Abstract

In this paper we describe measurements and modeling of $^{18}$O in CO$_2$ and H$_2$O pools and fluxes at a tallgrass prairie site in Oklahoma. We present measurements of the $\delta^{18}$O value of leaf water, depth-resolved soil water, atmospheric water vapor, and Keeling plot $\delta^{18}$O intercepts for net soil-surface CO$_2$ and ecosystem CO$_2$ and H$_2$O fluxes during three periods of the 2000 growing season. Daytime discrimination against C$^{18}$OO, as calculated from measured above-canopy CO$_2$ and $\delta^{18}$O gradients, is also presented. To interpret the isotope measurements, we applied an integrated land-surface and isotope model (ISOLSM) that simulates ecosystem H$_2^{18}$O and C$^{18}$OO stocks and fluxes. ISOLSM accurately predicted the measured isotopic composition of ecosystem water pools and the $\delta^{18}$O value of net ecosystem CO$_2$ and H$_2$O fluxes. Simulations indicate that incomplete equilibration between CO$_2$ and H$_2$O within C$_4$ plant leaves can have a substantial impact on ecosystem discrimination. Diurnal variations in the $\delta^{18}$O value of above-canopy vapor had a small impact on the predicted $\delta^{18}$O value of ecosystem water pools, although sustained differences had a large impact. Diurnal variations in the $\delta^{18}$O value of above-canopy CO$_2$ substantially affected the predicted ecosystem discrimination. Leaves dominate the ecosystem $^{18}$O-isoflux in CO$_2$ during the growing season, while the soil contribution is relatively small and less variable. However, interpreting daytime measurements of ecosystem C$^{18}$OO fluxes requires accurate predictions of both soil and leaf $^{18}$O-isofluxes.

Nomenclature

- $C_i$ = leaf internal CO$_2$ concentration (µmol m$^{-3}$)
- $C_{lH}$, $C_{lL}$ = CO$_2$ concentrations at the high and low sampling points (µmol m$^{-3}$)
- $F_{al}$, $F_{la}$ = CO$_2$ fluxes into and out of the leaf (µmol m$^{-2}$ s$^{-1}$)
- $F_{gr}$, $F_{sam}$, $F_s$ = growth, stem, and net soil-surface CO$_2$ fluxes (µmol m$^{-2}$ s$^{-1}$)
- $I$ = ecosystem $^{18}$O-isoflux (µmol m$^{-2}$ s$^{-1}$ %)
- $R_{ar}$, $R_{cr}$, $R_{eq}$ = CO$_2$ $^{18}$O isotopic ratios in the atmosphere, chloroplast, net ecosystem flux, and in equilibrium with leaf water
- $z_0$ = e-folding depth for soil CO$_2$ source (m)
- $\delta_{ar}$, $\delta_{cr}$, $\delta_{lH}$, $\delta_{lL}$, $\delta_{al}$, $\delta_{sam}$, $\delta_{s}$ = $\delta^{18}$O values of atmospheric CO$_2$, net ecosystem CO$_2$ flux, leaf water; CO$_2$ at the high sampling point, CO$_2$ at the low sampling point, net leaf CO$_2$ flux, stem respiration CO$_2$ flux, and soil CO$_2$ flux (%)
- $\Delta_c$ = difference in $\delta^{18}$O values of chloroplast and atmospheric CO$_2$ (%)
- $\Delta_{eq}$ = difference in $\delta^{18}$O values of equilibrium chloroplast and atmospheric CO$_2$ (%)

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Introduction

Terrestrial ecosystem carbon fluxes dominate large-scale spatial and temporal variations in the $\delta^{18}O$ value of atmospheric CO$_2$. Ocean gas exchange, biomass and fossil fuel burning, and stratospheric reactions also impact $\delta_a$, although their influence is much smaller (Francey & Tans, 1987; Farquhar et al., 1993; Ciais et al., 1997a; Peylin et al., 1999). At the global scale, a simple mass balance can be used to estimate the relative impact of these fluxes. The net ocean exchange, fossil fuel and biomass burning, and stratospheric fluxes are each less than 150 Pg C yr$^{-1}$%o, while the photosynthetic and soil respiratory fluxes are each on the order of 1000 Pg C yr$^{-1}$%o (Tans, 1980; Farquhar et al., 1993). Using a global network of flask data, Francey & Tans (1987) inferred that terrestrial carbon fluxes interacting with soil and leaf water drive the large (~1.5%) observed interhemispheric gradient in $\delta_a$. Simultaneously, Friedli et al. (1987) showed that terrestrial fluxes strongly influence measured variations in $\delta_a$ above Switzerland.

Experimental and theoretical advances in our understanding of respiratory and photosynthetic influences on $\delta_a$ followed these studies. In both respiration and photosynthesis, the exchange of oxygen isotopes between water and dissolved CO$_2$ imparts the $\delta^{18}O$ value of water to the CO$_2$ molecules. Hesterburg & Siegenthaler (1991) first investigated the interactions of soil CO$_2$ with soil water and developed a model to predict the $\delta^{18}O$ value of soil-respired CO$_2$. Tans (1998) expanded on this model to incorporate the influence of ‘abiotic’ or ‘invasion’ fluxes and developed analytical solutions for the $\delta^{18}O$ value of soil-gas CO$_2$ and surface CO$_2$ fluxes for a range of environmental conditions. Miller et al. (1999) performed a series of detailed measurements to quantify the effective kinetic fractionation of CO$_2$ diffusion out of the soil and demonstrated the importance of the invasion flux in soil chamber measurements. By applying the analytical solutions of Tans (1998), Stern et al. (2001) estimated the importance of abiotic CO$_2$ exchange between the atmosphere and soil for a variety of ecosystems. To quantify leaf C$^{18}O_2$ exchanges, Farquhar & Lloyd (1993) developed equations describing interactions between leaf CO$_2$ fluxes and $^{18}O$ in leaf water. Leaf C$^{18}O_2$ exchanges are dominated by the influx of CO$_2$ molecules into leaves, isotopic exchange with leaf water, and ‘retrodiffusion’ (i.e., molecules leaving the leaf without being fixed by photosynthesis, but having a different $\delta^{18}O$ value than when they entered).

Some of these results have been incorporated in global modeling studies of surface C$^{18}O_2$ fluxes and $\delta_a$. In the first such study, Farquhar et al. (1993) confirmed the importance of photosynthesis and respiration on $\delta_a$. Ciais et al. (1997a, b) modeled net ecosystem C$^{18}O_2$ fluxes and coupled them to a 3-D tracer-transport model to examine seasonal and latitudinal variations in $\delta_a$. Using the same modeling framework, Peylin et al. (1999) explored the influence of specific geographic regions on temporal and latitudinal variations in $\delta_a$. They argued that seasonal variations in northern hemisphere $\delta_a$ are dominated by carbon exchanges in the Siberian taiga region, where soil and leaf water are strongly depleted in $^{18}O$. Despite these modeling advances, a number of uncertainties remain, including the large interannual variability and apparent downward trend in global measurements of $\delta_a$ (Gillon & Yakir, 2001; Stern et al., 2001). Furthermore, the models of ecosystem C$^{18}O_2$ fluxes used in these global-scale studies have not been adequately tested at the site level.

Several ecosystem-scale studies have reported using measurements of $^{18}O$ in H$_2$O and CO$_2$ to better understand controls on the $\delta^{18}O$ value of CO$_2$ exchanged with the atmosphere or to partition measured net CO$_2$ fluxes into gross fluxes (for reviews, see Yakir & Sternberg, 2000; Dawson et al., 2002). Yakir & Wang (1996) used simultaneous measurements of $^{18}O$ and $^{13}C$ to partition net CO$_2$ fluxes between soil and plant components in several crop fields. Flanagan et al. (1995) described measurements of $^{18}O$ in water pools and CO$_2$ at two heights in a pine forest canopy. They reported that predictions from a mixing model that included the various ecosystem CO$_2$ sources were consistent with observed diurnal variations in C$^{18}O_2$ concentrations within the canopy. Using discrimination calculations based on measurements of $^{18}O$ in soil, stem, and leaf water, Flanagan et al. (1997) estimated that mid-day discrimination against C$^{18}O_2$ during photosynthesis was similar among the three boreal forest types, but that CO$_2$ released during soil respiration was less depleted than expected due to interactions with an extensive moss layer. In a tropical forest site, Harwood et al. (1998) reported leaf-level measurements of the
The δ18O value of CO2 fluxes and their relationship to vapor pressure deficits and stomatal conductance. Harwood et al. (1999) used Keeling plot analysis in a UK forest site to demonstrate that heterogeneity in ecosystem water pools likely accounted for variations in the δ18O value of CO2 fluxes. Keeling plots and measurements of 18O in ecosystem water pools have also been used to quantify soil and leaf contributions to the net ecosystem latent heat flux (Wang & Yakir, 2000).

The studies mentioned above were conducted in forest and agricultural ecosystems; much less information exists on 18O exchanges in H2O and CO2 in grasslands, which cover close to 25% of the earth’s land surface. Several recent studies indicate that C18OO exchanges may be more complicated than originally thought, particularly in C4 grasslands. For example, incomplete isotopic equilibration (termed disequilibrium, Θeq) between CO2 and leaf water due to low carbonic anhydrase (CA) enzyme activity may be common in most grasses (Gillon & Yakir, 2000, 2001). In this notation, Θeq varies between 0 and 1, and Θeq = 1 indicates complete equilibration. Gillon & Yakir (2001) report an average leaf disequilibrium in C4 plants, excluding outliers, of 0.38, while Helliker (2001) estimated Θeq to range from 0.6 to 0.7 in both leaf-level and whole-plant experiments with the C4 grass Andropogon gerardii. Additionally, large variations in leaf water isotopic composition along the leaf length were reported by Helliker & Ehleringer (2000), further complicating predictions of photosynthetic C18OO exchanges in grasslands.

In this paper, we describe a set of isotopic measurements and simulations in a C4-dominated tallgrass prairie ecosystem located in north-central Oklahoma, USA. After describing the experimental methods and measurements, we apply a mechanistic land-surface and isotope model (ISOLSM; Riley et al., 2002) to interpret the physiological and biophysical controls on measured δ18O values of CO2 and H2O pools and fluxes. We also demonstrate the importance of incomplete equilibration between leaf water and CO2 on ecosystem C18OO fluxes.

Materials and methods

Site description

Measurements were made in a tallgrass prairie pasture in Oklahoma, USA (36°56′N, 96°41′W) during three sampling campaigns in 2000: May 6–10, June 4–7, and July 18–21. The site is in a region with various land uses and covers, including crops, sparse trees, and other grasslands; it has not been grazed since 1996, but is burned every spring. The maximum leaf area index (LAI) is about 3.0 and the maximum net ecosystem exchange during the growing season is about 35 μmol m–2 s–1. The site and collection of meteorological forcing and flux data are described in detail in Suyker & Verma (2001).

C4 grasses constituted at least 78% of the species present in a vegetation cover survey conducted in 1997 (Suyker & Verma, 2001). However, this proportion varies seasonally. Still et al. (2003a) used night-time 13C measurements to estimate the fraction of ecosystem respiration resulting from C4-derived carbon. In 2000, these measurements indicated that the C4 contribution increased from 67% in early spring to 77% in mid-summer. Daytime measurements of above-canopy 13C gradients showed a similar seasonal increase in the fraction of net ecosystem exchange attributable to C4 plants.

CO2 measurements

Night-time CO2 Keeling plots

We collected air samples at four heights above the surface (0.5, 1.5, 2.5, and 4.5 m) several times during the night when both plant and heterotrophic respiration were occurring. The 0.5 m sampling level was directly above the grassland canopy. Each air sample was collected over a 2-min interval, so that all four levels were sampled in less than about 10 min. Each set of four samples was used to create a single Keeling plot intercept. Further details of field sampling are described in Still et al. (2003a). Air samples were collected and stored in 100 ml glass flasks (Kontes Custom Glass Shop, Hayward, CA, USA) and returned to the Carnegie Institution of Washington for concentration and isotopic analysis. This analysis was conducted using a system that simultaneously measures CO2 mixing and isotope ratios in small air samples (Ribas-Carbo et al., 2002). The measurement precision for CO2 concentration with this system is 0.4–0.7 ppm, and for δ18O values of CO2 is 0.05%.

Using the night-time data, we constructed mixing plots (Keeling plots) to estimate the isotopic composition of the net ecosystem CO2 flux, δe (%o). This approach (Keeling, 1958; Keeling, 1961) assumes that the system can be represented as a simple mixture of atmospheric CO2 and the CO2 produced by ecosystem respiration. The intercept from a linear regression between the δ18O value of the CO2 concentration and the reciprocal of the CO2 concentration provides an estimate of the isotopic composition of the respiration source. We used a geometric mean regression that incorporates errors in both the concentration and isotopic composition measurements to calculate the intercept (Friedli et al., 1987; Sokal & Rohlf, 1995;
Daytime discrimination

We sampled daytime CO₂ concentration and δ¹⁸O values at the highest (4.5 m) and lowest (0.5 m) tower levels during the 2000 growing season. The sample collection was the same as that used for nighttime collections, except that only two levels were sampled for each measurement.

The average measured CO₂ concentrations and isotopic ratios sampled at each height during a one to three hour period were used for each discrimination calculation. On a typical day, fewer than 10 gradient pairs with sufficient concentration and isotope gradients could be sampled due to strong winds at the site. The net ecosystem discrimination against C¹⁸O₂, \( \Delta_e^{18} \) (‰), was calculated as (derived in Still et al., 2003a; see also Evans et al. (1986); Lloyd & Farquhar (1996):

\[
\Delta_e^{18} = \frac{-1000C_H(\delta_H - \delta_L)}{1000(C_H - C_L) + (\delta_H C_H - \delta_L C_L)}.
\]

where \( C_H \) and \( C_L \) (\( \mu \text{mol} \text{ m}^{-2} \)) are the CO₂ concentrations at the high and low sampling points, respectively, and \( \delta_H \) and \( \delta_L \) (‰) are the δ¹⁸O values of CO₂ at the high and low sampling points, respectively.

Soil-surface CO₂ flux

We measured the δ¹⁸O value of the soil-surface CO₂ flux on two occasions in July 2000. The measurement protocol was designed to minimize pressure artifacts (Lund et al., 1999) and to average over the small-scale variation in \( C_3 \) and \( C_4 \) abundance. We used a modified Licor 6400 soil respiration system (Still et al., 2003a). A balloon was placed on the inside of the chamber over the pressure equalization port and a septum was attached so that air could be withdrawn from the chamber through a small column of magnesium perchlorate into pre-evacuated 100 mL flasks. When a sample was taken, atmospheric air flowed into the balloon, equalizing the pressure inside and outside the chamber. The chamber was placed on open patches of soil between grass tussocks. Before sampling, respired CO₂ was allowed to accumulate in the chamber for a time (the same for each replication) sufficient to reach a concentration of approximately 700 ppm. Seven flasks from the chamber were taken, one each from seven separate soil patches. Two flasks were also filled with ambient air (one at the beginning and one at the end of the sampling sequence). The data were combined for Keeling plot analysis (geometric mean regression, nine points per curve) to obtain a flux-weighted average of the isotopic composition of CO₂ respired from the sampled surface area.

Using the method described in Miller et al. (1999), we calculated the impact of invasion (excess chamber CO₂ diffusing into the soil, equilibrating with soil water, and diffusing back into the chamber) on the soil-surface isoflux to be small (less than 0.5%), primarily because soil moisture in the top 15 cm was low at the time of this measurement (less than 25% water-filled pore space).

H₂O measurements

Atmospheric water vapor

Atmospheric water vapor samples were collected and analyzed for ¹⁸O composition. The water vapor mixing ratio was determined by averaging the micrometeorological measurements at each height over the sampling period. For ¹⁸O composition, water vapor was collected from four heights so that each Keeling plot consisted of four samples. The sampling methodology is described in detail in Helliker et al. (2002). Briefly, atmospheric air was pulled through a dry-ice-cooled glass condenser for 15 min. The samples were then sealed and shipped to the SIRFER laboratory at the University of Utah (http://ecophys.biology.utah.edu/sirfer.html). Pure CO₂ was injected into condensers (to a final concentration of 10%) and allowed to equilibrate for 48 hours. The δ¹⁸O value was determined by on-column injection through a continuous flow isotope ratio mass spectrometer. Keeling plots for water vapor were calculated analogously to those for CO₂.

Leaf and soil water

Soil water, bulk leaf water, and plant stem water were collected and analyzed for ¹⁸O composition. Soil water was sampled with a soil corer to 20 cm depth. We subsampled each core in four intervals: 0–2.5, 2.5–5, 5–10, and 10–20 cm. These soil plugs were placed in glass vials, sealed with parafilm, and stored for isotopic analysis. The leaf water isotopic composition was determined by collecting upper leaves from the dominant plants (\( C_3 \): Solidago missouriensis; \( C_4 \): Andropogon gerardii, Panicum virgatum, and Sorghastrum nutens) at mid-day and storing them in glass vials as with the soil samples. The leaf and soil samples were analyzed at SIRFER at the University of Utah. Water was extracted from the sample with cryogenic distillation and its
$^{18}$O composition was determined by the CO$_2$-H$_2$O equilibration method of Socki et al. (1992) with modifications described in Helliker & Ehleringer (2000).

**ISOLSM simulations**

ISOLSM couples the land-surface model LSM1.0 (Bonan, 1996) with modules that predict the $^{18}$O composition of canopy water vapor, leaf water, and vertically resolved soil water; CO$_2$ oxygen isotope exchanges with soil and leaf water; leaf photosynthetic C$^{18}$OO fluxes; soil CO$_2$ and C$^{18}$OO diffusive fluxes (including abiotic soil exchange); and ecosystem exchange of H$_2^{18}$O and C$^{18}$OO with the atmosphere. A detailed description of the processes simulated in ISOLSM can be found in Riley et al. (2002). Briefly, the depth-resolved $^{18}$O isotopic ratio of soil water is solved by an explicit numerical solution to the $H_2^{18}$O mass balance. The model accounts for equilibrium fractionation during evaporation and fractionation through the laminar layer at the soil surface. Rain and irrigation inputs are treated as boundary conditions on the soil water $^{18}$O balance. A semi-implicit numerical scheme is used to simulate the soil-gas diffusion and CO$_2$ interactions with $^{18}$O in the soil water. For the simulations shown here, the model calculates the energy balance, photosynthetic CO$_2$ flux, soil moisture and temperature, and the $\delta^{18}$O value of soil moisture with a time step of 100 s, while the soil-gas diffusion model uses a time step of 20 s. Predictions of the $\delta^{18}$O value of leaf water, $\delta_1$ (%), are based on the predicted stem water and canopy water vapor isotopic composition and the Craig-Gordon model (Craig & Gordon, 1965) with modifications for leaves as described by Flanagan et al. (1991). The canopy water vapor $^{18}$O composition is determined diagnostically based on fluxes from the atmosphere, leaves, and the soil surface. As mentioned earlier, incomplete equilibration between leaf water and CO$_2$ can occur in C$_4$ grass leaves as a result of low CA activity. Gillon & Yakir (2000) showed that a reasonable approximation for leaf disequilibrium is $\Theta_{eq} = \Delta_c/\Delta_{eq}$, where $\Delta_c = (R_c/R_\alpha - 1) 1000$, $\Delta_{eq} = (R_{eq}/R_\alpha - 1) 1000$, and $R_c$, $R_\alpha$, and $R_{eq}$ represent the isotopic ratios of the background atmosphere, chloroplast CO$_2$ and CO$_2$ in equilibrium with leaf water, respectively. We apply these relationships to calculate an equivalent $\delta^{18}$O value of leaf internal CO$_2$ that reflects the reduced leaf discrimination due to disequilibrium.

We used measurements from the site to specify soil characteristics and the vertical root distribution. ISOLSM is forced with measurements of air temperature, wind speed, CO$_2$ concentration, vapor pressure, downward short-wave and long-wave radiation, precipitation or irrigation amount and its isotopic ratio, and the $\delta^{18}$O value of above-canopy vapor and CO$_2$. We conducted the simulations presented here assuming a 100% C$_4$ canopy, as C$_4$ plants dominate the net ecosystem exchange during the growing season. Since we did not have continuous measurements of the isotopic composition of atmospheric vapor, we assumed a value 7% less than the predicted stem water isotopic composition. Actual values are impacted by many factors other than evapotranspiration (e.g., horizontal and vertical atmospheric advection), and show diurnal variations of up to 4% (Helliker et al., 2002). We also lacked measurements of the isotopic composition of above-canopy CO$_2$ and assumed a constant value of 0% for the results shown here, although diurnal variations of up to 2% are common (Helliker et al., 2002). We test the sensitivity of model predictions to variations in the $\delta^{18}$O values of atmospheric CO$_2$ and H$_2$O below.

**Results and discussion**

In this section, we present experimental results and discuss comparisons between measured and simulated latent heat, sensible heat, and CO$_2$ fluxes; the $^{18}$O composition of water in leaves and stems; vertically resolved soil water $^{18}$O composition; and H$_2^{18}$O and C$^{18}$OO exchanges with the atmosphere. We also apply ISOLSM to examine biological and physical controls on these exchanges.

**Ecosystem CO$_2$ and latent and sensible heat fluxes**

Model predictions of ecosystem CO$_2$ and latent and sensible heat fluxes impact predictions of ecosystem H$_2^{18}$O and C$^{18}$OO stocks and fluxes. For example, sustained inaccuracy in the predicted ecosystem latent heat flux can result in inaccurate predictions of near-surface soil water isotopic composition. Such errors can propagate to impact stem and leaf water isotopic composition predictions and therefore the ecosystem exchanges of C$^{18}$OO. The model accurately simulated the magnitude and dynamics of CO$_2$ and latent and sensible heat fluxes over the growing season. For example, Fig 1(a) and (b) show comparisons between measured and modeled fluxes over a 10-day period beginning May 1, 2000.

**Isotopic composition of ecosystem water pools**

Figure 2 shows the predicted and measured depth-resolved soil water isotopic composition over the 3-month period. We initialized the modeled soil water isotopic composition using measurements taken at the beginning of May 2000. The model reasonably predicts
the $\delta^{18}O$ value of soil water measured in the subsequent periods. The 10–20 cm soil layer water isotopic composition is predicted to be $\sim 5$ and 3% too light in the June and July measurement periods, respectively, while the soil water isotopic composition between 2.5 and 5 cm is predicted to be $\sim 2\%$ too light in the July measurement period. The predictions are dependent on the assumed rooting activity depth profile and the $\delta^{18}O$ value of atmospheric water vapor, as described in Riley et al. (2002). The impact of errors in the rooting activity is difficult to evaluate since the activity profile at this site is not known. Errors in the imposed atmospheric water vapor $\delta^{18}O$ value could easily result in an error in the predicted near-surface soil water isotopic composition of $2\%$ after 3 months of simulation.

The temporal resolution of the measurements shown in Fig. 2 does not allow us to conclude that predicted diurnal variations in soil water isotopic composition between 0 and 2.5 cm, which are as large as 5%, are accurate. However, we observed comparable diurnal variability in measurements of the $\delta^{18}O$ value of near-surface soil water taken in the summer of 2001 in a sorghum field in Oklahoma (data not shown). These variations are driven by soil evaporation, and are largest when evaporation is large, e.g., following precipitation. Nonetheless, more diurnal measurements of soil water $^{18}O$ composition are required to test these model predictions adequately. Accurately predicting the near-surface soil water isotopic composition is important since it influences the isotopic composition of the net soil-surface CO$_2$ and H$_2$O fluxes.

Predicted and measured leaf and stem water isotopic compositions for the dominant C$_4$ grasses are shown in Fig. 3 for the 3 days in May, June, and July for which we have measurements. $\delta_l$ and the $\delta^{18}O$ value of stem water are accurately predicted in May and July, while $\delta_l$ is predicted to be $\sim 3\%$ too heavy in the June sampling. The predicted $\delta_l$ typically increases from early morning to mid-afternoon by between 10% and 20%, and then relaxes back to a night-time steady value. We have observed similar patterns and magnitudes of diurnal variation in sorghum leaf water $^{18}O$ composition in this area (data not shown). The leaf water isotopic composition is substantially more variable than that of soil water (particularly deeper than 5 cm; Fig. 2) over the afternoon, resulting in more variable $\delta^{18}O$ values of leaf CO$_2$ fluxes than of soil CO$_2$ fluxes.

**Ecosystem H$_2$O fluxes**

The predicted and measured evapotranspiration (ET) flux isotopic composition is shown in Fig. 4 for the 3 days when H$_2$O Keeling plots were available. The predicted ecosystem water flux isotopic composition shows strong diurnal variation, consistent with the variable soil evaporation isotopic composition and fraction of total ET attributable to soil evaporation. The $\delta^{18}O$ value of the net ecosystem vapor flux will be more variable the larger the contribution of soil
evaporation to the total ET flux. $\delta^{18}O$ values of canopy and above-canopy atmospheric vapor and soil-surface evaporation and transpiration are shown for a typical day in Fig. 5. The soil evaporation isotopic composition is typically lightest at about 11 in the morning and increases throughout the day. This increase is caused by the concurrently increasing near-surface soil water isotopic composition and soil-surface equilibrium-partitioning coefficient (due to increased soil temperature). The perturbations in canopy water vapor and soil evaporation $\delta^{18}O$ values at about day 180.6 occur because of a rapid change in measured downward short-wave radiation over this period, probably caused by clouds. At any particular time, the canopy water vapor isotopic composition depends on $H_2^{18}O$ and $H_2O$ fluxes between the canopy air and (1) overlying atmosphere, (2) leaves, and (3) soil surface (see Eqn (11) of Riley et al. (2002)). Typically, the predicted canopy air space vapor isotopic composition in the morning is close to that of the background above-canopy vapor, increases until about mid-day as a result of the heavier transpiration flux, and then returns to the background value as the ecosystem latent heat flux diminishes in the late afternoon.

**Soil respiration $^{18}CO_2$ fluxes**

The measured and predicted $\delta^{18}O$ values of soil-respired CO$_2$ are presented in Fig. 6. In these simulations, we imposed soil respiration profiles that decay exponentially with depth. We assume that the root respiration profile follows the root distribution profile with an $\epsilon$-folding depth, $z_0$ (m), of 0.2 m, and that the microbial respiration has a profile defined by $z_0 = 0.05$ m. Thus, about 75% of the predicted soil respiration occurs in the top 15 cm of soil. In reality, the depth distribution of respiration will depend on the distribution of root activity, soil moisture and...
temperature, and microbial substrate availability, among others. The \( \delta^{18}O \) value of the net soil-surface \( \text{CO}_2 \) flux is sensitive to the depth distribution of \( \text{CO}_2 \) production. For example, if a larger fraction of respiration occurs near the surface, the \( \delta^{18}O \) value of the net soil-surface CO\(_2\) flux will become more enriched as a result of equilibration with more enriched near-surface soil water.

The decrease in the measured \( \delta^{18}O \) value of soil-respired \( \text{CO}_2 \) between days 200 and 201 is caused by a small precipitation event with a \( \delta^{18}O \) value of \(-2.6\%\) (indicated by the arrow in Fig. 6). This precipitation input is reflected in the simulated \( \delta^{18}O \) value of soil water as a decline in the top soil layer and as a small increase in the second soil layer. The small increase in the \( \delta^{18}O \) value of soil water in the 2.5–5 cm layer results from advection of the heavier soil water (before the precipitation event) from 0–2.5 cm. As the \( \text{CO}_2 \) diffuses through the top soil layer, it interacts with this lighter soil water and thereby acquires a lighter isotopic composition. Note that this result contradicts the observation of Miller et al. (1999) that the \( \delta^{18}O \) value of water in the top 5 cm of soil does not substantially impact the \( \delta^{18}O \) value of the soil-surface \( \text{CO}_2 \) flux. The decrease in the \( \delta^{18}O \) value of soil-respired \( \text{CO}_2 \) resulting from the precipitation event is accurately captured by ISOLSM. In general, the impact of a precipitation event on the \( \delta^{18}O \) value of soil-respired \( \text{CO}_2 \) depends on the precipitation flux, \( \delta^{18}O \) value of precipitation and antecedent soil moisture, and the fraction of soil respiration occurring in the near-surface soil.

**Ecosystem \( ^{13}\text{CO}_2 \) fluxes**

Figures 7(a)–(c) show predicted and measured \( \delta^{18}O \) values of the net ecosystem \( \text{CO}_2 \) flux (Keeling plot intercepts) for the three periods where measurements were made (predicted values are shown when the magnitude of the ecosystem \( \text{CO}_2 \) flux is greater than 2 \( \mu \text{mol m}^{-2} \text{s}^{-1} \)). Three simulation scenarios are shown: the first assumes complete equilibration within the leaf (\( \text{\( \Theta_{eq} = 1.0 \) and the second and third assume \( \Theta_{eq} = 0.5 \) and 0.35, respectively. In Fig. 7, only measurements with \( R^2 \) values greater than 0.6 and \( \text{CO}_2 \) gradients (between 0.5 and 4.5 m height) greater than 15 ppm are included (Table 1).

The \( \delta^{18}O \) value of the predicted ecosystem \( \text{CO}_2 \) flux varied substantially during the day and between days due primarily to variations in \( \delta_1 \) (also shown in Fig. 7) and leaf internal \( \text{CO}_2 \) concentration, \( C_i \) (\( \mu \text{mol m}^{-3} \)). At night the predicted \( \text{CO}_2 \) flux isotopic composition remained relatively constant since the soil water isotopic composition and soil temperature are relatively constant. The sharp transitions in the \( \delta^{18}O \) values of the net ecosystem \( \text{CO}_2 \) flux during the morning and evening occur when the system switches between being dominated by respiration and photosynthesis. During the day, photosynthetic uptake and retrodiffusion dominate ecosystem \( \text{CO}_2 \) and \( ^{13}\text{CO}_2 \) exchange. Lower
values of $\Theta_{eq}$ resulted in significantly more positive $\delta^{18}$O values of daytime ecosystem CO$_2$ fluxes. Note that a negative $\delta^{18}$O value of the daytime ecosystem flux enriches the atmosphere. Leaf water $\delta^{18}$O values are relative to the V-SMOW standard; CO$_2$ flux $\delta^{18}$O values are relative to the V-PDB-CO$_2$ standard.

Using a two-component mixing model (Keeling plot) to estimate the $\delta^{18}$O value of respired CO$_2$ from measurements can be misleading, since (1) changes in the $\delta^{18}$O value of ecosystem respiration can occur independently of changes in CO$_2$ concentration and (2) the water pools driving these isotopic changes can be spatially and temporally heterogeneous (Amundson et al., 1998; Tans, 1998). As a result, extrapolation of the linear regression to infinite CO$_2$ concentration may not give an accurate estimate of the isotopic composition of respired CO$_2$. This decoupling of atmospheric CO$_2$ mole fraction and the isotopic composition of respired CO$_2$ can be caused by temporal changes in the leaf or soil water isotopic compositions over the measurement period. $\delta_1$ is more likely to change over the night than the $\delta^{18}$O value of soil water (particularly below ~5 cm depth). It is unlikely that changes in leaf and soil water isotopic compositions affected our measurements at a particular time because each of our night-time estimates was based on measurements collected along a vertical spatial gradient over a short time interval. However, this effect can impact our interpretation of measurements throughout the night, as discussed below. The abiotic invasion of C$^{18}$OO into soils and horizontal atmospheric advection can also impact the expected linear Keeling plot relationship. These potential confounders indicate that care must be taken when testing the accuracy of model predictions against $\delta^{18}$O Keeling plot intercepts. Despite these concerns, the majority of our Keeling plots seem to follow the two-component model assumption, as demonstrated by the high $R^2$ values shown in Table 1.

The May 2000 ecosystem CO$_2$ flux isotopic compositions are notable since the Keeling plot intercepts tend toward more negative values throughout the night, contrary to model predictions. We believe that this measured trend is real. The CO$_2$ gradients in these Keeling plots (Table 1) are less than the threshold recommended by Pataki et al. (2003). However, that recommendation was based on the decrease in standard error of Keeling plot intercepts with increasing CO$_2$ gradients. The threshold they recommend (75 ppm) corresponds to a standard error of the intercept of 1%; the standard errors of our three night-time intercepts are 0.2%, 0.9%, and 1.0%, despite the relatively small CO$_2$ gradients. The inability of the model to capture this night-time trend may reflect (a) more rapid relaxation than is predicted by the model of leaf water isotopic composition back to the relatively depleted source water, thereby impacting leaf dark respiration; (b) an inaccurate prediction of night-time leaf stomatal

Table 1 $R^2$ values and differences in CO$_2$ concentrations between 0.5 and 4.5 m for the night-time CO$_2$ Keeling plot intercepts shown in Fig. 7

<table>
<thead>
<tr>
<th>Date</th>
<th>Time (hours)</th>
<th>$\Delta$CO$_2$ (ppm)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/9/2000</td>
<td>21:37</td>
<td>65</td>
<td>0.99</td>
</tr>
<tr>
<td>5/10/2000</td>
<td>12:10</td>
<td>25</td>
<td>0.97</td>
</tr>
<tr>
<td>5/10/2000</td>
<td>2:50</td>
<td>22</td>
<td>0.99</td>
</tr>
<tr>
<td>6/5/2000</td>
<td>21:11</td>
<td>128</td>
<td>0.83</td>
</tr>
<tr>
<td>6/6/2000</td>
<td>12:23</td>
<td>118</td>
<td>0.62</td>
</tr>
<tr>
<td>7/18/2000</td>
<td>21:37</td>
<td>47</td>
<td>0.90</td>
</tr>
<tr>
<td>7/19/2000</td>
<td>12:20</td>
<td>118</td>
<td>0.98</td>
</tr>
<tr>
<td>7/19/2000</td>
<td>3:32</td>
<td>31</td>
<td>0.85</td>
</tr>
<tr>
<td>7/20/2000</td>
<td>21:47</td>
<td>16</td>
<td>0.72</td>
</tr>
<tr>
<td>7/21/2000</td>
<td>12:27</td>
<td>9</td>
<td>0.97</td>
</tr>
</tbody>
</table>
conductance; (c) changes in the isotopic composition of soil respiration not accurately predicted by the model; (d) incorrect prediction of invasion due to inaccurate estimates of the $\delta^{18}O$ value of net soil-surface CO$_2$ fluxes; or (e) advection (i.e., temporal heterogeneity in background atmospheric $\delta^{18}O$ values resulting from advection of air from adjacent areas). We do not have sufficient information to evaluate the relative impact of these mechanisms on the trend in these measurements.

**Daytime discrimination**

The measured (Eqn (1)) and predicted daytime ecosystem discrimination values ($\Delta_e^{18}$) are shown in Figs 8(a)–(c). The predicted $\Delta_e^{18}$ is calculated as

$$\Delta_e^{18} = \left( \frac{R_a}{R_e} - 1 \right) 1000 = \frac{\delta_a - \delta_e}{1 + \delta_e/1000},$$

where $R_e$ (–) is the isotopic ratio of the net ecosystem CO$_2$ flux. Comparing predicted and measured ecosystem discrimination indicates that leaf disequilibrium may be substantial. In May, June, and July, $\Theta_{eq}$ values of 0.5, 0.35, and 0.35, respectively, force model predictions closer to measured values. Care must be taken in interpreting this observation since other modeled state variables (e.g., $\delta_l$ and $C_i$) also have substantial impacts on $\Delta_e^{18}$ and may be inaccurately represented in the model. For example, our modeled $\delta_l$ is higher than that observed in June, which will result in an overestimate of leaf discrimination. Further, our assumption of isotopic steady state in the leaf may result in an overestimate of $\delta_l$ during transient environmental conditions. Errors in simulating $C_i$ are potentially more troublesome due to the non-linear relationship between $C_i$ and leaf discrimination against C$_{18}$OO (Farquhar & Lloyd, 1993). C$_3$ plants have higher $C_i$ than C$_4$ plants and, as a result, larger leaf discrimination values. Therefore, the diminishing proportion of C$_3$ plants over the season may also cause the progression toward lower measured $\Delta_e^{18}$; this effect is not included in the modeling predictions shown here.

We examine more closely the factors contributing to the predicted $\Delta_e^{18}$ over the course of a single day in Figs 9(a) and (b). In Fig. 9(a), $\Theta_{eq}$ = 0.5 and $\Delta_e^{18}$ and $\Delta_l^{18}$ (%) represent the net discrimination of C$_{18}$OO from soil and leaves, respectively, and are calculated analogously to $\Delta_e^{18}$. The predicted $\delta_l$ and $C_i$ are shown in Fig. 9(b).
net ecosystem discrimination increases from ~5% before sunrise to about 20% at 20% before sunrise and remains relatively constant until the afternoon. The abrupt shifts in early morning and later afternoon occur as the system transitions between being dominated by photosynthesis and respiration; the net ecosystem isoflux is relatively small during these periods. Note that, although soil ‘discrimination’ is calculated to be positive, soil respiration typically makes the atmosphere lighter, in contrast to photosynthesis. Diurnal variations in soil respiration typically makes the atmosphere lighter, although soil ‘discrimination’ is calculated to be positive, relatively small during these periods. Note that, although soil ‘discrimination’ is calculated to be positive, soil respiration typically makes the atmosphere lighter, in contrast to photosynthesis. Diurnal variations in \( \Delta_{18}^{\text{soil}} \) are small. With respect to impacts on \( \Delta_{18}^{\text{leaf}} \), the increase (decrease) in \( \delta^1 \) is opposed by the decrease (increase) in \( \delta^1 \) during the morning (afternoon).

**Ecosystem isoflux**

The ecosystem \(^{18}\text{O}\)-isoflux, \( I \) (\( \mu\text{mol m}^{-2} \text{s}^{-1} \text{‰} \)), quantifies the net impact of ecosystem fluxes on the atmospheric \(^{18}\text{O}\) content:

\[
I = -(F_{al} - F_{la})\delta_{al} + (F_{g} + F_{sm})\delta_{sw} + F_{s}\delta_{s},
\]

where \( \delta_{al} \), \( \delta_{sw} \) and \( \delta_{s} \) (%) are the predicted \(^{18}\text{O}\) values of the net leaf, stem respiration, and net soil-surface \( \text{CO}_2 \) fluxes, respectively; \( F_{al} \) and \( F_{la} \) (\( \mu\text{mol m}^{-2} \text{s}^{-1} \)) are the predicted \( \text{CO}_2 \) fluxes into and out of the leaf, respectively; and \( F_{g} \), \( F_{sm} \), and \( F_{s} \) (\( \mu\text{mol m}^{-2} \text{s}^{-1} \)) are the predicted growth respiration, stem respiration, and net soil-surface \( \text{CO}_2 \) fluxes, respectively. The three groups of terms on the right-hand side of Eqn (3) describe the net leaf isoflux, above-ground respiratory isoflux, and net soil-surface respiratory isoflux, respectively.

The net leaf isoflux dominates the ecosystem isoflux (Fig. 10), which varies substantially over the course of the day. The predicted photosynthetic \( \text{CO}_2 \) exchange and \( \delta^1 \) each reach their maximum in the middle of the day, thereby reinforcing the net leaf isoflux magnitude. The net soil-surface isoflux is a small fraction of the ecosystem isoflux for several reasons. First, the net soil-surface \( \text{CO}_2 \) flux is a small fraction of the ecosystem \( \text{CO}_2 \) flux during this period. This tallgrass system maintains an approximately even carbon balance over the season through losses from soil microbial respiration and fire at other times of the year. In systems where diurnal respiratory and photosynthetic carbon fluxes are more balanced, the soil-surface isoflux will be a more significant contributor to the ecosystem isoflux. Second, the soil water isotopic composition at this site is not strongly depleted relative to the atmosphere (compared with, for example, boreal regions; Flanagan et al., 1997). Third, the mid-day leaf water is strongly enriched due to the low relative humidity and high \( \delta^{18} \) value of soil water, thus ensuring a large net leaf isoflux during the day. Finally, photosynthetic fluxes are much higher in productive grasslands than in many other ecosystems.

The relatively low soil moisture in this system leads to a lower effective diffusive fractionation and therefore a relatively enriched net soil-surface \( \text{CO}_2 \) flux. Concurrently, the lower soil moisture may cause a decrease in heterotrophic respiration, thereby reducing the soil isoflux. The net impact of these effects is difficult to discern without a model like ISOLSM that can explicitly simulate the impact of soil moisture and temperature on the \( \text{CO}_2 \) source strength and diffusivity as a function of depth. We will address these interactions and their impact on the \( \delta^{18} \) value of the soil-surface \( \text{CO}_2 \) flux in future work.

As mentioned earlier, \( \text{C}_4 \) plants have lower discrimination against \(^{18}\text{O}\) than \( \text{C}_3 \) plants. Thus, all else being equal, soil respiration has a relatively larger impact on the ecosystem isoflux in a \( \text{C}_4 \)-dominated system. In a related analysis, we applied ISOLSM to investigate the impact of \( \text{C}_3 \) vs. \( \text{C}_4 \) plant physiology in this tallgrass system (Still et al., 2003b). In addition to the impact on leaf discrimination due to different \( \text{CO}_2 \) concentrations in the leaf stomatal pore, the \( \text{C}_3 \) and \( \text{C}_4 \) systems also have slightly different predicted soil moitures and leaf temperatures for the same meteorological forcing. Soil moisture and leaf temperature impact the soil-surface and leaf isofluxes. In these simulations, the soil isoflux was a larger proportion of the ecosystem isoflux in the \( \text{C}_4 \) system, due primarily to the reduced daytime leaf discrimination.

**Diurnal variations in the \( \delta^{18} \) value of above-canopy \( \text{CO}_2 \)**

As part of our measurement campaigns in June and July, air samples from the 4.5 m high sampling port were collected in pre-dried and evacuated 100-mL glass flasks every 1.5–3 h and analyzed for their \( \text{CO}_2 \)
concentration and oxygen isotope composition ($\delta_{18}O$). Several features are immediately apparent in the isotopic composition data (Figs 11(a) and (c)): an average diurnal cycle with an amplitude of $\sim 1.5\%_{\text{oo}}$, an upward trend in the June period, and a downward trend in the July period. The diurnal cycle amplitude is large and roughly the same size as the interhemispheric $\delta_a$ gradient observed by the NOAA-CMDL network (Farquhar et al., 1993; Ciais et al., 1997a, b). During both periods, diurnal variations in $\delta_{18}O$ are closely coupled to variations in CO$_2$ concentration. This tight coupling implies that changes in $\delta_{18}O$ are dominated by leaf and soil fluxes and not by changes in the $\delta^{18}O$ value of water pools independently of flux variations. There was no precipitation during these two periods.

An examination of modeled ecosystem $^{18}O$-isofluxes (Figs 11(b) and (d)) over these periods shows that the observed $\delta^{18}O$ diurnal cycle in both periods is strongly modulated by leaf photosynthetic $^{18}O$-isofluxes, with a small and relatively invariant contribution from soil $^{18}O$-isofluxes. The weak trends in observed $\delta_{18}O$ in June and July follow trends in the modeled net leaf $^{18}O$-isoflux. Unfortunately, a full comparison between modeled $^{18}O$-isofluxes and observed $\delta_{18}O$ variations is not possible, since $\delta_{18}O$ is also influenced by (1) advection of air parcels from adjacent regions, which may have different vegetation cover and soil water $^{18}O$ composition, and (2) the atmospheric boundary layer height and turbulence conditions, which vary with surface heating and cooling. Coupling ISOLSM to a regional-scale meteorological model that simulates $^{18}O$ exchanges with CO$_2$ and H$_2$O is in progress and will facilitate analyses that include these processes.

**Sensitivity to the $\delta^{18}O$ value of atmospheric CO$_2$ and H$_2$O**

The simulations described above assume that the $\delta^{18}O$ value of atmospheric water vapor was $7\%_{\text{oo}}$ less than the predicted stem water isotopic composition, while the $\delta^{18}O$ value of atmospheric CO$_2$ was assumed to be constant at $0\%_{\text{oo}}$. Measurements at this site indicate that the $\delta^{18}O$ value of above-canopy H$_2$O and CO$_2$ can vary by $4\%_{\text{oo}}$ and $2\%_{\text{oo}}$, respectively, over the day (Helliker

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**Fig. 11** Measured CO$_2$ concentration and $\delta^{18}O$ value of CO$_2$ sampled at 4.5 m ($\delta_{18}O$) during the (a) June 4–7 and (c) July 18–21 measurement campaigns. Simulated net leaf and soil $^{18}O$-isofluxes (umol m$^{-2}$ s$^{-1}$%$_{\text{oo}}$) are also shown for these two periods (b, d). $\delta^{18}O$ values are relative to the V-PDB-CO$_2$ standard.

et al., 2002). To test the impact of this variation, we imposed changes of these magnitudes while maintaining the average isotopic composition over the day unchanged. The $^{18}$O composition of atmospheric H$_2$O was forced to increase linearly with time between 8:00 and 18:00 hours, with a daily average 7% lighter than stem water at 8:00 hours. For the atmospheric isotopic composition of CO$_2$, we imposed a time-dependent sinusoidal profile with a maximum at 14:00 hours and a daily average of 0%.

Imposing diurnal variation in the $^{18}$O value of atmospheric H$_2$O resulted in effectively no change in the soil water, stem water, and leaf water isotopic compositions, and therefore no change in the $^{18}$O value of the ecosystem CO$_2$ flux. Note that changes in the mean $^{18}$O value of atmospheric H$_2$O significantly impact the isotopic composition of ecosystem water pools. In contrast, imposing a varying $^{18}$O value of atmospheric CO$_2$ resulted in increases of about 2% in the $^{18}$O value of the mid-day ecosystem CO$_2$ flux, consistent with the increase in the atmosphere-to-leaf C$_{18}$OO fluxes. Note that an increase in the $^{18}$O value of the mid-day CO$_2$ flux will result in a lighter atmosphere. Night-time $^{18}$O values of the ecosystem CO$_2$ flux were relatively unaffected by the imposed variability in the $^{18}$O value of atmospheric CO$_2$.

**Conclusions**

In this paper, we present measurements and model predictions of CO$_2$ fluxes, latent and sensible heat fluxes, leaf and stem H$_2^{18}$O composition, vertically resolved soil water H$_2^{18}$O composition, and H$_2^{18}$O and C$_{18}$OO ecosystem fluxes in a tallgrass prairie in Oklahoma, USA. Generally, ISOLSM accurately predicted the dynamics and magnitude of these quantities over the 3-month simulation period. The paucity of measurements spanning the diurnal cycle makes it difficult to evaluate the short-term predictions of the model. However, the large predicted diurnal variations in the $^{18}$O values of ecosystem water pools and resultant C$_{18}$OO fluxes argue that care must be taken when applying discrete measurements of these quantities to partition net ecosystem fluxes into component gross fluxes.

Continuous $^{18}$O values of atmospheric CO$_2$ and H$_2$O are required inputs to the model, and this information was unavailable for this site. Previous measurements in this system have shown that these quantities can vary substantially over the course of the day. Our simple sensitivity analysis indicated that diurnal variability in the $^{18}$O value of atmospheric H$_2$O had a small impact on the isotopic composition of ecosystem water pools, although sustained changes can have significant impacts. Typical variations in the $^{18}$O value of atmospheric CO$_2$ increased the mid-day $^{18}$O value of the ecosystem CO$_2$ flux by up to 2%, night-time values were relatively unaffected by the change.

Our simulation results indicate that incomplete equilibration between CO$_2$ and leaf water is common in this system. Further work is required to quantify accurately the extent of disequilibrium and its impact on net ecosystem C$_{18}$OO fluxes. The ISOLSM simulations demonstrated that the ecosystem isoflux was dominated by leaf fluxes during the simulation period.

The development of ecosystem isotope models would benefit from further research on the biophysical and physiological controls on plant retro-diffused and soil-respired fluxes, as these fluxes account for the largest uncertainties in the atmospheric C$_{18}$OO budget. Although leaf retro-diffused fluxes are theoretically well understood for C$_3$ plants (Farquhar & Lloyd, 1993; Farquhar et al., 1993; Ciais et al., 1997b), recent experimental evidence suggests a more complicated picture for C$_4$ plants (Gillon & Yakir, 2000; Helliker & Ehleringer, 2000; Gillon & Yakir, 2001). In particular, the impact of partial equilibration of CO$_2$ with leaf water and variations in the $^{18}$O value of water along the leaf need to be addressed. Recent experimental (Miller et al., 1999) and theoretical (Tans, 1998; Stern et al., 1999; Stern et al., 2001; Riley et al., 2002) work has advanced our understanding of soil-respired C$_{18}$OO fluxes; further work is necessary to predict these fluxes across the range of soil types and environmental conditions found in real systems. These types of investigations will enhance our ability to use the $^{18}$O value of atmospheric CO$_2$ as a tracer of gross carbon exchanges and a constraint on land-surface biophysical processes.

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