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Influence of clouds and diffuse radiation on ecosystem-atmosphere CO₂ and CO¹⁸O exchanges

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[1] This study evaluates the potential impact of clouds on ecosystem CO₂ and CO₂ isotope fluxes (“isofluxes”) in two contrasting ecosystems (a broadleaf deciduous forest and a C₄ grassland) in a region for which cloud cover, meteorological, and isotope data are available for driving the isotope-enabled land surface model (ISOLSM). Our model results indicate a large impact of clouds on ecosystem CO₂ fluxes and isofluxes. Despite lower irradiance on partly cloudy and cloudy days, predicted forest canopy photosynthesis was substantially higher than on clear, sunny days, and the highest carbon uptake was achieved on the cloudiest day. This effect was driven by a large increase in light-limited shade leaf photosynthesis following an increase in the diffuse fraction of irradiance. Photosynthetic isofluxes, by contrast, were largest on partly cloudy days, as leaf water isotopic composition was only slightly depleted and photosynthesis was enhanced, as compared to adjacent clear-sky days. On the cloudiest day, the forest exhibited intermediate isofluxes: although photosynthesis was highest on this day, leaf-to-atmosphere isofluxes were reduced from a feedback of transpiration on canopy relative humidity and leaf water. Photosynthesis and isofluxes were both reduced in the C₄ grass canopy with increasing cloud cover and diffuse fraction as a result of near-constant light limitation of photosynthesis. These results suggest that some of the unexplained variation in global mean $\delta^{18}\text{O}$ of CO₂ may be driven by large-scale changes in clouds and aerosols and their impacts on diffuse radiation, photosynthesis, and relative humidity.

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1. Introduction

[2] While spatial and temporal variations in atmospheric CO₂ and its ¹³C/¹²C composition have received considerable attention from the carbon cycle community [e.g., Ciais et al., 1995; Fung et al., 1997; Rayner et al., 1999, 2008; Randerson

et al., 2002a, 2002b; Scholze et al., 2003], much less is known about the ¹⁸O/¹⁶O composition of atmospheric CO₂ ($\delta^{18}\text{O}_a$; symbols defined in Table 1). Although global simulations of $\delta^{18}\text{O}_a$ and its controlling processes have made good progress [Farquhar et al., 1993; Ciais et al., 1997a, 1997b; Peylin et al., 1999; Cuntz et al., 2003a, 2003b; N. Buenning et al., Modeling the response of the terrestrial biosphere and $\delta^{18}\text{O}$ of atmospheric CO₂ to flux, humidity, and isotope hydrology changes, manuscript in preparation, 2009], fundamental spatial and temporal variations of $\delta^{18}\text{O}_a$ are poorly captured by state-of-the-art global model simulations. One example of unexplained behavior is the phase shift between seasonal cycles of CO₂ and $\delta^{18}\text{O}_a$ observed at high northern latitudes, though a recent study showed how this shift is sensitive to boreal forest plant functional type composition and the $\delta^{18}\text{O}$ of plant source water [Welp et al., 2006]. A second, outstanding example of unexplained variation is the large, multiyear variation in mean $\delta^{18}\text{O}_a$ observed at many stations. The pronounced downward excursion in global mean $\delta^{18}\text{O}_a$ observed during the early and mid-1990s averaged $\sim -0.1\text{‰ a}^{-1}$ for extratropical, marine boundary layer stations, implying isotope fluxes, or “isofluxes,” on the order of tens of Pmol CO₂‰ a⁻¹.

[3] Because $\delta^{18}\text{O}_a$ is strongly influenced by exchanges of CO¹⁸O between the atmosphere and terrestrial ecosystems

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Table 1. Nomenclature Used in the Paper^a

Variable	Description
$\delta^{18}O_a$	Background atmosphere $\delta^{18}O$ -CO ₂ (VPDB-CO ₂)
R_D/R_S	Diffuse fraction, the ratio of diffuse irradiance to total (global) irradiance or of diffuse PAR to total PAR
PAR	Photosynthetically Active Radiation (400–700 nm).
LAI	Leaf area index (m ² /m ²)
$^{18}\Delta$	Discrimination against CO ¹⁸ O during photosynthesis
ϵ_d	Kinetic fractionation during molecular diffusion of CO ¹⁸ O
$\delta^{18}O_c$	$\delta^{18}O$ value of CO ₂ in equilibrium with H ₂ O in leaves
C_a, C_i, C_c	CO ₂ concentrations in the atmosphere, stomatal pore, and in chloroplasts
F_{al}	Gross CO ₂ flux from atmosphere to leaf
F_{la}	Gross CO ₂ flux from leaf to atmosphere
A_{net}	Net leaf photosynthesis including leaf respiration ($F_{al}-F_{la}$)
$^{18}F_{al}$	Atmosphere-to-leaf isoflux ($\delta^{18}O$ in CO ₂)
$^{18}F_{la}$	Leaf-to-atmosphere isoflux ($\delta^{18}O$ in CO ₂)
$A_{net}^{18}\Delta$	Net photosynthetic isoflux
$\delta^{18}O_{lw}$	$\delta^{18}O$ value of leaf water (VSMOW)
$\delta^{18}O_{xy}$	$\delta^{18}O$ composition of source water in xylem (VSMOW)
$\delta^{18}O_{sw}$	$\delta^{18}O$ composition of soil water (VSMOW)
$\delta^{18}O_{cv}$	$\delta^{18}O$ composition of in-canopy water vapor (VSMOW)
$\delta^{18}O_v$	$\delta^{18}O$ composition of background, above-canopy water vapor (VSMOW)

^aHere $\delta = \left(\frac{R_{sam}}{R_{std}} - 1\right)$ and R_{sam} and R_{std} are the ratios of ¹⁸O/¹⁶O in a sample or standard, respectively. The $\delta^{18}O$ -CO₂ values are reported relative to the

during photosynthesis and respiration [Francey and Tans, 1987; Friedli et al., 1987; Farquhar et al., 1993; Ciais et al., 1997a, 1997b; Cuntz et al., 2003a, 2003b], several studies have related the downward excursion of $\delta^{18}O_a$ to terrestrial carbon cycle anomalies [Gillon and Yakir, 2001; Stern et al., 2001; Ishizawa et al., 2002; Flanagan, 2005]. However, water cycle anomalies can also affect $\delta^{18}O_a$, as the $\delta^{18}O$ of ecosystem-to-atmosphere CO₂ fluxes is determined by the $\delta^{18}O$ of leaf and soil water pools which interact with CO₂ during photosynthesis and respiration [Yakir and Sternberg, 2000]. Leaf and soil water $\delta^{18}O$ are in turn determined by the $\delta^{18}O$ of precipitation [Welker, 2000; Vachon et al., 2007] and water vapor and subsequent isotopic fractionations during evaporation and diffusion [Craig and Gordon, 1965; Allison et al., 1983]. Although either carbon or water cycle anomalies may drive $\delta^{18}O_a$, unexplained multiyear variations in $\delta^{18}O_a$ such as occurred in the 1990s likely result from linked perturbations to both cycles.

[4] Recent research has documented large variability in tropical cloud cover [e.g., Wielicki et al., 2002] on interannual timescales that span part of the $\delta^{18}O_a$ record. For example, satellite measurements of earth's shortwave and longwave radiation budgets over the 1990s suggest decreases in tropical mean cloudiness [Wielicki et al., 2002], in agreement with decreases in the monthly mean global cloud fraction over the 1990s (<http://isccp.giss.nasa.gov/climanal1.html>). Tropical cloud cover variability may be particularly relevant for understanding global $\delta^{18}O_a$ variations, as tropical terrestrial ecosystem CO₂ fluxes comprise a large fraction of global productivity. Other satellite-based analyses document increasing spring and summer cloud cover in the Arctic region [Wang and Key, 2003]. In addition, evidence from ground-based radiometers suggests secular changes in surface global irradiance, with a total reduction of ~4–6% from about 1960 to 1990 (“global dimming”) [Stanhill and Cohen, 2001; Liepert, 2002; Liepert et al., 2004] followed by a reversal from roughly 1990 onward that has been termed “global brightening” [Wild et al., 2005, 2007; Pinker et al., 2005; Roderick, 2006].

[5] Here we examine the hypothesis that these large-scale changes in cloud cover and irradiance account for part of the unexplained variation observed in $\delta^{18}O_a$, as clouds influence several environmental factors important in controlling biosphere-atmosphere CO₂ isofluxes. Clouds reduce total shortwave (global) irradiance (R_S) while also increasing diffuse irradiance (R_D) and the diffuse fraction (R_D/R_S , the ratio of diffuse irradiance to total or global irradiance [Roderick, 1999]). Numerous empirical and theoretical studies have noted the impact of changes in diffuse photosynthetically active radiation (PAR) on canopy carbon uptake via increases in photosynthesis of light-limited shade leaves and other associated changes in the environment [e.g., Price and Black, 1990; Hollinger et al., 1994, 1998; Gower et al., 1999; Choudhury, 2001; Roderick et al., 2001; Freedman et al., 2001; Gu et al., 1999, 2002, 2003; Rocha et al., 2004; Min, 2005; Urban et al., 2007; Oliveira et al., 2007; Knohl and Baldocchi, 2008]. In addition to increasing R_D/R_S and the contribution of shade leaves to canopy photosynthesis, clouds decrease radiant heating of upper canopy sun leaves, potentially increasing net photosynthetic rates [Roderick et al., 2001; Gu et al., 2002, 2003]. Increased cloudiness is often also associated with higher surface relative humidity via decreases in air and leaf temperature and increases in specific humidity [Freedman et al., 2001].

[6] Relative humidity will influence both photosynthetic CO₂ fluxes and the $\delta^{18}O$ of leaf water via impacts on stomatal conductance, and thus can have a disproportionate impact on ecosystem-atmosphere isofluxes. An increase in relative humidity generally increases stomatal conductance, which, coupled with increased shade leaf photosynthesis, should increase photosynthetic isofluxes. However, increased relative humidity will also decrease leaf water $\delta^{18}O$ because of a greater influx of depleted vapor, and this would decrease photosynthetic isofluxes.

[7] Thus, the net effect of changing cloud cover on biosphere-atmosphere CO₂ and CO₂ isofluxes exchanges is difficult to assess without high-frequency ecosystem CO¹⁸O flux measurements. However, these data are currently being

collected at only a few sites at present [Griffis *et al.*, 2008; McDowell *et al.*, 2008]. The focus of this study instead is to examine potential ecosystem isoflux responses using observed cloud cover, radiation, meteorological and water isotope data to drive an isotope-enabled ecosystem model (ISOLSM). We chose to focus on two contrasting ecosystems in the Southern Great Plains over a short time period for intensive investigation of the mechanisms underlying the modeled canopy isoflux response to changing cloud cover. For our analyses, we selected a 12-day period from 11 to 22 July 2004 (day of year (DOY) 193–204,) during which strong variations in daytime thick cloud cover occurred at our study site, from less than 10% on clear days to 100% on a cloudy day. In addition to cloud cover variations, we selected this period using the following criteria: constant LAI, only trace amounts of precipitation (since precipitation $\delta^{18}\text{O}$ is a primary driver of CO₂ isofluxes), and no large changes in air temperature and specific humidity due to the passage of differing air masses associated with storm fronts. By limiting variability from these factors, we decomposed the predicted isoflux response to cloud cover into its component processes.

2. Methods

2.1. Site Description

[8] To capture the relevant processes that determine the net impact of clouds on ecosystem CO¹⁸O isofluxes, we employed a comprehensive, isotope-enabled ecosystem model (ISOLSM) [Riley *et al.*, 2002, 2003; Still *et al.*, 2005] in the DOE Atmospheric Radiation Measurement (ARM) program's Climate Research Facility (ACRF) in the 140,000 km² Southern Great Plains (SGP) region of Oklahoma and Kansas [Ackerman and Stokes, 2003]. The SGP region is particularly amenable for such a study because of the great diversity of cloud property, aerosol, radiation, and meteorological measurements available, with the most intensive data collection at the Central Facility (CF) site near Lamont, OK (36° 36.30'N, 97° 29.10'W, 320 masl). Analysis of atmospheric data collected at the CF has shown large changes in irradiance driven by cloud cover from 1997 to 2004 [Dong *et al.*, 2006]. The SGP region also contains natural and agricultural ecosystems representing a variety of photosynthetic pathways and growth forms, including tallgrass prairies, broadleaf forests along riparian areas, and crops such as winter wheat, milo, and corn. Because we wanted to explore the impact of cloud cover variations on ecosystem-atmosphere isofluxes in two globally important but strongly contrasting natural vegetation types also represented within the SGP region, we chose broadleaf deciduous forests and C₄ grasslands for our model simulations.

2.2. Model Description

[9] ISOLSM is based on the NCAR Land Surface Model (LSM1.0) [Bonan, 1994; Bonan *et al.*, 1997], which was modified by Riley *et al.* [2002] to simulate the carbon and oxygen isotope composition of terrestrial ecosystem-atmosphere CO₂ and H₂O exchanges. The model simulates canopy radiation transfer using the two-stream approximation of Dickinson [1983] and Sellers [1985] to calculate direct and diffuse radiation fluxes in the visible and near-infrared wave bands. The canopy is divided into sunlit and shaded leaves using an extinction coefficient that accounts for scattering within the

canopy [Sellers, 1985]. The model does not vary leaf nitrogen and photosynthetic capacity between sun and shade leaves, as is done in some models [e.g., de Pury and Farquhar, 1997; Wang and Leuning, 1998]. The version of ISOLSM applied here differs from that described by Riley *et al.* [2002] by several changes made to the plant photosynthesis submodels. First, low- and high-temperature inhibition factors on the maximum catalytic capacity of Rubisco (V_{max}) from Sellers *et al.* [1996] have been included. Second, we implemented the method of Sellers *et al.* [1996] to smooth transitions between the three limiting assimilation rates (i.e., Rubisco, light, and export limited). Finally, iterations to estimate C_c and C_i , the leaf chloroplast and internal CO₂ concentrations, are now performed using net photosynthesis (i.e., accounting for leaf respiration occurring inside the leaf), as opposed to gross photosynthesis, as done in the original version of LSM1. Of these changes, the last had the largest impact, resulting in values for V_{max} and C_i that are much closer to measured values. Accurate C_i and C_c are critical for simulating isotopic fractionations against ¹³CO₂ and CO¹⁸O. ISOLSM models mesophyll (or internal) conductance in C₃ plants to be proportional to the maximum carboxylation capacity (V_{max} (in $\mu\text{mol m}^{-2} \text{s}^{-1}$)) following Evans and Loreto [2000], but without the soil moisture dependence implemented by Randerson *et al.* [2002b]. During light-saturated photosynthesis in forest sun leaves, the average drawdown from C_i to C_c was ~ 4 Pa over the study period, similar to the drawdown measured by Gillon and Yakir [2000].

[10] We have tested ISOLSM's H₂O and CO₂ flux predictions against several sets of measurements: (1) in the dominant vegetation types using measurements [Suyker and Verma, 2001] performed in the SGP as part of the AmeriFlux program [Riley *et al.*, 2003]; (2) against 3 years of surface measurements made during the FIFE campaign [Betts and Ball, 1998; Cooley *et al.*, 2005]; (3) in a tallgrass prairie site in Kansas [Lai *et al.*, 2006a]; (4) in an old growth conifer forest in Oregon [Aranibar *et al.*, 2006]; and in more recent measurements in wheat, pasture, and soy (W. J. Riley *et al.*, manuscript in preparation, 2009). We have also tested ISOLSM's isotopic predictions against available data in Great Plains grassland and cropland ecosystems (i.e., $\delta^{18}\text{O}$ in ecosystem water pools and fluxes, and $\delta^{18}\text{O}$ in ecosystem CO₂ fluxes [Riley *et al.*, 2003; Still *et al.*, 2005; Lai *et al.*, 2006a]). We have previously applied ISOLSM to examine (1) impacts of the atmospheric $\delta^{18}\text{O}$ value of H₂O and CO₂ on ecosystem discrimination against CO¹⁸O [Riley *et al.*, 2003]; (2) impact of carbonic anhydrase activity in soils and leaves [Riley *et al.*, 2002, 2003]; (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 CO₂ flux [Riley *et al.*, 2003; Riley, 2005]; (4) impacts of land use change on regional surface CO₂ and energy fluxes and near-surface climate [Cooley *et al.*, 2005]; and (5) the use of ¹³C measurements to improve model parameterizations [Aranibar *et al.*, 2006]. The isotope submodels in ISOLSM simulate the dominant processes impacting the $\delta^{18}\text{O}$ value of soil ($\delta^{18}O_{\text{sw}}$) and leaf H₂O ($\delta^{18}O_{\text{lw}}$) and CO₂ fluxes: advection of H₂¹⁸O in soil water and subsequent evaporation, leaf water isotopic enrichment, isotopic exchanges between H₂O and CO₂ in the soil and leaves, the transport of CO₂ and CO¹⁸O in the soil column, and the $\delta^{18}\text{O}$ of canopy water vapor ($\delta^{18}O_{\text{cv}}$). The xylem source water that supplies leaves,

$\delta^{18}O_{xy}$, is determined in ISOLSM by the vertical distribution of $\delta^{18}O_{sm}$, weighted by rooting density profiles for the various ecosystem types. $\delta^{18}O_{cv}$ is calculated at each time step as a function of vapor isotope exchanges with above-canopy air ($\delta^{18}O_v$), as well as isotope fluxes from canopy transpiration and soil and canopy evaporation when the canopy is wet [Riley *et al.*, 2002]. Further description of our leaf water $\delta^{18}O$ and photosynthetic isoflux calculations is given in section 3.

2.3. Cloud Cover, Radiation, Meteorology, and Water Isotope Forcing Data

[11] ISOLSM is forced with meteorological and water isotope data [Riley *et al.*, 2002, 2003], and it has recently been modified to ingest satellite measurements of vegetation characteristics such as the projected leaf area index (LAI). For the simulations reported here, radiation, cloud property, and aerosol data were acquired from instruments at the ARM Central Facility (CF) in Lamont, OK, which is the primary measurement facility within the ARM SGP region [Ackerman and Stokes, 2003]. The instrument array at the CF includes sensors to measure cloud presence and cloud radiative properties, which are necessary to explore the role of clouds in ecosystem-atmosphere CO¹⁸O exchanges. Radiation fluxes measured at the CF site include downwelling shortwave radiation (direct and diffuse) and downwelling longwave radiation. For our analysis, early morning and late afternoon values (solar angles less than 15°) were screened to minimize the impact of low solar angles on R_D/R_S .

[12] The ARM cloud data used are the daytime percent cover of clouds, as measured by the total sky imager (TSI), an instrument that measures the fractional sky coverage of thin and thick (opaque) clouds (i.e., the fraction of the hemispheric field of view that contains these cloud types) for daytime periods when the solar elevation exceeds 10 degrees. For this analysis, we focus on the percent cover of thick clouds, as these are both the dominant cloud types and have the largest impact on irradiance, R_D/R_S , temperature, and relative humidity. Min [2005] showed that diffuse radiation fluxes due to optically thick clouds have a greater impact on canopy photosynthetic efficiency than do fluxes from optically thin clouds. Because of temporal limitations on these data (i.e., only daytime cloud cover fractions are available from the TSI), we have restricted our analysis to daytime periods. Although nighttime clouds can affect the surface energy budget and carbon cycle through modulation of longwave energy fluxes [e.g., Dai *et al.*, 1999], the largest impacts of clouds on canopy isofluxes should occur during the day. Unfortunately, cloud-screened aerosol optical depth data from a Sun photometer [e.g., Niyogi *et al.*, 2004; Oliveira *et al.*, 2007] were not available for our study period to allow a separate assessment of aerosol impacts on isofluxes.

[13] The meteorological data used to force ISOLSM include air temperature, pressure, water vapor content, wind speed, and precipitation amount. These data were taken from the Oklahoma and Kansas Mesonet program. The Mesonet consists of 145 instrument platforms (as of April 2007) distributed throughout the two states. Each station measures relative humidity, wind speed and direction, air temperature, and atmospheric pressure, and reports these data as 5-min, 15-min, or half-hourly averages for the state of Oklahoma

and as hourly average for the state of Kansas. Additional external data sets required by ISOLSM include the following: (1) soil type from the 1 km USGS Statsgo soils database (i.e., 20% sand, 15% silt, and 65% clay around the CF); (2) monthly mean precipitation $\delta^{18}O$ values averaged over 2–5 years of data from analyses of archived water samples collected by the EPA National Atmospheric Deposition Program (NADP) network [Lynch *et al.*, 1995] between 1980 and 1990 and interpolated across the Great Plains region [Welker, 2000]; and (3) the atmospheric CO₂ concentration.

[14] The model simulations also require the $\delta^{18}O$ composition of above-canopy water vapor ($\delta^{18}O_v$) and background atmospheric CO₂ ($\delta^{18}O_a$). Neither quantity is measured continuously in this region. Many factors affect $\delta^{18}O_v$ [Lee *et al.*, 2006], including evapotranspiration and horizontal and vertical atmospheric advection, and diurnal variations of up to 4‰ have been measured in this area [Helliker *et al.*, 2002; Riley *et al.*, 2003]; smaller diurnal variations (1–2‰) have been observed over temperate forests [Lai *et al.*, 2006a; Lee *et al.*, 2006]. Other investigators have shown strong linear or log linear relationships between specific humidity and $\delta^{18}O_v$ [White and Gedzelman, 1984; Lee *et al.*, 2006]. However, we have no information on this relationship in the SGP region, as extensive $\delta^{18}O_v$ data are not available. Instead, for this set of simulations, we set $\delta^{18}O_v$ to be in a temperature-dependent isotopic equilibrium with the most recent precipitation event [e.g., Lee *et al.*, 2006]. Although our approach only crudely captures the processes that regulate $\delta^{18}O_v$, the sensitivity of ecosystem-atmosphere CO¹⁸O exchanges to diurnal variations in $\delta^{18}O_v$ has been examined in detail by Riley *et al.* [2003] and found to be small, partly because the more important vapor $\delta^{18}O$ is that of within-canopy vapor, $\delta^{18}O_{cv}$, which interacts directly with $\delta^{18}O_{lv}$. Riley *et al.* [2003] also showed that diurnal variations in $\delta^{18}O_a$ can impact CO₂ isofluxes. However, since we lacked consistent diurnal measurements of $\delta^{18}O_a$, we imposed a constant value of −0.5‰, which is similar to the zonal annual mean value from mid-latitude, northern hemisphere stations in the NOAA air sampling network [Cuntz *et al.*, 2003b], and is close to mean values measured 3–4 km above the surface by ARM and NOAA. There is no diagnostic solution for the canopy air space CO₂ and CO¹⁸O concentrations that is analogous to the H₂O and H₂¹⁸O solution [Riley *et al.*, 2002]. We therefore assume that canopy CO₂ and CO¹⁸O concentrations are the same as above-canopy values. To properly analyze potential feedbacks between leaf and canopy CO¹⁸O fluxes, a prognostic canopy airspace model would need to be used; to our knowledge, no previous work has addressed this issue.

2.4. Model Sensitivity Experiments

[15] Our primary objective was to better understand the effects of cloud cover and associated environmental factors such as diffuse radiation and relative humidity on ecosystem-atmosphere CO¹⁸O exchanges for two globally important and strongly contrasting biomes that should bracket the expected range of ecosystem responses to cloud cover: broad-leaf deciduous forests and C₄ grasslands. The two types differ in photosynthetic pathway (C₃ forest and C₄ grass), life form (tree versus grass), and canopy stature (canopy heights used in ISOLSM are 20 m and 0.5 m, respectively [Bonan, 1996]), thereby allowing us to explore a wide range of potential ecosystem CO₂ isoflux responses to cloud cover variations.

The LAI values we used are particularly important because a higher diffuse radiation fraction is more influential with higher canopy LAI, as more leaf area is in shade during sunny conditions dominated by direct beam radiation [cf. *Roderick et al.*, 2001; *Gu et al.*, 2002; *Alton et al.*, 2005; *Knohl and Baldocchi*, 2008]. To assess the sensitivity of our results to LAI in the broadleaf forest, we ran our base simulation with the mean value (5.0) for temperate broadleaf forests from *Asner et al.* [2003]. We also ran simulations with LAI values one standard deviation above and below the mean (i.e., LAI of 3.5 and 6.5, with all other driving variables were held constant). An LAI of 6.5 is not uncommon in temperate and tropical broadleaf forests, which together contribute substantially to global primary production [e.g., *Field et al.*, 1998] and thus are particularly relevant for understanding global $\delta^{18}O_a$ variations. We set the C₄ grass canopy LAI to 3.75. This value is typical of highly productive C₄ grasslands [*Suyker and Verma*, 2001] and C₄ corn crops [*Campbell et al.*, 1999]. To assess the C₄ grass canopy LAI sensitivity, we doubled the LAI (from 3.75 to 7.5) in one simulation and reduced it by 33% (to 2.5) in another.

[16] We also tested the sensitivity of our results to shade leaf temperatures, as ISOLSM does not separately calculate the energy balance of sun and shade leaves. Shade leaves can experience a very different radiation environment than sun leaves, leading to leaf temperature gradients in the canopy [*Gu et al.*, 2002; *Larcher*, 2003]. Shade leaf temperatures can be lower than sun leaf temperatures during sunny days. We tested the impact of this difference on our results by setting forest shade leaf temperatures to canopy air temperatures. Finally, we assessed the sensitivity of our results to the uniform distribution of leaf nitrogen and photosynthetic capacity (V_{\max}) between sun and shade leaves in ISOLSM. This uniformity could lead to larger shade leaf photosynthesis than would otherwise occur if these leaves become limited by Rubisco, which scales with leaf nitrogen. We halved V_{\max} in forest shade leaves in a separate simulation.

3. Results and Analysis

[17] We analyzed consecutive growing season days to understand how changes in cloud cover affected the physical environment and modeled ecosystem-atmosphere CO₂ fluxes and isofluxes in a broadleaf deciduous forest canopy and a C₄ grassland canopy. Our analysis is divided into four sections to clarify the processes impacting CO₂ fluxes and isofluxes: (section 3.1) cloud cover effects on R_D/R_S , PAR, temperature, and humidity; (section 3.2) the response of photosynthesis and respiration to cloud cover; (section 3.3) the response of leaf and soil water $\delta^{18}O$ to cloud cover; and (section 3.4) the response of CO₂ isofluxes to cloud cover.

3.1. Cloud Cover Impacts on R_D/R_S and the Physical Environment

[18] During the first 3 days (DOY 193–195) of the study period, the percent of the sky obscured by thick (opaque) and thin clouds was minimal (Figure 1a). During these mostly clear days, total irradiance was high, and the PAR flux was dominated by direct beam radiation except for early in the morning and early in the evening when diffuse radiation increased (Figure 1b). In this and subsequent figures, only daytime values are plotted. These clear-sky days provided a

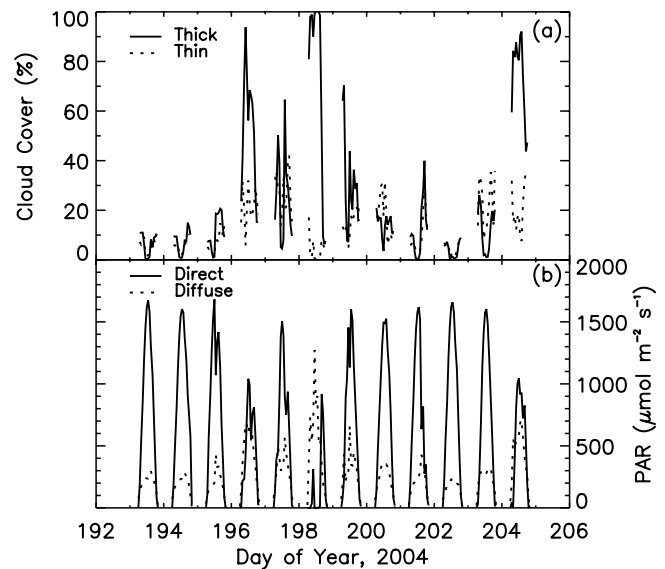


Figure 1. (a) The observed percent cover of thick (opaque) and thin clouds at the ARM Central Facility during daylight hours from DOY 193 to DOY 204 (11–22 July 2004). (b) Observed direct and diffuse PAR irradiance ($\mu\text{mol } \% \text{ m}^{-2} \text{ s}^{-1}$, using conversion factors of $4.6 \mu\text{mol photons J}^{-1}$ and $4.2 \mu\text{mol photons J}^{-1}$ for direct and diffuse radiation [*Larcher*, 2003]) on consecutive summer days (DOY 193–204) with contrasting cloud cover.

useful basis for comparison with subsequent days (DOY 196–199), which experienced increasing thick cloud cover and midday diffuse PAR irradiance, along with reduced direct and total shortwave irradiance. The peak diffuse PAR irradiance on partly cloudy days increased more than twofold from clear days. The magnitude of midday diffuse PAR irradiance was similar to direct PAR on DOY 196, and thick cloud cover exceeded 60% for several hours. DOY 198 was by far the cloudiest day of the study period, with thick cloud cover close to 100% for much of the day (Figure 1a) and irradiance dominated by diffuse fluxes (Figure 1b). The days before and after DOY 198 were both partly cloudy, with daily maximum thick cloud cover around 60%. DOY 199 is noteworthy, as the thick and thin clouds scattered and reflected direct beam irradiance, in the process increasing the diffuse irradiance enough to produce the highest midday shortwave irradiance measured in the study period (i.e., total PAR was greater than even the clear-sky days of 193, 194, and 202). This effect of unexpectedly high midday irradiance during partly cloudy periods has been observed elsewhere [*Gu et al.*, 1999, 2001; *Urban et al.*, 2007].

[19] The period from DOY 200–203 was mostly clear, with the lowest cloud cover of the study period measured on DOY 202 (Figure 1a). On this day, direct beam PAR was very high, about the same peak magnitude as on the other very clear day, DOY 193, but diffuse PAR was slightly lower. DOY 204 was partly to mostly cloudy (cover greater than 80% for much of the day), and it had high diffuse PAR irradiance (Figure 1b). This day preceded a heavy rain event on DOY 205. Stratifying the days by cloud cover thus produces the following classifications: clear (sunny) days (DOY 193–195, 200–203), partly cloudy days (DOY 196–197, 199, and 204), and a cloudy day (DOY 198).

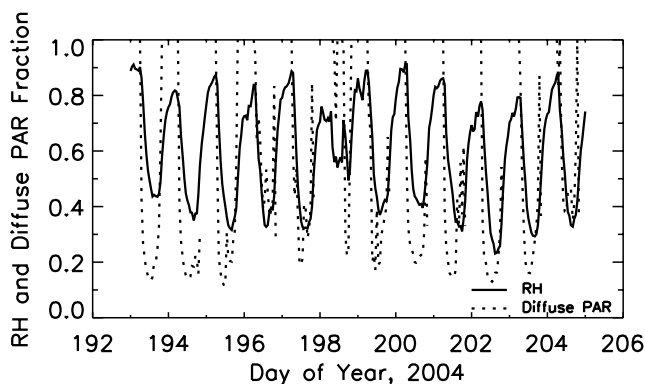


Figure 2. Observed background relative humidity (RH) and incident diffuse PAR fraction (R_D/R_S).

[20] Observed relative humidity and the diffuse PAR fraction (R_D/R_S), are shown in Figure 2. (Our analysis focuses on the observed diffuse PAR fraction, which we denote with the same notation (R_D/R_S) as the diffuse shortwave fraction following Roderick 1999; although diffuse PAR and shortwave fractions can differ slightly, during our study period they were indistinguishable from one another). Diurnal profiles of relative humidity largely followed the pattern of air temperature, and R_D/R_S followed predictable patterns on clear days with higher morning and evening values (Figure 2). Midday R_D/R_S was highest on the partly cloudy and cloudy days. Notably, the partly cloudy days (DOY 196–197, 199, and 204) did not have temperatures or humidities dramatically different from adjacent clear-sky days. Modeled leaf temperatures in the forest simulation tracked measured air temperatures, though they were higher by 1–3 K on sunny days (not shown).

[21] The increasing cloud cover during DOY 196–198 increased diffuse PAR and decreased direct and total PAR irradiance, producing a positive relationship between daytime R_D/R_S and the thick cloud cover fraction (Figure 3). Thin clouds and aerosols might also have affected R_D/R_S and contributed to some of the scatter shown in Figure 3. On partly cloudy days, midday R_D/R_S values were ~ 0.4 , compared to ~ 0.15 on clear days, and the highest midday R_D/R_S occurred on DOY 198, when it reached 1.0. The strong relationship between cloud cover and R_D/R_S has been observed in a variety of other studies, and results from radiation absorption, reflection and scattering by cloud droplets.

3.2. Photosynthetic Responses to Cloud Cover Changes

3.2.1. Broadleaf Deciduous Forest

[22] The effect of cloud cover on modeled broadleaf deciduous forest canopy photosynthesis was large. Despite the lower total PAR on partly cloudy and cloudy days (DOY 196–199, 204), simulated peak canopy photosynthesis was higher on these days than on sunny days (DOY 193–195 and 200–203; Figures 1b and 4a). This enhancement was due primarily to increases in shade leaf photosynthesis from increases in diffuse PAR on these days. There were minimal changes in modeled sun leaf photosynthesis on these days because the rate was light saturated for much of the day, and even relatively large decreases in direct PAR didn't impact sun leaf photosynthesis. During these periods, sun leaf photosynthesis was limited by the amount and capacity of

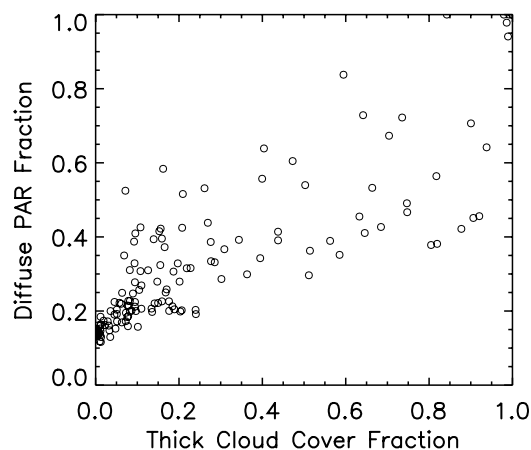


Figure 3. Observed daytime thick cloud cover fraction and incident diffuse PAR fraction (R_D/R_S) over the study period (DOY 193–204). Early morning and late afternoon values were screened to minimize the impact of low solar angles ($<15^\circ$) on R_D/R_S .

the primary photosynthetic enzyme, Rubisco [i.e., Collatz *et al.*, 1991]. Also, the leaf temperature was slightly lower on the partly cloudy days compared to the sunny days because of lower radiant heating, thereby decreasing leaf respiration and photorespiration rates. The temperature sensitivity of the maximum carboxylation capacity (V_{max}) is important for sun leaf photosynthesis, as it is usually light saturated and depends directly on V_{max} , while photorespiration affects both light-limited and light-saturated rates [Farquhar *et al.*, 1980; Collatz *et al.*, 1991].

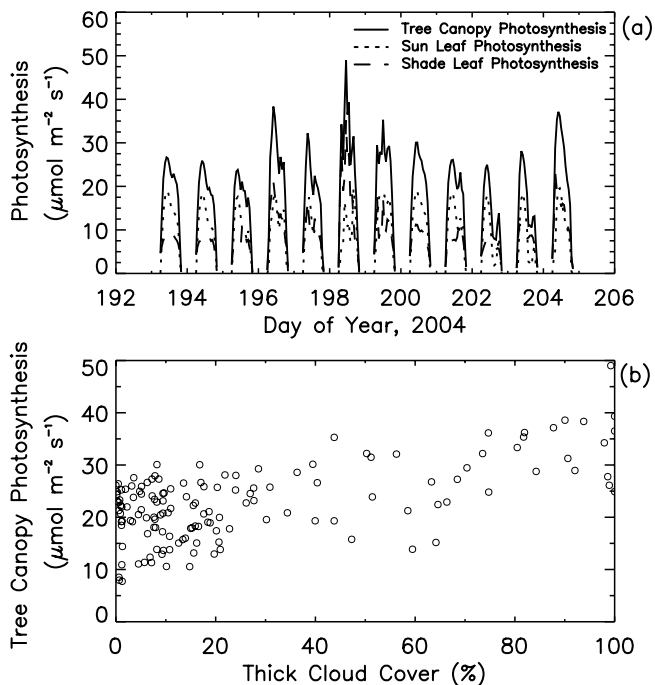


Figure 4. (a) Modeled broadleaf deciduous tree canopy photosynthesis per unit ground area ($\mu\text{mol m}^{-2} \text{s}^{-1}$) during DOY 193–204. (b) Modeled tree canopy photosynthesis ($\mu\text{mol m}^{-2} \text{s}^{-1}$) plotted against the thick cloud cover percentage for daylight hours from DOY 193 to DOY 204.

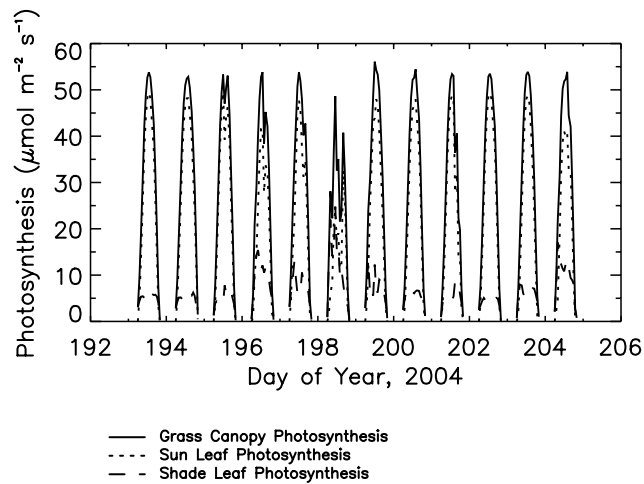


Figure 5. Modeled C₄ grass canopy photosynthesis ($\mu\text{mol m}^{-2} \text{s}^{-1}$) during DOY 193–204.

[23] In contrast to sun leaves, forest shade leaves responded strongly to the altered radiation regime induced by clouds: as cloud cover increased, diffuse PAR and shade leaf photosynthesis increased in tandem because shade leaf photosynthesis was light limited. On sunny days, peak shade leaf cumulative photosynthetic fluxes were less than half of sun leaf fluxes, whereas on partly cloudy and cloudy days the shade leaf fluxes equaled or exceeded the sun leaf values (Figure 4a). The overall positive simulated forest canopy photosynthetic response to increasing cloud cover (slope 0.15, $r^2 = 0.37$; Figure 4b) thus resulted primarily from increased shade leaf carbon uptake with increased R_D/R_S .

3.2.2. C₄ Grassland

[24] The C₄ grass canopy photosynthetic response to cloud variations was opposite that of the broadleaf deciduous forest canopy: increasing cloud cover generally led to decreased canopy photosynthesis. The negative response of C₄ photosynthesis to increasing R_D/R_S was stronger than its response to cloud cover (not shown). Although grass shade leaf photosynthesis responded positively to increased cloud cover due to increased diffuse PAR, sun leaf photosynthesis responded negatively to the decrease in direct beam radiation, and sun leaf photosynthesis was much larger than shade leaf photosynthesis during almost all cloud cover conditions (Figure 5).

[25] The modeled C₄ grass canopy photosynthesis closely followed daily irradiance patterns, in agreement with leaf and canopy-scale observations for C₄ plants [Suyker and Verma, 2001; Larcher, 2003]. In general, the highest predicted C₄ grass canopy photosynthesis rates occurred during the clear-sky days (DOY 193–195, 200–203), and the lowest rates occurred during the cloudiest days (DOY 196, 198, 204). The one important exception (on DOY 199, which was partly cloudy) proves the rule: peak insolation values on this day were the highest of the study period because of cloud scattering and reflection, and modeled peak C₄ grass photosynthesis was also highest on this day (Figure 5). Modeled peak canopy photosynthesis was large because of the high LAI values we imposed, although there are examples of well-watered and fertilized natural C₄ grassland and C₄ crop canopies exhibiting even higher productivity [Piedade et al.,

1991; Jones, 1992; Morison et al., 2000]. The net ecosystem exchange (NEE) values predicted by ISOLSM (not shown) ranged from -15 to $-35 \mu\text{mol m}^{-2} \text{s}^{-1}$, similar to NEE measured in a C₄ grass-dominated pasture in this region [Suyker and Verma, 2001].

[26] The fundamentally different response to cloud cover of the C₄ grass canopy (as opposed to the forest canopy) was at least partly due to canopy stature and the lower effective shade leaf area (and higher effective sun leaf area) in the much shorter grass canopy. Grass leaves have a more vertical orientation (erectophile morphology), and broadleaf deciduous tree leaves have a more horizontal orientation, so that at high solar angles the sun leaf area in grass canopies is higher than the comparable sun leaf area of broadleaf deciduous tree canopies [Jones, 1992; Larcher, 2003]. Another reason for the different response to irradiance is that both sun and shade leaf photosynthetic rates are almost always limited by light in the C₄ grass simulation. A hallmark of C₄ plants is their dominance in high-light and high-temperature environments such as grasslands and savannas [Long, 1999; Sage et al., 1999]. Photosynthesis in unstressed C₄ plants does not saturate on sunny days, unlike the typical light saturation for C₃ plants [Collatz et al., 1991, 1992].

[27] The decline in C₄ grass canopy photosynthesis with increasing cloud cover and R_D/R_S parallels the empirical results from eddy flux studies assessed by Niyogi et al. [2004], who found that increasing aerosol optical depth increased R_D/R_S and reduced R_S . This led to increases in net carbon uptake by C₃ ecosystems, but strong reductions in net carbon uptake for a C₄ natural grassland. Although not explicitly a response to cloud cover variations per se, this study supports our modeling results: increasing R_D/R_S and decreasing R_S reduces C₄ photosynthesis, without the diffuse light photosynthetic enhancement often seen in C₃ canopies. Our predictions also agree with Turner et al. [2003], who studied the relationship between measured gross primary production (GPP) and absorbed PAR in a cross-biome comparison. The C₄-dominated tallgrass prairie displayed a nearly linear relationship between GPP and APAR, unlike other biomes, which exhibited more typical light saturation responses (i.e., a hyperbolic relationship between GPP and APAR). Thus, decreases in R_S and increases in R_D/R_S , whether caused by clouds or aerosols, should decrease GPP in C₄ grasses, but not necessarily in C₃ plants.

3.2.3. Response of Canopy Light Use Efficiency to Cloud Cover and R_D/R_S Variations

[28] The response of forest photosynthesis to cloud cover and irradiance is related to how efficiently the canopy converts solar radiation to chemical energy, a quantity referred to as gross or GPP light use efficiency (LUE) ($\text{mol CO}_2 \text{ mol}^{-1} \text{ APAR}$). The broadleaf deciduous forest gross LUE was inversely proportional to irradiance. Indeed, the forest canopy strongly increased its gross LUE as R_D/R_S increased (Figure 6a). The daily averaged forest gross LUE for clear/sunny days (DOY 193–195, 200–203) was $0.031 \text{ mol CO}_2 \text{ mol}^{-1} \text{ APAR}$, for partly cloudy days (DOY 196–197, 199, 204) was $0.038 \text{ mol CO}_2 \text{ mol}^{-1} \text{ APAR}$, and for the cloudy day (DOY 198) was $0.048 \text{ mol CO}_2 \text{ mol}^{-1} \text{ APAR}$. This pattern follows the expectations of increasing LUE with increasing cloud cover and R_D/R_S demonstrated previously in eddy flux [e.g., Hollinger et al., 1994; Gu et al., 2002; Rocha et al., 2004; Min, 2005] and modeling [Norman

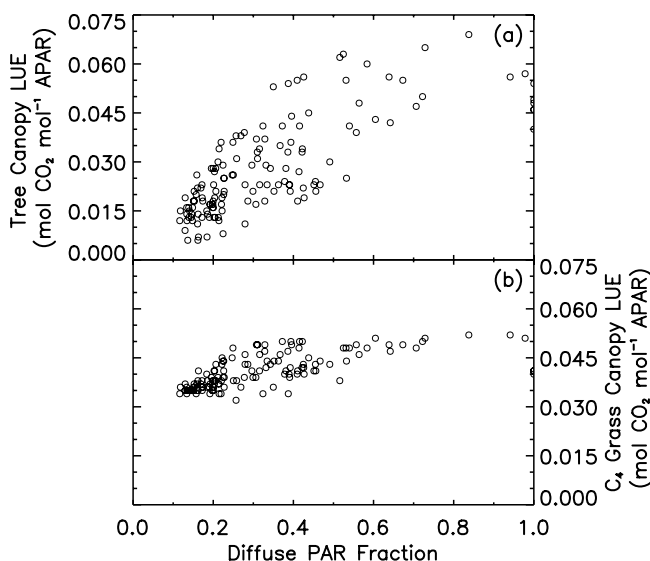


Figure 6. (a) Modeled gross LUE (mol CO₂ mol⁻¹ APAR) in the broadleaf deciduous tree canopy plotted against observed R_D/R_S during daylight hours (solar angles $>15^\circ$). (b) Modeled C₄ grass canopy gross LUE (mol CO₂ mol⁻¹ APAR) plotted against observed R_D/R_S during daylight hours.

and Arkebauer, 1991; Choudhury, 2001] studies. The increase of LUE with R_D/R_S depends on canopy structure and openness [Alton et al., 2005], and, as we show below, on photosynthetic pathway.

[29] During periods of high R_D/R_S , both sun and shade leaves in the forest were light limited and thus displayed a linear response to APAR. The linear slope between photosynthesis and APAR is defined as the quantum yield of photosynthesis [Larcher, 2003]. In C₃ plants the highest intrinsic quantum yield is ~ 0.085 mol CO₂ mol⁻¹ incident PAR, and its temperature sensitivity is largely driven by photorespiration [Collatz et al., 1998; Ehleringer et al., 1997]. Therefore, canopy LUE under low light closely follows the temperature-dependent photorespiration rate. Forest LUE values reached their lowest values around midday when sun leaves were light saturated and leaf temperatures were high. Forest canopy LUE dropped nonlinearly with temperature and reached its lowest values on the sunniest, hottest days when R_D/R_S was lowest (Figure 6a).

[30] The C₄ canopy maintained high gross LUE over the study period, and was relatively insensitive to variations in cloud cover, irradiance, and leaf temperature. Since C₄ sun and shade leaf photosynthesis was almost always light limited, the relationship between canopy photosynthesis and APAR was linear across the entire PAR range, and thus canopy LUE was very close to the leaf quantum yield. The intrinsic modeled leaf C₄ quantum yield is 0.06 mol CO₂ mol⁻¹ incident PAR [Collatz et al., 1998], although natural C₄ monocots can occasionally exceed this value [Ehleringer et al., 1997]. C₄ plants typically maintain nearly constant quantum yields across a range of temperatures under low-light conditions [Ehleringer et al., 1997; Collatz et al., 1998]. During most daytime hours of the study period, the C₄ grass canopy LUE varied from ~ 0.035 – 0.05 mol CO₂ mol⁻¹ APAR, and, unlike the forest canopy, there was no consistent

relationship with cloud cover or leaf temperature. There was a relationship with R_D/R_S , although it was weak compared with the forest LUE response to R_D/R_S (Figures 6a and 6b).

3.3. Leaf and Soil Water $\delta^{18}\text{O}$ Responses to Cloud Cover Changes

[31] The simplest formulation for leaf water $\delta^{18}\text{O}$ is captured in the steady state prediction for $\delta^{18}\text{O}$ of an evaporating surface, in this case within leaves [Craig and Gordon, 1965; Farquhar et al., 1989; Yakir and Sternberg, 2000]:

$$\delta^{18}O_{lws} = \delta^{18}O_{xy} + \varepsilon_k + \varepsilon^* + (\delta^{18}O_{cv} - \varepsilon_k - \delta^{18}O_{xy}) \frac{e_a}{e_i}. \quad (1)$$

In this equation, $\delta^{18}O_{xy}$ and $\delta^{18}O_{cv}$ are the ¹⁸O/¹⁶O composition of stem xylem (source) water and within-canopy atmospheric water vapor; ε_k is the weighted mean of kinetic fractionations against H₂¹⁸O molecules diffusing through the stomata and across the leaf boundary layer (32 and 21‰, respectively [Cappa et al., 2003]); ε^* is the equilibrium fractionation between liquid and vapor phases over a saturated surface (~ 9.4 ‰ at 298K [Horita and Wesolowski, 1994]); and e_a and e_i are the water vapor pressures (Pa) in the canopy atmosphere and inside leaf stomata, respectively.

[32] Bulk leaf water $\delta^{18}\text{O}$ is often not accurately represented by a steady state formulation [Dongmann et al., 1974; Zundel et al., 1978; Wang et al., 1998; Harwood et al., 1998; Cernusak et al., 2002; Cuntz et al., 2003a; Barbour et al., 2004; Farquhar and Cernusak, 2005; Cernusak et al., 2005; Seibt et al., 2006]. Dongmann et al. [1974] first proposed a nonsteady state leaf water model; our treatment in ISOLSM follows closely from their work, and describes the change in leaf water $\delta^{18}\text{O}$ as an asymptotic approach to a steady state value. The nonsteady state leaf water $\delta^{18}\text{O}$ at time t (i.e., $\delta^{18}O_{lw}(t)$) is calculated implicitly from the steady state estimate ($\delta^{18}O_{lws}(t)$) and the nonsteady state $\delta^{18}O_{lw}$ (i.e., $\delta^{18}O_{lw}(t-1)$) from the previous time step as follows:

$$\delta^{18}O_{lw}(t) = e^{-\frac{\Delta t}{\tau}} \delta^{18}O_{lw}(t-1) + \left(1 - e^{-\frac{\Delta t}{\tau}}\right) \delta^{18}O_{lws}(t). \quad (2)$$

Here, τ is the leaf water time constant (s) and in practice Δt is the model time step (s). τ is calculated separately for sun and shade leaves as the ratio between the leaf stock of water interacting with transpiration (M_l) and the gross water vapor flux out of leaves:

$$\tau = \frac{M_l}{\left(\frac{e_s}{RT_s}\right) g_s}. \quad (3)$$

Here, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T_s is vegetation temperature (K), and g_s is stomatal conductance (sun or shade leaf, m s⁻¹). The leaf water content, M_l , of both sun and shade leaves is set to a constant value of 10 mol m⁻², which is consistent with limited available observations from a temperate needleleaf forest [Seibt et al., 2006] and a tropical broadleaf forest [Förstel, 1978]. In reality, the water content of the average shade leaf is undoubtedly different from the average sun leaf, since there are well-known differences in specific leaf area between sun and shade leaves [Chapin et al., 2002; Larcher, 2003]. However, we lacked data to reliably

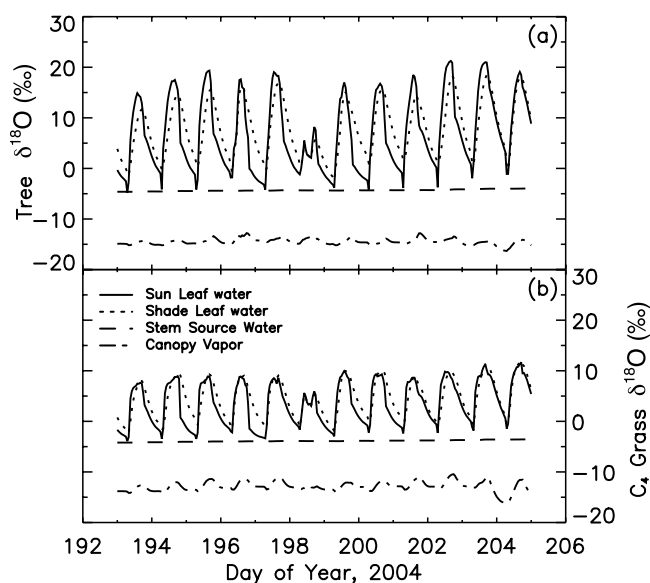


Figure 7. (a) Shown is $\delta^{18}\text{O}$ (‰, relative to VSMOW) of leaf water ($\delta^{18}O_{lw}$) for sun and shade leaves and stem source water ($\delta^{18}O_{xy}$) and canopy vapor ($\delta^{18}O_{cv}$) in the broadleaf deciduous forest canopy simulation. (b) The same quantities plotted for the C₄ grass canopy simulation.

and accurately set this difference and assumed a constant value in both biomes and leaf types.

3.3.1. Broadleaf Deciduous Forest

[33] Simulated nonsteady $\delta^{18}O_{lw}$ for forest sun and shade leaves varied by over 20‰ during the study period (Figure 7a: all $\delta^{18}\text{O}-\text{H}_2\text{O}$ values are reported relative to the Vienna SMOW (VSMOW) scale). The diurnal cycle of $\delta^{18}O_{lw}$ for sun and shade leaves was inversely related to canopy relative humidity. Assuming steady state and no leaf boundary layer fractionation, the change in $\delta^{18}\text{O}$ of an evaporating leaf at steady state will be roughly -0.4‰ for each percent change in relative humidity [Craig and Gordon, 1965]. This slope will be slightly smaller when including isotopic fractionation across the leaf boundary layer and nonsteady state effects. Over the study period, the slope of the linear regression for daytime sun leaf $\delta^{18}O_{lw}$ versus canopy relative humidity was -0.39‰ per % change in relative humidity. By contrast, the slope for shade leaves was lower, approximately -0.28‰ per % change in relative humidity. $\delta^{18}O_{cv}$ varied diurnally between -13‰ and -16‰ in response to canopy transpiration, soil evaporation, and exchange with above-canopy air. This variation was dampened by a 3-h canopy turnover time imposed to account for turbulent air mass exchange between the canopy and atmosphere [Riley et al., 2002].

[34] The sun and shade $\delta^{18}O_{lw}$ differed from the steady state ($\delta^{18}O_{lws}$) and from each other during most of the day (both leaves had the same water content, were at the same temperature, and were exposed to the same canopy vapor pressure and isotopic composition). This difference occurs because the leaf water time constant depends on the stomatal conductance of each leaf type (equation (3)), which is linked to the photosynthetic rate. For much of the day, sun leaf $\delta^{18}O_{lw}$ was close to steady state. Shade leaf $\delta^{18}O_{lw}$ generally lagged sun leaf $\delta^{18}O_{lw}$, with smaller lags on partly cloudy and cloudy days when shade leaf photosynthesis and transpira-

tion were higher because of enhanced diffuse PAR (e.g., DOY 196, 204). Both sun and shade leaves remained elevated above source stem water, especially in the early evening and through much of the night.

[35] As is apparent from $\delta^{18}O_{xy}$ (Figure 7a), variation in modeled soil water $\delta^{18}\text{O}$ ($\delta^{18}O_{sw}$) was minimal across the study period. Even in the upper soil layers where $\delta^{18}O_{sw}$ can strongly increase because of evaporative enrichment [Allison et al., 1983; Riley, 2005], $\delta^{18}O_{sw}$ did not vary greatly because transpiration dominated evapotranspiration in these high-LAI simulations. The magnitude and variability of soil-respired CO₂ isofluxes was fairly minimal, in agreement with earlier Great Plains modeling studies [Riley et al., 2002, 2003; Lai et al., 2006a; Still et al., 2005], and will not be discussed further.

3.3.2. C₄ Grassland

[36] There was an unanticipated difference between the broadleaf forest and C₄ grassland $\delta^{18}O_{lw}$, with peak C₄ grassland $\delta^{18}O_{lw}$ over the period never exceeding 12‰, whereas peak forest $\delta^{18}O_{lw}$ routinely exceeded 18‰ (Figures 7a and 7b), despite identical precipitation $\delta^{18}\text{O}$, radiation, and meteorological forcing (including above-canopy relative humidity). The difference is due to feedbacks between transpiration and within-canopy relative humidity. The canopy relative humidity (not shown) was substantially higher in the C₄ grassland. Canopy relative humidity is calculated in ISOLSM from the canopy temperature and vapor pressure, which depends on exchanges with background vapor pressure, as well as transpiration and soil and canopy evaporation. The canopy relative humidity in the C₄ grassland simulation never dropped below 55% over the study period, whereas modeled canopy relative humidity in the broadleaf forest was only slightly elevated from the measured above-canopy humidity, reaching values below 40% near midday. The higher average daytime relative humidity in the C₄ canopy (relative to the broadleaf forest canopy) depleted $\delta^{18}O_{lw}$.

[37] The higher relative humidity in the C₄ canopy was due to higher transpiration fluxes. Although C₄ plants typically exhibit water use efficiencies roughly twice those of comparable C₃ plants [Percy and Ehleringer, 1984], this difference was overcome by much higher photosynthetic fluxes in the C₄ grass canopy compared to the forest canopy (Figures 4a and 5). The higher relative humidity in the C₄ grass canopy was also due to a lower aerodynamic conductance between the grass canopy and overlying atmosphere compared to the taller and aerodynamically rougher forest, leading to a greater offset between the canopy relative humidity and the background atmosphere. The effect of these differences is also apparent in the greater diurnal cycle of canopy vapor $\delta^{18}\text{O}$ ($\delta^{18}O_{cv}$) in the C₄ grassland (Figure 7b), as it was more strongly influenced by transpiration. The greater diurnal cycle in $\delta^{18}O_{cv}$ also contributed to the transpiration feedback on $\delta^{18}O_{lw}$, although the feedback was primarily due to the change in canopy relative humidity.

3.4. Response of Photosynthetic Isofluxes to Cloud Cover and R_p/R_s

[38] Leaf CO₂ isofluxes depend on both photosynthesis and discrimination against CO¹⁸O. Discrimination against CO¹⁸O ($^{18}\Delta$) depends upon the $\delta^{18}\text{O}$ value of CO₂ in equilibrium with H₂O inside leaf chloroplasts ($\delta^{18}O_c$) and the ratio of chloroplast CO₂ to atmospheric CO₂ concentrations

(C_c/C_a). Gaseous CO₂ equilibrates with liquid water in the mesophyll cells lining the bottom of the stomatal pore via the activity of the carbonic anhydrase enzyme. This equilibration labels CO₂ with the isotopic signature of leaf water plus an equilibrium offset [Farquhar and Lloyd, 1993; Farquhar et al., 1993; Gillon and Yakir, 2000; Affek et al., 2005], and has been shown to be lower in C₄ grasses [Gillon and Yakir, 2001]. The discrimination can be estimated as [Farquhar and Lloyd, 1993; Farquhar et al., 1993; Ciais et al., 1997a; Gillon and Yakir, 2000; Yakir and Sternberg, 2000]

$$^{18}\Delta = \varepsilon_d + \frac{C_c}{C_a - C_c} (\delta^{18}O_c - \delta^{18}O_a). \quad (4)$$

ε_d is the weighted kinetic fractionation accompanying diffusion of CO¹⁸O molecules across the stomata, boundary layer, and the mesophyll walls ($\sim 7.4\%$ [Farquhar and Lloyd, 1993; Gillon and Yakir, 2001]), $\delta^{18}O_c$ is calculated from $\delta^{18}O_{lw}$ and a temperature-dependent fractionation factor [Brenninkmeier et al., 1983], and $\delta^{18}O_a$ is the $\delta^{18}O$ value of background atmospheric CO₂. The $\frac{C_c}{C_a - C_c}$ term arises from mass balance of CO¹⁸O molecules, and when multiplied by net leaf uptake, quantifies the back diffusion or retro-diffusion flux of CO₂ molecules, which have a different $\delta^{18}O$ from when they entered the leaf. This change occurs because only some of the CO₂ entering the leaf is fixed by photosynthesis, while the remainder diffuses out after full or partial isotopic equilibration with leaf water [Farquhar et al., 1993; Flanagan et al., 1994; Gillon and Yakir, 2001].

[39] These bidirectional fluxes, termed F_{al} (atmosphere-to-leaf) and F_{la} (leaf-to-atmosphere), together sum to net photosynthesis, A_{net} (which includes leaf respiration). Each of these global fluxes (roughly 300 and 200 Pg C a⁻¹ for F_{al} and F_{la} , respectively [Ciais et al., 1997a]) is larger than any other carbon flux term in the contemporary carbon budget. Equation (4) can be recast as a function of F_{al} and F_{la} :

$$^{18}\Delta = \frac{F_{la}}{A_{net}} (\delta^{18}O_c - \varepsilon_d - \delta^{18}O_a) + \frac{F_{al}}{A_{net}} \varepsilon_d. \quad (5)$$

[40] The first, right-hand side term captures the effective discrimination associated with the return, or retro-diffused, flux from leaves, and its sign and magnitude vary directly with changes in $\delta^{18}O_c$. The combined net photosynthetic isoflux, in units of $\mu\text{mol } \text{‰} \text{m}^{-2} \text{s}^{-1}$, is the product of photosynthetic discrimination ($^{18}\Delta$) and net leaf photosynthesis (A_{net}):

$$A_{net} \ ^{18}\Delta = F_{la} (\delta^{18}O_c - \varepsilon_d - \delta^{18}O_a) + F_{al} \varepsilon_d = {}^{18}F_{la} + {}^{18}F_{al}. \quad (6)$$

[41] Bidirectional CO₂ isofluxes across leaf stomata can occur during nighttime periods [e.g., Cernusak et al., 2004; Barbour et al., 2007]. Although this effect is potentially important, accurate quantification requires a model with a canopy air space and prognostic calculations of CO₂ and CO¹⁸O concentrations throughout the night [e.g., Seibt et al., 2006], along with a model that accurately predicts stomatal conductance and the concentration of CO₂ in the substomatal

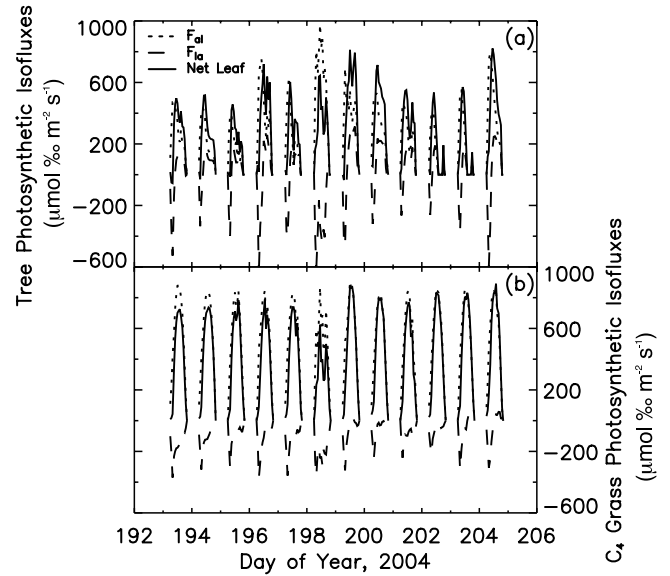


Figure 8. (a) Modeled photosynthetic isofluxes ($\mu\text{mol } \text{‰} \text{m}^{-2} \text{s}^{-1}$), $^{18}F_{al}$ and $^{18}F_{la}$, and their sum ($A_{net} \ ^{18}\Delta$) for the broadleaf tree canopy. (b) The same quantities plotted for the C₄ grass canopy.

air spaces (C_i) and inside leaf chloroplasts (C_c) when photosynthesis is zero. For this study, we focused on daytime isofluxes only.

3.4.1. Broadleaf Deciduous Forest

[42] The $^{18}\Delta$ diurnal cycle (not shown) was strongly related to $\delta^{18}O_{lw}$ enrichment as canopy relative humidity declined with increasing air temperature. There was a decline in $^{18}\Delta$ with increasing cloud cover that followed from a small decrease in $\delta^{18}O_{lw}$ on partly cloudy days, and a large decrease in $\delta^{18}O_{lw}$ on the cloudy day (Figures 1a and 7a). Neither C_c nor leaf temperature (the other components of $^{18}\Delta$) varied appreciably with cloud cover for either leaf type. The bidirectional leaf CO₂ fluxes, F_{al} and F_{la} , varied diurnally with photosynthesis and increased strongly with cloud cover, particularly for shade leaves. The $^{18}F_{al}$ and $^{18}F_{la}$ isofluxes were often in opposition: the gross flux into stomata ($^{18}F_{al}$) always enriched atmospheric $\delta^{18}O_a$ (i.e., was always positive in δ notation), whereas the retro-diffused flux ($^{18}F_{la}$) depleted $\delta^{18}O_a$ in the morning (i.e., a negative isoflux) and enriched it in the afternoon (Figure 8a). The early morning depletion occurred because $\delta^{18}O_{lw}$ (and thus $\delta^{18}O_c$) was relatively depleted from the previous night when it approached $\delta^{18}O_{xy}$ (Figure 7a); also, early morning canopy relative humidity was still high, and the transpiration flux was reduced because of low light levels, thus affecting the leaf water time constant. At this site, where we imposed a fixed $\delta^{18}O_a$ consistent with the measured annual zonal mean (-0.5%), $\delta^{18}O_c$ must exceed $\sim 7.0\%$ before the retro-diffused isoflux ($^{18}F_{la}$) has a positive isotopic forcing (i.e., enriches $\delta^{18}O_a$).

[43] As relative humidity decreased in the late morning, $\delta^{18}O_c$ became more enriched until it exceeded the $\sim 7\%$ threshold and the leaf-to-atmosphere isoflux ($^{18}F_{la}$) reinforced the atmosphere-to-leaf isoflux ($^{18}F_{al}$). The forest sun leaf $\delta^{18}O_{lw}$ corresponding to this $\delta^{18}O_c$ threshold occurred at a canopy relative humidity of $\sim 60\%$. Only on the cloudiest

and coolest day (DOY 198) did $\delta^{18}O_{lw}$ stay below this value throughout the day (Figures 7a and 8a). The greatest $\delta^{18}O_{lw}$ enrichment occurred on the sunniest, hottest day when canopy relative humidity was lowest (DOY 202), and $^{18}F_{la}$ was mostly positive. Because of high leaf temperatures on DOY 202, however, A_{net} and net leaf isofluxes ($A_{net}^{18}\Delta$ or $^{18}F_{al} + ^{18}F_{la}$) were lowest of the study period.

[44] If $\delta^{18}O_{lw}$ and $\delta^{18}O_c$ are sufficiently negative, the net leaf isoflux can deplete $\delta^{18}O_a$. The $\delta^{18}O_c$, where negative net photosynthetic isotope fluxes ($^{18}F_{al} + ^{18}F_{la} < 0$) occur is a function of $\delta^{18}O_a$, the C_i/C_a ratio, and ε_d . $\delta^{18}O_c$ values more depleted than approximately -4.2‰ caused net forest photosynthetic isofluxes to be negative. During the 12-day study period, negative CO₂ isofluxes occurred only briefly on DOY 193 when $\delta^{18}O_{lw}$ approached $\delta^{18}O_{xy}$ and photosynthesis was just beginning (Figure 8a). Because the $\delta^{18}O$ of growing season precipitation is rarely more depleted than -5‰ at these latitudes [Welker, 2000; Bowen and Wilkinson, 2002], forest photosynthetic isofluxes will almost always enrich $\delta^{18}O_a$. At higher latitudes where precipitation $\delta^{18}O$ is lower, leaf CO₂ isofluxes can deplete $\delta^{18}O_a$ [e.g., Francey and Tans, 1987; Farquhar et al., 1993; Ciais et al., 1997b], because of $^{18}F_{la}$ outweighing $^{18}F_{al}$.

[45] The net photosynthetic isoflux ($A_{net}^{18}\Delta$, solid line in Figure 8a) generally followed the daily variations in canopy photosynthesis (Figure 4a), with larger isofluxes on partly cloudy days (DOY 196–197, 199, 204) than on clear, sunny days (DOY 193–195, 201–203), an effect driven by shade leaves. However, the cloudy day (DOY 198) exhibited intermediate CO₂ isofluxes: although it had the largest peak photosynthesis, this was countered by the lowest $\delta^{18}O_{lw}$ and $^{18}\Delta$ of the study period (Figures 4a, 7a, and 8a). Partitioning the net leaf isoflux ($A_{net}^{18}\Delta$) into $^{18}F_{al}$ and $^{18}F_{la}$ (equation (6)) reveals the canopy response to cloud cover in more detail. The $^{18}F_{al}$ isoflux increased strongly with increasing cloud cover because of an increase in shade leaf and canopy photosynthesis with cloud cover. By contrast, $^{18}F_{la}$ did not exhibit a strong relationship with cloud cover during daytime hours of the study period. Indeed, both negative and positive $^{18}F_{la}$ values occurred for a range of cloud cover, as $\delta^{18}O_{lw}$ and thus $\delta^{18}O_c$ alternated from relatively depleted values in the morning to enriched values in the afternoon after they crossed the $\sim 7.0\text{‰}$ threshold. Thus, for the sum of $^{18}F_{al}$ and $^{18}F_{la}$ (i.e., $A_{net}^{18}\Delta$), no clear response to cloud cover occurred. When net photosynthetic isofluxes are plotted against R_D/R_S , however, there was a weak negative relationship, with the highest isofluxes centered at an R_D/R_S of ~ 0.4 . This was driven by $^{18}F_{la}$, which peaked around this value in our simulations; at R_D/R_S values above ~ 0.6 , $^{18}F_{la}$ was always negative. The peak isoflux at an R_D/R_S of 0.4 was not driven solely by photosynthetic responses to diffuse irradiance, as peak canopy photosynthesis occurred at higher R_D/R_S values. Rather, it was the combination of enhanced photosynthesis with higher $\delta^{18}O_{lw}$ due to lower canopy relative humidity at this particular R_D/R_S . These conditions occurred around midday on the partly cloudy days (DOY 196, 199, 204) that have the largest peak and cumulative daily isofluxes.

3.4.2. C₄ Grassland

[46] There were large differences in leaf isofluxes between the forest and C₄ grassland simulations that arose from differences in the internal CO₂ concentrations between these different physiological types, as well as differences in their

$\delta^{18}O_c$ values (section 3.3). Comparing chloroplast CO₂ concentrations between C₃ and C₄ plants is difficult since the C₄ pathway concentrates CO₂ around Rubisco in the bundle sheath cell chloroplasts, and raises CO₂ concentrations to much higher levels than occur in mesophyll cell chloroplasts of C₃ plants [von Caemmerer and Furbank, 2003]. For these simulations, we used the C_i value calculated in ISOLSM. Typical C_i/C_a ratios for C₄ plants range from 0.2 to 0.4, whereas those for most C₃ plants are 0.6–0.8 [Pearcy and Ehleringer, 1984; Collatz et al., 1991, 1992]. At similar photosynthetic rates, F_{la} can be much higher in C₃ than C₄ plants [Still et al., 2005; Hoag et al., 2005]. For example, a C_i/C_a ratio of 0.8 produces a F_{la} four times larger than a ratio of 0.2 produces for the same net leaf flux.

[47] The C₄ grass photosynthetic isoflux, dominated by $^{18}F_{al}$ from sun leaves, is almost always larger and less variable than the forest isoflux (Figure 8b). However, $^{18}F_{la}$ is smaller in the grass than in the forest, and it remains negative throughout the day and never reinforces $^{18}F_{al}$, except for three brief periods on DOY 199, 203, and 204 (Figures 8a and 8b). This negative isotopic forcing on the atmosphere is due to the lower $\delta^{18}O_{lw}$ (Figures 7a and 7b) and the larger ε_d in the C₄ grass simulation. $\delta^{18}O_c$ must exceed a threshold value of $\sim 7.9\text{‰}$ before the $^{18}F_{la}$ from C₄ plants has a positive isotopic forcing on the atmosphere. However, because leaf temperatures exceeded 30°C on the days with highest $\delta^{18}O_{lw}$ (DOY 199, 200, 202), and the CO₂-H₂O fractionation has a sensitivity of -0.2‰ K^{-1} [Brenninkmeier et al., 1983; Ciais et al., 1997a], $^{18}F_{la}$ is almost always negative during the study period (Figure 8b).

[48] Because the magnitude of $^{18}F_{la}$ will be much smaller in C₄ plants compared to C₃ plants because of lower C_i/C_a ratios [Still et al., 2005] and reduced equilibration between CO₂ and H₂O from lower carbonic anhydrase activity [Gillon and Yakir, 2001], photosynthesis by C₄ plants will almost always enrich $\delta^{18}O_a$. The positive isotopic forcing associated with $^{18}F_{al}$ will in almost every case be much larger than the negative isotopic forcing from $^{18}F_{la}$. Because C₄ plants are largely restricted to tropical and subtropical savannas and grasslands [Still et al., 2003], the $\delta^{18}O$ of precipitation and thus of plant xylem water ($\delta^{18}O_{xy}$), is relatively enriched [Bowen and Wilkinson, 2002]. For example, Ometto et al. [2005] measured Amazonian C₄ pasture grasses with $\delta^{18}O_{xy}$ values between -3‰ and -9‰ , and mean values around -5‰ . These values, and measurements from C₄-dominated tallgrass prairies in Oklahoma and Kansas [Helliker et al., 2002; Riley et al., 2003; Lai et al., 2006b], are similar to the mean predicted $\delta^{18}O_{xy}$ at our site (Figure 7). Given a typical midday C₄ plant C_i/C_a ratio of 0.3 and assuming complete equilibration, $\delta^{18}O_c$ at this site would have to be below approximately -17.3‰ for net C₄ photosynthetic isofluxes to deplete $\delta^{18}O_a$. Using precipitation $\delta^{18}O$ regressions from Bowen and Wilkinson [2002], $\delta^{18}O_{lw}$ and thus $\delta^{18}O_c$ values that are sufficiently depleted occur above $\sim 60^\circ\text{N}$. Although C₄ plants do grow north of 50°N [e.g., Schwarz and Redmann, 1988; Beale and Long, 1995], they are uncommon and do not substantially affect regional carbon fluxes.

[49] While C₄ grass photosynthesis decreased slightly with increasing cloud cover, net photosynthetic isofluxes ($A_{net}^{18}\Delta$) exhibited no clear relationship with cloud cover. $^{18}\Delta$ did not vary with cloud cover, as an increase in the F_{al} component of $^{18}\Delta$ due to an increase in C_c with cloud cover

was countered by a decrease in the F_{la} component of $^{18}\Delta$ driven by the slight decrease of $\delta^{18}O_{lw}$ and $\delta^{18}O_c$ with cloud cover. Over the study period, the flux-weighted mean C_4 grassland canopy $^{18}\Delta$ was $\sim 12\text{‰}$, with $\sim 2/3$ of this from ε_d . There was a weak negative response of $A_{net}^{18}\Delta$ to increasing R_D/R_S , just as there was between C_4 canopy photosynthesis and R_D/R_S . In both cases, peak uptake occurred at R_D/R_S values between 0.2 and 0.4, and declined sharply above 0.4. There was a strong positive relationship (slope = 0.46; $r^2 = 0.89$) between the net C_4 photosynthetic isoflux and incident PAR (i.e., the canopy isotope light response curve; Figure 9).

3.5. Sensitivity to Leaf Area Index

3.5.1. Broadleaf Deciduous Forest

[50] We examined the sensitivity of our results to LAI given the importance of this canopy characteristic in the response to clouds and R_D/R_S as highlighted by earlier studies [e.g., Rocha et al., 2004; Urban et al., 2007; Knohl and Baldocchi, 2008]. We altered LAI values throughout the study period, with other model driving data unchanged from control simulations. Relative to the control, forest canopy photosynthesis and transpiration declined in the low-LAI simulation and increased in the high-LAI one, driven by the shade leaf response. The changes in canopy transpiration lowered or raised canopy relative humidity by a few percent relative to the base case. The impact of changing LAI on canopy relative humidity and $\delta^{18}O_{lw}$ was most dramatic on the cloudy day (DOY 198) when R_D/R_S and diffuse PAR were highest. This day exhibited the highest peak shade leaf and canopy photosynthesis in the base LAI simulation, and also the greatest humidification of the canopy from transpiration (since wind speed and exchange with the atmosphere was not different from adjacent days). On DOY 198, peak daytime steady state $\delta^{18}O_{lw}$ values were raised by 1.4‰ in the low-LAI (3.5) simulation relative to the base case, and lowered by 0.3‰ in the high-LAI (6.5) simulation.

[51] Taken in isolation, this transpiration feedback on $\delta^{18}O_{lw}$ would increase (decrease) $^{18}\Delta$ in the lower- (higher-) LAI simulations. However, the retroflux scalar (equation (4)) was lowered in the reduced LAI simulation as the relative contribution of shade leaves with slightly higher C_c values

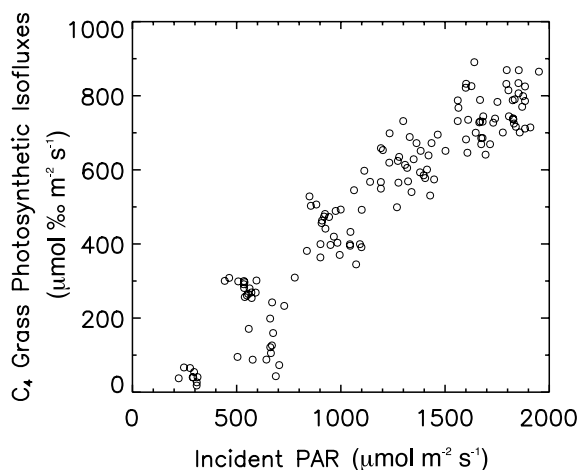


Figure 9. Modeled daytime net photosynthetic isofluxes ($A_{net}^{18}\Delta$, $\mu\text{mol } \text{‰} \text{m}^{-2} \text{s}^{-1}$) plotted against the observed daytime incident PAR for the C_4 grass canopy simulation.

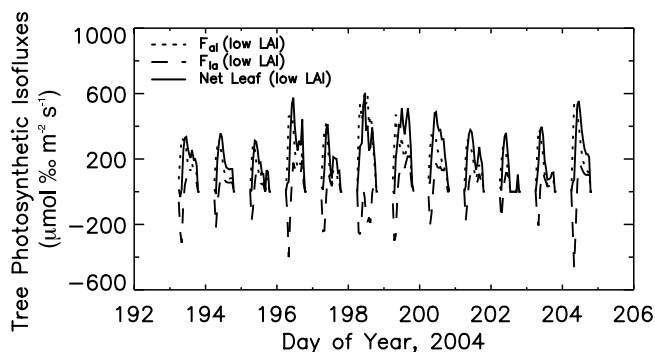


Figure 10. Modeled net photosynthetic isofluxes ($\mu\text{mol } \text{‰} \text{m}^{-2} \text{s}^{-1}$), $^{18}F_{al}$ and $^{18}F_{la}$, and their sum for the low-LAI (3.5) broadleaf tree canopy simulation.

declined relative to the base LAI. The effect of these differences was to quantitatively reduce the importance of $^{18}F_{la}$ in the reduced LAI simulations, and as a result, net photosynthetic isofluxes ($A_{net}^{18}\Delta$) were more dominated by $^{18}F_{al}$. Because $^{18}F_{al}$ scales with leaf photosynthesis and is unaffected by $\delta^{18}O_{lw}$, it exhibited a positive correlation with cloud cover; as LAI was reduced, a coherent relationship between $A_{net}^{18}\Delta$ and cloud cover emerged. Indeed, in the low-LAI simulation, net photosynthetic isofluxes on DOY 198 reached higher peak values than on the partly cloudy days (DOY 196, 199, 204) that had the highest isofluxes in the base LAI case (Figure 10). This resulted from a combination of enhanced shade leaf photosynthesis and enriched $\delta^{18}O_{lw}$ due to a reduced transpiration feedback on canopy relative humidity. $\delta^{18}O_{lw}$ and $\delta^{18}O_c$ were even high enough on DOY 198 in the low-LAI simulation to briefly surpass the $\sim 7.0\text{‰}$ forest threshold (section 3.4.1), and $^{18}F_{la}$ reinforced $^{18}F_{al}$ to enrich $\delta^{18}O_a$ (Figure 10).

3.5.2. C_4 Grassland

[52] We also assessed the sensitivity to LAI in the C_4 grass canopy, with other driving variables held constant. For these simulations, we decreased the LAI from the base case by one third (to a LAI of 2.5) and increased it twofold (to a LAI of 7.5). The reduced LAI lowered canopy photosynthesis and transpiration in the C_4 grassland relative to the base case. The expected response led to several changes that modified photosynthetic isofluxes, primarily via the same transpiration feedback on canopy relative humidity and $\delta^{18}O_{lw}$ that was found for the forest simulations. In particular, $\delta^{18}O_{lw}$ values increased in the reduced LAI simulations as the transpiration flux was lowered and the canopy relative humidity more closely tracked the observed, above-canopy humidity shown in Figure 2. Unlike the forest simulations, reducing LAI did not strengthen the relationship between leaf isofluxes and cloud cover. The negative response of C_4 photosynthesis to increasing cloud cover and R_D/R_S was similar for the different LAI values, and the isotope light response curve remained linear in all LAI simulations (Figure 9).

4. Discussion and Conclusions

[53] Terrestrial ecosystems are likely to respond to changes in irradiance, temperature, relative humidity, and R_D/R_S driven by changes in cloud cover. For example, Min and Wang [2008] showed that interannual cloud cover variations

drive interannual carbon fluxes in a temperate broadleaf forest. Clouds influence other ecological processes like shoot growth and reproduction [Graham *et al.*, 2003], photosynthesis of understory species [Johnson and Smith, 2006, 2008], tree growth [Williams *et al.*, 2008], and range boundaries [Fischer *et al.*, 2009]. At the leaf scale, diffuse light is used less efficiently for photosynthesis than direct light [Brodersen *et al.*, 2008], whereas at the canopy scale, the opposite response is observed. Yakir and Israeli [1995] documented how artificially reducing irradiance reduced growth but increased ¹³C discrimination in an experimental plantation; this result is buttressed by work showing that increasing R_D/R_S in a multilayer canopy model increases C_i/C_a and ¹³C discrimination [Knobl and Baldocchi, 2008].

[54] Our results illustrate the myriad impacts that clouds have on biosphere-atmosphere CO¹⁸O exchanges. We examined a sequence of midsummer days in which the light intercepted by the canopy varied from irradiance dominated by direct beam radiation (sunny) to days with high total irradiance but an increasing diffuse fraction (partly cloudy) to days in which almost all irradiance was diffuse (cloudy). This variation allowed a detailed examination of the mechanisms that drive ecosystem isotopic states and exchanges, and to explore how ecological properties influence the mechanisms and responses. Although this study only examined a portion of the growing season, we can hypothesize that, when integrated to a larger scale, clouds have a substantial impact on biosphere-atmosphere CO¹⁸O exchanges through their varied impacts on direct and diffuse radiation, leaf temperature, relative humidity, leaf water enrichment, and bidirectional leaf fluxes (F_{al} and F_{la}). These effects vary strongly with canopy structure, LAI, precipitation $\delta^{18}O$, and photosynthetic pathway.

[55] The forest canopy increased photosynthesis with increasing cloud cover and R_D/R_S , whereas the C₄ grass canopy exhibited a negative response to both increasing cloud cover and R_D/R_S . The LUE of the forest canopy was strongly related to R_D and leaf temperature, whereas the grass canopy LUE was relatively insensitive to environmental conditions. Compared to sunny conditions, the forest canopy exhibited larger photosynthetic isofluxes on partly cloudy days. The response of forest leaf isofluxes to cloud cover depends strongly on LAI, primarily via a feedback of transpiration on canopy relative humidity and $\delta^{18}O_{lw}$. Whereas the relationship between forest canopy photosynthesis and cloud cover (i.e., Figure 4b) became stronger with increasing LAI, the relationship between canopy photosynthetic isofluxes ($A_{net}^{18}\Delta$) and cloud cover weakened with increasing LAI.

[56] In contrast, photosynthesis and isofluxes in the C₄ grass canopy declined with increasing cloud cover and R_D/R_S , regardless of LAI. This opposite response resulted primarily from the lower effective shade leaf LAI in the lower-stature grass canopy compared to the broadleaf forest, as well as the near-constant light limitation on photosynthesis in C₄ sun and shade leaves. These different responses represent a fundamental functional distinction between these globally important vegetation types.

[57] It is important to acknowledge some of the modeling limitations in the work reported here. One deficiency is the lack of a separate energy balance and leaf temperature calculation for shade leaves. High LAI values are not uncommon

in many forests, and the fraction of canopy photosynthesis attributable to shade leaves increases with LAI. An incorrect shade leaf temperature will impact canopy CO¹⁸O exchanges in several ways. First, $\delta^{18}O_{lw}$ is sensitive to leaf temperature because of its impact on the saturation vapor pressure inside leaves. Second, each 1°C increase in leaf temperature reduces the equilibrium liquid-vapor fractionation by ~0.07‰ for typical ambient temperatures [Horita and Wesolowski, 1994], and also reduces the equilibration fractionation between CO₂ and H₂O by -0.2‰ [Brenninkmeier *et al.*, 1983]. Leaf temperature also influences the leaf surface relative humidity and stomatal conductance, which in turn impacts C_i and bidirectional CO₂ fluxes across stomata. Finally, leaf temperature affects photosynthesis and respiration [Collatz *et al.*, 1991, 1992]. However, we tested the sensitivity of our results by varying shade leaf temperature and found the impact to be small (not shown).

[58] We also tested the impact of varying photosynthetic capacity (V_{max}) between sun and shade leaves. When we halved shade leaf V_{max} in the forest simulation, there was no change in shade leaf or total canopy photosynthesis, simply because shade leaf photosynthesis is always light limited. This prediction confirms the results of Leuning *et al.* [1995], who showed with a multilayer canopy model that total photosynthesis of shaded leaves is insensitive to the nitrogen distribution within a canopy. And, as shown by de Pury and Farquhar [1997], even with nitrogen and photosynthetic capacity distributed between sun and shade leaves as a function of optical depth in the canopy, the photosynthetic rate of shade leaves is always limited by light (i.e., by electron transport rate) and not by Rubisco.

[59] We contend that these model limitations have small impacts on our conclusions. One could test this assumption by conducting similar site-scale analyses with a one-dimensional, multilayer canopy models that also included turbulent transport and leaf nitrogen variations within the canopy [e.g., Baldocchi and Bowling, 2003; Knobl and Baldocchi, 2008]. However, for predictions of the impact of cloudiness on ecosystem-atmosphere CO¹⁸O exchanges at regional to global scales, a sun/shade model like ISOLSM that has already been integrated into global climate models [Noone *et al.*, 2004; Buenning *et al.*, manuscript in preparation, 2009] is preferable for computational reasons.

[60] Although the differences in the response to cloudiness between C₃ and C₄ vegetation is largely due to differing F_{al} and F_{la} and photosynthetic rates, there are additional physiological and anatomical differences that would further impact CO¹⁸O exchanges that we did not consider. The differences between forest and grassland isofluxes would have been even larger if we had reduced the C₄ grass carbonic anhydrase activity [Gillon and Yakir, 2001]. For the work presented here we assumed complete equilibration between CO₂ and $\delta^{18}O_{lw}$ for both vegetation types, as we were interested primarily in ecosystem responses to changes in cloud cover as mediated by canopy structure and photosynthetic pathway. Also, we lacked field data on equilibration in this region, and recent studies suggest conflicting results for assigning appropriate values in modeling studies. Gillon and Yakir [2001] suggest a mean equilibration value of 0.4 for C₄ grasses; recent work with C₄ corn plants suggests values closer to C₃ plants [Affek *et al.*, 2005]. Laboratory measurements with both wild-type and transgenic individuals

of a C₄ dicot also suggest higher values from *in vitro* carbonic anhydrase assays [Cousins *et al.*, 2006]. Moreover, a recent phylogenetic analysis suggests that reduced carbonic anhydrase activity may not be simply a trait of grasses with the C₄ photosynthetic pathway, but may be more widespread among tropical grass lineages, including several widespread and productive C₃ grass species [Edwards *et al.*, 2007]. We also did not consider the large δ¹⁸O_{hw} enrichment observed along leaf veins of C₄ grasses [Helleriker and Ehleringer, 2000], which can affect leaf CO¹⁸O fluxes.

[61] This study demonstrates the complex responses of terrestrial ecosystems to changes in cloud cover, particularly with respect to oxygen isotope fluxes of CO₂. The broadleaf forest and C₄ grassland are predicted to have fundamentally different responses to changes in cloud cover. Our findings also identify a potentially important feedback of transpiration on canopy relative humidity, δ¹⁸O_{cvs}, and δ¹⁸O_{hw}, and thus on leaf-to-atmosphere CO₂ isofluxes. We believe that some of the unexplained variation in δ¹⁸O_a is driven by changes in clouds given the strong responses we show here and decadal-scale changes in cloud cover and aerosols observed in many locations.

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