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Journal

Geochimica et Cosmochimica Acta, 58(1)

ISSN

0016-7037

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Publication Date

1994

DOI

10.1016/0016-7037(94)90472-3

Geochimica et Cosmochimica Acta Vol. 58, pp. 393–399

0016-7037/94/\$6.00 + .00

A model for soil $^{14}CO_2$ and its implications for using ^{14}C to date pedogenic carbonate

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(*Received March* 17, 1993; *accepted in revised form July* 31, 1993)

Abstract—A diffusion-reaction model for soil $^{14}CO_2$ is described that analyzes the $^{14}CO_2$ distribution in soils. It shows that the ^{14}C content of soil CO_2 is not the same as that of atmospheric CO_2 and varies with depth depending on various factors. The most important factors affecting the ^{14}C content of soil CO_2 include the ^{14}C content of soil organic matter, the relative contribution of root respired CO_2 to total CO_2 production, soil respiration rate, atmospheric CO_2 concentration and $^{14}CO_2$ content, and soil properties such as temperature and moisture content etc. The ^{14}C content of soil CO_2 not only can be a sensitive indicator of the residence time of decomposing organic matter in the soil, but also determines the ^{14}C content of pedogenic carbonate. Our model suggests that soil CO_2 could be enriched or depleted in ^{14}C relative to atmospheric CO_2, depending on the relative contribution of root respiration to total soil respiration and on the turnover rate of the soil organic matter contributing to the soil CO_2. Therefore, the initial ^{14}C dates of soil carbonate could differ from the true ages of pedogenesis. The processes and factors considered by the model are a first step in determining whether the ^{14}C content of soil carbonate could lead to reliable dates of pedogenesis.

INTRODUCTION

CARBON DIOXIDE IS PRODUCED by decomposition of organic matter and by root respiration in soils. As a result, CO_2 concentrations in soils are higher than atmospheric CO_2 concentrations. Diffusion is considered the major mechanism by which gases move in soils (KIRKHAM and POWERS, 1972; JURY et al., 1991). It has been previously shown that the distribution of CO_2 and its stable isotopic species (e.g., $^{12}CO_2$, $^{13}CO_2$) in soils can be described by a diffusion-reaction model (CERLING, 1984, 1991; SOLOMON and CERLING, 1987; CERLING et al., 1989; QUADE et al., 1989). Since the $\delta^{13}C$ value of CO_2 produced by root respiration is essentially the same as that of CO_2 produced by decomposition of soil organic matter, the $\delta^{13}C$ value of soil CO_2 is determined by soil respiration rate and the $\delta^{13}C$ value of soil organic matter, which is more or less constant with depth and time in a stable soil ecosystem (CERLING, 1984, 1991; CERLING et al., 1989; QUADE et al., 1989).

However, in the case of the radioactive carbon isotope (^{14}C), the model needed to describe the $^{14}CO_2$ profile will be more complicated. First of all, the ^{14}C content of CO_2 produced by root respiration is not necessarily the same as that of CO_2 derived from organic matter decomposition. While root respiration CO_2 can be assumed to be nearly identical with the atmospheric ^{14}C level (DÖRR and MÜNNICH, 1986), the ^{14}C content of CO_2 derived from organic matter decomposition may, depending on the carbon residence time in the soil, be depleted by radioactive decay or even enriched by the contribution of ^{14}C produced in the late 1950s and early 1960s by atmospheric testing of thermonuclear weapons (bomb ^{14}C) (DÖRR and MÜNNICH, 1986). In other words, the $\delta^{14}C$ value of CO_2 produced by organic matter decomposition should be determined by the ^{14}C content of soil organic matter, which is a mixture of compounds with different turnover rates (TRUMBORE et al., 1990; TRUMBORE, 1993). Moreover, the $\delta^{14}C$ value of organic matter changes with depth and time (GOH et al., 1976; O'BRIEN and STOUT, 1978; TRUMBORE, 1993), suggesting that the CO_2 produced at different depths should have different ^{14}C contents depending on the ^{14}C content of soil organic matter at that depth and also on the relative contribution of root respiration to the total CO_2 production. HAAS et al. (1983) and THORSTENSON et al. (1983) observed lower ^{14}C contents in respired CO_2 during winter time due to oxidation of older soil organic matter in the absence of significant root respiration. However, their model failed to describe the $^{14}CO_2$-depth profile observed in their study. DÖRR and MÜNNICH (1986) also observed an annual ^{14}C variation of soil-respired CO_2, which they suggested is controlled by the seasonally varying contribution of root respiration and CO_2 produced by microbial decomposition of organic matter.

Presently, there is no adequate model describing the $^{14}CO_2$ distribution in soils. Previous studies on soil CO_2, and $\delta^{13}C$ values of soil CO_2, and pedogenic carbonates indicate that the CO_2 and carbonate in a soil system are in isotopic equilibrium. This implies that any detrital carbonate dissolved in the soil is overwhelmed by soil CO_2 and the isotopic composition of pedogenic carbonate is determined by the isotopic composition of soil CO_2 (CERLING, 1984, 1991; CERLING et al., 1989; QUADE et al., 1989; AMUNDSON et al., 1989; CERLING and QUADE, 1992). If this is the case, the ^{14}C content of pedogenic carbonate should also be determined by ^{14}C content of soil CO_2 and inherited dead carbon should not affect the age of soil pedogenic carbonate. Therefore, a better understanding of $^{14}CO_2$ distribution in soils would have very important implications not only in the study of organic carbon cycling in soils, but also in the application of ^{14}C to date soil carbonate. Furthermore, the ^{14}C content of soil CO_2 is an important parameter in modeling variations of atmo-

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spheric ^{14}C content as well as for determining the initial value for ^{14}C groundwater dating, because groundwater recharges through soils.

In this study, we incorporate the $^{14}CO_2$ isotopic species into a diffusion-reaction model which is expanded on the $\delta^{13}C$ (CO_2) model of CERLING (1984). The purpose of our modeling is (1) to help us better understand the $^{14}CO_2$ distribution in soils; (2) to evaluate the different factors affecting soil $^{14}CO_2$ such as the relative contribution of root respired CO_2 to total CO_2 production, soil respiration rate, ^{14}C content of soil organic matter, atmospheric CO_2 concentration and $^{14}CO_2$ content, soil properties, and temperature etc.; and (3) to explore the potential application of using soil pedogenic carbonate to ^{14}C date soils or landforms.

A DIFFUSION-REACTION MODEL FOR $^{14}CO_2$

Carbon dioxide is produced in soils by biological processes and is transported to the atmosphere by diffusion (KIRKHAM and POWERS, 1972; JURY et al., 1991). The diffusion mechanism applies to its isotopic species $^{12}CO_2$, $^{13}CO_2$, and $^{14}CO_2$ as well (HAAS et al., 1983; THORSTENSON et al., 1983; CERLING, 1984, 1991; CERLING et al., 1989; QUADE et al., 1989). Different isotopic species of CO_2 react and diffuse independently of each other according to their own concentration gradient and their own sources and sinks (HAAS et al., 1983; THORSTENSON et al., 1983). Since the concentration of $^{14}CO_2$ in a soil profile is controlled by the production and decay of $^{14}CO_2$, and by diffusion through the soil to the atmosphere, the concentration of $^{14}CO_2$ can be described by a diffusion-reaction equation:

$$\frac{\partial C_s^{14}}{\partial t} = D_s^{14}\frac{\partial^2 C_s^{14}}{\partial z^2} + \Phi_s^{14} - \lambda C_s^{14}, \qquad (1)$$

where C_s^{14} represents the $^{14}CO_2$ concentration in the soil air (moles/cm^3), D_s^{14} is the diffusion coefficient of $^{14}CO_2$ in the soil (cm^2/sec), Φ_s^{14} is the production of $^{14}CO_2$ in the soil by organic matter decomposition and root respiration (moles/cm^3/sec), and λ the decay constant of ^{14}C (3.84×10^{-12}/sec). Since the term λC_s^{14} is much smaller compared to the other terms on the right side of the equation, the above equation can be reduced to

$$\frac{\partial C_s^{14}}{\partial t} = D_s^{14}\frac{\partial^2 C_s^{14}}{\partial z^2} + \Phi_s^{14}. \qquad (2)$$

To model $^{14}CO_2$, information is needed regarding the production of $^{14}CO_2$ (Φ_s^{14}) in a soil. With the simplified assumption that soil CO_2 is primarily produced (a) by root respiration with practically no difference in ^{14}C from atmospheric CO_2, and (b) by decomposition of soil organic matter with the same ^{14}C content as decomposing organic matter, the relative contribution of these two reservoirs to the soil $^{14}CO_2$ production can be calculated with a two-component mixing model following the equation: $(^{14}C/^{12}C)_z = F^*(^{14}C/^{12}C)_{o.m.} + (1-F)^*(^{14}C/^{12}C)_{atm.}$, where $(^{14}C/^{12}C)_z$ is the ^{14}C content of biologically produced CO_2 in the soil at depth z; F is the relative contribution of CO_2 from organic matter decomposition, the fraction of CO_2 derived from root respiration is $1 - F$; and $(^{14}C/^{12}C)_{o.m.}$ and $(^{14}C/^{12}C)_{atm}$ are ^{14}C content of decomposing organic matter and the atmosphere, respectively. The production of $^{14}CO_2$ can then be described by:

$$\Phi_s^{14}(z) = \Phi^{12}\left(\frac{^{14}CO_2}{^{12}CO_2}\right)_z$$

$$= \Phi^{12}\left[F\left(\frac{^{14}CO_2}{^{12}CO_2}\right)_{o.m.} + (1-F)\left(\frac{^{14}CO_2}{^{12}CO_2}\right)_{atm}\right] \qquad (3)$$

$$\Phi^{12} = \Phi^* - \Phi^*\left(\frac{C^{13}}{C^{12}+C^{13}}\right)_\Phi = \Phi^*\cdot(1-\hat{\delta})$$

and

$$\hat{\delta} = \left(\frac{\left(\frac{\delta^{13}C_\Phi}{1000}+1\right)R_{PDB}}{1+\left(\frac{\delta^{13}C_\Phi}{1000}+1\right)R_{PDB}}\right),$$

where Φ^* and Φ^{12} are the total CO_2 and $^{12}CO_2$ production rates, respectively; $\delta^{13}C_\phi$ is the $\delta^{13}C$ value for respired CO_2, and R_{PDB} is the ratio ($^{13}C/^{12}C$) in the isotopic standard PDB.

Defining $R = {}^{14}C/^{12}C$, Eqn. 3 becomes

$$\Phi_s^{14}(z) = \Phi^{12}[R^*_{o.m.}F + (1-F)^*R_{atm}]. \qquad (4)$$

Using the notation,

$$\delta^{14}C = \left(\frac{R_{sample}}{R_{std}} - 1\right) \times 1000,$$

where $\delta^{14}C$ is the permil value for ^{14}C content (STUIVER and POLACHE, 1977), and R_{std} is the absolute $^{14}C/^{12}C$ ratio in the isotopic standard (NBS oxalic acid). The $\delta^{14}C$ notation here is the same as that used in oceanography and is not corrected for $\delta^{13}C$. Substituting the notation into Eqn. 4,

$$\Phi^{14}(z) = \Phi^{12}\left[F\left(\frac{\delta^{14}C_{o.m.}}{1000}+1\right)(R_{std}) + (1-F)\left(\frac{\delta^{14}C_{atm}}{1000}+1\right)(R_{std})\right]. \qquad (5)$$

Assuming that the soil can be approximated as a one-dimensional box with a non-flux boundary at depth L, the following boundary conditions exist:

$$C_s^{14} = C_a^{14} \quad \text{at} \quad z = 0$$

and

$$\frac{\partial C_s^{14}}{\partial z} = 0 \quad \text{at} \quad z = L.$$

For the condition that the ^{14}C content of decomposing organic matter diminishes with depth in a linear fashion, i.e., $\delta^{14}C_{o.m.} = A + Bz$, which is the case in most soils (O'BRIEN and STOUT, 1977; TRUMBORE et al., 1990; SCHARPENSEEL et al., 1989), and that Φ^* and F is constant with depth, the steady-state solution to Eqn. 2 is

$$C_s^{14} = \frac{1}{D_s^{14}}\left[-(\Phi^{12})(R_{std})\cdot F \times \left(\frac{A+1000}{2000}z^2 + \frac{B}{6000}\cdot z^3\right) - \frac{E\cdot z^2}{2} + G\cdot z\right] + C_a^{14}, \qquad (6)$$

where

$$E = (\Phi^{12})(R_{std})(1 - F)\left(\frac{\delta^{14}C_{atm}}{1000} + 1\right)$$

and

$$G = (\Phi^{12})(R_{std})\cdot F\cdot\left(\frac{A + 1000}{1000}\cdot L + \frac{B}{2000}\cdot L^2\right) + E\cdot L.$$

According to CERLING (1984), the steady-state solutions for diffusion-reaction equations for CO$_2$ and ^{13}CO$_2$, with boundary conditions of $C_s^* = C_a^*$ and $C_s^{13} = C_a^{13}$ at $z = 0$, and $\frac{\partial C_s^*}{\partial z} = 0$ and $\frac{\partial C_s^{13}}{\partial z} = 0$ at $z = L$, are as follows:

$$C_s^* = \frac{\Phi^*}{D_s^*}\left(Lz - \frac{z^2}{2}\right) + C_a^* \qquad (7)$$

$$C_s^{13} = \frac{\Phi^{13}}{D_s^{13}}\left(Lz - \frac{z^2}{2}\right) + C_a^{13}, \qquad (8)$$

where C_a^* and C_a^{13} are CO$_2$ and ^{13}CO$_2$ concentrations in the atmosphere; C_s^* and C_s^{13} are corresponding concentrations in the soil air; and D_s^* and D_s^{13} are diffusion coefficients for CO$_2$ and ^{13}CO$_2$, respectively.

The diffusion coefficient for CO$_2$ in soil is related to that in air (D_{air}) by

$$D_s^* = D_{air}\epsilon\rho,$$

where ϵ is the free air porosity in the soil, and ρ is a tortuosity factor (KIRKHAM and POWERS, 1972; JURY et al., 1991). D_{air} varies with temperature and pressure (BIRD et al., 1960):

$$D_{air} = D_{air}^0\left(\frac{P^0 T}{P T^0}\right)^{1.823},$$

where D_{air}^0 is the diffusion coefficient for CO$_2$ in air under standard conditions (T^0 = 25°C and P^0 = 1 bar pressure) and is taken to be 0.144 cm^2/s.

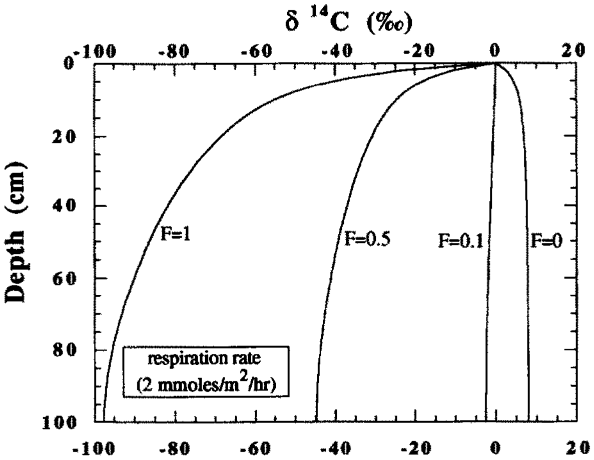

FIG. 1. δ^{14}C value of soil CO$_2$ vs. depth for a model soil. It shows that the δ^{14}C values of soil CO$_2$ vary with depth from the (pre-atomic bomb) atmospheric value at the soil-atmosphere interface to more negative or more positive values at depth depending on the value of F.

Table 1 Parameters for the model soil described in the text

$\delta^{14}C_{o.m.}$	-10	-50	-100	-150	-200	-225	-250	-275	-300	-325
depth(cm)	10	40	60	80	100	120	140	160	180	200

$\delta^{14}C_{o.m.}$=1.1176-1.7317*depth
Temperature=15°C
Pressure=1atm
Respired CO$_2$: δ^{13}C=-26‰
Atmospheric CO$_2$: 300ppm, δ^{13}C=-6‰
Porosity = 0.5
tortuosity factor = 0.61

The diffusion coefficients of ^{14}CO$_2$ and ^{12}CO$_2$ are related by

$$\frac{D_s^{12}}{D_s^{14}} = \left[\left(\frac{M(\mathrm{air}) + M(^{12}\mathrm{CO_2})}{M(\mathrm{air}) \times M(^{12}\mathrm{CO_2})}\right)\left(\frac{M(\mathrm{air}) \times M(^{14}\mathrm{CO_2})}{M(\mathrm{air}) + M(^{14}\mathrm{CO_2})}\right)\right]^{1/2}$$

$$= 1.00868.$$

Using Eqns. 6, 7, and 8 and using various values of soil respiration, an atmospheric CO$_2$ concentration of 300 ppm, and atmospheric δ^{13}C and δ^{14}C values of −6‰ (pre-industrial value) and 0‰ (pre-bomb value), respectively, it is possible to calculate ^{14}CO$_2$ (δ^{14}C) profiles in soils for various conditions.

Figure 1 shows how the δ^{14}C value of soil CO$_2$ varies with depth in a model soil where the ^{14}CO$_2$ concentration is diffusion-controlled. The parameters for the model soil are listed in Table 1. This diagram displays several important features:

1) The δ^{14}C value of soil CO$_2$ is not necessarily the same as that of atmospheric CO$_2$, although it has been assumed so in previous studies using ^{14}C to date soil carbonate. However, the present-day analytical precision at best is ±3‰, and for most accelerator labs the analytical precision is ±8‰. Therefore, when F is small, for example F = 0.1, the δ^{14}C value of soil CO$_2$ can be considered the same as that of atmospheric CO$_2$.
2) The δ^{14}C values of soil CO$_2$ are not constant with depth.
3) The δ^{14}C values of soil CO$_2$ depend on the δ^{14}C values of soil organic matter, soil respiration, and the relative contribution of CO$_2$ derived from organic matter decomposition to total CO$_2$ production (F).
4) When the fraction of CO$_2$ derived from organic matter decomposition (F) ≠ 0, the δ^{14}C values of soil CO$_2$ vary continuously from the atmospheric value at the soil-atmosphere interface to more negative values at depth. Increasing the value of F, the δ^{14}C values of soil CO$_2$ at any depth become more negative.
5) When $F = 0$, the δ^{14}C values of soil CO$_2$ vary continuously from the atmospheric value at the soil-atmosphere interface to more positive values at depth. This increase in δ^{14}C values is a result of diffusion effects on the different isotopic species (CERLING et al., 1991). If the ^{14}C data are corrected for isotope fractionation using ^{13}C data (i.e., Δ^{14}C in STUIVER and POLACH, 1977), this diffusion component will not be seen.

Figure 2 shows how the δ^{14}C values of soil CO$_2$ vary with soil respiration rates. It is evident that at a given value of F, the higher the soil respiration, the more the δ^{14}C values of soil CO$_2$ deviate from that of atmospheric CO$_2$.

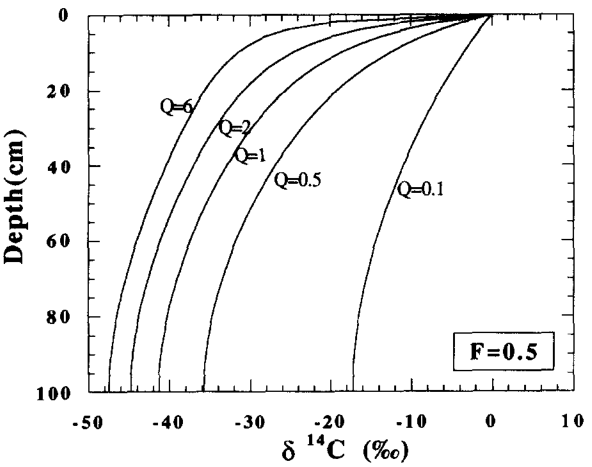

FIG. 2. Variations of the $\delta^{14}C$ values of soil CO_2 with soil respiration rates at a constant F value. The model shows that the higher the soil respiration rate, the more the $\delta^{14}C$ values of soil CO_2 deviate from that of the atmospheric CO_2.

When all soil CO_2 is derived from root respiration and/or decomposition of short-lived organic matter which has the same ^{14}C content as the atmospheric CO_2, the $\delta^{14}C$ values of soil CO_2 are relatively enriched (up to 8.5‰ at 15°C) compared to $\delta^{14}C$ values of atmospheric CO_2 (Fig. 3) due to diffusion effects. The lower the respiration rate or the higher the value of the diffusion coefficient, the less enriched the $\delta^{14}C$ values of soil CO_2 are relative to the $\delta^{14}C$ values of atmospheric CO_2. When soil respiration = 0, the $\delta^{14}C$ values of soil CO_2 are the same as the $\delta^{14}C$ values of atmospheric CO_2. Again, considering the present-day analytical precision of ±8‰ for ^{14}C analysis, this diffusion effect on ^{14}C content of soil CO_2 would be beyond detection.

These figures show soil $^{14}CO_2$ relationships for pre-industrial atmospheric conditions. To use this model to evaluate present-day soil conditions, one must change the atmospheric boundary conditions for CO_2, $^{12}CO_2$, and $^{14}CO_2$. In our test of the model against empirical data given below, various $^{14}C_{atm}$ values are used, based on the reported data.

OBSERVATIONS IN SOILS

It is important to establish if the above $^{14}CO_2$ model is valid in soils. Presently, there are few $^{14}CO_2$ depth profiles available. In Fig. 4, the ^{14}C data (reported as $A^{14}C$, percent modern carbon (pmc) = $(\delta^{14}C/1000 + 1)(1 - 2*(25 + \delta^{13}C)/1000)*100$) for soil CO_2 and CO_2 concentrations (data obtained in May) from site #6 in HAAS et al. (1983) and THORSTENSON et al. (1983) are plotted (different symbols represent different sampling dates) and compared to our model calculation (solid line). Since there were no $^{14}C_{o.m.}$ data and no CO_2 production information reported in their study, we assumed that the $^{14}CO_2$ production is an exponential function of depth as $\Phi_s^{14}(z) = \Phi_s^{14}(0)e^{-bz}$ with $\frac{\partial C_s^{14}}{\partial z} = 0$ at $z = L$ ($L = 380$ cm was used in the model calculation), where $\Phi_s^{14}(0)$ is the production of $^{14}CO_2$ at surface and b is a constant (we use $b = 0.003$ in the model calculation). We also assume that production of CO_2 is an exponential function of depth in their soil as $\Phi_s^*(z) = \Phi_s^*(0)e^{-z/chz}$ with $\frac{\partial C_s^*}{\partial z} = 0$ at $z = L'$ ($L' = 520$ cm was used in the model calculation), where $\Phi_s^*(0)$ is the production of CO_2 at surface and chz is the attenuation depth (we use $chz = 300$ cm in the model calculation). The solution to the diffusion Eqn. 2 with the assumed production function and boundary conditions are:

$$C_s^{14} = \frac{\Phi_s^{14}(0)}{(D_s^{14})b^2}(1 - e^{-zb}) - \frac{\Phi_s^{14}(0)(z)}{(D_s^{14})b}e^{-Lb} + C_a^{14} \quad (9)$$

$$C_s^* = \frac{\Phi_s^*(0)(chz^2)}{D_s^*}(1 - e^{-z/chz}) - \frac{\Phi_s^*(0)(chz)(z)}{D_s^*}e^{-L'/chz} + C_a^*, \quad (10)$$

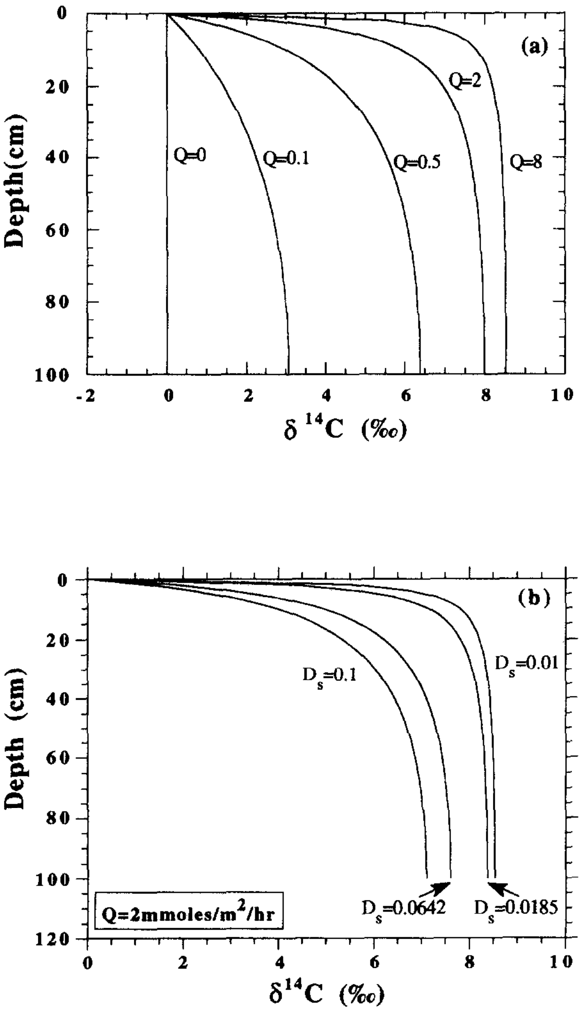

FIG. 3. $\delta^{14}C$ value of soil CO_2 vs. depth for soils where all CO_2 is derived from root respiration and/or decomposition of short-lived organic matter. It can be seen that the $\delta^{14}C$ values of soil CO_2 are relatively enriched compared to $\delta^{14}C$ values of atmospheric CO_2 due to diffusion effects. Figure 3 (a) shows that the lower the respiration rate, the less enriched the $\delta^{14}C$ values of soil CO_2 are relative to the $\delta^{14}C$ values of atmospheric CO_2. Figure 3 (b) shows the effect of varying diffusion coefficient on the ^{14}C content of soil air.

where C_s^{14} and C_s^* are $^{14}CO_2$ and CO_2 concentrations in the soil; C_a^{14} and C_a^* are corresponding concentrations in the atmosphere; and L and L' are the depth of the non-flux boundaries for $^{14}CO_2$ and CO_2, respectively (the non-flux boundary is a boundary where CO_2 or $^{14}CO_2$ concentration gradient equals to zero). Other assumed parameters used in our model calculation are listed in Table 2. In their study, THORSTENSON et al. (1983) concluded that the measured $^{14}CO_2$ profiles cannot be readily explained with a diffusion model due to some as yet unexplained mechanisms. However, Fig. 4 suggests that our curve fits their data reasonably well, except for one datum point at the 15.9 meter depth. This point represents a groundwater CO_2 sample and, therefore, may be contaminated by carbon from other sources. The goodness of the fit is adequate to strongly suggest that vertical diffusion is indeed the dominant mass-transport mechanism affecting $^{14}CO_2$ and CO_2 distribution in this soil. It should be noted that $\delta^{14}C$ value of atmospheric CO_2 (the upper boundary condition) is greater than 0‰ (the boundary condition used in Figs. 1-3). This is because present atmospheric ^{14}C content is elevated above natural levels by nuclear weapons testing and use.

Table 2 Parameters used in Figures 4 and 5

	Site#6	Forest soil	Pasture soil
Respiration rate (mmoles/m2/hr)	2	13	10
Temperature (°C)	15	27	27
Pressure (atm)	1	1	1
Porosity	0.5	0.55	0.5
F		0.66	0.55
Diffusion coefficient (cm^2/sec)	0.04	0.095	0.09
$\delta^{13}C_{o.m.}$	-26‰	-26‰	-26‰
^{14}C of respired CO_2 (PMC)	129		
^{14}C of atmospheric CO_2 (PMC)	130	114.5	114.5
CO_2 production function	exponential	constant	constant

Forest soil: $A^{14}C_{o.m.}$ (percent modern carbon)=115+0.005*depth
Pasture soil: $A^{14}C_{o.m.}$ (percent modern carbon)=100+0.035*depth
Atmospheric CO_2: 350ppmv, $\delta^{13}C$=-7

Figure 5 compares the $^{14}CO_2$ and CO_2 data from two Oxisol profiles (a forest soil and a 17-year-old pasture soil which is a degraded forest soil) from Paragominas in Brazil (NEPSTAD et al., unpubl. data) and our model calculations. The CO_2 samples were collected in May, 1992 by Trumbore, Davidson,

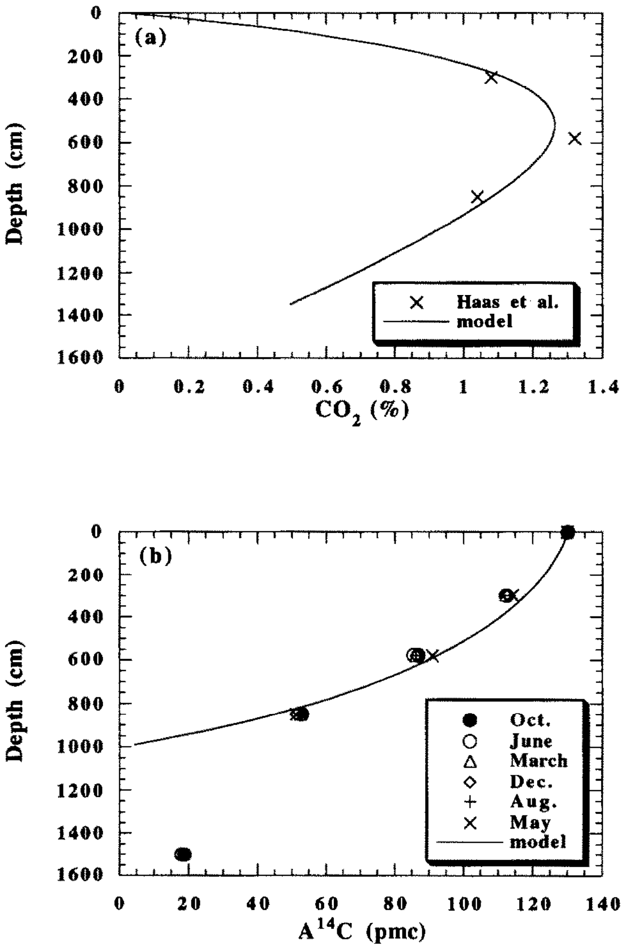

FIG. 4. Comparisons of (a) CO_2 and (b) $^{14}CO_2$ data from site #6 in HAAS et al. (1983) with model calculation. Different symbols represent different sampling dates and the curve is our model calculation. The goodness of the fits suggests that diffusion is indeed the dominant mechanism affecting the CO_2 and $^{14}CO_2$ distribution in the soil. The datum point at 15.9 meter depth represents a groundwater sample and, therefore, may be contaminated by carbon from other sources.

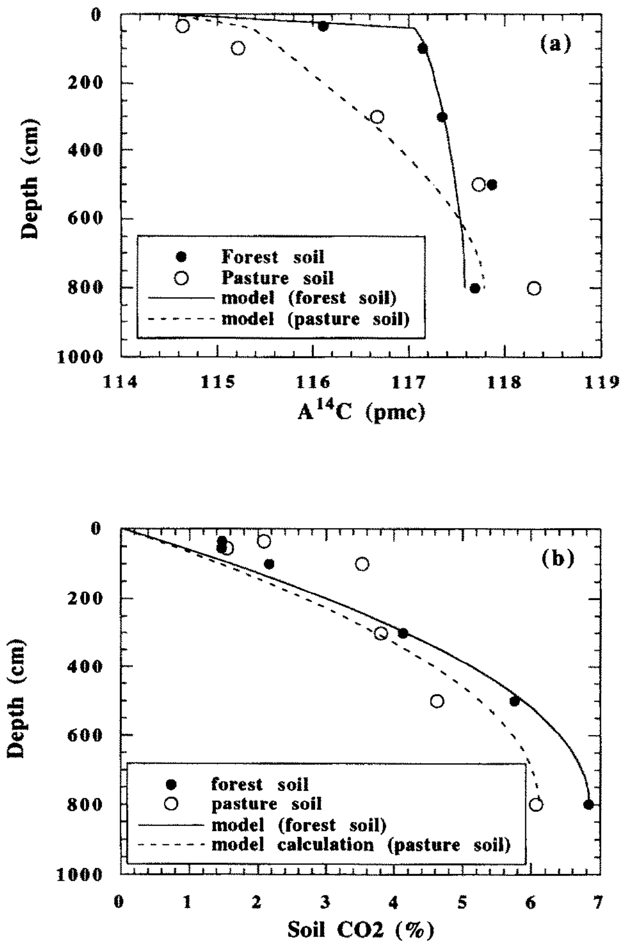

FIG. 5. Comparison of (a) $^{14}CO_2$ and (b) CO_2 (%) data from two Oxisol profiles from Paragominas in Brazil with model calculations. The solid dots represent a forest soil and the open circles a pasture soil (a degraded forest soil). For each soil, the $^{14}CO_2$ and CO_2 data are fitted using the same set of parameters (i.e., same respiration rate, diffusion coefficient, porosity, temperature, and pressure). Diffusion appears to be the dominant mechanism controlling the $^{14}CO_2$ and CO_2 distributions in these two soils.

and Nepstad. The measured CO_2 respiration rates for May are 25 mmoles/m^2/h for the forest soil and 10 mmoles/m^2/h for the pasture soil. For each soil, the $^{14}CO_2$ and CO_2 data are fitted using the same set of parameters (i.e., respiration rate, diffusion coefficient, porosity, temperature, and pressure) (Table 2). The measured CO_2 respiration rate for the forest soil seems too high because it requires an unreasonably high diffusion coefficient and/or porosity to produce the observed soil $^{14}CO_2$ and CO_2 profiles. The high respiration rate reflects the decomposition of abundant litter on the forest floor which could have contributed significant amounts of CO_2 to the total CO_2 flux measured at the soil surface and higher production of CO_2 in the upper 2 meters of the soil. In our model calculation we used a value of 13 mmoles/m^2/h for respiration rate for the forest soil which gives a reasonable fit to both the $^{14}CO_2$ and CO_2 data. Again, vertical diffusion appears to be the dominant mass-transport mechanism affecting $^{14}CO_2$ and CO_2 distribution in these soils. However, unlike the data of HAAS et al. (1983), the ^{14}C content of soil CO_2 is greater than present atmospheric values. Since soil CO_2 is produced by root respiration and decomposition of soil organic matter which is a heterogeneous mixture of compounds turning over at different rates, the observed ^{14}C profiles here suggest that the fractions of soil organic matter whose turnover contribute the most to the soil CO_2 contains a considerable quantity of bomb-produced ^{14}C.

IMPLICATIONS FOR ^{14}C DATING OF SOIL CARBONATE

Dates from soil carbonates have been considered unreliable estimates of the age of pedogensis because of unknown initial $^{14}C/^{12}C$ ratios in the carbonate and the possibility of subsequent contamination with environmental ^{14}C (CALLEN et al., 1983). Comparison of carbonate ^{14}C ages with ^{14}C ages of coexisting organic matter suggests that radiocarbon dates calculated from pedogenic carbonate in arid areas were about 500 to 7000 radiocarbon years too old (WILLIAMS and POLACH, 1969). On the other hand, radiocarbon dates of pedogenic carbonate from the sub-humid part of southeastern Australia were much younger than either the known age of deposition in which the carbonate is segregated, or the likely age of pedogenesis (BOWLER and POLACH, 1971). These discrepancies have been attributed to an initial low ^{14}C content of soil carbonate due to the limestone dilution effect and/or secondary contamination by environmental ^{14}C. The limestone dilution effect (BARTLETT, 1951; BROECKER and WALTON, 1959) states that soil carbonate derives half of its C from dead calcium carbonate and another half from atmospheric CO_2, suggesting that radiocarbon age of such carbonate would be about one half-life of ^{14}C (about 5570 years) older than the true age. However, studies on soil CO_2 and $\delta^{13}C$ of soil CO_2 and pedogenic carbonates indicate that the CO_2 and its isotopic species in a soil system are in isotopic equilibrium. This implies that C derived from dissolving detrital carbonate is ultimately lost through isotopic exchange with soil CO_2 and isotopic composition of pedogenic carbonate is determined by the isotopic composition of soil CO_2 (CERLING, 1984, 1991; CERLING et al., 1989; QUADE et al., 1989; CERLING and QUADE, 1992). We have shown that ^{14}C content of soil CO_2 can be depleted or enriched relative to that of atmospheric CO_2 depending on various factors. Soil carbonate formed during the early development of a soil, when ^{14}C content of soil organic matter is about the same as that of the atmospheric CO_2, could have ^{14}C ages younger than the true age of the pedogensis. On the other hand, carbonate formed later on in a soil, could have ^{14}C ages older than the true age of the carbonate precipitation. Elsewhere, we (AMUNDSON et al., 1993) explore in detail the effects of our diffusion/reaction model on carbonate ^{14}C ages.

CONCLUSIONS

The distribution of $^{14}CO_2$ in soils can be described by a diffusion-reaction model. The ^{14}C content of soil CO_2 varies with depth depending on many factors: the ^{14}C content of soil organic matter, the relative contribution of root respiration to total CO_2 production, soil respiration rate, atmospheric CO_2 concentration and ^{14}C content, soil properties, temperature, etc. Our model suggests that ^{14}C ages of pedogenic carbonate could be older or younger than the true age of pedogensis. While there are other factors that can also affect the ^{14}C age of a carbonate sample (such as sample thickness, i.e., the total time required to form the sample being measured), our basic understanding of the initial ^{14}C contents of pedogenic carbonates is the first step to critically evaluating their potential as indicators of landform age.

Editorial handling: E. J. Reardon

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