

Ecological Applications, 10(2), 2000, pp. 412–422
© 2000 by the Ecological Society of America

CARBON ISOTOPE RATIOS IN BELOWGROUND CARBON CYCLE PROCESSES

JAMES R. EHLERINGER,^{1,4} NINA BUCHMANN,² AND LAWRENCE B. FLANAGAN³

¹*Department of Biology, University of Utah, 257 S 1400 E, Salt Lake City, Utah, USA 84112-0840*

²*Max-Planck-Institut für Biogeochemie, PO Box 100164, 07701 Jena, Germany*

³*Department of Biological Sciences, University of Lethbridge, 4401 University Drive, Lethbridge, Alberta, T1K 3M4 Canada*

Abstract. Analyses of carbon isotope ratios ($\delta^{13}\text{C}$) in soil organic matter (SOM) and soil respired CO_2 provide insights into dynamics of the carbon cycle. $\delta^{13}\text{C}$ analyses do not provide direct measures of soil CO_2 efflux rates but are useful as a constraint in carbon cycle models. In many cases, $\delta^{13}\text{C}$ analyses allow the identification of components of soil CO_2 efflux as well as the relative contribution of soil to overall ecosystem CO_2 fluxes. $\delta^{13}\text{C}$ values provide a unique tool for quantifying historical shifts between C_3 and C_4 ecosystems over decadal to millennial time scales, which are relevant to climate change and land-use change issues. We identify the need to distinguish between $\delta^{13}\text{C}$ analyses of SOM and those of soil CO_2 efflux in carbon cycle studies, because time lags in the turnover rates of different soil carbon components can result in fluxes and stocks that differ in isotopic composition (disequilibrium effect). We suggest that the frequently observed progressive $\delta^{13}\text{C}$ enrichment of SOM may be related to a gradual shift in the relative contributions of microbial vs. plant components in the residual SOM and not to differential SOM degradation or to microbial fractionation during decomposition. Clarifying this mechanism is critical for applying $\delta^{13}\text{C}$ analyses to quantification of SOM turnover rates. Across latitudinal gradients, large differences should occur in the $\delta^{13}\text{C}$ values of CO_2 effluxing from soils, but as of yet a global database is lacking with which to test this prediction. Such a global database would be a useful input for global carbon cycle models that rely on δ values to constrain source and sink relations.

Key words: below ground processes and global change; C_3 and C_4 ecosystems; carbon cycle; carbon isotope ratio; ecosystem processes; global change; soil organic carbon; soil organic matter.

INTRODUCTION

Over the past decade, attention has focused on quantifying components of the global carbon cycle and of sink/source relationships in the terrestrial biosphere (Keeling et al. 1989, Tans et al. 1990, Schimel et al. 1994, Ciais et al. 1995, 1997, Enting et al. 1995, Schimel 1995, IPCC 1996, Walker and Steffen 1996, Fung et al. 1997, Walker et al. 1999). On a global basis, the carbon contained within soils of terrestrial ecosystems far exceeds that within aboveground biomass; yet proportionally less is known about the processes influencing soil carbon dynamics (Anderson 1992, Schimel et al. 1994, Jobbágy and Jackson 2000). As more emphasis is placed on better understanding the carbon cycle across different ecological scales, ranging from patch, stand, and landscape to global levels, stable isotope analyses of carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) will

be increasingly applied to help meet the challenge of closing gaps in our understanding of soil carbon turnover and belowground processes (Balesdent and Mariotti 1996, Boutton 1996, Amundson et al. 1998, Allen et al. 2000, Jackson et al. 2000).

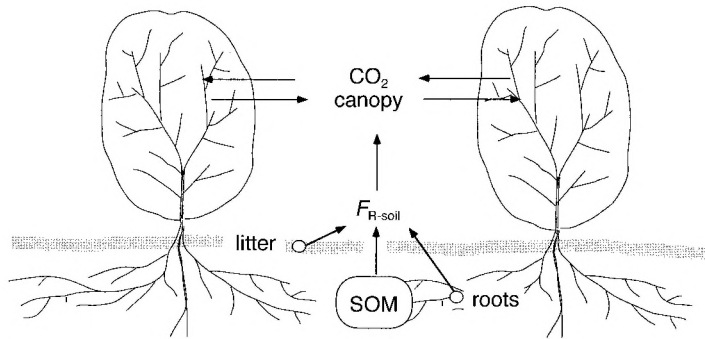
Stable isotopes are best viewed as a tool for constraining magnitudes of different processes and for source identification, but not as a tool for directly assessing flux rates. Their application is useful across a range of scales, such as at the patch scale to distinguish between autotrophic and heterotrophic components of soil respiration (e.g., Lin et al. 1999) or at the global scale to separate terrestrial and oceanic CO_2 flux components (e.g., Ciais et al. 1995). Long-term reconstruction of ecosystem dynamics (e.g., historical patterns of C_3/C_4 vegetation) represent another area where the application of stable isotope analyses have proved useful (Arrouays et al. 1995, Feigl et al. 1995, Gregorich et al. 1995, Martinelli et al. 1996, Neill et al. 1996).

Global $\delta^{13}\text{C}$ data sets spanning different ecosystems and land-use histories for soils are lacking at the mo-

Manuscript received 15 April 1999; revised 21 May 1999; accepted 24 May 1999. For reprints of this Invited Feature, see footnote 1, p. 397.

⁴ E-mail: ehleringer@biology.utah.edu

FIG. 1. A diagram of the various sources for carbon dioxide within a forest ecosystem. Soil carbon dioxide efflux components include decomposition of litter, oxidation of soil organic matter, and respiration by roots.



ment, although information is available for above-ground components (Lloyd and Farquhar 1994, Buchmann et al. 1998, Buchmann and Kaplan 1999). Yet soil CO₂ efflux constitutes a major component of the annual biospheric CO₂ contribution to the atmosphere (Schimel 1995) and flux $\delta^{13}\text{C}$ values are not necessarily uniform over time or space. Inputs of the ecosystem-dependent and seasonal changes in the $\delta^{13}\text{C}$ values of soil CO₂ efflux may well influence the extent to which different land surfaces are interpreted as being carbon sinks in model simulations. In this contribution, we focus on the application of $\delta^{13}\text{C}$ to address soil CO₂ effluxes in the carbon cycle, including the significance of disequilibrium between flux and soil organic matter $\delta^{13}\text{C}$ values associated with land-use change and atmospheric CO₂ change. We believe that establishment of a global $\delta^{13}\text{C}$ soil database and a mechanistic explanation for why $\delta^{13}\text{C}$ values vary with soil organic matter (SOM) in the soil profile will significantly improve our understanding of soil carbon turnover and will find immediate applicability in carbon cycle models, especially under land-use change situations.

BACKGROUND INFORMATION

^{13}C with its one additional neutron is far less abundant than ^{12}C , but still represents $\sim 1.1\%$ of all the carbon on Earth. By convention isotope ratios are expressed in delta notation (δ) with units of per thousand (‰) as

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000\text{‰} \quad (1)$$

where R is the molar ratio of the heavy to light isotope of the sample or standard. A similar equation describes oxygen isotope ratios, but in that case R is $^{18}\text{O}/^{16}\text{O}$. The standards for carbon and oxygen are the Pee Dee Belemnite (PDB) and Standard Mean Ocean Water (SMOW).

As illustrated in Fig. 1, soil CO₂ efflux ($F_{R\text{-soil}}$) can be viewed as the result of three independent component processes:

$$F_{R\text{-soil}} = F_{\text{root}} + F_{\text{SOM}} + F_{\text{litter}} \quad (2)$$

where CO₂ efflux components (F) are root respiration (including rhizosphere), oxidation of soil organic matter (SOM), and decomposition of surface litter. At this fine scale, the challenge is to develop approaches to partition soil CO₂ efflux into its various components, and particularly into autotrophic and heterotrophic soil respiration (e.g., Höglberg and Ekblad 1996, Lin et al. 1999). Understanding how individual components respond to fluctuations in resource levels and to other environmental parameters under natural conditions is critical to our ability to predict SOM responses to future climatic conditions.

At regional and global scales, soil respiration is a significant component of biospheric CO₂ fluxes to the atmosphere (Schlesinger 1977, Davidson 1994, Raich and Potter 1995, Flanagan et al. 1996, Flanagan and Ehleringer 1997, Lavigne et al. 1997). The isotopic composition of soil CO₂ efflux influences both the overall isotopic composition of CO₂ leaving ecosystems and biosphere-atmosphere CO₂ fluxes at regional and global scales (Ciais et al. 1995, 1997, Fung et al. 1997). The extent to which an ecosystem functions as a source or sink for atmospheric CO₂ depends on the net ecosystem exchange (NEE), which is the balance between gross photosynthesis and total ecosystem respiration. However, the $\delta^{13}\text{C}$ values of the gross ecosystem flux and the heterotrophic soil CO₂ efflux need not be identical. It is reasonable to assume that autotrophic respiration of both aboveground (e.g., leaves, stems) and belowground (e.g., roots) components is derived from recently fixed carbon and therefore carries the isotopic signature of recently formed plant compounds. Yet the $\delta^{13}\text{C}$ of autotrophic respiration ($\delta^{13}\text{C}_{R\text{-root}}$) is not likely to be similar to other components of $\delta^{13}\text{C}_{R\text{-soil}}$, because of differential carbon turnover rates of the autotrophic and heterotrophic processes. Inherent in most regional and global carbon-balance models is the assumption that the $\delta^{13}\text{C}$ of above- and belowground CO₂ fluxes within an ecosystem or region differ because of time-constant differences in soil and vegetation carbon turnover rates (Tans et al. 1990, Ciais et al. 1995, 1997, Enting et al. 1995, Fung et al. 1997). This is known

as the disequilibrium factor and is considered to be a consequence of current vegetation fixing CO_2 from an atmosphere whose value today averages approximately -8‰ , whereas 30–100 years ago at the time when much of the soil carbon was produced, the $\delta^{13}\text{C}$ of CO_2 in the atmosphere had a value of approximately -6.5‰ . Disequilibrium value estimates used in carbon cycle models range between 0.18‰ (cultivated ecosystems) and 0.54‰ (evergreen forests) (Fung et al. 1997). If there were additional differences in the $\delta^{13}\text{C}$ values of soil and vegetation CO_2 fluxes, the magnitude of terrestrial source/sink relations could change. As an indicator of the importance of knowing the disequilibrium factor in global carbon cycle modeling, Fung et al. (1997) calculated that the isotopic disequilibrium alone would account for a 0.5 Pg C/yr shift in the magnitude of the middle northern hemisphere carbon sink.

RELATIONSHIPS BETWEEN $\delta^{13}\text{C}$ VALUES OF LEAVES AND SOM

The $\delta^{13}\text{C}$ values of SOM ($\delta^{13}\text{C}_{\text{SOM}}$) reflect contributions from plant foliage/stems, roots, and the consequences of subsequent processes within the soil. As a source input into the soil, leaf carbon isotope ratio ($\delta^{13}\text{C}_p$) values reflect the integration of fractionation events during CO_2 fixation and diffusional constraints imposed by stomata (Farquhar et al. 1989). Photosynthetic fractionation effects are small in C_4 plants and their $\delta^{13}\text{C}_p$ values vary between -10‰ and -15‰ relative to an atmospheric CO_2 substrate of approximately -8‰ (the value today). In contrast, photosynthetic fractionation is greater for C_3 plants with $\delta^{13}\text{C}_p$ values between -21‰ and -30‰ , often reflecting the consequences of stomatal constraints associated with soil water deficits (Farquhar et al. 1989, Ehleringer et al. 1993). Both C_3 and C_4 photosynthetic contribution to SOM can be distinguished using $\delta^{13}\text{C}$ analyses (Tieszen et al. 1997).

Within leaves, the overall ^{13}C content is primarily determined by the initial photosynthetic carbon fixation (Farquhar et al. 1989). There appears to be no subsequent autotrophic or mitochondrial carbon isotope fractionation associated with respiration (Lin and Ehleringer 1997). Yet ^{13}C fractionation can occur during secondary metabolism when there are metabolic branch points, such as in the biosynthesis of compounds derived from acetyl-CoA (DeNiro and Epstein 1977, Winkler et al. 1978, O'Leary 1981, Schmidt and Gleixner 1998). As a result, lipids and lignins are generally depleted by 3–6 ‰ relative to that of the average $\delta^{13}\text{C}_p$ values; sucrose, starch, cellulose, and hemicellulose tend to be slightly enriched in ^{13}C . Since foliage, wood, fruit, and roots differ in their chemical composition, these organs can differ in $\delta^{13}\text{C}$ values by 2–3‰. During foliage senescence, translocation processes can lead to changes in the $\delta^{13}\text{C}_p$ values (Andreux et al. 1990, Bal-

esdent et al. 1993, Buchmann et al. 1997a, b). An enrichment factor of $+0.12\text{‰}$ has been incorporated into some of the carbon balance models to account for the differences in $\delta^{13}\text{C}$ between leaves and litter (e.g., Ciais et al. 1995). However, this shift may be less important than the isotopic changes observed during later stages of decomposition (see below).

THE $\delta^{13}\text{C}$ VALUES OF SOM AND OF SOIL CO_2 EFFLUX

Reconstruction of historical vegetation changes are often obtained through pollen and packrat-midden records (Davis 1981, Betancourt et al. 1990). Shifts between C_3 and C_4 ecosystems are recorded in $\delta^{13}\text{C}$ values of SOM (Balesdent and Mariotti 1996, Boutton 1996, Tieszen et al. 1997), soil carbonates (Cerling and Quade 1990), and silica bodies (Kelly et al. 1991). These studies clearly established the utility of $\delta^{13}\text{C}$ analyses for quantifying C_3/C_4 grassland dynamics and movements in forest–grassland boundaries, especially in tropical and subtropical ecosystems where recent vegetation changes are most common (e.g., Kapos et al. 1993, McPherson et al. 1993, Mariotti and Peterschmitt 1994, Victoria et al. 1995, Desjardins et al. 1996, Schwartz et al. 1996, Boutton et al. 1998). In these instances, $\delta^{13}\text{C}$ values have provided unique information that could not have been obtained from pollen and packrat-midden records. Yet these $\delta^{13}\text{C}$ observations also point to a challenge when integrating carbon flux information, since SOM and flux $\delta^{13}\text{C}$ values need not be the same during transitional periods (Neill et al. 1996, Rochette and Flanagan 1997, Buchmann and Ehleringer 1998). An inherent constraint on ^{13}C data interpretation is that recalcitrant SOM components have much longer turnover rates and potentially different $\delta^{13}\text{C}$ values than components with faster turnover rates. Thus, one should not expect the carbon isotopic composition of soil CO_2 efflux and SOM to be the same.

Balesdent and Mariotti (1996) recognized this constraint and showed that the rate of change in $\delta^{13}\text{C}$ values differed among particle-size fractions, which are thought to represent different stages of SOM oxidation. They showed that following 13 years of maize cultivation, the $\delta^{13}\text{C}$ values of 200–2 000 μm topsoil particles had become 10‰ more enriched in ^{13}C , whereas 0–10 μm particles had become enriched only by 2‰. On a decadal scale, agricultural displacement of native ecosystems, agricultural crop rotation patterns, and forest-to-pasture conversions have all been shown to have a substantial impact on $\delta^{13}\text{C}_{\text{SOM}}$ and on $\delta^{13}\text{C}$ values of soil CO_2 efflux (Schimel et al. 1994, Balesdent and Mariotti 1996, Neill et al. 1996, Rochette and Flanagan 1997, Buchmann and Ehleringer 1998). Given the extensive forest-to-pasture and grassland-to-crop conversions (IPCC 1996) and the frequent agricultural practice of interannual C_3 – C_4 crop rotations in temperate regions (Cox and Atkins 1979), it is possible

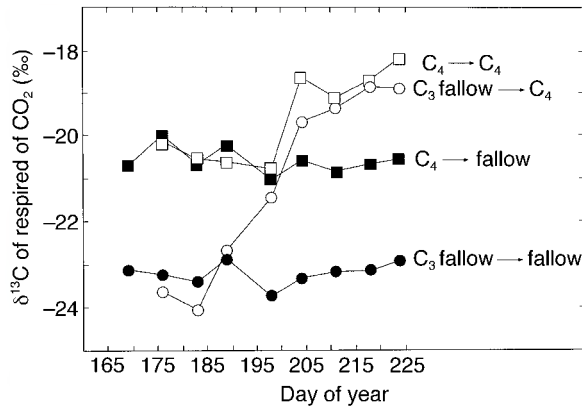


FIG. 2. The carbon isotope ratio of soil carbon dioxide efflux throughout the growing season for a fallow, control plot that previously had a C_3 vegetation, a plot where corn (C_4) has been planted and the previous year the plot had been fallow, a field allowed to remain fallow but which had previously had corn (C_4) growing on it, and a field that had previously had corn growing in it and again is cropped with corn (L. B. Flanagan, unpublished data).

that significant fractions of the land surface in tropical, subtropical, and temperate regions may exhibit a difference between the $\delta^{13}C$ values of SOM and soil CO_2 .

The input $\delta^{13}C$ value of roots or falling litter directly influences $\delta^{13}C_{SOM}$, but does not allow for immediate quantification of the disequilibrium factor. Understanding the rate of decomposition of plant litter inputs is particularly important in agricultural soils where there has been a C_3 -to- C_4 conversion, such as conversion to tropical pastures and corn, millet, or sorghum crops. Consider the $\delta^{13}C$ values of SOM and soil CO_2 efflux associated with land-use change such as planting of corn (C_4) on a soil that developed exclusively from C_3 organic inputs (Fig. 2). The $\delta^{13}C$ values of corn ($-11.8‰$) and C_3 SOM ($-25.7‰$) provide an example of large $\delta^{13}C$ differences between SOM and soil CO_2 efflux within a particular soil (Rochette and Flanagan 1997). Consequently current autotrophic respiration is quantifiable by changes in the $\delta^{13}C$ values of the soil CO_2 efflux. Respiration from plots with corn resulted in CO_2 with a $\delta^{13}C$ value more enriched than that of microbial respiration breaking down C_3 organic matter. When a C_4 crop is in place, the $\delta^{13}C$ values of soil CO_2 efflux are $-17.5‰$ to $-18.5‰$, while the $\delta^{13}C$ values of soil CO_2 efflux from the two fallow soils remained at $-20‰$ ($C_4 \rightarrow$ fallow) and $-22.5‰$ (C_3 fallow $\rightarrow$ fallow). Rochette and Flanagan (1997) calculated that the CO_2 respired by the root and rhizosphere was $\sim 55\%$ of total soil CO_2 efflux, an amount equivalent to 24–35% of crop net CO_2 assimilation during most of the growing season. Here $\delta^{13}C$ analyses to directly assess flux components are most useful in helping to clarify the differences between current soil flux components from current SOM values. In these transitional eco-

systems, we expect to see the greatest seasonal changes in the $\delta^{13}C$ values of soil CO_2 effluxes as the contributions of the current and historical vegetation predominate during different seasons. Abandoned pastures in tropical regions represent the opposite situation where the land-use reversion was C_4 to C_3 , but the differential $\delta^{13}C$ effects on soil CO_2 efflux were similar (Neill et al. 1996).

The challenge of estimating the $\delta^{13}C$ of soil CO_2 efflux in the face of land-use changes, especially in crop rotation systems with C_4 corn ($-12.8‰$) and C_3 alfalfa ($-28.2‰$), is compounded when soil CO_2 efflux rates are crop dependent. Buchmann and Ehleringer (1998) observed that soil CO_2 efflux rates were higher in alfalfa ($9.4 \mu mol \cdot m^{-2} \cdot s^{-1}$) compared to corn ($2.8 \mu mol \cdot m^{-2} \cdot s^{-1}$) stands. At the same time, they observed that after cultivation of corn on the same plot for 2 yr and alfalfa on a plot for 5 yr that $\delta^{13}C_{SOM}$ values in the upper 5 cm were $-15.0‰$ and $-23.6‰$, respectively. Yet the $\delta^{13}C$ values of CO_2 efflux were indistinguishable: $-22.8‰$ for current C_4 and $-22.3‰$ for current C_3 stands. Thus, for the plot with a C_4 crop, 62% of the CO_2 efflux was associated with the previous C_3 crop, whereas for the plot with the current C_3 crop, only 35% of the CO_2 efflux was associated with the previous C_4 crop.

Changing dynamics in C_3 and C_4 vegetation types of both agricultural and forest/pasture ecosystems will introduce additional uncertainty into global carbon flux estimates. This is an important point to reiterate, because as a first approximation for estimating biospheric CO_2 fluxes, it is tempting to substitute the more easily measured $\delta^{13}C$ value of current vegetation or of SOM for the harder-to-measure $\delta^{13}C$ value of soil CO_2 efflux.

Elevated CO_2 studies represent a disequilibrium situation between soil CO_2 efflux and SOM $\delta^{13}C$ values. Yet this disequilibrium can be used to better understand partitioning of the belowground flux components. Lin et al. (1999) measured both carbon and oxygen isotope ratios and soil CO_2 efflux directly coming off the soil surface in order to estimate the three soil components contributing to the overall soil CO_2 efflux (Fig. 3). In their study, 4-yr-old Douglas-fir saplings were grown under controlled conditions with elevated CO_2 and elevated air temperature treatments in all four combinations. The use of a ^{13}C -labeled CO_2 (source of approximately $-35‰$ in contrast to the $-8‰$ under outside growth conditions) resulted in new root materials whose $\delta^{13}C$ values were 8–10‰ more negative than the ambient treatments (open circles, Fig. 3). As a result, the $\delta^{13}C$ values of root respiration under elevated CO_2 treatments should have been 8–10‰ more negative than that of the ambient control plots. The $\delta^{18}O$ values of water (and therefore also of $C^{18}O^{16}O$) varied with depth in the soil profile (Tans 1998). Litter soil water was evaporatively enriched, but soil water deeper than 10 cm depth was not. Lin et al. (1999) capitalizing on

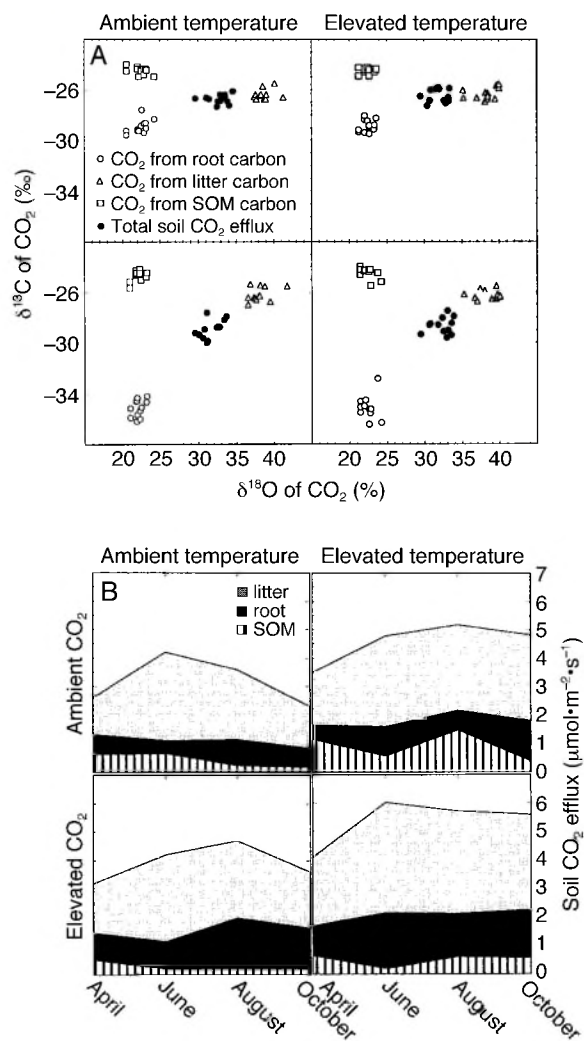


FIG. 3. (A) Carbon and oxygen isotope ratios of carbon dioxide from roots, litter, and soil organic matter for a terracost with plants grown under combinations of elevated atmospheric carbon dioxide and temperature. Soils were from a Douglas-fir forest. (B) Calculated soil carbon dioxide efflux rates for soils grown under a combination of ambient and elevated air temperatures and atmospheric carbon dioxide levels. The figure is modified from Lin et al. (1999).

these differences in soil water measured the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in soil CO₂ efflux (closed circles, Fig. 3) and then used the differences in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in soil CO₂ efflux components to partition the overall efflux into its various components (Fig. 3, right). Litter decomposition dominated the soil CO₂ efflux, in part because of the young age of the trees (and therefore limited overall biomass) in this reconstructed experimental ecosystem. The elevated CO₂ treatments exhibited greater root respiration rates as have been observed in more traditional soil efflux studies. The value of isotopes in this analysis was quantifying changes in the

small-component root respiration signal from the more-dominant litter decomposition signal in response to changes in soil temperature and/or elevated CO₂ treatments.

¹³C ENRICHMENT OF SOM IN C₃ ECOSYSTEMS

$\delta^{13}\text{C}$ differences between soil and vegetation are expected, even in the absence of the extreme case of C₃/C₄ conversions. One of the most common observations in C₃ ecosystems is a progressive enrichment in $\delta^{13}\text{C}$ values associated with litter decomposition and SOM oxidation (Fig. 4). It is not uncommon within a forest ecosystem to see a 1–3‰ enrichment in $\delta^{13}\text{C}$ values between leaf litter and old (deeper) SOM (Nadelhoffer and Fry 1988, Balesdent and Mariotti 1996, Boutton 1996, Buchmann et al. 1997b). Buchmann et al. (1997b) observed that the extent of ^{13}C enrichment in SOM was not a function of $\delta^{13}\text{C}_p$ input values, but instead was positively correlated with soil moisture, suggesting that some aspect of decomposition was influencing ^{13}C enrichment.

Leaf litter and SOM $\delta^{13}\text{C}$ values have been investigated across a broad range of ecosystems (Balesdent et al. 1993, Balesdent and Mariotti 1996, Boutton 1996, Bird et al. 1996, Bird and Pousai 1997). The Balesdent et al. (1993) observations are consistent with each of the other studies and are particularly instructive; they observed a general linear relationship between leaf litter and SOM $\delta^{13}\text{C}$ values (Fig. 5). However, Balesdent et al. (1993) noted that in order to obtain a 1:1 relationship between $\delta^{13}\text{C}$ values of litter input and observed $\delta^{13}\text{C}$ values of soil carbon, an offset correction factor was required that was related to the soil carbon content. In their studies as in others, there appeared to be a progressive enrichment in soil $\delta^{13}\text{C}$ values among C₃ ecosystems negatively related to residual soil carbon content.

The progressive ^{13}C enrichment in SOM is most evident when examining soil depth profiles (Fig. 4) and is thought to be related to decomposition, which is defined here as the sum of litter decomposition and humification (i.e., humus formation). The humus fractions (i.e., humic acids, fulvic acids, humins) can also differ in their $\delta^{13}\text{C}$ values, compared to the bulk soil $\delta^{13}\text{C}_{\text{SOM}}$ values (Nissenbaum and Schallinger 1974, Deines 1980). Even though the absolute SOM content decreases with depth (Jobbágy and Jackson 2000), the $\delta^{13}\text{C}$ values of the remaining SOM within C₃ ecosystems all tend to increase with increasing soil depth. It is well accepted that organic matter particle size decreases with depth and that SOM at depth is in a more advanced stage of decomposition as well (Melillo et al. 1989, Schlesinger 1997). Thus, changes in $\delta^{13}\text{C}$ values of SOM occur during decomposition that may be useful in estimating turnover rates of soil carbon (Balesdent and Mariotti 1996, Bernoux et al. 1998).

Yet the mechanistic basis for this $\delta^{13}\text{C}$ -enrichment

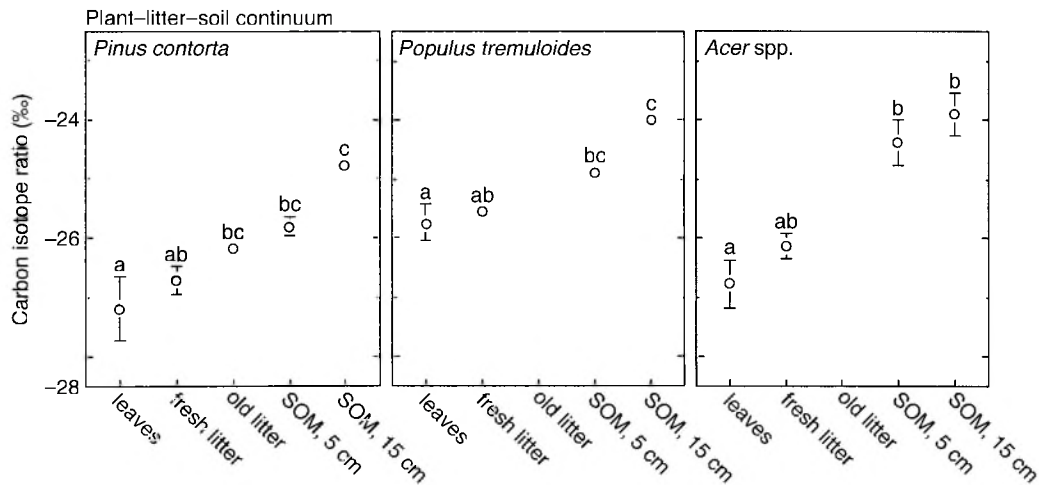


FIG. 4. Carbon isotope ratios of leaves, fresh litter, old litter, and soil organic matter at 5 and 15 cm depths for *Pinus contorta*, *Populus tremuloides*, and *Acer spp.* ecosystems of northern Utah. Vertical lines indicate ± 1 SE. Lowercase letters indicate statistical differences among components within an ecosystem. The figure is modified from Buchmann et al. (1997b).

observation in soil carbon has been the subject of controversy for the past two decades. Understanding the factor(s) leading to a change in soil $\delta^{13}\text{C}$ values is a critical step in deciphering soil carbon processes and inferring turnover rates of soil carbon. Four hypotheses have been discussed in the literature. We expand on the fourth hypothesis, which is consistent with the available data, and, if correct, suggests why SOM might exhibit differential ^{13}C enrichment among ecosystems.

Hypothesis 1: influence of atmospheric change.—The $\delta^{13}\text{C}$ ratios of atmospheric CO_2 have been decreasing since the dawn of the Industrial Revolution because

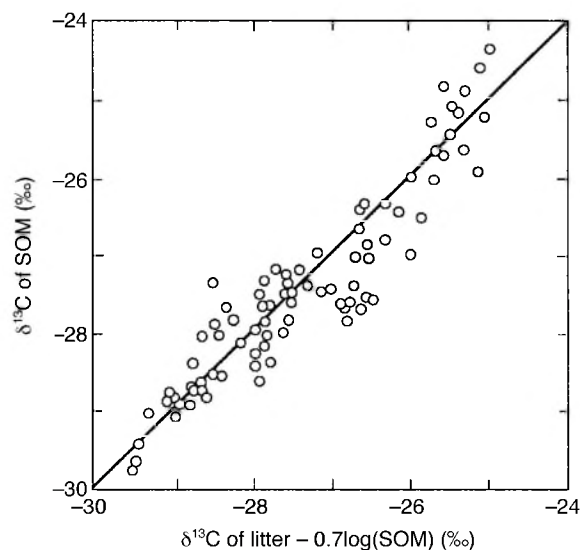


FIG. 5. The relationship between the carbon isotope ratio of litter input into an ecosystem and the carbon isotope ratio of soil organic matter (SOM). The figure is modified from Balesdent et al. (1993).

of the combustion of ^{13}C -depleted fossil fuels (Friedli et al. 1987, Troler et al. 1996). Since SOM at deeper soil depths is older (Trumbore 2000), the carbon in these deeper soil layers should have originated at a time when the $\delta^{13}\text{C}$ values of atmospheric CO_2 were more positive. Using this analogy, $\delta^{13}\text{C}_{\text{SOM}}$ values in deeper horizons should be heavier relative to surface litter $\delta^{13}\text{C}$ values. If so, knowing the differences in $\delta^{13}\text{C}$ values between surface and lower layer SOM values might then be used as a means to estimate soil carbon turnover rates, assuming other factors did not also influence $\delta^{13}\text{C}_{\text{SOM}}$ values (Balesdent and Mariotti 1996, Bernoux et al. 1998). However, the decrease in the $\delta^{13}\text{C}$ ratios of atmospheric CO_2 has been approximately -1.3‰ between 1744 and 1993 (Friedli et al. 1987, Troler et al. 1996), which is much smaller than the typical $\delta^{13}\text{C}$ differences of up to 3‰ observed in soil profiles. At this point, it is debatable how much of the $\delta^{13}\text{C}$ values of SOM in soil profiles can be attributed to changes in the $\delta^{13}\text{C}$ of atmospheric CO_2 vs. other processes described below, but the hypothesis that all the change is the result of atmospheric influences clearly results in miscalculation of soil carbon turnover rates.

Hypothesis 2: microbial fractionation during litter decomposition.—If microbial reactions preferentially used lighter (i.e., ^{13}C depleted) carbon sources in metabolic reactions associated with litter decomposition and SOM oxidation, then the residual SOM should become progressively more positive in its $\delta^{13}\text{C}$ values. Rayleigh distillation analyses are frequently used to quantify the kinetic or enzymatic fractionation associated with a process. Plotting $\delta^{13}\text{C}_{\text{SOM}}$ values vs. the natural logarithm of SOM concentration has often revealed linear relationships, consistent with the notion of a small fractionation against ^{13}C -containing com-

TABLE 1. Carbon isotope ratios ($\delta^{13}\text{C}$) of earthworms and fungi raised on different media and substrates. These data reveal a tendency for ^{13}C enrichment of the organism relative to its substrate.

Organism	$\delta^{13}\text{C}_{\text{organism}}$ (‰)	$\delta^{13}\text{C}_{\text{substrate}}$ (‰)	Source
Basidiomycetes (soft rot fungus)	-22.7	-25.3	Gleixner et al. (1993)
Basidiomycetes (white rot fungus)	-23.0	-25.5	Gleixner et al. (1993)
<i>Millsonia anomala</i> (earthworm)	-11.8 -23.5	-12.8 -27.8	Martin et al. (1992)

pounds as SOM is metabolized in soils (e.g., Nadelhoffer and Fry 1988, Balesdent and Mariotti 1996, Höglberg and Ekblad 1996). However, there is no direct, compelling evidence of microbial fractionation during SOM breakdown. In fact, Lin and Ehleringer (1997) recently provided direct experimental evidence that there was no mitochondrial fractionation during respiration in autotrophs and presumably the same will occur in heterotrophs. Balesdent and Mariotti (1996) also noted that with existing $\delta^{13}\text{C}_{\text{SOM}}$ and [SOM] data, it is not possible to distinguish among microbial fractionation factors (hypothesis 2) and soil mixing (hypothesis 4).

Hypothesis 3: preferential microbial decomposition of litter and SOM.—Individual plant compounds can vary by as much as 10‰ in their $\delta^{13}\text{C}$ values (O’Leary 1981, Schmidt and Gleixner 1998). If SOM components were differentially digested by microbes, this could potentially contribute to the observed trends of increased $\delta^{13}\text{C}_{\text{SOM}}$ values with depth. While it is commonly observed that lignin:C ratios increase as SOM content decreases (Melillo et al. 1982), this mechanism is unlikely to explain observed changes in the $\delta^{13}\text{C}_{\text{SOM}}$. Lignins are actually lighter than bulk leaf values (O’Leary 1981, Schmidt and Gleixner 1998) and so the trend toward increased ^{13}C in residual SOM is opposite to that expected if the trend was due to a relative increase in lignin concentration of SOM.

Hypothesis 4: soil carbon mixing.—Both Wedin et al. (1995) and Balesdent and Mariotti (1996) suggested that there was mixing of new and older SOM components during soil carbon loss and as a result $\delta^{13}\text{C}_{\text{SOM}}$ values shifted during decomposition. We suggest that microbial and fungal carbon residues account for the observed ^{13}C enrichment in residual SOM. Although microbes and fungi are not likely to fractionate significantly against ^{13}C during respiratory metabolism, not all of the microbial and fungal carbon is necessarily derived directly from the decomposing soil organic matter. We expect that the $\delta^{13}\text{C}$ values of microbes and fungi should be heavier than their food source as a result of carboxylation reactions. This is because whenever a carboxylation reaction is involved in catabolism that CO_2 molecule is likely to have originated from the soil atmosphere, which is ^{13}C heavier than the ^{13}C content of the organic materials being decomposed (Cer-

ling et al. 1991). In fact, the CO_2 remaining in the soil that surrounds a microbe/fungus is expected to be 4.4‰ heavier than the metabolically produced CO_2 from decomposition at that location. Even if only a small fraction (for example 5% of the total biomass) of the microbe/fungus carbon was derived in this manner, its $\delta^{13}\text{C}$ value would be enriched by 1–1.5‰ relative to its substrate. Literature observations strongly suggest that invertebrates, microbes, and fungi are enriched in their $\delta^{13}\text{C}$ values relative to their substrate (Table 1; Macko and Estep 1984). If there is a general trend for the remaining SOM to become progressively enriched with microbial/fungi derived components over time, then we would expect that the residual SOM must also become ^{13}C enriched as a result. At this point, there are insufficient data to know whether or not this trend will be maintained in soils from C_4 ecosystems.

Overall, we believe that the observed changes in $\delta^{13}\text{C}_{\text{SOM}}$ values over time and with depth in C_3 ecosystems are the result of microbial incorporation as a progressively more significant component of the residual SOM (hypothesis 4) and the Suess effect (hypothesis 1). Neither hypothesis alone can explain the entire range of $\delta^{13}\text{C}_{\text{SOM}}$ values in a single ecosystem, but together provide a testable interpretation that may shed new light on the processes influencing soil carbon dynamics. Further experimentation is critical to testing this hypothesis, but it is essential to understand the basis of ^{13}C variation in soils if these data are to be correctly interpreted in carbon cycle studies. We feel that hypothesis 2 is not supported by any direct experimental evidence, such as measurements of evolved CO_2 , and that existing evidence indicates that there is little or no fractionation during metabolism. Hypothesis 3 is not supported by the available data, which indicate that the very compounds that are ^{13}C heavy (such as cellulose) are not among those components that become part of the older more recalcitrant soil carbon pool.

GLOBAL $\delta^{13}\text{C}$ PATTERNS OF SOM AND $F_{\text{R-soil}}$

While a global data set of soil $\delta^{13}\text{C}$ values does not yet exist, the existing literature clearly reveals that the $\delta^{13}\text{C}_{\text{SOM}}$ values need not remain constant across geographical transects. Strong latitudinal gradients in C_3/C_4 composition occur across grasslands throughout the

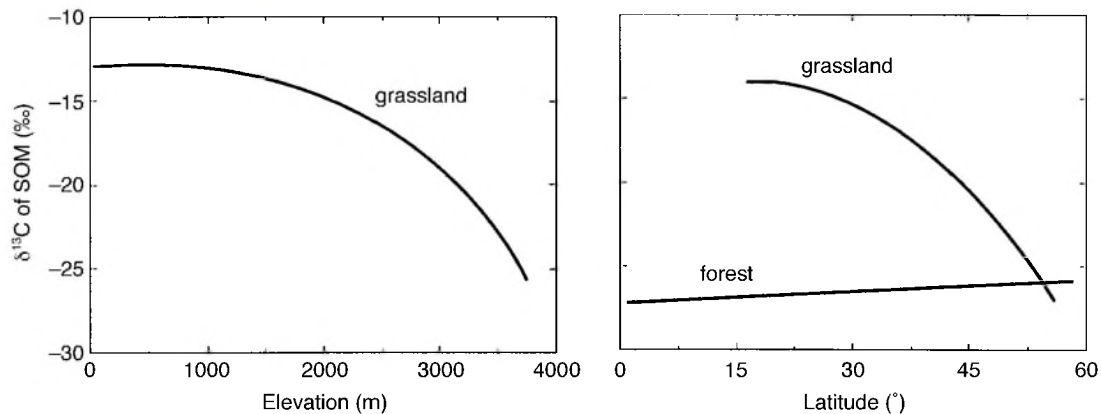


FIG. 6. Patterns of carbon isotope ratio of soil organic matter for grassland and forest ecosystems along elevation and latitude transects. The figure is based on data presented in Bird and Pousai (1997) and Tieszen et al. (1997).

world and are linearly correlated with growing season temperature (Ehleringer et al. 1997, Sage and Monson 1999). Consequently, C_4 -dominated grasslands occur at lower latitudes, while C_3 -dominated grasslands occur at higher latitudes (Fig. 6). Similar aboveground C_3/C_4 gradients exist along elevational transects, mirroring the changes in temperature with elevation (Bird et al. 1994, Tieszen et al. 1997). When long-term, C_3/C_4 potential primary productivity data and $\delta^{13}C_{SOM}$ data are compared, a significant correlation existed between both parameters along latitudinal gradients across the Great Plains of North America (Tieszen et al. 1997). The $\delta^{13}C$ values of C_3 and C_4 end members along these gradients were $-25.5‰$ and $-14‰$, respectively. Grassland $\delta^{13}C_{SOM}$ data from Bird and Pousai (1997) extend these grassland observations to lower latitudes and show the continued prevalence of the C_4 grassland $\delta^{13}C_{SOM}$ values in tropical latitudes. Latitude and elevation are to a large degree interchangeable. As a result, along the elevational transect in Papua New Guinea, Bird et al. (1994) observed a similar pattern as was seen in the latitudinal grassland gradients: along these elevation gradients (0–4000 m) C_3 and C_4 end members were $-26‰$ and $-13‰$, respectively. To the extent that these grasslands have not been impacted by land-use changes, it is reasonable to assume that $\delta^{13}C$ values of aboveground and soil CO_2 fluxes will be similar, once corrected for soil turnover effects described previously.

In contrast, Bird et al. (1996) and Bird and Pousai (1997) have shown that there is limited variation in "corrected" $\delta^{13}C_{SOM}$ values of forest ecosystems across a 0–70° latitudinal transect (Fig. 6). The correction factor eliminated the 1–2‰ effect associated with "old" recalcitrant SOM (Bird et al. 1996), which is not a significant component of soil CO_2 efflux. As a consequence, the $\delta^{13}C$ values of CO_2 effluxing from soils are expected to vary by $\sim 14‰$ as a function of both ecosystem type and latitude. In high-latitude eco-

systems, there is only a small difference in the $\delta^{13}C$ values of soil CO_2 efflux from different ecosystems.

CONCLUSION

While the theory describing aboveground ^{13}C fractionation events in ecological systems has been developed, less is understood about belowground ^{13}C fractionation events, and the integrated database that will allow us to fully incorporate soil CO_2 flux data into carbon cycle models is still lacking. Uncertainties in the estimates of $\delta^{13}C$ values in various pools may translate into inferred CO_2 flux differences, creating the need for a global database of soil and vegetation $\delta^{13}C$ flux data. Unanswered questions remain that must be addressed before $\delta^{13}C$ analyses can be fully applied to soil turnover studies. In particular, we need a better understanding of the mechanism(s) leading to ^{13}C enrichment in SOM. Nevertheless, it is clear that $\delta^{13}C$ analyses will play a central role in carbon flux studies as efforts are made to understand the magnitudes of CO_2 flux components across ecological scales.

LITERATURE CITED

- Allen, A. S., J. A. Andrews, A. C. Finzi, R. Matamala, D. D. Richter, and W. H. Schlesinger. 2000. Effects of free-air CO_2 enrichment (FACE) on belowground processes in a *Pinus taeda* forest. *Ecological Applications* 10:437–448.
- Amundson, R., L. Stern, T. Baisden, and Y. Wang. 1998. The isotopic composition of soil and soil-respired CO_2 . *Geoderma* 82:83–114.
- Anderson, J. M. 1992. Responses of soils to global change. *Advances in Ecological Research* 22:163–210.
- Andreux, F., C. C. Cerri, P. B. Vose, and V. A. Vitorello. 1990. The distribution of ^{13}C and ^{15}N in plants and soil profiles. Pages 262–265 in A. F. Harrison, P. Ineson, and O. W. Heal, editors. *Nutrient cycling in terrestrial ecosystems*. Elsevier, Amsterdam, The Netherlands.
- Arrouays, D., J. Balesdent, A. Mariotti, and C. Girardin. 1995. Modelling organic carbon turnover in cleared temperate forest soils converted to maize cropping by using ^{13}C natural abundance measurements. *Plant and Soil* 173:191–196.
- Balesdent, J., C. Girardin, and A. Mariotti. 1993. Site-related

- $\delta^{13}\text{C}$ of tree leaves and soil organic matter in a temperate forest. *Ecology* **74**:1713–1721.
- Balesdent, J., and A. Mariotti. 1996. Measurement of soil organic matter turnover using ^{13}C natural abundance. Pages 83–111 in T. W. Boutton and S.-I. Yamasaki, editors. *Mass spectrometry of soils*. Marcel Dekker, New York, New York, USA.
- Bernoux, M., C. C. Cerri, C. Neill, and J. F. L. de Moreas. 1998. The use of stable isotopes for estimating soil organic matter turnover rates. *Geoderma* **82**:43–58.
- Betancourt, J. L., T. R. Van Devender, and P. S. Martin, editors. 1990. *Packrat middens the last 40 000 years of biological change*. University of Arizona Press, Tucson, Arizona, USA.
- Bird, M. I., A. R. Chivas, and J. Head. 1996. A latitudinal gradient in carbon turnover times in forest soils. *Nature* **381**:143–146.
- Bird, M. I., S. G. Haberle, and A. R. Chivas. 1994. Effect of altitude on the carbon-isotope composition of forest and grassland soils from Papua New Guinea. *Global Biogeochemical Cycles* **8**:13–22.
- Bird, M. I., and P. Pousai. 1997. Variations of $\delta^{13}\text{C}$ in the surface soil organic carbon pool. *Global Biogeochemical Cycles* **11**:313–322.
- Boutton, T. W. 1996. Stable carbon isotope ratios of soil organic matter and their use as indicators of vegetation and climate change. Pages 47–82 in T. W. Boutton and S.-I. Yamasaki, editors. *Mass spectrometry of soils*. Marcel Dekker, New York, New York, USA.
- Boutton, T. W., S. R. Archer, A. J. Midwood, S. F. Zitzer, and R. Bol. 1998. $\delta^{13}\text{C}$ values of soil organic carbon and their use in documenting vegetation change in a subtropical savanna ecosystem. *Geoderma* **82**:5–41.
- Buchmann, N., J. R. Brooks, L. B. Flanagan, and J. R. Ehleringer. 1998. Carbon isotope discrimination of terrestrial ecosystems. Pages 203–221 in H. Griffith, editor. *Stable isotopes integration of biological, ecological and geochemical processes*. BIOS Scientific, Oxford, UK.
- Buchmann, N., and J. R. Ehleringer. 1998. CO_2 concentration profiles and carbon and oxygen isotopes in C_3 and C_4 crop canopies. *Agricultural and Forest Meteorology* **89**:45–58.
- Buchmann, N., J.-M. Guehl, T. Barigah, and J. R. Ehleringer. 1997a. Interseasonal comparison of CO_2 concentrations, isotopic composition, and carbon cycling in an Amazonian rainforest (French Guiana). *Oecologia* **110**:120–131.
- Buchmann, N., W.-Y. Kao, and J. Ehleringer. 1997b. Influence of stand structure on carbon-13 of vegetation, soils, and canopy air within deciduous and evergreen forests in Utah, United States. *Oecologia* **110**:109–119.
- Buchmann, N., and J. O. Kaplan. 1999. Carbon isotope discrimination of terrestrial ecosystems—how well do observed and modeled results match? In E.-D. Schulze, S. P. Harrison, M. Heimann, E. A. Holland, J. Lloyd, I. C. Prentice, and D. Schimel, editors. *Global biogeochemical cycles in the climate system*. Academic Press, San Diego, California, USA, *in press*.
- Cerling, T. E., and J. Quade. 1990. Global ecologic and climatic change during the neogene: stable isotopic evidence from soils. *Chemical Geology* **84**:164–165.
- Cerling, T. E., D. K. Solomon, J. Quade, and J. R. Bowman. 1991. On the isotopic composition of carbon in soil carbon dioxide. *Geochimica et Cosmochimica Acta* **55**:3403–3405.
- Ciais, P., et al. 1997. A three-dimensional synthesis study of $\delta^{18}\text{O}$ in atmospheric CO_2 . 1. Surface fluxes. *Journal of Geophysical Research* **102**:5857–5872.
- Ciais, P., P. P. Tans, J. W. C. White, M. Troler, R. J. Francey, J. A. Berry, D. R. Randall, P. J. Sellers, J. G. Collatz, and D. S. Schimel. 1995. Partitioning of ocean and land uptake of CO_2 as inferred by $\delta^{13}\text{C}$ measurements from the NOAA Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network. *Journal of Geophysical Research* **100**:5051–5070.
- Cox, G. W., and M. D. Atkins. 1979. *Agricultural ecology*. W.H. Freeman, San Francisco, California, USA.
- Davidson, E. A. 1994. Climate change and soil microbial processes: secondary effects are hypothesized from better known interacting primary effects. Pages 155–168 in M. D. A. Rounsevell and P. J. Loveland, editors. *Soil responses to climate change*. Volume 123. Springer-Verlag, Heidelberg, Germany.
- Davis, M. B. 1981. Quaternary history and the stability of forest communities. Pages 132–153 in D. C. West, H. H. Schugart, and D. B. Botkin, editors. *Forest succession: concepts and application*. Springer-Verlag, New York, New York, USA.
- Deines, P. 1980. The isotopic composition of reduced organic carbon. Pages 329–406 in P. Fritz and J. C. Fontes, editors. *Handbook of environmental isotope geochemistry*. Volume 1. Elsevier, Amsterdam, The Netherlands.
- DeNiro, M. J., and S. Epstein. 1977. Mechanism of carbon isotope fractionation associated with lipid synthesis. *Science* **197**:261–263.
- Desjardins, T., A. C. Filho, A. Mariotti, A. Chauvel, and C. Girardin. 1996. Changes of the forest–savanna boundary in Brazilian Amazonia during the Holocene revealed by stable isotope ratios of soil organic carbon. *Oecologia* **108**:749–756.
- Ehleringer, J. R., T. E. Cerling, and B. R. Helliker. 1997. C_4 photosynthesis, atmospheric CO_2 , and climate. *Oecologia* **112**:285–299.
- Ehleringer, J. R., A. E. Hall, and G. D. Farquhar. 1993. *Stable isotopes and plant carbon/water relations*. Academic Press, San Diego, California, USA.
- Enting I. G., C. M. Trudinger, and R. J. Francey. 1995. A synthesis inversion of the concentration and $\delta^{13}\text{C}$ of atmospheric CO_2 . *Tellus* **47B**:35–52.
- Farquhar, G. D., J. R. Ehleringer, and K. T. Hubick. 1989. Carbon isotope discrimination and photosynthesis. *Annual Review of Plant Physiology and Plant Molecular Biology* **40**:503–537.
- Feigl, B. J., J. M. Melillo, and C. C. Cerri. 1995. Changes in the origin and quality of soil organic matter after pasture introduction in Rondonia (Brazil). *Plant and Soil* **175**:21–29.
- Flanagan, L. B., J. R. Brooks, G. T. Varney, S. C. Berry, and J. R. Ehleringer. 1996. Carbon isotope discrimination during photosynthesis and the isotope ratio of respired CO_2 in boreal ecosystems. *Global Biogeochemical Cycles* **10**:629–640.
- Flanagan, L. B., and J. R. Ehleringer. 1997. Ecosystem–atmosphere CO_2 exchange: interpreting signals of change using stable isotope ratios. *Trends in Ecology and Evolution* **13**:10–14.
- Friedli, H., U. Siegenthaler, D. Rauber, and H. Oeschger. 1987. Measurements of concentration, $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of tropospheric carbon dioxide over Switzerland. *Tellus* **39**:80–88.
- Fung, I., et al. 1997. Carbon 13 exchanges between the atmosphere and the biosphere. *Global Biogeochemical Cycles* **11**:507–533.
- Gleixner, G., H.-J. Danier, R. A. Werner, and H.-L. Schmidt. 1993. Correlations between the ^{13}C content of primary and secondary plant products in different cell compartments and that in decomposing Basidiomycetes. *Plant Physiology* **102**:1287–1290.
- Gregorich, E. G., B. H. Ellert, and C. M. Monreal. 1995. Turnover of soil organic matter and storage of corn residue carbon estimated from natural ^{13}C abundance. *Canadian Journal of Soil Science* **75**:161–167.

- Högberg, P., and A. Ekblad 1996. Substrate-induced respiration measured *in situ* in a C_3 -plant ecosystem using additions of C_4 -sucrose. *Soil Biological Biochemistry* **28**: 1131–1138.
- IPCC. 1996. Climate change 1995. The science of climate change. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK.
- Jackson, R. B., et al. 2000. Belowground consequences of vegetation change and their treatment in models. *Ecological Applications* **10**:470–483.
- Jobbágy, E. G., and R. B. Jackson. 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications* **10**:423–436.
- Kapos, V., G. Ganade, E. Matsui, and R. L. Victoria. 1993. $\delta^{13}C$ as an indicator of edge effects in tropical rainforest reserves. *Journal of Ecology* **81**:425–432.
- Keeling, C. D., R. B. Bacastow, A. F. Carter, S. C. Piper, T.P. Whorf, M. Heimann, W. G. Mook, and H. Roeloffzen. 1989. A three-dimensional model of atmospheric CO_2 transport based on observed winds. I. Analysis of observational data. Pages 165–236 in D. H. Peterson, editor. Aspects of climate variability in the Pacific and the western Americas. AGU Monograph 55, American Geophysical Union, Washington, D.C., USA.
- Kelly, E. F., R. G. Amundson, B. D. Marino, and M. J. DeNiro. 1991. Stable isotope ratios of carbon in phytoliths as a quantitative method of monitoring vegetation and climate change. *Quaternary Research* **35**:222–233.
- Lavigne, M. B., M. G. Ryan, D. E. Anderson, D. D. Baldocchi, P. M. Crill, D. R. Fitzgerald, M. L. Goulden, S. T. Gower, J. M. M. Massheder, J. H. McCaughey, M. B. Rayment, and R. G. Strieg 1997. Comparing nocturnal eddy covariance measurements to estimates of ecosystem respiration made by scaling chamber measurements at six coniferous boreal sites. *Journal of Geophysical Research* **102**: 28977–28985.
- Lin, G., and J. R. Ehleringer. 1997. Carbon isotopic fractionation does not occur during dark respiration in C_3 and C_4 plants. *Plant Physiology* **114**:391–394.
- Lin, G., J. R. Ehleringer, P. T. Rygielwicz, M. G. Johnson, and D. T. Tingey. 1999. Elevated CO_2 and temperature impacts on different components of soil CO_2 efflux in Douglas-fir terracosms. *Global Change Biology* **5**:157–168.
- Lloyd, J., and G. D. Farquhar. 1994. ^{13}C discrimination during CO_2 assimilation by the terrestrial biosphere. *Oecologia* **99**: 201–215.
- Macko, S. A. and M. Estep. 1984. Microbial alteration of stable nitrogen and carbon isotopic composition of organic matter. *Organic Geochemistry* **6**:787–790.
- Mariotti, A., and E. Peterschmitt. 1994. Forest savanna ecotone dynamics in India as revealed by carbon isotope ratios of soil organic matter. *Oecologia* **97**:475–480.
- Martin, A., A. Mariotti, J. Balesdent, and P. Lavelle. 1992. Soil organic matter assimilated by geophagous tropical earthworm based on $\delta^{13}C$ measurements. *Ecology* **73**:118–128.
- Martinelli, L. A., L. C. R. Pessenda, E. Espinoza, P. B. Camargo, E. C. Telles, C. C. Cerri, R. L. Victoria, R. Aravena, J. Richey, and S. Trumbore. 1996. Carbon-13 variation with depth in soils of Brazil and climate change during the Quaternary. *Oecologia* **106**:376–381.
- McPherson, G. R., T. W. Boutton, and A. J. Midwood. 1993. Stable carbon isotope analysis of soil organic matter illustrates vegetation change at grassland/woodland boundary in southeast Arizona, USA. *Oecologia* **93**:95–101.
- Melillo, J. M., J. D. Aber, A. E. Linkins, A. Ricca, B. Fry, and K. Nadelhoffer. 1989. Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter. *Plant and Soil* **115**:189–198.
- Melillo, J. M., J. D. Aber, and J. F. Muratore. 1982. Nitrogen and lignin control of hardwood leaf litter decomposition dynamics. *Ecology* **63**:621–626.
- Nadelhoffer, K. J., and B. Fry. 1988. Controls on natural nitrogen-15 and carbon-13 abundances in forest soil organic matter. *Soil Science Society of America Journal* **52**: 1633–1640.
- Neill, C., B. Fry, J. M. Melillo, P. A. Steudler, J. F. L. Moraes, and C. C. Cerri. 1996. Forest- and pasture-derived carbon contributions to carbon stocks and microbial respiration of tropical pasture soils. *Oecologia* **107**:113–119.
- Nissenbaum, A., and K. M. Schallinger. 1974. The distribution of the stable carbon isotope ($^{13}C/^{12}C$) in fractions of soil organic matter. *Geoderma* **11**:137–145.
- O'Leary, M. H. 1981. Carbon isotope fractionation in plants. *Phytochemistry* **20**:553–567.
- Raich, J. W., and C. S. Potter. 1995. Global patterns of carbon dioxide emissions from soils. *Global Biogeochemical Cycles* **9**:23–36.
- Rochette, P., and L. B. Flanagan. 1997. Quantifying rhizosphere respiration in a corn crop under field conditions. *Soil Science Society of America Journal* **61**:466–474.
- Sage, R. F., and R. K. Monson. 1999. C_4 plant biology. Academic Press, San Diego, California, USA.
- Schimel, D. S. 1995. Terrestrial ecosystems and the carbon cycle. *Global Change Biology* **1**:77–91.
- Schimel, D. S., B. H. Braswell, E. A. Holland, R. McKeown, D. S. Ojima, T. H. Painter, W. J. Parton, and A. R. Townsend. 1994. Climatic, edaphic, and biotic controls over storage and turnover of carbon in soils. *Global Biogeochemical Cycles* **8**:279–293.
- Schlesinger, W. H. 1977. Carbon balance in terrestrial detritus. *Annual Review of Ecology and Systematics* **8**:51–81.
- Schlesinger, W. H. 1997. Biogeochemistry: an analysis of global change. Academic Press, San Diego, California, USA.
- Schmidt, H.-L., and G. Gleixner. 1998. Carbon isotope effects on key reactions in plant metabolism and ^{13}C -patterns in natural compounds. Pages 13–25 in H. Griffiths, editor. Stable isotopes integration of biological, ecological, and geochemical processes. BIOS Scientific Publishers, Oxford, UK.
- Schwartz, D., H. de Foresta, A. Mariotti, J. Balesdent, J. P. Massimba, and C. Girardin. 1996. Present dynamics of the savanna-forest boundary in the Congolese Mayombe: a pedological, botanical and isotopic (^{13}C and ^{14}C) study. *Oecologia* **106**:516–524.
- Tans, P. P. 1998. Oxygen isotopic equilibrium between carbon dioxide and water in soils. *Tellus* **50B**:163–178.
- Tans, P. P., I. Y. Fung, and T. Takahashi. 1990. Observational constraints on the global atmospheric CO_2 budget. *Science* **247**:1431–1438.
- Tieszen, L. L., B. C. Reed, N. B. Bliss, B. K. Wylie, and D. D. DeJong. 1997. NDVI, C_3 and C_4 production, and distribution in Great Plains grassland land cover classes. *Ecological Applications* **7**:59–78.
- Troler, M., J. W. C. White, P. P. Tans, K. A. Masarie, and P. A. Gemery. 1996. Monitoring the isotopic composition of atmospheric CO_2 : measurements from the NOAA Global Air Sampling Network. *Journal of Geophysical Research* **101**:25897–25916.
- Trumbore, S. E. 2000. Age of soil organic matter and soil respiration: radiocarbon constraints on belowground C dynamics. *Ecological Applications* **10**:399–411.
- Victoria, R. L., F. Fernandes, L. A. Martinelli, M. d. C. Piccolo, P. B. deCamargo, and S. Trumbore. 1995. Past vegetation changes in the Brazilian Pantanal arboreal—grassy

- savanna ecotone by using carbon isotopes in the soil organic matter. *Global Change Biology* **1**:165–171.
- Walker, B., and W. Steffen. 1996. Global change and terrestrial ecosystems. Cambridge University Press, Cambridge, UK.
- Walker, B., W. Steffen, J. Canadell, and J. Ingram, editors. 1999. The terrestrial biosphere and global change. Cambridge University Press, Cambridge, UK.
- Wedin, D. A., L. L. Tieszen, B. Dewey, and J. Pastor. 1995. Carbon isotope dynamics during grass decomposition and soil organic matter formation. *Ecology* **76**:1383–1392.
- Winkler, F. J., E. Wirth, E. Latzko, H. L. Schmidt, W. Hoppe, and P. Wimmer. 1978. Influence of growth conditions and development on $\delta^{13}\text{C}$ values in different organs and constituents of wheat, oat, and maize. *Zeitschrift für Pflanzenphysiologie* **87**:255–263.