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RADIOCARBON ANOMALIES FROM OLD CO_2 IN THE SOIL AND CANOPY AIR

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ABSTRACT. The canopies of forests and cultivated fields can retard the ventilation of CO_2 respired from the soil. The plants in dense canopies can then acquire a small fraction of their carbon by recycling some of the respired CO_2. Furthermore, some plants can assimilate a small fraction of their carbon by uptake of CO_2 in the soil via their roots. In tectonically active areas, the diffuse flux of CO_2 from geological sources may be comparable to that from normal soil respiration. In such areas, both the canopy and root uptake effects may allow plants to acquire a measurable fraction of their carbon from geological sources. Because this "old" carbon lacks radiocarbon, its assimilation would increase the apparent ^{14}C ages of the plants. These effects may account for some of the discrepancies between archaeological and ^{14}C dates.

INTRODUCTION

The preferred materials for radiocarbon dating of ancient sites are short-lived organic samples, such as seeds and twigs, found in secure archaeological context. Even in such cases, however, the ^{14}C ages from a collection of apparently identical samples sometimes range over a century or more. Such discordant results are usually ascribed to sample contamination or different laboratory procedures. This paper aims to show that some of them may also reflect actual differences in the initial uptake of ^{14}C by otherwise identical samples, due to the assimilation by plants of "old" carbon from the soil or the canopy air.

Carbon dioxide emitted from subsoil geological sources (hereafter "old CO_2") contains effectively no ^{14}C. Plants growing in the immediate vicinity of such emissions can assimilate enough old CO_2 to produce apparent ^{14}C age increments of thousands of years (Bruns et al. 1980; Saupé et al. 1980; Calderoni and Turi 1998; Pasquier-Cardin et al. 1999; Cook et al. 2001; Saurer et al. 2003; Garnett and Billett 2007). Where old CO_2 issues from a concentrated source at the surface, the uptake by plants only a few hundred meters away may be negligible, due to rapid dilution of the gas in the ambient air.

In other cases, the uptake of old CO_2 appears to occur over larger areas. Chatters et al. (1969) obtained ^{14}C data indicating that plants growing several kilometers from the nearest known volcanic vents on Hawaii acquired more than 5% of their carbon from old CO_2. Sulerzhitsky (1971) reported similar results based on ^{14}C data from trees growing many kilometers from known gas vents on Kamchatka and Kunashir Island. He suggested that the distribution of local ^{14}C anomalies may be due to concealed sources of CO_2, and that the relief of the terrain, the strength and direction of winds during the growing season, and the nature of the vegetation cover strongly affect the phenomenon.

In the cases cited above, the local concentration of old CO_2 was high enough for its uptake by plants to be readily detected. However, if diffuse weak sources are more prevalent than concentrated ones, the resulting augmentation of ^{14}C ages would often be only a few decades, or near the margin of detection.

Diffuse emission of CO_2 from geological sources occurs in many parts of the world, usually associated with zones of active tectonics, seismicity, and high heat flow (Irwin and Barnes 1980; Kerrick 2001; Mörner and Etiope 2002). Degassing of old CO_2 occurs widely, for example, in central and southern Europe, Turkey, the western United States, Peru, and Tibet. Sources of diffuse emissions include mantle degassing, metamorphism of sedimentary carbonates, and oxidation of sedimentary organic deposits, including peat and oil. The diffuse flux of old CO_2 from the soil is often comparable to the CO_2 flux from normal soil respiration (Etiope 1997).

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This paper suggests 2 mechanisms by which forests and cultivated fields may incorporate old carbon from diffuse sources: (1) uptake in the soil by plant roots and (2) photosynthesis of old CO_2 detained in the canopy air. In tectonically active areas, these pathways may augment the apparent ^{14}C ages of plants by relatively small but measurable amounts.

ROOT UPTAKE OF CARBON

Many plants acquire a small fraction ρ of their total carbon via their roots (Enoch and Olesen 1993; Cramer 2002). Evidence for such assimilation has been reported for peas and barley (Stolwijk and Thimann 1957), cocklebur (Skok et al. 1962), tomato (Stemmet et al. 1962; Cramer and Richards 1999), willow (Vuorinen et al. 1992), pine (Ford et al. 2007), and other plants. Quantitative comparison of these results can only be very sketchy, however, due to the wide range of experimental conditions. Some plants were grown in hydroponic solutions and others in soils. Diverse experiments exposed the roots to labeled carbon in a variety of chemical forms and concentrations and for different periods of time. The results, however, suggest that ρ for whole plants generally ranges from about 0.1% to a few percent.

The carbon assimilated by roots is present in the form of gaseous CO_2 in soil air, or dissolved inorganic carbon (DIC), which consists of CO_2 and its equilibrium products in solution (carbonic acid, bicarbonate and carbonate ions, in proportions depending on pH). In a recent experiment, Ford et al. (2007) grew pine seedlings in soil containing ^{13}C-labeled DIC and found that $\rho \approx 0.8\%$. In discussing root uptake, the term "soil CO_2" will refer to either gaseous carbon dioxide or DIC.

The average concentration of carbon dioxide in the soil air due to respiration depends on the surface and soil biota, temperature, and depth. During the growing season, it is usually in the range 0.2% to 8%, compared to 0.036% in the normal atmosphere (Buyanovsky and Wagner 1983; Hamada and Tanaka 2001; Bekele et al. 2007). In tectonically active areas, the respired CO_2 may be augmented by a contribution from old CO_2. To quantify the problem, we define g as the fractional contribution of old CO_2 to the total concentration of soil CO_2, where $0 < g < 1$.

The fraction φ of total plant carbon due to root uptake of old carbon is then the fraction ρ of plant carbon acquired by root uptake multiplied by g, or $\varphi = \rho g$. If the root uptake ρ were a constant independent of the soil CO_2 concentration, then φ would increase linearly with g, up to a maximum value of ρ when $g = 1$. However, such an approach appears to be unrealistic for 2 reasons. First, experiments suggest that ρ increases with the concentration of soil CO_2. Cramer and Richards (1999) grew tomato seedlings in nutrient solutions containing ^{14}C-labeled DIC. They found that plants grown in solutions aerated with 5000 ppm CO_2 had ρ values about 10 times greater than plants aerated with 360 ppm CO_2 (normal air). This suggests that ρ varies nearly in proportion to soil CO_2 concentration. Vuorinen and Kaiser (1997) obtained similar results for willow and barley plants. Increasing g, which entails higher CO_2 concentrations, would therefore increase ρ, but only up to a point.

Here, we encounter the second problem. As g approaches unity, the contribution of old CO_2 to the soil overwhelms that due to normal respiration. For example, when $g = 0.9$, the total concentration of CO_2 in the soil is 10 times the amount due to respiration. The excess CO_2 might then inhibit root growth and respiration for some plants, due to hypoxia and other adverse effects (Stolwijk and Thimann 1957). In that case, ρ would have to decline as g approaches 1, and so would φ.

These considerations suggest that φ initially increases with g to some maximum value and thereafter declines as g approaches unity. The limited data suggest that the maximum ρ is less than a few per-

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cent. In that case, the corresponding ^{14}C age increments due to root uptake of old CO_2 would not exceed a few hundred years.

CANOPY EFFECT ON VENTILATION AND CO_2 ASSIMILATION

The second factor that can augment ^{14}C ages is the assimilation by photosynthesis in the canopy of old CO_2 emitted from the ground. In forests and cultivated fields, dense foliage tends to suppress winds and atmospheric mixing near the ground. The relative stillness of the air in a forest is often evident even to the unaided senses. The suppression of ventilation within forest and crop canopies produces a measurable stratification of both the concentration and stable carbon isotope ratio of CO_2 during the course of the diurnal cycle, reflecting the periodic depletion of CO_2 by photosynthesis and its augmentation by respiration (Brooks et al. 1997; Buchmann and Ehleringer 1998; Buchmann et al. 2002).

Most of the respired gas in a canopy is emitted from the soil, with a smaller contribution from foliage and stems above ground. Normally, nearly all of the CO_2 emitted from the soil is from respiration by roots and heterotrophic microbes. The retardation of ventilation by the canopy allows the plants to recycle some of the respired CO_2 by photosynthesis (Wickman 1952; Keeling 1961; Lloyd et al. 1996). Most of the carbon respired from the soil in temperate forests has been in the ground for only about a decade (Gaudinski et al. 2000; Trumbore 2000), so the recycling of some of it produces only a negligible ^{14}C age increment in the plants.

However, in areas where old CO_2 is emitted from the ground, it will mix with the normal flux of CO_2 respired by the ecosystem, diluting the canopy air with respect to ^{14}C. A forest or cultivated field growing in such an area will assimilate some of the old CO_2 that remains in the canopy along with the respired gas, augmenting the apparent ^{14}C age of the plant material. The long-term average uptake of old CO_2 would then vary nearly in proportion to that of respired CO_2.

We can therefore quantify to first order the uptake in a canopy of old CO_2 by using an index that measures the recycling of respired CO_2. The recycling index r is defined as the ratio of the respired flux of CO_2 fixed by photosynthesis to the total photosynthetic flux (Schleser and Jayasekera 1985; Lloyd et al. 1996; Greaver et al. 2005). This quantity depends on the aerodynamic characteristics of a canopy (determined by the leaf area index, canopy height, tree spacing, etc.) and the local meteorology on diurnal through seasonal timescales.

Calculations based on stable carbon isotope ratios have led to estimates of r. Published values range from about 1.8 to 6% for boreal forests (Lloyd et al. 1996; Brooks et al. 1997), 4 to 18% for tropical forests (Sternberg et al. 1989; Lloyd et al. 1996), and 18% for a densely planted crop of sunn hemp (Greaver et al. 2005). In general, the recycling index r increases with the density of a canopy and decreases with its exposure to winds. Dense forests or thickets would have larger values of r, open canopies would have smaller values particularly if exposed to wind, while isolated trees would not recycle any respired carbon.

A plant that acquired only 1% of its carbon from old CO_2 would have an apparent ^{14}C age increment of 80 yr. The above data alone therefore suggest that in areas where the diffuse emission of old CO_2 is comparable to that from soil respiration, plants in dense canopies may take up enough old carbon to increase their apparent ^{14}C ages by a few hundred years.

As represented in Figure 1, the flux of CO_2 into a volume of canopy air is the sum of 4 contributions: turbulent mixing from the troposphere (T); respiration from the soil (R_s); respiration of foliage and stems above ground (R_a); and emission from geological sources (G). The soil respiration R_s includes

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autotrophic respiration by roots and heterotrophic respiration of soil organics by microbes. The flux of CO_2 leaving the volume of canopy air is the sum of turbulent mixing back to the troposphere (F) and photosynthetic assimilation by foliage (P).

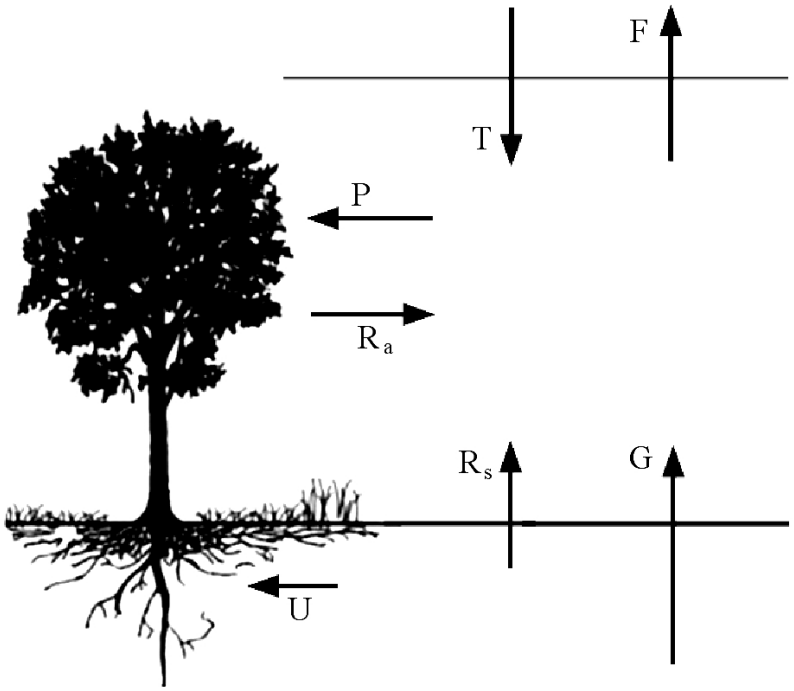

Figure 1 The flux of CO_2 into a volume of canopy air is the sum of 4 contributions: turbulent mixing from the overlying troposphere (T); soil respiration (R_s); respiration of foliage above ground (R_a); and emission from geological sources (G). The flux of CO_2 leaving the volume of canopy air is the sum of turbulent mixing back to the troposphere (F) and photosynthetic assimilation by foliage (P). A small amount of non-photosynthetic assimilation of CO_2 also occurs below ground in the roots (U). Tree illustration courtesy of T Dawson.

These fluxes vary with the season, weather, and time of day. The most obvious example is that $P = 0$ at night. The flux G also varies with barometric pressure and, on longer timescales, due to changes in the geological "plumbing," including fault permeability. The total ecosystem respiration at any time is $R = R_s + R_a$.

The CO_2 in a canopy is a time-variable mixture of contributions from the free troposphere, from respiration by the ecosystem, and (when present) from old CO_2. Respired CO_2 is depleted in ^{13}C relative to the troposphere, reflecting the isotope fractionation by photosynthesis in plants. During the night, when turbulent mixing is usually lowest, the concentration of CO_2 increases to well above that in the troposphere, and the stable isotope ratio $\delta^{13}C$ decreases in close step, as respired CO_2 accumulates within the relatively undisturbed lower canopy (Berry et al. 1997). During the day, turbulent mixing reduces the CO_2 concentration, and photosynthesis further lowers it below tropospheric levels.

Figure 2a shows the diurnal variation in the concentration (solid line) and the carbon isotope ratio (dashed line) of CO_2 measured at 1 m above the ground in the canopy of a characteristic Mediterra-

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nean savanna-type oak woodland in May 2004 (Werner et al. 2006). Although differing in detail, other canopy types show similar diurnal variations in CO_2 concentration. These include boreal forests in Manitoba (Brooks et al. 1997), a pine plantation near Ottawa (Berry et al. 1997), and fields of corn and alfalfa in Utah (Buchmann and Ehleringer 1998).

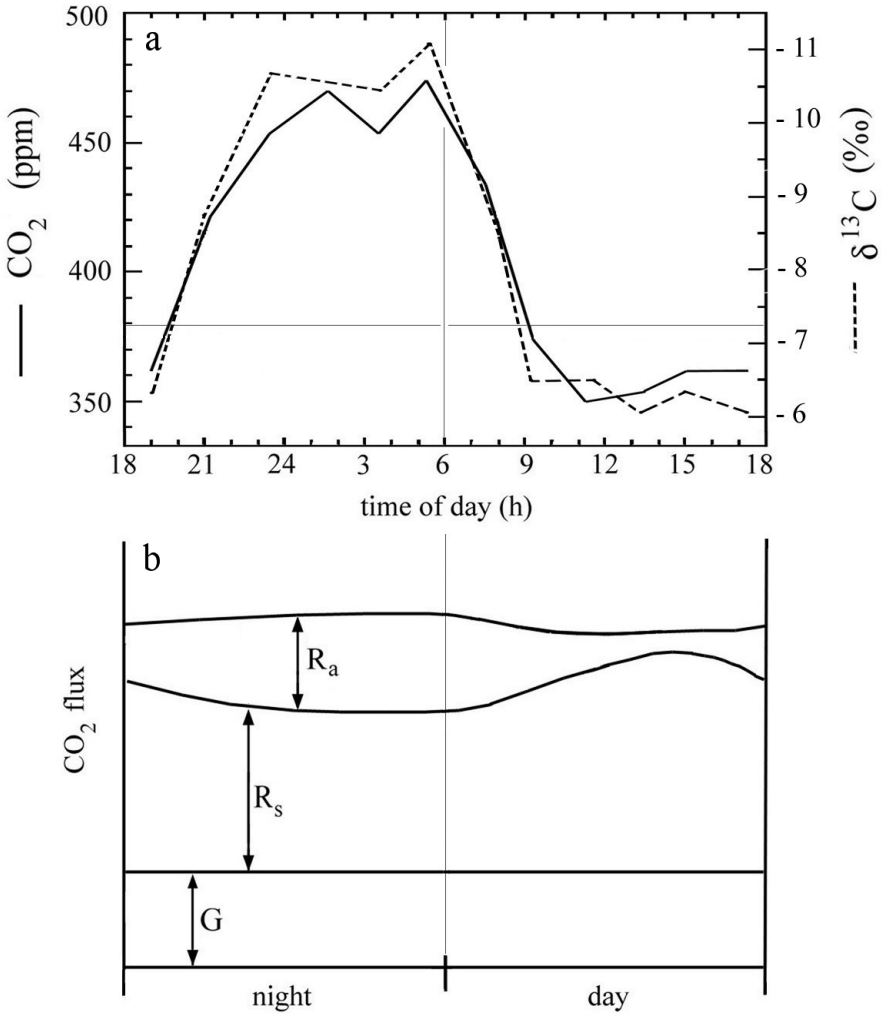

Figure 2 (a) The daily variation in the concentration (solid line) and stable carbon isotope ratio $\delta^{13}C$ (dashed line) of CO_2 measured 1 m above the ground in the canopy of a characteristic Mediterranean savanna-type oak woodland in May 2004 (Werner et al. 2006). During the night, CO_2 increases and $\delta^{13}C$ decreases in step, as respired CO_2 accumulates within the relatively undisturbed lower canopy. After sunrise (thin vertical line), CO_2 begins to decline, due to uptake by photosynthesis and mixing with the troposphere. For a few hours after dawn, however, both curves still reflect the accumulation of CO_2 respired during the night. By midday, photosynthesis in the canopy has reduced the concentration of CO_2 to below the background troposphere level (thin horizontal line). (b) Schematic plot of the flux during 24 hr of CO_2 respired above ground (R_a), respired from the soil (R_s), and emitted from old CO_2 (G). The latter is taken here to be constant. During the day, R_s increases due in part to rising soil temperature, while R_a decreases due to suppression of leaf respiration by photosynthesis. However, the total respired flux ($R = R_s + R_a$) may be relatively constant.

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After sunrise (thin vertical line in Figure 2a), the concentration of CO_2 begins to decline and its $\delta^{13}C$ increases, due to uptake by photosynthesis and mixing with the troposphere. In the first few hours after dawn, however, both curves still show the presence of CO_2 respired and accumulated in the canopy during the night, with concentrations near the ground substantially greater than the tropospheric average (thin horizontal line). Photosynthesis will then incorporate a significant amount of respired gas. Although the excess of respired CO_2 is strongest near the ground, where direct sunlight is least intense, assimilation by photosynthesis occurs at all levels in the canopy, and is actually more efficient for diffuse than for direct sunlight (Gu et al. 2002).

By midday, vigorous photosynthesis together with convective mixing have reduced the concentration of CO_2 to well below the average tropospheric value. This indicates that the canopy air still maintains some stratification near the ground, despite the daytime mixing with the troposphere. If old CO_2 is constantly emitted from the ground, some of it may then be assimilated by photosynthesis near the ground even in the afternoon.

The nocturnal excursions in CO_2 concentration and $\delta^{13}C$ diminish with increasing elevation in the canopy, but the effects of respiration and photosynthesis on both parameters remain detectable even a few meters above the top of the canopy (Buchmann and Ehleringer 1998; Werner et al. 2006). The nocturnal suppression of ventilation by the canopy is responsible for most of the variation in the curves for both CO_2 concentration and $\delta^{13}C$.

Ecosystem respiration also follows a diurnal cycle. Figure 2b is a schematic plot of the fluxes over 24 hr of CO_2 respired above ground (R_a), respired from the soil (R_s), and emitted as old CO_2 through the soil (G). The latter flux is shown here as constant. Soil respiration R_s increases in the afternoon, mainly due to increased soil temperatures, while the aboveground respiration R_a is lower in the daytime, due to reduction of leaf respiration during photosynthesis (Atkin et al. 1997).

Field observations of diurnal variations in soil respiration R_s have been reported for an oak grass savanna in California (Tang et al. 2005), a pine forest in the Rhine Valley (Kodama et al. 2008), and a winter wheat field in the Lhasa River valley of Tibet (Shi et al. 2006). A boreal spruce forest in northern Sweden showed no diurnal variations in R_s (Betson et al. 2007). Since $R_s > R_a$ and the two are generally out of phase, we will approximate their sum as nearly constant. In that case, the canopy air would maintain a nearly constant ratio between old CO_2 and that from total respiration.

ANALYTICAL TREATMENT

This section examines how the apparent ^{14}C age increment Δt of a plant exposed to diffuse emission of old CO_2 depends on 3 principal factors: the total plant carbon fraction ρ acquired by root uptake; the canopy recycling index r; and the fraction g of the total soil CO_2 due to geological sources. All 3 quantities depend strongly on the local environment and the first two are poorly known at best. However, we can still examine a range of plausible values for them, which yield order of magnitude estimates for the associated ^{14}C age increments. The reader can skip this analytical treatment and still follow the subsequent sections. All symbols are defined in the Appendix.

Emission of old CO_2 dilutes the normal ^{14}C concentration of the soil and canopy air, and uptake by roots and/or photosynthesis of the mixture can then increase the apparent ^{14}C age of the plant material. Suppose that a living plant acquires a fraction φ of its carbon from old CO_2. Then, at any time t after the plant dies, the radioactivity of its carbon relative to the initial value will be

$$\exp(-t_a/\tau) = (1-\varphi)\exp(-t/\tau) + \varphi\exp(-t_g/\tau) \quad (1)$$

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where t_a is the apparent ^{14}C age of the plant material, t_g is the age of the old carbon (effectively infinite), and $\tau = 8033$ yr is the conventional decay time used for ^{14}C dating. It follows that

$$\varphi = 1 - \exp(-\Delta t/\tau) \tag{2}$$

where Δt is the apparent ^{14}C age increment of the plant material,

$$\Delta t = t_a - t = -\tau \ln(1 - \varphi) \tag{3}$$

For example, incorporation of a fraction $\varphi = 1\%$ of old carbon in a plant results in an apparent ^{14}C age increment of about $\Delta t = 80$ yr.

Consider first the effect of root uptake of old carbon. Let the total concentration of CO_2 in the soil be

$$C = C_{geo} + C_{res} \tag{4}$$

where C_{geo} and C_{res} are the contributions from old CO_2 and normal soil respiration, respectively. Then, the fraction of soil CO_2 due to geological sources is

$$g = C_{geo}/C \tag{5}$$

Let

$$k = C_{geo}/C_{res} \tag{6}$$

be the ratio of old to respired CO_2; then,

$$1/g = 1/k + 1 \tag{7}$$

Taking ρ as the fraction of total plant carbon assimilated via root uptake, then the portion of that due to old carbon is

$$\varphi = \rho g \tag{8}$$

However, as discussed above, ρ depends on the total soil CO_2 concentration, and hence on g. The total concentration relative to the amount due only to normal respiration is $C/C_{res} = 1/(1-g)$, which exceeds 10 when $g > 0.9$.

Although ρ varies with total soil CO_2 concentration, we have insufficient data to model this dependence. However, we can still examine a range of possible cases by assigning pairs of values for ρ and g as if they were independent. For example, if half the soil CO_2 is old ($g = 0.5$), then constant root uptake values of $\rho = 1\%$ and 2% would give $\Delta t \approx 40$ and 80 yr, respectively.

We turn now to the uptake of old carbon by the canopy effect. In the absence of old CO_2 emission, let $\bar{R}$ and $\bar{R}_s$ denote the normal CO_2 fluxes into the canopy from total ecosystem respiration and from soil respiration, respectively, averaged over a year. The flux of soil respiration is approximately proportional to that of the total ecosystem respiration, so

$$\bar{R}_s = \beta \bar{R} \tag{9}$$

where published values of β generally range from 0.6 to 0.9 (Law et al. 1999; Bolstad et al. 2004; Yuste et al. 2005; Zha et al. 2007). We take $\beta = 0.75$ as a representative value.

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Let $\hat{T}$ and $\hat{R}$ be the integrated amounts of plant carbon assimilated per year in a canopy by photosynthesis of CO_2 derived from the troposphere and from total respiration, respectively. The recycling index is the proportion of total plant carbon refixed from the CO_2 of ecosystem respiration, relative to the total photosynthetic carbon, and is given by

$$r = \frac{\hat{R}}{\hat{T} + \hat{R}} \tag{10}$$

We regard r as a constant characterizing the physical properties of a canopy and its local pattern of meteorology, independent of whether or not the soil emits old CO_2. The total flux of CO_2 assimilated per year is $\hat{T} + \hat{R}$, which equals the flux R respired back into the canopy, when averaged over a year for an ecosystem in equilibrium. Then, from Equation 10,

$$\hat{R} = r\overline{R} \tag{11}$$

Let $\overline{G}$ be the average flux into the canopy of old CO_2, and let $\hat{G}$ be the portion of that flux assimilated per year by photosynthesis. It will be useful to quantify the flux of old CO_2 in terms of the normal soil respiration flux $\overline{R}_s$ in the absence of old CO_2, using the ratios

$$k = \overline{G}/\overline{R}_s \tag{12}$$

and

$$g = \overline{G}/(\overline{R}_s + \overline{G}) \tag{13}$$

in analogy with Equations 6 and 5. Because the concentration of CO_2 in the soil is roughly proportional to its flux from the ground (Jassal et al. 2005), the flux ratio between contributions by old and respired CO_2 is comparable to the ratio of their concentrations.

The values of $\hat{R}$ and $\hat{G}$ depend, respectively, on the amounts of CO_2 from respiration and from geological emission during the night that remain in the canopy air in the first hours after dawn. That depends on the exchange of canopy air with the troposphere. But on the assumption that both R and G are nearly constant through the diurnal cycle, such factors of micrometeorology should not affect the ratio k. Photosynthesis in the canopy should respond to $\hat{G}$ in nearly the same way that it responds to the respired flux R (see Equation 11). It follows that $\hat{G} = rG$. The assimilation by the ecosystem of carbon from the 2 sources will then be in nearly the same ratio as the fluxes, and

$$k = \hat{G}/\beta\hat{R} \tag{14}$$

This approximation greatly simplifies the analysis.

The addition of old CO_2 to the canopy air allows an ecosystem to incorporate and respire more carbon, due in effect to CO_2 fertilization. A fraction r of the old CO_2 respired by the system will be reassimilated by photosynthesis. This further increases the contribution of old CO_2 to the ecosystem, but the effect is of second order in r and has a negligible influence on the apparent ^{14}C ages. Other second-order effects are similarly neglected.

The ratio of carbon assimilated from old CO_2 in the canopy to total carbon assimilated by the ecosystem is then approximately

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$$\varphi_o = \frac{\hat{G}}{\hat{T} + \hat{R} + \hat{G}} \tag{15}$$

Using Equations 10 and 14, we can rewrite this as

$$\varphi_o = \frac{1}{1/\beta rk + 1} \tag{16}$$

where r and k are both measurable in principle. Equation 16 shows that increasing either the ratio k or the recycling index r (for example, by increasing the leaf density and thereby suppressing ventilation of the canopy) will increase the proportion of plant carbon assimilated from old CO_2, and hence the apparent ^{14}C age of a sample. Note that $\varphi_o \approx \beta rk$ when $rk << 1$.

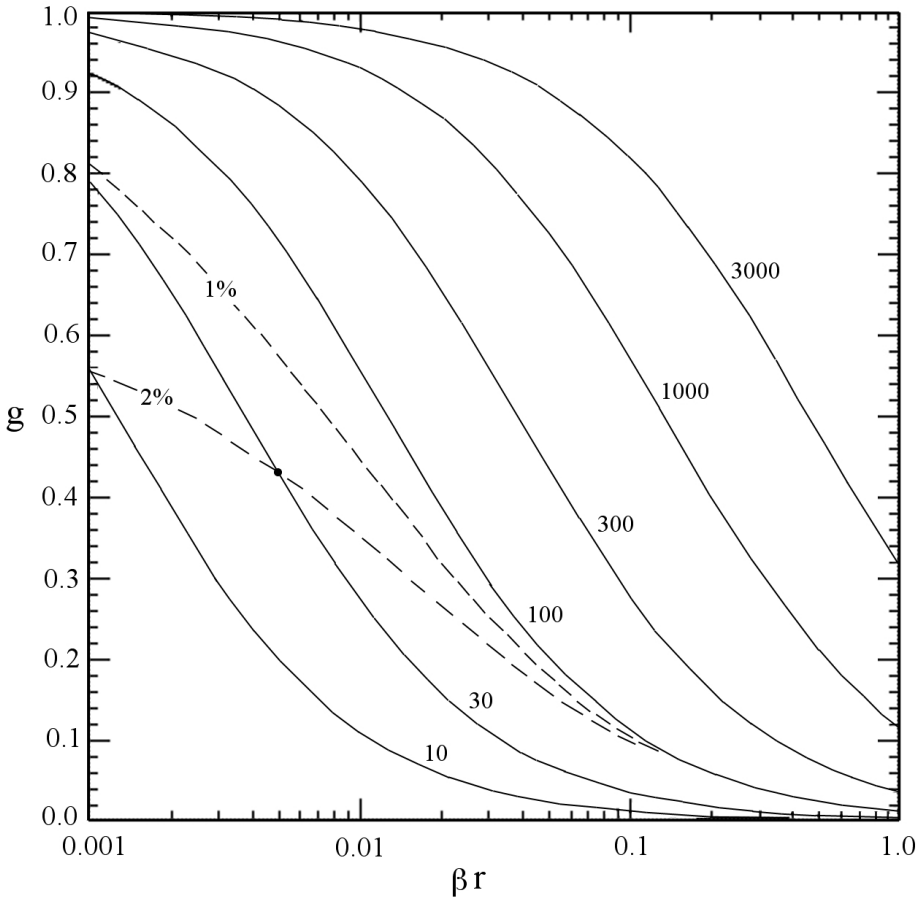

Figure 3 The curves represent a set of apparent ^{14}C age increments Δt, labeled in years, plotted as a function of βr, the ratio of carbon assimilated from soil respiration to total carbon assimilation, and the proportion g of total CO_2 emission from the soil that derives from geological sources. The recycling index r increases with the density of a canopy. The fraction β of total ecosystem respiration due to soil respiration is typically about ¾. The solid curves show the age increments in the absence of carbon uptake by roots. The dashed curves show the increments including root uptake for 2 values of ρ, labeled in percent, for the case where Δt = 100 yr. Increasing ρ increases the value of Δt corresponding to any point on the diagram, especially when r is small.

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Figure 3 plots curves of constant Δt as a function of g and βr, where we take g and r to represent the influences of the old CO_2 flux and canopy suppression of ventilation, respectively. The solid curves, labeled with Δt values in years, are calculated using Equations 2, 7, and 16. For example, consider a canopy characterized by $r = 0.04$ in a geological setting with $g = 0.30$. A value of $\beta = 0.75$ gives $\beta r = 0.03$, and the estimated ^{14}C age increment of a plant grown in such an environment would be $\Delta t = 100$ yr from the canopy effect alone. Using the same value of r but with $g = 0.56$ would give $\Delta t = 300$ yr.

Finally, if both the canopy effect and root uptake are present, the proportion φ of total plant carbon derived from old CO_2 is the sum of their contributions,

$$\varphi = (1 - \rho)\,\varphi_o + \rho g \tag{17}$$

where the first term on the right represents the canopy contribution and the second term represents root uptake. Note that $\varphi = \varphi_o$ as $\rho \to 0$ (no root uptake) and $\varphi \to \rho g$ as $\varphi_o \to 0$ (no canopy recycling, $r = 0$).

The dashed curves in Figure 3 show the combined effect of assimilation by both the canopy and roots, for the case $\Delta t = 100$ yr and 2 values of the root uptake ρ (labeled in %), taken here as a fixed quantity independent of g. For values of $\beta r > 0.1$ (strong canopy suppression of ventilation), both dashed curves approach the solid curve for $\Delta t = 100$ yr, indicating that root uptake would make a small contribution to the apparent age increment. In more open canopies, with lower values of r, root uptake would make a larger relative contribution. For example, for $\beta r = 0.005$ and $g = 0.43$ (the dot in Figure 3), the age increment Δt would be 30 yr with no root uptake, but 100 yr with root uptake at $\rho = 2\%$.

Similar curves for other values of Δt and constant ρ can be plotted by solving Equations 16 and 17 for

$$\beta r = \frac{1/g - 1}{(1 - \rho)/(\varphi - \rho g) - 1} \tag{18}$$

where φ is found from Equation 2.

DIFFUSE EMISSION OF OLD CO_2: EXAMPLES FROM ITALY

Non-volcanic CO_2 emissions from the western side of the Italian peninsula are among the most prolific and intensively studied in the world (Chiodini et al. 1999, 2004; Minissale 2004). Analyses of $\delta^{13}C$ in groundwaters of Tuscany and Campagnia indicate that the flux to the atmosphere of deep-source CO_2 ranges from 1 to 6 g m^{-2} d^{-1} over areas of hundreds of square kilometers (Gambardella et al. 2004; Frondini et al. 2008). This is a significant contribution compared to the average CO_2 flux of soil respiration for Mediterranean woodlands and heath, about 7 g m^{-2} d^{-1} (Raich and Schlesinger 1992).

Much of this old CO_2 flux is focused locally in springs and vents (Rogie et al. 2000), but a portion of it, as yet only poorly quantified, takes the form of diffuse soil emission. Consider a hypothetical case in which diffuse emission contributes an average CO_2 flux of $G = 3$ g m^{-2} d^{-1}. Suppose this occurs in an area with a soil respiration flux of $R_s = 7$ g m^{-2} d^{-1}. Then, this example would give $k = G/R_s = 0.43$ and $g = 0.30$. Figure 3 suggests that plants growing in such an area with a recycling index of $r = 0.04$ and $\beta = 0.75$ could have an average ^{14}C age increment of about 100 yr due to the canopy effect alone.

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Etiope and Lombardi (1995) measured soil gas concentrations of CO_2 in surveys of 6 faulted clay basins in central and southern Italy. The areas surveyed in each basin ranged from 120 to 380 km^2. In each basin, the investigators found local areas with positive soil-gas anomalies, typically about a kilometer in size, and preferentially located close to or directly above linear faults and fracture zones. Each of these areas may be the surface expression of gas dispersing through the permeable sedimentary strata from a single point or line source in the bedrock at a depth comparable to the surface dimensions of the anomalous area. On contour maps of soil gas concentration, these anomalies occupy about 10 to 30% of the area surveyed in each basin. Ciotoli et al. (1999) and Guerra and Lombardi (2001) provide additional gas contour maps of Italian basins.

For each basin, Etiope and Lombardi tabulated the maximum CO_2 concentration found in the soil of an anomalous area and the mean concentration in the basin. We denote these quantities by C_{max} and C_{res}, respectively, and take the latter to represent the normal soil respiration. Then, the average contribution due to old CO_2 within an anomaly is approximately $C_{geo} \approx 0.5(C_{max} - C_{res})$.

Because gas fluxes are nearly proportional to the corresponding concentrations of CO_2 in the soil, we can estimate the old CO_2 index from Equations 4 and 5 as

$$g \approx (C_{max} - C_{res}) / (C_{max} + C_{res}) \tag{19}$$

Table 1 gives the relevant CO_2 concentration data measured by Etiope and Lombardi for the 6 Italian basins, and our estimates of the corresponding g ratios. The latter values are quite comparable among the anomalies, around 0.8. Reference to Figure 3 shows that the corresponding ^{14}C age increments for the canopy effect could exceed 100 yr for $\beta r > 0.004$. Root uptake alone, with a constant value of $\rho = 0.8\%$, could give age increments of ~50 yr.

Table 1 CO_2 soil concentrations for selected regions in Italy. C_{res} is the mean soil gas concentration of CO_2 in a region, C_{max} is the maximum concentration measured for an anomalous area in the region, g is the average proportion of total soil CO_2 due to old CO_2 in an anomalous area (estimated from Equation 19), and k is the corresponding ratio of old to respired CO_2 in the soil. The values of C_{res} and C_{max} are from the tabulation of Etiope and Lombardi (1995).

Location	C_{res} (%)	C_{max} (%)	g	k
Siena Basin	1.13	15.9	0.87	6.7
Medium Tiber Valley	0.93	14.1	0.88	7.3
Roveto Valley	1.0	7.0	0.75	3.0
Ofanto Basin	1.33	15.5	0.84	5.25
Pisticci	0.5	4.8	0.81	4.3
Gela	0.8	6.5	0.78	3.5

Etiope (1999) observed the actual CO_2 fluxes within one of the Siena Basin anomalous areas, located in a grassy field over faulted basement rock. There, he measured an average total soil flux of 85 g m^{-2} d^{-1}. In a nearby control area with similar vegetation but no evidence of faults, he measured an average background flux of 7 g m^{-2} d^{-1}. If we assume that the latter represents the normal flux of soil respiration R_s and the difference is the old CO_2 contribution, then Equation 13 gives a maximum $g = 0.92$ within the anomaly.

For some regions during particular eras, ^{14}C dates from organic material in archaeological strata often appear to be older than dates based on archaeological typology. In Italy, for example, this has led to uncertainties in the archaeological chronology. Because degassing of old CO_2 is widespread there, such emissions may account for some of the discrepancies.

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Guidi et al. (1996) surveyed the Italian Bronze and Iron Age data and concluded that "almost all cultures and phases show a chronology which is longer and earlier than traditionally expected . . . Radiocarbon dates provide no confirmation of the precise subdivisions provided by chronotypology and in some cases directly contradict them." The most discordant examples include the Iron Age sites of Bolsena Gran Carro, Fidenai, and Satricum, in Etruria and Latium.

All 3 sites lie within a region (~220 × 60 km) of deep-source CO_2 emissions identified by Chiodini et al. (2004) as the "Tuscan Roman degassing structure." Bolsena Gran Carro in particular lies on a tectonic lineament bounding a major volcanic caldera (Gambardella et al. 2004), and gas emissions measured nearby have radon and $\delta^{13}CO_2$ values indicating a deep source (Minissale et al. 1997).

Diffuse degassing of old CO_2 and its assimilation by plants may thus account for some of the ^{14}C anomalies in Italy and other seismically active regions. Etiope (1999) noted that "soils within the active tectonic bounds of the Earth . . . cover at least 25% of the land surface, and if these areas have geogas [old CO_2] fluxes similar to those observed in the present study [of the Siena Basin], the global soil emission of carbon would be significantly higher than the estimate based on soil respiration only . . .".

DISCUSSION AND CONCLUSIONS

This paper suggests that plants growing in tectonically active areas can assimilate old carbon from the diffuse emission of old CO_2, either by root uptake in the soil or by photosynthesis in the canopy. Such assimilation may be sufficient to produce detectable ^{14}C age increments, but it remains to demonstrate whether it actually occurs in the field.

A possible test involves the stable isotope ^{13}C. Old CO_2 usually has a higher $^{13}C/^{12}C$ ratio than atmospheric CO_2. This may explain the inverse correlation between ^{14}C and ^{13}C reported for plants growing in the vicinity of strong sources of old CO_2 emissions (Bruns et al. 1980; Saupé et al. 1980; Calderoni and Turi 1998; Pasquier-Cardin et al. 1999; Saurer et al. 2003). However, in areas with diffuse emissions such a correlation may be too weak to detect, particularly if $\delta^{13}C$ for the old CO_2 is close to that of atmospheric CO_2.

While areas with detectable levels of old CO_2 emission can extend over kilometers, the soil CO_2 concentration may vary by an order of magnitude or more over horizontal distances of only a meter, due to the limited lateral diffusion of gas through fine-grained soil (Vodnik et al. 2006). The expected result is that while old CO_2 levels sufficient to produce measurable ^{14}C age increments would be found within large areas, plants grown even in the same cultivated field may show a substantial range of apparent ages.

The diffuse flux of old CO_2 generally varies in time and space (e.g. Guerra and Lombardi 2001; Saurer et al. 2003), and its absence in a given area today tells us little about whether it was present in the past. In tectonically active areas, the intermittent emission of old CO_2 may thus introduce an irreducible level of uncertainty in ^{14}C dating. In such areas, however, if short-lived samples from the same stratigraphic horizon yield a wide range of ^{14}C ages, the lower values may be the least altered by old CO_2.

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APPENDIX

C = total soil gas CO_2 concentration.

C_{geo} = soil gas concentration of old CO_2.

C_{res} = soil gas concentration of respired CO_2.

g = ratio of old to total CO_2.

G = flux of old CO_2 from soil.

$\overline{G}$ = average flux of old CO_2.

$\hat{G}$ = average flux of old carbon assimilated by photosynthesis.

k = ratio of old to respired CO_2.

r = ratio of recycled to total CO_2 assimilated by photosynthesis.

R = ecosystem flux of respired CO_2.

$\overline{R}$ = average ecosystem flux of respired CO_2.

$\hat{R}$ = average ecosystem flux of respired carbon assimilated.

R_a = flux of CO_2 respired above ground.

R_s = flux of CO_2 respired from soil.

$\overline{R}_s$ = average flux of CO_2 respired from soil.

T = flux of CO_2 from troposphere to canopy air.

$\hat{T}$ = average flux of carbon from troposphere assimilated by photosynthesis.

Δt = apparent increment in ^{14}C age.

β = ratio of soil respiration to total ecosystem respiration.

ρ = fraction of total plant carbon assimilation due to root uptake.

φ = fraction of total plant carbon derived from old CO_2.

φ_o = fraction of total photosynthetic carbon derived from old CO_2.

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