Hydrologic control of the oxygen isotope ratio of ecosystem respiration in a semi-arid woodland

J. H. Shim¹, H. H. Powers¹, C. W. Meyer¹, A. Knohl², T. E. Dawson³, W. J. Riley⁴, W. T. Pockman⁵, and N. McDowell¹

¹Earth and Environmental Sciences Division, Los Alamos National Laboratory, MS-J495, Los Alamos, NM 87545, USA
²Chair of Bioclimatology, Georg-August University of Göttingen, Göttingen, Germany
³Department of Integrative Biology, University of California, Berkeley, CA, USA
⁴Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA
⁵Department of Biology, University of New Mexico, Albuquerque, NM 87131-0001, USA

Correspondence to: J. H. Shim (jeeshim@gmail.com)

Received: 19 September 2012 – Published in Biogeosciences Discuss.: 2 January 2013
Revised: 8 May 2013 – Accepted: 18 June 2013 – Published: 23 July 2013

Abstract. We conducted high frequency measurements of the δ¹⁸O value of atmospheric CO₂ from a juniper (Juniperus monosperma) woodland in New Mexico, USA, over a four-year period to investigate climatic and physiological regulation of the δ¹⁸O value of ecosystem respiration (δR). Rain pulses reset δR with the dominant water source isotope composition, followed by progressive enrichment of δR. Transpiration (ET) was significantly related to post-pulse δR enrichment because the leaf water δ¹⁸O value showed strong enrichment with increasing vapor pressure deficit that occurs following rain. Post-pulse δR enrichment was correlated with both ET and the ratio of ET to soil evaporation (ET/ES). In contrast, the soil water δ¹⁸O value was relatively stable and δR enrichment was not correlated with ES. Model simulations captured the large post-pulse δR enrichments only when the offset between xylem and leaf water δ¹⁸O value was modeled explicitly and when a gross flux model for CO₂ retro-diffusion was included. Drought impacts δR through the balance between evaporative demand, which enriches δR, and low soil moisture availability, which attenuates δR enrichment through reduced ET. The net result, observed throughout all four years of our study, was a negative correlation of post-precipitation δR enrichment with increasing drought.

1 Introduction

Terrestrial ecosystems play an important role in global carbon cycling, and atmospheric oxygen isotope composition of CO₂ (δa) has emerged as a promising tool to detect biosphere–atmosphere CO₂ fluxes at tissue, ecosystem, regional and global scales (Francey and Tans, 1987; Yakir and Wang, 1996; Tans and White, 1998; Farquhar et al., 1993; Buenning et al., 2011; Cuntz et al., 2003a; Welp et al., 2011). δa has been used to distinguish the contributions of photosynthesis and respiration (Tans and White, 1998; Yakir and Wang, 1996) and of nocturnal foliar and soil respiration (Bowling et al., 2003a) to net ecosystem exchange. The δ¹⁸O value of terrestrial CO₂ fluxes (δg) may provide a stronger terrestrial signal than δ¹³C in some ecosystems (Fung et al., 1997; Ogée et al., 2004), but prediction of δg is complex (Still et al., 2009) because it depends on prediction of both ecosystem water and C dynamics (Riley et al., 2003, 2005; Lai et al., 2006). The utility of oxygen isotopes in carbon cycle research can be improved, however, by a better understanding of plant physiological effects on the gross and net leaf fluxes of C¹⁸O₁⁶O (Flanagan et al., 1997; Gillon and Yakir, 2000; Cernusak et al., 2004).

δR depends on the ⁰¹⁸O composition of the net CO₂ effluxes from foliage, stem, and soils. These effluxes are strongly influenced by the ⁰¹⁸O compositions of their respective water pools through oxygen atom exchange between CO₂ and H₂O after equilibrium and diffusive fractionation (Brenninkmeijer et al., 1983; Tans, 1998; Farquhar et al., 1993). Carbonic anhydrase (CA) catalyzes this CO₂–H₂O isotopic equilibration inside foliage (Flanagan et al., 1997) and soil (Riley et al., 2002; Seibt et al., 2006; Wingate et al., 2009).

δSW is often reset to the isotopic content of precipitation, which varies strongly with condensation temperature, storm origin, and
storm tracks (Rozanski et al., 1982; Wingate et al., 2010). Subsequently, a vertical gradient in δsw is often established because soil evaporation leads to isotopic enrichment (increasing δ18O value; Sharp, 2005) in the upper layers (Walker et al., 1988; Mathieu and Bariac, 1996). Soil water that is taken up by plant roots is transported through the xylem unfractionated in most terrestrial ecosystems (Dawson and Ehleringer, 1991). Leaf water becomes enriched relative to xylem water because of fractionation during evapotranspiration (Wang and Yakir, 1995; Roden and Ehleringer, 1999; Flanagan et al., 1997). At night, leaf water can become more enriched than that predicted by the Craig–Gordon model, due to the lag in relaxation of the daytime leaf water enrichment toward the nighttime value (Cernusak et al., 2002; Farquhar and Cernusak, 2005). Cuntz et al. (2003b) incorporated such a lag into a global model of δ18O value in atmospheric CO2. They concluded that the leaf-respired δ18O value becomes further enriched above source water due to CO2 retro-diffusion (the process where CO2 enters foliage through stomata, equilibrates with leaf water, and escapes from the leaf without altering the net CO2 flux; Cernusak et al., 2004). Lastly, assuming an accelerated soil hydration rate from soil surface CA activity improved agreement between predicted and observed 18O composition of atmospheric CO2 (Wingate et al., 2009).

δR is impacted by evaporative enrichment of ecosystem water pools. Evapotranspiration drives greater isotopic enrichment in foliage than in soils due to the much smaller water pool of foliage. This enrichment results in foliar respiration being more 18O enriched than soil respiration, and the isotopic disequilibrium between the δ18O values of soil and leaf-respired CO2 is enhanced during dry periods (Wingate et al., 2010). For example, the δ18O values of branch and soil respiration increased during a post-precipitation dry period by 170‰ and 18‰ (Vienna Pee Dee Belemnite-CO2), respectively, in a Pinus dominated ecosystem in Europe (Wingate et al., 2010). Thus, δs may carry a strong signal of drought impacts on the hydrology of terrestrial systems.

A reasonable hypothesis is that δR increases during seasonal droughts when precipitation (P) minus potential evapotranspiration (EP; Ellis et al., 2010) is most negative. Testing this hypothesis requires long-term datasets to capture a large range of P − EP. A further reasonable hypothesis is that drought imparts a δR enrichment dependent on the ratio of canopy transpiration to soil evaporation (ET/ES) because of their differential responses to drought (Wingate et al., 2010). ET and ES represent the two main fluxes of water from the ecosystem to the atmosphere. The ET/ES ratio is fundamentally important because it is mechanistically linked to vegetation and ecosystem water balance processes and is sensitive to disturbances such as climate extremes and woody encroachment (Huxman et al., 2005). Therefore, the magnitude of δR enrichment over the several days after pulse events should be linked to ET and ES because these fluxes impact the δ18O values of source water pools (i.e., leaves and soil water) with which CO2 interacts.

To our knowledge, no study has combined long-term δR, P − EP, and ET/ES observations with an analysis of terrestrial ecosystem drought response. ET/(ES + ET) has been estimated from observations for a relatively small number of locations in water-limited regions, and those field estimates vary greatly in methodology (Reynolds et al., 2000, Wilson et al., 2001). There have been a few high-resolution, continuous monitoring studies of δR (Griffis et al., 2005; Welp et al., 2006; Wingate et al., 2010), but none from arid ecosystems that would be expected to strongly exhibit drought signals. Semi-arid woodlands in the southwestern USA are dominated by pulse-driven precipitation patterns and prolonged and severe drought periods (Seager et al., 2007; Rauscher et al., 2008); thus a logical expectation is that these woodlands exhibit large variation in δR, P − EP, and ET/ES.

We measured δR in a juniper (Juniperus monosperma) woodland over a four-year period to investigate precipitation-pulse-driven eco-hydrological responses. Along with direct measurements of ET, we improved and applied ISOLSM (Riley et al., 2002), an isotope-enabled land-surface model, to estimate ES and interpret δR observations. We hypothesized that (1) δR would be related to P − EP; however, (2) this relationship would be moderated by rainfall-pulse-driven changes in ET or ET/ES. Our overarching goal is to move towards better understanding of the mechanisms determining the δ18O compositions of terrestrial CO2 fluxes and the atmosphere, allowing for potential use of these signatures for monitoring the impacts of drought on terrestrial ecosystems.

2 Methods

2.1 Field site

The field site is a píñon pine–one-seed juniper (Pinus edulis–Juniperus monosperma) woodland located in northern New Mexico at Los Alamos National Laboratory (35.85° N, 106.27° W, elevation 2140 m). Approximately 97% of the mature píñon trees died in October 2002 (Breshears et al., 2005; McDowell et al., 2008a), resulting in a large necromass component to the ecosystem. The understory is dominated by C3 forbs that have increased substantially since the píñon mortality, with a minor component (~10% cover) of native C4 grass (Bouteloua gracilis). Average leaf area index of the understory during the growing season is ~0.25 m² m⁻² and juniper leaf area index is ~1.1 m² m⁻²; maximum canopy height is ~5.5 m and stand density is about 371 trees ha⁻¹ (McDowell et al., 2008a). The site is located on a ~200 m wide mesa with a slope of ~5%. The soils are a Hackroy clay loam derived from volcanic tuff, with depths ranging from 30 to 130 cm. The climate is continental with warm summers and cold winters. Mean annual precipitation is
The use of isotope-enabled land models to interpret
forcing and net isotope exchanges with the atmosphere, as long as an awareness of these uncertainties is maintained.

2.2 Micrometeorology and $E_T$ calculation

We collected meteorological measurements at 30 s and recorded averages every 30 min including air temperature, relative humidity (RH), soil water content (SWC) at 2 cm depth, and rainfall (Texas Electronics, Texas, USA). Soil water content was also measured at depths of 20–100 cm twice per month using neutron probes (503DR Hydrophobe Neutron Moisture Probes, Campbell Pacific Nuclear, Inc., Pacheco, CA, USA). Pre-dawn leaf water potential ($\Psi_{pd}$) was measured once per month using a Scholander-type pressure chamber (PMS Instruments Co., Corvallis, OR, USA) on six mature juniper trees.

Canopy-scale transpiration, $E_T$, was estimated by measuring sap flux density with Granier heat dissipation probes (Granier, 1987; Phillips and Oren, 2001). A detailed description of sap flux methodology is described in Shim et al. (2011). Transpiration was scaled to the canopy level as

$$E_T = J_s A_s / A_g,$$

where $J_s$ is sap flux (g m$^{-2}$ s$^{-1}$), $A_s$ is sapwood area (m$^2$), and $A_g$ is the ground area (m$^2$). Site-specific $A_s / A_g$ was from McDowell et al. (2008a) and did not change considerably during the study due to the low growth rate of these trees.

2.3 Incorporation of the Isotope Land-Surface Model (ISOLSM)

The use of isotope-enabled land models to interpret $\delta^{18}O$ values of ecosystem water and CO$_2$ fluxes at the site level is fraught with potential uncertainties (Ogée et al., 2004) stemming from challenges in (1) simulating the underlying bulk water and CO$_2$ fluxes (Schwalm et al., 2010; Tang and Zhuang, 2008); (2) equilibrium and kinetic fractionations (Cappa et al., 2003); (3) above-canopy isotopic forcing (Welker, 2000); (4) vertical soil distributions of $^{18}O$ and CO$_2$ production (Riley et al., 2002; Riley, 2005); and (5) leaf water $^{18}O$ and interactions with CO$_2$ (Cernusak et al., 2003; Farquhar and Cernusak, 2005). The problem becomes even more acute when isotope-enabled land models are integrated into global models (e.g., Buening et al., 2012; Wingate et al., 2009). Despite these complications, we contend these models can be helpful to investigate relationships between forcing and net isotope exchanges with the atmosphere, as long as an awareness of these uncertainties is maintained.

With that philosophy in mind, we applied ISOLSM (Riley et al., 2002) to investigate land-to-atmosphere C$^{18}O$ exchanges in the period immediately following precipitation events. ISOLSM has been used in a number of studies to evaluate controls on the $^{18}O$ composition of ecosystem C and H$_2$O exchanges at site, regional, and global scales (Riley et al., 2002, 2003; Riley, 2005; Buening et al., 2011; Henderson-Sellers et al., 2006; Lai et al., 2006; McDowell et al., 2008b; Still et al., 2005, 2009).

Here, we briefly describe the methods used in ISOLSM; details of the model formulation can be found in Riley et al. (2002). In addition to simulating fluxes of CO$_2$, H$_2$O, radiation, sensible heat, and latent heat, ISOLSM predicts separately each component of the ecosystem CO$_2$ and H$_2$O isotope effluxes. Site-level climate observations sufficient to force ISOLSM continuously for the three years of this study were unavailable. Therefore, the necessary inputs (wind speed, humidity, temperature, pressure, solar and long-wave radiation) to drive ISOLSM were obtained from the North American Regional Reanalysis product (NARR; http://www.emc.ncep.noaa.gov/mmb/remen/). The NARR is a meteorological assimilation framework designed to produce consistent climate data for the North American region. It assimilates, at a 3 h time step, a suite of high-resolution meteorological observations into a coupled atmosphere (Eta) and land (NOAH) model. ISOLSM interpolates the resulting climate forcing to its half-hour internal time step, so no gap filling of climate forcing was required.

As with almost every other long-term C and H$_2$O isotope modeling exercise ever performed, we did not have continuously observed $\delta^{18}O$ values of precipitation or above-canopy atmospheric humidity. For this study, as in Still et al. (2009), we used the monthly mean precipitation $\delta^{18}O$ values averaged over 2–5 yr from analyses of archived water samples collected by the EPA National Atmospheric Deposition Program (NADP) network (Lynch et al., 1995) between 1980 and 1990 and interpolated across the US (Welker, 2000). Many factors affect the $\delta^{18}O$ value of vapor ($\delta^{18}Ov$; Lee et al., 2006; Helliker et al., 2002; Lai et al., 2006; White and Gedzelman, 1984). We set $\delta^{18}Ov$ to be in a temperature-dependent isotopic equilibrium with the most recent precipitation event (Still et al., 2009). We note that the sensitivity of ecosystem–atmosphere C$^{18}O$ exchanges to diurnal variations in $\delta^{18}Ov$ is relatively small (Riley et al., 2003). Accelerated CO$_2$–H$_2$O isotopic exchange (by carbonic anhydrase) in soils and foliage is an important factor impacting $\delta_R$. We set the CO$_2$–H$_2$O isotopic hydration to 100% (Wingate et al., 2009; also see Farquhar and Cernusak, 2012) because seasonal and temporal variability in hydration activity is unknown. We set the soil setting point depth to 0–2.5 cm soil depth and applied a 7.2‰ diffusive offset reflecting disequilibrium between CO$_2$ and water near the surface (Miller et al., 1999).

We incorporated the one-way flux model proposed by Cernusak et al. (2004) to calculate the $\delta^{18}O$ value of leaf CO$_2$
fluxes $(\delta_{LR})$:

$$
\delta_{LR} = \frac{\theta \left( \delta_{CW} (1 + \epsilon_w) + (1 - \theta) \delta_{CO} - \frac{C_w}{C_a} (\delta_a - \bar{\theta}) - \bar{\sigma} \right)}{(1 + \bar{\sigma}) (1 - \frac{C_w}{C_a})},
$$

(2)

where $\theta$ is the proportion of chloroplast CO$_2$ that is isotope-equilibrated with chloroplast water (assumed to be 1 for the simulations here); $\delta_{CW}$, $\delta_{CO}$, and $\delta_a$ are the $\delta^{18}O$ values of chloroplast water (‰), of CO$_2$ in the chloroplast that has not equilibrated with local water, and the CO$_2$ mole fractions in the ambient atmosphere, respectively; $C_a$ and $C_c$ are the CO$_2$ in the ambient air and in the chloroplasts (µmol mol$^{-1}$), respectively; and $\epsilon_w$ is the equilibrium $^{18}O$ fractionation between CO$_2$ and water that is dependent on temperature (Brenninkmeijer et al., 1983). $\bar{\sigma}$ is the weighted mean discrimination against C$^{18}$O for diffusion from the chloroplast to the atmosphere (Farquhar and Lloyd, 1993):

$$
\bar{\sigma} = \frac{(C_c - C_t) a_w + (C_t - C_a) a + (C_s - C_a) a_b}{C_c - C_a},
$$

(3)

where $a_w$ is the summed discriminations against C$^{18}$O during liquid phase diffusion and dissolution (0.8 ‰); $a$ and $a_b$ are the discriminations against C$^{18}$O during diffusion through the stomata and the boundary layer (8.8 and 5.8 ‰, respectively); and $C_t$ and $C_s$ are CO$_2$ in the leaf intercellular spaces and at the leaf surface (µmol mol$^{-1}$), respectively.

We imposed a two-hour turnover time to the leaf water pool to account for the delayed equilibrium of leaf water with xylem water after transpiration ceases (Cuntz et al., 2003a; Farquhar and Cerneusak, 2005; Lai et al., 2006). We used the model default value of minimum nighttime stomatal conductance (Bonan, 1996), which was supported by limited direct measurements (data not shown). We discuss the uncertainty resulting from these assumptions in the Discussion section.

We calculated the fractional contribution of each isoflux, i.e., leaf, soil, and stem, to the total ecosystem isoflux from the specific sources predicted by ISOLSM by multiplying the $\delta^{18}O$ values of leaf, soil and stem CO$_2$ fluxes by leaf, soil, and stem respiration rates, respectively.

### 2.4 Drought index

We used the difference between precipitation ($P$) and estimated potential evapotranspiration ($E_P$) as a hydroclimatic index. We employed the Hamon (1961) method for $E_P$ estimation.

$$
E_P = 13.97D^2 P_t,
$$

(4)

where $E_P$ is potential evapotranspiration (mm day$^{-1}$), $D$ is the number of daylight hours in units of 12 h for a given day, and $P_t$ is the saturated water vapor density term calculated by

$$
P_t = \frac{4.95 e^{0.062 T_a}}{100},
$$

(5)

where $T_a$ is daily mean air temperature ($°C$). This index is well suited for regions with high interannual variability and extremely warm seasons during which evaporative loss dominates the hydrologic budget despite significant precipitation (Ellis et al., 2010).

### 2.5 Tunable diode laser system

A description of the tunable diode laser absorption spectrophotometer (TDL, TGA100A, Campbell Scientific Instruments, Logan, UT, USA) operation and sampling system is provided in Shim et al. (2011). Briefly, air samples were continuously collected from the canopy airspace of the piñon–juniper woodland at 0.05, 1.0, 1.5 and 3.0 m height. The fetch for the sample area is representative of the local vegetation at our sampling location because the (dead) piñon–juniper ecosystem extends for approximately 73 km$^2$ around the tower site. The lead salt laser within our TDL system was tuned to absorption lines of 2308.225 cm$^{-1}$, 2308.171 cm$^{-1}$, and 2308.416 cm$^{-1}$ for CO$_2$, CO$_2$, and C$^{12}$O$^{18}$O$^{16}$O, respectively. The TDL sampled two calibration cylinders for 35 s each followed by four sample inlets and one quality control cylinder for 34 s each, resulting in a sample collected for each height every four minutes. The first 20 s of all samples were discarded to omit transients associated with valve switching and to ensure complete purging of the sample cell of the previous sample. To assess the net error associated with CO$_2$ and $\delta^{18}$O measurements, we sampled a quality control cylinder during each sample cycle. This cylinder was sampled with the piñon–juniper field inlets and treated as an unknown. Precisions ($1\sigma$ standard deviation) for the unknown cylinders were $0.18 \mu$mol mol$^{-1}$ for CO$_2$ and $0.16$ ‰ for $\delta^{18}$O value ($n = 6000$).

A linear two-point gain and offset correction was applied to the sample data as described by Bowling et al., (2003b). Working calibration cylinders were propagated from World Meteorological Organization traceable gases obtained from the National Oceanic and Atmospheric Administration Earth System Research Lab; [CO$_2$] was from 344.88 to 548.16 µmol mol$^{-1}$ and the $\delta^{18}$O value from $-8.16$ to $-16.42$ ‰. The mole fractions of the isotopologues CO$_2$, CO$_2$, and C$^{12}$O$^{18}$O$^{16}$O within our calibration gases spanned the range observed in the field samples. The secondary standards (Scott-Marin, Inc., USA) were propagated weekly from our two primary standards throughout 2006 and analyzed for drift in CO$_2$ and $\delta^{18}$O value within the cylinders. Cylinder drift was negligible, averaging 0.00001 ‰ day$^{-1}$, with maximum drift of 0.00005 ‰ day$^{-1}$ ($n = 12$ cylinders). We switched to approximately monthly propagation of secondary cylinders beginning in 2007.

We employed a two-ended mixing model to estimate $\delta_R$ (Keeling, 1958; Flanagan et al., 1996; Zobitz et al., 2006). $\delta_R$ represents the $^{18}$O composition of the net ecosystem flux associated with respiration as well as abiotic invasion flux between leaves and the atmosphere (Francey and Tans, 1987).
and soils and the atmosphere (Tans, 1998). We used measurements of CO$_2$ and $^{18}$O taken between 20:00 and 04:00 h and data from four inlets located at 0.05, 1.0, 1.5 and 3.0 m together to examine nightly $\delta_R$. Model I regressions were used to avoid negatively skewed intercepts (Zobitz et al., 2006). To assess the stability of isotopic sources for each night, we compared Keeling intercepts to the isotopic mixing line proposed by Miller and Tans (2003) (MT2003 hereafter). The MT2003 approach estimates $\delta_R$ as the slope of a linear regression between the product of $^{18}$O and [CO$_2$] versus [CO$_2$] and offers an advantage when the Keeling approach violates the assumption of a stable background (Miller and Tans, 2003; Lai et al., 2004). Determining $\delta_R$ from a Keeling or a MT2003 regression from model I regressions gave similar results for our 4 yr data record ($r^2 = 0.99$, see Fig. A5); therefore we retained our analysis via the Keeling approach. An independent check on the assumption of stable source values was conducted using ISOLSM, which revealed that the sources were relatively stable (mean standard error ($\%e$) = 1.5, 0.1, and 0.1 for $^{18}$O of foliar, soil and stem respiration, respectively; see Fig. A6). We screened the data to include only values with ranges of 10 ppm for CO$_2$ and 2 %e for $^{18}$O (Schaeffer et al., 2008). Using this filter, 64 % of the nightly datasets were retained between April 2005 and October 2008.

2.6 Analyses of pulse responses

To determine the $\delta_R$ response to precipitation pulses, we compared the $\delta_R$ prior to a rain event to the subsequent days after that event and lasting up to 11 days, but not including subsequent rain events. The number of days after precipitation pulses was not significantly different by season ($F = 0.6$, $P = 0.5$, ANOVA). Analysis within individual pulse events avoids confounding multiple precipitation events when analyzing the coupling of $\delta_R$ to meteorological or physiological parameters. Rain events differed in $\delta^{18}$O value due to varying $\delta^{18}$O values of source water, temperature, and storm tracks (Rozanski et al., 1982); thus we report $\delta_R$ responses to pulse precipitation events as the maximum $\delta_R$ change over the week following a rain event (see an inset in Fig. 2). This approach allows comparison of the rate and magnitude of $\delta_R$ changes after each pulse event across the four years.

We conducted correlation analyses of $\delta_R$ with $E_T$, vapor pressure deficit (VPD), RH, and SWC for each pulse event to determine the degree and speed of coupling between $\delta_R$ and hydrologic drivers (Bowling et al., 2002; Shim et al., 2011). We considered all possible subsets from 1 day after a pulse event up to 11 days, for all four years. We considered correlations ranging from instantaneous (e.g., $\delta_R$ from day x paired with $E_T$ from day x) to lagged responses (e.g., $\delta_R$ from day x correlated with $E_T$ from day x-1, x-2, and so on). Responses of $\delta_R$ lagged up to 11 days behind driving variables were considered. The number of days used in these analyses varied with the length of time between rain events.

All correlations were conducted as linear regression models using the least squares method. We present all relationships with significance ($p < 0.1$ (Flanagan et al., 1996; McDowell et al., 2004; Shim et al., 2011).

2.7 $\delta^{18}$O of precipitation, foliage, stem, and soils

Samples of precipitation, foliage, stem, and soil water were collected and analyzed for $^{18}$O composition in 2006 and 2007. Precipitation was collected from a sealed collection vial at the base of a rain funnel immediately after rain events. Foliage, stem and soil samples at 2, 7, and 10 cm were collected on a monthly basis as part of the Moisture Isotopes in the Biosphere and Atmosphere project. $\delta^{18}$O values of the soil water profile were measured at 5 depths: 2, 5, 7, 10 and 15 cm on day of year (DOY) 151 in 2006. Samples were cryogenically extracted on a vacuum line and analyzed with a Thermo Delta Plus XL mass spectrometer at the UC Berkeley stable isotope laboratory where long-term external precision (over more than 5 yr) is ±0.24 ‰. All oxygen isotope ratios in this paper for water and CO$_2$ are referenced to the Vienna Standard Mean Ocean Water (V-SMOW) scale (Coplen, 1996) and are presented in dimensionless units of ‰.

3 Results

3.1 Climate regimes over four years and associated patterns of $P - E_p$, $E_S$, $E_T/E_S$ and $\delta_R$

The pre-monsoon periods (~April–June) typically had relatively wet soil at depth (20–40 cm) from snowmelt but dry soil near the surface due to small precipitation inputs and long inter-pulse durations (Fig. 1a, Table A1.). There was substantial interannual variation, however, with a particularly dry pre-monsoon period in 2006 and relatively wet pre-monsoon period in 2007 (Fig. 1b, and Shim et al., 2011). The mid-summer monsoon seasons (typically July and August) were characterized by frequent rainfall events and subsequently dynamic SWC (Fig. 1). Again, there was substantial interannual variation, with relatively strong monsoon precipitation in 2006 characterized by an early onset of monsoon rains and particularly short (<5 days) inter-pulse duration (Table A1). 2007 was the driest monsoon season of the four years, with lowest SWC, highest VPD and $T_{soil}$, and longest inter-pulse durations. $P - E_p$ declined rapidly after pulse events and was particularly low in 2007 and 2008. As a reminder, $P - E_p$ here in Fig. 1b was calculated on a daily time step, and in Fig. 8b the daily value was averaged over the period extending from one rain event to the day before the next rain event, never extending more than 11 days. Post-monsoon periods were relatively similar between years and were characterized by decreasing rainfall and declining $T_{soil}$.

Pre-dawn leaf water potential ($\Psi_{pd}$) tended to track SWC at 20 cm depth, with least negative values in spring, most

www.biogeosciences.net/10/4937/2013/

Biogeosciences, 10, 4937–4956, 2013
negative values in August, and rebounded in early September (Fig. 1a; \( p < 0.001, r^2 = 0.3 \)). SWC at 20 cm depth followed seasonal variation in \( P - E_P \) (Fig. 1b; \( p < 0.001, r^2 = 0.3 \)).

Mean daily \( E_T \) (mm d\(^{-1}\)) from days 100 to 304 were 0.7 ± 0.1, 0.5 ± 0.1, and 0.3 ± 0.1 in 2006, 2007, and 2008, respectively. \( E_T \) increased after rainfall events throughout the three years of sapflow measurements (Fig. 1c). Average maximum changes in \( E_T \) (mm d\(^{-1}\)) after pulses were 0.6 ± 0.2, 0.4 ± 0.1 and 0.4 ± 0.2 during pre-monsoon, monsoon, and post-monsoon periods, respectively. \( E_T \) did not exceed 0.3 mm day\(^{-1}\) when \( \Psi_{pd} \) was \( \leq -1 \) MPa in monsoon and post-monsoon seasons, but did reach higher values for the same \( \Psi_{pd} \) during the pre-monsoon seasons (Fig. A1); this is consistent with the relatively anisohydric behavior of juniper trees (McDowell et al., 2008a). Similarly, \( E_T \) responses to VPD were only strong when SWC \( \geq 15 \% \), with relatively shallow responses when soil moisture was low (i.e., < 15%; Fig. 3a).

Modeled \( E_S \) generally showed rapid spikes and subsequent gradual decreases after rainfall events (inset in Fig. 1c). As \( E_S \) declined, \( E_T \) consistently increased, resulting in increasing \( E_T/E_S \) (Fig. 1c, 59% of rain events) because soil evaporation responds rapidly to pulses, while the vegetation response was more gradual and long-lived because it takes longer for water to infiltrate, reach the rooting zone, transport through xylem, and transpire through the leaves (Reynolds et al., 2004). Strong positive responses of \( E_T \) to VPD became evident when SWC > 15% (Fig. 3a). Average maximum changes in \( E_T/E_S \) after pulses were 4.3 ± 1.3, 1.4 ± 0.4 and 5.5 ± 2.5 during pre-monsoon, monsoon, and post-monsoon periods, respectively. \( E_T/E_S \) peaks were associated with elevated soil moisture after snowmelt and during relatively wet monsoon periods due to high values of \( E_T \) (Fig. 1a and c, Table A1.).

After filtering atmospheric CO\(_2\) \( ^{18} \)O (\( \delta_a \)) by our QC (Quality Control) criteria, 64% of the nights were retained for \( \delta_R \) calculation from April 2005 through October 2008 (547 nights). Nightly measured \( \delta_R \) averaged 46.7\% ± 0.6, 50.7\% ± 0.7, 52.6\% ± 1.2, and 44.8\% ± 2.3 in 2005, 2006, 2007, and 2008, respectively. \( \delta_R \) generally became depleted immediately after rainfalls and subsequently enriched until the next rain event (Fig. 2). Average maximum
3.2 Patterns of water pool $\delta^{18}$O and relationships of $\delta_R$ and hydrologic drivers after pulses

Juniper foliage water consistently had the highest $\delta^{18}$O values (mean 17.6 ± 0.2‰), followed by soil water (mean $-2.2 \pm 1.0$‰) and juniper stem water ($-8.7 \pm 0.6$‰) (Tukey’s test, $F = 225.1$, $p < 0.001$, Table 1). Foliar water $\delta^{18}$O value was positively correlated with VPD ($r^2 = 0.7$, $p < 0.001$), but there was no correlation of mean 0–15 cm soil water $\delta^{18}$O value with VPD (Fig. 2b).

$\delta_R$ showed progressive enrichments with increasing VPD and $E_T$ and decreasing RH at the intraseasonal scale (Table 2 and Fig. A2), indicating the importance of evaporative demand and transpiration on $\delta_R$. Despite the clear dependence of $\delta_R$ on these drought-related parameters, there were no significant relationships between $\delta_R$ and $P - E_P$ when including all nights from DOY 100–273 over the four years (Fig. A3), though a clear pattern emerges of a wide $\delta_R$ range.

\[ \delta_R \text{ enrichment after pulses was 28.7, 18.9, and 25.6‰ during pre-monsoon, monsoon and post-monsoon periods, respectively.} \]
during wetter periods and a limited range during drought. Thus, $P - E_P$ by itself was not a good predictor of $\delta_R$, perhaps due to the variable $\delta^{18}O$ of rainfall events. $\delta_R$ on the day of rain events followed annual $\delta^{18}O$ precipitation trends ($r^2 = 0.4$, $p = 0.001$). Indeed, pulse events induced an immediate decrease in $\delta_R$ (Fig. 4b). Following these immediate depletions, $\delta_R$ subsequently became enriched following nearly all pulse events (Fig. 4c). Similarly, $E_T$ increased following rain events (Fig. 4a). The largest and smallest enrichments occurred in pre-monsoon and monsoon seasons, respectively (Fig. 5a–c). The normalized $\delta_R$ enrichment was correlated with $E_T$ (Fig. 5d–f).

The model accurately captured the temporal $\delta_R$ dynamics of the post-pulse $\delta_R$ enrichment ($r^2 = 0.7$; Fig. 6). Simulated depletion in $\delta_R$ immediately following precipitation events was often underestimated (mean underestimate of

$7.2 \pm 1.6 \text{‰};$ Fig. A7). The $\delta_R$ prediction accuracy improved greatly after the one-way flux model proposed by Cernusak et al. (2004) was incorporated to estimate leaf $C^{18}O$ fluxes ($p < 0.001$ for all, $r^2 = 0.2$ and 0.5 for net flux model and
Fig. 5. (a–c) Seasonal patterns of normalized $\delta_R$ enrichment after rain pulses (the pulses are on day zero). $\delta_R$ values were normalized by $\delta_R$ on the day of the rain event to make all starting values zero over the four years. (d–f) The seasonal relationships between post-rain-pulse normalized $\delta_R$ and $E_T$. Maximum $E_T/E_S$ values and $r^2$ values for the same period are added in each legend. Maximum $E_T/E_S > 2$ is expressed as bold.

one-way flux model, respectively; Fig. A4). The higher accuracy of the one-way flux model is consistent with large enrichment of chloroplast CO$_2$. ISOLSM predicted that foliar C$^{18}$O flux was the dominant contributor to post-pulse $\delta_R$ enrichment during pre- and post-monsoon periods over the three years, whereas soil C$^{18}$O flux was the dominant contributor during monsoon periods (Fig. 7).

Consistent with our expectations, $\delta_R$ enrichment was correlated with $E_T/E_S$ (Fig. 8a). A stronger relationship between $\delta_R$ and $P - E_P$ emerged after accounting for precipitation effects on ecosystem water pools by calculating the maximum $\delta_R$ change between the day of the rain event and the subsequent dry period (see methods, $r^2 = 0.4$, $p = 0.001$, Fig. 8b). This also highlights that increasing precipitation and decreasing potential evapotranspiration both lead to larger enrichment of $\delta_R$ after rain events.

4 Discussion

$\delta_R$ did not simply increase with larger values of $P - E_P$ (Fig. A3). Rather, the relationship between $\delta_R$ and $P - E_P$ was heavily moderated by precipitation events (Fig. 8b). Further, the four-year semi-continuous $\delta_R$ observations exhibited strong coupling of $\delta_R$ with hydrological attributes of local weather ($P - E_P$, VPD, and RH) and ecosystem physiology ($E_T$ and $E_T/E_S$) at daily (Figs. 3, 5, Fig. A2), seasonal (Fig. 5, Fig. A2) and interannual scales (Figs. 3, 5, Fig. A2). The wide $\delta_R$ range at more positive $P - E_P$ and narrow range at more negative $P - E_P$ (Fig. A3) appears to be the result of multiple factors, most notably resetting of water pool $\delta^{18}$O values by rain (Fig. 5b), and regulation of subsequent enrichment by transpiration and soil evaporation (Figs. 1, 2, 5, 8). The magnitude of post-pulse $\delta_R$ enrichment varied with seasonal and interannual climate (Figs. 1, 5) due
<table>
<thead>
<tr>
<th>Day of year</th>
<th>VPD</th>
<th>SWC_2 cm</th>
<th>RH</th>
<th>$E_T$</th>
<th>Pulse size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>125–132 (2005)</td>
<td>0.33 (0,+)</td>
<td>0.81 (0,−)</td>
<td>0.87 (0,−)</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>135–143 (2005)</td>
<td>0.71 (0,+)</td>
<td>0.53 (0,−)</td>
<td>0.79 (0,−)</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>198–206 (2005)</td>
<td>0.36 (0,+)</td>
<td>0.50(0,−)</td>
<td>0.67 (0,−)</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>207–213 (2005)</td>
<td>0.50 (0,+)</td>
<td>0.43 (0,−)</td>
<td>0.45 (0,−)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>234–244 (2005)</td>
<td>0.27 (0,+)</td>
<td>0.71 (0,−)</td>
<td>0.51 (0,−)</td>
<td>21.9</td>
<td></td>
</tr>
<tr>
<td>Post-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>245–253 (2005)</td>
<td>0.83 (1,+)</td>
<td>0.81 (0,−)</td>
<td>0.9 (1,−)</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>271–278 (2005)</td>
<td>~0 (0,−)</td>
<td>0.78 (0,−)</td>
<td>0.05 (0,+)</td>
<td>0.63 (0,−)</td>
<td>61.7</td>
</tr>
<tr>
<td>282–287 (2005)</td>
<td>0.94 (0,+)</td>
<td>0.02 (0,−)</td>
<td>0.94 (0,−)</td>
<td>0.36 (0,−)</td>
<td>9.9</td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>118–123 (2006)</td>
<td>0.86 (1,+)</td>
<td>0.52 (1,+)</td>
<td>0.83 (1,−)</td>
<td>0.69 (1,+)</td>
<td>6</td>
</tr>
<tr>
<td>125–131 (2006)</td>
<td>0.69 (2,+)</td>
<td>0.93 (0,−)</td>
<td>0.43 (2,−)</td>
<td>0.53 (0,+)</td>
<td>2.3</td>
</tr>
<tr>
<td>135–141 (2006)</td>
<td>0.86 (2,+)</td>
<td>0.98 (4,−)</td>
<td>0.89 (3,−)</td>
<td>0.95 (4,+)</td>
<td>1.6</td>
</tr>
<tr>
<td>160–167 (2006)</td>
<td>0.39 (3,−)</td>
<td>0.76 (2,+)</td>
<td>0.73 (1,+)</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>173–178 (2006)</td>
<td>0.06 (0,+)</td>
<td>0.53 (0,+</td>
<td>0.14 (1,+)</td>
<td>0.44 (0,+)</td>
<td>16.4</td>
</tr>
<tr>
<td>Monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>184–191 (2006)</td>
<td>0.34 (0,+)</td>
<td>~0 (0,+)</td>
<td>0.38 (0,−)</td>
<td>0.34 (0,+)</td>
<td>29.1</td>
</tr>
<tr>
<td>217–222 (2006)</td>
<td>0.74 (0,+)</td>
<td>0.72 (0,+)</td>
<td>0.73 (0,−)</td>
<td>0.42 (0,+)</td>
<td>31</td>
</tr>
<tr>
<td>225–230 (2006)</td>
<td>0.07 (0,+)</td>
<td>0.75 (0,+)</td>
<td>0.07 (0,−)</td>
<td>~0 (−)</td>
<td>28.3</td>
</tr>
<tr>
<td>231–235 (2006)</td>
<td>0.82 (0,+)</td>
<td>0.1 (0,+)</td>
<td>0.76 (0,−)</td>
<td>0.03 (0,+)</td>
<td>16.8</td>
</tr>
<tr>
<td>236–241 (2006)</td>
<td>0.98 (0,+)</td>
<td>~0 (0,+)</td>
<td>0.98 (0,−)</td>
<td>0.27 (0,+)</td>
<td>29.1</td>
</tr>
<tr>
<td>243–248 (2006)</td>
<td>0.23 (0,+)</td>
<td>0.06 (0,+)</td>
<td>0.22 (0,−)</td>
<td>0.01 (0,+)</td>
<td>10.6</td>
</tr>
<tr>
<td>Post-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>249–255 (2006)</td>
<td>0.88(1,+)</td>
<td>0.86(3,−)</td>
<td>0.99(1,−)</td>
<td>0.69(4,+)</td>
<td>13.4</td>
</tr>
<tr>
<td>254–259 (2006)</td>
<td>0.73(0,+)</td>
<td>0.83(0,−)</td>
<td>0.92(0,−)</td>
<td>0.41(0,+)</td>
<td>1</td>
</tr>
<tr>
<td>282–286 (2006)</td>
<td>0.95(0,+)</td>
<td>0.83(0,+)</td>
<td>0.96(0,−)</td>
<td>0.87(0,+)</td>
<td>9</td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>103–106 (2007)</td>
<td>0.94(0,+)</td>
<td>0.57(0,+)</td>
<td>0.93(0,−)</td>
<td>0.97(0,+)</td>
<td>4.3</td>
</tr>
<tr>
<td>128–133 (2007)</td>
<td>0.82(0,+)</td>
<td>0.62(0,+)</td>
<td>0.75(0,−)</td>
<td>0.22(0,−)</td>
<td>16.3</td>
</tr>
<tr>
<td>134–140 (2007)</td>
<td>0.54(0,+)</td>
<td>0.74(3,−)</td>
<td>0.54(0,−)</td>
<td>0.19(0,−)</td>
<td>9.6</td>
</tr>
<tr>
<td>140–150 (2007)</td>
<td>0.17(3,−)</td>
<td>0.24(1,+)</td>
<td>0.67(3,+)</td>
<td>0.16(3,−)</td>
<td>8.6</td>
</tr>
<tr>
<td>162–166 (2007)</td>
<td>0.4(0,+)</td>
<td>0.89(0,+)</td>
<td>0.34(0,−)</td>
<td>0.17(0,+)</td>
<td>11.2</td>
</tr>
<tr>
<td>Monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200–206 (2007)</td>
<td>0.19(0,+)</td>
<td>0.62(0,+)</td>
<td>0.26(0,−)</td>
<td>0.5(0,+)</td>
<td>6</td>
</tr>
<tr>
<td>211–216 (2007)</td>
<td>0.87(0,+)</td>
<td>0.25(0,+)</td>
<td>0.71(0,−)</td>
<td>0.6(0,+)</td>
<td>20.6</td>
</tr>
<tr>
<td>218–223 (2007)</td>
<td>0.73(0,+)</td>
<td>0.67(0,+)</td>
<td>0.75(0,−)</td>
<td>0.47(0,+)</td>
<td>11.2</td>
</tr>
<tr>
<td>224–229 (2007)</td>
<td>0.85(0,+)</td>
<td>~0(0,+)</td>
<td>0.92(0,−)</td>
<td>0.22(0,−)</td>
<td>8.9</td>
</tr>
<tr>
<td>230–234 (2007)</td>
<td>0.79(0,+)</td>
<td>0.28(0,−)</td>
<td>0.78(0,−)</td>
<td>0.08(0,+)</td>
<td>4.8</td>
</tr>
<tr>
<td>236–240 (2007)</td>
<td>0.07(0,+)</td>
<td>0.05(0,−)</td>
<td>0.08(0,−)</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>241–246 (2007)</td>
<td>0.4(0,+)</td>
<td>0.41(2,−)</td>
<td>0.41(2,+)</td>
<td>22.1</td>
<td></td>
</tr>
<tr>
<td>Post-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>247–254 (2007)</td>
<td>0.82(−)</td>
<td>0.55(3,+)</td>
<td>0.62(2,+)</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>260–266 (2007)</td>
<td>0.36(2,−)</td>
<td>0.88(4,+)</td>
<td>0.3(0,−)</td>
<td>40.1</td>
<td></td>
</tr>
<tr>
<td>271–276 (2007)</td>
<td>0.84(1,−)</td>
<td>0.8(0,−)</td>
<td>0.61(1,+)</td>
<td>10.9</td>
<td></td>
</tr>
</tbody>
</table>
in part to constraints on the $E_T$ response (Figs. 1, 2, 4, 8 and Fig. A1) and changes in $E_T/E_S$ (Fig. 8a). These patterns support the contention of strong hydrological regulation of ecosystem function in semi-arid regions (Weltzin and Tissue, 2003) and suggest that long-term monitoring of $\delta_R$ has promise for understanding drought responses and detecting drought induced eco-physiological changes. Below, we explore the potential mechanisms driving the drought signal of $\delta_R$.

Rain reset near-surface soil and source (i.e., xylem water) $\delta^{18}O$ values, causing immediate $\delta_R$ depletions followed by subsequent enrichment as the ecosystem dried (Figs. 1, 4, 5), consistent with previous results from short-term (i.e., 60 minutes) post-pulse measurements of the $\delta^{18}O$ value of soil CO$_2$ effluxes at our site (Powers et al., 2010). ISOLSM was not consistently accurate in simulating $\delta_R$ depletions within hours of the rainfall events, for several reasons. First, comparisons between the available precipitation $\delta^{18}O$ measurements at the site for the time periods presented in our study in 2006 indicate that the ISOLSM forcing precipitation isotope composition was, on average, 3.1 ‰ more enriched than observed (Fig. A7). Therefore, the imposed $\delta^{18}O$ value of above-canopy vapor following precipitation would also be too enriched in the simulations (Riley et al., 2002). ISOLSM precipitations were less dynamic than observations, particularly depletions during pulse events. Second, pulse events often trigger a brief large burst of soil CO$_2$ efflux (i.e., the Birch effect (Birch, 1964)) in arid and semi-arid ecosystems, which can impact $\delta_R$ for short periods. Modeling the Birch effect is difficult because it cannot be simply formulated using only soil temperature and moisture, as done in ISOLSM and many terrestrial ecosystem models. Despite these caveats, the model simulations are useful because we focus not on the immediate few hours following rainfall but on the multi-day responses following rainfall. 93 % of our analysis periods (in which data was used in the results) contained zero rainfall because nearly all rain events occurred during the day from convective storms and the data analysis was for periods starting the subsequent nights after a rain event. ISOLSM captured the measured $\delta_R$ within 7 days of the precipitation ($r^2 = 0.7$; Fig. 6) after we (1) imposed a two-hour turnover time to the leaf water pool considering leaf water may be enriched several hours after transpiration ceases due to slow

![Image](image-url)

**Fig. 6.** Comparison between measured and modeled maximum $\delta_R$ changes within 7 days of precipitation.

<table>
<thead>
<tr>
<th>Day of year</th>
<th>VPD</th>
<th>SWC,2 cm</th>
<th>RH</th>
<th>$E_T$</th>
<th>Pulse size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>107–114 (2008)</td>
<td>0.66(+), 0.6(-)</td>
<td>0.6(0,+), 0.4(0,+)</td>
<td>0.94(+), 0.94(+), 3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>134–140 (2008)</td>
<td>0.64(+), 0.76(+), 0.29(1,+), 0.66(3,+), 4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>142–147 (2008)</td>
<td>0.1(0,+), 0.86(0,+), 0.13(0,+), 0.7(0,+), 2.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>148–155 (2008)</td>
<td>~0(0,+), 0.09(0,+), 0.03(0,+), 0.64(+), 3.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>235–245 (2008)</td>
<td>0.06(1,+), 0.75(1,+), 0.59(1,+), 0.20(0,+), 28.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>197–206 (2008)</td>
<td>0.46(0,+), 0.69(0,+), 0.04(0,+), 0.93(0,+), 21.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>207–215 (2008)</td>
<td>0.46(0,+), 0.85(0,+), 0.42(0,+), 0.13(0,+), 4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>216–225 (2008)</td>
<td>0.03(0,+), 0.70(0,+), 0.02(0,+), 0.46(0,+), 50.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>222–229 (2008)</td>
<td>0.48(+), 0.27(4,−), 0.42(3,−), 0.62(+), 38.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>228–234 (2008)</td>
<td>0.03(0,+), 0.87(0,+), 0.62(+), 0.61(+), 12.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>235–245 (2008)</td>
<td>0.06(+), 0.75(+), 0.59(+), 0.20(0,+), 28.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Post-monsoon</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>243–251 (2008)</td>
<td>0.46(+), 0.22(2,−), 0.18(4,−), 0.74(+), 22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>263–268 (2008)</td>
<td>0.01(0,+), 0.32(0,+), 0.07(0,+), 0.01(0,+), 3.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>269–274 (2008)</td>
<td>0.13(0,+), 0.28(0,+), 0.16(0,+), 0.11(0,+), 3.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>284–293 (2008)</td>
<td>0.79(0,+), 0.89(0,+), 0.86(0,+), 0.62(0,+), 28.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Continued.
turnover of the leaf water pool (Cuntz et al., 2003a; Lai et al., 2006) and (2) incorporated a one-way flux model proposed by Cernusak et al. (2004).

Comparison of modeled and observed $\delta_R$ at this site in 2006 demonstrated that nocturnal isotope equilibration of $\text{CO}_2$ with leaf water $\delta^{18}\text{O}$ value and subsequent atmospheric retro-flux may drive large enrichment in $\delta_R$ (McDowell et al., 2008b). The higher accuracy of the one-way flux model is consistent with large enrichment of chloroplast $\text{CO}_2$ (Cernusak et al., 2004). This one-way flux model is similar to $\text{CO}_2$ invasion and retro-flux in soils (Tans, 1998; Riley et al., 2005; Seibt et al., 2006). Stomata are assumed to be closed at night in many isotope land models; however, accumulated evidence has shown that stomata are leaky at night in many species (Barbour et al., 2005; Dawson et al., 2007). Limited nocturnal, leaf-level measurements of stomatal conductance ($g_c$) confirmed that junipers do maintain some degree of stomatal conductance after sundown (up to 0.11 mol m$^{-2}$ s$^{-1}$, SE = 0.003, unpublished data). Markedly improved $\delta_R$ prediction by ISOLSM suggests nocturnal $g_c$ leads to high $\text{CO}_2$ retro-diffusion and a faster exchange of leaf water with atmospheric water vapor at night, and the $\delta^{18}\text{O}$ composition of leaf water may not be in equilibrium with xylem water at night (Cernusak et al., 2004; Seibt et al., 2006; Lai et al., 2006; Cuntz et al., 2007).

The $\delta_R$ values over four years of study showed $\delta_R$ enrichment following pulse events in 95% of the observations (Fig. 2). Correlations of $\delta_R$ with VPD and RH over the subsequent days after pulse events and lasting up to 11 days were stronger than for SWC (Table 2). These relationships suggest that declines in atmospheric vapor content following precipitation pulses were a stronger driver of $\delta_R$ patterns than the availability of soil moisture per se (i.e., water content), consistent with observations from more mesic sites (Bowling et al., 2003a, b; Wingate et al., 2010).

The underlying drivers of the correlations of VPD and RH with $\delta_R$ are likely driven by both soil evaporation and canopy transpiration. The post-pulse normalized $\delta_R$ enrichment correlated strongly with $E_T/E_S$ over the three years from DOY 100 to 273 (Fig. 8a). Post-pulse $\delta_R$ enrichment was relatively small when $E_T/E_S < 2$, due in part to $E_T$ constraints and a higher contribution of soil $\text{C}^{18}\text{O}$ flux to total isoflux (Figs. 1, 5 – see legend). Post-pulse $\delta_R$ enrichment was significantly larger when $E_T$ and its relative contribution to ecosystem-scale evapotranspiration were large (Figs. 5, 8a) consistent with leaf-level observations in droughted plants. This $\delta_R$ enrichment was likely a result of the enrichment of foliar water as well as retro-diffusion with atmospheric $\text{CO}_2$. With active transpiration, water transpired by foliage is more enriched than soil water (Table 1, Wingate et al., 2010) because evaporation results in more efficient accumulation of heavier water molecules in leaf water than soil water (Table 1, Wang and Yakir, 1995; Barbour et al., 2005; Wingate et al., 2010). In our system, this enrichment resulted in a strong relationship between VPD and foliar water $\delta^{18}\text{O}$ values, but no relationship between VPD and soil water $\delta^{18}\text{O}$ values (Fig. 3b). This more enriched foliar water is likely to persist several hours at night after transpiration ceases, as suggested by ISOLSM.

The post-pulse normalized $\delta_R$ enrichment correlated well with $E_T/E_S$ over the three years from DOY 100 to 273 (Fig. 8a). The magnitudes of post-pulse $E_T$ and $\delta_R$ enrichment were larger and more frequently observed during pre-monsoon periods than during monsoon periods (Fig. 5). Strong positive responses of $E_T$ to VPD were more common when more soil water was available (Fig. 3a). Strong responses of $E_T/E_S$ to pulses corresponded with high $\Psi_{pd}$ and lower VPD (not shown). All of these factors were most common pre-monsoon when snowmelt had recharged the entire soil water profile (Fig. 1). The source partitioning analysis...
Fig. 8. (a) The relationship between maximum $\delta_R$ change within 7–11 days after each pulse and mean $E_T/E_S$ change for the same periods. The regression equation is $\delta_R = 15.4 + 6.0 \times E_T/E_S$, $r^2 = 0.4$. (b) Relationships between maximum $\delta_R$ change and the drought index $P - E_P$. Each data point represents the combination of maximum $\delta_R$ change and mean $P - E_P$ over the same period, with each subset starting on the day of the rain pulse and extending to the day before the next rain pulse.

from ISOLSM provides evidence of higher foliar contribution to total ecosystem isoflux relative to soil and stem components during pre-monsoon periods (Fig. 7). Both $E_T$ and $E_S$ responded strongly to spring rains despite their small size, yet $E_T/E_S$ frequently exceeded 2 because of transient $E_S$ spikes and more sustained increases in $E_T$ (Fig. 1c in inset, Fig. 5 in legend).

Soil isoflux contributed relatively more than leaf isoflux to the ecosystem signal during the monsoon periods (Fig. 7). The monsoon periods typically had more negative $\Psi_{pd}$, lower soil water content deep in the soil profile (Fig. 1), and higher temperatures, thus only particularly large rain events or many rainy days in a row triggered significant $\delta_R$ responses. $E_T$ increased within a few days after monsoon rains, but the $E_T$ amplitudes were small and post-pulse $E_T/E_S$ usually remained below 1.5 (particularly for the dry 2007 and 2008 monsoon seasons, Figs. 1c, 5). The least $\delta_R$ enrichment after rain events was observed during seasons when the post-rainfall $E_T$ response was small and the drought index $P - E_P$ was highly negative (Fig. 8b). While $\delta_R$ was strongly related to atmospheric vapor pressure deficit, the degree of enrichment appears constrained by the trees’ capacity to increase $E_T$ (Figs. 1, 5e, Fig. A1, Ferrio et al., 2009). However, further manipulative studies that alter VPD and $E_T$ separately are needed to test models of $\delta^{18}O$ exchange.

Coupling of $\delta_R$ with VPD, RH, and $E_T$ occurred more rapidly, and more frequently, than observed for the $\delta^{13}C$ value of ecosystem respiration ($\delta^{13}C_R$) at this ecosystem for the same years (Table 2, Fig. A2, Shim et al., 2011). This more rapid coupling is likely due to the immediate exchange of oxygen atoms between respiring $CO_2$ and water pools, leading to fast incorporation of the water isotopic signature into ecosystem respiration (Wingate et al., 2010). In contrast, $\delta^{13}C_R$ is derived from the relatively slower transport of carbon from foliage to the mean location of respiration (foliage, stems, roots, and heterotrophic biomass), including additional lags due to autotrophic and heterotrophic storage (Bowling et al., 2008). These storage effects, in particular, make deciphering the information derived from $\delta^{13}C_R$ measurements more difficult because $\delta^{13}C_R$ is frequently uncoupled from climate, at least in this semi-arid woodland (Shim et al., 2011). Thus, the relative value of $\delta_R$ is enhanced not only by its unique representation of terrestrial hydrology, but also because its dependence on climate and physiology is more easily detected.

5 Conclusions

In our system, the $\delta^{18}O$ value of ecosystem respiration ($\delta_R$) was highly variable (Fig. 2); this variability was reduced as drought increased ($P - E_P$, Fig. A3). Evaporative demand plays a significant role in the $\delta_R$ enrichment following rain events, and this response was strongly influenced by $E_T$ and $E_T/E_S$ (Figs. 5, 8) due in part to strong leaf water enrichment (Fig. 3) and subsequent foliar respiration and retro-diffusion (Figs. 5, Fig. A4). Conditions that limit $E_T$ subsequently limit the $\delta_R$ enrichment post-rain events (Figs. 1, 2, 5, 6), resulting in reduced enrichment when $P - E_P$ is more negative (Fig. 8b). Thus, deciphering the drought signal associated with $\delta_R$ requires consideration of episodic dynamics of precipitation pulses, their impacts on the $\delta^{18}O$ value of source water pools, and the magnitude of $E_T$ responses.
Appendix A

Table A1. Seasonal rain pulse sizes and inter-pulse duration shown as the percentage of events and durations, respectively. The numbers within parentheses are the number of rain events. The maximum days column shows the maximum number of days between pulse events.

<table>
<thead>
<tr>
<th>Year/season</th>
<th>Pulse sizes (%)</th>
<th>Inter-pulse durations (%)</th>
<th>Maximum days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1–5 mm</td>
<td>5–15 mm</td>
<td>15–30 mm</td>
</tr>
<tr>
<td>2005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td>100 0 0 0 0</td>
<td>0 22 78 19</td>
<td></td>
</tr>
<tr>
<td>Monsoon</td>
<td>85 5 5</td>
<td>22 56 22 14</td>
<td></td>
</tr>
<tr>
<td>Post-monsoon</td>
<td>82 0 9 9</td>
<td>50 25 25 14</td>
<td></td>
</tr>
<tr>
<td>2006</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td>100 0 0 0</td>
<td>14 50 36 16</td>
<td></td>
</tr>
<tr>
<td>Monsoon</td>
<td>61 25 14 0</td>
<td>29 64 7 10</td>
<td></td>
</tr>
<tr>
<td>Post-monsoon</td>
<td>78 22 0 0</td>
<td>33 50 17 8</td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td>86 14 0 0</td>
<td>18 55 27 21</td>
<td></td>
</tr>
<tr>
<td>Monsoon</td>
<td>76 20 4 0</td>
<td>33 47 20 18</td>
<td></td>
</tr>
<tr>
<td>Post-monsoon</td>
<td>75 25 0 0</td>
<td>20 80 0 5</td>
<td></td>
</tr>
<tr>
<td>2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-monsoon</td>
<td>91 9 0 0</td>
<td>14 29 57 26</td>
<td></td>
</tr>
<tr>
<td>Monsoon</td>
<td>69 19 12 0</td>
<td>46 40 14 8</td>
<td></td>
</tr>
<tr>
<td>Post-monsoon</td>
<td>100 0 0 0</td>
<td>20 20 60 10</td>
<td></td>
</tr>
<tr>
<td>Means ± SE</td>
<td>83.6 ± 3.7</td>
<td>11.6 ± 3.0</td>
<td>3.7 ± 1.5</td>
</tr>
</tbody>
</table>

Fig. A1. The relationship between monthly juniper pre-dawn leaf water potential (Ψpd) and ET by season. The number of data points is limited because not all monthly Ψpd observations had corresponding ET data.
Fig. A2. Correlations of $\delta_R$ with VPD, RH, SWC, and $E_T$. Correlations were displayed individually for each rain event from day zero to day $N$ just before the next rain event. We present only significant best fits of regressions from lag analysis. Numbers after DOY in the figure legends represent slopes for each subset.
Fig. A3. Relationships between δ_R and P − EP. All nocturnal Keeling plot intercepts that passed QC criteria from DOY 100 to 273 were included.

Fig. A4. The relationships between modeled δ_R and observed δ_R. Dark and open circles represent model output after and before the one-way flux model (Cernusak et al., 2004) was incorporated, respectively. Data are included from DOY 100 to 273.

Fig. A5. 1 : 1 Relationships of δ_R calculations from the Keeling plots (intercept approach) and Miller/Tans formulation (slope approach).
Fig. A6. ISOILSM simulation for nocturnal $\delta_R$ (filled circle), $\delta^{18}O$ of foliar-respired CO$_2$ (open circle), $\delta^{18}O$ of soil-respired CO$_2$ (filled triangle) and $\delta^{18}O$ of stem-respired CO$_2$ (open triangle).

Fig. A7. Pulse precipitation events and associated $\delta^{18}O$ of precipitation in 2006 for the time periods presented in this manuscript.

Acknowledgements. We appreciate the technical and field support provided by Steve Sargent, Karen Brown, and numerous undergraduate interns during the four years of this study. Funding for this project was derived from LANL-Laboratory Directed Research and Development (LDRD), the Institute for Geophysical and Planetary Research (IGPP), and the Department of Energy, Office of Science, Office of Biological and Environmental Research (DOE-BER).

Edited by: C.-K. Kang

References


