}$  in soil water and precipitation, when combined with measurements of precipitation and soil moisture content, could be used to partition ET into transpiration and evaporation by using a simple isotopic mass balance approach. Ferretti *et al.* (2003) confirmed the utility of such an approach in a mixed  $\text{C}_3/\text{C}_4$  grassland. The steady state/mixing approach depends on measuring concentrations and the  $\delta^{18}\text{O}_{\text{vp}}$  at multiple heights within the canopy to determine  $\delta^{18}\text{O}$  values of the total ET



**Figure 1.** A schematic illustration of oxygen isotope ratios in major water pools of a forest. Values of the oxygen isotope ratio ( $\delta^{18}\text{O}$ ) are approximations for a site located near the coast of the Pacific Northwest in the United States. The  $\delta^{18}\text{O}$  values of transpired water depend on the condition under which water transferred from a leaf to the atmosphere.

flux using a linear mixing model (Moreira *et al.* 1997). Transient  $\delta^{18}\text{O}$  signatures of water fluxes from various ecosystem water pools may limit the application of the latter approach in forests where transpiration of large trees may not rapidly approach a steady state, a critical assumption that is not always achieved in natural conditions (Flanagan, Marshall & Ehleringer 1993).

Isotopic steady state requires that the  $\delta^{18}\text{O}$  of transpired water ( $\delta^{18}\text{O}_T$ ) equal that of source water (Flanagan *et al.* 1991; Yakir 1992). Nevertheless, transpiration at isotopic non-steady state does not assure such a requirement (Fig. 1). Direct  $\delta^{18}\text{O}$  measurements of leaf-transpired water are rare. Harwood *et al.* (1999) measured  $\delta^{18}\text{O}_T$  from leaves within an oak forest using a leaf cuvette. They showed that averaged  $\delta^{18}\text{O}_T$  values equal that of source water, indicating that leaf-transpiration signal was close to an isotopic steady state when integrated over many hours (e.g. 1 d). When individual  $\delta^{18}\text{O}_T$  values were examined, they found a negative correlation with VPD. Harwood *et al.*'s (1999) study suggests that instantaneous  $\delta^{18}\text{O}_T$  values are more variable, particularly when environmental conditions change rapidly. According to Flanagan *et al.* (1991), the isotope ratio of water transpired by a leaf ( $R_T$ ) could be modelled (see their eqn 5) by Eqn 1:

$$R_T = \frac{\left(\frac{R_w}{\alpha^*} e_i - R_a e_a\right)}{\alpha_k (e_i - e_a)} \quad (1)$$

where  $\alpha^*$  and  $\alpha_k$  are the isotope fractionation factors associated with the equilibrium effect between vapour and liquid water and the kinetic effects for diffusion through the stomatal pore, respectively,  $R_w$  is the molar ratio of the heavy to light isotopes of liquid water at the sites of evaporation,  $R_a$  is the molar ratio of the heavy to light isotopes of water vapour,  $e$  is the partial pressure of water vapour and the subscripts  $i$  and  $a$  refer to the leaf intercellular air space and ambient air, respectively. A list of symbols used in the current study is presented in Appendix A. In delta notation, the oxygen isotope ratio of transpired water is expressed as:

$$\delta^{18}\text{O}_T = \left(\frac{R_T}{R_{\text{smow}}} - 1\right) \cdot 1000 \quad (2)$$

where  $R_{\text{smow}}$  is the standard molar ratio of oxygen isotope on the standard mean ocean water (SMOW) scale (= 0.0020052). A recent work by Cappa *et al.* (2003) suggested a revised value of  $\alpha_k = 1.032$  for oxygen from the original value (1.0285) reported by Merlivat (1978). Values of  $\alpha^*$  were dependent on temperature and were calculated based on Majoube (1971). Equation 1 can also be used to predict  $\delta^{18}\text{O}$  of soil evaporation (Moreira *et al.* 1997). In this case, values of  $R_w$  refer to the liquid water where evaporation occurs in the soil.

Understanding the  $^{18}\text{O}$  value of leaf water is essential for isotope-flux analyses. To predict  $\delta^{18}\text{O}_T$ , the isotope ratio of leaf water at sites of evaporation ( $R_e$ ) is needed. By assuming an isotopic steady state,  $R_T$  is equal to the isotope ratio

of source water, and Eqn 1 can be rearranged to derive an equation for isotopic enrichment during leaf transpiration (Dongmann *et al.* 1974; White 1983). Flanagan *et al.* (1991) used a similar approach but included a boundary-layer effect between leaf surface and the surrounding air to predict  $\delta^{18}\text{O}$  values of leaf water, given by Eqn 3:

$$R_e = \alpha^* \left[ \alpha_k R_x \left( \frac{e_i - e_s}{e_i} \right) + \alpha_{kb} R_x \left( \frac{e_s - e_a}{e_i} \right) + R_a \left( \frac{e_a}{e_i} \right) \right] \quad (3)$$

where  $\alpha_{kb}$  is the kinetic isotope fractionation factor associated with diffusion in the boundary layer (= 1.021) (Cappa *et al.* 2003),  $R_x$  is the molar ratio of the heavy to light isotopes of xylem water and the subscript  $s$  refers to the leaf surface.

Many studies have reported observed  $\delta^{18}\text{O}$  values of bulk leaf water less enriched than Craig-Gordon steady state predictions (Dongmann *et al.* 1974; Leaney *et al.* 1985; Bariac *et al.* 1989; Walker *et al.* 1989; Flanagan & Ehleringer 1991; Yakir 1992; Roden & Ehleringer 1999), for which recent studies have suggested two possible explanations. The first is that the discrepancy between measured and steady-state predicted  $\delta^{18}\text{O}$  of leaf water is at least partially justified by the Péclet effect (Farquhar & Lloyd 1993; Barbour *et al.* 2000, 2004), which takes into account the opposite water flow between fractionated and non-fractionated water by diffusion and advection transport. The Péclet correction considers the mixing of various water pools within leaves (Yakir, DeNiro & Gat 1990; Yakir 1992; Gan *et al.* 2002; Farquhar & Gan 2003) that lowers the  $\delta^{18}\text{O}$  value compared to that at the sites of evaporation. Gan *et al.* (2002) used cotton leaves growing at different humidities to show that there were considerable spatial variations of leaf water enrichment within a leaf. They showed progressive  $\delta^{18}\text{O}$  enrichment in vein water along the direction of water flow. Helliker & Ehleringer (2000) also reported the progressive enrichment of leaf water in grasses. Recently, Farquhar & Gan (2003) developed a model incorporating both longitudinal and radial Péclet effects with the progressive enrichment along evaporating leaf cells.

The second explanation is that the assumption of steady state may not be valid in many field conditions following changes in humidity and leaf energy balance. The  $\delta^{18}\text{O}$  of leaf water could be in a transient state due to slower water turnover time within leaves than the environmental change. As a result, at any given time, observed  $\delta^{18}\text{O}$  of leaf water is no longer in equilibrium but is dependent on the  $\delta^{18}\text{O}$  value at the previous time step. Such a lag in response has been observed in natural conditions (Langendörfer *et al.* 2002). Previous studies have proposed models to address this issue (Dongmann *et al.* 1974; White 1983; Cernusak, Pate & Farquhar 2002; Farquhar & Cernusak 2005). Cuntz *et al.* (2003) incorporated the effects of lag into models for investigating global patterns of  $\delta^{18}\text{O}$  in atmospheric  $\text{CO}_2$ . A transient model that considers time-dependency of leaf water  $\delta^{18}\text{O}$  can be expressed as Eqn 4 (Dongmann *et al.* 1974):

$$\delta_{\text{en}}(t) = \delta_e(t) - [\delta_e(t) - \delta_{\text{en}}(t-1)] \exp\left(-\frac{\Delta t}{\tau_c}\right) \quad (4)$$

where  $\delta_{\text{en}}(t)$  and  $\delta_{\text{en}}(t-1)$  represent non-steady state oxygen isotope ratios of leaf water at the sites of evaporation at time  $t$  and  $t-1$ , respectively, with  $\Delta t$  being the time interval (Dongmann *et al.* 1974; Förstel *et al.* 1975; Farris & Strain 1978; Bariac *et al.* 1994; Cuntz *et al.* 2003).  $\delta_c(t)$  is the steady state oxygen isotope ratio of leaf water at time  $t$ , predicted by Eqn 3.  $\tau = W/T$  represents turnover time of leaf water, where  $W$  is the leaf water content on a leaf area basis and  $T$  is transpiration rate. In  $\zeta = \alpha^* \cdot \alpha_{\text{kv}} \cdot (1 - rh)$ ,  $rh$  is relative humidity and  $\alpha_{\text{kv}}$  is an effective kinetic fractionation factor of water vapour ( $\approx 0.974$ ) (Cuntz *et al.* 2003). Values of  $\tau$  can be directly estimated if measurements of leaf water volume and transpiration rate are available.

Very few studies have examined atmospheric vapour  $^{18}\text{O}$  budget in forest canopies. Given the interplay between evaporation, atmospheric mixing and transpiration, it is not clear how variable transpiration under isotopic non-steady state would affect  $\delta^{18}\text{O}$  of canopy water vapour. In this paper, we present diurnal measurements of  $\delta^{18}\text{O}$  in atmospheric water vapour for three summer days in coniferous forests in the Pacific Northwest region of the United States. Continuous measurements of  $\delta^{18}\text{O}_{\text{vp}}$  are labour intensive. We focus on a mechanistic understanding of the diurnal variation in  $\delta^{18}\text{O}_{\text{vp}}$  measured above and within canopies, addressing two questions: (1) do  $\delta^{18}\text{O}$  values of canopy water vapour reflect the biospheric impact (or are such signals swamped by atmospheric mixing)? and (2) what are the mechanisms that drive temporal variations of  $\delta^{18}\text{O}_{\text{vp}}$ ? We derive a mass balance equation for water vapour  $^{18}\text{O}$  within plant canopies. We then assess water vapour  $^{18}\text{O}$  budget with the aid of eddy covariance measurements to estimate transpiration and evaporation fluxes, and by principles of turbulent transport to estimate contributions from the uploft atmosphere. We use two classes of models (steady state versus non-steady state) to describe the  $\delta^{18}\text{O}$  of leaf water and compare their impacts on the  $\delta^{18}\text{O}_{\text{vp}}$  budget calculation.

## THEORY

### Oxygen isotope ratio of water vapour within a forest canopy

To derive a mass balance equation for  $^{18}\text{O}$  of atmospheric vapour inside a forest, we considered a column of air extending from the soil surface to some height above the canopy. Assuming horizontal advection of water vapour is negligible, the mass conservation of water vapour inside the canopy can be written as:

$$M_c \frac{dv_c}{dt} = F_+ - F_- + F_T + F_E \quad (5)$$

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 vapour in the column,  $F$  represents component fluxes,  $F_+$  is the one-way flux of water vapour entering the canopy,  $F_-$  is the flux of water vapour leaving the top of the canopy and  $F_T$  and  $F_E$  are fluxes of transpiration and evap-

oration, respectively. Here, our focus is the entire canopy air column and therefore, we assume the column is well-mixed during the day with respect to water vapour concentration. A mass balance equation can also be written for  $\text{H}_2^{18}\text{O}$ , as shown in Eqn 6.

$$M_c \frac{dR_c v_c}{dt} = R_+ F_+ - R_- F_- + R_T F_T + R_E F_E \quad (6)$$

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 above,  $R_-$  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. The oxygen isotope ratio of air leaving the top of the column may be different from the air at the bottom of the canopy. However, under well-mixed conditions, we can assume  $R_- = R_c$ . This assumption is analogous to the one made by Lloyd *et al.* (1996) in their derivation of the canopy  $\delta^{13}\text{C}$  budget. Multiplying Eqn 5 by  $R_c$  and subtracting from Eqn 6 we obtain:

$$M_c v_c \frac{dR_c}{dt} = (R_+ - R_c) F_+ + (R_T - R_c) F_T + (R_E - R_c) F_E. \quad (7)$$

Dividing by the isotope standard, we can rewrite Eqn 7 in  $\delta$  notation with a good approximation, as:

$$M_c v_c \frac{d\delta_c}{dt} = (\delta_+ - \delta_c) F_+ + (\delta_T - \delta_c) F_T + (\delta_E - \delta_c) F_E. \quad (8)$$

We have derived a mass balance equation to describe temporal variations of averaged atmospheric vapour  $\delta^{18}\text{O}$  within plant canopies ( $\delta_c$ ). Equation 8 can be solved for  $\delta_c$  if  $v_c$ ,  $\delta_+$ ,  $\delta_E$ ,  $\delta_T$ ,  $F_+$ ,  $F_T$  and  $F_E$  are all known. Values of  $\delta_T$  and  $\delta_E$  can be modelled using Eqn 1. In the current study, values of  $v_c$ ,  $F_T$  and  $F_E$  can be estimated from direct meteorological measurements of vapour concentration and water vapour fluxes. However, water vapour flux from the air above and its associated isotope ratio remain to be known.

### Estimates of one-way flux from the atmosphere above

One-way flux can be measured by the relaxed eddy accumulation method (Oncley *et al.* 1993). Using the formulation of a relaxed eddy accumulation, the net turbulent flux is given by Eqn 9:

$$F_{\text{net}} = \overline{w'v'} = \beta \sigma_w (v_+ - v_-) \quad (9)$$

where  $\beta$  is a constant that can be derived from the distribution of vertical wind fluctuation ( $w'$ ),  $v'$  is the deviation away from mean mole fraction of water vapour,  $\sigma_w$  is the standard deviation of the vertical velocity,  $v_+$  is the mean mole fraction of water vapour in all downdraft events (i.e. when  $w' < 0$ ), and  $v_-$  is the mean mole fraction of water vapour in the updraft events (i.e. when  $w' > 0$ ).

If we assume the mean scalar concentration probability distribution is symmetric (i.e. zero-skewness), the gross

fluxes in ( $F_+$ ) and out ( $F_-$ ) of the canopy can be given by Eqn 10:

$$\begin{aligned} F_+ &= \beta\sigma_w v_{\text{ref}} + \frac{F_{\text{net}}}{2} \\ F_- &= \beta\sigma_w v_{\text{ref}} - \frac{F_{\text{net}}}{2} \end{aligned} \quad (10)$$

where  $F_{\text{net}}$  is the net flux and  $v_{\text{ref}}$  represents a reference concentration. Notice that  $F_{\text{net}} = F_+ - F_-$  follows the definition of a net flux. Appendix B provides a full description of the assumptions made for deriving gross fluxes. On the basis of turbulent similarity theories (Stull 1988; Wesson, Katul & Lai 2001), we can derive an expression that directly relates incoming gross flux to the net flux:  $F_+ = 3.0F_{\text{net}}$  and  $F_+ = 2.1F_{\text{net}}$  on 30 and 31 July 2002, respectively. Day 2 (31 July) has a smaller incoming flux from the atmosphere above relative to the net flux, because of the smaller turbulent energy to move vapour (see Appendix B). These relationships allow us to estimate the one-way flux of water vapour entering the canopy air column by using direct measurements of eddy covariance systems and velocity statistics. Only  $F_+$  is needed in our calculation for  $\delta_c$  (see Eqn 8).

### Estimates of $F_T$ and $F_E$

Eddy covariance (EC) measurements were made both above- and below-canopies at the Wind River Canopy Crane Research Facility (WRCCRF) during our investigation period (Paw U *et al.* 2004). We used direct measurements from the below-canopy EC system to represent soil evaporation ( $F_E$ ). This may have slightly overestimated the contribution of soil evaporation because below-canopy EC measurements include transpiration from a portion of understory species. The EC system above the canopy measured total evapotranspiration. By subtracting below-canopy EC measurements, the difference represents overstory transpiration ( $F_T$ ). We note that the mass balance equation of water vapour (Eqn 1) assumes fair weather conditions (no precipitation). Hence, canopy interception and direct evaporation from wet leaf surfaces are not considered.

## MATERIALS AND METHODS

### Study site

Oxygen isotope measurements were collected in the summer of 2002 in an old-growth ( $\approx 500$  years old) coniferous forest in the southern Washington ( $45^\circ 49' \text{N}$ ,  $121^\circ 58' \text{W}$ ; elevation = 371 m), roughly 160 km from the Pacific coast (Shaw *et al.* 2004). The dominant overstory species are *Pseudotsuga menziesii* (Douglas-fir), *Tsuga heterophylla* (western hemlock) and *Thuja plicata* (western red cedar). There is a diverse group of understory species, which includes western hemlock, *Acer circinatum* (vine maple), *Abies amabilis* (Pacific Silver fir), and *Taxus brevifolia* (Pacific yew). The average tree height was 52 m for Douglas-fir and 19 m for western hemlock (Shaw *et al.* 2004). A

75-m-tall construction crane was installed in 1995, providing access to the upper canopy. This region is characterized by a maritime Pacific climate with dry summer and wet winter periods. The long-term mean annual temperature is  $8.7^\circ \text{C}$ , and mean annual precipitation in this region is 2467 mm with  $< 5\%$  falling between June and August; hence a significant decline in surface soil moisture occurs through the summer (Shaw *et al.* 2004). Stand leaf area index was estimated as 8.6, with  $\approx 56\%$  distributed in the middle and upper canopy (Thomas & Winner 2000). Soils were classified as sandy loams of volcanic origin. Further details on the climate, site description and canopy structure can be found elsewhere (Shaw *et al.* 2004); the information is also available online (<http://depts.washington.edu/wrccrf/>). In addition, oxygen isotopes, relative humidity, air temperature and sapflux were measured at a nearby young Douglas-fir forest (hereafter identified as the 'young stand'), which originated from clear-cutting followed by replanting. The average canopy height was 16 m in this 25-year-old forest.

### Meteorological measurements

The 30 min averages of air temperature ( $T_a$ ), relative humidity ( $rh$ ), wind speed and wind direction were measured at seven different heights (2, 10, 20, 40, 60, 70 and 80 m) in the old-growth stand. The mole fraction of water vapour was determined at different heights using  $T_a$  and  $rh$  measurements. Soil temperature at 0, 15 and 30 cm below ground and soil moisture content from 0 to 30 cm below ground were also logged at 30 min intervals. Air temperature and relative humidity were measured 30 m above ground in the young stand.

Two identical eddy covariance systems were mounted at 67 m on the crane tower and at 3 m, 35 m west of the tower. Vertical  $\text{H}_2\text{O}$  and  $\text{CO}_2$  exchange were calculated from the velocity vector, sonic temperature and the concentrations of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at 10 Hz, which were measured using Solent Gill HS 3-D sonic anemometers and fast-response LiCor 6262 infrared gas analysers (IRGAs) (Li-Cor, Lincoln, NE, USA). The IRGAs were located within 1 to 5 m of the sample orifice, with high flow rates of  $10 \text{ L min}^{-1}$  to minimize signal loss. The below-canopy eddy covariance system measured understory (3 m and below) and soil fluxes, and the above-canopy eddy covariance system measured fluxes in the ecosystem. Water vapour covariance exchange data were corrected for spectral drop-off and effects that Webb, Pearman & Leuning (1980) described, but both of these corrections were small, with relative magnitudes of only a few percent. Further details of the system can be found in Paw U *et al.* (2004).

### Sapflow and leaf water content measurements

We measured sapflow with constant-heat sapflow sensors (Granier 1987) following general procedures described in Phillips *et al.* (2002). Sensors (20 mm) were installed in the outer sapwood of 26 trees at the old-growth site and of nine

trees at the young site. Trees were selected to represent the range of species and size classes at each location. Measurements were recorded every 20 min and converted to half-hour increments through interpolation. Sapflux density is often different in the inner section of sapwood compared to the outermost sapwood. We estimated the radial variation in sapflow using an equation derived by Phillips *et al.* (2002) for Douglas-fir and by Moore *et al.* (2004) for western hemlock. We applied the algorithm for western hemlock to the other species (which tend to share many ecophysiological characteristics with hemlock, and in any event, contribute a relatively small proportion to total stand-level transpiration). From this we calculated the average sapflux per unit sapwood area for the different species and size classes and scaled to the stand level by multiplying this value by the sapwood basal area within that class.

Leaf water content was determined by measuring the difference between the fresh and the dry weight of the needles. For the old-growth Douglas-fir trees at the canopy crane, the average water content of the current age class of needles when they are fully turgid is 1.14 g water per gram dry weight of leaf. At a typical midday water potential of  $-2.6$  MPa, their relative water content is about 0.81, so the midday water content falls to about 0.93 g of water per gram dry weight of leaf. McDowell *et al.* (2002) reported a mean specific leaf area of foliage for the entire canopy of  $69 \text{ cm}^2 \text{ g}^{-1}$  at the canopy crane site and  $60 \text{ cm}^2 \text{ g}^{-1}$  at the young stand site, giving out a midday leaf water content of 7.49 and 8.61 mol water  $\text{m}^{-2}$  leaf area in the old-growth and young forests, respectively.

### Oxygen isotope measurements

Samples of various ecosystem water pools were collected for oxygen isotope ratio analyses, including atmospheric water vapour, xylem water, leaf water and soil water in the old-growth forest for two consecutive days, 30 and 31 July. A similar set of samples was also collected in the young forest on 1 August. Leaf water and atmospheric water vapour were collected as close as possible in time. Samples were stored in a dry-ice cooler while in the field and in a freezer upon returning to the laboratory before analyses.

#### Atmospheric water vapour

Atmospheric water vapour was cryogenically captured and analysed for oxygen isotope ratios using the sampling protocol described by Helliker *et al.* (2002). Canopy air was collected from three heights: 0.5, 20 and 60 m, representing the lower, middle and top portion of the canopy, respectively. Air from these heights was passed through sampling glass tubes placed in a dewar of crushed dry ice, allowing water vapour to condense on the inner walls of the glass tubing. The airflow rate was set at  $5 \text{ cc s}^{-1}$ . The sampling time was about 30 min, which was long enough to collect sufficient water volume ( $\geq 50 \mu\text{L}$ ) for isotope ratio analyses in the laboratory (Helliker *et al.* 2002), and was consistent with the averaging intervals of meteorological measurements.

#### Xylem, leaf and soil water

Xylem was collected by sampling small, non-green stems approximately 6 cm long and 5–7 mm in diameter, generally collected from three to five trees of each of the dominant overstorey species near the top of the canopy at each site. Stem and foliage samples were collected at least once in the morning (usually between 0800 and 1200 h). Foliage samples for leaf (needle) water analyses were collected from both the top of the canopy and mid-canopy heights, utilizing the same branch from which xylem water samples were collected. Both sets of samples were immediately placed in glass vials after collection, sealed with caps, wrapped with Parafilm (Pechiney Plastic Packaging, Menasha, WI, USA) and kept refrigerated or frozen until subsequent stable isotope ratio analyses. Soil samples were collected in general from the top 30 cm with a profile at 10 cm increments. A trench was excavated and soil samples were collected along the vertical sidewall of the trenches; as with xylem and leaf water collections, the samples were immediately stored in glass vials, wrapped with Parafilm and stored cold or frozen.

#### Stable isotope analyses

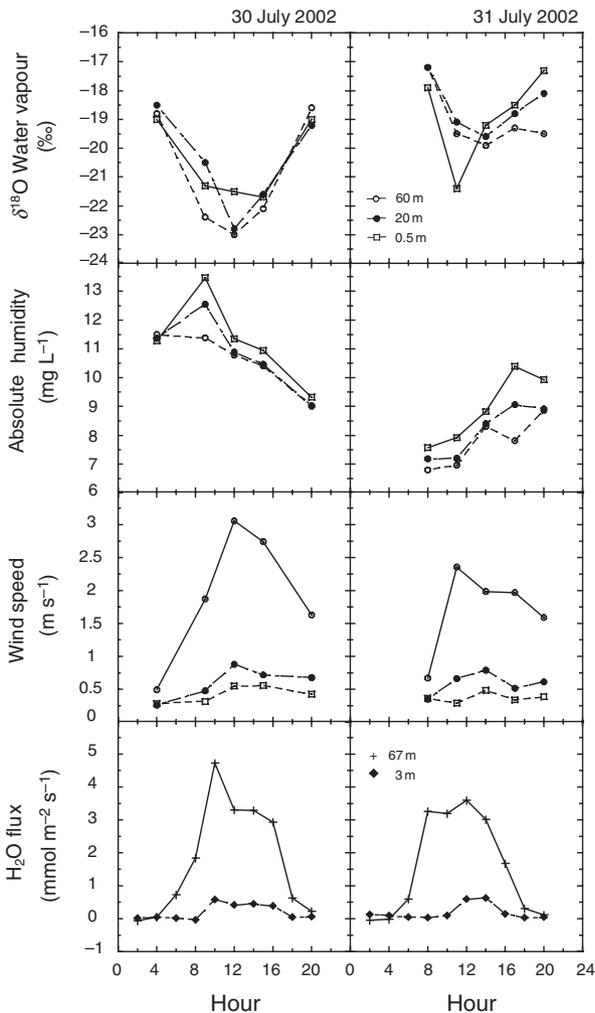
All of the water samples were extracted in the laboratory using a cryogenic vacuum distillation apparatus (Ehleringer, Roden & Dawson 2000). In order to measure the  $\delta^{18}\text{O}$  of water samples, the samples were equilibrated with  $\text{CO}_2$  (Compston & Epstein 1958). Samples were equilibrated with dilute  $\text{CO}_2$  ( $\text{CO}_2 : \text{N}_2 = 1:9$ ) for 48 h at  $25^\circ\text{C}$ . Batches of nine samples were calibrated against three working water standards during each analysis run by using an EA-CF-IRMS method described by Fessenden *et al.* (2002). Precision of the  $\delta^{18}\text{O}$  analyses is  $\pm 0.2\%$ . All observations were reported in delta notations, with  $\delta^{18}\text{O}$  values reported relative to V-SMOW (Coplen 1996).

## RESULTS

### Diurnal variations of $\delta^{18}\text{O}$ in canopy water vapour

The  $\delta^{18}\text{O}_{\text{vp}}$  measured within forest canopies represent an integrated signal from three major contributing sources: plant transpiration, ground evaporation and the mixing with the atmosphere above. We measured  $\delta^{18}\text{O}_{\text{vp}}$  profiles at three heights in the old-growth stand on two summer days in 2002 (Fig. 2). A large diurnal variation in  $\delta^{18}\text{O}_{\text{vp}}$ , exceeding 4‰ over the course of a day, was consistently detected at all heights on 30 July 2002. Values of  $\delta^{18}\text{O}_{\text{vp}}$  gradually decreased in the morning, and then increased almost symmetrically in the afternoon. This diurnal pattern was also observed the following day, although the overall  $\delta^{18}\text{O}_{\text{vp}}$  values were slightly more positive and the midday depletion was less pronounced.

Figure 2 also shows absolute humidity (air moisture content), ecosystem water fluxes measured by eddy covariance systems and wind speeds at multiple heights. An increase in air moisture content and a decrease in  $\delta^{18}\text{O}_{\text{vp}}$  values occurred concurrently during early morning hours (e.g.



**Figure 2.** Diurnal variations in the oxygen isotope ratio of water vapour, absolute humidity, wind speed and ecosystem water fluxes observed in the old-growth forest on two summer days in July 2002. Measurements from three different heights were shown for all variables. Ecosystem water fluxes were measured by an above- and a within-canopy eddy covariance system.

0400–0900 h on 30 July). This implied an accumulation of water inputs from transpiration which isotopically depleted water vapour within the canopy. However, the coupling between vapour concentration and  $\delta^{18}\text{O}_T$  values was not consistent. Values of  $\delta^{18}\text{O}_T$  maintained a decreasing trend from 0900 to 1200 h, but air moisture contents decreased at all heights during these hours. In the afternoon of 30 July, the negative correlation between values of  $\delta^{18}\text{O}_T$  and air moisture contents was resumed, with a decreasing vapour content and an increasing  $\delta^{18}\text{O}_T$  value. Such a negative correlation was consistent only for a portion of the day on 31 July. The daily mean values of  $\delta^{18}\text{O}_{vp}$  differed by  $\approx 2\%$  between the two days, with the second day values more positive than those of the first day (Fig. 2). The humidity also differed significantly between the two days.

Ecosystem water fluxes, measured by above-canopy and understory eddy covariance systems, indicated small contri-

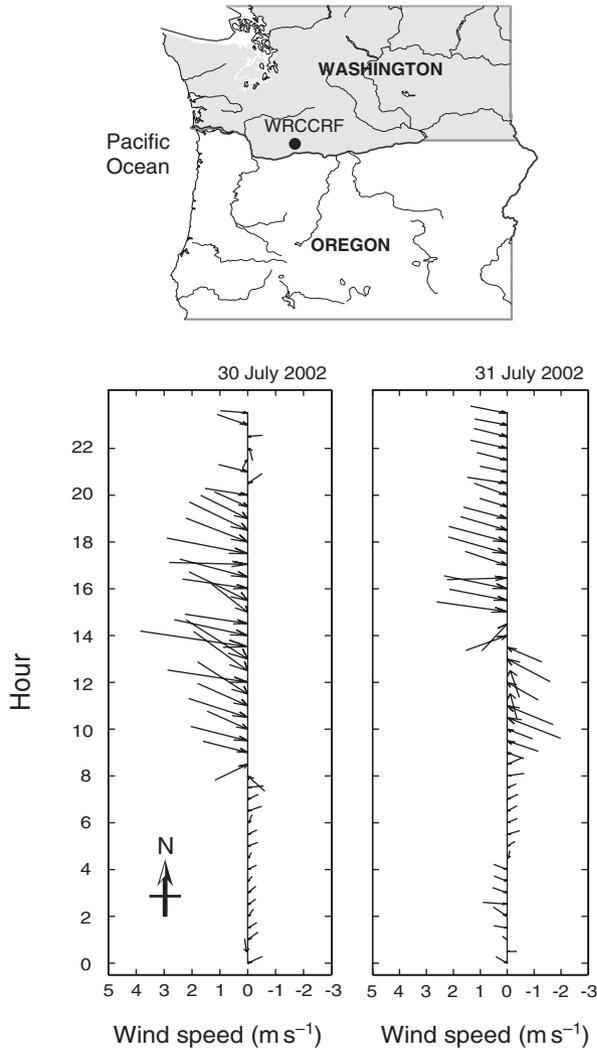
butions from understory species and soil evaporation. This is consistent with the notion that soil evaporation contributes a small proportion to the total ET because of the low radiation loads on the forest floor (Denmead 1984; Blanken *et al.* 1997). The difference between upper and lower eddy covariance measurements indicated overstory transpiration responsible for  $>85\%$  of total ET during these two days.

Values of  $\delta^{18}\text{O}_{vp}$  and wind speed at the top level appeared to be correlated. Mean wind speeds decreased inside the canopy, but the vertical mixing remained, as evidenced by the small vertical gradient of absolute humidity. The effect of wind on  $\delta^{18}\text{O}_{vp}$  was further examined by using wind direction data (Fig. 3); we assumed that the above canopy wind velocity was representative of the regional velocity field. Before dawn on the first day, a light easterly wind blew from inland towards the ocean but quickly shifted to a westerly wind after 0800 h. The dominant ocean-to-land wind continued the rest of the daylight hours. On the second day, the dominant wind was coming from the east until 1400 h, and then quickly shifted to the opposite direction. If our assumption is correct that tower-based wind measurements represented regional atmospheric patterns, we may expect a change in the  $\delta^{18}\text{O}$  of background atmospheric water vapour between air masses travelling towards inland or towards the ocean. Differences in the wind pattern during the morning hours may explain the 2‰ variation in the daily mean values of  $\delta^{18}\text{O}_{vp}$  and the contrasting pattern of air moisture contents between the two days. However, they did not provide a satisfactory explanation for the observed diurnal pattern in  $\delta^{18}\text{O}_{vp}$  both above and within the canopy (Fig. 2). Whether surface evapotranspiration could contribute to the observed diurnal pattern in  $\delta^{18}\text{O}_{vp}$  will be examined next.

### $\delta^{18}\text{O}$ of leaf water

To investigate effects of transpiration on the  $\delta^{18}\text{O}$  variation of canopy vapour, we first consider  $^{18}\text{O}$  enrichment of leaf water. Under steady state conditions,  $\delta^{18}\text{O}$  values of incoming and outgoing water are the same, and a Craig–Gordon type model (e.g. Eqn 3) is often used to predict  $\delta^{18}\text{O}$  of leaf water (Roden & Ehleringer 1999). We do not have diurnal measurements of leaf water  $\delta^{18}\text{O}$  in the old forest in spite of a crane available for accessing the canopy; it is costly and impractical to sample leaf water several times a day. However, the  $\delta^{18}\text{O}$  of water vapour, leaf water and xylem water were concurrently measured four times on 1 August 2002 in the young stand. The averaged  $\delta^{18}\text{O}$  value of xylem water was  $-10.3 \pm 0.6\%$  ( $n = 41$ ). Figure 4 shows VPD sap flux, and  $\delta^{18}\text{O}_{vp}$  values. We observed a 4‰ depletion of the  $\delta^{18}\text{O}_{vp}$  value in the young stand over a 10-h period. Leaf water  $\delta^{18}\text{O}$  was modelled using meteorological data every 20 min. At times when  $\delta^{18}\text{O}_{vp}$  was not measured,  $\delta^{18}\text{O}_{vp}$  values were interpolated for predicting leaf water  $\delta^{18}\text{O}$  based on measurements shown in Fig. 4.

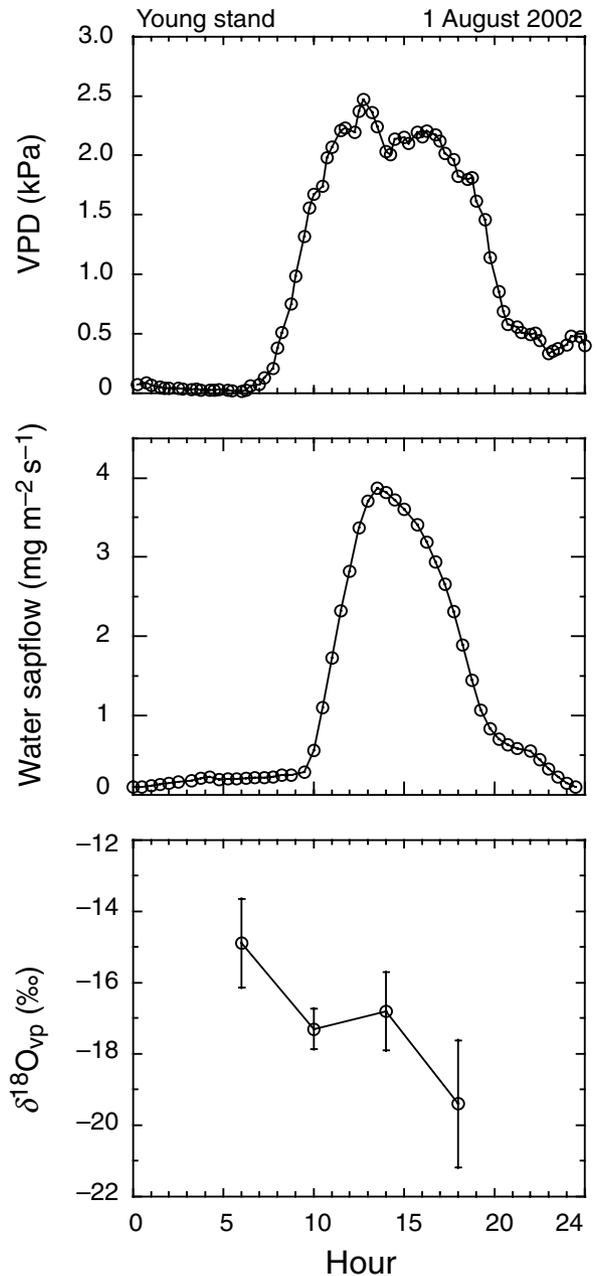
We compared the modelled  $\delta^{18}\text{O}$  of leaf water at the sites of evaporation with the measured bulk leaf water in Fig. 5. Figure 5 shows that, in general, leaf water  $\delta^{18}\text{O}$  predicted



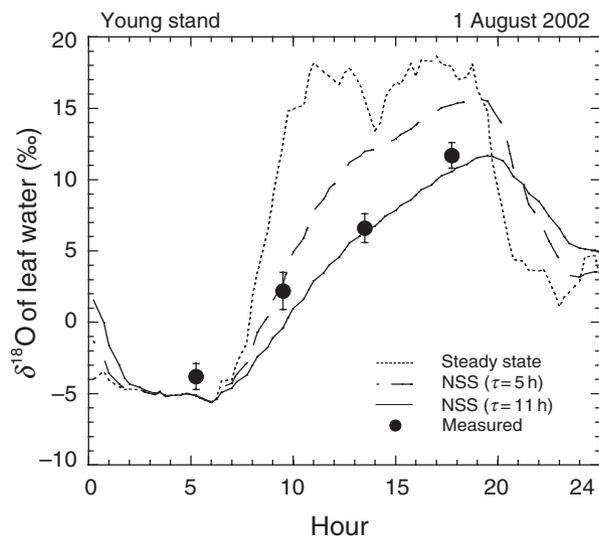
**Figure 3.** Half-hourly wind speed and dominant wind direction measured at 80 m above ground in an old-growth forest on 30 and 31 July 2002, indicated by the magnitude and incoming direction of vectors, respectively.

by a steady state model overestimated measured  $\delta^{18}\text{O}$  values of bulk leaf water during the day and underestimated  $\delta^{18}\text{O}$  value of bulk leaf water at night. The overestimation was greatest in the morning, reaching as much as 7‰. Previous studies showed observed  $\delta^{18}\text{O}$  values of bulk leaf water less enriched than Craig–Gordon predictions during the day (Dongmann *et al.* 1974; Leaney *et al.* 1985; Bariac *et al.* 1989; Walker *et al.* 1989; Flanagan & Ehleringer 1991; Yakir 1992; Roden & Ehleringer 1999), but few studies have reported a discrepancy as large as the one shown in Fig. 5. We also considered the Péclet effect (Farquhar & Lloyd 1993), with the transpiration rate derived from whole-tree sapflow measurements divided by the canopy leaf area (Phillips *et al.* 2002). Including the Péclet effect offered little improvement to the discrepancy between measured and modelled  $\delta^{18}\text{O}$  of leaf water (not shown).

The assumption of isotopic steady state is satisfied when the ratio of transpiration to leaf water volume is small (short turnover time of leaf water), which has been shown in shorter canopies (Yakir & Wang 1996). In tall forests under natural conditions, the steady state assumption is not always satisfied (Flanagan *et al.* 1993) because turnover time of leaf water may be much longer. To better describe measured  $\delta^{18}\text{O}$  of leaf water, we tested a different model that does not rely on the steady state assumption. This class of model is generally termed ‘non-steady state’ (Dongmann



**Figure 4.** Diurnal measurements of vapour pressure deficit (VPD), water sapflux and the oxygen isotope ratio of water vapour ( $\delta^{18}\text{O}_{\text{vp}}$ ) measured in a 25-year-old stand of Douglas-fir trees.



**Figure 5.** Comparison between measured and predicted oxygen isotope ratio ( $\delta^{18}\text{O}$ ) values of leaf water for the young stand on 1 August 2002. The averaged  $\delta^{18}\text{O}$  value of xylem water was  $-10.3 \pm 0.6\text{‰}$  ( $n = 41$ ). Both steady state and non-steady state (NSS) predictions were shown for comparison. The NSS model was run with two cases of turnover time of leaf water ( $\tau$ ; see text).

*et al.* 1974; White 1983; Cernusak *et al.* 2002; Farquhar & Cernusak 2005). We chose to use the model by Dongmann *et al.* (1974) in this study because we did not have enough information to describe diurnal changes in leaf water contents, which is required by other models (Cernusak *et al.* 2002; Farquhar & Cernusak 2005). Midday leaf water content was calculated to be  $8.61 \text{ mol water m}^{-2}$  leaf area in the young forest. Using the sapflux-estimated transpiration rate, we determined the turnover time of leaf water ( $\tau$ ) for needles of Douglas-fir trees in the young stand between 1230 and 1430 h on 1 August 2002 (Table 1). Table 1 shows that  $\tau$  was  $\approx 11$  h, which is considerably longer than values ( $\approx 2$  h) reported for a 150-year-old *Picea abies* forest in Russia (Langendörfer *et al.* 2002).

Using the measured  $\tau$ , we modelled the  $\delta^{18}\text{O}$  of leaf water at the sites of evaporation using a non-steady state approach and compared it to the bulk leaf water measurements in Fig. 5. In general, the modelled  $\delta^{18}\text{O}$  values conformed better with the measurements when we used  $\tau = 11$  h than when we assumed steady state conditions. It conformed best during midday, when biometric measurements were made to determine  $\tau$ . The non-steady state prediction slightly underestimated the  $\delta^{18}\text{O}$  of bulk leaf water in the morning and late afternoon hours, suggesting that the values of  $\tau$  are not constant; hence, changes in leaf water content may also be important (Cernusak *et al.* 2002; Farquhar & Cernusak 2005).

For the rest of this study, we refer steady state and non-steady state to predictions from a Craig–Gordon type model (i.e. Eqn 3) and a model that describes the  $\delta^{18}\text{O}$  of leaf water approaching steady state (i.e. Eqn 4; Dongmann *et al.* 1974). Predicted leaf water  $\delta^{18}\text{O}$  provide a basis for estimating  $\delta^{18}\text{O}_T$ , which in turn, affect the  $\delta^{18}\text{O}$  of canopy

water vapour. We would examine how steady state and non-steady state descriptions of leaf water influence  $^{18}\text{O}$  budget of water vapour inside the canopy.

### $\delta^{18}\text{O}$ of transpiration and soil evaporation

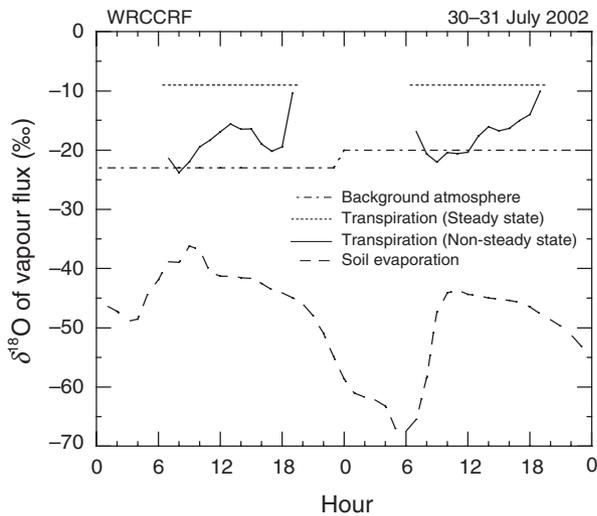
Gat & Matsui (1991) showed that large transpirational fluxes could contribute a significant amount of water into the canopy boundary layer with distinct isotopic signatures, altering the  $\delta^{18}\text{O}$  values of atmospheric moisture. Contributions of local evapotranspiration to the  $^{18}\text{O}$  budget of canopy water vapour depend on the input of  $^{18}\text{O}$ -isoflux.  $^{18}\text{O}$ -isoflux is defined as the product of a water flux and its associated  $\delta^{18}\text{O}$  value relative to mean  $\delta^{18}\text{O}_{\text{vp}}$  within the canopy as shown by terms on the right hand side (RHS) of Eqn 8. To quantify isoflux resulting from transpiration and soil evaporation, we first need to estimate the  $\delta^{18}\text{O}$  values of transpired water and water evaporated from the soil surface.

Figure 6 shows the modelled  $\delta^{18}\text{O}$  values of transpiration and soil evaporation at the canopy crane site. The  $\delta^{18}\text{O}$  of xylem water was  $-8.7 \pm 1.3\text{‰}$  ( $n = 36$ ). Averaged  $\delta^{18}\text{O}_{\text{vp}}$  from three measurement heights were interpolated for every 30 min interval, along with averaged air temperature and relative humidity in this calculation. Leaf water  $\delta^{18}\text{O}$  predicted by both steady and non-steady models (not shown) were used to model  $\delta^{18}\text{O}_T$  using Eqn 1. Modelled  $\delta^{18}\text{O}_T$  values are shown in Fig. 6 for the times when transpiration became significant. The utility of Eqn 1 is demonstrated by the modelled  $\delta^{18}\text{O}_T$  value assuming steady state in Fig. 6, where the dotted line indicates model calculations based on Eqn 1, which matches the required theoretical value ( $= \delta^{18}\text{O}$  of xylem water,  $-8.7\text{‰}$ ). When the values of  $\delta^{18}\text{O}_T$  were modelled based on non-steady state assumptions, they were about  $-22\text{‰}$  in the morning, but they gradually increased during the afternoon, approaching the steady state value. This is consistent with the modelled diurnal pattern of leaf water enrichment where non-steady state predictions intersect with steady state values in the later afternoon before diverging again at night, as demonstrated in Fig. 5. Modelled  $\delta^{18}\text{O}_T$  values are comparable to mea-

**Table 1.** Turnover time of leaf water in needles of Douglas-fir trees in the young stand.

| Time | Sapflux<br>( $\text{mg m}^{-2} \text{ leaf s}^{-1}$ ) | Lag time ( $\tau$ )<br>(h) |
|------|---|----------------------------|
| 1230 | 3.709   | 11.608                     |
| 1300 | 3.874   | 11.113                     |
| 1330 | 3.818   | 11.278                     |
| 1400 | 3.720   | 11.574                     |
| 1430 | 3.602   | 11.954                     |

Turnover time ( $\tau$ ) was determined as  $\tau = W/T$ , where  $W$  is the measured leaf water content ( $8.61 \text{ mol water m}^{-2}$  leaf area) and  $T$  is transpiration rate, represented by sapflux measurements. Here values were reported for midday hours using sapflux measurements collected on 1 August 2002.



**Figure 6.** Modelled oxygen isotope ratios of vapour fluxes from various ecosystem components above and within the old-growth forest at the Wind River Canopy Crane Research Facility (WRCCRF).

measurements reported in an oak forest by Harwood *et al.* (1999).

Equation 1 can also be used to predict the  $\delta^{18}\text{O}$  values of soil evaporation (Moreira *et al.* 1997), based on averaged soil water  $\delta^{18}\text{O}$  between 0 and 30 cm below ground ( $-9.1 \pm 1.8\text{‰}$ ;  $n = 21$ ). Measured  $\delta^{18}\text{O}_{\text{vp}}$  at 0.5 m were interpolated for every 30 min interval. We used air temperature and relative humidity measured at 2 m above ground in this calculation. Modelled  $\delta^{18}\text{O}$  of soil evaporation varied between  $-35$  and  $-67\text{‰}$  during the two days, with the majority of daytime values ranging between  $-40$  and  $-45\text{‰}$ . These  $\delta^{18}\text{O}$  signals, even compared to modelled  $\delta^{18}\text{O}_{\text{T}}$  under non-steady state conditions, were relatively depleted. The separation between  $\delta^{18}\text{O}$  values of canopy transpiration and soil evaporation provides a labelling capacity of using  $\delta^{18}\text{O}$  in ecosystem studies (Yakir & Sternberg 2000).

### $\delta^{18}\text{O}$ of background atmospheric vapour

Little is known about an accurate  $\delta^{18}\text{O}$  value representing the uploft atmosphere before entering the canopy column. To estimate  $\delta^{18}\text{O}$  values of background atmospheric vapour, we assumed that:

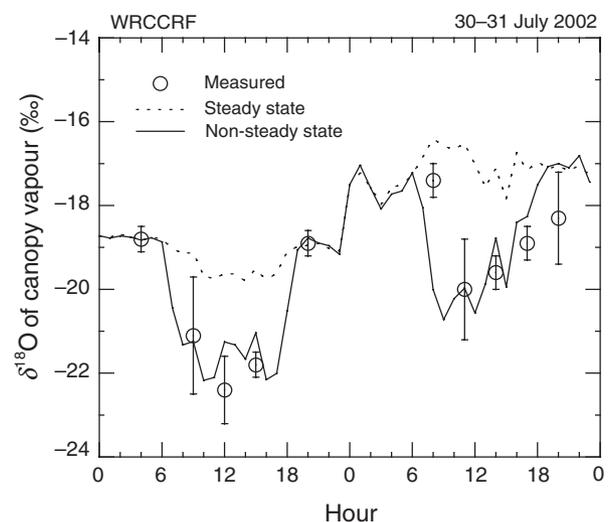
- 1 background atmospheric vapour has a constant  $\delta^{18}\text{O}$  value throughout the day as long as dominant wind direction remained unchanged, and
- 2 the canopy air column is well mixed by convective turbulence at midday when background atmosphere has the greatest impact on the  $\delta^{18}\text{O}_{\text{vp}}$  within the canopy.

The second assumption allowed us to estimate  $\delta^{18}\text{O}$  values of background atmospheric vapour by considering measured  $\delta^{18}\text{O}_{\text{vp}}$  values at midday. Averaged midday  $\delta^{18}\text{O}_{\text{vp}}$  values were  $-22.4 \pm 0.8\text{‰}$  and  $-20.0 \pm 1.2\text{‰}$  based on

measurements from three heights for the two days, respectively. We therefore assumed constant  $\delta^{18}\text{O}$  values of  $-23$  and  $-20\text{‰}$  for the two days representing oxygen isotope ratios of uploft atmospheric vapour (Fig. 6). These values correspond to a range between  $-10$  and  $-13\text{‰}$  in precipitation if atmospheric vapour can be assumed in equilibration with precipitation, given the fractionation associated with condensation is  $\approx -10\text{‰}$  at  $20^\circ\text{C}$ . These inferred precipitation  $\delta^{18}\text{O}$  values are well within the range ( $-5$  to  $-15\text{‰}$  in July and August) reported by the National Atmospheric Deposition Program for this region (Welker 2000).

### Comparison between modelled and measured $\delta^{18}\text{O}_{\text{vp}}$

On the basis of  $\delta^{18}\text{O}$  values of vapour fluxes shown in Fig. 6, and measured transpiration and evaporation fluxes shown in Fig. 2, we compared modelled and measured  $\delta^{18}\text{O}_{\text{vp}}$  values in the old-growth forest (Fig. 7). Initial values of the  $\delta^{18}\text{O}_{\text{vp}}$  were assumed as the average value of first observations in the morning for each of the two days,  $-18.7\text{‰}$  and  $-17\text{‰}$ , respectively. The  $\approx 2\text{‰}$  difference reflects the overall difference for the daily mean values of the  $\delta^{18}\text{O}_{\text{vp}}$  between the two days, likely a consequence of changes in the regional atmospheric wind pattern (Fig. 3). In general, the modelled  $\delta^{18}\text{O}_{\text{vp}}$  captured the diurnal variation fairly well in the case of a non-steady state description of leaf water  $\delta^{18}\text{O}$ . Modelled  $\delta^{18}\text{O}_{\text{vp}}$  values were slightly worse on the second day, which could be attributed to the more complicated atmospheric conditions that might have compromised our assumptions with respect to a constant  $\delta^{18}\text{O}$  of uploft atmospheric vapour throughout the day. In fact, based on the wind direction analysis (Fig. 3), assuming a constant  $\delta^{18}\text{O}$  of atmospheric vapour on 31 July would be incorrect because the dominant wind shifted towards inland at about 1400 h, which was more similar to the conditions



**Figure 7.** Comparison of modelled and measured oxygen isotope ratios of water vapour within the old-growth forest.

on 30 July. Hence, it was likely that the  $\delta^{18}\text{O}$  of atmospheric vapour was not  $-17\%$  later in the afternoon as we have assumed for the morning hours of 31 July, but more depleted and closer to the value for 30 July ( $-18.7\%$ ). If this adjustment was made, the apparent overestimation would be justifiable in the late afternoon of 31 July. Similarly, the underestimation in the early morning could be because of our incorrect choice of initial value for the  $\delta^{18}\text{O}_{\text{vp}}$ , since the earliest measurements were not made until 0800 h on day 2.

The model overestimated  $\delta^{18}\text{O}_{\text{vp}}$  when the steady state approach was used to predict the  $\delta^{18}\text{O}$  of leaf water. The diurnal fluctuation of  $\delta^{18}\text{O}_{\text{vp}}$  was also largely dampened in this case. Midday values of  $\delta^{18}\text{O}_{\text{vp}}$  were enriched by 2–3‰ when modelled using steady-state assumptions compared to the non-steady state scenario. The discrepancy between steady state and non-steady state calculations was a result of the difference in the  $\delta^{18}\text{O}$  of transpiration flux shown in Fig. 6. Values of  $\delta^{18}\text{O}_{\text{T}}$  were more than 10‰ greater when modelled assuming steady state compared with non-steady state assumptions. The more enriched signal resulted in greater  $^{18}\text{O}$ -isoflux to the canopy air column. In short,  $\delta^{18}\text{O}$  values of water vapour within a forest canopy reflect the balance of isofluxes from individual water inputs.

## DISCUSSION

### $\delta^{18}\text{O}$ of leaf water in isotopic non-steady state

Interpreting comparisons in Fig. 5 requires caution. Bulk leaf water is an ill-defined entity because it is a mixture of fractionated and non-fractionated water pools (Yakir 1992; Yakir *et al.* 1994; Gan *et al.* 2002). Predictions from current models specifically describe the enrichment at the *sites of evaporation*. The agreement between non-steady state predictions and bulk leaf water measurements cannot be used as proof that transpiration is not at isotopic steady state. Many other factors can affect the  $\delta^{18}\text{O}$  of leaf water. For example, Helliker & Ehleringer (2000) reported progressive  $\delta^{18}\text{O}$  enrichment in leaf water extracted from segments of grass blades. Effects of progressive enrichment were also observed in the vein xylem water in cotton leaves (Gan *et al.* 2002). Farquhar & Gan (2003) recently developed a one-dimensional model to account for both longitudinal and radial Péclet effects, including progressive enrichment along the leaf. These efforts have dramatically increased our ability to a mechanistic understanding of the  $^{18}\text{O}$  spatial pattern in leaf water.

It was our objective to contrast predictions with and without assuming isotopic steady state, not to justify predictions from a non-steady state description by comparing modelled results with bulk leaf water measurements. Interestingly, when turnover time of leaf water was independently estimated, a non-steady state description seemed to agree better with bulk leaf water  $\delta^{18}\text{O}$ . This agreement is especially interesting given that Péclet effects are insignificant for the needles of these Douglas-fir trees during periods of low to moderate transpiration rates.

Wang, Yakir & Avishai (1998) showed that, conifers usually possess smaller Péclet numbers relative to other evergreen and deciduous species from the same geographical location. They found that deviations between the  $\delta^{18}\text{O}$  value in chloroplast water and that predicted by the Craig–Gordon model decreased with decreasing Péclet number. Our modelled results are consistent with conclusions in Wang *et al.* (1998).

Farquhar & Cernusak (2005) suggested a non-steady state model incorporating the Péclet effect. Their model showed a more pronounced non-steady state effect at night, when compared to a dataset collected from a uniform stand of *Lupinus angustifolius* L. var. *Tangil* (Cernusak *et al.* 2002). Their non-steady state treatment was less important during the day when stomata were relatively open. The substantial non-steady state effect shown in Fig. 5 contrasted to the measurements from Cernusak *et al.* (2002) and the model calculation in Farquhar & Cernusak (2005), likely because of the species differences (leaf thickness, leaf water contents) between the two studies. Summer water stress commonly occurs in the Pacific Northwest coniferous forests (Unsworth *et al.* 2004). Partial stomatal closure at midday, indicated by the low sapflux rate, contributed to the considerable non-steady state effect on the measured  $\delta^{18}\text{O}$  of leaf water in this study. By contrast, measurements by Cernusak *et al.* (2002) were made when stomata were relatively open at daytime hours.

Modelled  $\delta^{18}\text{O}$  values of leaf water remained enriched relative to xylem water at night (Fig. 5), suggesting leaf water did not fully equilibrate with xylem water even several hours after transpiration stopped. This lagged response during night-time was observed by Cernusak *et al.* (2002) and predicted by the non-steady state model described therein. It is important to consider the non-steady state enrichment during night-time if one is to use  $\delta^{18}\text{O}$  signatures to partition ecosystem respiration into above- and below-ground contributions. Ignoring the lag response could lead to an overestimate of above-ground respiration.

### Modelled $\delta^{18}\text{O}$ of soil evaporation

Modelled  $\delta^{18}\text{O}$  of soil evaporation showed a large range of diurnal fluctuation (Fig. 6). We are not aware of any direct measurements of  $\delta^{18}\text{O}$  of soil evaporation ( $\delta_{\text{E}}$ ) in the literature. According to Eqn 1, predicted  $\delta_{\text{E}}$  depend on vapour pressure difference between the surface of evaporation and the ambient air, shown in the denominator of Eqn 1. At the surface where evaporation occurs, water vapour is assumed at saturation. Hence, when water vapour in the ambient air approaches saturation (e.g. during night-time), the denominator becomes close to zero, causing the very negative  $\delta_{\text{E}}$  values at night. This numeric instability partly explains the large range in our modelled  $\delta_{\text{E}}$ . Because we did not measure  $\delta^{18}\text{O}_{\text{vp}}$  at night, we interpolated measurements made between late afternoon and early morning. This may also have contributed to uncertainties with respect to night-time  $\delta_{\text{E}}$  values.

We performed a sensitivity analysis by considering all the variables associated with Eqn 1 and highlighted the results below. In general, model calculations are more robust during daytime, when lower relative humidity occurs. At night, relative humidity, the  $\delta^{18}\text{O}$  of source water and the  $\delta^{18}\text{O}_{\text{vp}}$  all have large effects on modelled  $\delta_{\text{E}}$ . This is because the denominator in Eqn 1 approaches zero at night, magnifying uncertainties in these calculations. We do not know whether these night-time effects would be reduced if cross interactions (i.e. relative humidity  $\times$   $\delta^{18}\text{O}$  of source water) were appropriately considered. Despite the large uncertainty associated with night-time  $\delta_{\text{E}}$  values, modelled  $\delta_{\text{E}}$  were relatively more robust during the day (uncertainties within  $\pm 5\%$ ). This is reassuring with respect to the daytime comparison between modelled and measured the  $\delta^{18}\text{O}$  of water canopy in Fig. 7.

Values of the  $\delta^{18}\text{O}$  of soil water averaged over the top 10, 20 and 30 cm were  $-8.1 (\pm 1.7)$ ,  $-8.7 (\pm 1.9)$  and  $-9.1 (\pm 1.8)$ , respectively. The averaged soil moisture content in the top 30 cm was  $0.15 \text{ m}^3 \text{ m}^{-3}$  during our study period, suggesting substantial drying in the surface soil layers. We do not know at what depth evaporation to be effective, but given the small difference in the  $\delta^{18}\text{O}$  value of soil water confined between 0 and 10 and 0–30 cm, we believe this difference is not sufficient to explain the large range of the modelled  $\delta^{18}\text{O}$  of soil evaporation. Direct measurements aiming at validating modelled  $\delta_{\text{E}}$  in different environmental conditions would be desirable for future research.

### $\delta^{18}\text{O}$ variation of canopy water vapour

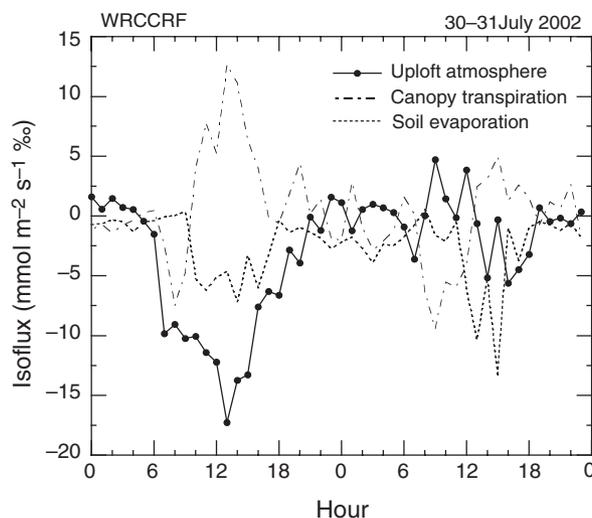
We observed diurnal variations in  $\delta^{18}\text{O}_{\text{vp}}$  as high as 4‰ above and within an old-growth coniferous forest for two consecutive summer days (Fig. 2). Yakir (1998) reported diurnal patterns of  $\delta^{18}\text{O}_{\text{vp}}$  similar to our observations over a small *Acacia saligna* plantation, where the diurnal  $\delta^{18}\text{O}_{\text{vp}}$  variation was related to changes in wind direction. Harwood *et al.* (1999) also showed similar diurnal variations in  $\delta^{18}\text{O}_{\text{vp}}$  from measurements in an oak forest, with smaller midday depletion of  $< 2\%$ . No discussion was given of the diurnal  $\delta^{18}\text{O}_{\text{vp}}$  pattern in Harwood *et al.* (1999).

We expect isotopic compositions of air masses to differ, depending on the history of the air mass trajectory prior to the arrival at the site where water vapour measurements were made. Lawrence *et al.* (2004) measured  $\delta^{18}\text{O}$  of atmospheric vapour in the tropics and found  $\delta^{18}\text{O}$  values of atmospheric vapour highly dependant on the air mass trajectory 24–48 h prior to the measurements. This is because isotopes (deuterium and oxygen) in atmospheric vapour often undergo equilibrium reactions with water pools (e.g. a rainstorm) which they encountered along the travelling path. Consequently, the isotope ratio of atmospheric water vapour at least partially reflects that of the surface water, which differs considerably in space due to factors such as the continental effect. Over the course of a day, however, when the regional wind pattern does not dramatically change, isotopic composition of background atmosphere should remain nearly constant (Lawrence *et al.* 2004). The

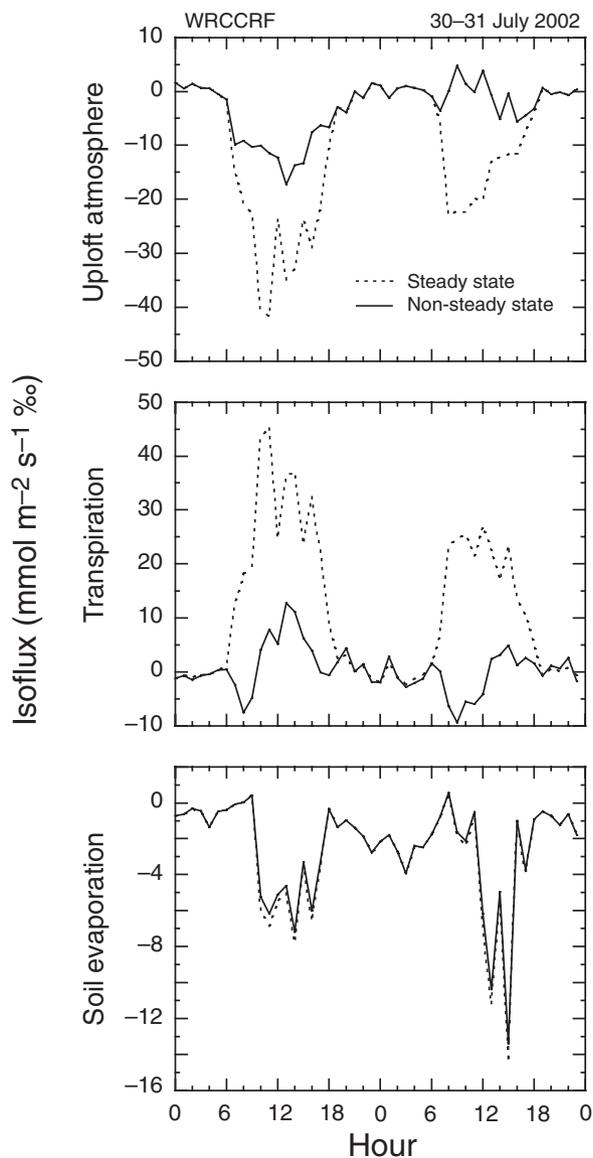
relative contributions of uploft atmosphere and local evapotranspiration on the  $\delta^{18}\text{O}$  of canopy water vapour depend on the input of their respective  $^{18}\text{O}$ -isofluxes.

### $^{18}\text{O}$ -isoflux of evaporation, transpiration and uploft atmosphere

Figure 8 illustrates modelled isoflux of transpiration, soil evaporation and the air entering into the canopy (terms on the RHS of Eqn 8) for the scenario of *non-steady state* leaf  $^{18}\text{O}$  enrichment. Following our sign convention a positive flux represents water vapour entering the canopy air column; a negative isoflux would therefore deplete  $^{18}\text{O}$  contents of water vapour within the canopy. In the morning of day 1 when a 4‰ depletion of the canopy  $\delta^{18}\text{O}_{\text{vp}}$  was observed, the air entering the canopy from the atmosphere above carried a large isoflux of isotopically depleted vapour, primarily responsible for driving  $\delta^{18}\text{O}_{\text{vp}}$  values more negative. Before 0900 h, transpiration also contributed a significant amount of  $^{18}\text{O}$ -depleted isoflux into the canopy. This was consistent with our observations from absolute humidity shown in Fig. 2, where we expected an accumulation of water inputs from transpiration depleting  $\delta^{18}\text{O}_{\text{vp}}$  values. Nonetheless, the isoflux from transpiration became positive after 1000 h and continued until the rest of the day. This isoflux with  $^{18}\text{O}$ -enriched vapour would offset impacts from the atmosphere above, and was the main cause for the increasing  $\delta^{18}\text{O}_{\text{vp}}$  in the afternoon. The isoflux associated with soil evaporation was about 1/3 of magnitude compared to the other isofluxes, which also contributed significantly. Although fluxes of soil evaporation only accounted for  $< 15\%$  of total ET, the isoflux of soil evaporation should not be ignored when evaluating canopy vapour  $^{18}\text{O}$  due to the very depleted  $\delta^{18}\text{O}$  signature of soil evaporation (Fig. 6).



**Figure 8.** Modelled  $^{18}\text{O}$ -isoflux with a non-steady state description of leaf water enrichment at the Wind River Canopy Crane Research Facility (WRCCRF) site.



**Figure 9.** Comparison of modelled  $^{18}\text{O}$ -isoflux with scenarios of steady state and non-steady state leaf water enrichment.

Modelled isofluxes showed a smaller diurnal variation on day 2 when compared to that on day 1 (Fig. 8). Transpiration carried an isoflux of  $^{18}\text{O}$ -depleted vapour in the morning until 1200 h, which was the major contributor for the decreasing  $\delta^{18}\text{O}_{\text{vp}}$  during these hours. This isoflux became positive in the afternoon, causing  $\delta^{18}\text{O}_{\text{vp}}$  values to increase. In contrast to day 1, the air entering the canopy was associated with a smaller isoflux with  $^{18}\text{O}$ -enriched vapour in the morning. Impacts from the atmosphere above were not as strong on day 2, as depicted by the smaller ratio of incoming flux relative to the net flux. Consequently, isoflux associated with uploft atmospheric vapour was significantly smaller on day 2 compared to that on day 1. The magnitude of isoflux associated with soil evaporation was very comparable to, or greater than, the other isofluxes. This again

shows the importance of including effects of soil evaporation in assessing  $^{18}\text{O}$  contents of water vapour in forest canopies.

Impacts of leaf water  $\delta^{18}\text{O}$  on modelled  $\delta^{18}\text{O}_{\text{vp}}$  were examined by comparing isoflux of individual water pools in Fig. 9. Leaf water  $\delta^{18}\text{O}$  predicted by the steady state assumption were more enriched than those from the non-steady state model in the day. The  $\delta^{18}\text{O}$  of transpired water under steady state was also more enriched (Fig. 6), which consequently produced greater isoflux of transpiration (Fig. 9). Based on model calculations, transpiration always induced  $^{18}\text{O}$ -enriched isoflux under steady state conditions. This was because  $\delta^{18}\text{O}_{\text{vp}}$  values were never as enriched as transpired water at steady state (or the source water), so that  $\delta_{\text{t}} - \delta_{\text{c}} > 0$ . This large amount of positive isoflux increased  $\delta^{18}\text{O}_{\text{vp}}$  values, exceeding  $\delta^{18}\text{O}$  value of the atmosphere above and causing isoflux associated with the air entering the canopy to remain negative ( $\delta_{\text{t}} - \delta_{\text{c}} > 0$ ). Calculations of isoflux appeared to be sensitive to descriptions of leaf water because values of  $\delta_{\text{r}}$ ,  $\delta_{\text{t}}$  and  $\delta_{\text{c}}$  were close to each other (Fig. 6); a small change in  $\delta_{\text{c}}$  could change the sign of isofluxes. Steady state assumption had less impacts on the isoflux of soil evaporation, because the difference ( $\delta_{\text{E}} - \delta_{\text{c}}$ ) was relatively large compared to ( $\delta_{\text{t}} - \delta_{\text{c}}$ ) and ( $\delta_{\text{r}} - \delta_{\text{c}}$ ).

Net contributions of each water flux to the canopy  $^{18}\text{O}$  budget can be examined by daily sums of isoflux. To demonstrate this point, we used modelling results from the non-steady state case. On day 1, daily sums of isoflux were  $-128.7$ ,  $39.0$  and  $-53.6 \text{ mmol m}^{-2} \text{ s}^{-1} \text{ ‰}$  for  $F_{\text{oi}}$ ,  $F_{\text{T}}$  and  $F_{\text{E}}$ , respectively. On day 2, the daily sums were  $-6.6$ ,  $-15.3$  and  $-66.7 \text{ mmol m}^{-2} \text{ s}^{-1} \text{ ‰}$  for  $F_{\text{oi}}$ ,  $F_{\text{T}}$  and  $F_{\text{E}}$ , respectively. The air entering the canopy from the atmosphere above was a net 'sink' (depleting  $^{18}\text{O}$  contents) on both days, but with a much greater impact on day 1. Transpiration contributed as a net source to the  $^{18}\text{O}$  content of canopy vapour on day 1, but a net sink on day 2. This is consistent with the gradual build-up of water vapour contents inside the canopy on day 2, as shown in Fig. 2. This change partially reflected the 2‰ increase in the  $\delta^{18}\text{O}$  of background atmospheric vapour so that values of  $\delta_{\text{r}}$ ,  $\delta_{\text{t}}$ , and  $\delta_{\text{c}}$  interacted differently on day 2. Soil evaporation contributed as a source of isotopically depleted vapour on both days. The greater contribution from soil evaporation on the second day reflected slightly larger differences between  $\delta_{\text{E}}$  and  $\delta_{\text{c}}$  in the term  $(\delta_{\text{E}} - \delta_{\text{c}})F_{\text{E}}$ .

The mass balance approach shown in this paper has not previously been used for assessing the  $^{18}\text{O}$  budget of atmospheric water vapour in forests. Our modelling analyses showed that both atmospheric mixing and local evapotranspiration are important to the  $\delta^{18}\text{O}$  temporal variation of water vapour within a forest canopy. The atmosphere appears to have the largest impact on the  $\delta^{18}\text{O}$  of canopy vapour, with strong turbulent mixing when the atmosphere above induces the greatest  $^{18}\text{O}$ -isoflux into the canopy (i.e. day 1 in Fig. 8). Depending on atmospheric conditions, transpiration could either increase or decrease  $\delta^{18}\text{O}$  values of water vapour. Soil evaporation often has small contributions ( $< 10\%$ ) to total evapotranspiration flux in forest ecosystems. Nevertheless, its effects on the  $\delta^{18}\text{O}$  of water

vapour cannot be ignored. Impacts of the biosphere on  $\delta^{18}\text{O}$  of water vapour within a forest canopy are clearly demonstrated by our modelling exercise with the comparison between different descriptions of leaf water enrichment.

Oxygen isotopes have become increasingly popular for the application of partitioning water fluxes. It needs to be emphasized that partitioning ET using  $^{18}\text{O}$  or  $^2\text{H}$  requires precise estimates of the end members, i.e. the isotope ratios of transpired and evaporated vapour. The  $\delta^{18}\text{O}$  value of transpiration *only* equals that of the source water when transpiration occurs at isotopic steady state. Our measurements suggest that turnover time of leaf water can be extensive in the needles of Douglas-fir trees, which would likely violate the steady state assumption.

Large uncertainties remain in the determination of  $\delta^{18}\text{O}$  values of soil evaporation. Environmental variables including isotope ratios of atmospheric vapour adjacent to the soil surface are required for predicting the  $\delta^{18}\text{O}$  of soil evaporation. It is, however, not a trivial task to obtain such measurements at present given the heterogeneity of the soil cover. Direct measurements in future research are required to validate modelled  $\delta^{18}\text{O}$  values of soil evaporation.

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## APPENDIX A: LIST OF SYMBOLS

|                        |   |
|------------------------|---|
| EC                     | eddy covariance   |
| ET                     | evapotranspiration flux (mmol m <sup>-2</sup> s <sup>-1</sup> )                           |
| <i>e</i>               | partial pressure of water vapour (kPa)  |
| <i>e<sub>a</sub></i>   | partial pressure of water vapour in the air (kPa)   |
| <i>e<sub>i</sub></i>   | partial pressure of water vapour in the leaf intercellular space (kPa)                    |
| <i>e<sub>s</sub></i>   | partial pressure of water vapour at the leaf surface (kPa)                                |
| <i>F</i>               | water vapour flux (mmol m <sup>-2</sup> s <sup>-1</sup> )                                 |
| <i>F<sub>+</sub></i>   | one-way flux of water vapour entering the canopy  |
| <i>F<sub>-</sub></i>   | one-way flux of water vapour leaving the canopy   |
| <i>F<sub>E</sub></i>   | flux of soil evaporation  |
| <i>F<sub>T</sub></i>   | flux of transpiration   |
| <i>F<sub>net</sub></i> | net flux of water vapour above the canopy   |
| <i>M<sub>c</sub></i>   | number of moles of air per unit ground area   |
| <i>R</i>               | molar ratio of heavy to light isotopes ( <sup>18</sup> O/ <sup>16</sup> O)                |
| <i>R<sub>+</sub></i>   | molar ratio of heavy to light isotopes of water vapour of the atmosphere above the canopy |
| <i>R<sub>-</sub></i>   | molar ratio of heavy to light isotopes of water vapour of air leaving the canopy          |
| <i>R<sub>a</sub></i>   | molar ratio of heavy to light isotopes of water vapour in the air                         |

|                                   |  |
|-----------------------------------|--|
| $R_c$                             | molar ratio of heavy to light isotopes of water vapour inside a well-mixed canopy air column |
| $R_E$                             | molar ratio of heavy to light isotopes of water vapour from soil evaporation                 |
| $R_e$                             | molar ratio of heavy to light isotopes of leaf water at the sites of evaporation             |
| $R_x$                             | molar ratio of the heavy to light isotopes of xylem water                                    |
| $R_T$                             | molar ratio of heavy to light isotopes of transpired water by a leaf                         |
| $R_{\text{snow}}$                 | standard molar ratio of oxygen isotope   |
| $R_w$                             | molar ratio of heavy to light isotopes of liquid water at the sites of evaporation           |
| $rh$                              | relative humidity (%)  |
| $T$                               | transpiration rate ( $\text{mmol m}^{-2} \text{s}^{-1}$ )                                    |
| $T_a$                             | air temperature ( $^{\circ}\text{C}$ )   |
| $u_*$                             | friction velocity ( $\text{m s}^{-1}$ )  |
| VPD                               | vapour pressure deficit (kPa)  |
| $v_c$                             | average mole fraction of water vapour inside the canopy                                      |
| $v'$                              | fluctuation of mole fraction of water vapour   |
| $v_+$                             | mean mole fraction of water vapour in down-draft wind  |
| $v_-$                             | mean mole fraction of water vapour in updraft wind   |
| $\hat{v}$                         | departure from the mean state of water vapour concentration                                  |
| $\bar{v}$                         | average concentration of water vapour  |
| $v_*$                             | scaling parameter of water vapour transport  |
| $v_{\text{ref}}$                  | reference concentration of water vapour  |
| $W$                               | leaf water content ( $\text{mol water m}^{-2}$ leaf area)                                    |
| $w'$                              | fluctuation of vertical wind speed ( $\text{m s}^{-1}$ )                                     |
| $\alpha^*$                        | equilibrium fractionation factor   |
| $\alpha_k$                        | kinetic fractionation factor   |
| $\alpha_{\text{kb}}$              | diffusional kinetic fractionation factor in the boundary layer                               |
| $\alpha_{\text{kv}}$              | effective kinetic fractionation factor of water vapour                                       |
| $\beta$                           | empirical coefficient (= 0.6)  |
| $\sigma_w$                        | standard deviation of the vertical velocity ( $\text{m s}^{-1}$ )                            |
| $\sigma_v$                        | standard deviation of water vapour concentration   |
| $\tau$                            | turnover time of leaf water (h)  |
| $\lambda$                         | dimensionless scaling group (scalar variance similarity)                                     |
| $\zeta$                           | scaled fractionation parameter   |
| $\delta^{18}\text{O}$             | oxygen isotope ratio (‰)   |
| $\delta_c(t)$                     | steady state oxygen isotope ratio of leaf water at time $t$ (‰)                              |
| $\delta_{\text{en}}(t)$           | non-steady state oxygen isotope ratio of leaf water at time $t$ (‰)                          |
| $\delta_{\text{en}}(t-1)$         | non-steady state oxygen isotope ratio of leaf water at time $t-1$ (‰)                        |
| $\delta^{18}\text{O}_T$           | oxygen isotope ratio of transpired water (‰)   |
| $\delta^{18}\text{O}_{\text{vp}}$ | oxygen isotope ratio of water vapour (‰)   |
| $\delta_+$                        | oxygen isotope ratio of the atmosphere above the canopy (‰)                                  |

|            |   |
|------------|---|
| $\delta_-$ | oxygen isotope ratio of air leaving the canopy (‰)                                |
| $\delta_c$ | oxygen isotope ratio of water vapour inside a well-mixed canopy air column (‰)    |
| $\delta_E$ | oxygen isotope ratio of soil evaporation (‰)                                      |
| $\delta_T$ | oxygen isotope ratio of transpired water (‰); same as $\delta^{18}\text{O}_T$ (‰) |
| $\Delta t$ | time interval   |

## APPENDIX B

Using the formulation of a relaxed eddy-accumulation, the net turbulent flux is given by

$$F_{\text{net}} = \overline{w'v'} = \beta\sigma_w(v_+ - v_-). \quad (\text{B1})$$

Let us assume that the mean scalar concentration probability distribution is symmetric (or zero-skewness) so that

$$\begin{aligned} v_+ &\approx v_{\text{ref}} + \hat{v} \\ v_- &\approx v_{\text{ref}} - \hat{v} \end{aligned} \quad (\text{B2})$$

where  $v_{\text{ref}}$  is now a reference concentration, and  $\hat{v}$  is the departure from the mean state because updrafts (or downdrafts) are transporting air parcels with enriched (or depleted) water vapour. With this approximation,

$$\hat{v} = \frac{F_{\text{net}}}{2\beta\sigma_w} \quad (\text{B3})$$

hence, the gross fluxes in ( $F_+$ ) and out ( $F_-$ ) of the canopy are given by

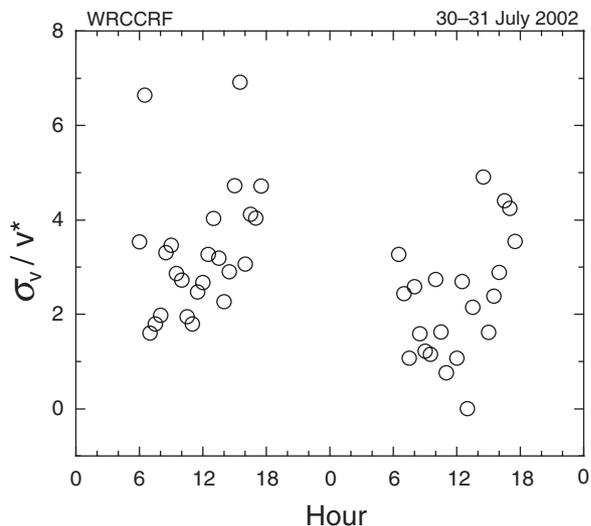
$$\begin{aligned} F_+ &= \beta\sigma_w v_+ = \beta\sigma_w v_{\text{ref}} + \frac{F_{\text{net}}}{2} \\ F_- &= \beta\sigma_w v_- = \beta\sigma_w v_{\text{ref}} - \frac{F_{\text{net}}}{2} \end{aligned} \quad (\text{B4})$$

Because we are interested in ‘movement’ of air (updrafts or downdrafts), a reference concentration that reflects background ‘activity’ rather than a background state (or number of molecules) is preferred; a possible choice is  $v_{\text{ref}} = \sigma_v$ , the turbulent standard deviation of concentration. This choice naturally reflects the reference ‘energy’ (which indicates the strength of turbulent activity) of water vapour parcel movements rather than absolute number of molecules (e.g.  $\bar{v}$ ). The choice  $v_{\text{ref}} = \sigma_v$  is based on dimensional arguments rather than a physical measurement of concentration. With this reference state, it is possible to relate the gross fluxes to the net flux as follows:

On the basis of similarity theories (e.g. Monin & Obukhov 1954), a dimensionless scaling group (called scalar variance similarity) can be shown as:

$$\frac{\sigma_v}{v_*} = \lambda \quad (\text{B5})$$

where  $\lambda$  is a constant (Stull 1988),  $v_* = F_{\text{net}}/u_*$  is defined as a scaling parameter for water vapour (Stull 1988). For can-



**Figure B1.** 30-min average values of dimensionless scalar variance similarity during daytime hours (0600–1700 h) measured above the old-growth forest.

opy flows in approximately near-neutral conditions, Wesson *et al.* (2001) found that  $\lambda = 3.5$  for sensible heat in a pine forest. We calculated 30-min averages of  $\lambda$  for water vapour using measurements above the canopy (Fig. B1). By assuming neutral conditions we calculated an averaged  $\lambda$ -value during daytime (0600–1700 h) as 3.3 and 2.1 on 30 July and 31 July, respectively, which were used in the current study.

Replacing this similarity result (Eqn B5) in Eqn B4 yields,

$$F_+ = \left( \beta \sigma_w \frac{\lambda}{u_*} + \frac{1}{2} \right) \cdot F_{\text{net}} \tag{B6}$$

$$F_- = \left( \beta \sigma_w \frac{\lambda}{u_*} - \frac{1}{2} \right) \cdot F_{\text{net}}$$

Values of  $\beta$  and  $\sigma_w$  can be taken from literatures as  $\beta = 0.6$  (Oncley *et al.* 1993) and  $\sigma_w \sim 1.25u_*$  (Raupach 1988).  $F_+$  can be related to  $F_{\text{net}}$  by using averaged  $\lambda$ -values on 30 July 2002 as  $F_+ = 3.0F_{\text{net}}$  and on 31 July 2002 as  $F_- = 2.1F_{\text{net}}$ .