Chapter 4

Insights from Stable Isotopes on the Role of Terrestrial Ecosystems in the Global Carbon Cycle

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4.1 Introduction

The use of isotopic tracers in organic matter, water, and atmospheric gases has become an important component of the study of ecology and global change. Physiological and physical processes discriminate against heavy isotopes in predictable ways, so that measurements of isotopes at natural abundance, i.e., naturally occurring concentrations as opposed to artificial labeling experiments, can provide useful information about biological and physical processes at various spatial and temporal scales. Here we review recent progress in the application of naturally occurring stable isotopes in understanding ecosystem physiology and its role in biogeochemistry at ecosystem and global scales, with an emphasis on analyses of isotopes of carbon and oxygen in atmospheric carbon dioxide, a key component of the GCTE core project.

First, it is useful to review the basis for the application of stable isotopes in ecology and to provide some definitions of commonly used terminology. Isotopes of a single element contain differing numbers of neutrons. Some isotopes are stable while others are radioactive. We will focus here on two commonly used stable isotopes in the biological sciences: carbon-13 and oxygen-18. The most abundant isotope of carbon is ^{12}C which constitutes 98.9% of terrestrial carbon atoms; 1.1% of carbon is found as ^{13}C. In oxygen, 99.8% is ^{16}O, and the next most abundant form is ^{18}O constituting 0.2% of oxygen atoms (Fritz and Fontes 1980).

Isotopes are useful in ecology because they influence the physical and chemical properties of molecules. Light isotopes form weaker chemical bonds than heavy isotopes, so chemical reactions with substrates containing light isotopes occur more rapidly than with substrates containing heavy isotopes. This results in a difference in the abundance of heavy isotopes between the substrate and product of the reaction, and is called kinetic fractionation. In an equilibrium reaction, such as equilibration between liquid and gaseous water, the gaseous phase contains more of the light isotope and the liquid phase contains more of the heavy isotope, which results in equilibrium fractionation. There is also diffusive fractionation, which reflects the observation that molecules containing light isotopes diffuse more quickly than their heavier counterparts. A mechanistic understanding of fractionation in biological and physical processes is the basis of using isotopes as tracers of ecosystem processes (Fritz and Fontes 1980; Kendall and McDonnell 1998).

Isotopic measurements are generally expressed as the molar ratios of heavier isotopes to lighter ones (R). Such ratios are difficult to resolve in an absolute sense, and are usually expressed as relative ratios in delta (δ) notation:

$$\delta = (R_{sample} / R_{standard} - 1) \quad (4.1)$$

where R_{sample} and $R_{standard}$ are the heavy-to-light molar ratios of the sample and of an international standard. If $R_{sample} < R_{standard}$ then δ is negative. For example, plants utilizing the C_3 photosynthetic pathway (the majority of terrestrial plants) typically have values of $\delta^{13}C$ that range from –21 to –35‰, where the symbol ‰ denotes per mil (parts per thousand), while atmospheric CO_2 is currently about –8.0‰ (Keeling et al. 2005) relative to the common standard for carbon stable isotopes, a belemnite from the Pee Dee formation in South Carolina (PDB).

A change in isotopic composition as a result of fractionation can be expressed as a discrimination (Δ):

$$\Delta = (\delta_{source} - \delta_{product}) / (1 + \delta_{product}) \quad (4.2)$$

where δ_{source} and $\delta_{product}$ are the isotope ratios of the source and product, respectively. With these definitions as a reference we can explore recent progress in the application of stable isotopes to understanding the role of terrestrial ecosystems in the carbon cycle.

4.2 Ecosystem Carbon Cycles

Measurements of the isotopic composition of air sampled near soils and plant canopies can provide information about ecosystem carbon cycles. The isotopic composition of respiration can be applied toward understanding physiological and environmental controls on the flow of carbon through various pools by applying a mechanistic understanding of carbon isotope fractionation. In addition, when different ecosystem pools or fluxes have dis-

tinct isotopic signatures, carbon isotopes can be used as a tracer to distinguish between components of the ecosystem carbon cycle.

Currently, a common protocol at a number of sites around the world is to repeatedly sample canopy air at night to obtain estimates of the isotopic composition of ecosystem respiration (see http://basinisotopes.org). We will denote the carbon isotope composition of CO_2 from ecosystem respiration as $\delta^{13}C_R$, and the oxygen isotope ratio of ecosystem respiration as $\delta^{18}O_R$. $\delta^{13}C_R$ is estimated by extracting the isotopic composition of plant- and soil-respired CO_2 from background air with a numerical method derived by Keeling (1958, 1961).

Consider CO_2 inside a forest canopy as a mixture of background CO_2 (not derived from any local sources) and CO_2 released by plant and soil respiration:

$$C_a = C_b + C_R \tag{4.3}$$

where C represents CO_2 concentration (mole fraction of dry air), and subscripts a, b and R represent the total CO_2, the background CO_2 and the ecosystem respired sources, respectively. Based on conservation of mass, we can write:

$$\delta^{13}C_a C_a = \delta^{13}C_b C_b + \delta^{13}C_R C_R \tag{4.4}$$

where $\delta^{13}C$ denotes δ of carbon-13 relative to carbon-12. Substituting $C_R = C_a - C_b$ from Eq. 4.3 to 4.4,

$$\delta^{13}C_a = \frac{C_b(\delta^{13}C_b - \delta^{13}C_R)}{C_a} + \delta^{13}C_R \tag{4.5}$$

Equation 4.5 is a linear function of $1/C_a$, allowing us to estimate $\delta^{13}C_R$ as the intercept of a linear regression with $1/C_a$ as the independent variable. A number of studies have investigated $\delta^{13}C_R$ over a wide range of ecosystems (Buchmann et al. 1997a; Buchmann et al. 1997b; Fessenden and Ehleringer 2002; Flanagan et al. 1996; Harwood et al. 1999; Quay et al. 1989; Sternberg et al. 1989). Pataki et al. (2003b) synthesized measurements from 33 sites and discussed the assumptions inherent in the collection and interpretation of $\delta^{13}C_R$, which include the critical assumption that $\delta^{13}C_b$ and $\delta^{13}C_R$ remain constant during the sampling period. Miller and Tans (2003) also illustrated uncertainties associated with measurement and analytical errors regarding the two-source mixing approach.

Advances in isotope ratio mass spectrometry have increasingly permitted analysis of CO_2 isotopes in smaller air volumes with greater automation, allowing for more frequent sampling (Ehleringer and Cook 1998; Schauer et al. 2003; Tu et al. 2001). Intensive measurements of $\delta^{13}C_R$ over short time-periods, as well as longer-term monitoring on a weekly basis, have led to recent advances in our understanding of ecosystem carbon cycling. Correlations between $\delta^{13}C_R$ and environmental variables have provided evidence that a large proportion of carbon fixed in photosynthesis cycles rapidly through forested ecosystems (Bowling et al. 2002; Ekblad and Högberg 2001; Lai et al. 2005; Ometto et al. 2002). Ekblad and Högberg (2001) observed a correlation between $\delta^{13}C$ of soil-respired CO_2 and atmospheric humidity that lagged by 1–4 days, which they interpreted as an indication of the influence of recent photosynthesis on root respiration. These results were supported by Bowling et al. (2002), who observed a correlation between whole ecosystem $\delta^{13}C_R$ and time-lagged atmospheric vapor pressure deficit (VPD) in several ecosystems in Oregon, USA. VPD strongly influences stomatal conductance, photosynthesis, and the ratio of stomatal conductance to photosynthesis, and therefore $\delta^{13}C$ of assimilate through its influence on C_i/C_a, the ratio of leaf intercellular to ambient CO_2 concentration (see Box 4.1). Scartazza et al. (2004) and Fessenden and Ehleringer (2003) showed that $\delta^{13}C_R$ is also influenced by soil moisture, presumably through the influence of drought on stomatal closure. Although changes in the proportion of above- and belowground respiration and influences of declining soil moisture on the isotopic composition of soil respiration are alternative explanations, Scartazza et al. (2004) show that soil moisture-driven variations in $\delta^{13}C_R$ were related to $\delta^{13}C$ of phloem sugar. Notably, the relationship between $\delta^{13}C_R$ and soil moisture showed a similar slope in two disparate coniferous forests in the eastern and western coastal regions of the United States (Fig. 4.1). Integrated over time, these relationships lead to spatial variability in $\delta^{13}C_R$ as a function of water availability (Fig. 4.2).

In addition to providing a greater mechanistic understanding of ecosystem physiology and its influence on carbon cycling, measurements of the isotopic composi-

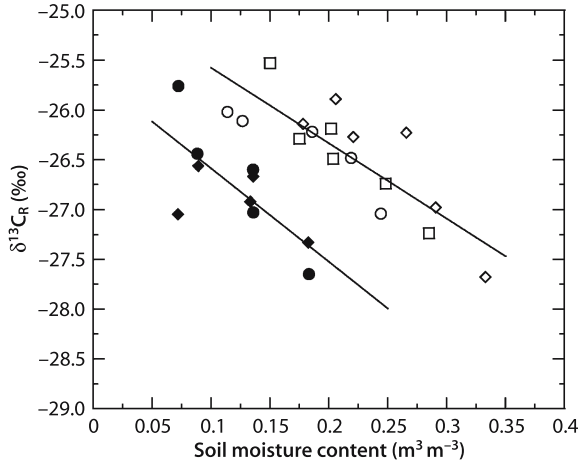

Fig. 4.1. Relationship between the monthly mean carbon isotope composition of ecosystem respiration ($\delta^{13}C_R$) and average soil moisture content during the growing season at two coniferous forests: the Wind River Canopy Crane Facility in Washington, USA (*open symbols*) and Howland Forest in Maine, USA (*closed symbols*). Measurements from different years are indicated by different symbols as *squares* (2001), *circles* (2002) and *diamonds* (2003) (from Lai et al. 2005, reproduced by permission of Blackwell Publishing)

tion of CO_2 can be used to partition ecosystem fluxes into specific component parts (Bowling et al. 1999; Bowling et al. 2001; Lai et al. 2003; Lloyd et al. 1996; Ogée et al. 2003; Yakir and Wang 1996). During daylight hours, Net Ecosystem Exchange (NEE) of CO_2 reflects the balance between photosynthesis (A) and respiration (R):

$$F_{NEE} = F_A + F_R \tag{4.6}$$

where F represents a flux of CO_2. A similar mass balance can be applied to the isotopes of CO_2:

$$\delta^{13}C_{NEE}F_{NEE} = F_\delta = \delta^{13}C_A F_A + \delta^{13}C_R F_R \tag{4.7}$$

where F_δ represents an "isoflux", analogous to net ecosystem exchange of $^{13}CO_2$ (μmol m^{-2} s^{-1} ‰) (Bowling et al. 2001). Values of $\delta^{13}C_{NEE}$, $\delta^{13}C_A$ and $\delta^{13}C_R$ denote the carbon isotope ratios associated with NEE, photosynthetic and respiratory fluxes, respectively.

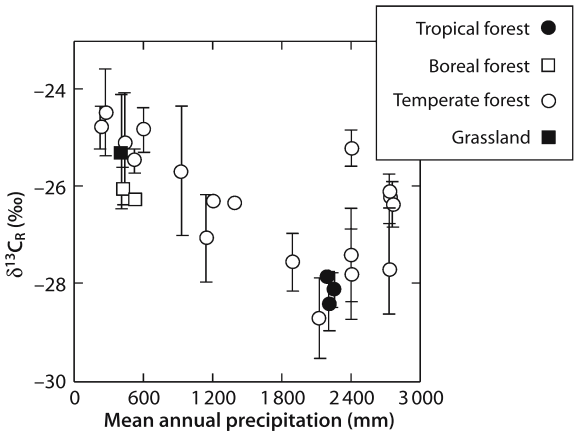

Fig. 4.2. The carbon isotope composition of ecosystem respiration ($\delta^{13}C_R$) at several sites throughout North and South America in relation to mean annual precipitation. *Error bars* show the standard error of all observations for a given site. A correlation is observed across all sites, with the exception of coniferous forests in the northwestern United States, where rainfall exceeds 2 400 mm yr^{-1} (from Pataki et al. 2003b, reproduced by permission of the American Geophysical Union)

F_{NEE} is routinely measured at numerous sites around the world as part of the FLUXNET suite of networks (http://daac.ornl.gov/FLUXNET). To apply Eq. 4.6 and 4.7 to solving for F_A and F_R, methods to measure or estimate the isotopic composition of the individual fluxes are required. Equation 4.5 is commonly used to determine $\delta^{13}C_R$ as discussed earlier. Quantifying $\delta^{13}C_{NEE}$ and $\delta^{13}C_A$, however, is more challenging (Bowling et al. 2003a). Yakir and Wang (1996) used $\delta^{13}C$ and $\delta^{18}O$ measurements to partition F_{NEE} of agricultural fields. They estimated $\delta^{13}C_{NEE}$ and $\delta^{13}C_A$ by measuring the isotopic composition of plants and soil samples, which integrate over seasonal time scales. However, to partition F_{NEE} at half-hourly intervals, capturing diurnal variations in $\delta^{13}C_{NEE}$ and $\delta^{13}C_A$ is necessary (Bowling et al. 2001). Using an aerodynamic approach to estimate canopy conductance and Fick's law of diffusion to estimate C_i, Bowling et al. (2001) calculated $\delta^{13}C_A$ for the whole-canopy:

$$\delta^{13}C_A = \delta^{13}C_a - a - (b - a)\frac{C_i}{C_a} \tag{4.8}$$

which combines Eqs. 4.2 and 4.12. An estimate of canopy-scale $\delta^{13}C_A$ can also be achieved by coupling biochemical photosynthesis models with a stomatal conductance model (Lai et al. 2003). Finally, if another parameter is known such as F_R, which can be modeled as a function of temperature, Eqs. 4.6 and 4.7 can be used to solve for $\delta^{13}C_A$ (Bowling et al. 2003a).

Carbon isotopes are particularly useful for discerning photosynthetic pathways because there is considerable contrast in $\delta^{13}C$ ratios between C_3 and C_4 plants (Box 4.1). In the context of ecosystem respiration, measurements of $\delta^{13}C$ can be used to partition contributions

Box 4.1. Isotopic discrimination in photosynthesis

Discrimination of ^{13}C in photosynthesis occurs in two steps. First, discrimination occurs during diffusion of CO_2 into the stomatal pores, followed by enzymatic discrimination in carboxylation by RuBP carboxylase (Rubisco). For plants utilizing the C_3 photosynthetic pathway, these effects can be represented as:

$$\Delta^{13}C_P = a + (b - a) \cdot C_i / C_a \tag{4.12}$$

where C_i/C_a denotes the ratio of intercellular to ambient CO_2 partial pressure, a the fractionation in diffusion, and b the net fractionation of carboxylation (Farquhar et al. 1982). Because a and b are known (4.4 and 27‰, respectively) photosynthetic discrimination of C_3 plants can be predicted with estimates of C_i/C_a, which is affected by photosynthetic rates and stomatal conductance. It should be noted that this approach neglects resistance to CO_2 transfer from the sub-stomatal cavity to the mesophyll, which may be significant in some species (Ethier and Livingston 2004).

Photosynthetic discrimination by C_4 plants may also be quantified with estimates of C_i/C_a. However, the "leakiness" of the unique C_4 anatomy must also be considered, as it affects the extent to which fractionation of Rubisco influences $\Delta^{13}C_P$, in addition to the C_4 enzyme PEP carboxylase. This is represented as:

$$\Delta^{13}C_P = a + (b_4 + b_3\phi - a) \cdot C_i / C_a \tag{4.13}$$

where b_4 denotes the fractionation factor of PEP carboxylase (−5.7‰), b_3 is the fractionation factor of Rubisco (30‰), and ϕ is the leakiness of bundle sheath cells, where C_4 photosynthesis takes place (Farquhar 1983). Rubisco has a small influence on photosynthetic fractionation in most C_4 plants, and the fractionation of PEP carboxylase is also fairly small. Thus, $\Delta^{13}C_P$ in C_4 plants is significantly lower than in C_3 plants, making these pathways isotopically distinct. Typical values of $\Delta^{13}C_P$ range from 13 to 25‰ in C_3 plants and 2.5 to 5‰ in C_4 plants (Dawson et al. 2002; Farquhar et al. 1989; Lloyd and Farquhar 1994).

of plants utilizing different photosynthetic pathways in C_3-C_4 mixtures (e.g., grassland and savannas), which are mainly distributed in sub- and tropical regions (Still et al. 2003a; Still et al. 2003b). The fraction of C_3 (λ) contributing to total ecosystem respiration can be estimated by:

$$\delta^{13}C_R = \lambda\delta^{13}C_3 + (1-\lambda)\delta^{13}C_4 \quad (4.9)$$

where $\delta^{13}C_3$ and $\delta^{13}C_4$ denote the $\delta^{13}C$ ratios of C_3 and C_4 species, respectively. Still et al. (2003b) used this approach to estimate that C_4 species contributed 60 to nearly 100% of the total respiration between May and September in a tallgrass pasture in central Oklahoma, U.S.A. Lai et al. (2003) found a comparable range of C_4 contributions in a tallgrass prairie with similar species composition and climate. The contribution of C_3 vs. C_4 plants is critical to the application of measurements of $^{13}CO_2$ at a global scale, as we will discuss in the next section.

4.3 The Global Carbon Cycle

There is a high degree of short-term interannual variability associated with the rate of increase in atmospheric CO_2 concentration (Fig. 4.3). We know from statistics of energy use that CO_2 emissions from fossil fuel combustion are increasing at a nearly steady rate from year to year (Andres et al. 2000; IPCC 2001). The principal sources of interannual variability are therefore ocean fluxes and terrestrial ecosystem processes. Isotopes of carbon dioxide are useful to distinguish between these components on regional and global scales.

We have discussed that photosynthesis of terrestrial plants discriminates against $^{13}CO_2$ (Box 4.1), leaving heavier $^{13}CO_2$ behind in the atmosphere, while the process of respiration returns isotopically light carbon to the atmosphere. In contrast, fractionation of CO_2 dissolution into the ocean is small, on the order of 2‰ (Inoue and Sugimura 1985; Wanninkhof 1985; Zhang et al. 1995). Therefore, gradients of $\delta^{13}C$ of CO_2 in the atmosphere may be used to distinguish between terrestrial and oceanic sinks if the magnitude of photosynthetic discrimination and the isotopic composition of respiration can be estimated well enough on a global scale. Because C_3 and C_4 photosynthesis differ greatly in fractionation of $^{13}CO_2$, this requires robust estimates of the proportion of productivity of C_3 vs. C_4 plants globally. However, the information gained from applying these estimates can be significant. Figure 4.3 shows the rate of change of $\delta^{13}C$ of atmospheric CO_2 in addition to the rate of change of atmospheric CO_2 concentration for the last two decades. The close correlation between the two time-series strongly suggests that terrestrial processes have dominated the short-term interannual variability in the growth rate of atmospheric CO_2. By applying mass balance to atmospheric observations of CO_2 and its isotopic composition, sources and sinks of CO_2 can be inferred:

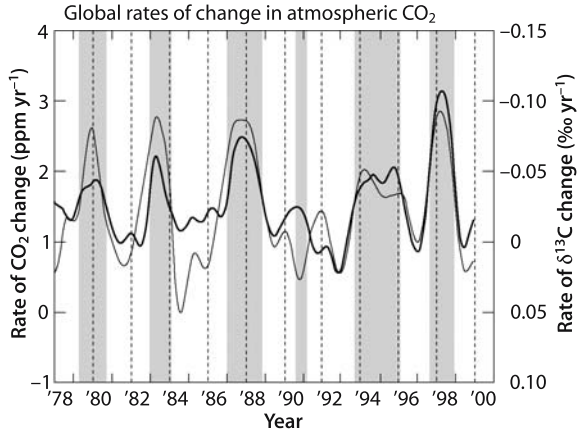

Fig. 4.3. The rate of change in atmospheric CO_2 concentration (*bold line*, *left axis*) and the rate of change in the carbon isotope composition ($\delta^{13}C$) of atmosphere CO_2 (*right axis*) (from Keeling et al. 2005, used by permission)

$$\frac{\partial}{\partial t}C_a = F_{FF} + F_{DEF} + F_{ao} + F_{oa} + F_{ab} + F_{ba} \quad (4.10)$$

$$\begin{aligned} C_a\frac{\partial}{\partial t}\delta^{13}C_a = &(\delta^{13}C_{FF} - \delta^{13}C_A)F_{FF} \\ &+(\delta^{13}C_{DEF} - \delta^{13}C_A)F_{DEF} \\ &+\varepsilon_{ao}(F_{ao} + F_{oa}) + D_oF_{oa} \\ &+ - \Delta_p(F_{ab} + F_{ba}) + D_bF_{ba} \end{aligned} \quad (4.11)$$

where the subscripts 'FF' and 'DEF' denote the fossil fuel- and land-use change-derived releases of CO_2 to the atmosphere, subscripts 'AO' and 'OA' denote the one-way ocean-atmosphere fluxes, and subscripts 'AP' and 'BA' denote the one-way biosphere-atmosphere fluxes (Francey et al. 1995; Fung et al. 1997; Tans et al. 1993). Also included in order to solve Eqs. 4.10 and 4.11 for the oceanic and terrestrial fluxes are symbols to denote CO_2 emissions from fossil fuel combustion, $\delta^{13}C_{FF}$; CO_2 emissions from land-use change, $\delta^{13}C_{DEF}$; fractionation factors associated with the net oceanic, ε_{ao}; and terrestrial discrimination, Δ_p; and two "disequilibrium" terms, D_o and D_b. These latter terms express the extent to which older carbon, dissolved in ocean waters or fixed in photosynthesis in the past and later released, has a more enriched $\delta^{13}C$ than current carbon due to the dilution of atmospheric CO_2 by fossil fuel combustion in the last century.

Mass balances expressed in Eqs. 4.10 and 4.11 have been applied in a number of global studies of carbon sources and sinks that utilized atmospheric measurements to infer regions of carbon uptake (Battle et al. 2000; Ciais et al. 1995; Francey et al. 1995; Fung et al. 1997; Tans et al. 1993). A limitation to this approach is that the parameterization of Δ_p, the discrimination associated with net carbon uptake by the terrestrial biosphere, is diffi-

cult to validate with measurements. Ecosystem studies commonly measure the isotopic composition of the one-way, nighttime flux, $\delta^{13}C_R$, but estimating the signature of photosynthetic discrimination from direct measurements is difficult at whole ecosystem scales. For lack of data to the contrary, Δ_P has been generally fixed as a constant value in global mass balance studies (Battle et al. 2000; Francey et al. 1995; Tans et al. 1993). However Randerson et al. (2002) demonstrated that if large-scale regional changes in Δ_P covary with changes in gross fluxes, as could occur during climatic anomalies such as the El Niño Southern Oscilliation (ENSO), applying constant values of Δ_P to Eq. 4.11 could introduce significant errors into global mass balance calculations. Modifying the mass balance approach to explicitly consider gross fluxes and their time varying anomalies could improve top-down estimates of carbon sinks from atmospheric measurements (Randerson et al. 2002).

It has been noted that the peaks in atmospheric CO_2 growth rate have generally been associated with the occurrence of ENSO events (Francey et al. 1995; Keeling et al. 2005; Keeling et al. 1995), which brings warm, dry conditions to highly productive tropical regions (Dai et al. 1997; Ropelewski and Halpert 1987). One hypothesis for the underlying correlation between ENSO conditions and terrestrial sources and sinks of carbon has been that drought conditions, and in particular dry atmospheric conditions, in tropical regions have resulted in reduced productivity and subsequently smaller terrestrial sinks in tropical forests during ENSO years. Measurements of $\delta^{13}C$ of atmospheric CO_2 have generally supported this hypothesis (Fig. 4.3), which would also be expected based on the data in Fig. 4.1 and 4.2. However, recent work utilizing carbon monoxide and methane tracers in addition to measurements of CO_2 concentration and $\delta^{13}C$ of CO_2 suggests that an increased occurrence of biomass burning and wildfire during ENSO years, also associated with drought, may also be an important mechanism (Van der Werf et al. 2004).

The oxygen isotopic composition of CO_2 also has great potential to distinguish between components of the carbon cycle, namely, between assimilation and respiration of the terrestrial biosphere. The oxygen isotopic signature of assimilation and respiration are generally very different – more so than the carbon isotope signatures in ecosystems that contain only C_3 plants. However, oxygen isotopes have been applied less frequently in global carbon studies, largely because of the complexity of modeling oxygen fractionation effects at the global scale.

CO_2 and water in the liquid phase equilibrate isotopically so that the isotopic composition of CO_2 is strongly influenced by the isotopic composition of water where water is abundant, as in plants and soils (Amundson et al. 1998; Farquhar and Lloyd 1993; Farquhar et al. 1993; Hesterberg and Siegenthaler 1991). Assimilation and respiration have different isotopic signatures because leaf water is enriched in oxygen-18 relative to soil water due to the evaporative effects of transpiration. Approximately two-thirds of the CO_2 that diffuses into leaves is not fixed by photosynthesis, but this CO_2 does equilibrate with leaf water and diffuses back into the atmosphere with an isotopically enriched signature that is distinct from that of respired CO_2 which has equilibrated with soil water (Farquhar and Lloyd 1993; Flanagan et al. 1997; Francey and Tans 1987). Quantifying these processes in global models requires hydrologic models that predict the isotopic composition of regional precipitation, as well as ecological models and models of atmospheric transport.

Despite this complexity, there has been recent progress in quantifying the oxygen isotopic composition of CO_2 on a global basis for carbon cycle applications. Ciais et al. (1997a) combined a global biospheric model with global climate model simulations to estimate monthly global surface fluxes of ^{18}O in CO_2 from the terrestrial biosphere. Integrated with an atmospheric tracer transport model, this approach yielded results that agreed well with atmospheric observations, and led to the conclusion that the temporal and spatial patterns of $\delta^{18}O$ of CO_2 in the atmosphere were largely attributable to terrestrial ecosystem processes (Ciais et al. 1997b; Peylin et al. 1999). Cuntz et al. (2003a,b) expanded global simulations of ^{18}O fluxes with a well-integrated suite of model components that provided estimates on the diurnal time-scale. These advances will likely provide a basis for utilizing observations of $\delta^{18}O$ of atmospheric CO_2 to constrain carbon sources and sinks and distinguish between assimilation and respiration components of terrestrial fluxes.

Further research is needed on an interesting aspect of the atmospheric CO_2 record, which showed a decline in $\delta^{18}O$ of CO_2 of about 0.5‰ in the mid-1990s (Gillon and Yakir 2001; Ishizawa et al. 2002). Gillon and Yakir (2001) found variations in the activity of the enzyme of carbonic anhydrase, which catalyzes oxygen isotope exchange between CO_2 and water, suggesting that full equilibration is not reached in many species, particularly C_4 grasses. The authors concluded that large-scale conversions of forested ecosystems to pastures dominated by C_4 plants during the 1990s could have led to a global decline in $\delta^{18}O$ of atmospheric CO_2 of 0.02‰ yr^{-1}. Ishizawa et al. (2002) pointed out that such conversions can only partially explain the observed decline in $\delta^{18}O$ of CO_2, and that an additional mechanism could be an increase in both photosynthesis and respiration of the terrestrial biosphere. Advances in global modeling of $\delta^{18}O$ of CO_2 and additional observations of mechanisms of ecosystem fractionation and the isotopic composition of atmospheric CO_2 will likely lead to further interpretation and application of variations in $\delta^{13}C$ and $\delta^{18}O$ of CO_2 for understanding the role of the terrestrial biosphere in the carbon cycle.

4.4 Future Directions

Research on the application of stable isotopes in ecosystem and global carbon cycles was synthesized and coordinated by the Biosphere-Atmosphere Stable Isotope Network (BASIN) of GCTE beginning with an initial workshop in 1997. The BASIN network (http://basinisotopes.org) is carrying forward with additional coordination and synthesis of traditional aspects of data collection, such as the isotopic composition of ecosystem respiration, as well as other applications of stable isotopes in understanding the role of terrestrial ecosystems in biogeochemistry. Data are increasingly available on the isotopic composition of other gases present in the atmosphere in lower concentrations than CO_2, and therefore more difficult to measure. Stable isotopes of methane (Snover and Quay 2000), N_2O (Perez et al. 2000; Perez et al. 2001), and hydrogen (Rahn et al. 2002), for example, are providing additional information on the role of ecosystem physiology in land-atmosphere interactions. Also promising are new studies on the isotopic composition of non-methane hydrocarbons such as isoprene (Affek and Yakir 2003; Goldstein and Shaw 2003), and the highly abundant atmospheric components, water vapor (Moreira et al. 1997; Yepez et al. 2003) and diatomic oxygen (Angert et al. 2003; Stern et al. 2001), which are strongly influenced by terrestrial processes.

Monitoring of a wider variety of ecosystem types will also provide a broader information base for understanding the influence of the land surface on the atmosphere and scaling from ecosystems to regional and global scales. Data from tropical ecosystems, semi-arid systems, and human-dominated ecosystems have been sparsely represented in the BASIN network, but new datasets in these areas are increasingly available (Ometto et al. 2002; Pataki et al. 2003a; Yepez et al. 2003). New technologies also promise to increase spatial and temporal coverage of the isotopic composition of the atmosphere. Automated samplers for collecting atmospheric samples have recently been deployed in a number of ecosystems and have demonstrated the dynamic influence of ecosystems processes on the atmosphere and the utility of long-term monitoring (Lai et al. 2005; Lai et al. 2003; Schauer et al. 2003). These monitoring programs will be greatly extended by the application of optical measurements of rare isotopes with instruments such as Tunable Diode Lasers (TDL) that measure $^{13}CO_2$ concentrations in real time. TDL and similar technologies will increase analytical capabilities severalfold in terms of sample number, allowing large numbers of samples to be collected over short time-periods in a number of locations throughout plant canopies (Bowling et al. 2003b).

Results from atmospheric monitoring programs in ecosystems are being incorporated into a growing number of models of isotopic fractionation and its influence on the atmosphere (Baldocchi and Bowling 2003; Riley et al. 2003; Suits et al. 2005). These linkages have been largely indirect, that is, as isotopic measurements improved our basic understanding of fractionation and its physical and physiological basis, new theoretical and empirical relationships have been incorporated into ecosystem-atmosphere models. However, direct linkages between isotopic data-streams and ecological models are emerging as data assimilation or "data-model fusion" techniques are becoming common in ecological and biogeochemical applications. Similar to approaches already common in global scale studies of the carbon cycle, these quantitative methods optimize the solution for a given set of equations, e.g., a mass balance of ecosystem carbon sources and sinks, using available datasets as constraints. This method has been used to model ecosystems fluxes (Raupach 2001; Styles et al. 2002), estimate the mean residence time of carbon pools (Barrett 2002; Luo et al. 2003), and partition fluxes into their component parts (Luo et al. 2004). The increasing temporal and spatial coverage of isotopic measurements in various ecosystems will likely be directly incorporated into improved estimates of ecosystem-scale physiological and biogeochemical parameters with these methods.

Measurements of the isotopic composition of trace gases in the atmosphere and within and above terrestrial ecosystems have provided new insights into ecosystem functioning and the role of the terrestrial biosphere in the carbon cycle. These insights have included partitioning carbon cycle components such as terrestrial and oceanic carbon sinks, photosynthetic and respiratory components of NEE, and C_3 and C_4 contributions to ecosystem respiration. Improvements in both measurement techniques and ecosystem- to global-scale models are rapidly resulting in refined estimates of these aspects of the carbon cycle and the underlying mechanisms for their spatiotemporal variations. This is a rapidly evolving area of research, and one in which the GCTE core project made an important and lasting contribution through its support of the BASIN network.

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In Memoriam

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