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Seasonal exchange of CO$_2$ and $\delta^{18}$O-CO$_2$ varies with postfire succession in boreal forest ecosystems

L. R. Welp, J. T. Randerson, and H. P. Liu

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[1] Seasonal cycles of atmospheric CO$_2$ and $\delta^{18}$O-CO$_2$ at high northern latitudes have the potential to serve as indicators of ecological change in response to climate changes. Effective interpretation of these observations requires an understanding of how different species and ecosystems contribute to biosphere-atmosphere exchange. Here we examined the effect of postfire stand age in boreal forest ecosystems on the seasonal distribution of CO$_2$ and $\delta^{18}$O-CO$_2$ fluxes. We measured net CO$_2$ fluxes in a 3-year burn scar, a 15-year trembling aspen stand, and an 80-year black spruce stand in interior Alaska using eddy covariance. By combining measurements of the oxygen isotopic composition of ecosystem water pools at each stand with measured CO$_2$ fluxes, we predicted half-hourly $\delta^{18}$O-CO$_2$ fluxes and used a one-box atmosphere model to make relative comparisons of the effect of stand age on the shape and amplitude of the seasonal cycle of CO$_2$ and $\delta^{18}$O-CO$_2$. A shorter growing season and higher rates of net ecosystem uptake during midsummer at the 15-year stand resulted in a larger seasonal CO$_2$ amplitude and a delay in the drawdown of atmospheric CO$_2$ as compared with the 80-year stand. Reduced levels of gross primary production isoforcing from the 15-year stand during spring and early summer caused atmospheric $\delta^{18}$O-CO$_2$ to increase more gradually between April and June as compared with fluxes from the 80-year stand. Our analysis suggests that increased boreal forest disturbance would delay the phase of CO$_2$ drawdown at high northern latitudes, but would advance the phase of $\delta^{18}$O-CO$_2$ drawdown.

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1. Introduction

[2] Climate change caused by increased greenhouse forcing over the next century is expected to be greatest in arctic and boreal regions, in part from temperature-albedo feedbacks linked with reduced snow and ice cover [Cess et al., 1991; Arctic Climate Impact Assessment (ACIA), 2004]. Indeed, observed rates of warming in the Arctic over the last few decades have been 50% larger than the global mean [Intergovernmental Panel on Climate Change (IPCC), 2001], and acceleration of this trend is predicted as greenhouse gas concentrations increase [ACIA, 2004]. Evidence that warmer spring temperatures during recent decades have lengthened the terrestrial growing season comes from satellite-derived observations of Normalized Difference Vegetation Index (NDVI) [Myneni et al., 1997; Tucker et al., 2001; Zhou et al., 2001; Bogaert et al., 2002; Hicke et al., 2002; Nemani et al., 2003; Slayback et al., 2003; Angert et al., 2005], passive microwave satellite observations and modeling of soil freeze/thaw transitions [McDonald et al., 2004; Smith et al., 2004], analysis of atmospheric carbon dioxide time series [Keeling et al., 1996; Randerson et al., 1997; Angert et al., 2005], and phenology records [Walther et al., 2002].

[3] The increased growing season length may allow for greater rates of photosynthesis and carbon accumulation during spring and summer [Frolking et al., 1996; Randerson et al., 1999; Kimball et al., 2001; Myneni et al., 2002; Tanja et al., 2003; White and Nemani, 2003], whereas warming air and soil temperatures may stimulate higher rates of respiration [Chapin et al., 1996; Goulden et al., 1998]. Warming of northern continental interiors may also increase fire activity [Stocks et al., 1998; Gillett et al., 2004; Flannigan et al., 2005], causing a decrease in the mean age of forests and a shift in species composition. The combined effect of these multiple changes in northern ecosystem processes on biome-level carbon fluxes remains challenging to measure or predict. In this respect, atmospheric trace gas observations have the potential to serve as an important top-down constraint of large-scale ecological change.

[4] The seasonal cycles in concentrations of atmospheric CO$_2$ and heavy stable isotopologues ($^{13}$CO$_2$ and C$^{18}$OO) at high northern latitudes integrate carbon fluxes from boreal and arctic biomes across both North America and Eurasia. Thus they record, and have the potential to help diagnose,
terrestrial ecosystem processes and their response to climate change at the biome scale. Here we focus on two of these tracers, CO₂ and C³¹⁸O₂, and the sensitivity to species composition of the boreal forests as it varies with postfire stand age. These two tracers are complementary; the seasonal cycle of atmospheric CO₂ is sensitive to the net carbon balance of ecosystems, whereas the seasonal cycle of C³¹⁸O₂ is sensitive to the magnitude of the gross CO₂ fluxes (i.e., photosynthesis and respiration) and the hydrological cycle. Effective use of these tracers as large-scale ecological indicators of climate change [Menzel and Fabian, 1999; Walther et al., 2002] requires improved understanding of the processes that control CO₂ and C³¹⁸O₂ fluxes in northern ecosystems.

6] Typically, the concentration of CO₂ in northern latitudes decreases from May through August, owing to photosynthetic uptake exceeding ecosystem respiration during summer months. Increasing concentrations follow from September through April as a result of slow, continuous ecosystem respiration fluxes to the atmosphere and negligible rates of photosynthesis [Bolin and Keeling, 1963]. From the 1960s through the latter part of the 1990s, the seasonal cycle of atmospheric CO₂ measured at high northern latitudes increased in amplitude (peak-to-trough) and the phase advanced [Conway et al., 1994; Keeling et al., 1996; McDonald et al., 2004].

6] Two classes of mechanisms have been proposed to account for the observed changes in the seasonal cycle of CO₂. The first involves direct climate controls on the timing and magnitude of northern ecosystem fluxes, including temperature, radiation, the timing of soil thaw, and drought [Keeling et al., 1996; Randerson et al., 1999; McDonald et al., 2004; Angert et al., 2005]. The second involves a change in distribution of plant functional types caused by increases in disturbance [Zimov et al., 1999]. Measurements from Siberian shrub and forest tundra ecosystems show that species assemblages associated with early stages of succession have enhanced rates of photosynthetic uptake during the summer in addition to enhanced respiratory losses during fall, partly from the removal of the less productive and more insulating moss layer. On the basis of these results, Zimov et al. [1999] hypothesize that increased disturbance in arctic and boreal biomes has increased the abundance of early successional ecosystems and this, in turn, has contributed to the observed increases in the CO₂ seasonal amplitude.

7] In contrast to the CO₂ record, the much shorter C³¹⁸O₂ record (measured and reported as δ¹⁸O-CO₂) shows no unidirectional, fossil fuel–controlled trend (as there is for CO₂ and δ¹³C) and intrannual variability in the annual mean and seasonal amplitude is much larger [Trolier et al., 1996; Ciais and Meijer, 1998]. The seasonal cycle and latitudinal gradient of δ¹⁸O-CO₂ are controlled largely by gross CO₂ exchange with the terrestrial biosphere as well as isotopic fractionation of meteoric water and climatic factors such as temperature and humidity [Francey and Tans, 1987; Ciais and Meijer, 1998; Peylin et al., 1999; Riley et al., 2002; Cuntz et al., 2003a].

8] When CO₂ diffuses into a leaf, it rapidly reaches isotopic equilibrium with the evaporatively enriched leaf water pool because carbonic anhydrase catalyzes CO₂ hydration [Mills and Urey, 1940; Farquhar et al., 1993; Yakir and Sternberg, 2000]. Only a portion of the CO₂ entering the leaf gets fixed as organic matter before the remainder diffuses back out of the leaf and returns to the atmosphere. This retrodiffusive flux is approximately twice as large as gross primary production and carries the leaf water isotopic signature [Francey and Tans, 1987; Friedli et al., 1987; Farquhar et al., 1993]. Similarly, CO₂ produced by soil respiration is in contact with soil water for a sufficient time to equilibrate with water in the upper layers of the soil surface before diffusing into the atmosphere [Hesterberg and Siegenthaler, 1991; Tans, 1998; Miller et al., 1999]. Leaf water is isotopically enriched as compared with soil water because of greater evaporation rates at the leaf surface than the soil surface. As a result, photosynthesis typically enriches atmospheric δ¹⁸O-CO₂ (more positive) and respiration depletes δ¹⁸O-CO₂ (more negative) [Ciais et al., 1997]. This large difference between the δ¹⁸O of leaf water carried by the photosynthetic CO₂ flux and soil water carried by the respiratory CO₂ flux, has the potential to be used to partition net CO₂ fluxes into one-way gross flux components [Ogee et al., 2004]. Successful partitioning of measured net CO₂ fluxes into foliar and soil components using δ¹⁸O has been demonstrated at the site level over discrete periods of time during the growing season [Yakir and Wang, 1996; Bowling et al., 2003b]. In principle, a similar partitioning at the global scale is possible; however, photosynthetic and respiratory end-members vary widely and are incompletely known.

9] For both CO₂ and δ¹⁸O-CO₂, the role of different ecosystems and their contribution to biome-level fluxes remain poorly understood. Here we examine the effects of boreal forest postfire stand age on the seasonal cycle of CO₂ and δ¹⁸O-CO₂ using a combination of CO₂ flux and oxygen isotope measurements from three stands in a fire chronosequence in interior Alaska. Species composition varies with time since fire and has the potential to influence rates of carbon uptake [Littvak et al., 2003; Bond-Lamberty et al., 2004], respiration rates [Wang et al., 2002; O’Neill et al., 2003], growing season length [Falge et al., 2002], and leaf diffusion properties such as stomatal conductance [Ewers et al., 2005], as well as the use and cycling of meteoric water by the ecosystem [Flanagan et al., 1997]. Each of these differences could lead to changes in the seasonality of CO₂ or δ¹⁸O-CO₂ fluxes. We estimate atmospheric iso forcing for each of our three stands following the approach described by Flanagan [2005]. We examine, in detail, differences in biosphere-atmosphere exchange between a deciduous broadleaf forest and an evergreen conifer forest. In a final step, we investigate stand age effects on the seasonal cycles of CO₂ and δ¹⁸O-CO₂ using a one-box atmospheric model. This allowed us to explore the Zimov et al. [1999] hypothesis in the context of changes in species composition within boreal forest ecosystems.

2. Site Description

10] We measured water isotopes and CO₂ fluxes at three stands that were part of a fire chronosequence in interior Alaska, near the town of Delta Junction (63°54′N, 145°40′W). This is an area of discontinuous permafrost that experiences seasonal extremes in climate. Temperature measurements at nearby Big Delta (64°00′N, 145°44′W),
from 1937 to 2004 by the Western Regional Climate Center, show the average daily minimum temperature in January was \(-24^\circ\text{C}\) and the average daily maximum during July was \(21^\circ\text{C}\) (Western U.S. climate historical summaries, 2004, Western Regional Climate Center, http://www.wrcc.dri.edu/climsum.html) (hereinafter referred to as WRCC data, 2004). For the 30-year period, from 1971 to 2000, the average annual precipitation in this region was 303 mm and the growing season length (air temperatures above freezing) was approximately 115 days from mid-May to early September (WRCC data, 2004). Our sites were located on relatively well drained silty loam soil [King et al., 2002], and were burned 3 years, 15 years, and approximately 80 years prior to the 2002 growing season. During the summer of 2002, rainfall measured by two tipping bucket rain gauges was 12 mm in May, 66 mm in June, 45 mm in July, 97 mm in August, and 53 mm in September [Liu et al., 2005]. Total precipitation during the 2002 calendar year was approximately 305 mm. Time series of average daily maximum photosynthetic photon flux density (PPFD) above the canopy, relative humidity, and 2 m air temperature are shown in Figure 1, along with soil temperatures at a depth of 10 cm at each stand. Differences in soil temperature between stands were caused partly by differences in canopy structure and leaf area that controlled the amount of shortwave radiation absorbed by the soil/moss surface.

[11] The most recently disturbed stand (the 3-year stand) was burned during the 1999 Donnelly Flats fire (\(63^\circ54'\text{N}, 145^\circ44'\text{W}\)) [Liu et al., 2005]. In 2002, 30% of the ground surface was covered by bunch grasses (Festuca altaiaca) and deciduous shrubs less than 1 m tall. Charred dead spruce boles remained standing and partial moss cover consisted of Polytrichum ssp. and Ceratodon ssp.

[12] The intermediate aged stand (the 15-year stand) burned during the 1987 Granite Creek fire (\(63^\circ55'\text{N}, 145^\circ23'\text{W}\)) and, by 2002, was dominated by an overstory of deciduous aspen trees (Populus tremuloides) with a mean canopy height of 5 m and willow shrubs (Salix spp.). The understory vegetation included smaller shrubs (Ledum palustre, Rosa acicularis, Vaccinium uliginosum and Vaccinium vitisidaea), grasses (Festuca spp. and Calamagrostis lapponica) and moss (Polytrichum ssp.) [Liu et al., 2005]. The understory also included regrowing black spruce (Picea mariana). By 2002, some of the dead spruce boles remained standing, but most had fallen over.

[13] The mature conifer end-member of our study (the 80-year stand) was an approximately 80-year-old stand of black spruce (Picea mariana) (\(63^\circ53'\text{N}, 145^\circ44'\text{W}\)), 5 km south of the 3-year stand and less than 20 km southwest of the 15-year stand [Liu et al., 2005]. The mean canopy height was 4 m, and the sparse understory consisted of shrubs (Ledum palustre, Vaccinium uliginosum and Vaccinium vitisidaea). The dominant ground cover was feathermoss (Pleurozium schreberi and Rhizidium rugosum) and lichen (Cladonia spp. and Stereocaulon ssp.). Moss and fibrous organic layer thickness was approximately 11 cm [Manies et al., 2004].

3. Methods
3.1. Eddy Covariance and Micrometeorological Measurements

[14] Eddy covariance measurements of net ecosystem exchange (NEE) \(\text{CO}_2\) fluxes were made using an open-path \(\text{CO}_2\) analyzer (LiCor 7500, LI-COR, Inc., Lincoln, Nebraska) and a 3-D sonic anemometer (CSAT3, Campbell Scientific, Inc., Logan, Utah) at each stand. Vertical and horizontal wind velocity, sonic temperature, and \(\text{CO}_2\) and water vapor concentrations were recorded at 10 Hz on a Campbell CR5000 data logger. Corrections were made to the \(\text{CO}_2\) fluxes to account for density effects [Webb et al., 1980] and buoyancy temperature and crosswind effects [Liu et al., 2001]. Energy balance closure during the summer of 2002 (June–August) was 80% at the 3-year stand, 83% at the 15-year stand, and 86% at the 80-year stand [Liu et al., 2005]. Instrument configuration and sampling heights are summarized in Table 1 of Liu et al. [2005].

[15] Micrometeorological observations that we used to develop and drive the \(\text{CO}_2\) flux partitioning and isoflux models included \(\text{CO}_2\) and latent heat fluxes, wind speed above and inside the canopy, PPFD (LI 190, LI-COR, Inc., Lincoln, Nebraska), precipitation, air temperature and relative humidity above and inside the canopy, and soil temperature at 10 cm depth. Micrometeorological data was 86% complete at the 3-year stand, nearly 100% at the 15-year stand and 95% at the 80-year stand. Air and soil temperature, relative humidity, PPFD, and wind speed data were gap filled using linear interpolation of points surrounding the missing data for short gaps (e.g., less than 3 hours), or using measurements recorded at one of the other nearby tower locations for extended periods of missing data (with the exception of soil temperature which was linearly interpolated for midday periods of missing data). We filtered NEE measurements for periods of low turbulence using a minimum \(u^*\) threshold of 0.2 m s\(^{-1}\) [Goulden et al., 1997]. We also excluded periods with rain or dust that potentially interfered with the operation of the infrared gas analyzer. Combined with instrument data gaps, the filtering procedure yielded 30-min NEE measurements for 51% of the growing
season (April–September) at the 3-year stand, 46% at the 15-year stand, and 57% at the 80-year stand.

3.2. Isotopic Measurements

[16] We collected precipitation using rain collectors that consisted of a 7.5-cm-diameter funnel with 20 cm of 1/4 inch ID Tygon tubing feeding into a 500-mL Nalgene bottle. The funnel and bottle were supported inside a PVC pipe. We constructed a vent from 30 cm of 1/4 inch ID Tygon tubing, allowing for rapid filling of the bottle while minimizing fractionation due to evaporation. We emptied the collectors weekly into borosilicate glass vials with screw caps sealed with Parafilm. The vials were stored in a refrigerator until analysis. We collected snow samples from both the top and bottom of the snow pack weekly during winter and stored them in the same way as the summer rain samples. We analyzed precipitation and extracted leaf, stem, and soil water samples for $\delta^{18}O$ by continuous flow GC-IRMS on a Finnigan MAT Delta S mass spectrometer (Thermo Finnigan, Bremen, Germany) following the method described by Fessenden et al. [2002]. We injected 0.5 mL of water by syringe into 7-mL vials flushed with 10% CO$_2$ in N$_2$. The vials were capped with Hycar rubber stoppers and allowed to equilibrate by shaking in a 25°C constant temperature water bath for a minimum of 12 hours. We prepared isotopic standards in the same manner as the unknown samples. We used a gas-tight syringe to inject 200–300 µL of headspace into a HP/Agilent Technologies 6890 Series Gas Chromatograph G1530A with a 25-m Poroplot-Q capillary column (0.32 mm diameter). The CO$_2$ effluent from the GC passed through a Finnigan GC Combustion III and Nafion drying trap before entering the mass spectrometer.

[17] We collected atmospheric water vapor cryogenically by pulling air through a 9-mm OD glass tube cold finger (with an inner 6-mm OD tube) sitting in crushed dry ice. We maintained the flow rate through the cold finger at 0.3 L min$^{-1}$ for approximately 2 hours [Helliker et al., 2002]. Water condensed on the inner portion of the 9-mm tube and the outer portion of the 6-mm tube. Both glass tubes were removed from the dry ice and sampling apparatus and sealed with a rubber stopper/septum and wrapped with Parafilm. Samples were stored in a freezer until analysis. To measure the $\delta^{18}O$ of the condensed water vapor, the sample tubes were removed from the freezer and allowed to reach room temperature over a period of 1 to 3 hours. We injected $\sim$1 mL of pure CO$_2$ through the stopper/septum to bring the internal CO$_2$ concentration to $\sim$10%. Standards were prepared in 7-mL-headspace vials, as previously described, and both standards and samples were allowed to equilibrate at room temperature for at least 48 hours. We used a gas-tight syringe to inject 80 µL of the headspace from the water vapor tubes into the Delta S GC-IRMS. Sample $\delta^{18}O$-H$_2$O values were calculated relative to known standards equilibrated at the same time. The reproducibility for this method was ±0.5‰.

[18] We collected bulk soil water samples from soil pits at 2.5, 5, 10, 15, and 30 cm depths, using borosilicate glass vials sealed with Parafilm. We also sampled dominant tree species for stem (xylem) and leaf water isotopic composition. Stems, leaves, and needles collected for isotopic analysis were stored in 25-mL screw-cap borosilicate glass vials and sealed with Parafilm. We collected stem samples from nongreen, woody stems to minimize effects of evaporative enrichment. Petioles were removed from the broadleaf leaves to minimize the effects of non-evaporatively-enriched stem water contributions. Samples were frozen until water was extracted by cryogenic vacuum distillation [Ehleringer et al., 2000].

3.3. Isotopic Modeling of Water Pools

[19] We measured $\delta^{18}O$ of atmospheric and ecosystem water pools during two field campaigns in 2002, although to predict the seasonal and annual isoforcing of $\delta^{18}O$-CO$_2$, we needed continuous estimates of the isotopic composition of the water pools. Therefore it was necessary to model the $\delta^{18}O$ of precipitation, water vapor, soil and xylem water, and leaf water at 30-min intervals. We used the measured $\delta^{18}O$ of precipitation collected at Delta Junction during 2002 to create a temperature regression based on the mean air temperatures of the week prior to sample collection (because samples were collected weekly) (Figure 2). We compared our isotopic data to four IAEA GNIP stations at Fort Smith (60°00’N, 111°97’W), Mayo (63°37’N, 135°52’W), Whitehorse (60°72’N, 135°52’W), and Yellowknife (62°28’N, 114°27’W), spanning the years 1961–1993 (IAEA/WMO, Global network of isotopes in precipitation, GNIP database, 2004, available at http://isohis.iaea.org). These stations were chosen because they are at similar latitudes as our field sites and also are interior (noncoastal) locations. The regression of weighted monthly $\delta^{18}O$ of precipitation on the monthly mean air temperature was nearly identical to that calculated from our own isotopic measurements (Figure 2a). The isotopic temperature dependence from Delta Junction was then applied to the monthly mean air temperature measured at the stands to construct an estimated seasonal cycle of $\delta^{18}O$ of meteoric water (Figure 2b). In our model, soil water $\delta^{18}O$ was set equal to the $\delta^{18}O$ of precipitation. As will be discussed later, this assumption ignores short-term isotopic variations in the top soil layers due to natural variability in precipitation and evaporation between rain events [Riley et al., 2002].

[20] Atmospheric water vapor $\delta^{18}O$ was assumed to be depleted relative to modeled precipitation $\delta^{18}O$ by −8‰ based on the mean difference between water vapor and precipitation isotopic measurements made during June and August (Figure 3). We also assumed that there was no diurnal cycle in water vapor $\delta^{18}O$ on the basis of our measured water vapor $\delta^{18}O$ profiles that showed considerable variability, but no clear diurnal trends (data not presented).

[21] Leaf water $\delta^{18}O$ becomes enriched during the day owing to evaporative enrichment during transpiration. The level of leaf water enrichment was estimated first using the Craig-Gordon steady state model of isotopic fractionation [Craig and Gordon, 1965], expanded to include leaf boundary layer effects [Flanagan et al., 1991]. The steady state $^{18}O/^{16}O$ ratio of leaf water (H$_2^{18}O$H$_2^{16}O$) at the sites of evaporative enrichment ($R_{ev}$) is given by

$$R_{ev} = \alpha_s \left[ \alpha_a \frac{R_{tot} (e_t - E_i)}{e_i} + \alpha_b R_{tot} \left( \frac{E_t - E_o}{e_i} \right) + R_{atm} \left( \frac{E_o}{e_i} \right) \right].$$

(1)
where $R_{a}$ and $R_{wx}$ are the $^{18}O/^{16}O$ ratios of water vapor in the atmosphere and xylem water respectively and $e$ is the water vapor pressure (subscripts $a$, $s$, and $i$ correspond to the free atmosphere, leaf surface and intercellular spaces respectively), $\alpha^*$ is the temperature-dependent equilibrium fractionation factor between liquid water and water vapor, $\alpha_{kb}$ is the kinetic fractionation associated with diffusion of water vapor in air (1.032) [Cappa et al., 2003] and $\alpha_{kb}$ is the kinetic fractionation associated with diffusion through the boundary layer ($\alpha_{kb} = \alpha^* k_{b}$). We used the mean 30-min air temperature and relative humidity measured at each stand above the canopy to drive this model of predicted leaf water enrichment.

Measurements of leaf water $\delta^{18}O$ tend to show a lag relative to that calculated with the Craig-Gordon approximation [Dongmann et al., 1974; Lai et al., 2006]. Therefore, we also employed a transitory model where the $\delta^{18}O$ of leaf water is a mixture of the Flanagan modified Craig-Gordon steady state prediction at that time and at the previous time step [Dongmann et al., 1974; Cuntz et al., 2003a; Lai et al., 2006].

\[
R_{nss}(t) = R_{ss}(t)/C_0 R_{nss}(t)/C_0 R_{nss}(t)/C_0 R_{nss}(t)/C_0 1/C_2/C_3 e/z D t/t; (2)
\]

where $R_{nss}(t)$ is the non-steady-state prediction of the isotopic ratio of leaf water at time $t$, $R_{ss}(t)$ is the Craig-Gordon steady state solution at time $t$, $R_{nss}(t)/C_0 1$ is the isotopic ratio of leaf water at time $t$/C_0 1, and $z$ is represented by the following equation:

\[
z = \alpha^* \alpha_{kv} h(t); (3)
\]

where $h$ is the humidity in the canopy air. Here $\alpha_{kv}$ is the effective kinetic fractionation through the stomata and boundary layer ($\alpha_{kv} = 1/(0.032 r_s + 0.021 r_b)/(r_s + r_b)$ where $r_s$ and $r_b$ are the stomatal and boundary layer resistances to water vapor diffusion, and 0.032 and 0.021 are scalars corresponding to the respective isotopic fractionation factors) [Cappa et al., 2003].

The turnover time of leaf water ($\tau$ in equation (2)) is proportional to the volume of leaf water divided by the transpiration rate and $D$ is the 30-min time step of the model. We used a $\tau$ of 2 hours based on reducing residuals between measured and modeled leaf water values. Leaf water turnover time probably varies with species and should vary diurnally
with transpiration rate; however, we had limited data to make this evaluation and therefore decided to use a constant $\tau$ for all stands. For comparison, Cuntz et al. [2003a] used a $\tau$ of $\sim$3 hours globally, and Lai et al. [2006] solved for a $\tau$ of 11 hours for conifers in the Pacific Northwest.

### 3.4. Partitioning CO$_2$ Fluxes

[24] NEE measurements at each stand were partitioned into ecosystem respiration ($R_e$) and gross primary productivity (GPP) components using $Q_{10}$ and Michaelis-Menten models, respectively. We used a temperature dependent $Q_{10}$ respiration model that was mathematically equivalent to a Van’t Hoff exponential model [Lloyd and Taylor, 1994].

$$R_e = R_e Q_{10}^{(t-25)},$$

(4)

where $T$ is the 10-cm soil temperature, $T_0 = 10^\circ$C, $R_e$ is the base respiration rate and $Q_{10}$ is a temperature sensitivity parameter. Nighttime growing season (April–September) NEE measurements and 10-cm soil temperatures from 3 years of combined measurements (2002–2004) were used to solve for stand-specific $Q_{10}$ values. Using these $Q_{10}$ values and nighttime NEE measurements, we then solved for $R_e$ values during 15-day windows moving by 5-day increments during the growing season (April–September). Winter $R_e$ was predicted by using the growing season $Q_{10}$ and half the mean growing season $R_e$. For each stand, these $R_e$ and $Q_{10}$ values were used with 10-cm soil temperature to estimate $R_e$ at the half-hourly time step of our model.

[25] Gross primary production (GPP) was modeled after Zha et al. [2004],

$$GPP = \left(\frac{A_{\text{max} \cdot \alpha \cdot \text{APAR}}}{A_{\text{max} \cdot \alpha \cdot \text{APAR}}}\right) \cdot VPD_{\text{scalar}},$$

(5)

where $\text{APAR}$ ($\mu$mol photons m$^{-2}$ s$^{-1}$) is absorbed photosynthetically active radiation ($\text{APAR} = \text{PPFD} \times \text{FPAR}$, where $\text{FPAR}$ is the fraction of PAR absorbed by the vegetation), GPP and $A_{\text{max}}$ (maximum photosynthetic capacity) are both in $\mu$mol CO$_2$ m$^{-2}$ s$^{-1}$ and $\alpha$ is a quantum efficiency (mol CO$_2$/mol photons). Many studies have explored the effect of vapor pressure deficit (VPD) and humidity levels on leaf-level gas exchange [Jarvis and McNaughton, 1986]; therefore we included a dependence on VPD in the assimilation model to better represent diurnal variations in water stress. (This $VPD_{\text{scalar}}$ was not included by Zha et al. [2004].)

$$VPD_{\text{scalar}} = 1 - 0.5 \left(\frac{VPD}{VPD_{\text{max}}}\right),$$

(6)

The value of $VPD_{\text{scalar}}$ (unitless) decreased linearly with increasing VPD until reaching $VPD_{\text{max}}$ above which it remained constant at 0.5. For each stand, we fixed $VPD_{\text{max}}$ at 3 kPa. This resulted in a very conservative reduction of GPP during afternoon periods of high VPD. The GPP model behaves linearly when $\alpha \times \text{APAR}$ is much smaller than $A_{\text{max}}$ and saturates when $\alpha \times \text{APAR}$ approaches $A_{\text{max}}$. $A_{\text{max}}$ and $\alpha$ were solved for every week during the growing season using PPDF data recorded by the micrometeorological towers and FPAR derived from MODerate Resolution Imaging Spectroradiometer (MODIS) observations [Myneni et al., 2002]. Table 1 lists values of the model parameters for each stand used to calculate GPP and $R_e$ fluxes for 2002.

### 3.5. Atmospheric Modeling

[26] We used a simple one-box atmosphere model to isolate the relative effect ecosystem exchange from each forest type has on the seasonal cycle of CO$_2$ and $\delta^{18}$O-CO$_2$ of the atmosphere. The atmospheric box represents the high northern latitude atmosphere in which one age class of forest (e.g., the 3-year stand, the 15-year stand, or the 80-year stand) interacts with the atmosphere in each model run. The mass of air in the atmospheric box ($M_a$) was matched the amplitude at the Point Barrow station of the NOAA CMDL network [Conway et al., 1994]. $M_a$ was the same for each stand and model simulation. The conceptual experiment presented here is roughly equivalent to covering the entire boreal forest land area with a single age class of forest, and mixing the resulting biospheric fluxes into the entire atmosphere contained between 59°N and 70°N. Observations at the Point Barrow station represent well-mixed background values of CO$_2$ and $\delta^{18}$O-CO$_2$ at high northern latitudes (because gases are sampled from ocean wind sectors under well-mixed conditions) and will be used later to give a reference framework for our results. No atmospheric boundary conditions were imposed (i.e., there was no mixing from other latitudes). The change in atmospheric CO$_2$ is predicted from modeled $R_e$ and GPP fluxes (mol m$^{-2}$ 30 min$^{-1}$) starting with an atmospheric CO$_2$ concentration at 370 ppm.

$$\frac{d(C_o M_o)}{dt} = GPP + R_e,$$

(7)

where $C_o$ is the molar ratio of CO$_2$ in the one-box model, and $M_o$ is the mass of air in the atmospheric box (equivalent to $5.4 \times 10^5$ mol air m$^{-2}$).

### Table 1. Model Parameters Used to Partition NEE Into GPP and $R_e$ Components

<table>
<thead>
<tr>
<th>Stand</th>
<th>$Q_{10}$ $^a$ Unitless</th>
<th>$R_e^{a,b}$ $^c$</th>
<th>$\alpha^{a,d}$</th>
<th>$\alpha^{e,f}$ mol CO$_2$/mol photons</th>
<th>$FPAR^{g,h}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-year</td>
<td>2.1</td>
<td>1.0</td>
<td>-3.6</td>
<td>-0.04</td>
<td>60</td>
</tr>
<tr>
<td>15-year</td>
<td>3.9</td>
<td>2.3</td>
<td>-11.2</td>
<td>-0.08</td>
<td>84</td>
</tr>
<tr>
<td>80-year</td>
<td>4.7</td>
<td>5.0</td>
<td>-9.6</td>
<td>-0.09</td>
<td>84</td>
</tr>
</tbody>
</table>

$^a$ $Q_{10}$ and $R_e$ are solved using 10-cm soil temperatures.

$^b$ $R_e$ was separately estimated for 5-day intervals during the growing season; here we report the mean over the growing season.

$^c$ $\alpha$ and FPAR are June–August means.

$^d$ The units are per mol of absorbed photons (incident PPFD x FPAR).
[27] To determine the total isotopic effect of biospheric CO₂ fluxes on the atmosphere, net isofluxes (in units of moles C per 1000 C) were calculated at half-hour time steps as

\[ \frac{d(C_{\text{iso}} M_{C_{\text{iso}}})}{dt} = GPP(\xi_{\text{CO}_2} - \Delta_d) + R_{\text{iso}}(\xi_{\text{iso}} - \xi_{\text{diff}}). \]  

(8)

where \( \xi_{\text{CO}_2} \) is the \( ^{18} \)O of CO₂ in the one-box model (initialized at -1.4%o VPDB-CO₂), \( \xi_{\text{iso}} \) is the \( ^{18} \)O of atmospheric CO₂ used in calculating the isofluxes and equivalent to the mean seasonal cycle of observations from the Point Barrow NOAA CMDL station, \( \Delta_d \) is the discrimination against \( ^{18} \)O during photosynthesis (defined later in equation (9)), \( \xi_{\text{si}} \) is the \( ^{18} \)O of CO₂ in equilibrium with soil water (%o VPDB-CO₂), and \( \xi_{\text{diff}} \) is the fractionation associated with diffusion of CO₂ out of the soil (%o).

[28] The seasonal cycle of \( \xi_{\text{CO}_2} \) was determined by dividing equation (8) by equation (7). For this modeling study, \( \xi_{\text{diff}} \) was assumed to be -7.2%o [Miller et al., 1999]. We assumed that the abiogenic retrodiffusion isoflux [Stern et al., 2000; Yakir and Sternberg, 2000] returns to the atmosphere without isotopically equilibrating.

[29] The seasonal cycle of \( \xi_{\text{CO}_2} \) was determined by dividing equation (8) by equation (7). For this modeling study, \( \xi_{\text{diff}} \) was assumed to be -7.2%o [Miller et al., 1999]. We assumed that the abiogenic retrodiffusion isoflux [Stern et al., 2000; Yakir and Sternberg, 2000] returns to the atmosphere without isotopically equilibrating. The discrimination associated with GPP, \( \Delta_d \), was first presented by Farquhar et al. [1993] and has been modified by Gillon and Yakir [2001] to include the effect of incomplete isotopic equilibration of CO₂ with H₂O by carbonic anhydrase. Gillon and Yakir [2001] showed that in most cases, hydration of CO₂ by carbonic anhydrase is not 100% efficient, and some of the CO₂ that diffuses into the leaf water returns to the atmosphere without isotopically equilibrating with leaf water. Although this effect is more pronounced in C₄ grasses, where carbonic anhydrase is only about 40% efficient, it is estimated to be approximately 88-99% for broadleaf and conifer C₃ trees.

\[ \Delta_d = \bar{\alpha} + \bar{\varepsilon} \left[ \theta_{\text{eq}}(\xi_{\text{CO}_2} - \xi_{\text{C}_2}) - \bar{\alpha} \left( \frac{1 - \theta_{\text{eq}}}{1 + \bar{\varepsilon}} \right) \right] \]  

(9)

Here \( \bar{\alpha} \) is the weighted mean of discrimination occurring during diffusion from ambient air to the sites of carboxylation in the chloroplast (estimated to be 7.4%o) and \( \xi_{\text{CO}_2} \) is the oxygen isotopic composition of CO₂ (%o VPDB-CO₂) in the chloroplast. The \( \xi_{\text{CO}_2} \) is assumed to be in isotopic equilibrium with enriched leaf water at the ambient air temperature (close to leaf temperature). The fraction of CO₂ entering the leaf that fully carboxylates with the leaf water pool before exiting is denoted as \( \theta_{\text{eq}} \). For the 3-year and 15-year stands, we used the mean of the ranges of values given for trees/shrubs by Gillon and Yakir [2001], \( \theta_{\text{eq}} = 0.96 \). Likewise, for the 80-year stand, the mean for conifers was \( \theta_{\text{eq}} = 0.93 \). \( C_e \) is the partial pressure of CO₂ and the subscripts \( a \) and \( c \) correspond to the CO₂ in ambient air and inside the chloroplast. We used the internal stomatal CO₂ ratio with the ambient CO₂ mixing ratio (\( C_i/C_a \)) as an estimate of \( C_i/C_a \) used to calculate \( \bar{\varepsilon} \) (equation (10)). We recognize that this is a simplification of the law of mass action that there is evidence that \( C_i \) and \( C_c \) can differ by 0.1 \( \times \) \( C_a \) to 0.2 \( \times \) \( C_a \) [Lloyd and Farquhar, 1994; Yakir and Sternberg, 2000; Cuntz et al., 2003a]. To address this, we conducted a sensitivity analysis in which we varied \( C_i \) and examined the impacts on \( ^{18} \)O-CO₂ isofluxes. \( C_i/C_a \) ratios were estimated from \( ^{13} \)C of plant tissue collected in the summer of 2002 using the relationship for \( C_i \) plants derived by Farquhar et al. [1989]. The \( ^{13} \)C discrimination was estimated at 20.9%o for dominant grasses at the 3-year stand, 22.0%o for aspen at the 15-year stand, and 21.2%o for black spruce at the 80-year stand. This translates to \( C_i/C_a \) ratios (or \( C_i/C_a \) estimates) of 0.71, 0.76 and 0.73, respectively. These estimates are broadly consistent with Dang et al. [1997] measurements of 0.81 for aspen and 0.71 for black spruce. Because the value of \( C_i/C_a \) sets the magnitude of the retrodiffusive flux of CO₂ out of the leaf and to the atmosphere, we wanted to include the effects of the diurnal cycle of \( C_i/C_a \) in our isoforcing calculations. We introduced a diurnal cycle in \( C_i/C_a \) (used to estimate \( C_i/C_a \)) using the Ball-Berry equation [Ball, 1988].

\[ \frac{1}{r_s} = \frac{m \times GPP \times h_s \times P}{C_i} + b, \]  

(11)

and a rearrangement of the diffusion representation of photosynthesis.

\[ \frac{C_i}{C_a} = \frac{1 + GPP \times \frac{(1.65_r + 1.37_{rs})}{LAI \times C_a}}{1}. \]  

(12)

In the preceding two equations, \( r_s \) is the resistance of water through the stomata (m² s⁻¹ μmol⁻¹ H₂O), and \( r_s \) is resistance through the laminar leaf boundary layer (m² s⁻¹ μmol⁻¹ H₂O). \( C_i \) and \( C_a \) are the partial pressures of CO₂ at the leaf surface (including the effect of \( r_s \) ) and in the atmosphere, \( h_s \) is relative humidity at the leaf surface, \( b \) is the residual conductance when GPP is zero, \( P \) is the atmospheric pressure and \( LAI \) is the unitless leaf area index which varies seasonally (from MODIS observations) and \( m \) is a constant. We solved for parameters \( m \) and \( b \) in equation (11) such that when entered into equation (12), the GPP-weighted annual mean \( C_i/C_a \) for each stand matched our estimates from the \( ^{13} \)C measurements. The sensitivity of the seasonal cycle of \( ^{18} \)O-CO₂ to the diurnal cycle of \( C_i/C_a \) will be explored further in this paper.

[29] In previous modeling studies, \( \xi_{\text{CO}_2} \) and \( \xi_{\text{CO}_2} \) have been “coupled” so that the model-predicted \( ^{18} \)O-CO₂ from the previous time step was used to calculate the discrimination in the next time step. We found it necessary to fix \( \xi_{\text{CO}_2} \) in equations (8) and (9) with observations from Point Barrow (rather than allowing it to change in response to the stand model isoforcing). This was necessary because atmospheric CO₂ is not in isotopic equilibrium with the extremely negative \( ^{18} \)O of water pools at high northern latitudes. In the coupled simulations that we first attempted, \( \xi_{\text{CO}_2} \) would reach values as negative as -4 to -5%o (VPDB-CO₂) by the end of 1 year because our model did not include mixing with air enriched in \( ^{18} \)O-CO₂ from the tropics. Because the calculated isofluxes were dependent on \( \xi_{\text{CO}_2} \) (through \( \Delta_d \) in equation (9)) it was necessary to keep \( \xi_{\text{CO}_2} \) consistent with current high-latitude observations to produce realistic fluxes. The discussions of our model results will be based on the resulting model-predicted \( \xi_{\text{CO}_2} \). Note that removing the seasonal cycle and using a constant value for \( \xi_{\text{CO}_2} \) for
the entire year (Point Barrow annual mean of −1.4%) yielded nearly identical results and did not change any of the conclusions of this study.

The purpose of the simple atmospheric model was to examine in isolation how biosphere-atmosphere fluxes that vary with stand age influence the atmospheric record. This approach provides insight about the role of species composition within boreal forests, and is not meant to replace a more realistic coupled biosphere-atmosphere model that includes atmospheric transport and fluxes from the ocean, stratosphere, fossil fuels, and other terrestrial ecosystems.

We linearly detrended our model results of seasonal cycles of CO$_2$ and $\delta^{13}$O (referred to as modeled $\delta^{18}$O-CO$_2$) to allow us to compare seasonal phasing across stands and with atmospheric observations. This is a common first step in the analysis of the seasonal cycle for atmospheric trace gases that also have a secular trend; it was required here because our local ecosystem fluxes were not in steady state with the atmosphere.

4. Results

4.1. CO$_2$ Fluxes

Measurements of NEE from the three stands are shown in Figure 4. In the spring, the onset of photosynthesis and net CO$_2$ uptake was delayed by approximately 3 weeks at the 15-year stand as compared with the 80-year stand. Leaf emergence of aspen at the 15-year stand occurred between 18 and 24 May 2002, day of year (DOY) 138–144. By DOY 146, the daily net CO$_2$ flux was negative. The carbon uptake period, as defined by negative daily net CO$_2$ fluxes, was significantly shorter at the younger stands; the 3-year stand was reduced by 9 weeks as compared to the 80-year stand and the 15-year stand was reduced by 7 weeks.

In midsummer from 18 June to 15 July 2002 (DOY 169–196), mean midday NEE (1000–1400 local solar time) was $-1.2$ μmol m$^{-2}$ s$^{-1}$ at the 3-year stand, $-5.7$ μmol m$^{-2}$ s$^{-1}$ at the 15-year stand, and $-4.2$ μmol m$^{-2}$ s$^{-1}$ at the 80-year stand. For this same period, integrated daily NEE was $-0.3$ g C m$^{-2}$ d$^{-1}$ at the 3-year stand, $-2.4$ g C m$^{-2}$ d$^{-1}$ at the 15-year stand, and $-1.3$ g C m$^{-2}$ d$^{-1}$ at the 80-year stand. Both the midday minima and daily NEE were reduced at the 3-year stand because of low leaf area. Midday NEE (1000–1400 local solar time) was 36% more negative at the 15-year stand than at the 80-year stand. Integrated over 24 hours, the difference was even larger. The daily NEE for the 15-year stand was 85% more negative because during the night, NEE fluxes from the two stands were similar in magnitude and offset the differences measured during midday.

The $R_e$ and GPP models described in the methods section were combined to form modeled half-hour NEE flux estimates. Weekly composite averages of the modeled fluxes are plotted with tower NEE diurnal averages in Figure 4. The model slightly underestimated the nighttime NEE maxima and the daytime NEE minima (Figure 4). Our calculated $Q_{10}$ values (Table 1) were between 2.1 to 4.7, and are within the range of $Q_{10}$ values reported for other boreal forest ecosystems [Wang et al., 2002].

The magnitude of the potential bias between the modeled and measured NEE during the growing season was examined by comparing differences in the cumulative

![Figure 4. Measured (black solid circles) and modeled (solid grey line) weekly mean NEE for the three stands in 2002. This plot shows mean diurnal cycles constructed from 7-day intervals of 30-min NEE data. The mean diurnal cycles are plotted sequentially to allow examination of the seasonality in GPP (indicated partly by the daytime minima) and $R_e$ (indicated partly by the nighttime maxima). The growing season at the 15-year stand is shorter and more intense (with a larger diurnal cycle in midsummer). Linear regression slopes between modeled and measured (weekly mean) NEE are 0.18 at the 3-year stand ($r^2 = 0.35$), 0.75 at the 15-year stand ($r^2 = 0.76$) and 0.59 at the 80-year stand ($r^2 = 0.72$). CO$_2$ fluxes at the 3-year stand are small, making them difficult to measure and model and resulting in poor correlation statistics.](image)

NEE (DOY 100–300) of the model fluxes with tower-measured NEE (Figure 5a). These results showed that the modeled NEE fluxes underpredicted the carbon uptake at each stand; however, without adding more complexity to our partitioning model, we considered this a reasonable fit to observations because it captured most of the seasonal change in net CO$_2$ fluxes (shape of the curves in Figure 5a) as well as variations in the diurnal cycle (Figure 4).

Although the modeled NEE fluxes should be used cautiously, especially in the winter, the integrated annual sums provided an estimate of the magnitude of the source or sink of CO$_2$ at each stand for the entire year (Figure 5b). Annual integrated sums of GPP and $R_e$, in addition to NEE, are summarized in Table 2.

4.2. Observations and Modeling of the $\delta^{18}$O of Water Pools

Figure 3 shows the range of precipitation, soil, xylem, leaf and water vapor isotope measurements from field campaigns during 2002, along with model estimates.
During the day, bulk leaf water δ18O was substantially enriched as compared to δ18O of precipitation. At night, non-steady-state estimates of leaf water δ18O decreased but did not fully return to xylem water values. Field measurements of δ18O of water vapor during midsummer ranged between −18‰ to −29‰ and the daily averages were approximately 6–9‰ less than the model predicted δ18O of precipitation (Figure 3). Each vapor δ18O value plotted is an average of vertical canopy profiles measured four times over the course of 1 day. To examine the model performance, measurements of leaf and xylem water from field campaigns in June and August are expanded along with model predictions in Figure 6. The different stand ages

Table 2. Annual Ecosystem Fluxes, Isofluxes, and Other Model Parameters

<table>
<thead>
<tr>
<th>Annual Value, Flux-Weighteda</th>
<th>3-Year</th>
<th>15-Year</th>
<th>80-Year</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>GPP</td>
<td>−16.1</td>
<td>−36.3</td>
<td>−41.2</td>
<td>mol m⁻² yr⁻¹</td>
</tr>
<tr>
<td>Rₑ</td>
<td>19.5</td>
<td>26.8</td>
<td>35.5</td>
<td>mol m⁻² yr⁻¹</td>
</tr>
<tr>
<td>$δ^{18}$O leaf water (GPP)</td>
<td>−0.6</td>
<td>−1.4</td>
<td>−0.5</td>
<td>% (VSMOW)</td>
</tr>
<tr>
<td>$δ^{18}$O soil water (Rₑ)</td>
<td>−18.3</td>
<td>−17.8</td>
<td>−18.1</td>
<td>% (VSMOW)</td>
</tr>
<tr>
<td>$δ^{18}$O leaf CO₂ (GPP)</td>
<td>1.6</td>
<td>0.3</td>
<td>1.6</td>
<td>% (VPDB-CO₂)</td>
</tr>
<tr>
<td>$δ^{18}$O soil CO₂ (Rₑ)</td>
<td>−15.4</td>
<td>−14.5</td>
<td>−14.1</td>
<td>% (VPDB-CO₂)</td>
</tr>
<tr>
<td>C/Cₐ (GPP)</td>
<td>0.71</td>
<td>0.76</td>
<td>0.73</td>
<td>unitless</td>
</tr>
<tr>
<td>Δ (GPP)</td>
<td>9.3</td>
<td>5.1</td>
<td>7.5</td>
<td>%</td>
</tr>
<tr>
<td>GPP(δ°C₀₂ - δₑ)</td>
<td>170</td>
<td>227</td>
<td>360</td>
<td>mol m⁻² yr⁻¹ %</td>
</tr>
<tr>
<td>Rₑ(δ°C₀₂ - δₑ)</td>
<td>−441</td>
<td>−581</td>
<td>−753</td>
<td>mol m⁻² yr⁻¹ %</td>
</tr>
<tr>
<td>Net Isoflux</td>
<td>−271</td>
<td>−354</td>
<td>−393</td>
<td>mol m⁻² yr⁻¹ %</td>
</tr>
</tbody>
</table>

aGross fluxes used for parameter flux weighting are in parentheses.

Figure 5. (a) A comparison between modeled NEE and measured NEE during the growing season, DOY 100–300. The solid lines are cumulative modeled NEE estimates, and the dotted lines are measured NEE values that were gap-filled with modeled estimates during periods of missing data. Modeled NEE has a bias toward decreased net carbon uptake at each stand. (b) Cumulative modeled NEE (starting at DOY 1) for the 3-year stand, 15-year stand, and 80-year stand. The sign convention is such that positive values are fluxes to the atmosphere and negative values are uptake by the ecosystem. The 3-year stand was a source with a flux of approximately 3.4 mol CO₂ m⁻² yr⁻¹ (40.8 g C m⁻² yr⁻¹) while the 15-year stand was a sink with a flux of approximately −9.5 mol CO₂ m⁻² yr⁻¹ (−114 g C m⁻² yr⁻¹). The mature 80-year stand was closer to steady state, but was still a sink of CO₂ with a flux of approximately −5.8 mol CO₂ m⁻² yr⁻¹ (−69.6 g C m⁻² yr⁻¹).

During the day, bulk leaf water δ18O was substantially enriched as compared to δ18O of precipitation. At night, non-steady-state estimates of leaf water δ18O decreased but did not fully return to xylem water values. Field measurements of δ18O of water vapor during midsummer ranged between −18‰ to −29‰ and the daily averages were approximately 6–9‰ less than the model predicted δ18O of precipitation (Figure 3). Each vapor δ18O value plotted is an average of vertical canopy profiles measured four times over the course of 1 day. To examine the model performance, measurements of leaf and xylem water from field campaigns in June and August are expanded along with model predictions in Figure 6. The different stand ages

Figure 6. Measured δ18O of leaf water and xylem water (symbols) are shown with model predictions (lines) during intensive field campaigns during (a) 16–22 June 2002 and (b) 10–16 August 2002. The leaf water model used in this study was a non-steady-state model with a leaf water turnover time of 2 hours. Modeled xylem water was set equal to the δ18O of precipitation.
show similar modeled leaf water $^{18}$O because of similarities in climate driver datasets (i.e., air temperatures, wind speeds, and relative humidity levels were similar at all three stands). The model did reasonably well at capturing the magnitude and diurnal variability of leaf water $^{18}$O, but overestimated enrichment levels on several days. Relative humidity contributed the most to variability in the leaf water $^{18}$O model predictions over weekly to monthly timescales. The seasonal maximum in leaf water isotopic enrichment (DOY ~150 in Figure 3) was linked to the seasonal minimum in relative humidity (DOY ~150 in Figure 1) and not to the seasonal maximum in $^{18}$O of modeled plant source water (precipitation) which occurred near DOY 200 in Figure 3.

4.3. Atmospheric Modeling

[37] The shorter and more intense growing season at the 15-year deciduous aspen stand caused a 30% increase in the peak-to-trough CO$_2$ seasonal amplitude, a delay in maximum CO$_2$ concentration, and an advance in minimum CO$_2$ concentration compared to the 80-year stand (Figure 7a). The “downward zero crossing time” of the phase (the day when the CO$_2$ concentration crosses the mean value of the seasonal cycle in its descending phase) was delayed by 13 days at the 15-year stand as compared with the 80-year stand. The amplitude of the seasonal cycle at the 3-year stand was small and was difficult to separate from the secular trend. The downward zero crossing time analysis for the 3-year stand yielded a delay of 9 days compared to the 80-year stand, however, small NEE fluxes at the 3-year stand substantially increased the error of the model prediction.

[38] Although we did not necessarily expect the one-box model results to match atmospheric observations because of the lack of transport in the model, we compared the box model results of CO$_2$ (and later $^{18}$O-CO$_2$) with the mean seasonal cycle of flask measurements from Point Barrow, Alaska, in Figure 7a. The 80-year stand exhibited a maximum in CO$_2$ in April close to the atmospheric observations, but the predicted minimum in September was delayed from observations by 1 month. The 15-year stand most closely matched the atmospheric observations with an identical spring maximum in May and minimum in August. The seasonal amplitude in CO$_2$ agreed well with observations because the mass of air in the one-box model was chosen so that the 80-year stand fluxes matched this feature of the atmospheric record. We used the same mass for the other two model simulations.

[39] To understand effects of photosynthesis and respiration on atmospheric $^{18}$O-CO$_2$, we considered the isotopic flux (or isoforcing) of each component separately (Figure 8). As described previously, photosynthesis normally enriches the atmosphere in $^{18}$O-CO$_2$, and respiration depletes the atmosphere. The large changes in isoforcing were constrained to periods of the year where there were large CO$_2$ fluxes, as the isoflux is the product of the one-way CO$_2$ flux and the isotopic composition of this flux. The combined net isoforcing on the atmosphere is shown in Figure 9. In terms of total net isoforcing, the 3-year stand had the effect of relative enrichment compared to the mature 80-year stand (also see Table 2). Although the recent fire disturbance at the 3-year stand decreased the atmospheric enrichment due to reduced assimilation, it diminished the depletion by reducing respiration even more. The overall effect was to enrich the atmosphere in $^{18}$O-CO$_2$ relative to the 80-year stand. The intermediate 15-year stand had a net isoforcing that was not substantially different from the 80-year stand.

[40] Using the modeled isofluxes for each forest, a seasonal cycle of $^{18}$O-CO$_2$ was predicted using the simple one-box model ($\delta_0^{18}$O) (Figure 7b). Since this is not a fully coupled model, the model results of $^{18}$O-CO$_2$ reflect isoforcing by each forest age stand prior to feedbacks with the atmosphere. All three stands exhibited maximum $^{18}$O-CO$_2$ in June and minimum in October. The zero crossing point of the seasonal cycle of the younger stands was advanced by 12 days relative to the 80-year stand (Figure 7b). The shape of the $^{18}$O-CO$_2$ seasonal cycle during spring and early summer is also noticeably different between the 15-year and 80-year stands. In part because of
was less than increased more rapidly from April forcing with the annual trend removed, (c) GPP and isoforcing positive (Figure 7d).

C Seasonal Cycle to was critical for predicting the GPP isoforcing leading to an in-

Cuntz et al. case by doubling the GPP isoforcing and because over a diurnal cycle.

WELP ET AL.: STAND AGE EFFECTS ON CO2 AND δ18O-CO2 (or similarly, case enriched the atmosphere factor included in cumulative isoforcing, and (e) GPP and (f) R is not in C = 0.75). We could easily adjust amplitude and phase to the by comparing model results from our e ratio weighted mean value by ±0.1 were Cumulative (a) GPP and (b) R was greater than the C was the same in both runs). The constant cumulative net annual isoflux at the 3-year [2003a] also e D components of the net exchange associated with R

seasonal cycles of GPP and R in equations (8) and (9). By comparing the detrended diurnal cycle in for the other stands. First, we tested the importance of the 15-year stand only; however, similar results were obtained used in our model. For clarity, we present results for the e-axis units in Figures 7a, 7b, 7e, and 7f are relative units; they are not absolute values. At no time during the year is the cumulative GPP isoforcing negative (Figure 7c) nor is the cumulative Rc isoforcing positive (Figure 7d).

the earlier onset of photosynthesis at the 80-year stand (Figure 4) that coincided with relatively low levels of humidity (Figure 1), this stand had substantially greater GPP isoforcing during May and June (Figure 8). As a consequence, δ18O-CO2 increased more rapidly from April to June for the 80-year stand than for the 15-year stand. Figure 7b also compares model predictions to atmospheric observations at Point Barrow, Alaska, the same values (δ18O(CO2)) used to calculate the photosynthetic discrimination in equations (8) and (9). By comparing the detrended seasonal cycles of GPP and Rc components of the net isoforcing (Figures 8e and 8f), it is clear that isotopic exchange associated with Rc has a larger effect on the seasonal cycle than isotopic exchange associated with GPP.

4.4. Sensitivity of the δ18O-CO2 Seasonal Cycle to C/Ca

[41] We examined the sensitivity of the predicted seasonal cycle of δ18O-CO2 amplitude and phase to the C/Ca ratio used in our model. For clarity, we present results for the 15-year stand only; however, similar results were obtained for the other stands. First, we tested the importance of the diurnal cycle in C/Ca by comparing model results from our standard approach (that included a diurnally variable C/Ca predicted using the Ball-Berry equation) with a model run that had a time-invariant C/Ca value set at the GPP-weighted annual average of the variable case (i.e., GPP weighted C/Ca was the same in both runs). The constant C/Ca case enriched the atmosphere δ18O-CO2 compared to the variable C/Ca case by doubling the GPP isoforcing and decreased the amplitude by 33% (Table 3). The increased GPP isoforcing component also delayed the zero point crossing by 17 days.

[42] This sensitivity was a result of the covariance of leaf water δ18O enrichment and C/Ca over a diurnal cycle. During midday when leaf water was most enriched, there were two negative feedbacks that limited GPP isoforcing. First, if there was no change in stomatal conductance, as GPP rates increased, C/Ca decreased, reducing the magnitude of the retrodiffusive flux. Second, stomatal conductance often decreased during midday in response to low levels of atmospheric humidity, and this also reduced C/Ca. Diurnal covariance between afternoon leaf water enrichment and decreased C/Ca was critical for predicting the GPP isoforcing component (equations (9) and (10)), and hence the seasonal cycle of δ18O-CO2. Cuntz et al. [2003a] also recognized the importance of C/Ca (or similarly, C/Ca) and noted that reasonable values of C/Ca could easily adjust the magnitude of the GPP isoforcing (through ε in equation (10)) by a factor of 2 (C/Ca = 0.67) or 3 (C/Ca = 0.75). We show here that it is possible to increase the GPP isoforcing by a factor of 2 without changing the GPP weighted C/Ca annual mean, but by simply removing the diurnal cycle in C/Ca.

Figure 8. Cumulative (a) GPP and (b) Rc components of CO2 forcing with the annual trend removed, (c) GPP and (d) Rc cumulative isoforcing, and (e) GPP and (f) Rc cumulative isoforcing with the annual trend removed. Note that the y-axis units in Figures 7a, 7b, 7e, and 7f are relative units; they are not absolute values. At no time during the year is the cumulative GPP isoforcing negative (Figure 7c) nor is the cumulative Rc isoforcing positive (Figure 7d).

Figure 9. Cumulative net annual isoflux at the 3-year stand, 15-year stand, and 80-year stand. All stands are predicted to deplete the atmosphere in δ18O-CO2 because ecosystem water pools in the far north are extremely depleted in δ18O. The atmospheric δ18O-CO2 is not in steady state with surface water pools at this latitude owing to mixing with southern air masses with higher δ18O-CO2.
5. Discussion

5.1. Disturbance-Induced Changes in CO₂ Seasonal Amplitude and Phase

We compared seasonal carbon exchange from the 15-year and 80-year stands to test the Zimov et al. [1999] hypothesis that disturbance could contribute substantially to the observed increase in the seasonal amplitude of atmospheric CO₂. Previous work from a boreal forest chronosequence in Canada showed that light-saturated CO₂ uptake in midsummer is greatest in intermediate stand ages [Litvak et al., 2003]. Falge et al. [2002] found that in temperate regions, broadleaf deciduous forest stands have a substantially shorter growing season that is characterized by high rates of net carbon uptake as compared with evergreen conifer forest stands. We measured an 85% increase in carbon uptake at the 15-year stand compared to the 80-year stand during the 31-day period from 18 June to 15 July (DOY 169–196). Together, these observations provide qualitative support for the Zimov et al. [1999] hypothesis, and the idea that plant functional type plays a key role in shaping the seasonal cycle of atmospheric CO₂ at high northern latitudes.

In terms of explaining observed increases in the CO₂ amplitude in the Arctic from 1961–1994 [Keeling et al., 1996], several factors suggest that disturbance-driven change in plant functional type within boreal ecosystems is probably not the dominant mechanism. From our one-box conceptual atmospheric model, replacing fluxes from the 80-year stand with fluxes from the 15-year stand caused an increase in the seasonal amplitude of CO₂ of 30%. This change represents a rough first guess at the expected effect of replacing all northern evergreen conifer forests with deciduous broadleaf forests. There is growing evidence that disturbance rates have increased in recent decades within the boreal forests of North America [Kurz and Apps, 1999; Kasischke and Stocks, 2000; Gillett et al., 2004] and Eurasia [Conard et al., 2002; Sukhinin et al., 2004]; however, actual shifts in the distribution of stand ages and plant functional types have been far more modest than the total stand replacement represented by our model simulations. In addition, only 42% of the seasonal cycle at Point Barrow and other Arctic observation stations originates from biosphere-atmosphere exchange with boreal forests; tundra ecosystems contribute another 14%, deciduous forests contribute 12%, and grassland ecosystems farther to the south contribute another 16% [Randerson et al., 1997].

Another metric of seasonal cycle change is the phase, which is often measured by the DOY that the seasonal cycle crosses from a positive value to a negative value in the spring (for a time series of CO₂ for which the secular trend from fossil fuel emissions has been removed). This “downward zero crossing time” of the atmospheric CO₂ seasonal cycle has advanced 7 days from 1975 to 1994 [Keeling et al., 1996]. The leading candidate for explaining both the advanced CO₂ phase as well as increased amplitude is increasing spring and summer air temperature at high northern latitudes [Keeling et al., 1996; McDonald et al., 2004; Angert et al., 2005]. A warmer climate simultaneously increases growing season length through earlier initiation of photosynthetic activity [Black et al., 2000; Tanja et al., 2003; White and Nemani, 2003] and net uptake rates during summer, and provides greater substrate for respiratory

### Table 3. Sensitivity Analysis of the δ¹⁸O-CO₂ Seasonal Cycle

<table>
<thead>
<tr>
<th>Model Simulation</th>
<th>GPP Isoforcing, mol m⁻² yr⁻¹ ‰₀</th>
<th>Rₑ Isoforcing, mol m⁻² yr⁻¹ ‰₀</th>
<th>Net Isoforcing, mol m⁻² yr⁻¹ ‰₀</th>
<th>δ¹⁸O-CO₂ Amplitude, ‰₀</th>
<th>Percent Amplitude Change</th>
<th>Zero Crossing Point</th>
<th>Day Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control, Cₒ/Cₘ = 0.76 time varying</td>
<td>227</td>
<td>−581</td>
<td>−354</td>
<td>1.2</td>
<td>0%</td>
<td>229</td>
<td>0</td>
</tr>
<tr>
<td>Cₒ/Cₘ = 0.76 constant</td>
<td>457</td>
<td>−581</td>
<td>−124</td>
<td>0.8</td>
<td>−33%</td>
<td>256</td>
<td>−17</td>
</tr>
<tr>
<td>Cₒ/Cₘ = 0.66 time varying</td>
<td>226</td>
<td>−581</td>
<td>−355</td>
<td>1.0</td>
<td>−17%</td>
<td>224</td>
<td>5</td>
</tr>
<tr>
<td>Cₒ/Cₘ = 0.86 time varying</td>
<td>213</td>
<td>−581</td>
<td>−368</td>
<td>1.9</td>
<td>58%</td>
<td>233</td>
<td>−4</td>
</tr>
</tbody>
</table>

Figure 10. (a) Daily GPP-weighted leaf δ¹⁸O-CO₂ and δ¹⁸O of atmospheric CO₂ (δₑ,i CO₂) and (b) daily Rₑ-weighted respired soil δ¹⁸O-CO₂ (diffusion fractionation of −7.2‰ has been included, δₑ,i CO₂ − δₑ,i CO₂) for the 15-year stand. Maximum leaf CO₂ (and leaf water) δ¹⁸O values in the beginning of the growing season (~DOY 150) were due to low humidity levels during this period (Figure 1c). This resulted in more positive Δₑ values on average earlier in the growing season and decreasing Δₑ toward the end of the season. Differences in the magnitude and seasonal distribution of GPP at each stand resulted in variations in the isoforcing among stands, even though the modeled δ¹⁸O of leaf water was similar across stands. Soil temperature differences resulted in different equilibrium fractionation factors between CO₂ and water, and therefore δ¹⁸O of soil respired CO₂ at each stand.
losses during fall, winter, and spring [Goulden et al., 1998]. However, deciduous broadleaf trees must grow new leaves each spring, and hence there is a delay in the start of the carbon uptake period as compared with evergreen conifers that retain needles year round. This directly delays the phase of the CO$_2$ seasonal cycle, by 13 days at the 15-year stand compared to the 80-year. Using arguments similar to those discussed earlier for the CO$_2$ amplitude, we present this as an upper bound of expected atmospheric change if all boreal evergreen forests were replaced by deciduous forests. Assuming a modest increase in the rate of disturbance, we predict a shift toward deciduous forest species should have delayed the seasonal CO$_2$ phase by perhaps a day or two. This suggests that spring warming may have advanced the phase of the seasonal cycle of CO$_2$ even more than that predicted in previous studies that did not account for disturbance-induced change in forest stand age and plant functional type.

5.2. Factors Controlling the Seasonal Cycle of δ$^{18}$O-CO$_2$

The modeled amplitudes of the δ$^{18}$O-CO$_2$ seasonal cycle imposed by surface fluxes at the 15-year stand and the 80-year stand were comparable (Figure 7b). Nonetheless, the phase and shape of the seasonal cycle was considerably different as a result of differences in isotopic exchange between the two stands. The δ$^{18}$O-CO$_2$ phase was advanced by 9 days at the 15-year stand relative to the 80-year stand (Figure 7b). Stand-level differences in both the GPP and $R_e$ isotopic fluxes contributed to differences in the phase and shape of the seasonal cycle (Figures 8e and 8f).

Because precipitation is considerably depleted in $^{18}$O at high northern latitudes, CO$_2$ in equilibrium with leaf water is close to atmospheric δ$^{18}$O-CO$_2$ (Figure 10a). The GPP isoforcing was only slightly positive and was even negative at times (when the δ$^{18}$O of leaf CO$_2$ is less than δ$_{\text{air}}$), depleting the atmosphere in δ$^{18}$O-CO$_2$. The flux-weighted annual mean Δ$_A$ was +5.1% for the 15-year stand and +7.5% for the 80-year stand. For comparison, these Δ$_A$ values were lower than other widely variable high-latitude estimates. Farquhar et al. [1993] predicted approximately +14% at 60°N, and Flanagan et al. [1997] estimated Δ$_A$ was +21% for the Canadian boreal forest during midday in July which was also higher than our model predictions of midday Δ$_A$ during July of approximately +17%.

In the Delta Junction study region, low spring relative humidity (Figure 1c) led to enriched leaf waters that gradually became more depleted as humidity increased throughout the summer (Figure 10a). Earlier initiation of GPP at the 80-year stand during the period of more enriched leaf water resulted in a more positive Δ$_A$ at that stand. Delays in leaf out at the 15-year stand led to less atmospheric enrichment associated with GPP in the early part of the growing season (Figure 8e). Thus the increase in δ$^{18}$O-CO$_2$ between April and June was considerably smaller for the 15-year stand as compared with the 80-year stand (Figures 7b and 8e). Changes in the phase also reflected differences in isotopic fluxes associated with $R_e$ (Figure 8f).

Specifically, the advance in phase of $R_e$ at the 15-year stand (Figure 8b) led to an advance in the phase of the $R_e$ isoforcing (Figure 8f).

5.3. Future Work

We developed a simple model for δ$^{18}$O-CO$_2$ isoforcing to extend the interpretation of our field measurements and to specifically investigate some of the effects of stand age on the seasonal cycle of δ$^{18}$O-CO$_2$. In this analysis, we simplified or omitted a number of processes that should be considered in future work. First, there is an active area of research currently focusing on non-steady-state leaf water enrichment models and observations [Cernusak et al., 2004; Farquhar and Cernusak, 2005] and the effects on canopy vapor δ$^{18}$O [Lai et al., 2006] and surface isofluxes [Seibt et al., 2006]. Differences in leaf morphology are likely to lead to different leaf water turnover times among broadleaves and conifer needles. More field experiments are required to accurately determine differences in the τ parameter (equation (2)). Recent work suggests nonzero nighttime stomatal conductance rates may have consequences for δ$^{18}$O-CO$_2$ isofluxes and that the magnitude of the effect may be different for broadleaf and conifer species [Barbour et al., 2005]. However, the degree to which concurrent increases in nighttime leaf and canopy boundary layer resistances offsets the impact of this mechanism for ecosystem δ$^{18}$O-CO$_2$ isofluxes remains unexplored.

A more complete representation of $R_e$ isoforcing may be obtained, in future, by partitioning foliar and stem components of $R_e$ [Flanagan et al., 1997; Bowling et al., 2003a, 2003b; Riley et al., 2003] and by including the effects of moss water on soil $R_e$ isoforcing [e.g., Flanagan et al., 1997]. $R_e$ isoforcing estimates could also be improved by including a more detailed representation of equilibration of CO$_2$ with surface soil water pools [Riley et al., 2002] and fluxes associated with abiotic atmosphere-soil CO$_2$ exchange [Tans, 1998; Miller et al., 1999; Stern et al., 2001]. A key factor that contributes to uncertainty in the GPP isoforcing term is our limited understanding of seasonal patterns of plant water use, including the use of snowmelt water by different plant species throughout the growing season [Sugimoto et al., 2002; Welp et al., 2005].

6. Conclusions

We measured NEE and the isotopic composition of atmosphere and ecosystem water pools at three stands in a boreal forest fire chronosequence. Our measurements and
model analysis provide evidence that species composition exerts a strong control on the shape of both the CO₂ and δ¹⁸O-CO₂ seasonal cycles at high northern latitudes. An expansion of the areas covered by deciduous forests in the boreal region, as a result of increased forest fire frequency, would increase the amplitude and delay the phase of the seasonal cycle of CO₂. Increases in high-latitude disturbance and spring warming have been proposed as potential explanations of observed increases in the amplitude of the seasonal cycle of atmospheric CO₂ [Keeling et al., 1996; Zimov et al., 1999; McDonald et al., 2004; Angert et al., 2005]. Our work implies that it must be a combination of these processes. Changes in the boreal disturbance regime over the last few decades, though not well characterized, seem too small to drive large changes in the seasonal amplitude, on the basis of our NEE measurements.

[54] Our analysis also provides evidence that the seasonal cycle of δ¹⁸O-CO₂ is sensitive to the seasonal timing of GPP and Rₚ surface fluxes, both of which are controlled by plant functional type (and thus stand age) within the boreal forest. In contrast to CO₂, an expansion of the areas covered by deciduous forests would advance the phase of the δ¹⁸O-CO₂ seasonal cycle. An increase in deciduous forest area would also weaken GPP isoforcing during the early part of the growing season and cause δ¹⁸O-CO₂ to increase more gradually between April and June. Important next steps include improving our understanding winter and summer precipitation use by different plant functional types and investigating the impact of changing plant functional types and climate on the δ¹⁸O-CO₂ seasonal cycle using a coupled model that includes atmospheric transport and mixing.

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References


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