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## CARBON ISOTOPE RATIOS IN BELOWGROUND CARBON CYCLE PROCESSES

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**Abstract.** Analyses of carbon isotope ratios ( $\delta^{13}\text{C}$ ) in soil organic matter (SOM) and soil respired  $\text{CO}_2$  provide insights into dynamics of the carbon cycle.  $\delta^{13}\text{C}$  analyses do not provide direct measures of soil  $\text{CO}_2$  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  $\text{CO}_2$  efflux as well as the relative contribution of soil to overall ecosystem  $\text{CO}_2$  fluxes.  $\delta^{13}\text{C}$  values provide a unique tool for quantifying historical shifts between  $\text{C}_3$  and  $\text{C}_4$  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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\delta$  values to constrain source and sink relations.

**Key words:** *below ground processes and global change;  $\text{C}_3$  and  $\text{C}_4$  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).

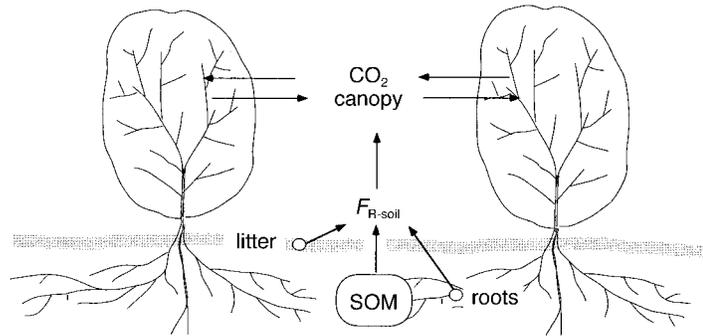
Stable isotopes are best viewed as a tool for constraining magnitudes of different processes and for source identification, but not as a tool for directly assessing flux rates. Their application is useful across a range of scales, such as at the patch scale to distinguish between autotrophic and heterotrophic components of soil respiration (e.g., Lin et al. 1999) or at the global scale to separate terrestrial and oceanic  $\text{CO}_2$  flux components (e.g., Ciais et al. 1995). Long-term reconstruction of ecosystem dynamics (e.g., historical patterns of  $\text{C}_3/\text{C}_4$  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-

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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 CO<sub>2</sub> efflux constitutes a major component of the annual biospheric CO<sub>2</sub> contribution to the atmosphere (Schimel 1995) and flux δ<sup>13</sup>C values are not necessarily uniform over time or space. Inputs of the ecosystem-dependent and seasonal changes in the δ<sup>13</sup>C values of soil CO<sub>2</sub> 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 δ<sup>13</sup>C to address soil CO<sub>2</sub> effluxes in the carbon cycle, including the significance of disequilibrium between flux and soil organic matter δ<sup>13</sup>C values associated with land-use change and atmospheric CO<sub>2</sub> change. We believe that establishment of a global δ<sup>13</sup>C soil database and a mechanistic explanation for why δ<sup>13</sup>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

<sup>13</sup>C with its one additional neutron is far less abundant than <sup>12</sup>C, but still represents ~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 <sup>18</sup>O/<sup>16</sup>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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> efflux into its various components, and particularly into autotrophic and heterotrophic soil respiration (e.g., Högberg 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 CO<sub>2</sub> 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 CO<sub>2</sub> efflux influences both the overall isotopic composition of CO<sub>2</sub> leaving ecosystems and biosphere-atmosphere CO<sub>2</sub> 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 CO<sub>2</sub> depends on the net ecosystem exchange (NEE), which is the balance between gross photosynthesis and total ecosystem respiration. However, the δ<sup>13</sup>C values of the gross ecosystem flux and the heterotrophic soil CO<sub>2</sub> 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 δ<sup>13</sup>C of autotrophic respiration (δ<sup>13</sup>C<sub>R-root</sub>) is not likely to be similar to other components of δ<sup>13</sup>C<sub>R-soil</sub>, 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 δ<sup>13</sup>C of above- and belowground CO<sub>2</sub> 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<sub>2</sub> 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 δ<sup>13</sup>C of CO<sub>2</sub> 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 δ<sup>13</sup>C values of soil and vegetation CO<sub>2</sub> 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 δ<sup>13</sup>C VALUES OF LEAVES AND SOM

The δ<sup>13</sup>C values of SOM (δ<sup>13</sup>C<sub>SOM</sub>) 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 (δ<sup>13</sup>C<sub>p</sub>) values reflect the integration of fractionation events during CO<sub>2</sub> fixation and diffusional constraints imposed by stomata (Farquhar et al. 1989). Photosynthetic fractionation effects are small in C<sub>4</sub> plants and their δ<sup>13</sup>C<sub>p</sub> values vary between -10‰ and -15‰ relative to an atmospheric CO<sub>2</sub> substrate of approximately -8‰ (the value today). In contrast, photosynthetic fractionation is greater for C<sub>3</sub> plants with δ<sup>13</sup>C<sub>p</sub> 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<sub>3</sub> and C<sub>4</sub> photosynthetic contribution to SOM can be distinguished using δ<sup>13</sup>C analyses (Tieszen et al. 1997).

Within leaves, the overall <sup>13</sup>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 <sup>13</sup>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 δ<sup>13</sup>C<sub>p</sub> values; sucrose, starch, cellulose, and hemicellulose tend to be slightly enriched in <sup>13</sup>C. Since foliage, wood, fruit, and roots differ in their chemical composition, these organs can differ in δ<sup>13</sup>C values by 2–3‰. During foliage senescence, translocation processes can lead to changes in the δ<sup>13</sup>C<sub>p</sub> values (Andreux et al. 1990, Bal-

esdent et al. 1993, Buchmann et al. 1997a, b). An enrichment factor of +0.12‰ has been incorporated into some of the carbon balance models to account for the differences in δ<sup>13</sup>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 δ<sup>13</sup>C VALUES OF SOM AND OF SOIL CO<sub>2</sub> EFFLUX

Reconstruction of historical vegetation changes are often obtained through pollen and packrat-midden records (Davis 1981, Betancourt et al. 1990). Shifts between C<sub>3</sub> and C<sub>4</sub> ecosystems are recorded in δ<sup>13</sup>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 δ<sup>13</sup>C analyses for quantifying C<sub>3</sub>/C<sub>4</sub> 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, δ<sup>13</sup>C values have provided unique information that could not have been obtained from pollen and packrat-midden records. Yet these δ<sup>13</sup>C observations also point to a challenge when integrating carbon flux information, since SOM and flux δ<sup>13</sup>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 <sup>13</sup>C data interpretation is that recalcitrant SOM components have much longer turnover rates and potentially different δ<sup>13</sup>C values than components with faster turnover rates. Thus, one should not expect the carbon isotopic composition of soil CO<sub>2</sub> efflux and SOM to be the same.

Balesdent and Mariotti (1996) recognized this constraint and showed that the rate of change in δ<sup>13</sup>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 δ<sup>13</sup>C values of 200–2 000 μm topsoil particles had become 10‰ more enriched in <sup>13</sup>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 δ<sup>13</sup>C<sub>SOM</sub> and on δ<sup>13</sup>C values of soil CO<sub>2</sub> 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<sub>3</sub>–C<sub>4</sub> crop rotations in temperate regions (Cox and Atkins 1979), it is possible

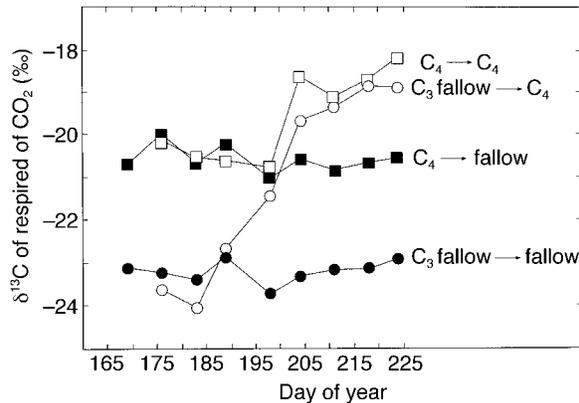


FIG. 2. The carbon isotope ratio of soil carbon dioxide efflux throughout the growing season for a fallow, control plot that previously had a  $C_3$  vegetation, a plot where corn ( $C_4$ ) has been planted and the previous year the plot had been fallow, a field allowed to remain fallow but which had 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 ( $9.4 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) compared to corn ( $2.8 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ) 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

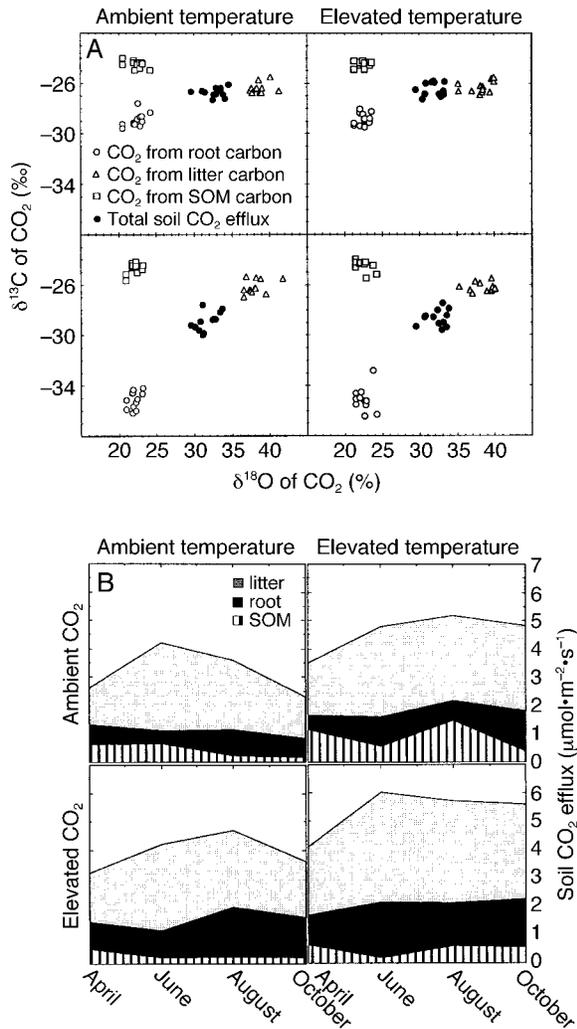


FIG. 3. (A) Carbon and oxygen isotope ratios of carbon dioxide from roots, litter, and soil organic matter for a terracost with plants grown under combinations of elevated atmospheric carbon dioxide and temperature. Soils were from a Douglas-fir forest. (B) Calculated soil carbon dioxide efflux rates 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 CO<sub>2</sub> efflux (closed circles, Fig. 3) and then used the differences in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in soil CO<sub>2</sub> efflux components to partition the overall efflux into its various components (Fig. 3, right). Litter decomposition dominated the soil CO<sub>2</sub> efflux, in part because of the young age of the trees (and therefore limited overall biomass) in this reconstructed experimental ecosystem. The elevated CO<sub>2</sub> 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 CO<sub>2</sub> treatments.

#### <sup>13</sup>C ENRICHMENT OF SOM IN C<sub>3</sub> ECOSYSTEMS

$\delta^{13}\text{C}$  differences between soil and vegetation are expected, even in the absence of the extreme case of C<sub>3</sub>/C<sub>4</sub> conversions. One of the most common observations in C<sub>3</sub> 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 <sup>13</sup>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 <sup>13</sup>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 C<sub>3</sub> ecosystems negatively related to residual soil carbon content.

The progressive <sup>13</sup>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 C<sub>3</sub> 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

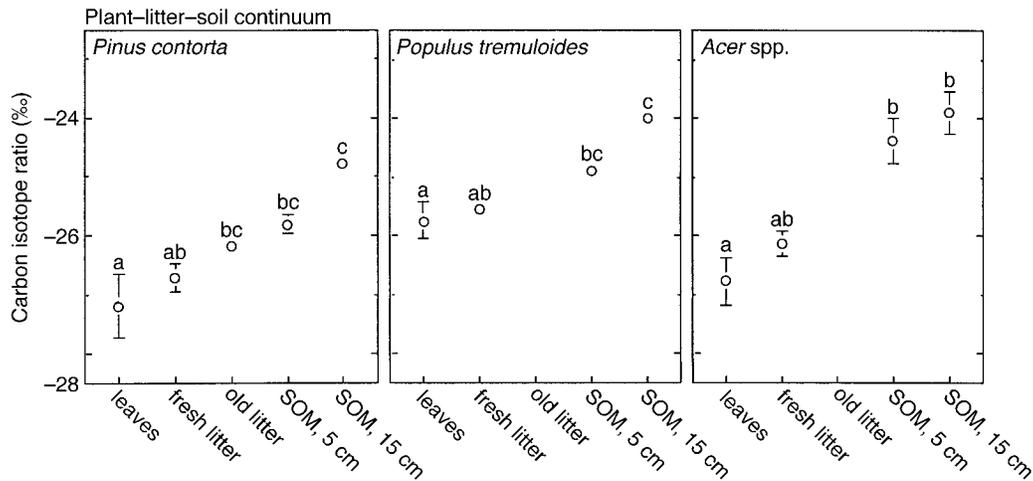


FIG. 4. Carbon isotope ratios of leaves, fresh litter, old litter, and soil organic matter at 5 and 15 cm depths for *Pinus contorta*, *Populus tremuloides*, and *Acer* spp. ecosystems of northern Utah. Vertical lines indicate  $\pm 1$  SE. Lowercase letters indicate statistical differences among components 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  $^{13}\text{C}$  enrichment among ecosystems.

*Hypothesis 1: influence of atmospheric change.*—The  $\delta^{13}\text{C}$  ratios of atmospheric  $\text{CO}_2$  have been decreasing since the dawn of the Industrial Revolution because

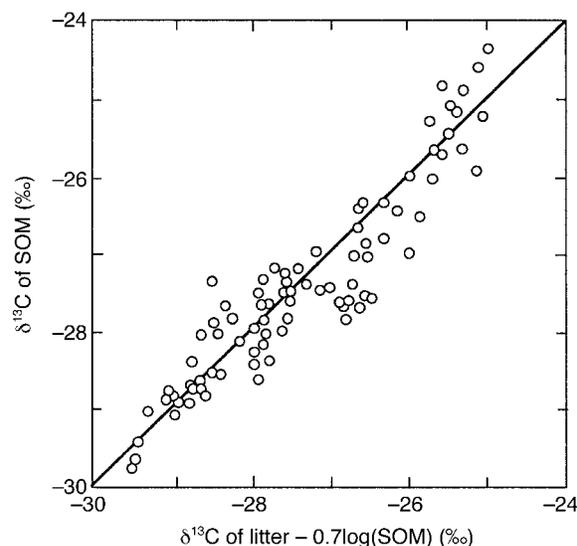


FIG. 5. The relationship between the carbon isotope ratio of litter input into an ecosystem and the carbon isotope ratio of soil organic matter (SOM). The figure is modified from Balesdent et al. (1993).

of the combustion of  $^{13}\text{C}$ -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  $\text{CO}_2$  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  $\text{CO}_2$  has been approximately  $-1.3\text{‰}$  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  $3\text{‰}$  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  $\text{CO}_2$  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.,  $^{13}\text{C}$  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  $^{13}\text{C}$ -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  $^{13}\text{C}$  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	-12.8	Martin et al. (1992)
	-23.5	-27.8	

pounds as SOM is metabolized in soils (e.g., Nadelhoffer and Fry 1988, Balesdent and Mariotti 1996, Högberg 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  $^{13}\text{C}$  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  $^{13}\text{C}$  enrichment in residual SOM. Although microbes and fungi are not likely to fractionate significantly against  $^{13}\text{C}$  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  $\text{CO}_2$  molecule is likely to have originated from the soil atmosphere, which is  $^{13}\text{C}$  heavier than the  $^{13}\text{C}$  content of the organic materials being decomposed (Cer-

ling et al. 1991). In fact, the  $\text{CO}_2$  remaining in the soil that surrounds a microbe/fungus is expected to be 4.4‰ heavier than the metabolically produced  $\text{CO}_2$  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  $^{13}\text{C}$  enriched as a result. At this point, there are insufficient data to know whether or not this trend will be maintained in soils from  $\text{C}_4$  ecosystems.

Overall, we believe that the observed changes in  $\delta^{13}\text{C}_{\text{SOM}}$  values over time and with depth in  $\text{C}_3$  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  $^{13}\text{C}$  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  $\text{CO}_2$ , 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  $^{13}\text{C}$  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 $F_{R\text{-soil}}$

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  $\text{C}_3/\text{C}_4$  composition occur across grasslands throughout the

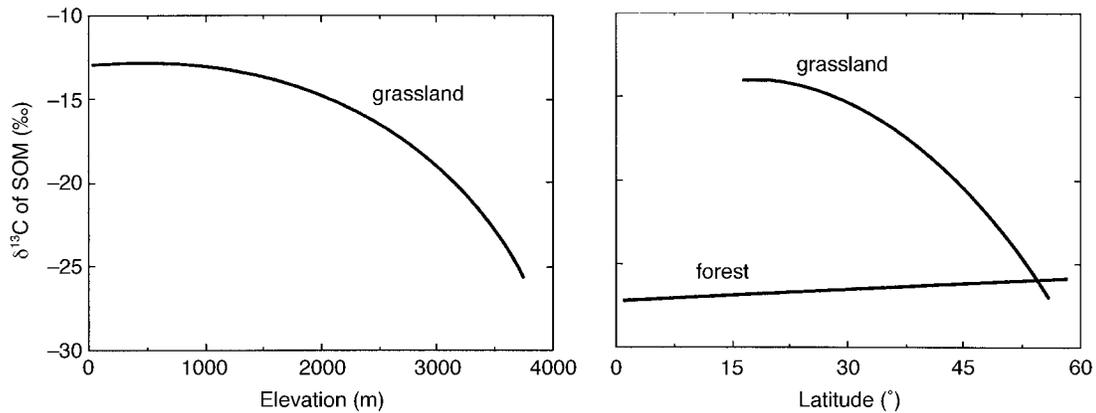


FIG. 6. Patterns of carbon isotope ratio of soil organic matter for grassland and forest ecosystems along elevation and latitude transects. The figure is based on data presented in Bird and Pousai (1997) and Tieszen et al. (1997).

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  $-25.5\text{‰}$  and  $-14\text{‰}$ , 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  $-26\text{‰}$  and  $-13\text{‰}$ , 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  $\sim 14\text{‰}$  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.

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