

# CO<sub>2</sub> concentration profiles, and carbon and oxygen isotopes in C<sub>3</sub> and C<sub>4</sub> crop canopies

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## Abstract

CO<sub>2</sub> concentrations ([CO<sub>2</sub>]), as well as carbon and oxygen isotope ratios ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) were measured within alfalfa (C<sub>3</sub>) and corn (C<sub>4</sub>) crop canopies (leaf area indices of 4.6 and 2.5, respectively). Daily fluctuations were observed within the canopy and extended into the canopy boundary layer (at heights 2 to 3 times higher than the maximum plant height). Photosynthetic demand for canopy CO<sub>2</sub> exceeded soil respiration to such an extent that daytime [CO<sub>2</sub>] values were depleted 15 to 50 ppm below tropospheric values;  $\delta^{13}\text{C}$  values of canopy air reached a maximum of 3‰ heavier than the tropospheric baseline values. Highly significant relationships were observed between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ratios of canopy air in both crop canopies. Leaf carbon isotope discrimination was significantly different between species, 20‰ (alfalfa) vs. 4‰ (corn). However, the relationships between 1/[CO<sub>2</sub>] and  $\delta^{13}\text{C}$ , as well as 1/[CO<sub>2</sub>] and  $\delta^{18}\text{O}$  of canopy air did not differ between the two crop species. Thus, ecosystem respiration had an average  $\delta^{13}\text{C}$  ratio of -21.6‰ and a  $\delta^{18}\text{O}$  ratio of 29‰. The  $\delta^{13}\text{C}$  values of soil-respired CO<sub>2</sub> were similar in both C<sub>3</sub> and C<sub>4</sub> crop stands (approximately -22.6‰). Ecosystem-level carbon isotope discrimination ( $\Delta_c$ ) estimates were indistinguishable between both crops (13.8‰ for alfalfa, and 13.2‰ for corn). Thus, the  $\Delta_c$  estimates, as well as the  $\delta^{13}\text{C}$  values of soil organic carbon and soil-respired CO<sub>2</sub> integrate <sup>13</sup>C contributions from the current standing plant cover, as well as from crops of previous years in this crop rotation system. Furthermore, this study clearly indicated that the carbon isotope ratios of carbon fixed and carbon released were not near the equilibrium values expected for the current crop at each site. The implications of this isotopic disequilibrium of a crop rotation agricultural system are discussed with respect to scaling canopy-level observations to global models for identifying C sinks. © 1998 Elsevier Science B.V.

*Keywords:* CO<sub>2</sub>;  $\delta^{13}\text{C}$ ;  $\delta^{18}\text{O}$ ; Carbon discrimination; Alfalfa; Corn; Land use; Soil carbon; Isotopic disequilibrium

## 1. Introduction

The carbon dioxide concentration ([CO<sub>2</sub>]) and its carbon isotope ratio ( $\delta^{13}\text{C}$ ) within plant canopies

changes diurnally as a result of photosynthetic depletion, plant and soil respiration inputs, and turbulent mixing of canopy air and the boundary layer or the troposphere. A number of abiotic and biotic factors such as turbulent mixing, light, water or plant life form influence both canopy [CO<sub>2</sub>] and  $\delta^{13}\text{C}$  profiles (McNaughton, 1989; Buchmann et al., 1996, 1997a). In general, the magnitude of intracanopy gradients of

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[CO<sub>2</sub>] and  $\delta^{13}\text{C}$  increase with increasing leaf area index (LAI) of forest canopies (Buchmann et al., 1996, 1997a), although the presence of understory vegetation might confound with this canopy leaf area effect. If turbulent mixing is low in highly productive canopies (with high LAI), a strong photosynthetic effect can be seen, manifesting itself as a depletion in canopy [CO<sub>2</sub>] below the tropospheric baseline concentration (e.g., Lemon, 1960; Keeling, 1961; Allen, 1971; Buchmann et al., 1996). Under these conditions, when [CO<sub>2</sub>]<sub>canopy</sub> are subtropospheric,  $\delta^{13}\text{C}_{\text{canopy}}$  are more enriched than those of the tropospheric background due to discrimination against  $^{13}\text{C}$  during photosynthesis (Farquhar et al., 1989).

In agricultural stands, it is well known that canopy [CO<sub>2</sub>] profiles are affected by crop LAI and foliage density (e.g., Lemon and Wright, 1969). In dense crop canopies for example, wind velocity decreases exponentially with decreasing height above the ground, due to increased boundary layer resistance for CO<sub>2</sub> transfer (Baldochi et al., 1981a,b); thus, limiting turbulent mixing with the troposphere (Keeling, 1961; Lemon, 1969; Monteith, 1973; Uchijima, 1976; Baldochi et al., 1981a,b; Norman, 1989). Furthermore, canopy photosynthesis increases with increasing LAI until light, water or nutrients become limiting (Schulze et al., 1994). Although micrometeorological studies of crop canopies have been conducted since the early 1960s, only limited information is available about  $\delta^{13}\text{C}_{\text{canopy}}$  values within or above crop stands (Yakir and Wang, 1996). Assuming equivalent LAI values for forest and crop canopies, we would expect the effect of LAI on canopy [CO<sub>2</sub>] to be greater in the shorter crop than in the taller forest canopy, due to differences in canopy coupling with the troposphere (Denmead, 1968; Jarvis and McNaughton, 1986). Given photosynthetic carbon isotope discrimination, we might further expect  $\delta^{13}\text{C}_{\text{canopy}}$  values within a dense crop canopy to be more positive than that of the troposphere. However, high soil respiration rates could offset this photosynthetic effect, because soil-respired CO<sub>2</sub> has a much more depleted  $\delta^{13}\text{C}$  value than the tropospheric CO<sub>2</sub>. Thus,  $\delta^{13}\text{C}_{\text{canopy}}$  values within a crop stand should be dependent on canopy leaf density (as it impacts turbulent mixing), on microclimatic factors influencing soil respiration (as

they affect soil temperature and soil moisture), and on crop photosynthetic pathway (since this affects leaf carbon isotope discrimination,  $\Delta_{\text{leaf}}$ , and therefore the  $\delta^{13}\text{C}$  value of plant litter).

C<sub>3</sub> or C<sub>4</sub> plants differ in carbon isotope discrimination values at both the individual leaf level ( $\Delta_{\text{leaf}}$ ) as well as at higher organizational levels, with C<sub>3</sub> canopies discriminating more than C<sub>4</sub> canopies (Lloyd and Farquhar, 1994). Although agricultural stands are important components of carbon fluxes on both regional and global scales, very limited information is available about carbon isotope discrimination of C<sub>3</sub> or C<sub>4</sub> crop systems (or 'ecosystems';  $\Delta_{\text{c}}$ ; Buchmann et al., 1997b) or about the daily variability of  $\delta^{13}\text{C}_{\text{canopy}}$  values within different crop stands (Yakir and Wang, 1996). Compounding this is the typical agricultural practice of crop rotation, which, in many areas, involves rotating between a legume (a C<sub>3</sub> crop with nitrogen fixation capacities) and corn (a C<sub>4</sub> crop with high nutrient demands). Thus, we initiated a study to explore  $\Delta_{\text{c}}$  values of a C<sub>3</sub> and a C<sub>4</sub> crop canopy under typical crop rotation conditions (i.e., periodic switching from C<sub>3</sub> to C<sub>4</sub> cover and vice versa). The shift in photosynthetic pathways of the crop might be expected to influence soil microbial activities and the  $\delta^{13}\text{C}$  of soil organic matter; therefore, the  $\delta^{13}\text{C}$  value of respired CO<sub>2</sub>. In this study, we compare daily fluctuations of [CO<sub>2</sub>],  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of canopy air among alfalfa (C<sub>3</sub>) and corn (C<sub>4</sub>) crop canopies, and determine  $\Delta_{\text{c}}$  for two crop rotation sites in a temperate, dry agricultural region (northern Utah, USA).

## 2. Methods

### 2.1. Sites

The study sites were located at the George B. Caine Dairy Teaching and Research Center of the Utah State University, Logan, Utah, USA (41°54'N, 111°49'W; 1577 m above MSL). Two corn canopies (*Zea mays* L.; about 17 m apart) and one alfalfa canopy (*Medicago sativa* L.) were studied July, 1994, and again in August, 1995. All three sites were located about 10–15 m away from the field borders, and about 800 m apart from each other. Soils could be classified as Aridisols. Air temperatures averaged 22.6°C (minimum: 10°C; maximum: 35°C), and there

was no precipitation during the July 1994 sampling period (Utah Climate Center, Logan, UT, USA). All measurements were taken at days with full sunlight and no clouds. Although wind speeds were not measured, no strong breezes were noticed by the author (N.B.). The field rotation scheme on this farm is to switch between C<sub>3</sub> (alfalfa) and C<sub>4</sub> (corn) on 5-year intervals. 1994 was the first year for corn on the corn site after five years of alfalfa, whereas the alfalfa field was in its fourth year. 1995 was therefore the second year for corn, and the fifth year for alfalfa at the respective sites.

### 2.2. Biomass and leaf area index

Plant biomass of the alfalfa canopy was determined by harvesting five 0.30 × 0.30 m plots. Plant material was dried for 48 h at 70°C, separated into leaves and stem/twigs, and weighed. Ten representative corn plants, covering the entire range of the height distribution of both corn sites, were cut, then separated into leaves and stems, dried, and weighed. Allometric relationships were used to calculate the plant biomass (stems:  $y = 11.65 \times \text{height}^{3.03}$ ,  $r^2 = 0.92$ ,  $n = 10$ ,  $P = 0.0009$ ; leaves:  $y = 22.21 \times \text{height}^{1.78}$ ,  $r^2 = 0.97$ ,  $n = 10$ ,  $P < 0.0001$ ). Stand density of the two corn sites was 15 plants per square meter. Canopy leaf area index (LAI) was measured in July 1994 with a plant canopy analyzer (LAI-2000; LiCor, Lincoln, NE, USA). Fifteen to twenty readings were taken for each replicate LAI measurement. A second LAI estimate was obtained from allometric relationships (by multiplying plant biomass per unit ground area with the specific leaf area).

No significant differences in average plant height or leaf area index (LAI, measured with LiCor) were found between the two corn sites (Table 1). However, plant biomass per unit area of site corn 1 was significantly lower than that of site corn 2. Both corn canopies were taller than the alfalfa canopy. Although corn biomass per unit area was greater than that of the alfalfa site, LAI of the alfalfa canopy was higher.

### 2.3. Soil analyses

Soil respiration rates were measured in August 1995 using a soil respiration chamber (LI-6000-09S;

Table 1  
Stand characteristics during mid-July 1994

	Corn 1	Corn 2	Alfalfa
Plant height (m)	1.44 ± 0.02 <sup>a</sup>	1.47 ± 0.10 <sup>a</sup>	0.80 ± 0.1
<i>Biomass (g/m<sup>2</sup>)</i>			
Total	1180 ± 50 <sup>a</sup>	1503 ± 67 <sup>b</sup>	688 ± 77
Leaves	643 ± 22 <sup>a</sup>	780 ± 28 <sup>b</sup>	335 ± 29
<i>LAI</i>			
LiCor	2.5 ± 0.2	2.7 ± 0.2	4.6 ± 0.2
Allometry	1.94	2.81	7.64
Leaves only	1.06	1.46	3.72
Stems only	0.88	1.35	3.92
<i>Soil moisture (% dw)</i>			
0–0.05 m	0.5 ± 0.4 <sup>a</sup>	0.6 ± 0.5 <sup>a</sup>	2.1 ± 0.8
0.05–0.10 m	4.5 ± 2.2 <sup>a</sup>	7.3 ± 5.1 <sup>a</sup>	3.8 ± 0.4

Leaf area index (LAI) was determined by two different methods (measured with a LiCor Plant Canopy Analyzer, and calculated with allometric relationships).

Different letters following the means represent significant differences between the two corn sites (Tukey–Kramer test at the 0.05-level).

LiCor, Lincoln, NE, USA) connected to a portable photosynthesis system (LI-6200). Three PVC tubes (0.25 m long, 0.10 m inside diameter) to which the chamber could be attached without leaks to the atmosphere, were inserted into the soil at each site, 24 h prior to measurement. The protocol recommended by LiCor (LI-6000-09S manual) was changed to five observations of 5 ppm change per measurement (pers. commun. J. Norman; for more details, see Matson, 1995). CO<sub>2</sub> concentrations ([CO<sub>2</sub>]) were scrubbed with soda lime in an open configuration until [CO<sub>2</sub>] level was 50 ppm below ambient. After closing the system, [CO<sub>2</sub>] was allowed to increase by 20 ppm before measurements were taken. Soil temperature was measured at 0.10 m soil depth. Four measurements were taken at the corn site, and seven measurements were taken at the alfalfa site.

Gravimetric soil water content was determined with five replicates per measurement in July 1994 and August 1995. Sampling containers were sealed in the field with Parafilm. The wet soil samples were weighed, then dried until weight constancy, and weighed again. Soil moisture is expressed as percent dry weight (% dw).

#### 2.4. Continuous CO<sub>2</sub> and temperature measurements

Canopy air was sampled from different heights within and above the canopy (corn: 0.02, 0.3, 0.5, 1.0, 1.4, 2.4 m height; alfalfa: 0.02, 0.30, 0.55, 0.75, 2.65 m height). Air was dried using magnesium perchlorate, and was drawn through tubing (Dekoron 1300; 0.625 cm outer diameter, nonbuffering ethylene copolymer coating; Aurora, OH, USA) at a flow rate of 10 ml/s, using a battery-operated 12 V pump (Spectrex, Redwood City, CA, USA). A relay driver (A6Rec-12; Campbell Scientific, Logan, UT, USA) switched between two manifolds with four solenoids each, providing sampling of air from five (alfalfa) or six (corn) heights and two standards (one CO<sub>2</sub>-free air source and a calibrated CO<sub>2</sub> source). A datalogger (21X; Campbell Scientific, Logan, UT, USA) controlled the opening and closing of these solenoids, and allowed measurements of the air from each height for 90 s. A run of the entire profile with five or six heights was completed within 10 min. [CO<sub>2</sub>] were measured each second with an infrared CO<sub>2</sub> gas analyzer (LI-6262; LiCor, Lincoln, NE, USA). The last 15 of the 90 readings of each height were averaged and stored. Every 3 h, both calibration gases were measured. The CO<sub>2</sub> standards were calibrated in the lab against a primary, certified CO<sub>2</sub> standard (Matheson Gas Products, USA; 357 ppmv). Air temperatures were measured at 1.30 (corn) and 1.20 m (alfalfa) height, and at soil temperatures in 0.05 m soil depth by using copper–constantan thermocouples. Thermocouples for air temperature were shielded against direct sunlight, but installation allowed free air movement. Canopy [CO<sub>2</sub>] were measured simultaneously in both corn canopies during July 10–12, 1994, and during July 12–13, 1994 in the alfalfa canopy.

For comparisons of above-canopy air to tropospheric baseline values, we used data collected on a weekly basis during daytime hours at Wendover (UT, 40°03'N 105°38'W; 3749 m above MSL) from the NOAA Cooperative Flask Sampling Network. [CO<sub>2</sub>] in July 1994 was 360.5 ppm,  $\delta^{13}\text{C}$  was  $-7.96\text{‰}$  (data provided by T. Conway and M. Trolier). No information about tropospheric  $\delta^{18}\text{O}$  was available. The precision of the NOAA data is  $< 0.5$  ppm for [CO<sub>2</sub>], and  $\pm 0.03\text{‰}$  for  $\delta^{13}\text{C}$ . Natural temporal variability for data, collected at the

same station over a one month period is  $< 0.2\text{‰}$  (pers. commun. M. Trolier). Variability between stations at a similar latitude is between 0.5 and 1 ppm and around  $0.25\text{‰}$  (see Conway et al., 1994; Ciais et al., 1995, respectively).

#### 2.5. Collection of canopy air for isotopic analyses

Canopy air was collected for isotopic analyses from the same heights as used for the continuous [CO<sub>2</sub>] measurements, but with a second set of tubing. Using a battery-operated 12 V pump (TD-3LS; Brailsford, Rye, NY, USA), air was dried using magnesium perchlorate and was drawn through the tubing and a preevacuated 1.7-l glass sampling flask (with two high-vacuum stopcocks) at a flow rate of 10 ml/s. After pumping for 20 min, both stopcocks of the flask were closed. Up to four flasks were collected at the same time using separate lines. Continuous [CO<sub>2</sub>] measured during the 20-min collection period were averaged, thus providing the corresponding [CO<sub>2</sub>] for a given flask sample. During the 4-day-period in July 1994, 15 flask samples were collected between 0700 and 2300 in each corn canopy, and 21 flasks between 0700 and 2300 in the alfalfa canopy.

#### 2.6. Collection of soil-respired CO<sub>2</sub> for isotope analyses

The setup described for soil respiration measurements was modified to collect soil-respired CO<sub>2</sub> for isotopic analyses. A closed system was designed where soil CO<sub>2</sub> efflux was drawn from the soil respiration chamber through the LI-6200 and an ethanol–dry ice water trap into a glass sampling flask and pushed back into the chamber. The 1.7-l flask was filled with CO<sub>2</sub>-free N<sub>2</sub>-gas and connected to the top inlet of the soil respiration chamber. The air within the entire system was scrubbed by soda lime for 10 to 20 min. As soon as [CO<sub>2</sub>] dropped below 50 ppm, the soda lime was taken out of line. The system's [CO<sub>2</sub>] was allowed to increase to approximately 350 ppm before the stopcocks of the flask were closed. Four flasks were collected at each site in August 1995.

## 2.7. Isotope analyses and calculations

During both years, soil samples were taken from 0–0.05 m and 0.05–0.10 m soil depth with three replicates per depth and site. Soils were acid-washed and then sieved (mesh size = 1 mm). Sun leaves of corn and alfalfa were sampled in both years with three replicates per site. In addition, all seven leaves of two corn plants (0.20–1.10 m height) were sampled in 1994. Plant materials were dried for 48 h at 70°C and then ground with mortar and pestle to a fine powder. A 2-mg subsample was combusted and analyzed for  $^{13}\text{C}/^{12}\text{C}$  using an isotope ratio mass spectrometer (delta S; Finnigan MAT, Bremen, Germany).

$\text{CO}_2$  of the flask samples was extracted cryogenically using a three-trap vacuum line (each trap with a double loop) and transferred into a sampling tube within 3 h after flask collection. Due to possible interferences at mass 44,  $\text{CO}_2$  was separated from  $\text{N}_2\text{O}$  by using a gas chromatograph (GC-14A; 3-M Poraplot Q column, Shimadzu, Kyoto, Japan) prior to isotope analysis. The  $\text{CO}_2$  gas was introduced manually into the mass spectrometer, and carbon and oxygen isotope ratios of canopy air ( $\delta^{13}\text{C}_{\text{canopy}}$ ,  $\delta^{18}\text{O}_{\text{canopy}}$ ) were analyzed from the same sample.

The isotope ratio ( $\delta X$ ) was calculated as

$$\delta X = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000\text{‰} \quad (1)$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  are the  $^{13}\text{C}:^{12}\text{C}$  or  $^{18}\text{O}:^{16}\text{O}$  ratios of the sample and the standard (PDB for carbon; SMOW for oxygen), respectively (Farquhar et al., 1989). The overall precision of the carbon isotope measurements was  $\pm 0.11\text{‰}$  for organic carbon,  $0.03\text{‰}$  for carbon and  $0.15\text{‰}$  for oxygen isotopes in gas samples.

Carbon isotope discrimination of a leaf ( $\Delta_{\text{leaf}}$ ) was calculated as

$$\Delta_{\text{leaf}} = (\delta^{13}\text{C}_{\text{air}} - \delta^{13}\text{C}_{\text{leaf}})/(1 + \delta^{13}\text{C}_{\text{leaf}}) \quad (2)$$

where  $\delta^{13}\text{C}$  is expressed in absolute units (e.g., 0.026 instead of 26), not in the per mil notation used in Eq. (1).  $\delta^{13}\text{C}_{\text{air}}$  was calculated for each height where foliage was collected by applying the linear regression equations ( $\delta^{13}\text{C}_{\text{canopy}}$  as a function of  $1/[\text{CO}_2]_{\text{canopy}}$ , see below) to the average  $[\text{CO}_2]$  between 0800 and 1800.

## 2.8. Empirical modeling of $\delta^{13}\text{C}_{\text{canopy}}$ and estimates of $\Delta_c$

Carbon isotope ratios of canopy air ( $\delta^{13}\text{C}_{\text{canopy}}$ ) were modeled by regressing the inverse of  $[\text{CO}_2]_{\text{canopy}}$  against the corresponding measured  $\delta^{13}\text{C}_{\text{canopy}}$  (Keeling, 1958; Sternberg, 1989):

$$\delta^{13}\text{C}_{\text{canopy}} = a \times \left( \frac{1}{[\text{CO}_2]_{\text{canopy}}} \right) + b \quad (3)$$

where  $a = (\delta^{13}\text{C}_{\text{trop}} - \delta^{13}\text{C}_{\text{resp}}) * [\text{CO}_2]_{\text{trop}}$  and  $b = \delta^{13}\text{C}_{\text{resp}}$ . This linear relationship describes the turbulent mixing of the two major  $\text{CO}_2$  sources within the canopy (tropospheric and respired  $\text{CO}_2$ ), and includes the photosynthetic effect due to discrimination during carbon assimilation.

The intercept of this linear regression is an indicator of the isotopic composition of respired  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{resp}}$ ) of the entire ecosystem, integrating over autotrophic and heterotrophic respiration. Thus, the intercept can be used to estimate ecosystem discrimination against the heavier  $^{13}\text{C}$  during photosynthesis of the entire ecosystem ( $\Delta_c$ ; Buchmann et al., 1997b). Provided no fractionation occurs during respiration (Lin and Ehleringer, 1997),  $\Delta_c$  can be calculated as

$$\Delta_c = (\delta^{13}\text{C}_{\text{trop}} - \delta^{13}\text{C}_{\text{resp}})/(1 + \delta^{13}\text{C}_{\text{resp}}) \quad (4)$$

The mixing model described by Eq. (3) can also be used for oxygen isotope ratios of canopy air ( $\delta^{18}\text{O}_{\text{canopy}}$ ; Yakir and Wang, 1996; Flanagan et al., 1997). Analogous to the mixing model for  $\delta^{13}\text{C}$ , the intercept of nighttime data describes the oxygen isotope ratio of ecosystem respiratory  $\text{CO}_2$  ( $\delta^{18}\text{O}_{\text{resp}}$ ), integrating leaf and soil respiration.

## 2.9. Estimates of fraction soil-respired carbon originating from $\text{C}_4$ or $\text{C}_3$ plant organic matter

Due to crop rotation, soil-respired carbon at both corn and alfalfa sites is a mixture of  $\text{C}_3$  and  $\text{C}_4$  plant organic matter. Knowing the two end members, the  $\delta^{13}\text{C}_{\text{leaf}}$  of alfalfa and corn, we used a mixing model to calculate the fraction soil-respired carbon that originated from  $\text{C}_3$  or  $\text{C}_4$  plant organic matter:

$$\delta^{13}\text{C}_{\text{soil respiration}} = x \times \delta^{13}\text{C}_{\text{corn}} + (1 - x)$$

$$\times \delta^{13}\text{C}_{\text{alfalfa}} \quad (5)$$

where  $\delta^{13}\text{C}_{\text{soil respiration}}$  represents the measured  $\delta^{13}\text{C}$  of soil  $\text{CO}_2$  efflux,  $\delta^{13}\text{C}_{\text{corn}}$  is the  $\delta^{13}\text{C}_{\text{leaf}}$  of corn sun leaves ( $-12.8\text{‰}$ ), and  $\delta^{13}\text{C}_{\text{alfalfa}}$  is the  $\delta^{13}\text{C}_{\text{leaf}}$  of alfalfa sun leaves ( $-28.2\text{‰}$ ).  $x$  represents the fraction (in %) originating from  $\text{C}_4$  organic matter;  $(1-x)$  describes the fraction originating from  $\text{C}_3$  plant matter.

2.10. Statistics

In general, continuous  $[\text{CO}_2]$  data are presented as the 10-min records. Data were smoothed with moving averages (intervals of seven data points) by using Microsoft Excel Version 4.0. The statistical package

JMP (Version 3, SAS Institute, Cary, NC, USA) was used for most of the data analyses. Analyses of variance (ANOVA) were done with multiple main factors such as species, site, height etc. If the interaction term was not significant ( $P > 0.05$ ), data were pooled and reanalyzed. The Student's  $t$ -test or Tukey–Kramer HSD (honestly significant difference) test (at the 0.05 level) were used to distinguish among the means of two or more groups, respectively. All linear regressions are stated with  $r_{\text{adjusted}}^2$ . When both  $x$  and  $y$  variables were associated with an error (such as for  $1/[\text{CO}_2]$  vs.  $\delta^{13}\text{C}$ ), slopes and intercepts were calculated by geometric mean regressions (Sokal and Rohlf, 1981). Slopes and intercepts

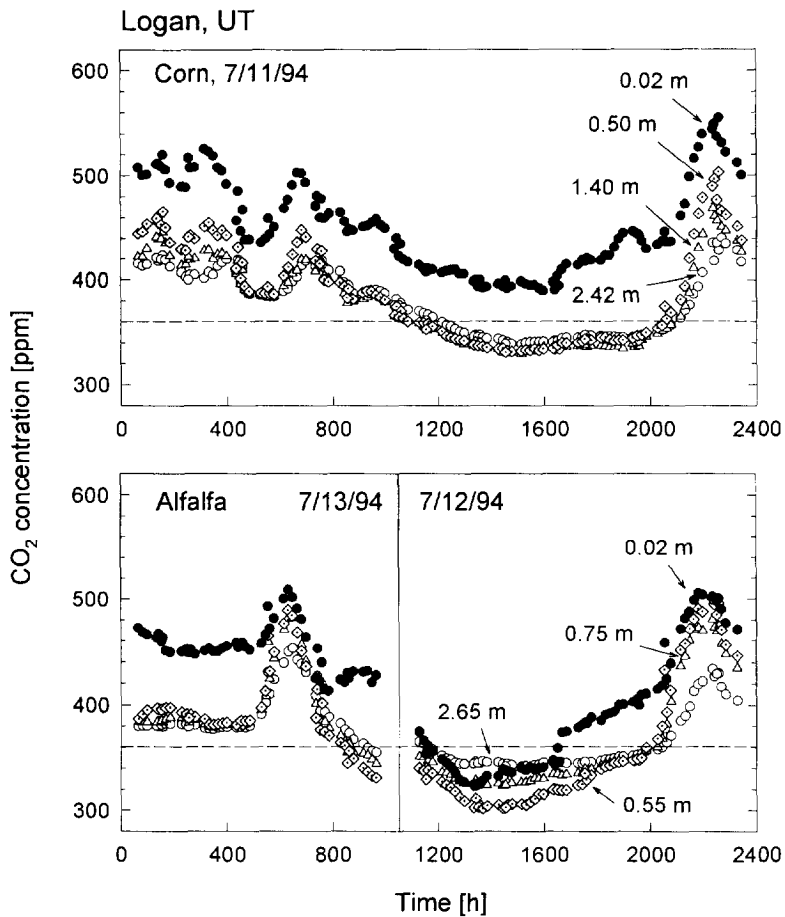


Fig. 1. Daily courses of  $\text{CO}_2$  concentrations within  $\text{C}_4$  (corn) and  $\text{C}_3$  (alfalfa) crop canopies. The dashed line represents the average daytime  $\text{CO}_2$  concentration of the troposphere (360.5 ppm, station Wendover, UT, USA; data provided by M. Trolier, University of Colorado, INSTAAR).

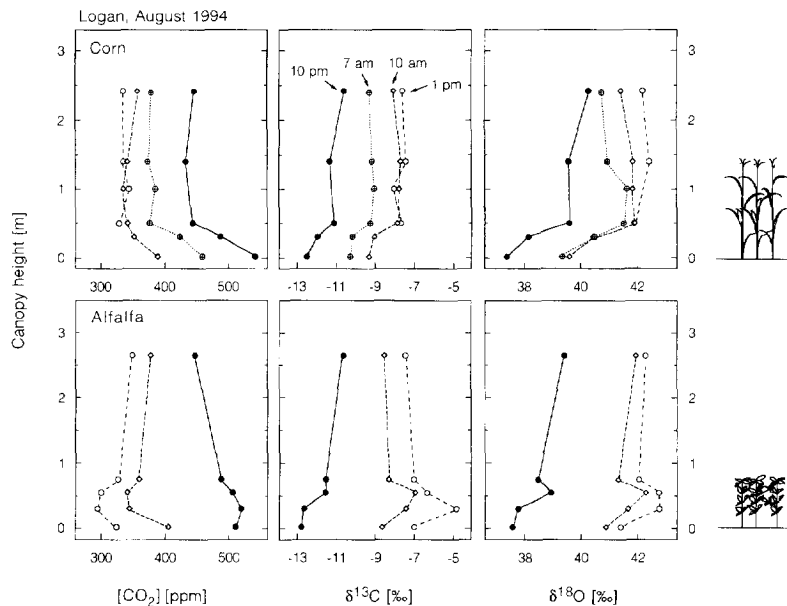


Fig. 2. Height profiles of  $[CO_2]$ ,  $\delta^{13}C$  and  $\delta^{18}O$  of canopy air within  $C_4$  (corn) and  $C_3$  (alfalfa) crop stands for different times during night and day. Original flask data are presented.

of regressions were tested against each other by introducing indicator variables ('dummy' variables) into a multiple regression model (Neter et al., 1985).

### 3. Results

$CO_2$  concentrations ( $[CO_2]$ ) within both crop canopies showed very pronounced daily variations, with daytime concentrations well below that of the average tropospheric baseline measured at Wendover (360.5 ppm; daytime only; Fig. 1). Between 1200 and 1800, all heights within the corn canopy (except at 0.02 m) dropped, on average, 16 to 26 ppm below the Wendover baseline value, including the 2.42 m height (1 m above the corn canopy, within boundary layer). Large daytime intracanopy gradients (calculated as the concentration difference between two heights) were observed in both corn canopies (about 60 ppm between 0.02 and 1.40 m), and in the alfalfa canopy (about 28 ppm between 0.02 and 0.75 m). The spatial variability within the corn field was low, since the two corn sites (approximately 17 m apart) showed very similar  $[CO_2]$  gradients (data not shown). Although the site corn 1 had a significantly

lower biomass than the site corn 2 (Table 1;  $t < 0.001$ ),  $[CO_2]$  profiles did not differ more than a total of 11 ppm at 1.40 m, 14 ppm at 0.50 m, and 21 ppm at 0.02 m within a 24-h period. The daytime depletion in canopy  $[CO_2]$  was even more pronounced in the alfalfa canopy, between 15 and 47 ppm below the Wendover baseline value, indicating very limited turbulent mixing with the troposphere. Moreover, concentrations just above the soil surface (0.02 m), as well as high above the alfalfa canopy (at 2.65 m height, 1.85 m above average plant height) showed the same daily pattern, indicating a strong influence of the crop canopy on the canopy boundary values. Soil respiration rates did not seem to be sufficiently high to offset photosynthetic depletion of  $CO_2$  within the canopies, perhaps in part due to the low soil moisture values during July 1994 (Table 1).

The strong vertical stratification of  $[CO_2]$  was also reflected in the carbon and oxygen isotope ratios of canopy air (Fig. 2). The highest  $[CO_2]$  and lowest  $\delta^{13}C$  and  $\delta^{18}O$  values occurred near the soil surface. The daytime depletion in canopy  $[CO_2]$  was reflected in  $\delta^{13}C$  values of about  $-7.4\text{‰}$  (corn) and between  $-6.3$  and  $-4.8\text{‰}$  (alfalfa), values well above the  $-7.96\text{‰}$  of the tropospheric baseline,

Table 2

Linear regressions of  $1/[CO_2]$  vs.  $\delta^{18}O$  of canopy air for  $C_4$  (corn) and  $C_3$  (alfalfa) crop canopies in August 1994

Site	Time	Regression	$r^2$	$n$	$F$
Corn	N	$y = 4598 (\pm 1633)^* x + 29.05 (\pm 3.56)$	0.57	7	7.9
Alfalfa	N	$y = 4985 (\pm 2187)^* x + 28.31 (\pm 4.45)$	0.63	4	5.2
Corn	D	$y = 3122 (\pm 699)^* x + 32.73 (\pm 1.94)$	0.51	20	20
Alfalfa	D	$y = 877 (\pm 481)^* x + 39.61 (\pm 1.40)$	0.17	17	3.3

Equations are given for night (N) and day (D) sampling times separately ( $\pm 1$  SE in parentheses).

The regression equations for corn, but not for alfalfa, were significant at the 0.05 level.

indicating a strong photosynthetic discrimination effect of both crop canopies. The vertical profiles of canopy  $[CO_2]$  and its isotopic composition were more pronounced in the alfalfa than in the corn stand, probably due to the higher foliage density of the alfalfa canopy (Table 1). The highest  $\delta^{13}C$  value of  $-4.8\text{‰}$  was measured within the main portion of the alfalfa canopy. High  $\delta^{18}O$  ratios of canopy  $CO_2$  were observed in both crop canopies (Fig. 2).  $\delta^{18}O$  ratios increased during the course of the day, probably due to isotopic exchange with enriched leaf water. In contrast, lower  $\delta^{18}O$  values near to the soil surface might indicate isotopic exchange of soil-respired  $CO_2$  with the more depleted soil water. Modeling the  $\delta^{18}O$  ratios of canopy air revealed only weak relationships between  $1/[CO_2]$  and the corresponding  $\delta^{18}O$  ratios (Table 2). The oxygen isotopic composition of ecosystem respiration was about 29‰ (nighttime only). During the day, this respiratory signal was more enriched (about 36‰). We found significant linear relationships between the  $\delta^{13}C$  and  $\delta^{18}O$  values of canopy air in both corn and alfalfa canopies ( $r^2 > 0.8$ ; Fig. 3), indicating tight coupling between water vapor and carbon dioxide fluxes. In spite of different photosynthetic pathways, no differences in this relationship were evident between the two crop species (slope:  $P = 0.16$ ; intercept:  $P = 0.11$ ).

Significant linear relationships were also found between  $1/[CO_2]$  and the corresponding  $\delta^{13}C$  of canopy air in both crop stands (Table 3, Fig. 4). The spread in the values was smaller for the corn than for the alfalfa canopy, perhaps reflecting a combination of both photosynthetic sink and turbulent transfer differences between the two canopies. Although the extent of the photosynthetic  $CO_2$  depletion and the  $^{13}C$  enrichment were larger in the alfalfa canopy than

in the corn canopy, regression equations of the relationship  $1/[CO_2]$  vs.  $\delta^{13}C$  were statistically similar (slope:  $P = 0.27$ ; intercept:  $P = 0.36$ ). No statistical

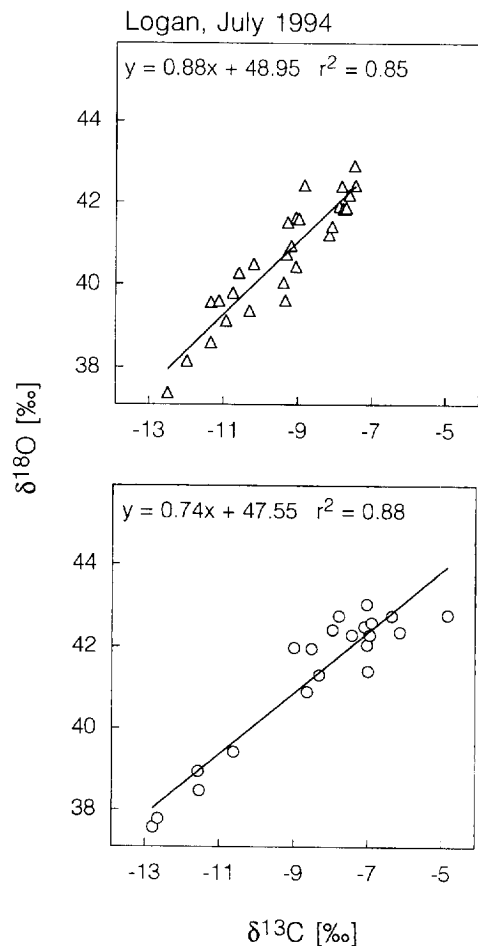


Fig. 3. Relationship between  $\delta^{13}C$  and  $\delta^{18}O$  of canopy air for  $C_4$  (corn) and  $C_3$  (alfalfa) crop canopies. Original flask data are presented.



Table 3

Linear regressions of  $1/[CO_2]$  vs.  $\delta^{13}C$  of canopy air for two  $C_4$  (corn) crop canopies and one  $C_3$  (alfalfa) crop canopy in August 1994

Site	Regression	$r^2$	$n$	$F$
Corn 1	$y = 4567 (\pm 302)^* x - 21.32 (\pm 0.81)^{**}$	0.94	15	215
Corn 2	$y = 4316 (\pm 341)^* x - 20.50 (\pm 0.89)^{**}$	0.91	15	147
Alfalfa	$y = 4775 (\pm 283)^* x - 21.46 (\pm 0.77)^{**}$	0.93	21	277
Overall	$y = 4805 (\pm 208)^* x - 21.62 (\pm 0.56)^{**}$	0.91	51	486

Equations are given with 1 SE in parentheses.

$P$  was  $< 0.0001$  for all equations.

Different letters following the equations represent significantly different regressions (Tukey–Kramer test at the 0.05 level).

differences were found in the slopes ( $P = 0.52$ ) and intercepts ( $P = 0.45$ ) between the two corn sites. Thus, calculated ecosystem discrimination ( $\Delta_e$ ) values were similar for the two different crop types, averaging 13.8‰ for alfalfa and 13.2‰ for corn canopies. One equation described both crop stands adequately ( $r^2 = 0.91$ ). This result implies that in spite of photosynthetic pathway differences between the two crops ( $C_3$  vs.  $C_4$ ), there were no differences apparent in the  $\delta^{13}C$  value of respired  $CO_2$  or the ecosystem discrimination.

Actual measurements of the  $\delta^{13}C$  of soil-respired  $CO_2$  supported this conclusion (Table 4). The  $\delta^{13}C$  value of soil  $CO_2$  efflux was  $-22.8‰$  in the corn stand, and  $-22.3‰$  in the alfalfa stand in the second

year of this study. Despite this similarity, we found significant differences in the  $\delta^{13}C$  of soil organic carbon (SOC) and of foliage, reflecting the photosynthetic pathway of the crop currently planted at each site (Table 4). Corn, as a  $C_4$  plant, showed less negative  $\delta^{13}C$  ratios due to a smaller carbon isotope discrimination during photosynthesis. Whereas alfalfa, as a typical  $C_3$  plant, exhibited much more negative  $\delta^{13}C$  values, indicating greater carbon discrimination. Thus, the similarity of the  $\delta^{13}C$  of soil  $CO_2$  efflux must be due to different percentages of  $C_3$  and  $C_4$  carbon sources respired by roots and soil microorganisms. For the corn stand, we calculated that 38% of the respired  $CO_2$  originated from  $C_4$  organic matter, either from root respiration or from decomposition of  $C_4$  litter (see Eq. (5)). However, 62% of the soil  $CO_2$  efflux was  $C_3$ -derived, i.e., old organic matter from alfalfa plants that grew on this site prior to corn cropping (crop rotation). For the alfalfa stand, only 35% of soil-respired  $CO_2$  originated from old organic matter, i.e.,  $C_4$  sources, but 65% was  $C_3$ -derived (Eq. (5)). Although soil moisture values and soil temperatures were similar for both crops, soil respiration rates at the alfalfa site were more than three times those at the corn site.

These differences among corn and alfalfa stands in the contribution of older to younger carbon sources might be mainly due to the time period since the last

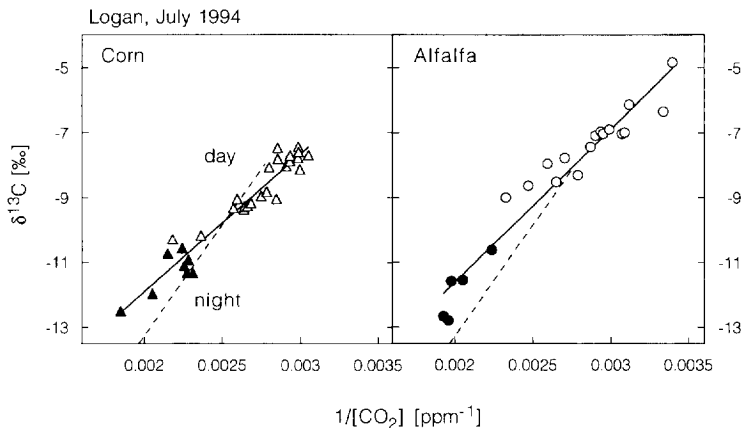


Fig. 4. Relationship between  $1/[CO_2]$  and  $\delta^{13}C$  of canopy air for  $C_4$  (corn) and  $C_3$  (alfalfa) crop canopies. Original flask data (day and night) are presented. The dashed line represents the hypothetical mixing line between tropospheric and respired  $CO_2$ . Data for the troposphere were provided by M. Troler (University of Colorado, INSTAAR; 360.5 ppm,  $-7.96‰$ ; station Wendover, UT, USA).  $\delta^{13}C_{leaf}$  of alfalfa plants was used as  $\delta^{13}C$  of respired  $CO_2$  for the hypothetical mixing line.

crop rotation. Although the  $\delta^{13}\text{C}$  of foliage stayed relatively constant (1.1‰ difference for alfalfa; and 0.3‰ for corn) during two consecutive years (1994 and 1995; Fig. 5), the  $\delta^{13}\text{C}$  of soil organic carbon changed by several permil. This shift in the carbon isotopic composition of SOC was 0.3‰ in 0–0.05 m depth, and 1.75‰ in 0.05–0.10 m for alfalfa, but 5.15‰ in 0–0.05 m, and 3.8‰ in 0.05–0.10 m for corn. This means that during the first year of corn cropping (in 1994), approximately half of SOC was old organic matter of  $\text{C}_3$  origin. In the second year of planting corn (1995), the fraction of young,  $\text{C}_4$ -derived material increased to 86%, while the fraction of old,  $\text{C}_3$ -derived material decreased to 14%. The change over from old to young organic matter was apparently slower in the alfalfa than in the corn soil. During the fourth year of growing alfalfa on the same site (1994), approximately 68% of SOC was young,  $\text{C}_3$ -derived, whereas 32% was old,  $\text{C}_4$ -derived material. During the fifth year of growing

Table 4

Soil moisture (%dw), soil temperature ( $^{\circ}\text{C}$ ), soil respiration rates ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) as well as  $\delta^{13}\text{C}$  (‰) of canopy air (0.05 m height), foliage, and soil organic carbon (SOC) in August 1995

	Corn	Alfalfa
<i>Soil moisture</i>		
0–0.05 m	33.2 ± 0.4 <sup>a</sup>	33.2 ± 2.3 <sup>a</sup>
0.05–0.10 m	48.2 ± 3.5 <sup>b</sup>	25.1 ± 1.5 <sup>a</sup>
0.10–0.20 m	24.8 ± 2.0 <sup>a</sup>	23.1 ± 0.2 <sup>a</sup>
<i>Soil temperature</i>		
0.10 m	20.4 ± 0.2 <sup>a</sup>	20.4 ± .04 <sup>a</sup>
<i>Soil respiration rate</i>		
	2.8 ± 0.3 <sup>a</sup>	9.4 ± 1.0 <sup>b</sup>
$\delta^{13}\text{C}$		
canopy air (0.05 m)	–8.6 ± 0.01 <sup>b</sup>	–9.2 ± 0.34 <sup>a</sup>
leaves	–12.8 ± 0.07 <sup>b</sup>	–28.2 ± 0.20 <sup>a</sup>
SOC (0–0.05 m)	–15.0 ± 0.73 <sup>b</sup>	–23.6 ± 1.00 <sup>a</sup>
$\text{CO}_2$ efflux	–22.8 ± 0.47 <sup>a</sup>	–22.3 ± 0.63 <sup>a</sup>
<i>Carbon-respired</i>		
% $\text{C}_4$	38	35
% $\text{C}_3$	62	65

Percentage of  $\text{C}_4$  or  $\text{C}_3$  carbon respired was estimated using Eq. (5).

Different letters following the means represent significant differences between species (*t*-test at the 0.05-level).

The year 1995 was the second year of corn cropping, and the fifth year of alfalfa. After five years, crop species are switched at each site.

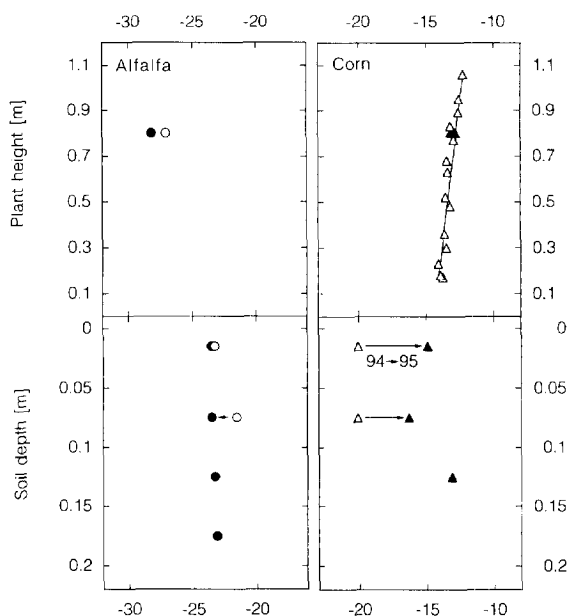


Fig. 5.  $\delta^{13}\text{C}$  of foliage and soil organic carbon for alfalfa and corn sites. Data from two consecutive years are presented (1994: open symbols; 1995: closed symbols). Two corn plants were sampled in 1994 for the height profile.

alfalfa (1995), about 70% of SOC was young,  $\text{C}_3$ -derived and about 30% was old,  $\text{C}_4$ -derived organic matter. Fine root turnover or simply agricultural practice (e.g., plowing stubble under after the harvest) might be responsible for these different isotopic shifts in SOC.

After accounting for source air effects, we calculated leaf carbon isotope discrimination ( $\Delta_{\text{leaf}}$ ) for sun leaves of both crop species.  $\Delta_{\text{leaf}}$  values of alfalfa leaves averaged 20‰, and  $\Delta_{\text{leaf}}$  values of corn foliage ranged from 4‰ for leaves at 1 m height to 5‰ for leaves at 0.2 m height. This pronounced height profile of  $\delta^{13}\text{C}_{\text{leaf}}$  within single corn plants (Fig. 5), with  $\Delta_{\text{leaf}}$  decreasing 1.54 to 1.93‰ per m height growth, may have been associated with increased shading of leaves lower in the canopy.

#### 4. Discussion

In both  $\text{C}_3$  and  $\text{C}_4$  crop canopies, the canopy photosynthetic sink strength was strong enough that midday values of canopy  $[\text{CO}_2]$  were well below

tropospheric baseline values. Coincident with this, atmospheric  $\delta^{13}\text{C}$  values were enriched above the troposphere. Soil respiration and turbulent mixing of canopy and boundary layer air apparently were insufficient to offset the photosynthetic demand of these highly productive stands during July 1994. While previous studies have reported similar canopy [ $\text{CO}_2$ ] changes (e.g., Lemon, 1960; Monteith, 1973), the high  $\delta^{13}\text{C}$  values of atmospheric air observed are new and unusually positive, but consistent with expectations based on Keeling-plot analyses (Keeling, 1958). The increased  $\delta^{18}\text{O}$  values of midcanopy air and the tight relationships between the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  ratios of canopy air support the interpretation of highly active gas exchange of both crop canopies, illustrating the close link between oxygen-18 fluxes in water and carbon dioxide at the leaf level (Farquhar et al., 1993). Before and during the photosynthetic fixation of  $\text{CO}_2$  in the leaf and the chloroplast,  $\text{CO}_2$  is in isotopic equilibrium with the leaf or chloroplast water (Farquhar et al., 1993; Yakir and Wang, 1996). At high vapor pressure deficits and therefore high transpiration rates (as in this study), evaporative enrichment of leaf water results in increased  $\delta^{18}\text{O}$  values of leaf water that equilibrates with  $\text{CO}_2$  leaving the leaves (Farquhar et al., 1993; Yakir and Wang, 1996). This pattern was reflected by higher  $\delta^{18}\text{O}$  ratios of canopy air during the day compared to the nighttime values. On the other hand, decreasing  $\delta^{18}\text{O}$  ratios close to the ground were found in many different ecosystems, ranging from agricultural systems to tropical and boreal forests (e.g., Yakir and Wang, 1996; Buchmann et al., 1997c; Flanagan et al., 1997), and generally indicate isotopic exchange with the more depleted soil water.

Integrating over the entire crop ecosystem, we found a  $\delta^{18}\text{O}$  ratio of ecosystem respiration at night of about 29‰ (both crops). For similar  $\text{C}_3$  and  $\text{C}_4$  crop canopies in Israel (wheat, cotton, corn), Yakir and Wang (1996) calculated the  $\delta^{18}\text{O}$  ratio of respiratory  $\text{CO}_2$  to be between 29 and 30‰. If plants and soils are in isotopic equilibrium at night, this estimate should reflect the isotopic composition of soil and stem water modified by fractionation during diffusion into the atmosphere. However, Flanagan et al. (1997) observed in boreal ecosystems that the  $\delta^{18}\text{O}$  ratios of nocturnal ecosystem respiration were more positive than those expected for soil-respired

$\text{CO}_2$  in isotopic equilibrium with soil water, indicating the influence of more enriched respiratory  $\text{CO}_2$  from vegetation. During the day, the intercepts for both corn and alfalfa canopies averaged about 36‰. Yakir and Wang (1996) found that the  $\delta^{18}\text{O}$  ratios of daytime ecosystem fluxes were consistent with modeled values for the  $\delta^{18}\text{O}$  of  $\text{CO}_2$  associated with photosynthesis. Thus, they further interpreted the intercept  $\delta^{18}\text{O}_{\text{resp}}$  obtained from daytime flask collections as the  $\delta^{18}\text{O}$  ratio of chloroplast water. More studies from different ecosystems are needed to further evaluate existing models and to apply carbon and oxygen isotopes to global models of carbon exchange of terrestrial ecosystems (Ciais et al., 1995).

The  $\delta^{13}\text{C}$  values of soil organic carbon (SOC) in these agricultural soils indicated that the respired carbon was a mixture of previous  $\text{C}_3$ – $\text{C}_4$  crop generations, with the soil isotope ratio dependent on both recent and long-term land use history. The carbon isotope ratio of soil-respired  $\text{CO}_2$  represented an integration that could not be adequately described without some knowledge of the previous crop rotation history. Surprisingly, calculations of the origin of respired carbon indicated that ~35–40% of the respiration at both sites originated from  $\text{C}_4$  material and about 60% from  $\text{C}_3$  material, although the cover crop was different between sites. These observations imply a moderate turnover rate for soil carbon and were within the range observed in previous studies (Schönwitz et al., 1986; Balesdent et al., 1987, 1990; Arrouays et al., 1995; Gregorich et al., 1995; Wedin et al., 1995; Neill et al., 1996; Rochette and Flanagan, 1997). Growing  $\text{C}_4$  crops on a  $\text{C}_3$  soil or converting  $\text{C}_3$  forests into  $\text{C}_4$  pastures has generally resulted in rapid shifts in the isotopic signal of soil-respired  $\text{CO}_2$  or soil organic matter. Schönwitz et al. (1986) reported that after one year of corn cultivation on a historically  $\text{C}_3$  site, only 30% of respired  $\text{CO}_2$  was of  $\text{C}_4$  origin. Corn cropping on soils whose initial organic matter was  $\text{C}_3$  resulted in a  $\delta^{13}\text{C}$  of SOC that were about 30% of  $\text{C}_4$  origin after 4 years (Wedin et al., 1995) and 22% after 13 years (Balesdent et al., 1987). Under tropical conditions, 85% of soil-respired  $\text{CO}_2$  was of  $\text{C}_4$  origin 3 years after forests were converted into  $\text{C}_4$  pastures (Neill et al., 1996). Soil carbon turnover rates have a clear impact on the extent to which older  $^{13}\text{C}$  signals are retained in the soil and subsequently lost through

soil respiration. This poses a challenge to biosphere–atmosphere studies attempting to predict the carbon isotope ratios of cultivated fields where  $C_3$ – $C_4$  crop rotations are routinely practiced.

The impact of this lag or ‘memory’ effect was not only evident in the values for  $\delta^{13}C$  of soil carbon and of soil-respired  $CO_2$  in the  $C_3$  and  $C_4$  crop canopies, but also in the ecosystem-level carbon isotope discrimination ( $\Delta_c$ ) estimates, which were indistinguishable between the two canopies. The  $\Delta_c$  estimate temporally and spatially integrates plant and soil processes at the ecosystem level; it incorporates the lag response of soils as well as any spatial variability in the aboveground component within the footprint of the sampling tower (Buchmann et al., 1997b). A comparison of our  $\Delta_c$  estimates with modeled values for  $^{13}C$  discrimination of canopy photosynthesis ( $\Delta_A$ ; Lloyd and Farquhar, 1994), yields different values for  $\Delta_A$  and  $\Delta_c$ , most likely reflecting the importance of the  $\delta^{13}C$  values of soil carbon on such biosphere–atmosphere calculations. The differences between the modeled single species canopy estimate ( $\Delta_A$ ) and our measured ecosystem estimate ( $\Delta_c$ ) were as large as 2–4‰ for pure  $C_3$  grasslands or agronomy ( $\Delta_A$ : 15.5–17.4‰ vs.  $\Delta_c$ : 13.8‰) and as large as 10‰ for  $C_4$  grasslands ( $\Delta_A$ : 3.3–3.5‰ vs.  $\Delta_c$ : 13.2‰). Thus, an appreciation of the isotopic signal recorded in the soil seems essential when scaling canopy level analyses to the region level for resolving global carbon budgets.

Since the uptake of  $^{13}C$ -carbon during photosynthesis and the carbon release through respiration are temporally decoupled, the terrestrial biota is at an isotopic disequilibrium (Enting et al., 1993, Enting et al., 1995). Even under constant climate conditions, the  $\delta^{13}C$  values of the terrestrial biosphere change over time because the atmospheric  $\delta^{13}C$  value becomes increasingly depleted as a result of the contribution of fossil fuel combustion to the atmosphere (Tans et al., 1990). This means, at any given time, the  $\delta^{13}C$  value of carbon released is not equal to the difference between the tropospheric  $\delta^{13}C$  value and the leaf carbon isotope fractionation, but the  $\delta^{13}C$  value of carbon released is more positive due to a more depleted tropospheric  $\delta^{13}C$  value. The results of this study also indicate that soil and canopy components of these crop systems were not at an isotopic equilibrium. However, in our case, the pri-

mary cause of a soil–canopy disequilibrium was land use changes, contributing another aspect to the overall isotopic disequilibrium. In general, the magnitude of the disequilibrium effect is dependent on the size of the carbon pools involved, their turnover rates, the fractionation and the isotopic signals of the carbon pools. The two major storage pools in terrestrial ecosystems are the living biomass and soil carbon. Thus, the disequilibrium exists for plant respiration, but also for litter decomposition. Since turnover times for soil carbon range from several years to decades (Bird et al., 1996; Trumbore et al., 1996), the timelag and therefore the disequilibrium factors will be greater for soil than for plant respiration. It would seem that detailed information about land use changes, particularly in agricultural regions, but also for systems that are generally considered undisturbed (Bush and Colinvaux, 1994) would be important when estimating the isotopic disequilibrium effect globally. The impact of land use history will be greatest if the vegetation changes from  $C_3$ - to  $C_4$ -dominated systems (or vice versa). Remote monitoring of clearcuts of tropical forests (mainly  $C_3$ ) and subsequent establishment of  $C_4$  pastures (Houghton, 1995; Neill et al., 1996), but also estimating crop rotation, which involves the switch between  $C_3$  and  $C_4$  crops in most temperate regions, will become increasingly important data for modeling the global carbon budget. The results of this study suggest that both the history of the land use as well as of the ecosystem carbon discrimination are going to be needed for evaluating isotopic exchange between the biosphere and the atmosphere.

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