Oxygen isotope content of CO_2 in nocturnal ecosystem respiration: 2. Short-term dynamics of foliar and soil component fluxes in an old-growth ponderosa pine forest

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[1] The oxygen isotope contents ($\delta^{18}O$) of soil, xylem, and leaf water and ecosystem respiration were studied in a ponderosa pine forest during summer 2001. Our goal was to assess whether $\delta^{18}O$ of CO_2 could be used to quantify the relative contributions of soil and foliar respiration to total nocturnal ecosystem respiration. The $\delta^{18}O$ in leaf and soil water showed enrichment over a 2-week sampling period as the weather became hot and dry (leaves 0.9 to 15.0‰, and soil −10.4 to −3.1‰), while $\delta^{18}O$ of xylem water remained constant (−12.9‰). Water in the soil was enriched in ^{18}O near the soil surface (−6.4‰ at 5 cm depth) relative to greater depths (−11.1‰ at 20 cm). The $\delta^{18}O$ of ecosystem respiration became gradually enriched over the 2-week sampling period (from 24.2 initially to 32.9‰ at the end, VSMOW scale). Soil respiration contributed 80 ± 12 percent to the total respiratory flux, close to estimates from scaled-up chamber data (77% [*Law et al.*, 2001a]). Quantitative application of the isotopic approach to determine respiratory proportions required direct measurement of $\delta^{18}O$ of soil and xylem water, air and soil temperature, and humidity. Better estimates of the isotopic signatures of component fluxes could be achieved with additional measurements and more detailed modeling. Results demonstrate that (1) there is variability in $\delta^{18}O$ of precipitation inputs to ecosystems, (2) immediately following a precipitation event, $\delta^{18}O$ of ecosystem respiration may reflect $\delta^{18}O$ of precipitation, (3) periods of hot dry weather can substantially enrich ecosystem water pools and subsequently alter the isotope content of CO_2 in ecosystem respiration, and (4) stable oxygen isotopes in CO_2 can be used to quantify the foliar and soil components of ecosystem respiration. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1615 Global Change: Biogeochemical processes (4805); 1818 Hydrology: Evapotranspiration; *KEYWORDS:* soil water, leaf water, carbon cycle, Oregon, $\delta^{18}O$, flux, Metolius

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1. Introduction

[2] Interactions between respired CO_2 and water pools in leaf tissue and the soil profile impart distinct oxygen isotope signatures to CO_2 in foliar and soil respiratory fluxes. Such isotopic labels may provide an opportunity to quantify the contributions of each component flux to total ecosystem respiration. However, we presently have a poor understanding of how the oxygen isotope content ($\delta^{18}O$) of total ecosystem respiration might be influenced by variation in $\delta^{18}O$ of precipitation and isotopic modification of soil and leaf water pools through evaporative enrichment. Such variation could contribute to a dynamic pattern in $\delta^{18}O$ of respiratory fluxes on timescales of hours to seasons. An understanding of these dynamics is a prerequisite to their quantitative application in separating foliar and soil respiratory contributions to total nocturnal ecosystem respiration.

[3] Factors influencing the oxygen isotope content of ecosystem respiration (δ_R) are discussed in a companion paper [*Bowling et al.*, 2003b]. *Keeling* [1958, 1961] observed that $\delta^{18}O$ of CO_2 in air within ecosystems varied, but did not correlate well with CO_2 concentration. This contrasted with the pattern observed for carbon isotopes of

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CO_2, and was an indication that different processes controlled the carbon and oxygen isotope ratios of respiratory CO_2. *Francey and Tans* [1987] and *Friedli et al.* [1987] suggested that isotopic exchange with vegetation and soils strongly influenced $\delta^{18}O$ of CO_2 in the atmosphere. Enrichment of leaf water in ^{18}O associated with transpiration was firmly established [*Dongmann et al.*, 1974; *Förstel*, 1978; *Farris and Strain*, 1978], and leaf-level gas exchange experiments demonstrated a strong connection between leaf water enrichment and exchange with CO_2. These and subsequent studies led to a firm mechanistic understanding of the factors controlling leaf water enrichment in ^{18}O and the accompanying isotopic effects on CO_2 during photosynthesis [*Flanagan et al.*, 1991; *Farquhar et al.*, 1993; *Farquhar and Lloyd*, 1993; *Roden and Ehleringer*, 1999; *Gillon and Yakir*, 2000a, 2000b].

[4] Theory behind the isotopic composition of CO_2 in soil profiles and soil fluxes is fairly well advanced [*Ciais et al.*, 1997; *Tans*, 1998; *Amundson et al.*, 1998], but there have been few experimental studies that measured $\delta^{18}O$ of the soil-respired flux (which we denote δ_{soil}). *Hesterberg and Siegenthaler* [1991] demonstrated that CO_2 within the soil was in isotopic equilibrium with soil water in an alpine grassland in Switzerland, and further measurements in other soil types suggest that isotopic equilibrium is reached at depth [*Amundson et al.*, 1998]. *Miller et al.* [1999] showed clearly that δ_{soil} was controlled by interaction with soil water.

[5] The above studies provide a solid basis from which we can begin to interpret isotopic patterns that are observed at the ecosystem scale. *Flanagan and Varney* [1995] and *Flanagan et al.* [1997] showed that diurnal variation in $\delta^{18}O$ within coniferous forests in Canada could be attributed to oxygen isotopic discrimination by photosynthesis and interactions between soil-respired CO_2 and soil water. Exchange with water within a thick moss layer present at some boreal black spruce forests also caused isotopic effects on CO_2 produced by respiration belowground [*Flanagan et al.*, 1997, 1999].

[6] Other studies have also observed pronounced diurnal and vertical variation in $\delta^{18}O$ of CO_2 within temperate deciduous forests [*Harwood et al.*, 1999; *Bowling et al.*, 1999], temperate coniferous forests [*Mortazavi and Chanton*, 2002], tropical forests [*Buchmann et al.*, 1997; *Sternberg et al.*, 1998], and agricultural crops [*Yakir and Wang*, 1996; *Buchmann and Ehleringer*, 1998]. In general, these studies have focused on the opposing isotopic influences of daytime photosynthesis and respiration on canopy CO_2. Photosynthesis tends to make canopy CO_2 more enriched in ^{18}O, while respiration depletes it of the heavy isotope (leaving the canopy with more negative $\delta^{18}O$). Very few studies have addressed the temporal or spatial variability of $\delta^{18}O$ in the nocturnal respiratory fluxes within a night [*Langendörfer et al.*, 2002; *Cuntz et al.*, 2003a].

[7] *Flanagan et al.* [1999] observed a shift of more than 5‰ in $\delta^{18}O$ of soil-respired CO_2 from one day to the next in a Canadian black spruce forest. They attributed the difference to the new isotopic input from rainfall that occurred on the night in between. This is reasonable since precipitation events are likely to alter $\delta^{18}O$ of soil water (and moss water in work by *Flanagan et al.* [1999]). The degree to which variability in precipitation inputs and isotopic modification of ecosystem water pools over time is transferred to ecosystem respiration has not been established.

[8] The companion paper [*Bowling et al.*, 2003b] examined seasonal and interannual variation in $\delta^{18}O$ of ecosystem respiration (δ_R) in several forests across a precipitation gradient in western Oregon. That study suggested a trend of more positive $\delta^{18}O_R$ at the dry inland sites relative to the mesic sites near the coast, indicating that fractionation due to evaporative enrichment overshadowed the original isotopic composition of precipitation as a first order control on δ_R. In the present study we focus on hourly to weekly variation in δ_R. The primary objectives were to (1) describe the natural variability in ecosystem water pools that influence $\delta^{18}O$ of respiratory fluxes, (2) demonstrate that isotopic variation in $\delta^{18}O$ of ecosystem water pools is transferred to $\delta^{18}O$ of respiratory fluxes in mechanistically predictable ways, and (3) evaluate the potential for using a measurement-based modeling approach to interpret $\delta^{18}O$ of atmospheric CO_2 in an ecosystem, to quantify the foliar and soil component fluxes of the total ecosystem respiratory flux. Observations are presented that were made over several time periods, but we focus particularly on a two-week period in summer 2001 when extensive measurements were conducted in a ponderosa pine forest in central Oregon.

2. Methods

2.1. The $\delta^{18}O$ of Precipitation in Oregon

[9] We sought to characterize natural variability in $\delta^{18}O$ of ecosystem water pools over various timescales (diel to annual), including $\delta^{18}O$ of precipitation. Our ecosystem measurements, however, focused on a short-term experiment at a single forest. Therefore, we characterized variability in $\delta^{18}O$ of precipitation using data collected at other sites in Oregon, and assume that these provide a reasonable indication of general variability. Precipitation samples were collected approximately weekly at three locations during 1996, 1997, and 2000 as part of the National Atmospheric Deposition Program (http://nadp.sws.uiuc.edu/). The sites were the Starkey and H. J. Andrews Experimental Forests, and the Alsea Guard Ranger Station [*Welker*, 2000], and are located along a strong precipitation gradient [*Taylor and Hannan*, 1999]. The $\delta^{18}O$ of precipitation was determined by isotope ratio mass spectrometry as described by *Welker* [2000]. No additional measurements were made at these sites.

2.2. Primary Study Site

[10] Research was conducted in a forest dominated by old-growth ponderosa pine (*Pinus ponderosa*) at the Metolius Research Natural Area in central Oregon, USA (44°30′N, 121°37′W, 915 m elevation). The Metolius forest is a component of the AmeriFlux network of ecosystem-atmosphere carbon exchange sites (http://public.ornl.gov/ameriflux/Participants/Sites/Map/index.cfm) and has been the focus of several ongoing studies [*Anthoni et al.*, 1999, 2002; *Law et al.*, 1999, 2000; *Irvine et al.*, 2002; *Irvine and*

Law, 2002]. The forest comprises two age classes of pines, roughly 50 yrs and 250 years. Soils are freely draining sandy loams with 65% sand, 25% silt, and 10% clay. The canopy is 10–34 m tall and fairly open with a leaf area index of 2.1 m^2 m^{-2} [*Law et al.*, 2001b]. A sparse understory of bitterbrush (*Purshia tridentata*), strawberry (*Fragaria vesca*), and bracken fern (*Pteridium aquilinum*) is present. The 30-year mean annual temperature is 8.1°C and mean annual precipitation is 524 mm. A suite of environmental variables (air and soil temperatures, humidity, etc.) are measured continuously at the Metolius site; details have been published elsewhere [*Anthoni et al.*, 1999, 2002]. A preliminary analysis of the oxygen isotope ratios of ecosystem respiration at this and other sites along a precipitation transect in Oregon has been previously published [*Ehleringer and Cook*, 1998]. During summer 2001, isotopic measurements were conducted every night from June 28 to July 10 (days 179 to 191) and are described in the following sections.

2.3. The $\delta^{18}O$ and CO_2 in Ecosystem Air Samples

[11] Air samples were collected at night, beginning 1 hour after sunset, at several heights within the forest (0.2, 0.8, and 11.4 m) from tubing (Dekoron 1300, GWS Supply, Appleton, Wisconsin) located on a scaffolding tower. Samples were collected in glass flasks (34–5671, Kontes Glass Co., Vineland, New Jersey) using a portable photosynthesis system (LI-6200, LI-COR, Inc., Lincoln, Nebraska) downstream of the flasks to provide an initial indication of CO_2 mole fraction ($[CO_2]$) in the flasks. The goal during sampling was to achieve a maximal range in $[CO_2]$ in flasks collected during a single night, which has been shown to minimize the uncertainty in estimates of the carbon isotope content of ecosystem respiration using the Keeling plot technique [*Pataki et al.*, 2003]. Ten samples were collected per night. On one night, two separate sampling sessions were performed, one early in the night (near the end of day 186) and one late in the night (early on day 187). All samples were chemically dried during collection using magnesium perchlorate to avoid isotopic exchange with minute quantities of liquid water in flasks [*Gemery et al.*, 1996]. Samples were analyzed for $\delta^{18}O$ of CO_2 via continuous-flow isotope ratio mass spectrometry (details given by *Bowling et al.* [2002]) with a precision of 0.15‰. Final analysis of $[CO_2]$ was performed in the laboratory using infrared gas analysis and the method of *Bowling et al.* [2001] with a precision of 0.3 μmol mol^{-1}.

2.4. The $\delta^{18}O$ of Ecosystem Respiration

[12] The isotopic composition of ecosystem respiration ($\delta^{18}O_R$ or δ_R) was calculated using a two-ended mixing model known as the Keeling plot approach [*Keeling*, 1958]. We assumed that air in an ecosystem with initial $[CO_2]$ and $\delta^{18}O$ background compositions of C_b and δ_b mixed with a nocturnal respiratory source that had a constant isotopic composition δ_R. As CO_2 increased within the nocturnal boundary layer, mole fraction and isotope ratio (C_m and δ_m) changed concomitantly and these changes were monitored with flask samples collected and analyzed as described above. *Keeling* [1958] showed that these changes could be graphically interpreted along a mixing line defined by

$$\delta_m = C_b(\delta_b - \delta_R)/C_m + \delta_R. \quad (1)$$

Geometric mean regressions were performed between measured $\delta^{18}O$ and the inverse of measured $[CO_2]$, and the y-intercept was taken as an estimate of δ_R.

[13] Samples collected at different heights in the forest were combined for a single Keeling plot. *Bowling et al.* [2003b] presented a set of data quality criteria to determine when Keeling plots can be interpreted with confidence for oxygen isotopes of CO_2. All Keeling plots in this study met those requirements, which included (1) significant linear regressions ($p < 0.01$, Student's t-test) and (2) air sampling durations less than 5 hours. Outliers on individual Keeling plots were removed as described by *Bowling et al.* [2002]. In the present study, the outlier test resulted in a maximum removal of 1 sample per Keeling plot. $[CO_2]$ ranges in Keeling plots in the present study ranged from 68 to 121 μmol mol^{-1}, and sampling durations varied from 1.1 to 3.8 hours.

2.5. The $\delta^{18}O$ of Xylem, Leaf, and Soil Water

[14] Xylem (stem), leaf, and soil samples were collected for analysis of $\delta^{18}O$ of water near the end of the air sampling period each night (2200–0100 local time (LT)). Samples were stored in glass vials wrapped with wax film, and kept refrigerated or frozen until analysis. Stem samples (5–7 cm long × 0.5–1 mm diameter) were collected from three trees in the 50-year age class on days 181, 186, and 191. Bark was removed upon collection. Leaf samples (from the same trees used for the stems) were collected in triplicate every night from days 179 to 191. Leaf and xylem water data are presented as means and standard errors of triplicate samples.

[15] Soil samples were bulked, averaged, and subsampled from 0–10 cm mineral soil depth collected with a small shovel. Soil samples were collected every 20 m along a 200-m transect, roughly 200 m east of the air-sampling tower. Ten soil samples were collected each night, one per transect location. Not all soil samples were analyzed; data are presented as means and standard errors of 3–10 replicates. On day 229, 2001 (a month after the intensive study period), samples were collected at several depths (5, 10, 15, and 20 cm, all ± 2 cm) in three separate soil pits to examine the depth profile of $\delta^{18}O$ of soil water. Water was extracted from all samples by cryogenic vacuum distillation in the laboratory, and $\delta^{18}O$ of the water was analyzed by isotope ratio mass spectrometry [*Fessenden et al.*, 2002].

2.6. Modeling of Leaf Water Enrichment and Respiratory CO_2 Fluxes

[16] *McDowell et al.* [2003] presented direct measurements of the carbon isotope content of leaf and soil respiration at the Metolius pine forest during the time period of the present study. However, the oxygen isotope content of respiration by leaves and particularly by soils is quite difficult to measure with confidence [*Flanagan et al.*, 1999; *Miller et al.*, 1999; *Mortazavi and Chanton*, 2002]. The bag-based chamber method used by *McDowell et al.* [2003]

to measure $\delta^{13}C$ of leaf respiration was unreliable for oxygen isotopes due to isotopic fractionation effects on $\delta^{18}O$ of CO_2 stored in the bags [*Bowling et al.*, 2003a]. We elected instead to model leaf and soil-respired fluxes based on established principles of oxygen isotopic fractionation in leaves and soils. Uncertainties associated with these modeled flux estimates are addressed in section 3.

[17] Evaporative enrichment of leaf water was modeled using the Craig-Gordon model [*Craig and Gordon*, 1965] as described by *Flanagan et al.* [1991, 1997]. As inputs to this model we (1) applied the average of all measured xylem water values (−12.9‰) as $\delta^{18}O$ of source water, (2) used air temperature and relative humidity data collected at 45 m height (canopy top), (3) assumed leaf temperature was equal to air temperature, and (4) estimated $\delta^{18}O$ of atmospheric water vapor in the following two ways. Initially, we assumed water vapor was in isotopic equilibrium with measured xylem water (−12.9‰) at the mean air temperature (19.7°C) observed during days 179 to 191 to obtain a constant $\delta^{18}O$ of vapor (δ_{vapor}) of −22.5‰. For liquid-vapor equilibrium fractionation we used *Majoube's* [1971] equations. At the Metolius forest the equilibrium assumption resulted in a relatively poor comparison between measured and modeled leaf water ($\delta_{modeled} = 1.18*\delta_{measured} - 4.7‰$, $r^2 = 0.88$, n = 13). We then chose a constant value for δ_{vapor} (−16.6‰) that minimized the residual error in the regression between measured and modeled values. The results compared more favorably with observations ($\delta_{modeled} = 0.97*\delta_{measured} - 0.04‰$, $r^2 = 0.88$, n = 13). Modeled leaf water results are presented for both cases, which we refer to as the equilibrium case ($\delta_{vapor} = -22.5‰$) and the best fit case ($\delta_{vapor} = -16.6‰$).

[18] The $\delta^{18}O$ of CO_2 in nocturnal leaf respiration was modeled by assuming complete isotopic equilibration between CO_2 and modeled leaf water at leaf (air) temperature. The equations of *Brenninkmeijer et al.* [1983] were used to describe the temperature-dependent equilibrium fractionation factor between liquid water and gaseous CO_2. An assumed 8.8‰ kinetic fractionation factor, based on kinetic theory of gaseous diffusion, was applied to account for diffusion of CO_2 from the leaf. We are unaware of studies which have experimentally addressed whether or not the 8.8‰ fractionation is fully expressed in the nocturnal leaf respiration flux. Recent work has shown that the degree of isotopic equilibration in leaves is dependent on carbonic anhydrase activity [*Gillon and Yakir*, 2001]. Lack of perfect isotopic equilibrium between leaf water and CO_2 would confound our modeled estimates, but carbonic anhydrase activity is generally high in conifers [*Gillon and Yakir*, 2001]. The $\delta^{18}O$ of leaf-respired CO_2 during daylight hours was not modeled since all our measurements and modeling of $\delta^{18}O$ in respiratory fluxes were conducted at night.

[19] The $\delta^{18}O$ of soil water was measured once per night, and extended in time to produce a continuous time series by assuming that the measured value was representative of a period 12 hours before and after the measurement. The $\delta^{18}O$ of the soil-respired flux was modeled similarly to leaf respiration. Complete isotopic equilibrium was assumed between CO_2 and measured $\delta^{18}O$ of soil water (0–10 cm depth) at measured soil temperature (15 cm depth). All oxygen isotope ratios in this paper (for water and for carbon dioxide) are referenced to the Vienna Standard Mean Ocean Water (VSMOW) scale [*Coplen*, 1996] and are presented in dimensionless "units" of ‰.

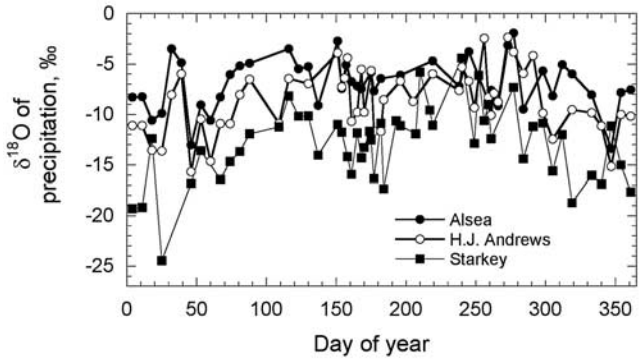

Figure 1. The $\delta^{18}O$ of precipitation in Oregon. Precipitation samples were collected in 1996, 1997, and 2000 at Alsea Guard Ranger Station (solid circles), and H. J. Andrews (open circles) and Starkey Experimental Forests (solid squares). The distances from the Pacific coast at the sites are 45, 150, and 450 km for Alsea, H. J. Andrews, and Starkey, respectively.

3. Results and Discussion

[20] To describe comprehensively the sources of variation that are likely to influence $\delta^{18}O$ of ecosystem respiration, we present data collected over a period of 3 years from three sites with widely varying annual precipitation that demonstrate the variability in $\delta^{18}O$ of individual precipitation events. We then show how environmental variables cause modification of $\delta^{18}O$ of leaf water and of water in the soil profile. Next, we describe how these water pools influence the isotopic composition of soil and foliar respiratory fluxes, and use this information to quantify their relative contributions to the total nocturnal respiration flux. Finally, we discuss the limitations of our approach in the context of other studies.

3.1. Variation in $\delta^{18}O$ of Precipitation, Leaf, and Soil Water and Implications for $\delta^{18}O$ of Respiration

[21] The isotopic composition of precipitation at three sites across Oregon is shown in Figure 1. In general, $\delta^{18}O$ of precipitation was more negative during the winter and less negative during the summer, a seasonal pattern that is generally observed at temperate locations where air and sea surface temperatures vary seasonally [*Rozanski et al.*, 1982; *Gat*, 1996; *Araguás-Araguás et al.*, 1998]. The site that was farthest from the Pacific coast (Starkey) generally exhibited more negative $\delta^{18}O$, and precipitation at the coastal site (Alsea) was less negative (as expected) based on the continental effect [*Rozanski et al.*, 1993; *Welker*, 2000; *Bowling et al.*, 2003b]. Temporal and spatial patterns such as these (winter/summer or coastal/inland patterns) are most easily discerned in long-term means, but means

Table 1. Week to Week Variability in $\delta^{18}O$ of Precipitation[a]

Location	Mean Difference, ‰	SD of Difference, ‰	Maximum Absolute Difference, ‰	Minimum Absolute Difference, ‰	n
Alsea	0.2	3.4	8.1	0.1	28
H. J. Andrews	0.0	4.1	9.7	0.1	34
Starkey	−0.8	4.1	12.1	0.0	31

[a]Statistics shown are calculated on the population of differences in $\delta^{18}O$ in subsequent 7-day periods ($\delta^{18}O_{week2} - \delta^{18}O_{week1}$).

generally obscure short-term variability. All three sites showed substantial variation from one week to the next (Figure 1) that was apparent in both winter and summer. The standard deviations of the week to week differences in $\delta^{18}O$ of precipitation at a single site were 3–4‰, and maximal weekly differences at the same site were as large as 12‰ (Table 1). Such variability is likely to have an important influence on the $\delta^{18}O$ of respired CO_2.

[22] During our intensive measurements in summer 2001, the weather at the Metolius forest was initially cool and humid. There was a 14.6-mm rain event with near-freezing temperatures on days 175–178, followed by rain-free conditions and progressively hotter and drier air for the remainder of the sampling period. Mean daily average temperatures increased from 14.4° to 22.8°C (days 179–191), while 24-hour average atmospheric vapor pressure deficit increased from 0.6 to 2.0 kPa over the same time period. Maximum daily vapor pressure deficit ranged from 1.2 to 4.5 kPa, providing prime conditions for evaporative enrichment of ^{18}O in leaf and soil water. A description of the environmental conditions and flux measurements during this time period can be found in a separate paper focused on the ^{13}C content of ecosystem respiration [*McDowell et al.*, 2003].

[23] To illustrate the influence of environmental variables on the isotope content of leaf water, weather conditions and $\delta^{18}O$ of leaf water on 3 days during the middle of this period at the pine forest are shown in Figure 2. Radiative input was strong with photosynthetically active radiation approaching 2000 W m^{-2}, and latent heat measurements from the flux tower at the site indicated similar diel patterns in evapotranspiration (not shown). Air temperatures varied on a diurnal basis by more than 20°C, and soil temperature amplitudes were damped relative to the air (5°C peak to peak at 15 cm depth, Figure 2b). Concomitant variation in relative humidity (Figure 2c) and leaf temperature combined to create very large (>25‰) diel changes in modeled $\delta^{18}O$ of leaf water (Figure 2d). The enrichment in ^{18}O of leaf water was caused by fractionation during transpiration. Lighter isotopes evaporated more readily, leaving behind relatively more of the heavier isotopes in the leaves. As transpiration diminished during the day, leaf water gradually mixed with stem water and $\delta^{18}O$ of leaf water became less enriched (less positive in $\delta^{18}O$, Figure 2d). The equilibrium vapor assumption resulted in an underestimation of $\delta^{18}O$ of leaf water compared to measurements, and the best fit case compared more favorably (Figure 2d). The daily range of modeled $\delta^{18}O$ of leaf water was much larger than the differences predicted by the models. As we will show, the large nocturnal range of $\delta^{18}O$ in leaf water results in a wide range of $\delta^{18}O$ in leaf-respired CO_2 over the course of a night.

[24] The $\delta^{18}O$ of water in the soil is shown in Figure 3. Open circles show observations over time in the 0–10 cm depth range during days 179–191. The depth profile was collected on day 229 and shows a pattern of more positive $\delta^{18}O$ of soil water near the surface relative to water in the soil at depth. This pattern is common in dry environments [*Allison et al.*, 1983] and was caused by isotopic fractionation associated with evaporation of soil water. Lighter molecules evaporated more easily, leaving the water in the profile more enriched in ^{18}O near the surface. We did not measure depth profiles during the intensive experiment period. However, the temporal variability observed at the 0–10 cm depth (Figure 3) was almost certainly accompanied by changes in the isotope content of soil water over the depth profile during this time (as shown for day 229 in Figure 3).

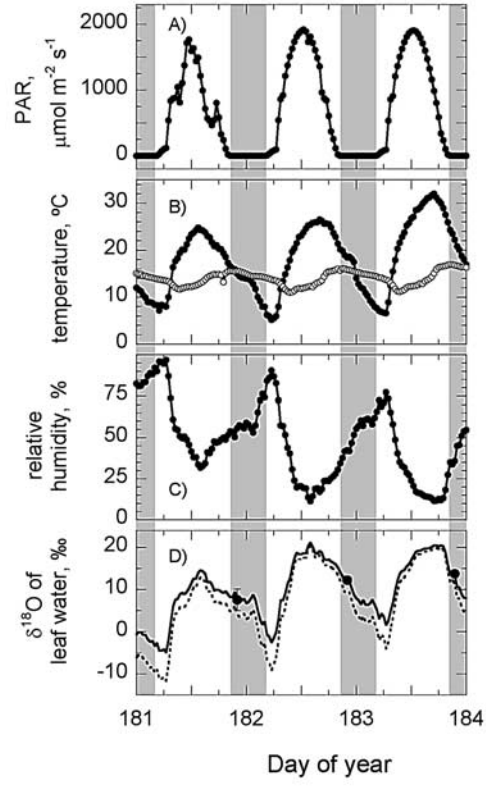

Figure 2. Diel meteorological and bulk leaf water evaporative enrichment patterns on days 181–184, 2001. (a) Photosynthetically active radiation. (b) Air (solid circles) and soil (open circles) temperature. (c) Relative humidity. (d) Modeled (lines) and measured (circles) $\delta^{18}O$ of bulk leaf water (error bars are smaller than the circles). The dashed modeled line was calculated using a constant δ_{vapor} of −22.5‰ (assuming vapor was in equilibrium with xylem water), and the solid line, −16.6‰ (fitted to minimize error between observed and modeled leaf water $\delta^{18}O$). Shading indicates night periods.

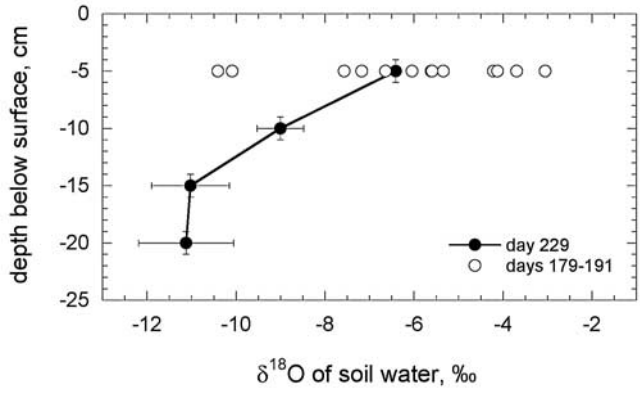

Figure 3. The $\delta^{18}O$ of water in the soil. The depth profile (solid circles, mean ± SE) was observed on day 229, 2001, collected at each depth in 2-cm slabs. The open circles show the range of observed values during days 179–191, bulked over the 0–10 cm depth range (see Figure 5 for the temporal pattern of data from days 179–191).

[25] One can imagine that variability in $\delta^{18}O$ of precipitation (Figure 1) combined with an isotopic profile in soil water that varies with depth (Figure 3) would lead to a new isotopic soil water profile following each rain event, followed by continuous changes during subsequent evaporative enrichment. The amount of rainfall, initial soil moisture content, and soil physical properties would dictate how far and how quickly the precipitation penetrated the soil. An ecosystem which experiences periods of hot dry weather interspersed with small rain events (such as our pine forest) is likely to have a complicated isotopic profile of soil water, and the resulting isotopic influence of this water pool on soil-respired CO_2 will be complex and quite dynamic.

3.2. The $\delta^{18}O$ of Ecosystem Respiration: Theory

[26] A representative Keeling plot from day 189 in the pine forest is shown in Figure 4. The $\delta^{18}O$ and $1/[CO_2]$ of samples collected in flasks are shown (solid circles) and represent mixing of background forest air (the single open circle) with respired CO_2 from all respiratory sources in the forest. On the basis of measured $\delta^{18}O$ of soil water (0–10 cm) and soil temperature, the modeled isotopic composition of the soil respiratory flux on this night was 27.7‰ (δ_{soil}, Table 2). On the basis of measurements of $\delta^{18}O$ of xylem and leaf water and environmental conditions, the modeled $\delta^{18}O$ of the leaf respiratory flux was 48.9‰ (δ_{leaf}, Table 2). If the soil-respired flux alone was added to the background atmosphere, it would mix along the lower dashed line. The upper dashed line shows the trajectory that would result from the addition of leaf-respired CO_2 to background air. The measured mixing line (the solid regression line in Figure 4) is a result of the combination of all respiratory component fluxes mixing with background air. The flux-weighted isotopic composition δ_R of the total ecosystem respiration flux was 33.6‰ (Table 2).

[27] If we neglect the contributions of respiration from live wood and woody decomposition (ignoring roughly 9% of the total flux [*Law et al.*, 2001a]), then δ_R should reflect the flux-weighted sum of the foliar and soil-respired components. This provides a way to estimate the fraction of the total flux produced by either component process. The total ecosystem respiration flux F_R comprises a flux from the soil (F_{soil}), and a flux from the foliage ($F_{foliage}$) so that

$$F_R = F_{soil} + F_{foliage} \tag{2}$$

$$1 = (F_{soil} + F_{foliage})/F_R. \tag{3}$$

Equations (2) and (3) represent conservation of mass for total CO_2. The processes controlling oxygen isotope fractionation in the soil do not allow us to distinguish between heterotrophic and autotrophic respiration belowground, so these are lumped together as a single flux F_{soil}. Each flux in equation (2) can be multiplied by its isotopic composition to represent conservation of mass for the heavy isotope $C^{18}O^{16}O$,

$$\delta_R F_R = \delta_{soil} F_{soil} + \delta_{foliage} F_{foliage}. \tag{4}$$

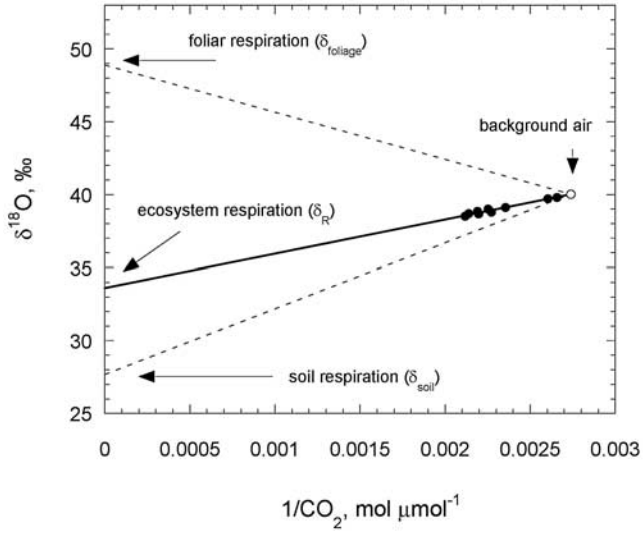

Figure 4. A graphical representation of the factors that influence $\delta^{18}O$ of CO_2 in air in an ecosystem. Data shown (solid circles) were collected at night on day 189, 2001. The solid line is the Keeling plot regression through the data, and the background air datum was selected arbitrarily (CO_2 = 365 μmol mol^{-1}) on the Keeling line. The intercept of the regression (δ_R) is interpreted as the oxygen isotopic composition of total ecosystem respiration. The isotopic signature of soil respiration (δ_{soil}) was calculated based on observed soil water $\delta^{18}O$ (0–10 cm depth) and soil temperature. The foliar signature ($\delta_{foliage}$) was calculated based on observed xylem water $\delta^{18}O$, air temperature and humidity, and the Craig-Gordon model of evaporative enrichment. Details of these calculations and appropriate fractionation factors are provided in the text. The dashed lines represent the theoretical mixing lines that would result if either (top) foliar or (bottom) soil respiration alone were added to the background air.

Table 2. Separation of Total Ecosystem Respiration Into Soil and Foliar Components Using $\delta^{18}O$ of Respiration[a]

Day of Year	$\delta^{18}O$ of Ecosystem-Respired CO_2 (δ_R), ‰	$\delta^{18}O$ of Leaf-Respired CO_2 ($\delta_{foliage}$), ‰	$\delta^{18}O$ of Soil-Respired CO_2 (δ_{soil}), ‰	Soil-Respired Fraction
179	24.2 ± 0.6	37.8 ± 1.1	23.7 ± 0.1	0.96
180	28.0 ± 0.4	37.6 ± 0.6	23.3 ± 0.1	0.67
181	28.2 ± 0.6	42.2 ± 0.7	27.1 ± 0.0	0.93
182	29.7 ± 0.3	46.2 ± 1.5	26.6 ± 0.3	0.84
183	31.3 ± 0.9	45.0 ± 2.3	25.9 ± 0.0	0.72
184	31.3 ± 0.3	49.2 ± 1.7	27.8 ± 0.0	0.84
185	30.1 ± 0.8	42.3 ± 0.3	29.3 ± 0.2	0.94
186[b]	32.5 ± 0.7	45.3 ± 1.7	27.2 ± 0.1	0.71
187[b]	32.9 ± 0.5	41.1 ± 0.4	27.5 ± 0.0	0.61
187	33.9 ± 0.3	44.8 ± 1.8	28.1 ± 0.1	0.65
188	31.9 ± 0.6	45.9 ± 0.2	29.3 ± 0.0	0.84
189	33.6 ± 0.4	48.9 ± 0.6	27.7 ± 0.1	0.72
190	31.1 ± 0.6	46.2 ± 0.7	30.3 ± 0.2	0.95
191	32.9 ± 0.3	46.1 ± 0.7	29.5 ± 0.0	0.80
Mean	30.83	44.2	27.4	0.80
SD	2.64	3.6	2.0	0.12

[a]Shown are $\delta^{18}O$ of respired CO_2 from the entire ecosystem and from the foliar and soil components, and the calculated fraction of total ecosystem respiration originating in the soil. Leaf-respired values were calculated assuming $\delta_{vapor} = -16.6‰$. Uncertainties in $\delta^{18}O_R$ are reported as the standard error of the Keeling plot intercept, and uncertainties in the leaf and soil respiration fluxes represent the standard deviation of all modeled values during the time of air sampling each night (sampling times varied from 1.1 to 3.8 hours). Actual error in the estimates is likely to be larger due to assumptions made in the modeling of the soil and leaf fluxes.
[b]Collected during two separate sampling sessions over one night.

Rearranging equation (4) yields

$$\delta_R = \left(\delta_{soil}F_{soil} + \delta_{foliage}F_{foliage}\right)/F_R, \quad (5)$$

and if we represent the fractional soil contribution to the total flux in equation (3) as $f = F_{soil}/F_R$ and the foliar contribution as $(1\text{-}f) = F_{foliage}/F_R$ we can write

$$\delta_R = (\delta_{soil})f + \delta_{foliage}(1\text{-}f). \quad (6)$$

Thus, if we can establish δ_{soil} and $\delta_{foliage}$ based on measurements and modeling, and if we can obtain a robust estimate of δ_R from a Keeling plot, then we can separate the relative contributions of the soil (f) and foliar ($1\text{-}f$) fluxes to the total ecosystem respiration flux using oxygen isotopes of CO_2.

[28] This approach is similar to isotopic methods developed to separate the transpiration and evaporation components of total evapotranspiration fluxes [*Yakir and Sternberg*, 2000, and references therein]. Three assumptions are made here. The first is that there is no isotopic variation imparted to atmospheric CO_2 by processes other than soil and foliar respiration. Such variation could result from interaction between CO_2 and rain or dew in a very stable boundary layer, by heterotrophic responses to pulse rain events [*Irvine and Law*, 2002], by changes in atmospheric conditions that lead to mixing from a distant source of CO_2 (e.g., smoke from fires or changes in measurement footprint), or from respiration by other sources that may not have the same isotope content (e.g., decomposition of coarse woody debris). Second, this approach assumes the isotopic signatures of soil and foliar respiration remain constant during the time period required to collect samples to construct the Keeling plot. This requirement may be relaxed if the variation in $\delta^{18}O$ of the respired fluxes is small relative to the isotopic distance between the two, as in Figures 4 and 6 and Table 2. Third, the relative proportions of the two fluxes (f and $1\text{-}f$ in equation (6)) must not change during the sampling period. For example, if leaf temperatures decreased over several hours during the night (decreasing leaf respiration rate) while soil temperatures (and respiration rate) remained fairly constant, the fractional contributions to total ecosystem respiration would change (see Figure 2b). *Bowling et al.* [2003b] argue that sampling duration should be minimized (<5 hours) to achieve theoretically realistic Keeling plot intercepts. Sampling over a short period (a few hours, as done in the present study) will minimize violation of the second and third assumptions above.

3.3. The $\delta^{18}O$ of Ecosystem Respiration: Application

[29] Two-week time series of $\delta^{18}O$ of xylem, soil, and stem water at the pine forest are shown in Figure 5, including direct measurements (symbols) and modeling or estimation (lines). Stem water remained isotopically constant, and comparison with nearby spring water samples suggests a groundwater or deep soil water source [*Anthoni et al.*, 1999; *Irvine et al.*, 2002; *Bowling et al.*, 2003b]. Initially, observed $\delta^{18}O$ of soil water was relatively depleted

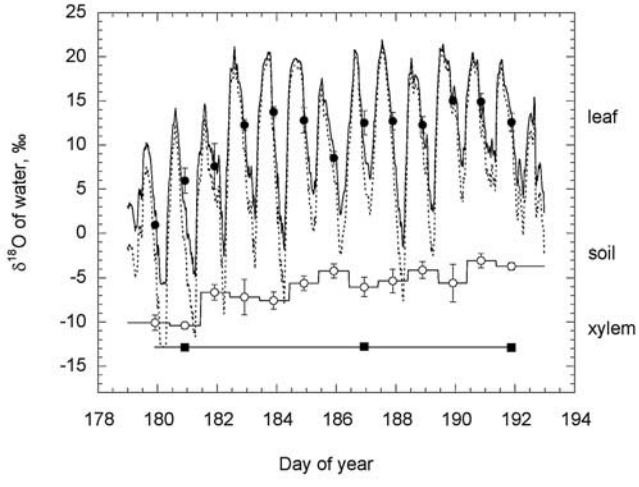

Figure 5. The $\delta^{18}O$ of leaf, xylem, and soil water over a 13-day period in July 2001. Rain fell on days 175–179, but the measurement period shown was rain-free. Data points are measured values (means ± SE, n = 3 to 10) of leaf water (solid circles), soil water (0–10 cm depth, open circles), and xylem water (squares) isotope content. Error bars are smaller than the symbols in some cases. The lines represent modeled data (for leaf water) or filled data (observed values were simply extended in time for xylem and soil water). The $\delta^{18}O$ of leaf water was modeled with the Craig-Gordon model assuming $\delta_{vapor} = -16.6$ ‰ (solid line, fitted to minimize error between observed and modeled leaf water $\delta^{18}O$) or −22.5‰ (dashed line, assuming vapor was in equilibrium with xylem water).

(−10.1‰ on day 179) but became enriched in ^{18}O by soil evaporation (−3.7‰ on day 191) as the weather became hot and dry. This gradual enrichment is likely to be associated with a complex soil depth profile like the one shown in Figure 3. The isotopic composition of the rain that fell just prior to our sampling period was not measured, but the value must have been near −10‰ to produce the observed soil values. The $\delta^{18}O$ of leaf water collected at roughly the same hour each night also showed gradual enrichment (0.9 to 12.6‰, Figure 5). However, the enrichment over the two weeks of the experiment was dwarfed by large diel changes in modeled $\delta^{18}O$ of leaf water (on some days greater than 25‰). In general, modeled $\delta^{18}O$ values for leaf water compared well with measurements considering the large diurnal range and the assumptions made in modeling leaf water.

[30] The data in Figures 1, 2, 3, and 5 illustrate the importance of short-term (hourly) environmental controls on $\delta^{18}O$ of leaf water, and also how leaf and soil water $\delta^{18}O$ can change in response to synoptic scale weather events (days to weeks). Changes in $\delta^{18}O$ of leaf and soil water pools will be directly conferred to respired CO_2.

[31] The nightly isotopic compositions of the respiratory fluxes are shown in Figure 6. Total ecosystem respiration was initially relatively depleted (24.2‰ on day 179) and became enriched in ^{18}O over the 2 weeks (32.9‰ on day 191) as soil and leaf water pools changed. The soil-respired flux changed from 23.7 to 29.5‰, and the leaf respired flux from 37.8 to 46.1‰. Changes in $\delta^{18}O$ of leaf water (Figure 5) and in leaf temperature caused large (4–16‰) changes in $\delta^{18}O$ of leaf respired CO_2 on all nights. By contrast, changes in soil temperature did not appreciably change $\delta^{18}O$ of the soil-respired flux. Shown in Table 2 are $\delta^{18}O$ values for each respiratory flux, with an indication of how much the isotopic compositions of the fluxes changed during the actual time air was sampled to construct Keeling plots. Although there was large variation over the whole night in $\delta^{18}O$ of leaf-respired CO_2, by minimizing the duration of air sampling (a few hours) the range of $\delta^{18}O$ variation was kept fairly small. The difference between $\delta^{18}O$ of the leaf and soil respiration fluxes varied from 13.1 to 21.4‰, much greater than the range of modeled values during sampling shown in Table 2.

[32] Application of equation (6) to determine the fraction of total ecosystem respiration attributable to soil surface respiration resulted in values ranging from 0.61 to 0.96 (Table 2). The variability in this fraction from night to night was likely caused by inadequate characterization of the isotopic endpoints δ_{soil} and $\delta_{foliage}$ and not by actual changes in the relative magnitudes of the soil and foliar respiration fluxes. Temporal variability in $\delta^{18}O$ of leaf water is substantial (Figure 5), and considerable spatial variability probably exists in δ_{soil} and $\delta_{foliage}$ as well. Variation in $\delta^{18}O$ of leaf water with height in the vegetation canopy has been noted in coniferous [*Allison et al.*, 1985] and tropical (J. P. Ometto et al., Oxygen isotope ratios of waters and respired CO_2 in Amazonian forest and pasture ecosystem, submitted to Ecological Applications, 2003) forests, but such variation is not always observed [*Flanagan and Varney*, 1995; *Bowling*, 1999].

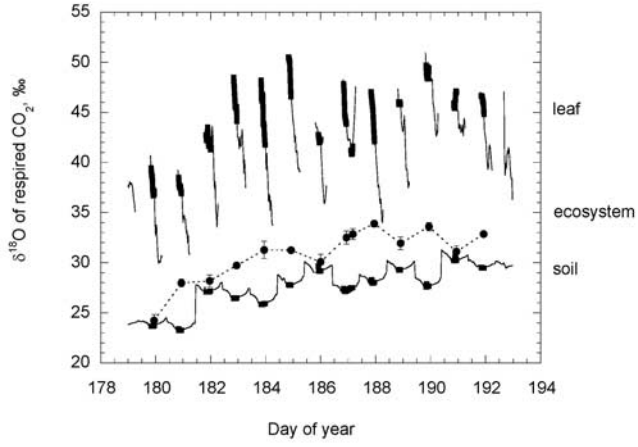

Figure 6. The $\delta^{18}O$ of CO_2 from nocturnal leaf, soil, and ecosystem respiration for the time period shown in Figure 5. Measured ecosystem respiration isotopic composition ($\delta^{18}O_R$, solid circles) are derived from nocturnal Keeling plots, one per night (except day 187, two per night). Error bars on the ecosystem data are smaller than the symbols in some cases. All other data in the figure are modeled. Modeled data for $\delta^{18}O$ in leaf (upper lines) and soil (lower line) respiration are based on the measurements and modeling in Figure 5. The thin lines represent $\delta^{18}O$ of foliar (upper thin lines) or soil (lower thin line) respiration during all nocturnal time periods, and the thick lines (upper and lower) show the subset of time periods during which flask samples were collected to determine $\delta^{18}O_R$. The modeled soil estimate (lower thin line) represents $\delta^{18}O$ of soil-respired CO_2 during all time periods, day and night, while the modeled leaf estimates (upper thin lines) are for nocturnal periods only. The variation in the modeled soil estimate is due to soil temperature variation and the stair-step pattern of the filled soil water $\delta^{18}O$ data in Figure 5. These data (upper and lower thick lines) show the variation in foliar and soil-respired isotope content that will influence the flask samples during collection.

[33] Averaged over the 2-week period, the soil fraction was 0.80 (standard deviation of the nightly soil fractions was 0.12), and the foliar contribution made up the remainder (0.20). The sensitivity of this fraction to δ_{soil} and $\delta_{foliage}$ is evident during the night that two separate sampling sessions were performed (days 186–187, Figure 6, Table 2). The Keeling plot intercepts (δ_R) and the modeled estimates of δ_{soil} did not differ during the two sessions (Table 2). However, a decrease in $\delta_{foliage}$ resulted in a smaller calculated fraction from the soil later in the night, which is unlikely, based on soil and air temperature data and their expected influence on soil and foliar respiration rates (not shown).

[34] Extensive measurements by *Law et al.* [1999, 2001a] suggest that, on an annual basis, soil, foliar, and woody respiration accounted for 77, 13, and 6%, respectively, of the total respiration flux at the Metolius pine forest, and decomposition of woody detritus was roughly 3%. Our estimate of the soil fraction is higher (80%), but we have

ignored the contribution of live woody respiration and decomposition of woody debris to the total ecosystem respiration flux (a total of 9% of ecosystem respiration). No published studies have addressed $\delta^{18}O$ of CO_2 respired by living or dead woody biomass, and we were uncertain how to describe isotopic effects from these sources. At present the quantitative application of Keeling plots in separating above and belowground components of ecosystem respiration is limited to an approach like ours.

[35] Clearly, the oxygen isotope content of ecosystem respiration and its foliar and soil components is dynamic in time. The $\delta^{18}O$ of leaf water can change over several hours within a single night (Figure 2), and from one night to the next based on changing environmental conditions (Figure 5). Soil evaporation alters the isotopic profile of soil water over a timescale of days to weeks (Figures 3 and 5). The $\delta^{18}O$ of precipitation is quite variable from event to event (Figure 1) and can change soil water $\delta^{18}O$. Heterotrophic activity can increase strongly in response to rain events [*Cui and Caldwell*, 1997; *Irvine and Law*, 2002; *Kelliher et al.*, 2003], and it is likely that autotrophic respiration of shallowly rooted plant species can increase as well [e.g., *Sala and Lauenroth*, 1982; *BassiriRad et al.*, 1999; *Schwinning et al.*, 2003]. These factors combine to create a complex array of soil water pools that directly influence the isotope content of respired CO_2. Despite this complexity, we were able to construct realistic estimates of the isotope ratios of the respired component fluxes with direct measurements of soil and xylem water $\delta^{18}O$, air and soil temperature, and humidity (Figure 6). These estimates allowed us, via equation (6), to quantify the foliar and soil respiratory contributions to total ecosystem respiration (Table 2), and our results are comparable to the scaled chamber estimates of *Law et al.* [1999, 2001a].

3.4. Model Assumptions and Limitations

[36] Our results suggest that some realistic understanding of ecosystem respiration may be achievable using oxygen isotopes of CO_2, subject to a few caveats. There are several simplifying assumptions made in our models which limit our ability to quantitatively determine the isotopic signatures of the respiration fluxes δ_{soil} and $\delta_{foliage}$.

[37] We did not directly measure δ_{vapor}, and hence some estimate of this parameter was required. The assumption that atmospheric water vapor is in equilibrium with local groundwater may be valid at humid inland locations but water vapor at coastal and arid regions is likely to depart from equilibrium with local groundwater [*Jacob and Sonntag*, 1991; *Flanagan*, 1993; *Gat*, 1996; *Araguás-Araguás et al.*, 2000]. This is a potentially serious problem that could alter our modeled estimates of $\delta_{foliage}$ by several ‰ or more [*Jacob and Sonntag*, 1991]. Direct measurements of δ_{vapor} should be made in future studies of this topic.

[38] The Craig-Gordon model of evaporative enrichment as applied to leaf water has been shown to be robust under a wide range of environmental conditions for a wide range of plant species [*Roden and Ehleringer*, 1999, and references therein]. However, most of these comparisons were made during the daytime when transpiration was active. Very few published studies have assessed the validity of the model at night [*Cernusak et al.*, 2002]. Recall that we initially assumed $\delta^{18}O$ of atmospheric water vapor was in equilibrium with local xylem water, and that led to an underestimation of bulk leaf water values (Figure 2). *Bowling* [1999] noted that the Craig-Gordon model underestimated bulk leaf water at night by 2‰ in white oak (*Quercus alba*) and red maple (*Acer rubrum*). The best fit assumption for δ_{vapor} resulted in a favorable match with observations (Figures 2 and 5), but is less than satisfying since it is a fit to make things match.

[39] The Craig-Gordon model assumes steady state conditions (leaf transpiration rate, δ_{vapor}, leaf temperature, etc.) which can be controlled in the laboratory, but such conditions are not likely to be met in the field [*Wang and Yakir*, 1995]. *Cernusak et al.* [2002] examined $\delta^{18}O$ of bulk leaf water in lupine (*Lupinus angustifolius*) in the field with repeated measurements through a night, and convincingly showed the steady state Craig-Gordon model underestimated $\delta^{18}O$ of leaf water at night by several ‰. They presented a non-steady-state variant of the model that reproduced observed leaf water isotope content throughout the night with minimal error. *Cernusak et al.'s* [2002] model was based on several parameters obtained from leaf level gas exchange measurements such as leaf transpiration rate, leaf conductance, and leaf water concentration, which unfortunately were not available in the present study. Further, our assumption that leaf temperature equals air temperature, a common assumption for conifers, is likely to fail at low wind speeds [*Martin et al.*, 1999]. Regardless, given the large difference in $\delta_{foliage}$ and δ_{soil}, meaningful determination of the soil respiration fraction (f) of total ecosystem respiration can still be achieved with errors of a few ‰ in $\delta^{18}O$ of leaf water.

[40] Variation with depth in $\delta^{18}O$ of soil water is quite important for $\delta^{18}O$ of CO_2 produced by soil respiration. CO_2 is produced at some depth in the soil or litter layer, and diffuses to the surface and out as a respiration flux. Respiratory CO_2 undergoes a hydration reaction and equilibrates isotopically with soil water, although equilibration may not be complete. Production rates of CO_2 by respiration differ with depth as respiratory substrate and nutrient availability, microbial and macrofaunal activity, and rooting depth vary. The degree to which the competing hydration and diffusion rates will influence isotopic exchange of CO_2 with soil water should also change as a function of depth. *Miller et al.* [1999] proposed the "setting point depth," a depth at which CO_2 in the surface flux is in apparent complete isotopic equilibrium with water in the soil profile. In reality, perfect equilibrium at a particular depth probably never occurs, and the CO_2 that effluxes from the soil surface represents a flux-weighted average of CO_2 in partial equilibria with water at various depths in the soil [*Miller et al.*, 1999].

[41] The $\delta^{18}O$ of respired CO_2 is influenced by the diffusion of CO_2 from the atmosphere that exchanges oxygen atoms with soil water and diffuses back out [*Tans*, 1998]. This has been referred to as "atmospheric invasion" [*Tans*, 1998] or "abiotic oxygen isotope exchange" [*Stern et al.*, 2001]. Invading CO_2 has an apparent oxygen isotopic

signature that mimics that of CO_2 produced by respiration, although it is not a direct product of biological respiration. The importance of invasion under natural conditions has not been established, but laboratory studies suggest it has a significant influence under stable atmospheric conditions and with soil chamber measurements of respired $\delta^{18}O$ [*Miller et al.*, 1999]. Modeling results suggest the invasion component of soil respiration can be as large as 0.7 μmol m^{-2} s^{-1} under some conditions [*Stern et al.*, 2001]. We have entirely ignored invasion in our simple model.

[42] Observations in Figure 3 show variation in $\delta^{18}O$ of soil water with depth (4.7‰ over 15 cm). A modeled estimate of $\delta^{18}O$ of soil-respired CO_2 that depends on measured $\delta^{18}O$ of soil water (such as the data we present in Figure 6) is potentially in error by several ‰ if the complexities of soil water $\delta^{18}O$ are not appropriately characterized. There can be very pronounced isotopic enrichment (or depletion following rain) in the top few centimeters of the soil [*Allison et al.*, 1983; *Bariac et al.*, 1994; *Melayah et al.*, 1996; *Miller et al.*, 1999], but it is not clear that extreme near-surface enrichment in soil water substantially alters ^{18}O of respired CO_2 [*Miller et al.*, 1999]. Diffusion of CO_2 produced very near the surface presumably occurs faster than the time required for isotopic changes by hydration.

[43] We used a simple approach to model $\delta^{18}O$ of soil-respired CO_2 which required measurements only of soil water $\delta^{18}O$ and soil temperature. *Tans* [1998], *Stern et al.* [2001], and other papers by these groups have established elaborate process models to predict δ_{soil} that compare well with observations in the laboratory [*Miller et al.*, 1999]. These models require information about soil water content and isotope ratio variation with depth, soil physical properties (porosity, tortuosity, diffusivity), and respiration rate (also as a function of depth). With detailed measurements of these parameters a more accurate estimate of δ_{soil} could be obtained.

[44] Efforts have been made to model the influence of terrestrial ecosystems on the oxygen isotope ratio of atmospheric CO_2 at regional, continental, and global scales [*Ciais et al.*, 1997; *Peylin et al.*, 1999; *Cuntz et al.*, 2002, 2003a, 2003b; *Styles et al.*, 2002; *Ishizawa et al.*, 2002]. These models are fundamentally dependent on knowledge of the isotopic composition of precipitation, which is also typically modeled [e.g., *Cuntz et al.*, 2003a, 2003b]. Results from the present study, *Bowling et al.* [2003b], and *Flanagan et al.* [1999] suggest that to adequately capture the dynamics of $\delta^{18}O$ of ecosystem respiration, models must be able to accurately characterize the seasonal and spatial variation in environmental factors such as temperature and humidity, and $\delta^{18}O$ of precipitation, soil water, and xylem water. Ecosystem-scale studies of $\delta^{18}O$ in respiration clearly must address the temporal variability in water pools and ecosystem fluxes that we have observed. Future studies that seek to use $\delta^{18}O$ in CO_2 to partition ecosystem respiration fluxes should make an effort to improve determination of δ_{soil} and $\delta_{foliage}$ via more extensive measurements and application of the latest improvements in modeling of leaf [*Roden and Ehleringer*, 1999; *Gillon and Yakir*, 2000a, 2000b; *Cernusak et al.*, 2002] and soil [*Tans*, 1998; *Amundson et al.*, 1998; *Miller et al.*, 1999; *Stern et al.*, 2001] isotopic effects on ^{18}O.

4. Conclusions

[45] We have examined the factors that influence short-term variation (hours to days) in the oxygen isotopic composition of ecosystem respiration. $\delta^{18}O$ of precipitation was variable from storm to storm, and in general this variability is expected to result in variation in $\delta^{18}O$ of soil water. Within a ponderosa pine forest, synoptic changes in air and soil temperature and humidity influenced $\delta^{18}O$ of soil water and leaf water over several days, and these water pools affected $\delta^{18}O$ of respired CO_2. Isotopic estimates of the fractional contribution of soil respiration to total ecosystem respiration in this forest averaged 80%, with large variability that might be explained by changes in physical (e.g., diffusion) and biological (e.g., heterotrophic) processes.

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