

Seasonal and interannual variations of carbon and oxygen isotopes of respired CO₂ in a tallgrass prairie: Measurements and modeling results from 3 years with contrasting water availability

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[1] We made weekly measurements of carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopes of atmospheric CO₂ in a C₃/C₄ tallgrass prairie during the growing season for 3 years with contrasting soil moisture conditions. Air samples above and within canopies were collected using 100-ml flasks at night to characterize isotopic composition of ecosystem respiration. We used a two-source mixing line (Keeling plot) approach to estimate isotope ratios of ecosystem respired CO₂ for both carbon ($\delta^{13}\text{C}_R$) and oxygen ($\delta^{18}\text{O}_R$). Measured net ecosystem CO₂ exchange (NEE) showed the largest net carbon uptake in 2004, followed by 2003 and 2002. This interannual difference in NEE strongly depends on the amount and distribution of precipitation received by this tallgrass prairie. Precipitation also affects the timing of the seasonal transition from C₃ dominance in spring to C₄ dominance in summer. Variations of $\delta^{13}\text{C}_R$ showed that C₄ plants dominated ecosystem respiration in 2003 and 2004, except in early spring when C₃ plants were more active. In contrast, contributions of C₃ plants were relatively higher for an extended period in the summer of 2002, when a severe drought occurred. Typically, C₃ forbs extract water and nutrients from soil layers below that of the C₄ grasses and remain photosynthetically active in periods when C₄ grasses have water stress that limits photosynthesis. Drought-reduced C₄ grass photosynthesis was lower than temperature-limited C₃ forb growth during this period. We used an integrated isotope land surface model (ISOLSM) to simulate (and compare to measurements) net CO₂ fluxes, $\delta^{18}\text{O}$ values of leaf and soil water, and $\delta^{18}\text{O}$ values of aboveground and soil respiration. The Keeling plot analysis becomes less reliable for estimating $\delta^{18}\text{O}_R$ values when the surface soil is dry. We suspect this is due to low CO₂ production in the soil when water is limiting, in which case the invasion (abiotic) effect is more significant. ISOLSM reasonably captured seasonal variations of measured $\delta^{18}\text{O}_R$ in all 3 years, indicating the model's consistency of predicting $\delta^{18}\text{O}_R$ in different soil water conditions. Model simulations also showed that nighttime $\delta^{18}\text{O}$ values of aboveground respiration were variable, often becoming very positive in water-stressed conditions primarily because of the low relative humidity and resultant elevated $\delta^{18}\text{O}$ values of leaf water.

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1. Introduction

[2] Measurements of the stable C and O isotope ratios of atmospheric CO₂ have been used to estimate gross carbon exchanges in terrestrial ecosystems, although problems with

the methods have been identified [Ogée *et al.*, 2004; Riley, 2005]. This opportunity of using stable isotopes of atmospheric CO₂ as tracers is particularly useful in grassland ecosystems where both C₃ and C₄ photosynthesis coexist. C₃ and C₄ plants have distinct carbon isotope ratios ($\delta^{13}\text{C}$), reflecting differences in physiology and in the fractionation expressed for major carboxylation enzymes [Farquhar *et al.*, 1989]. A number of studies have demonstrated the utility of using measured $\delta^{13}\text{C}$ values in CO₂ to partition ecosystem production into relative contributions of C₃ and C₄ photosynthesis over a growing season [e.g., Still *et al.*, 2003; Lai *et al.*, 2003].

[3] Friedli *et al.* [1987] concluded that ^{18}O exchange with leaf and soil water was responsible for the observed

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seasonal variation of ^{18}O in atmospheric CO_2 over Switzerland. *Francey and Tans* [1987] showed a latitudinal pattern of $\delta^{18}\text{O}$ in atmospheric CO_2 , and noted the potential of using the ^{18}O content of CO_2 for partitioning net ecosystem exchange (NEE) fluxes into photosynthetic and respiratory components. *Farquhar et al.* [1993] first laid out a mechanistic framework for global estimates of terrestrial discrimination against ^{18}O of CO_2 , and for global-scale terrestrial NEE partitioning using the ^{18}O content of CO_2 . Other global studies applying these concepts have followed [*Ciais et al.*, 1997; *Peylin et al.*, 1999; *Cuntz et al.*, 2003a, 2003b].

[4] These studies showed that a large portion of atmospheric CO_2 entering leaf intercellular air space exchanges oxygen molecules with leaf water before returning to the atmosphere. Consequently, CO_2 molecules diffusing out of leaf stomata are typically labeled with leaf water $\delta^{18}\text{O}$ signatures [*Francey and Tans*, 1987]. A similar ^{18}O equilibration process also occurs between atmospheric CO_2 and soil water [*Hesterberg and Siegenthaler*, 1991; *Tans*, 1998; *Amundson et al.*, 1998; *Miller et al.*, 1999; *Stern et al.*, 1999, 2001]. Leaf water usually has a higher content of ^{18}O relative to soil water because of evaporative enrichment [*Dongmann et al.*, 1974]. This distinction in the ^{18}O contents of leaf and soil water establishes the basis for using C^{18}OO as a tracer in terrestrial carbon studies. For example, differences in the oxygen isotope ratio of net CO_2 fluxes emitted from canopy and soil allow for partitioning nighttime respiration into aboveground and belowground compartments [*Mortazavi and Chanton*, 2002; *Bowling et al.*, 2003a]. Other studies have investigated diurnal and vertical fluctuations in $\delta^{18}\text{O}$ value of CO_2 within forest ecosystems [*Flanagan et al.*, 1997, 1999; *Buchmann et al.*, 1997; *Sternberg et al.*, 1998; *Harwood et al.*, 1999; *Bowling et al.*, 2003b]. Recently, *Ogée et al.* [2004] showed that uncertainties in the measurement and interpretation of atmospheric $\delta^{18}\text{O}$ values might limit our ability to use the isotopic approach for partitioning NEE.

[5] Previous studies have also investigated variations in the $\delta^{18}\text{O}$ value of CO_2 in grassland or agricultural systems. *Yakir and Wang* [1996] used measured $\delta^{18}\text{O}$ values of CO_2 to partition NEE fluxes into photosynthesis and respiration in different crop fields. *Riley et al.* [2002, 2003] used simulations from a mechanistic model to interpret temporal fluctuations of $\delta^{18}\text{O}$ in leaf water, water vapor, and canopy CO_2 fluxes observed in a tallgrass prairie in Oklahoma, USA. However, no continuous isotope measurements were made previously to examine seasonal and interannual variability in the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of canopy CO_2 in grassland systems.

[6] Temperature is the most important environmental variable determining the seasonal transition of the abundance of C_3 grasses in spring to C_4 grasses in summer in shortgrass prairies [*Kemp and Williams*, 1980] and in upland mixed grass prairies [*Ode et al.*, 1980]. The general distribution of C_4 grasses is more closely related to temperature than to any other factor [*Teeri*, 1988]. In tallgrass prairies, water availability also strongly influences carbon fluxes and ecophysiological processes [*Knapp*, 1984, 1985; *Kim and Verma*, 1991; *Steward and Verma*, 1992; *Axmann and Knapp*, 1993; *Knapp and Medina*, 1999]. The climate in the Flint Hills tallgrass prairie region possesses large interannual variation in water availability [*Borchert*, 1950]. That characteristic provides the motivation for investigating

how seasonal dynamics of C_3 and C_4 plants impact ^{13}C and ^{18}O contents in ecosystem CO_2 fluxes.

[7] *Lai et al.* [2003] showed considerable intraseasonal variations of the carbon isotope ratio of ecosystem-respired CO_2 ($\delta^{13}\text{C}_R$) in the Flint Hill tallgrass prairie. Their $\delta^{13}\text{C}_R$ measurements suggested a generally reduced impact from C_4 grass during a drought period in the early growing season of 2002. However, weekly values of $\delta^{13}\text{C}_R$ showed erratic fluctuations between signatures characterizing C_4 and C_3 -like photosynthesis.

[8] It is not clear whether the intraseasonal variation shown by *Lai et al.* [2003] is a consequence of the extreme drought conditions, during which time interpretation of isotope measurements requires caution.

[9] In this study we report measurements of carbon and oxygen isotopes of ecosystem-respired CO_2 in a tallgrass prairie, made continuously at weekly intervals for 3 years with contrasting precipitation input. Seasonal and interannual patterns of NEE fluxes (measured with eddy covariance) were also compared for the 3 years. We estimated carbon ($\delta^{13}\text{C}_R$) and oxygen ($\delta^{18}\text{O}_R$) isotope ratios of nocturnal ecosystem respiration using the Keeling plot approach. To interpret seasonal variations in the measured $\delta^{18}\text{O}_R$, we employed a mechanistic model that incorporates oxygen isotopes in a land surface model (ISOLSM [*Riley et al.*, 2002, 2003]). Factors that influence our interpretation of the seasonal variation in $\delta^{18}\text{O}_R$ are discussed.

2. Materials and Methods

2.1. Study Site

[10] This study was conducted in the Rannells Flint Hills Prairie near Manhattan, Kansas, USA ($39^\circ 12' \text{N}$, $96^\circ 35' \text{W}$, 324 m above sea level). The site has a mixture of C_3/C_4 photosynthesis and is burned during the last 10 days of April every year. The vegetation was dominated by C_4 grass species, primarily *Andropogon gerardii*, *Sorghastrum nutans*, and *Andropogon scoparius*. The C_3 species included *Carex*, a sedge, and numerous forb species including *Vernonia baldwinii*, *Artemisia ludoviciana*, *Ambrosia psilostachya*, and *Psoralea tenuiflora* var. *floribunda*. The 15-year average annual precipitation is 878 mm, with 74% occurring between April and September. The average canopy height, defined as the height of the tallest vegetation structure, was about 0.6 m at peak growth in 2002 and 2003, but extended to about 1.2 m in 2004 as a result of favorable growing conditions (i.e., more precipitation).

[11] From 2002 to 2004, NEE and, carbon and oxygen isotope values of ecosystem respiration were measured at the ungrazed site in the Rannells prairie. Measured NEE fluxes were averaged to a half-hourly basis, while values of $\delta^{13}\text{C}_R$ and $\delta^{18}\text{O}_R$ were estimated on weekly intervals. To demonstrate the seasonal and interannual variations of measured NEE fluxes, we calculated average daytime and nighttime NEE fluxes on a weekly basis. We assume that each weekly measurement of $\delta^{13}\text{C}_R$ and $\delta^{18}\text{O}_R$ was representative of the carbon and oxygen isotope ratios of respired CO_2 fluxes for that particular week.

2.2. Flux and Meteorological Measurements

[12] An open-path eddy covariance system consisting of a triaxial sonic anemometer (CSAT3, Campbell Scientific

Inc., Logan, Utah, USA) and a $\text{CO}_2/\text{H}_2\text{O}$ gas analyzer (LI-7500, LI-Cor Inc., Lincoln, Nebraska, USA) was used to measure fluxes of momentum, CO_2 , sensible, and latent heat above the canopy [Ham and Heilman, 2003]. A CR23X data logger (Campbell Scientific) recorded 10 Hz signals to compute 30-min average fluxes. Lai *et al.* [2003] described measurements of meteorological variables, including net radiation, air temperature, relative humidity, precipitation and soil temperature, in this tallgrass ecosystem. No correction was applied to the nighttime flux data since this site is generally windy (with calm night representing 0.1% of all sampling time). More details about eddy covariance measurements are given by Ham and Heilman [2003].

2.3. Oxygen Isotopes of Water Samples

[13] In May and July of 2002, two field experiments were conducted to collect samples for measuring $\delta^{18}\text{O}$ values of ecosystem water pools. Each experiment lasted for 3 days, and samples of water vapor, soil water, crown-root water, and bulk leaf water were collected 1–5 times a day to characterize diurnal patterns of $\delta^{18}\text{O}$ in each water pool. We collected foliage samples by clipping the whole grass blade and storing them in glass vials immediately after collection. Three replicates of grass blades from three dominant C_4 species were collected each time. We reported the average of 9 samples (± 1 S.D.) as the $\delta^{18}\text{O}$ value of canopy leaf water. Root water was sampled by collecting crown roots (the top portion of the rooting system where all fine roots converge). The $\delta^{18}\text{O}$ value of crown-root water represents $\delta^{18}\text{O}$ signatures of source water for this prairie. Profiles of soil samples were collected in general from the top 30 cm, with an increment of 10 cm from 5 soil pits. All water samples were stored in screw-cap glass vials carefully wrapped with Parafilm[®] to prevent evaporation and kept refrigerated or frozen until subsequent stable isotope ratio analyses.

[14] Atmospheric water vapor was cryogenically captured and analyzed for oxygen isotope ratios using the sampling protocol described by Helliker *et al.* [2002]. Air from three heights (0.5, 1, and 3 m above ground) was passed through sampling tubes placed in a dewar of crushed dry ice, allowing water vapor to condense on the inner walls of the glass tubing. The airflow rate was set at 5 cc s^{-1} with a sampling time of ~ 20 min. Water vapor tubes were sealed with a rubber stopper, and wrapped with Parafilm[®] on the outside. Samples of water vapor, crown-root water, and bulk leaf water were collected concurrently every 3–4 hours between 0800 and 2000 local standard time (LST) during the two field experiments.

[15] Water samples were extracted in the laboratory using a cryogenic vacuum distillation apparatus [Ehleringer *et al.*, 2000]. Each water sample equilibrated with dilute CO_2 ($\text{CO}_2:\text{N}_2 = 1:9$) for 48 hours at 25°C . Batches of 9 samples were calibrated against 3 working water standards during each analysis run using an EA-CF-IRMS method described by Fessenden *et al.* [2002]. Precision of the $\delta^{18}\text{O}$ analyses is $\pm 0.2\text{‰}$.

2.4. Flask Sampling and Isotope Analyses

[16] Air samples from three heights (0.1, 0.4, and 3 m) were collected using an automated sampling system, capable of filling 15 flasks on the basis of the specification of a

data logger [Schauer *et al.*, 2003]. Two flasks were collected 5-min apart in the midafternoon (usually between 1430 and 1530 LST) from the top intake. This flask pair was averaged for CO_2 concentration and $\delta^{13}\text{C}$ to estimate daytime canopy air. Beginning in March 2003, an extra pair of daytime flasks was collected on a separate day every week. Nighttime air samples were collected to attain a gradient of CO_2 concentration ≥ 50 ppm over the course of a night using 100 mL flasks (Kontes Glass Co., Vineland, New Jersey). Flasks were sealed with vacuum-tight Teflon stopcocks. The specified CO_2 range was typically achieved during the growing season. Nighttime sampling started an hour after sunset to avoid effects of photosynthesis, and air was drawn from 2 heights: 0.1 m and 0.4 m above ground. Flasks were filled at 5-min intervals, cycling between the bottom and middle inlets. A “panic” mode was initiated one hour before sunrise which filled all the remaining empty flasks before any photosynthetic uptake. If the specified CO_2 gradient was not met, the sampler resets and repeats the same procedure the following day. In general, there are 11 flask samples for each Keeling plot. Air was dried by flowing through a magnesium perchlorate trap before collection to minimize storage effect on the $\delta^{18}\text{O}$ of CO_2 [White *et al.*, 2002]. The majority of air samples were typically collected within the first 2 hours (~ 2000 – 2200 LST) after the sampling started. A field person then checked on the data logger and collected flasks the next day if they were successfully filled the night before.

[17] Flasks were collected for isotope analyses on weekly intervals between May and November and on a monthly basis for the rest of the year [Lai *et al.*, 2003, 2004, 2005]. Carbon and oxygen isotope ratios of CO_2 were analyzed on a continuous flow isotope ratio mass spectrometer (Finnigan MAT 252, San Jose, California), while CO_2 concentration was measured to a precision of 0.3 ppm using a bellow/IRGA system in 2002 [Lai *et al.*, 2003]. Beginning in 2003, a GC-IRMS system was deployed to analyze a flask for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and concentration of atmospheric CO_2 . Measurement precision was determined to be 0.06‰ for $\delta^{13}\text{C}$, 0.11‰ for $\delta^{18}\text{O}$ and 0.48 ppm for CO_2 concentration [Schauer *et al.*, 2005]. Precision of the GC-IRMS system significantly improved isotope ratio analyses (by $\sim 0.05\text{‰}$) but slightly degraded the precision for CO_2 concentration measurements (by ~ 0.2 ppm). This analytical modification improves the overall accuracy of the Keeling plot analysis because of the relative greater improvements in isotope precision as compared to a smaller decrease in the precision of concentration measurements.

[18] In this study, we report carbon isotope ratios on the VPDB scale; oxygen isotope ratios in water and CO_2 are both reported relative to the VSMOW scale [Coplen, 1996].

2.5. Isotope Ratios of Ecosystem Respiration

[19] A two-source mixing line approach, first developed by Keeling [Keeling, 1958, 1961], can be used to estimate the isotopic composition of ecosystem respiration (δ_R):

$$\delta_m = \frac{C_b(\delta_b - \delta_R)}{C_m} + \delta_R, \quad (1)$$

where C represents mixing ratios of CO_2 . Subscripts m and b represent measurements collected within the nocturnal

boundary layer and the background atmosphere, respectively. In theory, equation (1) can be applied for both carbon ($\delta^{13}\text{C}_R$) and oxygen ($\delta^{18}\text{O}_R$) isotopes; indeed, many ecosystem studies have adopted the mixing line approach to estimate $\delta^{13}\text{C}_R$ [Flanagan *et al.*, 1999; Buchmann *et al.*, 1997; Buchmann and Ehleringer, 1998; Bowling *et al.*, 2002; Ometto *et al.*, 2002; Pataki *et al.*, 2003] and $\delta^{18}\text{O}_R$ [Flanagan *et al.*, 1997, 1999; Buchmann and Ehleringer, 1998; Harwood *et al.*, 1999; Bowling *et al.*, 2003a, 2003b]. In this study, if the standard error of an estimated $\delta^{13}\text{C}_R$ value was greater than 2‰ (3‰ for $\delta^{18}\text{O}_R$), we excluded it from our analyses. We excluded 10 and 22% of the measured $\delta^{13}\text{C}_R$ and $\delta^{18}\text{O}_R$ values on this basis.

2.6. Brief Descriptions of ISOLSM

[20] ISOLSM [Riley *et al.*, 2002] is an updated version of the NCAR Land Surface Model (LSM1.0 [Bonan, 1994; Bonan *et al.*, 1997]) designed to simulate terrestrial ecosystem oxygen and carbon isotope exchanges in CO_2 and H_2O . We have successfully tested ISOLSM's CO_2 flux predictions in several of the dominant vegetation types using measurements performed in the Atmospheric Radiation Measurement Climate Research Facility (ACRF) as part of the AmeriFlux program [Riley *et al.*, 2003; Suyker and Verma, 2001] and against 3 years of surface measurements made during the FIFE campaign [Betts and Ball, 1998; Cooley *et al.*, 2005].

[21] The isotope submodels in ISOLSM simulate the dominant processes impacting the $\delta^{18}\text{O}$ value of the soil and leaf H_2O and CO_2 fluxes: advection and evaporation of H_2^{18}O in soil water, CO_2 and C^{18}OO soil-gas transport, leaf water enrichment, interactions between soil and leaf H_2^{18}O and CO_2 , and the $\delta^{18}\text{O}$ value of canopy air space vapor. We have applied ISOLSM to examine (1) impacts of the atmospheric $\delta^{18}\text{O}$ value of H_2O and CO_2 on ecosystem discrimination against C^{18}OO [Riley *et al.*, 2003], (2) impact of the enzyme carbonic anhydrase in soils [Riley *et al.*, 2002], (3) impacts of gradients in the $\delta^{18}\text{O}$ value of near-surface soil water on the $\delta^{18}\text{O}$ value of the soil-surface CO_2 flux [Riley, 2005; Riley *et al.*, 2003], (4) impacts of land use change on regional surface CO_2 and energy fluxes and near-surface climate [Cooley *et al.*, 2005], and (5) uncertainties associated with the use of ^{18}O in CO_2 measurements to estimate gross CO_2 fluxes from net ecosystem exchange measurements and atmospheric C^{18}OO measurements [Riley and Still, 2003].

[22] ISOLSM is forced with measurements of air temperature, pressure, and vapor content, wind speed, CO_2 concentration, downward shortwave and longwave radiation, precipitation amount and its isotopic ratio, and the $\delta^{18}\text{O}$ value of above-canopy vapor ($\delta^{18}\text{O}_v$) and CO_2 . We estimated downward longwave radiation using measured air temperature, shortwave radiation (SW) from measurements of photosynthetically active radiation (PAR), and a conversion factor (CF) of 0.46 with the relationship: $\text{SW} = \text{PAR}/\text{CF}$. Using satellite data, Pinker and Laszlo [1992] derived relationships between PAR and SW for the globe. They showed that, in most cases, CF is between 0.44 and 0.50, with the mean and median values being 0.46. For comparison, meteorological measurements from the ARM Central Facility (ww.arm.gov) between May and October of 2003 indicate a midday mean (standard deviation) of 0.43 (0.07), indicating that our choice is within the range of values expected for this area. In the absence of continuous meas-

urements of $\delta^{18}\text{O}_v$ we assumed a value 11‰ less than the predicted isotopic composition of source water. This assumption was based on averages of $\delta^{18}\text{O}_v$ and source water $\delta^{18}\text{O}$ measured during the two experiments in May and July 2002. The averaged $\delta^{18}\text{O}_v$ was -12.3‰ (± 1.2 ; $n = 11$) and -16.6‰ (± 1.2 ; $n = 10$), while the averages of source water $\delta^{18}\text{O}$ were -2.0‰ (± 1.3 ; $n = 99$) and -5.1‰ (± 1.8 ; $n = 90$) in May and July, respectively. Many factors other than evapotranspiration (e.g., horizontal and vertical atmospheric advection) impact $\delta^{18}\text{O}_v$, which can have diurnal variations of up to 4‰ in this area [Helliker *et al.*, 2002]. Our measurements in this grassland also showed diurnal variations about 4‰ in the two experimental periods in 2002. We assumed constant $\delta^{18}\text{O}_v$ values relative to the source water $\delta^{18}\text{O}$ in the ISOLSM simulations.

[23] We do not have $\delta^{18}\text{O}$ measurements of precipitation ($\delta^{18}\text{O}_p$) at this site, so we relied on two data sources for estimates of $\delta^{18}\text{O}_p$ values. Welker [2000] reported arithmetic averages of $\delta^{18}\text{O}_p$ from 3 years (1989–1991) at sites representative of the Gulf of Mexico storm track from Gulf coast of Texas, western Oklahoma, western Nebraska, and into southeastern Montana. We expect $\delta^{18}\text{O}_p$ values in Rannells Prairie to have similar seasonal characteristics and magnitude as those monitoring stations because it is in the pathway of this storm track. The averaged $\delta^{18}\text{O}_p$ values along this storm track ranged between -2 and -10‰ from Texas to Montana. The two stations closest to our site (western Oklahoma and western Nebraska) had average $\delta^{18}\text{O}_p$ values of -5 and -8‰ . Although $\delta^{18}\text{O}_p$ values showed considerable variations between summer and winter rains, summer precipitation was confined to a smaller range (less than 5‰). The second data source was based on a model output [Bowen *et al.*, 2005], which interpolates a global precipitation data set for water isotope analyses developed by IAEA. An online calculator for oxygen and hydrogen isotopes of precipitation at any locations is available at <http://www.waterisotopes.org>. On the basis of this model, $\delta^{18}\text{O}_p$ values varied between -4.4 and -5.5‰ between the month of May and August at our site (39.12°N , 96.35°W , elevation = 324 m), with an average of -5‰ . Hence we assumed a constant $\delta^{18}\text{O}_p$ of 5‰ in our model simulation throughout the growing season for all 3 years. The short-term variability of $\delta^{18}\text{O}_p$ is not considered in the model, which contributes to the uncertainty in the modeled soil and leaf water $\delta^{18}\text{O}$, and consequently, the modeled $\delta^{18}\text{O}$ of net CO_2 fluxes.

[24] The ISOLSM simulations predict $\delta^{18}\text{O}$ values of leaf water on the basis of predicted $\delta^{18}\text{O}$ values of source water and canopy water vapor using the Craig–Gordon model [Craig and Gordon, 1965] with modifications for leaves as described by Flanagan *et al.* [1991]. Gillon and Yakir [2000a, 2000b, 2001] showed that the presence of carbonic anhydrase is lower in C_4 relative to C_3 plants. Consequently, there is a lower degree of ^{18}O exchange between CO_2 and leaf water in C_4 grasses. We have used ISOLSM to evaluate the impact of incomplete equilibration between leaf water and CO_2 on ecosystem discrimination in a tallgrass prairie [Riley *et al.*, 2003]. For the work presented here we assume complete equilibration between CO_2 and leaf water; this assumption will not impact our results since our focus is on nighttime respiration.

[25] CO_2 in the soil profile approaches equilibrium with soil water with a characteristic time on the order of an hour

Table 1. Monthly Mean Concentrations, Carbon Isotope and Oxygen Isotope Ratios of CO₂ in Canopy Air Measured in the Rannells Prairie, Kansas^a

Month	CO ₂ , ppm			δ ¹³ C, ‰			δ ¹⁸ O, ‰		
	0.1 m ^b	0.4 m ^b	3 m ^c	0.1 m ^b	0.4 m ^b	3 m ^c	0.1 m ^b	0.4 m ^b	3 m ^c
2002									
5	445.7 (46.3)	407.7 (15.8)	371.4 (6.9)	-9.3 (0.4)	-9.0 (0.2)	-8.3 (0.1)	40.8 (1.3)	40.6 (0.8)	40.3 (0.6)
6	413.0 (14.7)	392.5 (3.8)	367.5 (0.5)	-8.7 (0.1)	-8.3 (0.1)	-8.1 (0.1)	38.8 (0.3)	39.3 (0.3)	39.5 (0.1)
7	431.1 (45.7)	404.2 (19.5)	373.4 (3.8)	-9.1 (0.6)	-8.8 (0.3)	-8.2 (0.3)	39.1 (1.0)	39.6 (0.6)	40.4 (0.6)
8	509.2 (73.8)	439.3 (56.3)	363.9 (6.0)	-9.6 (0.7)	-9.1 (0.5)	-8.1 (0.3)	38.4 (1.3)	39.3 (1.2)	40.1 (0.4)
9	503.1 (49.4)	455.1 (73.8)	366.8 (1.4)	-9.4 (0.4)	-9.0 (0.7)	-8.0 (0.1)	37.2 (1.2)	38.1 (1.2)	37.7 (1.7)
10	429.2 (19.3)	407.2 (16.5)	375.7 (2.3)	-9.1 (0.3)	-9.0 (0.4)	-8.5 (0.1)	38.2 (0.4)	38.7 (0.4)	38.6 (0.4)
2003									
5	420.4 (21.9)	402.1 (12.2)	379.1 (2.6)	-9.1 (0.3)	-8.8 (0.2)	-8.3 (0.1)	39.8 (0.6)	40.1 (0.6)	40.4 (0.3)
6	523.0 (73.4)	456.5 (76.2)	366.4 (5.2)	-9.9 (0.7)	-9.4 (0.7)	-8.2 (0.4)	37.9 (1.5)	38.4 (1.4)	40.2 (0.6)
7	554.3 (72.8)	457.1 (48.6)	361.7 (3.6)	-9.8 (0.4)	-9.1 (0.5)	-7.9 (0.2)	38.5 (0.6)	39.7 (1.0)	40.9 (0.3)
8	510.1 (31.8)	451.7 (29.7)	372.8 (9.1)	-9.8 (0.5)	-9.3 (0.6)	-8.2 (0.3)	38.1 (0.8)	39.2 (0.3)	40.6 (0.8)
9	509.3 (83.2)	406.8 (28.9)	370.3 (4.4)	-9.5 (0.6)	-8.6 (0.4)	-8.0 (0.2)	37.0 (1.5)	39.1 (1.6)	39.8 (0.9)
10	433.4 (23.8)	399.2 (16.9)	378.8 (5.8)	-9.2 (0.3)	-8.7 (0.4)	-8.4 (0.3)	39.4 (0.7)	39.8 (0.6)	39.4 (1.1)
2004									
5	405.3 (15.3)	399.2 (9.5)	376.7 (6.8)	-9.1 (0.3)	-9.0 (0.3)	-8.5 (0.2)	40.8 (1.0)	40.9 (1.0)	41.1 (1.0)
6	488.5 (76.2)	415.3 (20.1)	367.6 (7.1)	-9.8 (0.8)	-9.3 (0.6)	-8.2 (0.3)	38.4 (1.2)	40.0 (0.6)	40.7 (0.6)
7	663.1 (181.3)	434.6 (26.2)	358.2 (13.7)	-10.1 (0.6)	-9.2 (0.5)	-7.9 (0.4)	37.5 (0.6)	38.9 (0.6)	40.7 (0.6)
8	488.7 (81.3)	408.5 (35.7)	361.8 (8.6)	-9.4 (0.8)	-8.8 (0.6)	-8.0 (0.4)	37.8 (1.6)	39.3 (0.8)	40.6 (0.9)
9	484.9 (44.0)	434.1 (40.7)	368.5 (7.0)	-9.4 (0.4)	-8.9 (0.5)	-8.1 (0.2)	38.8 (0.8)	39.5 (0.7)	41.0 (0.5)
10	427.7 (17.4)	398.6 (7.3)	386.1 (6.9)	-9.6 (0.3)	-9.3 (0.3)	-9.0 (0.4)	39.4 (0.3)	39.7 (0.2)	39.7 (0.7)

^aValues in parenthesis are 1 S.D.

^bNighttime (usually between 2000 and 2200 LST) samples.

^cMid-afternoon (1430–1530 LST) samples.

[Riley, 2005]. It is important to note that the δ¹⁸O of CO₂ in canopy air is influenced by the δ¹⁸O value of the net soil-surface CO₂ flux, which, in turn, is impacted by the δ¹⁸O value of CO₂ in the soil profile. The δ¹⁸O value of soil-respired CO₂ (δ¹⁸O_s) will reflect (1) the δ¹⁸O value of CO₂ in complete equilibration with soil water at depth (δ¹⁸O_{se}); (2) the δ¹⁸O value of CO₂ in partial equilibrium with near-surface soil water; and (3) a theoretical diffusional fractionation, ε_D, of 8.7‰. Consequently, δ¹⁸O_s will equal δ¹⁸O_{se} depleted in ¹⁸O by some kinetic fractionation (ε_{Df}) between -8.7 and 0‰ [Amundson et al., 1998], i.e.,

$$\delta^{18}O_s = \delta^{18}O_{se} + \epsilon_{Df} \quad (\text{‰}). \quad (2)$$

Miller et al. [1999] determined an effective kinetic fractionation of CO₂ diffusing out of the soil to be 7.2‰ (with respect to water at about 10 cm depth) on the basis of a dynamic chamber experiment.

[26] Riley [2005] recently used a model simulation in a tallgrass prairie to show that gradients in the δ¹⁸O value of near-surface soil water have significant impacts on the δ¹⁸O value of the soil-surface CO₂ flux. For the work presented here, we use the relationship developed in that study with near-surface water-filled pore space (W (%)) to estimate ε_{Df}:

$$\epsilon_{Df} = -6.9 - 0.0152W. \quad (3)$$

3. Results and Discussion

3.1. Monthly Mean Concentrations, δ¹³C Values, and δ¹⁸O Values of Canopy CO₂

[27] Measured concentrations, δ¹³C values, and δ¹⁸O values of CO₂ in the canopy air were averaged and

presented as monthly means in Table 1. Mid-afternoon samples were collected from 3 m above ground, while nighttime samples were collected from 2 heights between inlets at 0.1 and 0.4 m. Mid-afternoon air showed consistently lower CO₂ concentrations, more positive δ¹³C, and usually higher δ¹⁸O compared to nighttime values. Photosynthetic uptake decreases CO₂ concentration while enriches ¹³C content in the atmosphere. The δ¹⁸O discrimination during photosynthesis, via CO₂ equilibration with ¹⁸O-enriched leaf water, possibly contributes to the more positive δ¹⁸O values of canopy CO₂ in the afternoon. At night, respiration releases ¹³C-depleted CO₂ into the atmosphere. The contrasting effect of photosynthesis and respiration on the carbon and oxygen isotopes was largely responsible for the difference between daytime and nighttime values of δ¹³C and δ¹⁸O. The seasonal minimum in the CO₂ concentration and the maximum in the δ¹³C value were in July for 2003 and 2004, but 2002 showed a different pattern. Whether this difference was related to changes in photosynthesis or respiration can be further investigated using meteorological and flux measurements.

3.2. Precipitation and Air Temperature

[28] Figure 1 shows monthly precipitation and averaged air temperature measured in the Rannells prairie during the growing season in 2002, 2003, and 2004. Monthly mean air temperature increased from about 13°C in April to a peak of 25°C in July, and then decreased again in the fall. Monthly averaged air temperature showed little interannual variation between 2002 and 2003, but was about 3°C cooler during July and August of 2004. The amount of precipitation varied tremendously among the 3 years. The amount of precipitation between April and September was 494, 653, 746 mm in 2002, 2003, and 2004, respectively, compared to

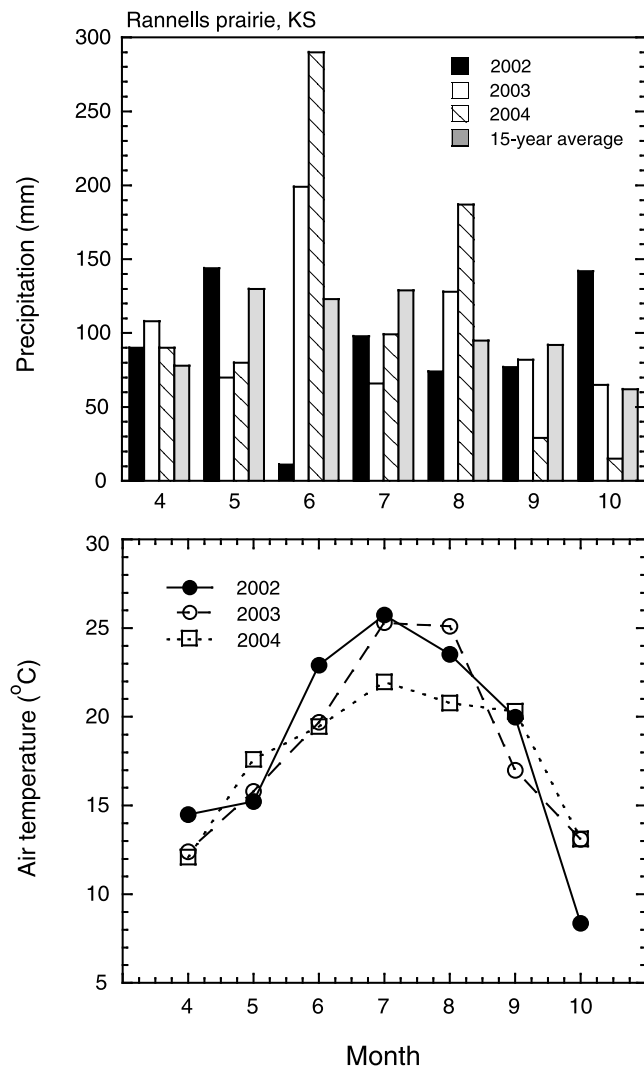


Figure 1. Monthly precipitation and averaged air temperature measured at the Rannells prairie site between 2002 and 2004.

the long-term average of 649 mm. Particularly, in the month of June, a record low precipitation input (~ 10 mm) was received in 2002. This was only 8% of the rainfall amount received for the same month averaged over 15 years. By contrast, twice the average rainfall was received in June of 2004. Hence we considered 2002 a drought year, 2003 a normal year, and 2004 a wet year in this ecosystem. These differences in precipitation have significant implications for the ecosystem carbon balance because the primary growth period for tallgrass prairie is during the first half of the season, and growth is fueled by both stored soil water and precipitation. Less than normal precipitation during the early growing season has a greater effect on biomass production than it would in the mid or late season.

3.3. Seasonal Patterns of NEE Fluxes

[29] Figure 2 shows seasonal and interannual variability of weekly averaged daytime and nighttime NEE fluxes. Substantial differences in weekly NEE fluxes were observed between years. Here negative fluxes represent carbon uptake by the prairie. The period shown here (May to mid-October) corresponds to the time when our study site appears to have the capacity to be a carbon sink (roughly defined as the growing season for this ecosystem).

[30] A prescribed control burn takes place yearly at the end of April. The burn removed accumulations of the current year litter layer and the mass of dead grasses, allowing soil to warm more quickly [Hulbert, 1988]. Uptake of CO_2 can be detected shortly after the burn in all 3 years. However, the capacity of carbon uptake varied significantly from year to year. In 2002, large negative NEE fluxes were observed in the early spring, but quickly diminished midway into June when a severe drought occurred at the site (Figure 1). This pattern likely resulted from decreased photosynthetic capacity under water stress conditions [Lai *et al.*, 2003]. Suyker and Verma [2001] showed that the apparent quantum yield of a tallgrass prairie in northern Oklahoma, which has similar species composition and environmental conditions as our site, was significantly lower when soil moisture was limiting. Nighttime fluxes were also decreased during the drought, likely

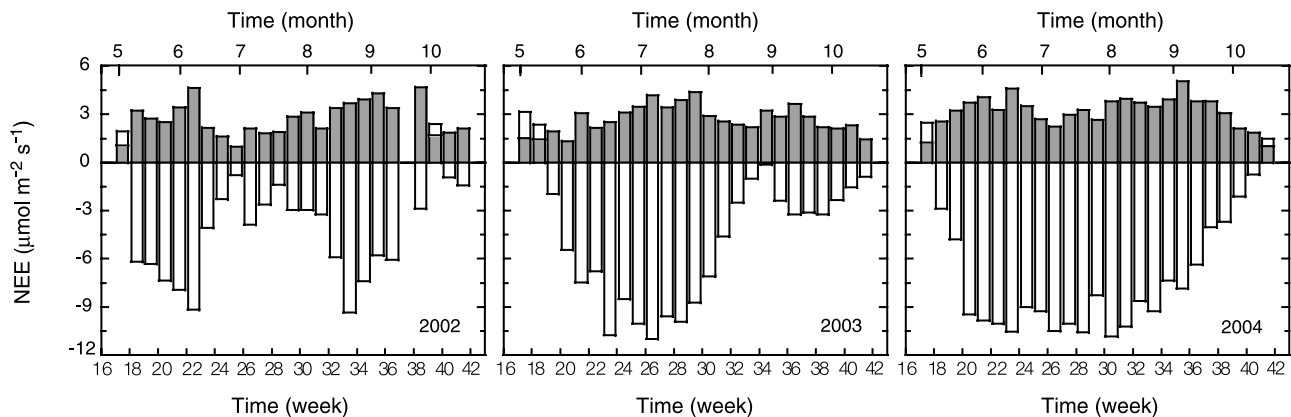


Figure 2. Net ecosystem exchange (NEE) of CO_2 fluxes measured by the eddy covariance system at the ungrazed site in the Rannells prairie between 2002 and 2004. Data shown are weekly averages of daytime fluxes (open) and nighttime fluxes (shaded). Negative fluxes represent carbon uptake by the prairie, occurring from May to mid-October as shown here between weeks 17 and 41.

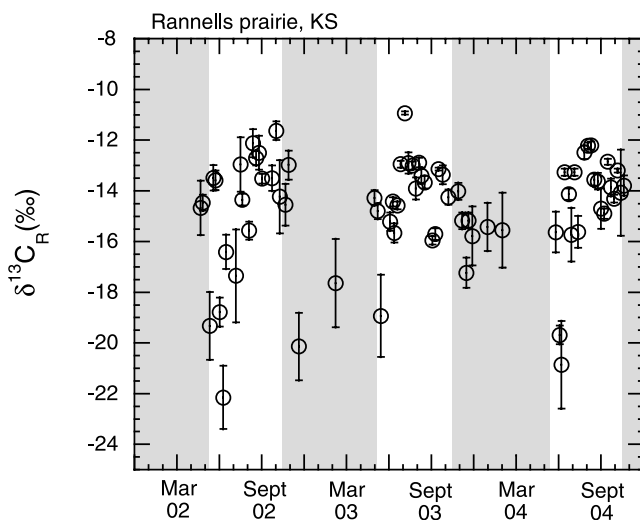


Figure 3. Weekly measurements of carbon isotope ratios of ecosystem respiration ($\delta^{13}\text{C}_R$, \pm S.E.). Shaded blocks indicate nongrowing season.

because of a combined effect of reduced autotrophic respiration and microbial activities. The drought caused daily sums of NEE flux to be nearly neutral [Lai et al., 2003].

[31] Ecosystem net C uptake increased toward the end of July, when water finally became available from precipitation. However, carbon uptake in 2002 was substantially reduced because of the drought during the otherwise peak growth period (see NEE in 2003 and 2004). On the contrary, we observed large uptake of atmospheric CO_2 by this prairie throughout the growing season in 2004, a wet year with no water limitation. The amount of carbon sequestered during the growing season was greatest in 2004, intermediate in 2003, and smallest in 2002. The rate of transition from carbon sink to carbon source is controlled by the gradual canopy senescence in the fall [Ham and Knapp, 1998]. Therefore the decrease of the NEE flux toward the end of August in 2003 (\sim week 34 in Figure 2) indicates a canopy response to a mild drought (discussed later).

[32] The pattern observed in 2003 was perhaps the most representative of this prairie ecosystem on the basis of average precipitation. Consistent with results from other studies [Knapp, 1984, 1985; Kim and Verma, 1991; Verma et al., 1992; Briggs and Knapp, 1995; Ham et al., 1995], Figures 1 and 2 suggest that the capacity of carbon sequestration of a tallgrass prairie is very sensitive to the amount and distribution of precipitation. Rainfall in May and June has a large impact on the interannual variability of CO_2 exchange in grassland ecosystems [Ham et al., 1995; Kim and Verma, 1991; Suyker and Verma, 2001]. In C_3/C_4 mixed grasslands, water availability could also affect interactions between C_3 and C_4 grasses. We investigate seasonal dynamics of C_3 and C_4 photosynthesis using carbon isotope measurements next.

3.4. Seasonal Patterns of $\delta^{13}\text{C}_R$ Measurements

[33] The seasonal transition of C_3 abundance in spring to C_4 dominance in summer has been shown in shortgrass and tallgrass ecosystems in North America Great Plains [Kemp and Williams, 1980; Ode et al., 1980; Barnes et al., 1983;

Monson et al., 1983]. Using atmospheric $\delta^{13}\text{C}$ measurements, Still et al. [2003] demonstrated that the apparent contribution of C_4 -derived carbon to ecosystem respiration increased from $\sim 40\%$ in spring to over 80% in fall 1999. Given the divergent pattern of water input, we expect significant differences in the carbon isotope ratio of ecosystem fluxes between the 3 years in this prairie. Figure 3 shows weekly measurements of $\delta^{13}\text{C}_R$. Values of $\delta^{13}\text{C}_R$ were more scattered during the summer of 2002, likely because of the impact of the drought on C_4 photosynthesis. Despite warmer temperature favoring C_4 photosynthesis in the summer [Ehleringer et al., 1997], water stress reduced photosynthetic uptake of C_4 grasses [Lai et al., 2003]. Contributions of C_3 plants were relatively higher for an extended period in 2002. Lai et al. [2003] showed that the more C_3 -like $\delta^{13}\text{C}$ signals were related to wind speeds and directions. Still et al. [2003] also noted the effect of wind on the $\delta^{13}\text{C}_R$ measurements in a tallgrass prairie in northern Oklahoma. An alternative explanation is that the more negative $\delta^{13}\text{C}$ signals observed in 2002 summer were due to the forb populations maintaining photosynthesis using deeper soil water. By contrast, values of $\delta^{13}\text{C}_R$ showed that C_4 plants dominated ecosystem respiration in 2003 and 2004, except in early spring when C_3 plants were more active because the cooler temperature favored C_3 grasses and forbs [Teeri, 1988; Ehleringer et al., 1997]. In 2003 and 2004 C_4 photosynthesis quickly became the major contributor as temperature increased. However, the timing of this shift from C_3 to C_4 photosynthesis depends on the timing of precipitation between years.

[34] We aggregated weekly $\delta^{13}\text{C}_R$ values and summarized this seasonal pattern on a monthly basis in Figure 4. We calculated the fraction of C_4 contribution (f) using a two-source mixing model [Still et al., 2003], i.e., $\delta^{13}\text{C}_R = f\delta^{13}\text{C}_4 + (1 - f)\delta^{13}\text{C}_3$, where $\delta^{13}\text{C}_3 = -27.9\text{‰}$ (± 0.54 S.E.) and $\delta^{13}\text{C}_4 = -12.3\text{‰}$ (± 0.19 S.E.) are measured carbon isotope ratios of leaf organic matter for C_3 and C_4 species, respectively [Lai et al., 2003]. In general, the fraction of C_4 contribution changed from about 50% in spring to greater than 85% in summer. A dip in this fraction occurred in May (June in 2002), partially reflecting the effect of the prescribed control burn that cleaned up the canopy floor where considerable amount of C_4 biomass from the year before would otherwise decompose. In contrast with the seasonal pattern in 2003 and 2004, the fraction of C_4 contribution continued to decrease in June 2002. Concurrently, this site had very low photosynthetic uptake (Figure 2). It is likely that drought-reduced photosynthesis of C_4 grasses surpassed temperature-limited growth of C_3 forbs during this period. In this system, $\delta^{13}\text{C}_R$ values seem to reflect the influence of microclimate on aboveground canopy on weekly timescales.

3.5. ISOLSM ^{18}O Predictions

[35] We used ISOLSM to simulate oxygen isotope ratios of ecosystem water pools and fluxes and gross and net CO_2 fluxes. Our goal in applying the model was to interpret the interannual differences in nighttime $\delta^{18}\text{O}_R$ values resulting from the complex interactions between H_2^{18}O pools and CO_2 fluxes. To estimate $\delta^{18}\text{O}_R$ values using the Keeling plot approach is sometimes difficult because the assumption of a two-source system is violated more often than for $\delta^{13}\text{C}$. The

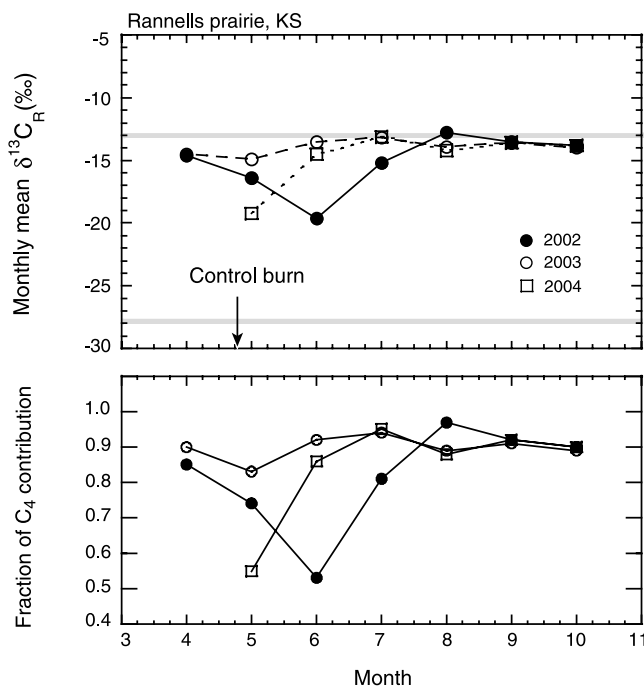


Figure 4. Comparison of monthly averages of $\delta^{13}\text{C}_R$ (top) and the fraction of C_4 contribution (bottom) for the 3 years. The arrow indicates the timing of a prescribed control burn conducted once a year at the Rannells prairie. The shaded lines indicate measured $\delta^{13}\text{C}$ boundaries based on leaf organic matter from dominant C_3 ($-27.9\text{‰} \pm 0.54$ S.E.) and C_4 ($-12.3\text{‰} \pm 0.19$ S.E.) species.

approach requires relative contributions of canopy and soil efflux to remain unchanged over the time when air samples were collected [Pataki *et al.*, 2003]. This assumption is particularly problematic when invasion (abiotic) fluxes are strong [Tans, 1998]. Here the invasion (abiotic) effect refers to the diffusion of atmospheric CO_2 into the soil, where it equilibrates isotopically with soil water before diffusing back out [Tans, 1998; Amundson *et al.*, 1998; Miller *et al.*, 1999; Stern *et al.*, 1999, 2001]. Even when the above assumption was met, measuring $\delta^{18}\text{O}_R$ remains a challenge because the $\delta^{18}\text{O}$ value of leaf (and to a lesser extent, soil) water can change over the course of a night, especially in grass species when progressive ^{18}O enrichment occurs [Helliker and Ehleringer, 2000]. Hence continuous measurements of $\delta^{18}\text{O}_R$ are rare and often difficult to interpret. To demonstrate that ISOLSM is a reliable tool for predicting ecosystem fluxes and isotope ratios, we compare model predictions with (1) measured NEE, latent heat (LE), and sensible heat (H) fluxes and (2) measured $\delta^{18}\text{O}$ values of leaf and source water. We then compare predictions to measured $\delta^{18}\text{O}_R$ values under conditions we believe met the assumptions describe above.

3.6. Comparisons Between Measured and Modeled Fluxes

[36] Figure 5 shows comparisons between measured and modeled NEE, LE, and H fluxes over the same 10-day period in 3 different years. The selected period addressed contrasting soil moisture conditions that were representative

of a dry (2002), a moderate (2003), and a wet year (2004). Despite a relatively larger ($\sim 20\%$) underestimation of LE and H in 2004, ISOLSM simulated diurnal patterns of NEE, LE, and H fluxes with robust agreements in contrasting soil moisture conditions. This agreement was typical for the entire season in all 3 years except during periods of intense precipitation. The greater model discrepancy during rain events is likely due to larger uncertainties in the measured or derived input variables (e.g., shortwave radiation) and fluxes. Nevertheless, Figure 5 provides confidence that ISOLSM correctly describes canopy conductances, soil fluxes, and the energy balance in variable soil moisture conditions for this site.

[37] Comparisons in Figure 5 also highlight the dynamics of NEE flux and the energy partitioning between LE and H in this tallgrass prairie. Canopy leaf area index (LAI) from clipped biomass collection was 1.8, 4.0, and $3.4 \text{ m}^2 \text{ m}^{-2}$ in this period for the 3 years, respectively. Midday NEE in drought periods was about 25% of that when water was not limiting (Figure 5). Given that nighttime respiration also decreased during drought (Figures 2 and 5), the reduction of midday NEE is likely not due solely to an increase in respiration. It appears that factors other than a smaller LAI also affect gross photosynthetic uptake in water stress conditions, likely because of a reduced quantum yield capacity [Suyker and Verma, 2001] or maximum carboxylation rate of Rubisco [Collello *et al.*, 1998].

[38] Contrasting LE fluxes suggest remarkably different water use strategies between C_3 forbs and C_4 grasses under different soil water conditions. The highest LE in 2004 was partially due to consistently higher soil evaporation based on model simulations. LE fluxes in the drought period were lower than those in the wettest year, but surprisingly higher than those in 2003 (Figure 5), a period with moderate water availability. Comparing NEE and LE patterns between years, it was interesting that the water use efficiency (WUE, roughly defined as NEE/LE here) at midday was the highest in 2003. C_4 plants are known to have higher WUE than C_3 plants [Downes, 1969; Long, 1985, 1999; Ehleringer and Monson, 1993]. Given the severe drought that occurred in the same period, we would have expected a more conservative water use in 2002. Lai *et al.* [2003] modeled NEE fluxes in this prairie and showed that C_3 forbs contributed relatively more to the NEE flux during drought because of their ability to access deep soil water [Weaver, 1958], which explained the higher LE and lower WUE when compared to 2003.

3.7. Comparisons Between Measured and Modeled $\delta^{18}\text{O}$ Values of Leaf and Source Water

[39] Figure 6 shows comparisons between measured and modeled $\delta^{18}\text{O}$ of leaf and source waters for two field experiments in 2002. Note that leaf and source water measurements were not made in 2003 or 2004. Modeled source water $\delta^{18}\text{O}$ values were relatively constant throughout each of our experiments, consistent with measurements. Modeled leaf water $\delta^{18}\text{O}$ values compared reasonably well with measurements in early morning and late afternoon, but the model predicted heavier than measured midday leaf water $\delta^{18}\text{O}$ values. The Craig-Gordon model has been shown to overpredict the $\delta^{18}\text{O}$ value of bulk leaf water in several ecosystem types [Dongmann *et al.*, 1974; Leaney *et*

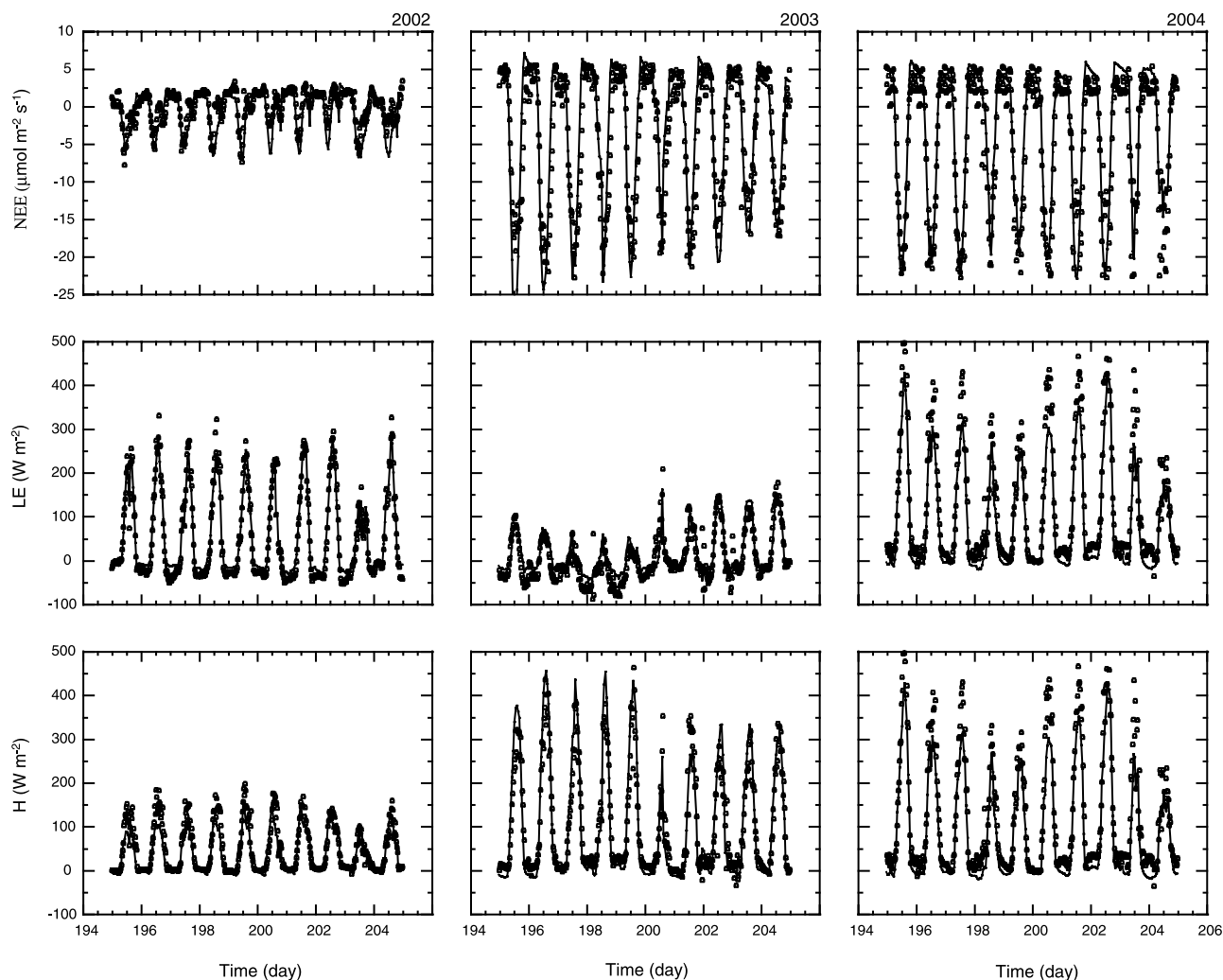


Figure 5. Comparisons between measured and modeled NEE, latent (LE), and sensible (H) heat fluxes for the same 10-day period in the 3 years. Open circles represent measurements, and solid lines are model results.

al., 1985; Bariac et al., 1989; Flanagan and Ehleringer, 1991; Yakir, 1992; Roden and Ehleringer, 1999]. This discrepancy was explained by a retrodiffusive flux that mixes fractionated water from the evaporation sites with the advected flux of nonfractionated water (Péclet effect [Farquhar and Lloyd, 1993]). In our sensitivity test, the discrepancy between modeled and measured leaf water $\delta^{18}\text{O}$ at midday was improved when we included the Péclet effect (not shown). However, for the current study, modeled leaf water $\delta^{18}\text{O}$ at night is a more critical parameter and relatively accurately predicted.

[40] Modeled $\delta^{18}\text{O}$ values of leaf water showed notable differences at night between the two periods (Figure 6). They remained enriched relative to the source water $\delta^{18}\text{O}$ throughout the night in May, but were closer to the $\delta^{18}\text{O}$ value of source water in July. Relative humidity was about 90% for both periods at night. Leaf water $\delta^{18}\text{O}$ estimates using the Craig-Gordon model are more sensitive to $\delta^{18}\text{O}$ values of above-canopy water vapor ($\delta^{18}\text{O}_v$) when relative humidity is high. Differences between $\delta^{18}\text{O}_v$ values in the two periods (about 4‰) can explain the difference between nighttime $\delta^{18}\text{O}$ values of leaf water in the model. We do not

have direct measurements of nighttime leaf water $\delta^{18}\text{O}$. Nevertheless, given the closer agreement between modeled and measured leaf water $\delta^{18}\text{O}$ in early morning and later afternoon, we believe ISOLSM adequately described leaf water $\delta^{18}\text{O}$ values at night for our estimates of nighttime $\delta^{18}\text{O}_R$ values. On this basis, we modeled $\delta^{18}\text{O}$ values of leaf water in the growing season for all 3 years using meteorological data from the flux tower, because we did not have temperature and relative humidity measurements at the canopy height in 2003 and 2004. We recognized the importance of a vertical gradient in water vapor concentration between the height of the canopy (0.5 m) and the sensor (3 m). A correction was applied to the tower-based relative humidity data using a second-order polynomial regression, developed on the basis of measurements from a vertical profile conducted in the summer of 2002 (data not shown).

3.8. Seasonal Patterns of Measured and Modeled $\delta^{18}\text{O}_R$

[41] Figure 7 shows comparisons between measured and modeled nighttime $\delta^{18}\text{O}_R$ and modeled soil moisture contents in the top 10 cm for the three growing seasons.

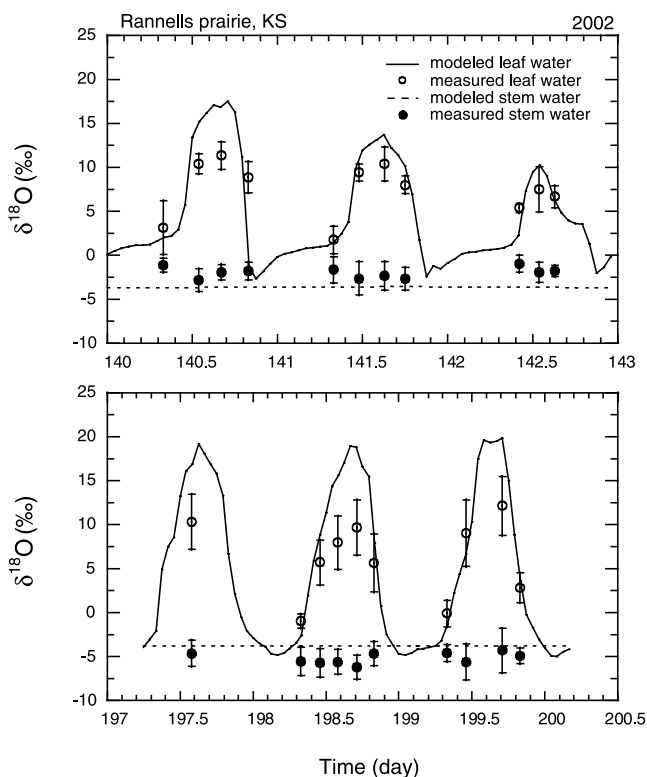


Figure 6. Comparisons between measured and modeled $\delta^{18}\text{O}$ values of leaf and source water for two 3-day periods in 2002.

Measured $\delta^{18}\text{O}_R$ showed considerable interseasonal and intraseasonal variations. ISOLSM $\delta^{18}\text{O}_R$ predicted these variations quite well, especially for the 2003 summer where the model successfully described a decreasing trend of $\delta^{18}\text{O}_R$ between DOY 150–190 and an increasing trend between DOY 190–240. We do not know the cause of the relatively less positive $\delta^{18}\text{O}_R$ value observed on DOY 244 ($22.7 \pm 0.5\%$, SMOW). This measurement was made immediately after a substantial rain event. It was likely that one precipitation had a relatively depleted $\delta^{18}\text{O}$ value, which was not described in the model. The model predicted the relatively smaller variation in $\delta^{18}\text{O}_R$ observed throughout 2004, as compared to 2003. Modeled $\delta^{18}\text{O}_R$ also showed close agreements with measurements in 2002 and 2004, indicating ISOLSM's consistency of predicting $\delta^{18}\text{O}_R$ in very different soil moisture conditions. This relatively good model versus measurement agreement gave us confidence in using ISOLSM to investigate factors affecting seasonal variations of $\delta^{18}\text{O}_R$.

[42] We could not obtain reliable $\delta^{18}\text{O}_R$ measurements from the Keeling plot analysis between DOY 160–207 in 2002. Air samples collected during this period had little or no correlation between $\delta^{18}\text{O}$ and $1/\text{CO}_2$ on a Keeling plot. We suspect this was due to low CO_2 production in the soil when water was limiting. Under these conditions, the amount of CO_2 exchanged between the atmosphere and the soil was likely much higher than the net CO_2 added from the soil. Consequently, the invasion (abiotic) effect was amplified. *Tans* [1998] used a model to demonstrate that strong invasion creates large errors when estimating $\delta^{18}\text{O}_R$ with a Keeling plot. Our results indicate that the decoupling between $\delta^{18}\text{O}$ values and CO_2 concentrations prevents reliable Keeling plot analysis when the soil surface

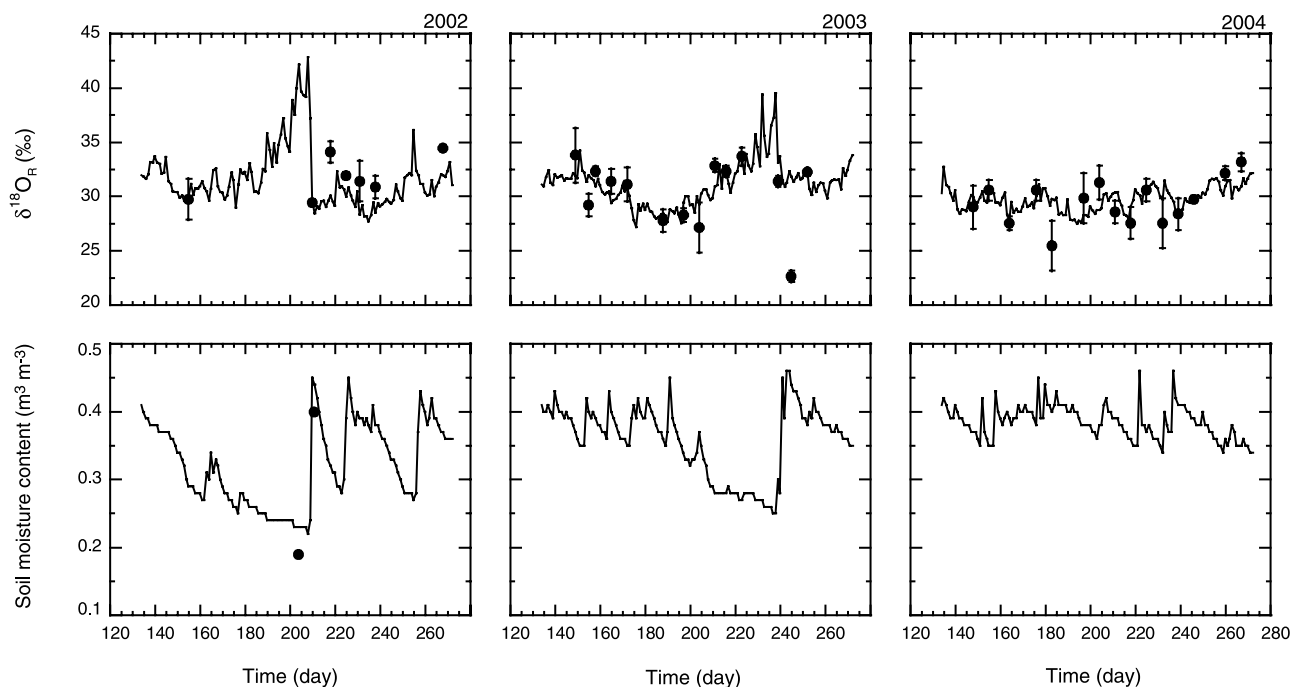


Figure 7. Comparisons between measured and modeled $\delta^{18}\text{O}_R$ values and modeled average soil moisture contents in the top 10 cm for the three growing seasons. Solid circles represent measurements, and solid lines are model results.

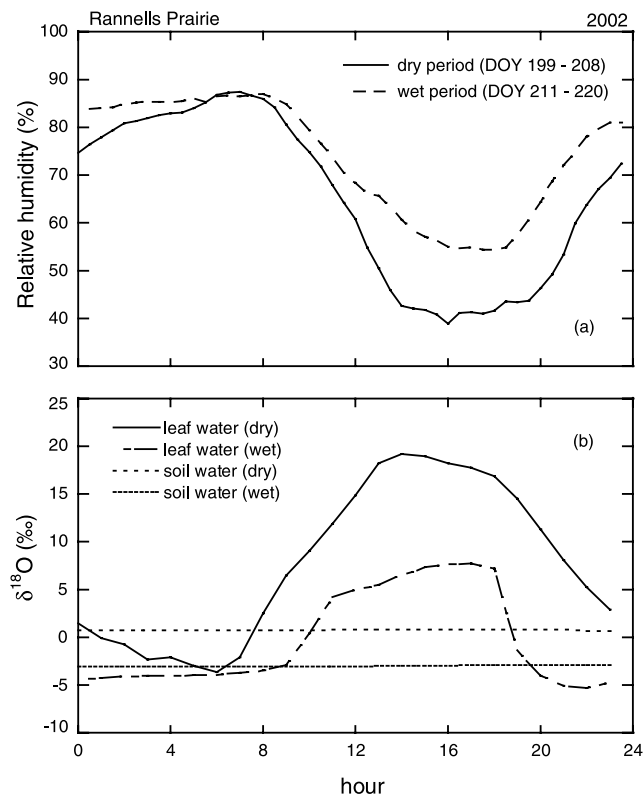


Figure 8. (a) Comparisons between measured relative humidity and (b) comparisons between modeled leaf and soil water $\delta^{18}\text{O}$ values in the top 10 cm between two periods with contrasting soil moisture conditions. Values reported are 10-day averages representing a dry (DOY 199–208) and a wet (DOY 211–221) period.

is dry. As described by *Miller et al.* [1999], the Keeling plot approach appears to be more robust for estimating $\delta^{18}\text{O}_R$ in moister soil conditions.

[43] The high $\delta^{18}\text{O}_R$ values occurring in 2002 just before day 210 contrast sharply with those that occur after day 210. The period before day 210 is very dry, with low soil moisture (Figure 7) and relative humidity (shown as 10-day averages before and after the precipitation event in Figure 8a). A substantial precipitation event on day 210 replenished soil moisture and increased relative humidity throughout the day. The near-surface soil water was heavier by about 4‰ preceding the precipitation event (Figure 8b) because of the period of sustained evaporative enrichment. This enrichment, and the impact of lower relative humidity over the course of the day, caused leaf water to become relatively enriched (Figure 8b) compared to the period after the precipitation event. Thus both components of nighttime respiration (above and belowground) were enriched, leading to the substantial enrichment of the total CO_2 respiration flux. If these modeled values were correct, a Keeling plot analysis would be ineffective because of the strong invasion effect.

[44] Measured and modeled $\delta^{18}\text{O}_R$ showed less seasonal variation in 2004, a wet year without water limitation in the growing season. When soil water was abundant, $\delta^{18}\text{O}_R$ values appeared to be affected by the relative contribution

of soil to total respiration (data not shown). This relationship is especially evident in the summer of 2003. $\delta^{18}\text{O}_R$ values were more positive when the contribution of soil respiration became greater, suggesting soil-respired CO_2 had higher $\delta^{18}\text{O}$ values than aboveground respiration. This observation is supported by model predictions, which showed more positive $\delta^{18}\text{O}$ in surface soil water than in nighttime leaf water. This modeling result contradicts the common assumption that leaf water $\delta^{18}\text{O}$ values are more enriched than soil water, which is often true during the day. At night, leaf water $\delta^{18}\text{O}$ could stay enriched relative to source water, particularly when the leaf water turnover rate is low [*Cernusak et al.*, 2002; *Farquhar and Cernusak*, 2005; *Lai et al.*, 2006]. Our measurements showed that $\delta^{18}\text{O}$ values of soil water in the top 10 cm could be enriched by nearly 6‰ from surface evaporation (data not shown). During these periods, the soil C^{18}OO flux is more ^{18}O enriched relative to aboveground respiration at night. The $\delta^{18}\text{O}$ signatures of soil-respired CO_2 and aboveground respiration are usually close to each other in this situation (within a few ‰).

3.9. Potential Sources of Errors in the Model

[45] *Riley et al.* [2002, 2003] modeled $\delta^{18}\text{O}$ values of soil water between 0 and 20 cm below the surface over an extended period in a tallgrass prairie in northern Oklahoma. They showed that $\delta^{18}\text{O}$ values of surface soil water (0–2.5 cm) were very responsive to evaporation and precipitation. Below 2.5 cm, diurnal fluctuations in the $\delta^{18}\text{O}$ value of soil water were much smaller. Previous studies showed that surface enrichment does not appear to affect $\delta^{18}\text{O}$ values of soil efflux because the equilibration process mostly occurs at depth [*Amundson et al.*, 1998; *Miller et al.*, 1999; *Stern et al.*, 1999, 2001]. In contrast, *Riley* [2005] used a model simulation to show that gradients in the $\delta^{18}\text{O}$ value of near-surface soil water have significant impacts on the $\delta^{18}\text{O}$ value of the soil-surface CO_2 flux. Further work needs to be done to characterize the impacts on $\delta^{18}\text{O}_R$ of competition between soil-gas diffusion and isotopic equilibration with near-surface soil water.

[46] Short-term variation in the $\delta^{18}\text{O}$ value of soil-respired CO_2 would likely be affected by the $\delta^{18}\text{O}$ value of individual rain events, which we did not specify in our simulations. Using predicted $\delta^{18}\text{O}$ values of source water to estimate above-canopy vapor also likely contributes to error, since vapor ^{18}O content is also impacted by horizontal advection, mixing with the free troposphere, and surface evaporation. Further, as mentioned earlier, diurnal variations in $\delta^{18}\text{O}_v$ can be large. In previous work we examined the impact of these variations on daily averaged leaf and near-surface soil water $\delta^{18}\text{O}$ values and found them to be smaller than impacts associated with errors in daily averaged values of above-canopy vapor $\delta^{18}\text{O}$ values [*Riley et al.*, 2003]. We do not expect that the assumption of a constant value for the $\delta^{18}\text{O}$ value of above-canopy CO_2 will substantially impact nighttime $\delta^{18}\text{O}_R$ [*Riley et al.*, 2003].

4. Conclusions

[47] In this study we showed carbon and oxygen isotopes of respired CO_2 fluxes measured in a tallgrass prairie. These measurements were made continuously on a weekly basis

during the growing season for 3 years with contrasting precipitation inputs. Measurements of NEE flux showed considerable seasonal and interannual variations. Consistent with previous studies, we found the timing and distribution of precipitation have large impacts on carbon exchange in this grassland. We found ISOLSM capable of predicting oxygen isotope ratios of ecosystem respiration ($\delta^{18}\text{O}_R$) in contrasting soil moisture conditions. Using Keeling plot analysis for estimating $\delta^{18}\text{O}_R$ is less reliable when surface soil is dry. ISOLSM modeled very positive $\delta^{18}\text{O}_R$ values under water stressed conditions. The combination of low relative humidity and high $\delta^{18}\text{O}$ enrichment in surface soil water during drought contributed to the very positive predicted $\delta^{18}\text{O}_R$ values.

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