

# Canopy-scale $\delta^{13}\text{C}$ of photosynthetic and respiratory $\text{CO}_2$ fluxes: observations in forest biomes across the United States

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## Abstract

The  $\delta^{13}\text{C}$  values of atmospheric carbon dioxide ( $\text{CO}_2$ ) can be used to partition global patterns of  $\text{CO}_2$  source/sink relationships among terrestrial and oceanic ecosystems using the inversion technique. This approach is very sensitive to estimates of photosynthetic  $^{13}\text{C}$  discrimination by terrestrial vegetation ( $\Delta_A$ ), and depends on  $\delta^{13}\text{C}$  values of respired  $\text{CO}_2$  fluxes ( $\delta^{13}\text{C}_R$ ). Here we show that by combining two independent data streams – the stable isotope ratios of atmospheric  $\text{CO}_2$  and eddy-covariance  $\text{CO}_2$  flux measurements – canopy scale estimates of  $\Delta_A$  can be successfully derived in terrestrial ecosystems. We also present the first weekly dataset of seasonal variations in  $\delta^{13}\text{C}_R$  from dominant forest ecosystems in the United States between 2001 and 2003. Our observations indicate considerable summer-time variation in the weekly value of  $\delta^{13}\text{C}_R$  within coniferous forests (4.0‰ and 5.4‰ at Wind River Canopy Crane Research Facility and Howland Forest, respectively, between May and September). The monthly mean values of  $\delta^{13}\text{C}_R$  showed a smaller range (2–3‰), which appeared to significantly correlate with soil water availability. Values of  $\delta^{13}\text{C}_R$  were less variable during the growing season at the deciduous forest (Harvard Forest). We suggest that the negative correlation between  $\delta^{13}\text{C}_R$  and soil moisture content observed in the two coniferous forests should represent a general ecosystem response to the changes in the distribution of water resources because of climate change. Shifts in  $\delta^{13}\text{C}_R$  and  $\Delta_A$  could be of sufficient magnitude globally to impact partitioning calculations of  $\text{CO}_2$  sinks between oceanic and terrestrial compartments.

*Keywords:* AmeriFlux,  $^{13}\text{C}$  discrimination, carbon dioxide, carbon isotope, net ecosystem exchange, temperate forests

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## Introduction

The  $\delta^{13}\text{C}$  values of atmospheric carbon dioxide ( $\text{CO}_2$ ) have emerged as an important, investigative tool for partitioning global patterns of  $\text{CO}_2$  source/sink relationships among terrestrial and oceanic ecosystems (Keeling *et al.*, 1989; Tans *et al.*, 1993; Ciais *et al.*, 1995). Interannual variability of terrestrial and oceanic  $\text{CO}_2$  fluxes has been inferred by observations from global

flask networks of atmospheric  $\text{CO}_2$  concentration and  $\delta^{13}\text{C}$  content using inversion techniques (Ciais *et al.*, 1995; Enting *et al.*, 1995; Francey *et al.*, 1995; Keeling *et al.*, 1995; Battle *et al.*, 2000), assuming that the photosynthetic discrimination against  $^{13}\text{CO}_2$  by terrestrial vegetation ( $\Delta_A$ ) remained constant (Lloyd & Farquhar, 1994; Fung *et al.*, 1997; Keeling *et al.*, 2001). Such an assumption simplifies the mass balance equation of global atmospheric  $^{13}\text{CO}_2$ , ignoring the potential covariance between variations in  $\Delta_A$  and gross primary production (GPP) fluxes with respect to changes in environmental conditions. Recent studies

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(Keeling *et al.*, 2001; Randerson *et al.*, 2002; Scholze *et al.*, 2003), reevaluated existing global CO<sub>2</sub> flask network observations. They predicted a more consistent, inter-annual interpretation of the available data, and less interannual variability in the partitioning of land and oceanic CO<sub>2</sub> fluxes if there were simultaneous regional reductions in Δ<sub>A</sub> and GPP during drought periods. The calculated partitioning of CO<sub>2</sub> fluxes between land and ocean is sensitive to even slight changes in globally averaged Δ<sub>A</sub> of less than 0.5‰ (Randerson *et al.*, 2002).

Improving our understanding of the magnitude of the terrestrial vs. oceanic CO<sub>2</sub> sink strength has implications for global CO<sub>2</sub> policies, while improving our understanding of climatic drivers for changes in Δ<sub>A</sub> will lead to a stronger mechanistic understanding of controls over gas exchange fluxes at ecosystem and regional scales. Historically, only sparse, discontinuous Δ<sub>A</sub> values have been available. As a consequence, δ<sup>13</sup>C data for terrestrial ecosystems have been derived from static organic matter observations (Lloyd & Farquhar, 1994).

Temporal variations in Δ<sub>A</sub> largely reflect physiological responses of overstory species to weather conditions, and provide information on the transfer of CO<sub>2</sub> from the atmosphere into organic matter in terrestrial ecosystems. CO<sub>2</sub> released from a terrestrial ecosystem, however, includes autotrophic and heterotrophic contributions from both above- and belowground components. Soil respired CO<sub>2</sub> integrates processes including litter decomposition, root and microbial respiration; each has distinct turnover rates (Trumbore *et al.*, 1996). Differences in turnover rates also incorporate the isotopic disequilibrium effect resulting from the gradual depletion of atmospheric δ<sup>13</sup>C because of fossil fuel burning (Fung *et al.*, 1997). As a result, the δ<sup>13</sup>C value of ecosystem respired CO<sub>2</sub> does not necessarily equate with the δ<sup>13</sup>C value of current photosynthate. To understand the carbon isotope budget, with respect to ecosystem-atmosphere CO<sub>2</sub> exchange, we need to consider δ<sup>13</sup>C signatures of ecosystem respiration (δ<sup>13</sup>C<sub>R</sub>) that include soil carbon (Buchmann *et al.*, 1998).

During daytime, plants discriminate against <sup>13</sup>C via photosynthesis (Δ<sub>A</sub>), leaving the atmospheric CO<sub>2</sub> more enriched in the <sup>13</sup>C content (Farquhar *et al.*, 1989). At night, much of these <sup>13</sup>C-depleted organic products are released back to the atmosphere through ecosystem respiration by plant materials and microbes (δ<sup>13</sup>C<sub>R</sub>). The latter can be estimated by a mixing process of adding respired carbon substrates to a constant starting point (Keeling, 1958) with simultaneous measurements of CO<sub>2</sub> and δ<sup>13</sup>C in the canopy air, given by

$$\delta^{13}C_m = \frac{C_a(\delta^{13}C_a - \delta^{13}C_R)}{C_m} + \delta^{13}C_R, \quad (1)$$

where C and δ<sup>13</sup>C represent concentration and carbon isotope ratio of CO<sub>2</sub>, respectively. Subscripts m and a represent measurements within the canopy boundary layer and the background air (defined later). Note that δ<sup>13</sup>C<sub>R</sub> represents δ<sup>13</sup>C signatures associated with ecosystem respiratory fluxes. During daytime, the biosphere-atmosphere CO<sub>2</sub> exchange represents the net balance of two gross fluxes – photosynthesis and respiration working in opposite directions. Considering canopy-atmosphere CO<sub>2</sub> exchange under daytime conditions, an equation based on the same mass balance principle (C<sub>m</sub> = C<sub>a</sub> + C<sub>s</sub>; δ<sub>m</sub>C<sub>m</sub> = δ<sub>a</sub>C<sub>a</sub> + δ<sub>s</sub>C<sub>s</sub>, where subscript s represents net sources) can be derived in which δ<sup>13</sup>C<sub>bio</sub> represents the δ<sup>13</sup>C signature associated with the net exchange CO<sub>2</sub> fluxes (NEE) (Bakwin *et al.*, 1998; Miller *et al.*, 2003), given by

$$(\delta^{13}C_m \cdot C_m - \delta^{13}C_a \cdot C_a) = \delta^{13}C_{bio}(C_m - C_a), \quad (2)$$

which has merit for analyzing a time series of air samples collected over multiple seasons or years during which C<sub>a</sub> and δ<sup>13</sup>C<sub>a</sub> vary with time (also see Fig. 3; Miller *et al.*, 2003). We cautiously note that δ<sup>13</sup>C<sub>bio</sub> and δ<sup>13</sup>C<sub>R</sub> are not equal because each represents the carbon isotope ratio associated with day- and night-time CO<sub>2</sub> exchange, respectively. Using a linear regression involving X = C<sub>m</sub> - C<sub>a</sub> and Y = δ<sup>13</sup>C<sub>m</sub>C<sub>m</sub> - δ<sup>13</sup>C<sub>a</sub>C<sub>a</sub>, we obtain δ<sup>13</sup>C<sub>bio</sub> as the slope of the regression.

To calculate δ<sup>13</sup>C<sub>bio</sub> using Eqn (2), additional information is necessary; that is, C<sub>a</sub> and δ<sup>13</sup>C<sub>a</sub> needs to be defined exclusively. We extract zonal-mean values of CO<sub>2</sub> concentration and δ<sup>13</sup>CO<sub>2</sub> from NOAA/CMDL's Globalview database to represent background air at the same latitude as each of our three local stations in our calculation of δ<sup>13</sup>C<sub>bio</sub> (Lai *et al.*, 2004). Globalview is a data product that interpolates marine boundary layer (MBL) measurements to weekly intervals and fills spatial data gaps by linear interpolation from nearby stations (Masarie & Tans, 1995; Globalview-CO<sub>2</sub>, 2003). Globalview MBL-CO<sub>2</sub> matrix has recently been incorporated to estimate net surface flux of CO<sub>2</sub> using an equilibrium boundary layer approach for a forested area in Wisconsin, USA (Helliker *et al.*, 2004), and is available on Internet via anonymous FTP to ftp://ftp.cmdl.noaa.gov/ccg/co2/GLOBALVIEW/.

At the ecosystem scale, when net and gross CO<sub>2</sub> fluxes are measured independently, the δ<sup>13</sup>C ratio associated with canopy-scale photosynthesis (δ<sup>13</sup>C<sub>p</sub>) can be estimated by (Lai *et al.*, 2004):

$$\delta^{13}C_{bio} \cdot NEE = \delta^{13}C_p \cdot GPP + \overline{\delta^{13}C_R} \cdot R \quad (3)$$

and

$$\Delta_A = \frac{\delta^{13}C_a - \delta^{13}C_p}{1 + \delta^{13}C_p/1000}, \quad (4)$$

where NEE and  $R$  represent net exchange and respiratory  $\text{CO}_2$  fluxes, respectively. In this study, we report the first long-term, weekly set of observations of ecosystem respired  $\delta^{13}\text{CO}_2$  from dominant forest ecosystems across the United States between 2001 and 2003. Using weekly measurements of mid-afternoon flasks (two to four flasks per week), a representative  $\delta^{13}\text{C}$  signature associated with NEE fluxes ( $\delta^{13}\text{C}_{\text{bio}}$ ) was estimated for the entire growing season (May–October) for each site. A flux-weighted mean  $\delta^{13}\text{C}_R$  value ( $\delta^{13}\text{C}_R$ ) representing the same period was calculated on a monthly basis. NEE fluxes were directly measured by the eddy covariance method and other flux components (GPP and  $R$ ) were derived based on site-dependent empirical functions (discussed in ‘Measurements of  $\text{CO}_2$  fluxes and other variables’). Combining isotope and flux measurements allowed us to estimate a canopy-scale  $\Delta_A$  using a measurement-based approach (i.e. Eqn (3)).

We investigated  $\delta^{13}\text{C}_R$  and  $\Delta_A$  in three contrasting terrestrial ecosystems, including a western coniferous forest (Wind River Canopy Crane Research Facility (WRCCRF), WA, 45°49'N, 121°58'W; Shaw *et al.*, 2004), a temperate deciduous forest (Harvard Forest, MA, 42°32'N, 72°11'W; Barford *et al.*, 2001), and an eastern coniferous forest (Howland Forest, ME, 45°15'N, 68°45'W; Hollinger *et al.*, 1999). These three sites comprise the major forest biomes that are considered to be potentially responsible for a large part of the missing carbon sink in northern temperate zones; each site was part of the AmeriFlux network. A new sampling system (Schauer *et al.*, 2003) had been developed which made possible unattended weekly monitoring of over 3200 atmospheric flasks at these sites during the reported measurement period.

## Materials and methods

### Flasks sampling

One of the challenges in monitoring ecosystem discrimination is the lack of sampling because of logistical requirements for night-time flask collection. To circumvent such a restriction, we used an automated air sampling system to collect 15 flasks weekly during the growing season and monthly when plants were dormant (Lai *et al.*, 2003; Schauer *et al.*, 2003). Two flasks were collected in the mid-afternoon (usually between 02:30 and 03:30 hours) from the top intake, roughly 2 m above the highest branches of the canopy. This flask pair was averaged for  $\text{CO}_2$  concentration and  $\delta^{13}\text{C}$  to estimate daytime canopy air. Beginning from March 2003, an extra pair of daytime flasks was collected on a separate day every week. Data screening

was carefully performed before further analyses. Measurements were first conditioned so that differences between the two members of a flask pair did not differ by more than five times of mass spectrometer precision in continuous flow mode (0.12% for  $\delta^{13}\text{C}$  in VPDB scale). A flawed flask pair was identified if the  $\text{CO}_2$  concentration of the two flask members differed by more than 2% of expected concentration ( $\sim 7$  ppm) based on *in situ* measurements. Ten percent of the daytime flask samples were excluded on this basis. Night-time sampling began an hour after sunset to ensure no photosynthesis effect on our estimates of  $\delta^{13}\text{C}_R$ . Pataki *et al.* (2003) suggested general guidelines to reduce errors when using the two-source mixing approach (i.e. Eqn (1)) for estimating  $\delta^{13}\text{C}_R$ , which is based on the fundamental assumption that the isotopic composition of two considered sources remains unchanged, or the contribution of multiple sources remains proportionally the same over the sampling period. Night-time samples were collected at two heights – one at 0.5 m above ground and the other at 1/2 of canopy height. Flasks were collected to satisfy a minimum  $\text{CO}_2$  gradient specified *a priori* in the datalogger program within the same night; that is, sampling began 1 h after sunset at 5 min intervals until all flasks were filled. A ‘panic’ mode was initiated 1 h before sunrise which filled all the remaining empty flasks before any photosynthetic uptake. If the specified  $\text{CO}_2$  gradient was not met, the sampler resets and repeats the same procedure the following day. The reliability of measured  $\delta^{13}\text{C}_R$  using the Keeling-plot approach diminishes as the  $\text{CO}_2$  gradient of a flask set decreases (Pataki *et al.*, 2003). In order to increase statistical confidence in  $\delta^{13}\text{C}_R$  measurements, we specified the expected  $\text{CO}_2$  gradient ( $\geq 75$  ppm during the growing season but no less than 20 ppm the rest of the year) in the datalogger program based on *in situ*  $\text{CO}_2$  profile measurements for each site. This expected  $\text{CO}_2$  gradient was calculated on a monthly basis. Since measurement errors were associated with both dependent and independent variables, we used the geometric mean regression for estimating each  $\delta^{13}\text{C}_R$  value (Sokal & Rohlf, 1995). Outliers were removed before the regression following procedures described in Bowling *et al.* (2002). Values of  $\delta^{13}\text{C}_R$  were not used if standard errors are greater than 3‰ for this study. Four percent of the measured  $\delta^{13}\text{C}_R$  values were excluded on this basis. Flasks were shipped back to Utah for stable isotope ratio analyses using a continuous-flow isotope ratio mass spectrometer (Delta S, San Jose, CA, USA), and  $\text{CO}_2$  concentrations were measured with high precision ( $\pm 0.2$  ppm) using a bellows/IRGA system (Bowling *et al.*, 2001). Since January 2003, all our flasks were analyzed for both  $\delta^{13}\text{C}$  ratio and  $\text{CO}_2$  concentration on a

GC-IRMS system, which has improved our precision to 0.06‰ for  $\delta^{13}\text{C}$  while retaining comparable precision of 0.48 ppm for  $\text{CO}_2$  concentration (Schauer *et al.*, 2005).

#### *Measurements of $\text{CO}_2$ fluxes and other variables*

Ancillary measurements in addition to the present isotopic analyses, including soil moisture,  $\text{CO}_2$ , carbon monoxide and eddy covariance fluxes are briefly described here. Soil moisture contents were measured by 6 CS610-L Time Domain Reflectometer (Campbell Scientific Inc., Logan, UT, USA) probes in the top 30 cm at Wind River Canopy Crane site, and with a profile of Hydra-Vitel soil moisture probes from 0 to 100 cm at the Howland Forest. *In situ* concentration measurements of  $\text{CO}_2$  at the Harvard Forest were measured with Li-Cor 6252- and 6262-infrared gas analyzers (Lincoln, NE, USA) and a Dasibi infrared absorbance instrument measured the carbon monoxide concentration (Munger *et al.*, 1996). For all three sites, NEE were measured by eddy covariance systems with standard configurations conforming with the guidelines of the AmeriFlux network (Goulden *et al.*, 1996a; Hollinger *et al.*, 2004; Paw *et al.*, 2004). Night-time eddy flux measurements are subject to low turbulent conditions, possibly underestimating ecosystem respiration (Goulden *et al.*, 1996b; Lavigne *et al.*, 1997). Ecosystem respiration derived from eddy covariance measurements therefore requires special attention. For this study, night-time eddy fluxes were first corrected for low turbulent conditions based on friction velocity ( $u^*$ ). The  $u^*$  correction is empirical and site dependent; the choice of  $u^*$  threshold for these forests were described in detail elsewhere (WRCCRF: Paw *et al.*, 2004; Harvard Forest: Goulden *et al.*, 1996b, Barford *et al.*, 2001; Howland Forest: Hollinger *et al.*, 2004). Here, we briefly summarize procedures used to estimate ecosystem respiration ( $R$ ) at these three sites. GPP fluxes were then calculated as  $\text{GPP} = \text{NEE} - R$ .

*Wind river canopy crane.* High wind-speed measurements of night-time fluxes were first selected; annual datasets were then used to derive an exponential fit with air temperature at 2 m (Paw *et al.*, 2004). Paw *et al.* (2004) showed that night-time fluxes became more scattered when  $u^* < 0.5 \text{ m s}^{-1}$ , whereas, above this threshold, nocturnal eddy fluxes were always positive. The half-hourly night-time  $\text{CO}_2$  fluxes were therefore replaced with the generated equation for periods when  $u^* < 0.5 \text{ m s}^{-1}$ . Sensitivity tests indicated that using a threshold of  $0.3 \text{ m s}^{-1}$  does not significantly change annual NEE estimates when compared with a threshold of  $0.5 \text{ m s}^{-1}$ .

*Harvard Forest.* Well-mixed night-time NEE data were selected using a  $u^*$  threshold at  $0.2 \text{ m s}^{-1}$ . The remaining

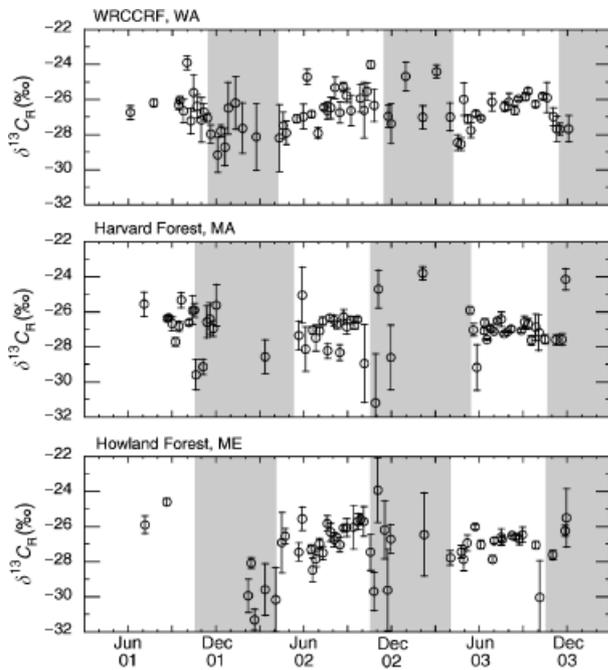
data were used to define a functional relationship between deviations from mean respiration ( $R_{\text{mean}}$ ) and deviations from the mean air temperature ( $T_{\text{mean}}$ ) over short intervals on a monthly basis, using the equation  $R = R_{\text{mean}} + k(T - T_{\text{mean}})$ , where  $k$  is the slope of a linear relationship between deviations in  $R$  from the mean and deviations in  $T$  from the mean (S. Urbanski *et al.*, unpublished data). Because relatively short time intervals were used to define the temperature dependence, the temperature ranges are narrow and the physiological state of the ecosystem (e.g. bud break in spring) is somewhat embedded in the equation.

*Howland Forest.* Night-time NEE data were first selected with a  $u^*$  threshold at  $0.25 \text{ m s}^{-1}$ . Missing nocturnal  $\text{CO}_2$  exchange values were obtained from second-order Fourier regressions between Julian day and nocturnal respiration using data from the entire year (Hollinger *et al.*, 2004). This approach gives an unbiased estimate and is superior to the Lloyd & Taylor (1994) approach in fitting the seasonality of respiration.

More information about eddy covariance fluxes at these three sites is available at <http://public.ornl.gov/ameriflux/Participants/Sites/Map/index.cfm>

## Results and discussion

Figure 1 shows weekly measurements of  $\delta^{13}\text{C}_R$  at the three AmeriFlux sites for our study period. There were pronounced seasonal dynamics in  $\delta^{13}\text{C}_R$  at the two coniferous forests (WRCCRF and Howland Forest). These carbon isotope variations far exceeded any observed variations in the leaf organic  $^{13}\text{C}$  content, which had varied insignificantly with time (Fessenden & Ehleringer, 2003). In contrast, seasonality was less obvious at the deciduous forest (Harvard Forest). Generally speaking, the most negative  $\delta^{13}\text{C}_R$  values occurred earliest in the growing season, while the least negative values occurred towards the late summer. These are  $\text{C}_3$ -dominated ecosystems and there were no  $\text{C}_4$  photosynthesis species in any of these three forests, which might otherwise have provided a potential explanation for the emergence of heavy  $^{13}\text{C}$  respiration during the warm, end-of-summer period. Recent studies suggested that respired  $\text{CO}_2$  from terrestrial ecosystems consists of a large portion of recently fixed carbon substrates (Ekblad & Högberg 2001; Högberg *et al.*, 2001; Bowling *et al.*, 2002), indicating a rapid recycling of recent photosynthesis into current respiration. That is, the  $\delta^{13}\text{C}$  signatures of respired  $\text{CO}_2$  measured on a given night reflects the gas exchange activities integrated over the past few days prior to the measurements. The seasonal trends in  $\delta^{13}\text{C}_R$  were suggestive of decreased ratios of intercellular to

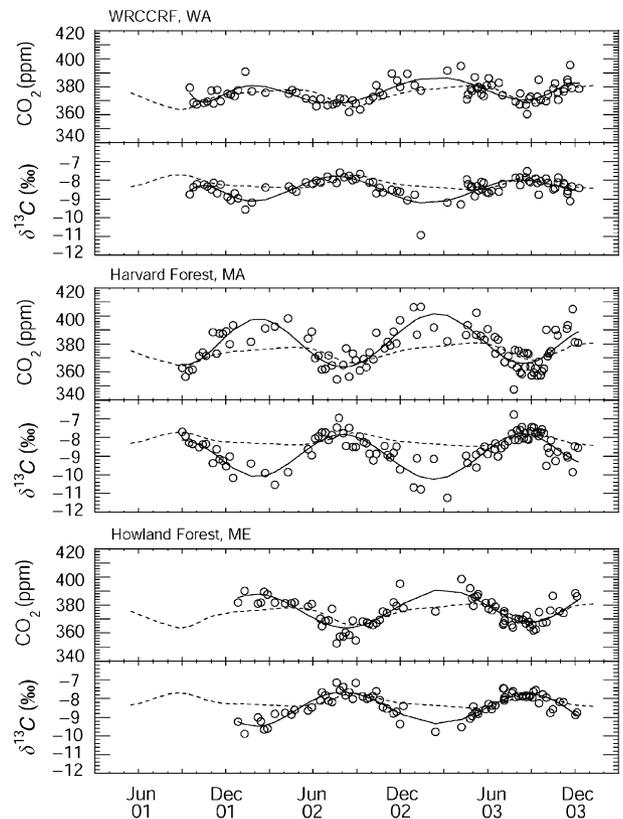


**Fig. 1** Carbon isotope ratios of ecosystem respired  $\text{CO}_2$  ( $\delta^{13}\text{C}_R$ ) measured at three forest biomes between June 2001 and December 2003. Error bars indicate one standard error and gray areas indicate dormant seasons based on phenological measurements.

ambient  $\text{CO}_2$  concentration by  $\text{C}_3$  autotrophic ecosystem components later in the season, most likely associated with partial stomatal closures (Farquhar *et al.*, 1989; Flanagan *et al.*, 1996). Using latent heat flux (LE) and vapor saturation deficit (vpd) measurements, canopy stomatal conductance was calculated by a 'big leaf' approximation using  $g = \text{LE}/\text{vpd}$  for the Howland Forest. The result revealed a decreased canopy-scale stomatal conductance as a severe drought progressed during the 2002 summer (data not shown). From soil moisture measurements, the pattern of summer drought was indeed obvious in the two coniferous forests. The correlation between  $\delta^{13}\text{C}_R$  and soil moisture content will be discussed later.

Values of  $\delta^{13}\text{C}_R$  appeared to be more scattered during wintertime. This is partially because of small  $\text{CO}_2$  gradients encountered in this period as a result of reduced respiratory fluxes. Errors associated with an individual Keeling intercept were greater (Fig. 1) when  $\text{CO}_2$  gradient was small (Pataki *et al.*, 2003). Nonetheless, on an annual time scale, the productivity is much reduced during winter which contributed little impacts in terms of the biospheric isoflux.

Figure 2 showed midday  $\text{CO}_2$  concentration and  $\delta^{13}\text{C}$  ratio in air above canopies at the three AmeriFlux sites. The concentration and  $\delta^{13}\text{C}$  of daytime  $\text{CO}_2$  above canopy, even under turbulent conditions in which the



**Fig. 2** Concentration and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in canopy air measured in the mid-afternoon. Open circles represent samples collected 2 m above the canopy fitted with a smooth curve (solid lines). Background troposphere (dash lines), represented here by Globalview marine boundary layer reference matrices derived from measurements within NOAA/CMDL network, were also shown for comparison.

convective boundary layer has grown to its maximum, clearly showed the impact of the biosphere on the atmosphere. A smooth curve consisting of second-order polynomial and annual harmonics was fit to observations (Thoning *et al.*, 1989). The seasonality of daytime measurements is the combined consequence of the relative balance between photosynthetic and respiratory activities and atmospheric transport at different times of the year. These observations suggest a strong correlation between  $\text{CO}_2$  concentration and  $\delta^{13}\text{C}$  in forest ecosystems, in particular during summer months. Figure 2 also showed remarkable differences in the intraannual amplitudes among the three sites, with the greatest seasonal swing at the Harvard Forest and the smallest at WRCCRF. These distinct patterns probably reflect differences in the source/sink strength as well as regional atmospheric mixing near the three forests.

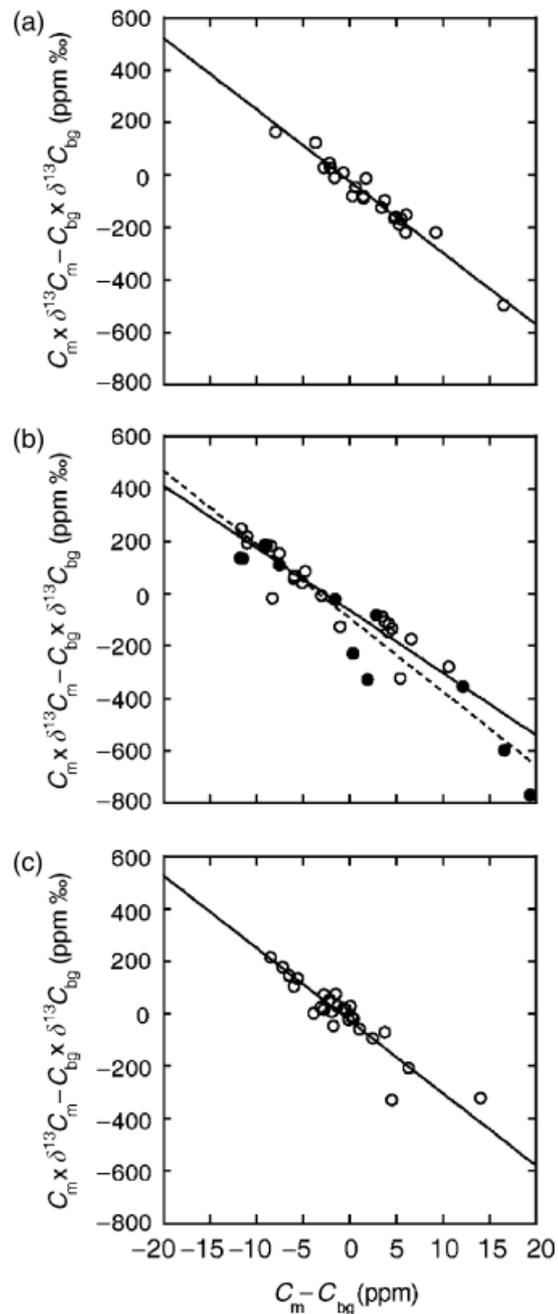
To highlight the terrestrial effect on atmospheric  $\text{CO}_2$  and  $\delta^{13}\text{C}$ , we superimpose our daytime measurements

with tropospheric values, represented by smooth curves fitted to MBL measurements within the NOAA/CMDL's network. Dashed lines shown in Fig. 2 were extracted from Globalview-CO<sub>2</sub> and  $-\delta^{13}\text{C}$  matrices for the same latitude as each of our local stations, representing values of  $C_a$  and  $\delta^{13}\text{C}_a$  (background atmosphere) for current analyses. The  $\delta^{13}\text{C}$  of above-canopy CO<sub>2</sub> became more enriched than background values with concurrent CO<sub>2</sub> drawdown between June and September at all sites, indicative of substantial regional photosynthetic activities during this period. CO<sub>2</sub> flask samples collected within the canopy roughness boundary layer are subject to considerable localized gas exchange activities and fossil fuel contributions relative to those from a remote marine site, as shown by the larger amplitudes of both CO<sub>2</sub> and  $\delta^{13}\text{C}$  signals. This was particularly apparent at the Harvard Forest site in winter. Note that differences between terrestrial and marine signals were the smallest at WRCCRF (merely ~160 km east of Pacific coast) and the greatest at Harvard Forest (~110 km west of Boston metropolitan area). We believe this is because of the collective effect of regional atmospheric mixing and CO<sub>2</sub> source inputs in respective areas.

Using daytime concentration and  $\delta^{13}\text{C}$  of CO<sub>2</sub> measured locally above canopies during the growing season (May–October) and values of  $C_a$  and  $\delta^{13}\text{C}_a$  represented by Globalview reference matrices (dashed curves in Fig. 2), we estimated an annual mean, canopy-scale  $\delta^{13}\text{C}_{\text{bio}}$  by Eqn (2). Estimates of  $\delta^{13}\text{C}_{\text{bio}}$  were robust with respect to instrument errors, but could be sensitive to choice of background air (Lai *et al.*, 2004). Figure 3 shows the graphic presentation of  $\delta^{13}\text{C}_{\text{bio}}$  estimates for the three forests, in which two distinct  $\delta^{13}\text{C}_{\text{bio}}$  values were derived using measurements between May and August (solid line) or May and October (dash line) for the Harvard Forest. Lai *et al.* (2004) showed that fossil fuel inputs became relatively important in the fall at Harvard Forest, which may have biased our estimates of  $\delta^{13}\text{C}_{\text{bio}}$  (Fig. 3b). Therefore, we adopted only measurements from May to August when calculating  $\delta^{13}\text{C}_{\text{bio}}$  for the Harvard Forest. The mean  $\delta^{13}\text{C}_R$  value ( $\delta^{13}\text{C}_R$ ) representing the entire growing season is flux weighted by the estimated respiration flux on a monthly basis (Fig. 4) using

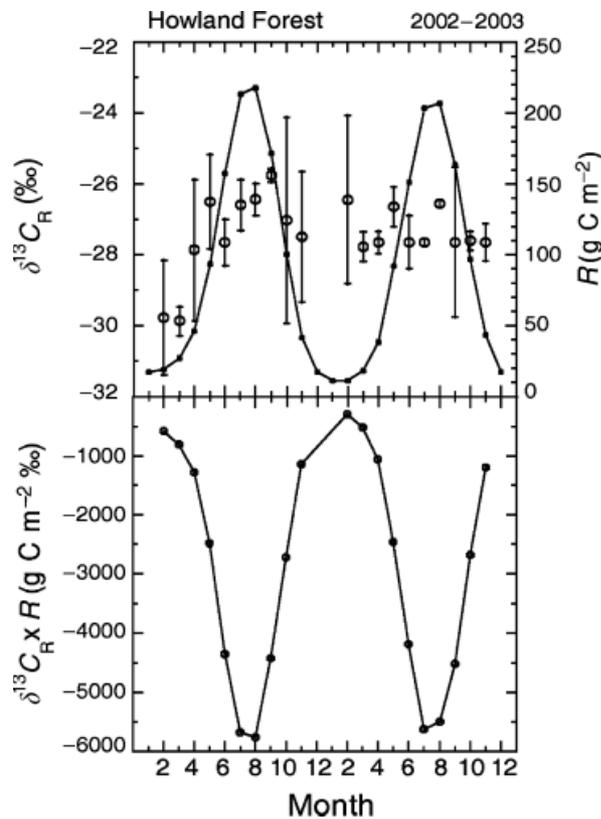
$$\overline{\delta^{13}\text{C}_R} = \frac{\sum \delta^{13}\text{C}_R \cdot R}{\sum R}. \quad (5)$$

Figure 4 clearly shows that the seasonality of ecosystem isoflux is mostly controlled by the flux component, and by the isotopic variation to a much less degree. The larger errors in the measured  $\delta^{13}\text{C}_R$  values during wintertime are mitigated by the smaller fluxes, result-



**Fig. 3** Relationship between deviations of local CO<sub>2</sub> mixing ratio and deviations of the product of CO<sub>2</sub> mixing ratio and  $\delta^{13}\text{C}$  from background troposphere for (a) Wind River Canopy Crane Research Facility (b) Harvard Forest and (c) Howland Forest. Measurements collected during the growing season in 2003 were used. Slopes of the linear regression represent estimates of  $\delta^{13}\text{C}_{\text{bio}}$ . At Harvard Forest, two distinct  $\delta^{13}\text{C}_{\text{bio}}$  values were derived, depending on measurement periods: May–August (solid line) or May–October (dash line).

ing in much reduced isoflux in winter. The sign of 'isoflux' is opposite to the 'flux' of substrates because of our definition in expressing isotopic composition.



**Fig. 4** A representative seasonal variation of ecosystem isoflux. Shown here are monthly-mean  $\delta^{13}\text{C}_R$ , ecosystem respiration ( $R$ ) and the respiratory isoflux ( $\delta^{13}\text{C}_R \times R$ ) at Howland Forest.

Values reported in Table 1 were *consistently* calculated using data collected only during the growing season (May–October) at WRCCRF and Howland forest. For the Harvard Forest, calculations were done using measurements collected between May and August. All the flux components were reported as the sum for the same period. The sign convention for fluxes is negative for carbon flow directed from the atmosphere to the ecosystem. Combining direct flux measurements of NEE and derived fluxes of GPP and  $R$ , we estimated  $\Delta_A$  using Eqns (3) and (4). The background tropospheric  $\delta^{13}\text{C}$  was represented by Globalview data product on the basis of MBL measurements. For our study sites, ranging from  $42^\circ 32' \text{N}$  to  $45^\circ 49' \text{N}$ , the annual-mean MBL  $\delta^{13}\text{C}$  is about  $-8\%$  with indistinguishable differences among the three sites (Lai *et al.*, 2004). Considerable gradients of  $\text{CO}_2$  concentration and  $\delta^{13}\text{C}$  ratio may exist for the air (source air) inside dense canopies. Nonetheless, such gradient is usually noticeable only within 1 m above forest floor (Buchmann *et al.*, 2002). Meanwhile, sunlit foliage at the top portion of canopies showed no correlation with canopy structure, suggesting temporal changes in  $\Delta_A$  mainly resulted from intrinsic water use efficiency instead of source air (Buchmann *et al.*, 1997b). In essence, we used the annual-mean MBL  $\delta^{13}\text{C}$  value ( $-8\%$ ) to represent  $\delta^{13}\text{C}_a$  in this study. We have a full year of isotope measurements for both day- and night-time conditions in 2002 and 2003. Therefore, we calculated  $\Delta_A$  for the 2 years and compared the results in Table 1. NEE flux

**Table 1** Estimates of growing season (May–October) mean  $\delta^{13}\text{C}$  of ecosystem respired  $\text{CO}_2$  ( $\overline{\delta^{13}\text{C}_R}$ ), net exchange  $\text{CO}_2$  fluxes ( $\delta^{13}\text{C}_{\text{bio}}$ ) and photosynthetic discrimination against  $^{13}\text{C}$  ( $\Delta_A$ ) at three AmeriFlux sites: Wind River Canopy Crane Research Facility (WRCCRF), Harvard Forest, and Howland Forest for 2002 and 2003

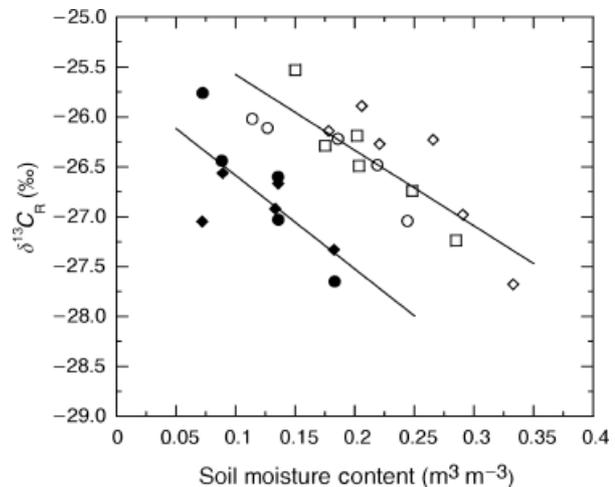
Site and year	$\overline{\delta^{13}\text{C}_R}$ ( $\pm$ SE‰)	$\delta^{13}\text{C}_{\text{bio}}$ ( $\pm$ SE‰)	NEE ( $\text{g C m}^{-2}$ )	GPP ( $\text{g C m}^{-2}$ )	$R$ ( $\text{g C m}^{-2}$ )	$\Delta_A$ (‰)	Errors of $\Delta_A$ ( $\pm$ SE‰)	
							(a)	(b)
<i>WRCCRF</i>								
2002	$-26.2 \pm 0.6$	$-27.1 \pm 2.7$	$-37$	$-646$	$610$	$18.8$	$1.3$	$4.9$
2003	$-26.4 \pm 0.4$	$-27.3 \pm 1.3$	$-$	$-$	$-$	$-$	$-$	$-$
<i>Harvard Forest*</i>								
2002	$-27.0 \pm 0.2$	$-28.3 \pm 2.5$	$-489$	$-1130$	$641$	$20.1$	$2.0$	$6.8$
2003	$-27.0 \pm 0.3$	$-23.7 \pm 1.9$	$-443$	$-1138$	$695$	$18.2$	$1.7$	$6.4$
<i>Howland Forest</i>								
2002	$-26.6 \pm 0.6$	$-27.8 \pm 2.4$	$-204$	$-1158$	$954$	$19.3$	$1.3$	$4.5$
2003	$-27.3 \pm 0.5$	$-27.7 \pm 2.3$	$-260$	$-1174$	$914$	$19.9$	$1.2$	$4.3$

Measured fluxes of net  $\text{CO}_2$  exchange (NEE), gross primary production (GPP) and ecosystem respiration ( $R$ ) represent accumulated values from May to October. The sign convention for fluxes is negative for carbon flow directed from the atmosphere to the ecosystem. Two sensitivity analyses were conducted assuming (a)  $\pm 5\%$  and (b)  $\pm 20\%$  SE for eddy covariance measurements regarding errors associated with measurement-based estimates of  $\Delta_A$ .

\*Includes only measurements between May and August.

measurements indicated net carbon gain in Harvard and Howland forests for our investigative period; while WRCCRF showed nearly neutral in 2002 (2003 NEE estimates were yet to be determined). Harvard Forest appeared to have the greatest net uptake of atmospheric  $\text{CO}_2$ , when compared using measurements only between May and August (data not shown) among the three sites. The estimated values of  $\Delta_A$  were 18.8, 20.1 and 19.3‰ for WRCCRF, Harvard Forest and Howland Forest, respectively, in 2002. These estimates are subject to uncertainties in both isotope and flux measurements. Eddy-covariance measured NEE fluxes are potentially plagued by a number of factors, including sensor limitation, atmospheric transport and topography effects. Although errors in flux measurements remain large ( $\pm 20\%$ ; Moncrieff *et al.*, 1996), on a relatively flat terrain, spatial variability in eddy covariance measurements over similar patches of forests may be as small as 5% (Hollinger *et al.*, 2004). We therefore performed a sensitivity test considering two cases: an optimized scenario with the assumption that errors in flux components can be measured within  $\pm 5\%$  and the other with a more common assumption of  $\pm 20\%$ . Table 1 shows uncertainties associated with our  $\Delta_A$  estimates by propagating errors through the calculation of Eqn (3). Errors in flux components radically affect the confidence in our estimates of  $\Delta_A$  using this measurement-based approach. For Harvard and Howland Forests, values of  $\Delta_A$  between 2002 and 2003 were marginally different given the large errors involved. When examined in detail, the 2‰ change in  $\Delta_A$  at Harvard Forest was mainly because of a 4.6‰ shift in  $\delta^{13}\text{C}_{\text{bio}}$  between the 2 years. This is somewhat contrasting to the calculation demonstrated by Lai *et al.* (2004), which concluded that calculations of  $\Delta_A$  are insensitive to estimates of  $\delta^{13}\text{C}_{\text{bio}}$ . The discrepancy between the calculation here and that of Lai *et al.* (2004) resides on the NEE flux term. When only summer months are considered, the magnitude of NEE is comparable with GPP or  $R$  (Table 1). As a result, the product of  $\delta^{13}\text{C}_{\text{bio}}$  and NEE (LHS of Eqn (3)) is comparable with the terms on the RHS. On an annual time scale, however, NEE is reduced as the ecosystem approaches a pseudobalance between  $\text{CO}_2$  uptake and release. The example adopted, in Lai *et al.* (2004), decadal carbon budgets that had smoothed-out temporal variability and consequently, showed less sensitivity to values of  $\delta^{13}\text{C}_{\text{bio}}$ .

Many environmental and biological factors influencing stomatal conductances have the potential to alter  $\Delta_A$  and  $\delta^{13}\text{C}_R$  on seasonal and annual time scales, and in turn causing significant perturbation to the atmospheric  $^{13}\text{C}$  budget. For instance, drought stress reduces stomatal conductances and consequently affects  $\Delta_A$  (Farquhar *et al.*, 1989). Furthermore, the degree of



**Fig. 5** Relationship between monthly mean  $\delta^{13}\text{C}_R$  and averaged soil moisture contents in the upper 30 cm soil at Wind River Canopy Crane Research Facility (WRCCRF) (open symbols) and upper 100 cm soil at Howland Forest (close symbols). Data shown here are between June and November for WRCCRF and between June and October for the Howland Forest measured in 2001 (square), 2002 (circle) and 2003 (diamond), respectively. Regression statistics are  $Y = -24.818 - 7.575X$ ,  $R^2 = 0.83$  for WRCCRF and  $Y = -25.661 - 9.428X$ ,  $R^2 = 0.74$  for the Howland Forest.

drought-induced  $\Delta_A$  variation differs among plant species (Farquhar *et al.*, 1989; Ehleringer, 1993). Water balance in terrestrial ecosystems has profound impact on processes of carbon exchange. Precipitation can be regarded as a direct measure of the amount of water input into an ecosystem. However, depending on how precipitation is quantified (e.g. with or without overstorey interception), ecological responses to precipitation may show a broad range (weak to strong) of correlation. Soil moisture ultimately influences plant growth and should be a more representative measure to the water availability. We observed a negative correlation ( $P < 0.05$ ) between monthly mean values of  $\delta^{13}\text{C}_R$  and soil moisture contents for low-to-medium range of soil water at both coniferous forests during the 3 years of our measurements (Fig. 5). Soil water availability explained about 80% of the variance in the respired  $^{13}\text{C}$  signal for the two coniferous forests. Such a relationship may be disrupted at high levels of soil water condition when net carbon uptake reduces (Hollinger *et al.*, 2004). An explanation for a positive relationship between  $\delta^{13}\text{C}_R$  values and soil moisture at high levels of water content may be because of anaerobic stress, which may also provide explanation for the relatively positive ( $> -25\%$ )  $\delta^{13}\text{C}_R$  values occasionally observed throughout the year (Fig. 1). Other factors (e.g. temperature, radiation and vapor pressure deficit) may have also affected the variability

in the observed  $\delta^{13}\text{C}_R$  (Bowling *et al.*, 2002). Global carbon models incorporating biological and physiological principles should explicitly consider these factors.

The sensitivity of  $\delta^{13}\text{C}_R$  values to available soil moisture contents implies a strong leaf-level stomatal control of photosynthetic gas exchange. Stomatal closure in response to decreased soil moisture has often been observed in single-plant studies (Farquhar *et al.*, 1989). That this response is so clearly detected in the ecosystem-scale observations is suggestive of a strong linkage between leaf-scale and ecosystem-scale gas exchange activities. The observed correlations between current canopy-scale gas exchange activity and soil moisture content are consistent with both previous single-plant and ecosystem-scale observations (Fessenden & Ehleringer, 2003; Unsworth *et al.*, 2004), where it appeared that canopy-scale transpiration was sensitive to soil moisture availability. Using sap flow and soil moisture measurements at WRCCRF, Unsworth *et al.* (2004) showed that transpiration of overstory species accounted for nearly 90% of surface soil water loss when soil moisture was not limiting. As soil moisture content decreased, the ratio of overstory transpiration to surface soil water loss diminished to <60%, clearly indicating stomatal closure with respect to drought. These observations were in support of our explanation for the pattern shown in Fig. 5. However, it must be noted that  $\delta^{13}\text{C}$  of  $\text{CO}_2$  leaving the soil also increases with decreasing soil water content (Fessenden & Ehleringer, 2003). It is difficult to quantify the relative contributions of the soil and the vegetation to an increase in  $\delta^{13}\text{C}_R$ , since both above- and belowground components respond to drought simultaneously in the same direction. At the moment, we could not address the potential impact of heterotrophic respiration on our  $\delta^{13}\text{C}_R$  measurements. On a different note, chamber-based measurements constantly show more enriched  $\delta^{13}\text{C}$  ratio of soil efflux when compared with that for the entire ecosystem (Buchmann *et al.*, 1997a; Flanagan *et al.*, 1999; Pataki *et al.*, 2003). A long-term, systematic measurement program to monitor  $\delta^{13}\text{C}$  ratio of soil efflux should be established in conjunction with ecosystem  $\delta^{13}\text{C}_R$  measurements to address these important research questions.

## Conclusions

We present 3 years of weekly  $\text{CO}_2$  concentrations and carbon isotope compositions in canopy air from an ongoing study of three forest biomes across the United States. Our study demonstrates that by collecting both day- and night-time flasks in the canopy boundary layer,  $\delta^{13}\text{C}$  signatures of various  $\text{CO}_2$  exchange processes can be quantified. In conjunction with eddy

covariance flux measurements, a measurement-based approach can be developed to directly estimate canopy-scale  $\Delta_A$ . Errors associated with  $\Delta_A$  estimates using our measurement-based approach remain large, but they provide a direct means to test model hypotheses and constrain model outputs.

We observed a broad range of weekly  $\delta^{13}\text{C}_R$  values (4–5.4‰) between May and September in our three study sites. The monthly mean values of  $\delta^{13}\text{C}_R$  showed a smaller range (2–3‰), but significantly correlated with monthly mean soil moisture contents at the coniferous sites. Region-wide water deficits that affect vegetation and the hydrologic cycle occur globally, such as those related with El Niño and Pacific Decadal Oscillation events. Such meteorological conditions may impose regional water stresses on vegetation (e.g. the western US; Barnett *et al.*, 2004; Schubert *et al.*, 2004) and consequently alter  $\Delta_A$ , which in turn affects GPP at the landscape or continental scales. From our atmospheric observations, it is apparent that the  $\delta^{13}\text{C}$  of biosphere–atmosphere  $\text{CO}_2$  exchange at the ecosystem scale responded to changes in water availability over both annual and interannual periods. Interannual climatic events (e.g. El Niño), that influence hydrological cycles on land, will likely be major factors driving the interannual variability in terrestrial discrimination and could affect our interpretation of the relative  $\text{CO}_2$  sink strength between marine and terrestrial ecosystems.

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