Effect of Climate on the Storage and Turnover of Carbon in Soils

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Executive Summary

Climate is, in many instances, the dominant variable controlling the storage of carbon in soils. It has proven difficult, however to determine how soil properties influenced by climate, such as soil temperature and soil moisture, actually operate to determine the rates of accumulation and decomposition of soil organic matter. Our approach has been to apply a relatively new tool, the comparison of ^{14}C in soil organic matter from pre- and post-bomb soils [Trumbore, in press (appended)], to quantify carbon turnover rates along climosequences. This report details the progress made toward this end by work under this contract.

1) We have completed studies of carbon turnover rates from sites located along elevation gradients in Hawaii and the western Sierra Nevada mountains in California. Elevation gradients were chosen as the most effective way to study climate influences on soils as they are constant in the soil forming factors of parent material and topography, but differ in vegetation and climate. Two manuscripts from this phase of the work are attached (one in preparation, summarizing both transects, and one in press in Ecology) have resulted from this study. One of these manuscripts (attached: Climate controls on soil carbon turnover), summarizes both climosequences, and the implications for response of soil carbon storage or release accompanying a temperature change, and serves as a summary of this research and its implications for the role of soils in the global carbon cycle.

2) We have completed a thorough study of the efficiency of different physically- and chemically-based fractionation methods at separating soil organic matter into pools which turn over on annual, decadal and centennial-millennial time scales. A preliminary manuscript summarizing this work (to be submitted to Radiocarbon) is also attached.

3) A separate modeling study to understand the controls of the ^{14}C-content of soil carbon dioxide was undertaken by Yang Wang, a postdoctoral researcher on this project. Two papers published from her work are attached. In addition, three graduate students and one undergraduate student at UCI have received part-time support from this grant.

Summary of Publications from this project:

Trumbore, S. E., O. A. Chadwick, and R. Amundson, Climate controls on soil carbon dynamics from climosequence studies, for submission to Global Biogeochemical Cycles, ms appended.

Townsend, A. R., P. M. Vitousek and S. E. Trumbore, The use of carbon isotopes to determine soil organic matter turnover along gradients of temperature and land-use on the Island of Hawaii. Accepted, *Ecology*.

Trumbore, S E, and Zheng, S. Comparison of fractionation methods for soil ^{14}C analysis inpreparaion for *Radiocarbon*, ms appended.

Trumbore, S E, Measurement of cosmogenic isotopes by Accelerator Mass Spectrometry: Applications to soil science (chapter 6 in *Mass Spectrometry of Soils*, T. Boutton and S. Yamasaki, eds, Marcel Dekker (New York) - in revision.

Wang, Y., R. Amundson and S. Trumbore, 1993. Processes controlling the 14C content of soil carbon dioxide: Model development. *Chemical Geology* 107:225-226.

Wang, Y., R. Amundson and S. Trumbore, A model for soil $^{14}CO_2$ and its implications for using ^{14}C to date pedogenic carbonate (in press) *Geochimica et Cosmochimica Acta*.

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Climate Control of Soil Carbon Dynamics

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ABSTRACT

Climate acts as one of the major controls of the storage and turnover of carbon in soils [Jenny, 1949; Jenkinson et al, 1991; Schimel et al, in press]. We investigated the importance of climate in determining the dynamics of soil organic matter by measuring carbon and ^{14}C in organic matter from soils spanning the range of elevations in the western slope of the Sierra Nevada National Forest, near Fresno, California. These soils form a 'climosequence', a series of soils which are similar to one another in soil forming properties such as parent material, soil age, and topography (relief, slope, sun angle), but experience different climate [Jenny et al, 1949]. The amount of soil organic matter in detrital and soil A horizon layers increases with elevation along this transect, primarily reflecting increases in the amount of low density and hydrolysable organic matter fractions (fast cycling carbon pools). Turnover times of these fast-cycling pools, derived from modeling the increase in ^{14}C in SOM since the end of atmospheric weapons testing in the early 1960's, show a marked decrease with increased elevation (decreasing temperature). The observed relation between temperature and organic matter turnover for the Sierra transect soils is similar to that observed in Histosols from an elevation transect in Hawaii [Townsend et al., in press]. Extrapolating this relation to predict the transient response of fast-cycling soil organic matter to a global temperature decrease of 1°C, we estimate a potential increase in the storage of carbon in fast-cycling pools of due to slowed decomposition rate of up to 1.3 PgC in one year.

INTRODUCTION

 Much of the uncertainty in recent assessments of the global carbon budget stems from the inability to measure directly the influence of the terrestrial carbon reservoirs. Soil organic matter (SOM) contains roughly two thirds of terrestrial carbon, two to three times more carbon than is present as CO_2 in the atmosphere [Schlesinger, 1977; Post et al., 1981; Eswaran et al, 1993]. One of the difficulties of understanding soil organic matter is that it consists of a complex mixture of compounds that accumulate and decompose at rates varying from months to millennia. The question of most importance to determining the role of soils in the global carbon cycle is how much of this mixture exchanges with atmospheric CO_2 on timescales of decades and less. Recent work using carbon isotopic approaches [O'Brien and Stout, 1978; Harkness et al., 1986; Balesdent et al, 1987; Scharpenseel et al., 1989; Trumbore et al, 1989; Vitorello et al., 1989; Jenkinson et al; 1992; Trumbore, 1993; Harrison et al., 1993; Townsend et al., in press], observations of carbon inventory changes in soils following land cover changes [Parton et al., 1987; Schimel, 1986; Davidson and Ackerman, 1993] and ecosystem modeling approaches [Jenkinson and Raynor, 1977, Parton et al., 1987; Van Bremen and Feijtel, 1990; McGuire et al., 1992; Potter et al., 1993; Schimel et al., 1994], has demonstrated that more than half of the soil organic matter in the upper 20-30cm of soils has turnover times of less than 100 years. Thus it is important to investigate carefully how the abundance and turnover time of these rapidly cycling components of SOM are controlled by such factors as vegetation, climate, soil texture and landform characteristics.

 Although SOM is an inhomogeneous mixture with a continuum of turnover times ranging from days to millennia, it is more tractable to model the soil by lumping components in to pools which turnover on annual (active pool), decadal to centennial (slow pool) or centuries to millennial (passive pool) timescales [Parton et al., 1987; Schimel et al, 1994]. The problem of quantifying soil organic matter dynamics then becomes one of determining the sizes and turnover times of these three pools, and understanding the physical and chemical bases underlying these divisions. Fast pools (mostly active plus some slow) determine the magnitude of annual carbon losses by decomposition, and thus at steady state will equal annual carbon inputs by detritus [Jenkinson et al., 1991; Schimel et al., 1994]. ^{14}C, the radioisotope of carbon (half-life = 5730 years), is useful in separating fast (active+slow) from passive carbon pools in soil organic matter.

The ^{14}C content of SOM collected before 1960 primarily reflects the influence of passive soil organic matter, in which carbon has resided in the soil long enough for significant radioactive decay. Passive pools may be isolated from bulk soil organic matter using physical and chemical fractionation procedures [Paul et al., 1964; Campbell et al., 1967; Martel and Paul, 1974; Goh et al., 1976, 1977, 1984; Scharpenseel et al., 1968a,b; 1984; Trumbore et al., 1989, 1990;Trumbore and Zheng, submitted]. The incorporation of ^{14}C produced in the early 1960's by atmospheric thermonuclear weapons testing ('bomb' ^{14}C) into soil organic matter during the past thirty years provides a direct measure of the amount of slow+active soil organic matter [Trumbore, 1993; Townsend et al, in press, O'Brien and Stout, 1984; Harrison et al., 1993]. A time-dependent modeling approach is used to link ^{14}C measurements of soil organic matter sampled prior to 1960 with that of contemporary samples. A large increase in ^{14}C content over the past thirty years indicates that significant portions of the soil organic matter are exchanging carbon with atmospheric CO_2 on decadal and shorter timescales. A comparison of ^{14}C in pre- and post-bomb soils also provides the best means to test the usefulness of various operationally defined separation procedures.

METHODS

Figure 1 shows the location of the Sierra Nevada climosequence, first described by Jenny et al. [1949]. Temperature and precipitation changes with elevation for the sites are summarized in Table 1, together with a description of vegetation and soil carbon inventories. Mean annual temperature decreases with elevation according to the atmospheric lapse rate. Precipitation increases rapidly to about 1000 m, then levels off. Most of the precipitation at higher elevations falls as snow. Vegetation also changes dramatically with elevation, from annual grasses in the Sierra foothills to pine forests at high elevation. Although we will summarize modeling results in terms of temperature controls on decomposition, it should be noted that other variables, such as the structure of vascular carbon inputs to the soil and precipitation also vary along the transect.

Soils sampled in 1958-1962 as part of the California Vegetation Survey were available from the archive at UC Berkeley. The samples were stored air-dry in sealed glass Mason jars. No samples of detritus were archived. We used the original field notes and topographic map locations to find and re-sample the same sites in 1992. Additional data on litterfall and detrital mass measured along the same climosequence are reported in Jenny et al [1949], although no data were available for elevations below 4000 m.

Soil carbon and surface detrital inventories were determined from %C and bulk density measurements (corrected for gravel contents of up to 35% at high elevation in soil A horizons). Per cent carbon data were determined by CO_2 evolution on *in vacuo* combustion at 900°C with cupric oxide wire. [14]C analyses were made by Accelerator Mass Spectrometry at the Center for AMS, Lawrence Livermore Laboratory, Livermore, California [Southon et al., 1992] from the purified CO_2. Graphite targets for AMS measurement were prepared using the sealed-tube, zinc reduction method modified from Vogel [1992]. [14]C data are reported as Δ^{14}C, the per mil difference in ^{14}C/^{12}C ratio between the sample and an absolute standard (oxalic acid decay-corrected to 1950; Stuiver and Polache, 1977). δ^{13}C values used to correct for mass-dependent fractionation effects were assumed to be -25‰ for all samples.

Soil organic matter was separated by density into fractions less and greater than 2.0 g/cc using sodium polytungstate [Trumbore, 1993; Trumbore and Zheng, in preparation]. The low density fraction consists of relatively undecomposed vascular plant matter and a small quantity of charcoal. The dense fraction (>2.0 g/cc) is predominantly mineral associated organic matter. Further treatment of the dense fractions (>2 g/cc) with a sequence of acid-base-acid (0.5N HCl; 0.1 N NaOH- Na; hot 6N HCl) isolated a residue which was always depleted in ^{14}C compared to the starting material. This residue was assumed to represent the Δ^{14}C value and minimum carbon content of the passive pool. We report carbon inventory and ^{14}C data for low density (LF) fraction, the hydrolysable organic matter with density >2.0 g/cc (HYD; calculated by mass balancing C and ^{14}C between the untreated dense fraction and the residue), and the hydrolysis residue (RES) in Table 2.

RESULTS

Changes in carbon inventory and ^{14}C with elevation are summarized in Table1 (litter), Table 2 (soil A horizon) and Figures 2a, b. The total amount of carbon in both litter and mineral soil A horizons increases substantially with elevation. The exception to this is the Chiquito soil (highest elevation), which showed evidence of surface erosion (rills and collection of detritus upslope of fallen tree trunks). Figure 2a compares the carbon inventory in surface detritus measured in this study with the data reported by Jenny et al. [1949].

The inventory of carbon in the soil A horizons (Figure 2b) equaled or was less than that in surface detritus at all elevations. Most of the increase in total

carbon inventory with elevation is due to increases in the low density(LF) and hydrolysable components (HYD). The amount of residual carbon after hydrolysis of the dense fraction in acids and bases (RES) is highest in the Musick soil, which also has the greatest clay content of any of the transect soils.

One of the assumptions implicit in our comparison of ^{14}C in pre- and post-bomb soils is that all organic matter pools have remained at steady state over the past 30 years. The carbon inventory data given in Table 1 and Figure 2b are for 1992 soils. Differences of carbon inventory between 1959 and 1992 profiles in mineral associated organic matter are less than 10% of the 1992 values for 3 of the 5 soils. The Chiquito, 1959 and Shaver, 1959 dense fractions had higher inventory than 1992 values by 100% and 65% respectively. Differences in LF inventory between 1959 and 1992 samples (which vary by less than 50% of the 1992 values in all cases) may be due to differences in sampling and in the treatment of samples prior to storage (for example, by selective removal of larger roots). The fractional distribution between hydrolysable and nondydrolysable components was the same for both soils, though total inventory of dense material differed between 1959 and 1992 soils. We assume the carbon isotopes within each modeled component (LF,HYD,RES) will be independent of the relative amount of the component present, making spatial heterogeneity less important within a soil unit than the relative mix of LF, HYD and RES components.

Detrital Layers

Jenny et al [1949] report litterfall data based on one year of litter collections at the sites above 1200 m elevation along this transect. Turnover times calculated by dividing carbon inventory by annual litterfall [Jenny et al., 1949], ranged from 8 to 115 years, and showed significantly faster turnover for deciduous than evergreen detritus (see Figure 3). As litterfall data were not available for the sites sampled in 1992, we assumed litter could be approximated as a homogeneous pool with a single average turnover time. We then compared the ^{14}C content observed in homogenized litter in 1992 to values predicted for a single pool at steady state with varying turnover times [see Harrison et al., 1993]. The measured ^{14}C data are compared in Figure 4a, with 1992 ^{14}C values predicted using the turnover times derived for the detrital layers measured by Jenny et al. [1947]. Good agreement between the two approaches and data sets is observed at mid-elevations, while at high elevations, the detrital layer in the 1992 Chiquito soil is probably affected by erosion (which causes an underestimate of turnover time). Turnover times for detritus based on ^{14}C will

include the residence time of needles and branches on trees (which may be up to several years for evergreens at high elevations).

Soil A Horizons

Figures 4b, 4c, and 4d show the ^{14}C increase between 1959 and 1992 for A horizon LF, HYD and RES fractions. Fractions with slowest turnover are expected to have the least ^{14}C initially, and the smallest increase in ^{14}C over the past 30 years. Based on these criteria, the RES fraction has the longest turnover time (and will be used in modeling as representing the passive pool). Low density carbon (LF; Figure 2b) shows the largest increase between 1959 and 1992 (the Fallbrook soil was collected in 1962. The ^{14}C values for atmospheric CO_2 in the 1950's and in 1992 (and therefore plant carbon fixed during these years) are indicated on Fig 4b by arrows at roughly -25‰ and +140‰ [Stuiver and Quay, 19xx; Camargo, in preparation]. ^{14}C values of LF in archived soils were less than the ^{14}C content of the atmosphere in the 1950's (which shows the effect of dilution with ^{14}C-free fossil-fuel derived CO_2; Suess,), indicating the presence of some inert or passive fraction (most probably charcoal, see below). ^{14}C values in 1992 LF generally decrease with elevation, ranging from slightly above present-day atmospheric values in the Fallbrook soil (lowest elevation) to below-1992 values at higher elevations. Fast turnover of LF at the low elevation site (Fallbrook) is evidenced by the presence of significant amounts of bomb ^{14}C in the 1962 archived soil. ^{14}C values in the hydrolysable dense organic matter (HYD fig 4c) are intermediate between RES and LF fractions.

Models

A three-component model was used to determine the distribution and turnover rates of carbon in active, slow and passive components needed to reproduce the observed increase in ^{14}C for density <2.0 and >2.0 fractions [described in detail in Townsend et al., in press; Trumbore et al., in preparation]. Turnover times in the model were constrained to be one year for the active pool, and by the observed ^{14}C content of the RES fraction in archived soils for the passive pool. The amount of RES carbon was also used to set the minimum size of the passive pool. The turnover time of the slow pool was then adjusted until both archived and 1992 ^{14}C values were matched. An additional constraint (which limited the amount of active SOM to close to zero everywhere but in the Fallbrook soil) was the total annual carbon flux through the soil. One estimate for this is obtained from the above-ground litterfall data of Jenny et al [1949], which ranged from 80 to 160 gC m^{-2} a^{-1} (1300 to 3000m elevation). A second estimate

was derived using the relation of temperature, precipitation and CO_2 flux from Raich and Schlesinger (1991). We assumed 50% of the total soil respiration, or roughly 200-300 gC m^{-2} a^{-1} as calculated using Raich and Schlesinger (1991) for these soils, was due to CO_2 released by decomposition.

We modeled LF (density <2.0) and HF (density >2.0 g/cc) fractions separately, as each contained slow and passive components. We derived total turnover times for active, slow and passive pools by adding together the amount of active, slow or passive carbon in LF with that in HF, and dividing the sum for each pool by the sum of annual carbon flux through it (calculated by summing contributions to the total flux (amount/turnover time) from active, slow and passive components of LF and HF). As only the Fallbrook soil showed a significant amount of carbon in the active pool, and to facilitate comparison with reults from other locations and models (see below), active+slow pool turnover times were combined in the same matter. The results are summarized in Table 3.

The modeling of the LF fraction was complicated by the presence of charcoal. As there were no fires at these sites between 1959 and 1992 collections, any charcoal present in the soil will contain pre-bomb carbon, which serves to dilute ^{14}C content of vascular plant remain components of LF. Visual inspection of the LF material revealed charcoal, but no attempt was made to quantify what proportion of the total carbon was in this form. In order to match both 1959 and 1992 LF ^{14}C values, between 5 and 15% of the carbon was required to be inert, with ^{14}C values of -50‰. Large amounts of active carbon (constrained as having one year turnover) were precluded by the high inventories of carbon in low density fraction, coupled with the knowledge that carbon inputs are probably of the order of 5% or less of LF carbon inventories.

The dense fraction ^{14}C content could be modeled reasonably well using the abundance and ^{14}C content of the RES fraction as representing the passive pool. The HYD fraction was then nearly all in the slow pool. Turnover rates in the HF slow pool were equal to or slightly greater than those in the LF slow pool for the same soil.

The turnover times for combined active+slow A horizons are plotted with surface detrital values in Figure 3. Fast cycling components of A horizon soil organic matter show an increase in turnover time with elevation similar to that observed in surface detritus.

The utility of the physical and chemical fractionation procedures at separation of SOM directly into active, slow and passive constituents is assessed in Table 3. The sum of active +slow carbon inventory is 77 to 98% of the sum of LF + HYD. Thus LF+HYD is a good predictor of the amount of active+slow carbon in these soils. This is not true for other soils, such as Histosols, which do not show large differences in ^{14}C on fractionation (Goh et al., 1977, 1984; Trumbore and Zheng, submitted).

Discussion

Figure 5a plots the turnover times of the active plus slow pools from the Sierra Nevada climosequence against mean annual temperature. The results from another elevation-based climosequence on Histosols in Hawaii [Townsend et al, in press] are also shown, along with a datum representing an Oxisol from the Amazon Basin, Brazil [Trumbore et al., in preparation]. Although these soils differ widely in vegetation cover, precipitation, and soil parent material, the strong relation between turnover time of the combined active + slow pools and temperature demonstrates that it is strong controlling factor on the dynamics of carbon in soils, as argued in recent modeling and data-based studies [Jenkinson et al; 1991, McGuire et al., 1992; Buol et al., 1993; Potter et al., 1993; Schimel et al., 1994]. Litter turnover times derived from ^{14}C for the Sierra soils also show a relation of decomposition to temperature similar to (or steeper than) that for soil A horizon active+slow pools (see Figure 3).

The carbon inventory contained in active+slow pools in these soils is plotted in Figure 5b. At each site, the active +slow carbon makes up more than 60% of the total carbon in the soil A horizon, and carbon inventory within each climosequence is inversely related to temperature. The slopes derived from the two climosequences are similar (excluding the Chiquito soil in the Sierra transect), although the absolute amount of carbon is much greater in the Hawaii climosequence soils.

The temperature relation to carbon abundance and turnover in active + slow pools observed in these regional scale elevation gradient studies are compared in Figures 5a and 5b with results derived from global ecosystem models [Potter et al., 1994; Schimel et al; 1994]. The carbon inventory and turnover rates of active+slow soil carbon pools derived from the CASA model [Potter et al., 1994, and Potter, personal communication, 1994], averaged into

10° latitude bands, are plotted using small cross symbols. The model-derived turnover times are a less strong function of mean annual temperature than the climosequence-based relation. Exponential fits to the climosequence (+Brazil soil) data give the following relation between turnover time and man annual temperature (MAT):

$$\text{Turnover(A+S)} = 74 \cdot \exp(-0.074 \cdot \text{MAT}) \qquad 1),$$

while a fit to the model-generated points is:

$$\text{Turnover(A+S)} = 41 \cdot \exp(-0.0546 \cdot \text{MAT}) \qquad 2).$$

The importance of soil organic matter and detrital pools in sequestering or releasing carbon given a temperature change may be estimated using equations (1) and (2), and the estimates of carbon storage by latitude taken from Potter et al [1994]. We assume that a transient temperature change, such as a decrease in MAT caused by a large volcanic eruption, will act to slow carbon losses from soil by decomposition, while leaving carbon inputs unchanged. The transient (one year of forcing) response of the global active+slow carbon pools is then estimated using the data in Table 4 for carbon inventory, and using turnover times calculated using equations 1 and 2:

$$\Delta(\text{carbon storage}) = \text{Inputs} - \text{Outputs}$$
$$= \text{C inventory/turnover(MAT)} - \text{C inventory/turnover(MAT-1)}$$

The data used for this calculation (Table 4) are lumped into 5 latitude bands, with distribution of land area by latitude derived from Potter et al. [1994].

The results for both the climosequence and model-derived relations for turnover vs. MAT show the potential for one-year storage of 1.2 to 1.3 Pg of carbon in active+slow pools of soil A horizons with a 1°C decrease in MAT. The largest changes in soil carbon storage occur at low latitudes (high MAT). Change in the carbon inventory in any given soil would be undetectable (<3% of A horizon inventory). Further storage would presumably occur in surface detrital layers, which have a similar or steeper response of turnover rates to MAT (Fig 3). These calculations ignore some important complicating factors, such as a probable slowing of carbon inputs

to the soil by vegetation at lowered MAT, and feedbacks between slowed decomposition and plant productivity (Schimel et al., 1994). In addition, the climosequences studied integrate long-term adjustment of ecosystems to climatic conditions, and transient responses may not be predictable from climate sensitivity derived from these data. However, they serve to illustrate that changes in MAT can potentially cause a globally important transient response by storing or releasing carbon from active+slow carbon pools. This response may provide a partial explanation for a slowing of the rate of atmospheric CO_2 increase in 1993, associated with global cooling following the eruption of Mt. Pinatubo [NOAA Climate Atlas, 1993].

Conclusions

Temperature is major control on the dynamics of organic matter which turns over on decadal and shorter timescales in soil A horizons. The relationship derived for turnover time vs temperature from climosequence studies is more sensitive to mean annual temperature changes than a relationship derived from the CASA global ecosystem model [Potter et al., 1994, Schimel et al; 1994].

The data presented here represent only two climosequences, from soils with very different vegetation, precipitation and temperature. Although more data are needed to provide a better understanding of climate controls on carbon turnover in soils, the data presented here demonstrate the usefulness of the climosequence approach. In particular, a better understanding of controls on carbon turnover in tropical soils is needed, as the response there is most sensitive. Comparison of the highest temperature points from climosequences in Figure 5a suggests considerable textural or vegetation controls may be important in these soils.

Fractionation of soil organic matter, while not a perfect indicator of the distribution of turnover times, is useful indicator of which physical portions of the soil organic matter are more labile and more refractory. In the Sierra transect sequence, low density and hydrolysable mineral-associated organic matter made up the active and slow pools (with the exception of charcoal present in the low density fraction), while the residue left after hydrolysis of mineral-associated organic matter in acids and bases provided a reasonable estimate for the size and turnover time of passive soil organic matter (once again, with the exception

of charcoal). These fractionation procedures appear to be most useful in soils with sandy or silty parent material; clay dominated soils, such as the Hawaii climosequence soils, do not show large differences in ^{14}C among these particular fractionation methods [Townsend et al., in press; Trumbore and Zheng, in preparation].

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Figure Captions

Figure 1. Location of Sierra Nevada Transect in Fresno County, CA. Approximate locations of the 5 soils on the elevation transect are also shown.

Figure 2. Carbon inventory in surface detrital (litter) layers (Fig. 2a), from this study and from Jenny et a [1947]. Figure 2b. Carbon inventory changes with elevation for the bulk A horizon soil organic matter (total), fractions with density <2.0 (LF), and hydrolysable (HYD) and nonhydrolysable components of the fraction with density >2.0 g/cc.

Figure 3. Changes in detrital layer turnover time with elevation along the Sierra transect. Turnover times from data in Jenny et al [1947] (squares) were calculated by dividing the detrital inventory by the annual litterfall (both were assumed to have the same %carbon). Turnover times for 1992 Sierra transect litter were determined from the 14C content of homogenized litter, assuming that litter may be represented using a single turnover time and is at steady state (Fig 4a). Estimated turnover times for A horizon active+slow components (derived later) are shown for comparison.

Figure 4. Comparison of carbon-14 contents for organic matter fractions isolated from Sierra Nevada transect soils (1950's and 1992). Negative $\Delta^{14}C$ values indicate that carbon in a given fraction has had sufficient time to undergo radioactive decay (half-life of radiocarbon is 5730 years), while positive values

indicate the presence of bomb-produced ^{14}C. Lowest initial ^{14}C values and the smallest increase in 14C over the past 30 years are observed in the RES fraction; highest initial 14C and greatest ^{14}C increase occur in the LF fraction.

Figure 5a. Estimated turnover times in active+slow pools (see Table 3) from modeling of ^{14}C increases in density <2.0 (LF) and density >2.0 fractions. Data from a similar elevation transect study in Hawaii [Townsend, Ph.D. dissertation, and Townsend et al., 1994 in press], and a single datum representing carbon dynamics derived from 14C and carbon flux measurements in the eastern Amazon basin [Trumbore et al., in preparation; Camargo et al., in preparation]. Crosses (identified in the legend as GLOBAL) are derived from results of the CASA global ecological model [Potter et al., 1994; and Potter, pers. comm.]. Curve fits used for equations 2 and 3 in the text are also shown. Figure 5b. Carbon inventory in active+slow pools for the same soils and model results. These represent >50% of the total soil carbon in all cases.

Table 1. Climate and vegetation of Sierra Nevada study sites

Soil	Elevation m	Temp °C	Precip mm	Litter gC m^{-2}	Vegetation
Fallbrook	470	17.8	31	637	annual grasses, blue oak
Ahwahnee	730	15.0	69	1456	blue oak, canyon live oak, manzonaita, red bud, poison oak
Musick	1240	11.7	94	4340	ponderosa pine, incense cedar, sugar pine, white fir, bear clover manzanita.
Shaver	1780	8.9	102	5042	white fir, ponderosa pine, sugar pine
Corbett	1950	8.0	106	5590*	white fir, ponderosa pine, sugar pine
Chiquito	2890	3.3	127	2389*	sierra junpier, western white pine, lodgepole pine

* affected by surface erosion.

Table 2. Carbon inventories and ^{14}C in fractonated soil organic matter.

Soil	depth of A1	clay %	ALF gC m^{-2}	HYD gC m^{-2}	RES gC m^{-2}	$\Delta^{14}C$ LF		$\Delta^{14}C$ HYD		$\Delta^{14}C$ RES	
						1959	1992	1959	1992	1959	1992
Fallbrook	12cm	10	747	480	60	+65 (1962)	+174	-23	+112	-170	-140
Musick	19 cm	22	3300	1203	597	-47	+132	-54	+31	-74	-70
Shaver	20 cm	8	5355	2075	159	-31	+130	-62	+98	-173	-143
Corbett	23 cm	8	5490	516	129	-32	+155	-28	+132	-116	-24
Chiquito	17 cm	8	3292	355	121	-40	+93	-	-43	-	-196

Soil inventory data are from 1992 collected profiles. Differences of carbon inventory between 1959 and 1992 profiles are up to less than 10% of the 1992 values, with following exceptions:Chiquito, 1959 and Shaver, 1959 dense fractions had higher inventory than 1992 vlaues by 100 and 65% respectively. Differences in LF inventory between 1959 and 1992 samples (which vary by less than 50% of the 1992 values in all cases) may be due to the treatment of sample after air-drying. We assume steady state profiles for all models.
The fractional distribution between hydrolyzable and nonhydrolyzable components was the same for both soils, though total inventory of dense material differed.

Table 3. Model results partitioning carbon into Active, Slow and Passive pools.

Soil	INVENTORY gC m^{-2}			TURNOVER, years		$\frac{A+S}{LF+HYD}$	$\frac{P}{RES}$
	A	S	P	A+S	P		
Fallbrook	103	1101	86	10	1700	0.98	1.4
Musick	0	3480	1620	38	162	0.77	2.7
Shaver	0	6383	1206	50	744	0.86	7.6
Corbett	0	5215	920	35	1000	0.87	7.1
Chiquito	0	3069	698	61	1927	0.84	5.8

Table 4. Predicted Chnage in Carbon Inventory from a 1°C change

Latitude	kgC m^{-2} in A+S	MAT °C	Land area 10^6 km^2	ΔC (Pg) (eq 2)	ΔC (Pg) (eq 3)
60-90 N	4.224	-5.0	21	0.058	0.087
60-30 N	3.647	10.0	36	0.256	0.294
30-0 N	2.331	24.3	43	0.556	0.491
0-30 S	2.667	24.2	29	0.424	0.375
30-60 S	1.003	27.0	3	0.020	0.017
Total	13.872	16.1	132	1.313	1.264

Estimates of carbon inventory and land area as a function of latitude arefrom Potter et al [1994] and C. Potter, pers. com, 1994. Changes in turnover time were calculated using equations 2 and 3 in the text. The calcuation of change in carbon inventory equals the carbon inventory/turnover time(MAT) minus carbon inventory/(MAT-1).
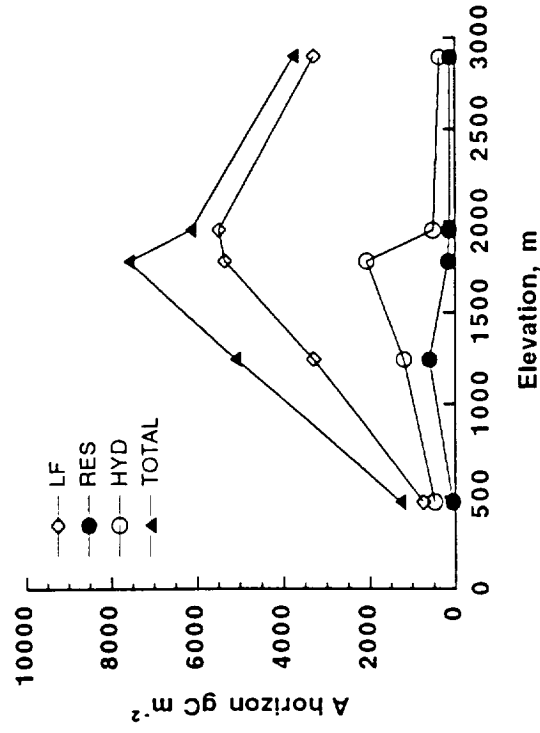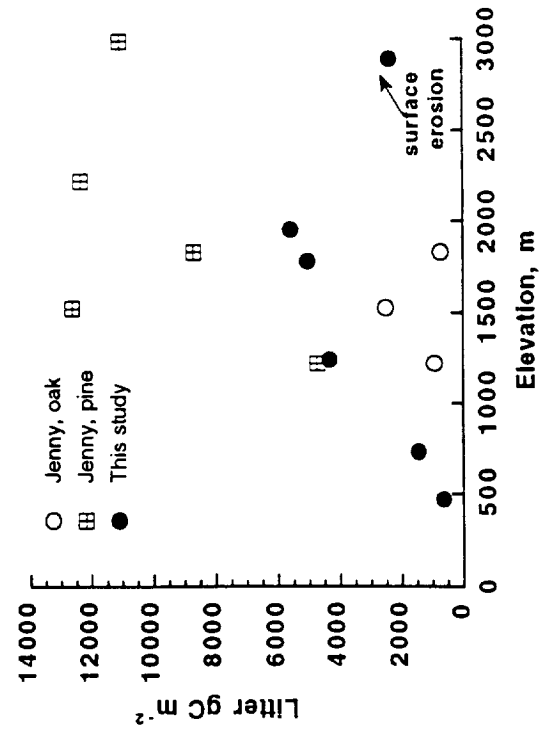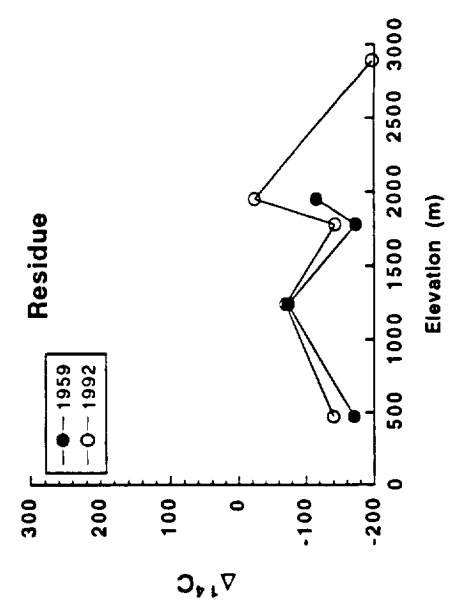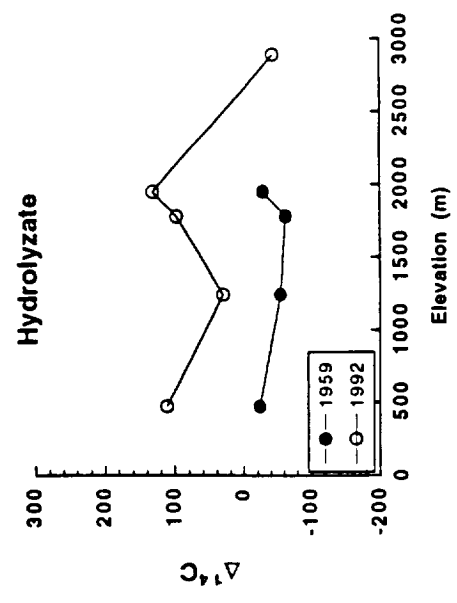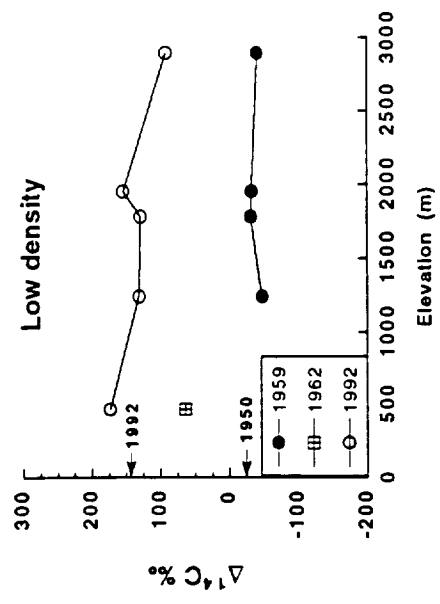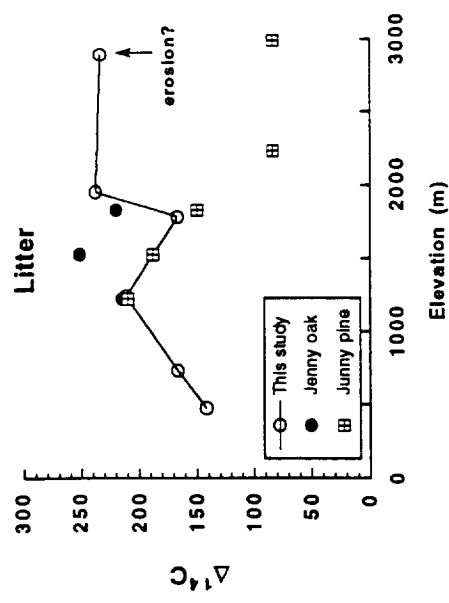
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PRECIPITATION

	T °C	P cm
	5.8	91
2000m	7.3	85
1500m	10.3	76
1000m	13.0	70
500m	15.0	60

After Fig 12.9, 12.10 in Jenny, 1980

Figure 1

Fig 2

Fig 3

Fig 4

Fig 5.,

Left plot: Turnover, S+A, years vs Mean Annual Temperature °C
Legend: Hawaii (○), Brazil (⊞), Sierra (●), GLOBAL (+)

Right plot: S+A Inventory, gC m⁻² vs Mean Annual Temperature °C
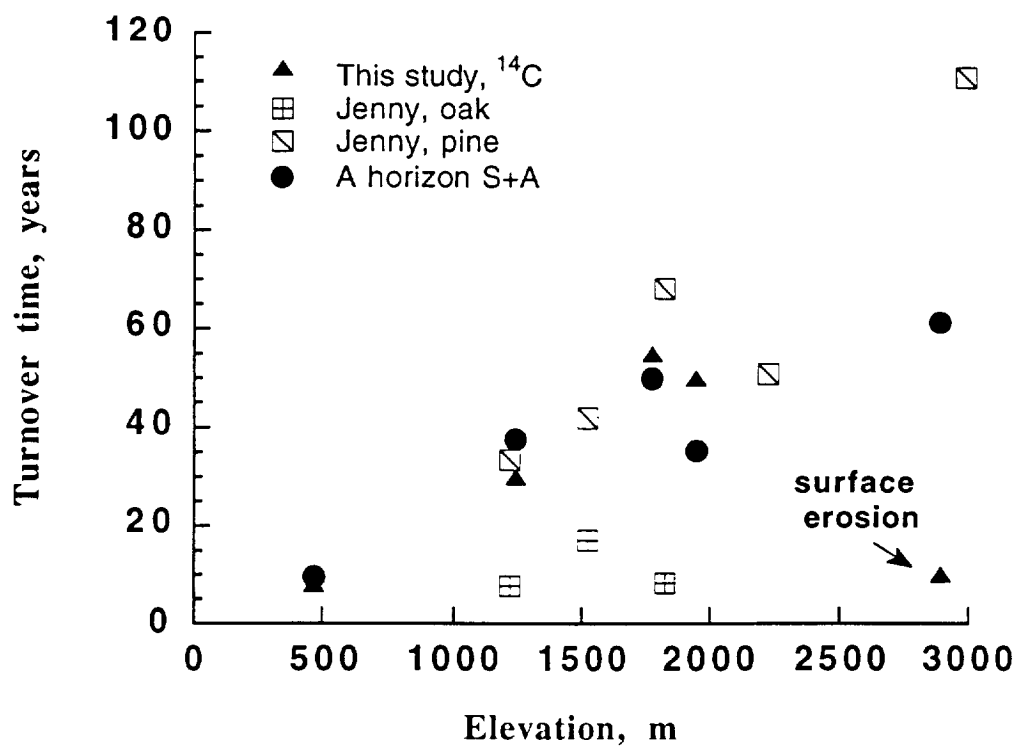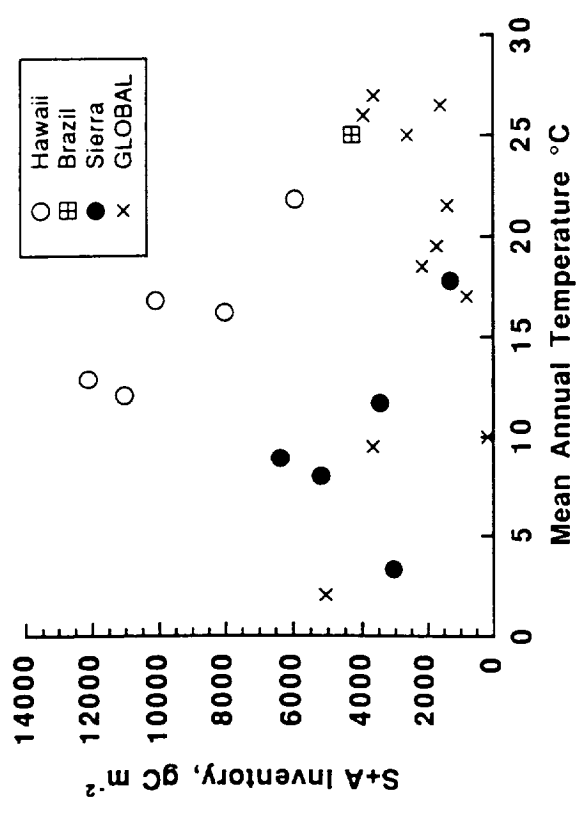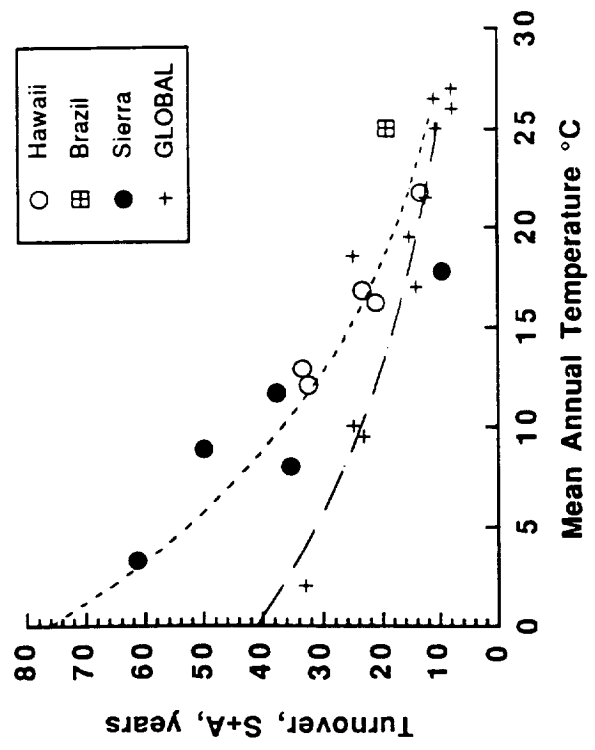Legend: Hawaii (○), Brazil (⊞), Sierra (●), GLOBAL (×)

Comparison of Fractionation Methods for Soil Organic Matter ^{14}C Analysis

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ABSTRACT ^{14}C measurements provide a useful test for determining the degree to which chemical and physical fractionation of soil organic matter are successful in separating labile and refractory organic matter components. Results from AMS measurements of fractionated soil organic matter made as part of several projects are summarized here, together with suggestions for standardization of fractionation procedures. While no single fractionation method will unequivocally separate soil organic matter into components cycling on annual, decadal and millennial timescales, a combination of physical (density separation or sieving) and chemical separation methods (combined acid and base hydrolysis) provides useful constraints for models of soil carbon dynamics in several soil types.

INTRODUCTION

Models describing the dynamics of accumulation and turnover of organic carbon generally recognize components of soil organic matter (SOM) which turn over on annual (active), decadal (slow), and centennial to millennial (passive) time scales [Jenkinson and Raynor, 1977, Parton et al., 1987; Van Bremen and Feijtel, 1990; O'Brien and Stout, 1978; McGuire et al., 1992; Potter et al., 1993; Schimel et al., 1994]. While these concepts have proven useful in explaining the magnitude and timing of changes in SOM following a perturbation such as land clearing for cultivation [Parton et al., 1987; Schimel, 1986; Cambardella and Elliott, ;Davidson and Ackerman, 1993], no recognized method now exists for determining how to apportion SOM into compartments which turn over on different time scales. To be useful for dividing soil organic matter into components useful for ecosystem modeling, a procedure must determine both the pool sizes and turnover rates.

Two methods are presently in use to partition soil organic matter into active, slow and passive pools. The first models the observed increase of ^{14}C during the 30 years since the end of atmospheric weapons testing, using

additional constraints derived from knowledge of carbon inputs to the system [O'Brien and Stout, 1978; Harkness et al., 1986; Balesdent et al, 1987; Scharpenseel et al., 1989; Trumbore et al, 1989; Vitorello et al., 1989; Jenkinson et al; 1992; Trumbore, 1993; Harrison et al., 1993; Townsend et al., in press]. The second relies on physical and/or chemical fractionation methods to separate SOM into pools which turn over on different time scales [Paul et al., 1964; Campbell et al., 1967; Martel and Paul, 1974; Goh et al., 1976, 1977, 1984; Anderson and Paul, 1984; Scharpenseel et al., 1968a,b; 1984a,b; Trumbore et al., 1989, 1990; Trumbore et al., in preparation]. Radiocarbon measurements of pre-bomb SOM fractions are interpreted as indicative of their turnover rates. A test of the efficiency of any fractionation method at isolating a relatively homogeneous (in terms of turnover) organic matter pool is a comparison of the observed ^{14}C increase since atmospheric weapons testing (Goh et al., 1984; Trumbore et al., 1989; Trumbore et al., in preparation). These tests have shown that, while no fractionation method is completely successful, separation of OM by density, followed by hydrolysis in 6N HCl, does result in a collection of compounds which are on average, turn over more slowly than the hydrolyzed portions of SOM [Campbell et al., 1967; Martel and Paul, 1974; Goh et al., 1976, 1977, 1984; Anderson and Paul, 1984; Scharpenseel et al., 1968a,b; 1984a,b; Trumbore et al., 1989, 1990].

This paper will summarize measurements of ^{14}C made of soil organic matter fractionated using different physical and chemical separation methods. Both archived (pre-bomb) and contemporary soil samples have been analyzed. The implications of these data for soil carbon cycling is discussed in other publications (see Table 1 for references). This paper is in essence a 'date list' which will make the original data available to those interested in the effects of fractionation methods on the ^{14}C content of SOM.

Summary of Fractionation Methods

All samples are sieved to remove components >2mm. Chemical and density separation procedures have been described before (Trumbore et al., 1989; Trumbore, 1993), and are summarized in Figure 1. Basically three kinds of fractionation techniques are used: separation by density, chemical extraction using acids and bases, and separation by size.

1. Density separation. The density separation extracts organic matter of low density (<1.6-2.0 g cm-3) by flotation in a heavy liquid. The low density material

consists of plant matter and charcoal [Sollins et al, 1983; Spycher et al, 1983]. Dense fractions contain mineral-associated organic matter, and some microbial cell debris [Sollins et al, 1983; Spycher et al, 1983]. In general, the low density material turns over more rapidly than much of the soil organic matter.

2. Chemical Fractionation. Operationally defined fractionation procedures for SOM rely on extraction using acids and bases, which are hypothesized to remove more labile components, leaving behind more refractory (and therefore more ^{14}C-depleted) constituents. The data presented here compare the ^{14}C content of residues after hydrolysis in acid (HCl) of varying strength, and in base (NaOH or NaOH-Na-pyrophosphate). Because the extraction of fresh plant material by these techniques leaves a residue [Ertel and Hedges, 1984], we have chosen to perform acid and base hydrolysis on SOM which has been separated previously by density, and to treat only the denser portion of the soil further.

3. Size separation. Recent work has tied the dynamics of decadal-cycling SOM to different size fractions (Cambardella and Elliott, 1993; 1994), which has led to speculation about the role of soil aggregates in limiting the decomposition of reactive SOM constituents by physically protecting organic matter from soil microbial activity [Oades, 1993]. In addition, the limited measurements of ^{14}C in size fractionated organic matter available from the literature [Anderson and Paul, 1984] suggest a relationship between the size of soil-associated organic material and stability of associated organic matter. Recently, Mayer [1994] has shown that organic matter content is related to BET surface area in many soils and sediments. If organic matter is protected by stabilization on clay surfaces, we might expect it to have lower ^{14}C values than organic matter which is more available for microbial attack.

For the size separation, we used the <2mm sieved samples, without prior density separation. We measured the ^{14}C content of three size fractions: <2mm but >63μ, <63μ but greater than 2μ, and less than 2μ. The largest fraction was separated by dry sieving; the fractions > and < 2μ were separated by settling from a suspension [Folk]. This procedure breaks apart soil aggregates.

Per cent carbon data were determined by CO_2 evolution on *in vacuo* combustion at 900°C with cupric oxide wire [Buchanon and Corcoran, 1959]. [14]C analyses were made by Accelerator Mass Spectrometry at the Center for AMS, Lawrence Livermore Laboratory, Livermore, California [Southon et al., 1992] from the purified CO_2. Graphite targets for AMS measurement were prepared

using the sealed-tube, zinc reduction method modified from Vogel [1992]. [14]C data are reported as $\Delta^{14}C$, the per mil difference in $^{14}C/^{12}C$ ratio between the sample and an absolute standard (oxalic acid decay-corrected to 1950; Stuiver and Polach, 1977). $\delta^{13}C$ values used to correct for mass-dependent fractionation effects were assumed to be -25‰ for all samples.

Nomenclature: We adopt a shorthand for describing the fractionation treatment experienced by a sample. The descriptors, denoted in Figure 1, are defined as follows:

BS = Bulk soil. Due the expense of AMS measurements, we often rely on measurements of the constituent fractions to derive a bulk soil ^{14}C number by mass balance.

LD = low density fraction (less than 2.0 g/cc).

HD = Dense fraction. The density of heavy liquid used in the separation is identified by accompanying LD data.

Chemical fractionation. All chemical fractionation procedures are performed on the HD fraction, and the data associated with them refers to the residue after a given chemical separation procedure. A refers to acid hydrolysis at room temperature in 0.5 N HCl; B refers to extraction with 0.1 N NaOH- 0.1 N sodium pyrophospate; C refers to hydrolysis in 6N HCl at 95°C. Often, we show data derived from the residue of a combination of chemical fractionation procedures: for example A+B+C refers to the residue after sequential hydrolysis in 0.5N acid, 0.1N NaOH and 6N HCl. When performing these procedures, the residue after each extraction step is rinsed thoroughly in distilled H_2O before moving on to the next procedure.

Samples

We present here summaries of fractionation of soils from several different types. Table 1 summarizes the source of soils, and data related to soil classification and site-specific characteristics, such as climate and parent material. References discussing the carbon cycling in these soils, or containing more information about the soils, are also listed.

Results

Tables 2 and 3 show the carbon and ^{14}C content of the fractionated soil organic matter. To better compare the effects of fractionation methods on the different soils, the results are also plotted in Figures 2 and 3.

Density separation

Low density components consist primarily of fine root hairs, charcoal (found in all LD fractions, but not quantified separately), and surface detritus mixed into the soil (in Oxisols BS-7, BS-9). Low density material makes up a large portion of the total soil carbon in A horizons of more coarse-textured soils and the Histosol (which had the highest total carbon content, Table 2). The ^{14}C content of LD material is close to atmospheric $^{14}CO_2$ values at the time of collection in both pre- and post-bomb soils, indicating rapid turnover of this fraction.

In general, ^{14}C values of the dense fraction (mineral associated) carbon decreased with depth in the soil, as has been previously observed (Scharpenseel et al., 1989). Bomb 14C is present in HD fraction for soils sampled in the 1990's, indicating the presence of at least some fast-cycling carbon associated with soil mineral phases.

Acid-Base hydrolysis

In the more heavy-textured soils (those excluding the Shaver soil from the Sierra Nevada, California), most of the carbon present is associated with mineral surfaces (HD fraction). Hydrolysis of the HD fraction in relatively mild acids (0.5N HCl) removes greater than 30% of the mineral-associated carbon for all soils studied (see Figure 2a). The removal is greatest in Spodic B horizons (the Michigan soils samples, B1-56 and A1-52), where more than 70% of the organic matter is solubilized in 0.5 N HCl. The carbon remaining is depleted in ^{14}C compared to the starting dense fraction material to varying degrees (Fig 3a). Least affected are the Histosol (Hawaii) samples, most affected are the Spodic B horizons. Subsequent hydrolysis in base and strong acid removes more carbon and ^{14}C (Fig 2b and Fig. 3 a-c). The residue after A+B+C treatments is, in all but two cases, the most depleted in ^{14}C of any treatment. Figure 3 summarizes the difference in ^{14}C content of residual carbon after various treatments, compared to the starting dense material (1:1 line on Figures). Use of A+B treatment (Fig 3b) removes almost as much carbon and ^{14}C as the A+B+C treatment, while treatments using only acids (A+C; Fig 3c) do not remove as much C and 14C as treatments including a base hydrolysis step. The Histosols and Oxisols are

affected by chemical fractionation less than more coarse textured soils. The difference between unfractionated dense material and the A+B or A+B+C residues is smaller in A horizons of soils than in B horizons. This is more noticeable in profiles previously published in Trumbore et al. [1990].

Size fractionation

      The results of size fractionation on splits of the same soils in which density- and chemical procedures were used are reported in Table 3. Most of the carbon in more coarse textured soils was associated with the $> 63\mu$ fraction (Figure 2b), while in heavy-textured soils (Oxisol), most of the carbon is in the fine silt and clay fractions ($<63\ \mu$). Size separations were not performed on the Histosol (Hawaii) soils; these are dominated by fine-grained material. Size-fractionation of soils did not affect ^{14}C values as much as chemical fractionation (Fig 3d). We did not see any consistent tendency for clay-sized particles to have $\Delta^{14}C$ values much greater or less than other size fractions, although clay fractions both enriched and depleted in ^{14}C were observed.

Conclusions and Suggestions for a standard fractionation scheme.

      The usefulness of different fractionation methods depends in part on the type of soil, in particular on soil texture (clay content). Separation by density will concentrate organic matter which turns over fast (decades and shorter timescales) in the low density fraction. In coarse textured soils with granitic parent material, such as the Shaver soil (Sierra Nevada), low density organic matter can make up the majority of the total soil carbon. The remaining HD material shows significant increase in ^{14}C in A horizons of contemporary soils due to incorporation of bomb ^{14}C. Chemical treatment, especially hydrolysis in acid and base, removes relatively ^{14}C-enriched components of the dense, mineral-associated organic matter. Once again, chemical treatment is most effective in coarser textured soils, in part because more of the total carbon is removed in the hydrolysis procedure. Chemical extraction with acids and bases did not change the ^{14}C content of Histosol organic matter, even though up to 90- 95% of the original carbon was removed. This may be useful in understanding how organic carbon is stabilized in allophane soils.

      Large differences in ^{14}C content were not observed between different size fractions. Most of the carbon in coarse-textured soils is in the larger size fractions

(>63μ), and probably is mostly low density vascular plant material, though ^{14}C values indicate that this organic matter is diluted by other (mineral associated) constituents.

We suggest the most informative fractionation procedure to be used in separating soil organic matter into faster and slower cycling components combines density and chemical separation procedures. Low density organic material (except for charcoal) turns over on timescales of decades and less (see Trumbore, 1993; Trumbore et al., in preparation; Camargo et al., in preparation). Extraction of dense material with acid and base will leave a residue which can provide a minimum estimate of the size and 14C content of a passive pool in ^{14}C modeling. This fractionation will be most useful in soils of medium to coarse texture.

Acknowledgments

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FIGURE CAPTIONS

Figure 1. Fractionation scheme used for 14C measurements.

Figure 2. Per cent of total carbon in the residues left after acid and base hydrolysis treatments of the dense fraction (Fig 2a), and after size fractionation of bulk soil (Fig 2b).

Figure 3. $\Delta^{14}C$ of HF (x axis) compared to that measured in the residue after various chemical treatments (identitifed in panels). The 1:1 line and the $\Delta14C$ values for A+B+C (most ^{14}C-depleted treatment) are given on each figure for comparison.

TABLE 1. Summary of Characteristics of Soils Analyzed in the Fractionation Study.

ID	Location	Date Collected	Clay content	Soil Order/ Horizon	Vegetation/ Climate	Parent Material	Depth Interval	Ref.
BS-7	Paragominas, Brazil	1992	>85%	Oxisol / A	tropical forest	sediments	30-35 cm	1, 2, 3
BS-9	"	"	"	Oxisol / B	"	"	100-105 cm	
H-13	Lapahoehoe, Hawaii	1992	ND	Histosol	tropical pasture	volcanic	0-10 cm	4
H-15	"		"	(allophane)	"	ash (15 -25 ka)	40 cm	
NS-11	Shaver Lake, California	1992	7-8%	Ultisol / A	dry temperate	granodiorite	5-10 cm	5, 6
NS-13	"	"	"	Ultisol / B	pine forest		20-40 cm	
OS-9	Shaver Lake, California	1959	7-8%	Ultisol / A	dry temperate	granodiorite	0-15 cm	5, 6
OS-10	"	"	"	Ultisol / B	pine		15-58 cm	
A1-52	Michigan	1992	<2%	Anspodosol / B	moist, cool	beach sand, 3ka	52 cm	7
B1-56	"	"	"	"	temperate forest	" , 10ka	56 cm	

references:
1. Nepstad et al., in press; 2. Camargo et al., in preparation; 3.Trumbore et al., in preparation;
4. Townsend et al., in press; 5. Trumbore et al., in preparation; 6. California soil and vegetation survey
7. Barrett and Schaetzl, in press

Table 2. Results of Chemical Fractionation Procedures

	BS-C Density gC m^{-2} cm^{-1}	LD<2.0 g/cc %C$_t$	LD<2.0 g/cc Δ^{14}C	HD(>2 g/cc) %C$_{gr}$	HD(>2 g/cc) Δ^{14}C	A only %C$_d$	A only Δ^{14}C	A+B %C$_d$	A+B Δ^{14}C	A+B+C %C$_d$	A+B+C Δ^{14}C	A+C %C$_d$	A+C Δ^{14}C
BS-7	132	<5%	+170	1.0	-102.4	61.7	-195.0	32.3	-316.4	14.1	-302.5	37.4	-254.8
BS-9	50	<1%	ND	0.4	-552.0	72.0	-615.0	49.9	-723.2	15.4	-852.6	18.6	-662.7
H-13	ND	ND	ND	11.0	4.0	46.5	-16.3	20.1	36.7	25.6	44.7	22.0	21.4
H-15	ND	ND	ND	4.2	-660.8	62.1	-705.9	12.6	-723.5	12.0	-758.9	13.8	-676.2
NS-11	462	91.7	+109.3	1.5	92.6	12.2	4.9	8.2	-56.7	5.2	-86.5	7.0	-164.2
NS-13	98	73.5	+169.5	0.4	32.7	40.9	-55.2	18.1	-153.7	11.4	-167.7	16.8	-115.1
OS-9	383	85.1	-35.8	2.1	-36.5	13.0	-93.9	5.9	-167.2	4.0	-173.6	4.2	-91.5
OS-10	92	59.8	-30.9	0.4	-123.0	39.4	-145.3	20.3	-249.7	13.6	-345.6	2.4	-193.4
A1-52	ND	<5%	ND	0.7	-148.7	25.6	-298.6	7.3	-287.0	2.6	-324.7	8.8	-256.9
B1-56	ND	<5%	ND	1.0	-123.7	12.4	-231.2	4.7	-316.8	3.8	-328.4	6.6	-309.3

Sample identification is given in Table 1. Carbon density is calculated from bulk density data and %C. ND denotes soils for which bulk density data were not available. The first fractionation procedure was separation in density <2.0 g/cc (LD) and >2.0 g/cc (Dense, HD fraction). %Ct denotes the % of total carbon in LD fractions (D% is 100-LD%). ^{14}C was measured in LD material only when it made up a significant amount of the total soil carbon. Hawaii soils were not separated by density; the bulk data are listed in the HD column, though most of this material is probably low density. The starting material for chemical fractionation procedures was the HD fraction (>2 g/cc). Gravimetric %C data are given for this fraction (%C$_{gr}$).

Chemical procedures are as follows:

A = residue after extraction with 0.5N HCl at 95°C for 12 hours.

B = residue after extraction at room temperature for 24 hours with 0.1 N NaOH-0.1N Na$_5$P$_2$O$_7$

C = residue after extraction with 6N HCl at 95°C for 12 hours.

Combinations of chemical procedures are shown. For example A+B denotes that the results given are for the residual organic matter following treatment with first A, then B.

%C$_d$ is the per cent of the carbon in the original untreated dense fraction which remains after the chemical treatment. ^{14}C data are reported as Δ^{14}C, the per mil deviation of the ^{14}C/^{12}C ratio to the ^{14}C/^{12}C ratio of oxalic acid standard in 1950. We have assumed δ^{13}C of -25‰ for the purpose of calculating Δ^{14}C for all samples, all vegetation cover for these soils was C3 plants. The one sigma error of the ^{14}C measurements is ± 10 ‰ to 15‰.

Table 3. Results of Size Fractionation Procedures

Sample	2mm > S > 63μ			63μ > S > 2μ			<2μ		
	%C	%C_t	$\Delta^{14}C$	%C	%C_t	$\Delta^{14}C$	%C	%C_t	$\Delta^{14}C$
BS-7	3.9	10.6	7.6	1.53	41.3	-92.5	1.0	48.1	-107.4
BS-9	0.4	33.3	-465.8	0.40	65.0	-499.7	0.52	1.6	-368.6
NS-11	11.2	61.3	82.9	3.48	38.7	67.5	-	-	
NS-13	0.8	69.5	11.0	1.71	29.1	41.7	4.5	1.4	73.8
OS-9	2.2	63.5	-54.4	4.73	36.3	-41.5	7.8	0.2	-55.1
OS-10	0.9	64.2	-108.1	1.79	34.2	-51.6	2.9	1.6	-271.3
A1-52	0.6	87.8	-128.8	12.55	12.2	-103.0	very little clay		
B1-56	0.6	93.1	-113.3	15.24	6.9	-91.6	very little clay		

Bulk Soil (sieved to <2mm)

Sieve
(63μ)

Density Separation
using heavy liquid

>63μ
<63μ

Suspension
(clays)

Light Fraction
undecayed vascular
plant material,
charcoal

Dense Fraction
cell wall debris,
mineral bound
organic matter

>2μ
<2μ

0.5 N HCl

RESIUDE
A

A+C

$0.1\ N\ NaOH\ -$
$0.1N\ Na_5P_2O_7$

RESIUDE
A+B

6N HCl (hot)

RESIUDE
A+B+C

Figure 1.

Carbon Distribution by Size

Soil

B1-56
A1-52
OS-10
OS-9
NS-13
NS-11
H-15
H-13
BS-9
BS-7

%C11
%C12
%C13

% Total Carbon in Fraction

0 20 40 60 80 100

Carbon in chemical fractions

Soil

B1-56
A1-52
OS-10
OS-9
NS-13
NS-11
H-15
H-13
BS-9
BS-7

A%CT
AB%CT
ABC%CT
AC%CT

Per cent of HF carbon

0 10 20 30 40 50 60 70 80

Fig 2

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

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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 or-

ganic 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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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):

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

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.
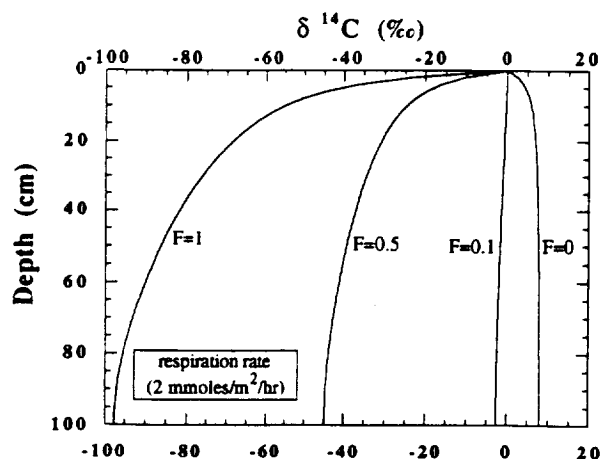

FIG. 1. $\delta^{14}C$ value of soil CO_2 vs. depth for a model soil. It shows that the $\delta^{14}C$ values of soil CO_2 vary with depth from the (pre-atomic bomb) atmospheric value at the soil-atmosphere interface to more negative or more positive values at depth depending on the value of F.

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

$\delta^{14}C_{o.m.} = 1.1176 - 1.7317 \cdot$ depth
Temperature = 15°C
Pressure = 1 atm
Respired CO_2: $\delta^{13}C = -26‰$
Atmospheric CO_2: 300ppm, $\delta^{13}C = -6‰$
Porosity = 0.5
tortuosity factor = 0.61

The diffusion coefficients of $^{14}CO_2$ and $^{12}CO_2$ are related by

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

$$= 1.00868.$$

Using Eqns. 6, 7, and 8 and using various values of soil respiration, an atmospheric CO_2 concentration of 300 ppm, and atmospheric $\delta^{13}C$ and $\delta^{14}C$ values of $-6‰$ (pre-industrial value) and 0‰ (pre-bomb value), respectively, it is possible to calculate $^{14}CO_2$ ($\delta^{14}C$) profiles in soils for various conditions.

Figure 1 shows how the $\delta^{14}C$ 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 $\delta^{14}C$ 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 $\pm3‰$, and for most accelerator labs the analytical precision is $\pm8‰$. Therefore, when F is small, for example $F = 0.1$, the $\delta^{14}C$ value of soil CO_2 can be considered the same as that of atmospheric CO_2.

2) The $\delta^{14}C$ values of soil CO_2 are not constant with depth.

3) The $\delta^{14}C$ values of soil CO_2 depend on the $\delta^{14}C$ 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) $\neq 0$, the $\delta^{14}C$ 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 $\delta^{14}C$ values of soil CO_2 at any depth become more negative.

5) When $F = 0$, the $\delta^{14}C$ 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 $\delta^{14}C$ 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., $\Delta^{14}C$ in STUIVER and POLACH, 1977), this diffusion component will not be seen.

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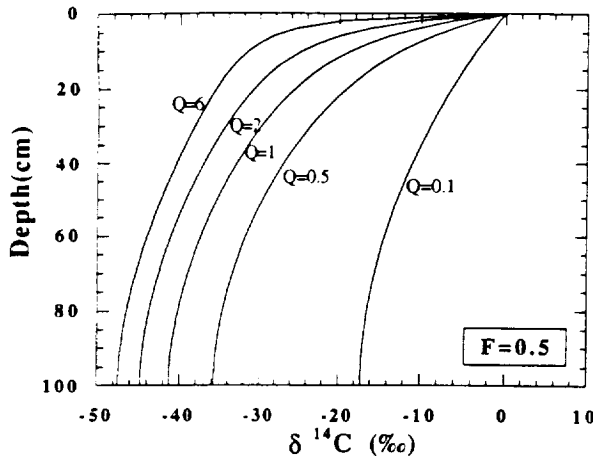
FIG. 2. Variations of the $\delta^{14}C$ values of soil CO_2 with soil respiration rates at a constant F value. The model shows that the higher the soil respiration rate, the more the $\delta^{14}C$ values of soil CO_2 deviate from that of the atmospheric CO_2.

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 $\dfrac{\partial C_s^{14}}{\partial z}$

= 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 $\dfrac{\partial C_s^*}{\partial z}$

= 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:

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

$$C_s^* = \frac{\Phi_s^*(0)(chz^2)}{D_s^*}(1 - e^{-z/chz})$$

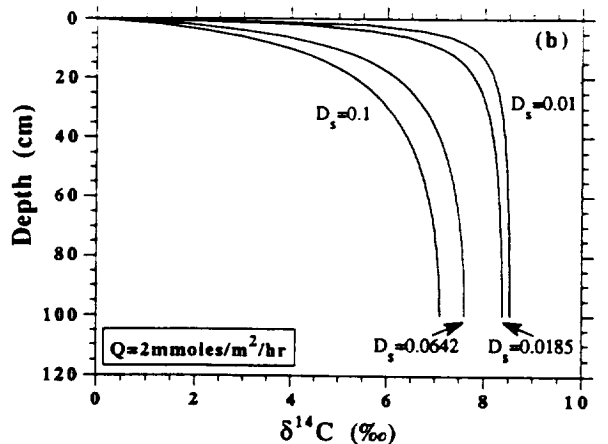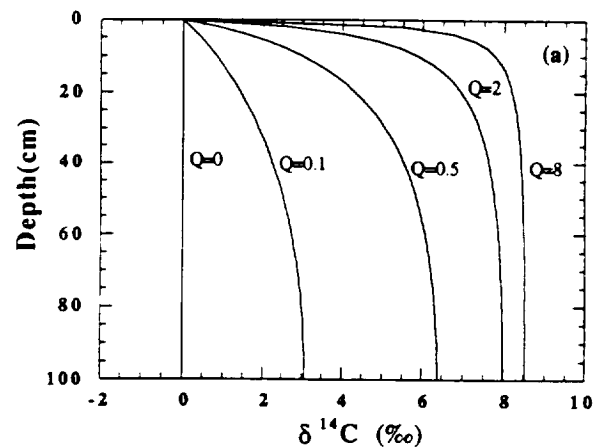$$- \frac{\Phi_s^*(0)(chz)(z)}{D_s^*}e^{-L'/chz} + C_a^*, \quad (10)$$

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.

3

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

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 (cm2/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

^{14}C content is elevated above natural levels by nuclear weapons testing and use.

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,
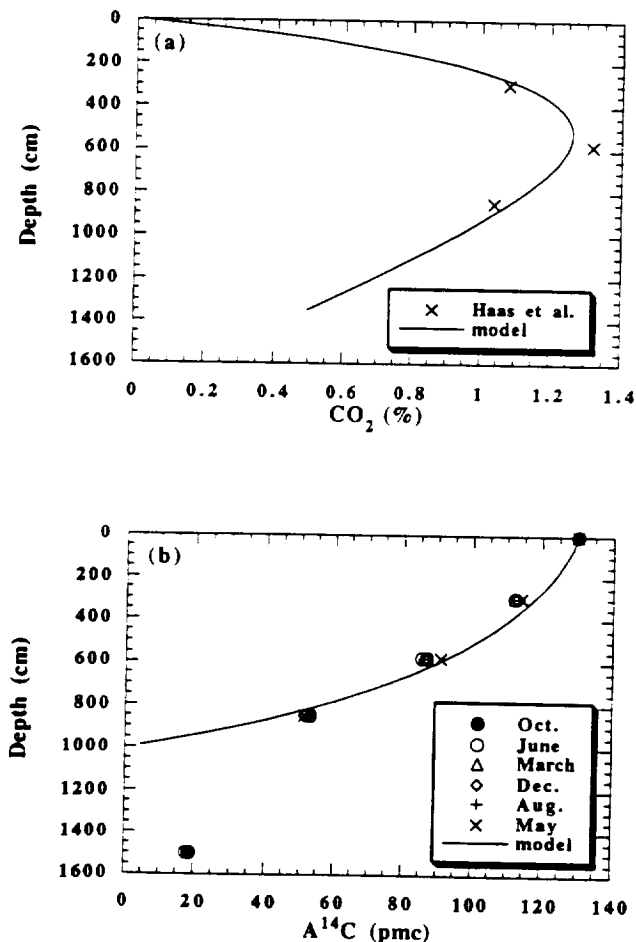

FIG. 4. Comparisons of (a) CO_2 and (b) $^{14}CO_2$ data from site #6 in HAAS et al. (1983) with model calculation. Different symbols represent different sampling dates and the curve is our model calculation. The goodness of the fits suggests that diffusion is indeed the dominant mechanism affecting 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.
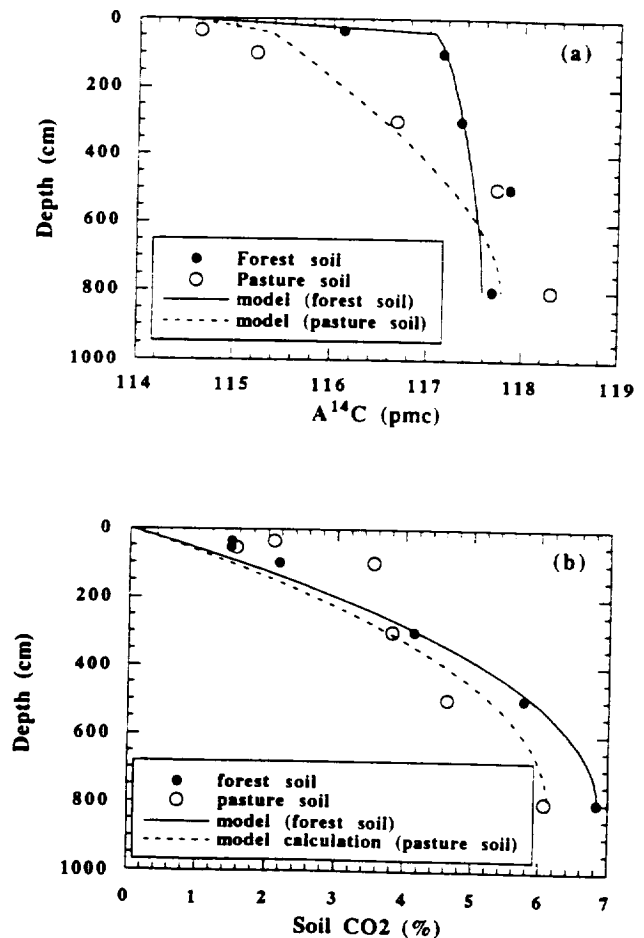
FIG. 5. Comparison of (a) $^{14}CO_2$ and (b) CO_2 (%) data from two Oxisol profiles from Paragominas in Brazil with model calculations. The solid dots represent a forest soil and the open circles a pasture soil (a degraded forest soil). For each soil, the $^{14}CO_2$ and CO_2 data are fitted using the 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/m²/h for the forest soil and 10 mmoles/m²/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/m²/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 PO-LACH, 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.

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Processes controlling the ^{14}C content of soil carbon dioxide: Model development

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Carbon-14 dates from soil carbonates have been considered unreliable estimates of the age of pedogenesis because of unknown initial ^{14}C/^{12}C ratios in the carbonate and the possibility of subsequent contamination with environmental [14]C. 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 ~ 500–7000 radiocarbon years too old. 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 was segregated, or the likely age of pedogenesis. 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 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 (~ 5570 yr) 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 the ^{14}C content of pedogenic carbonate should be determined by

[14]C content of soil CO_2 and inherited "dead carbon" should not affect the age of soil pedogenic carbonate.

We present here a diffusion-reaction model that analyzes the [14]CO$_2$ distribution in soils. Carbon dioxide is produced in soils by biological processes and is transported to the atmosphere by diffusion. The diffusion mechanism applies to its isotopic species [12]CO$_2$, [13]CO$_2$ and [14]CO$_2$ as well. Different isotopic species of CO_2 react and diffuse independently of each other according their own concentration gradient and their own sources and sinks. 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 (mol cm^{-3}); D_s^{14} is the diffusion coefficient of [14]CO$_2$ in the soil (cm^2 s^{-1}); Φ_s^{14} is the production of [14]CO$_2$ in the soil (mol cm^{-3} s^{-1}); and λ the decay constant of [14]C (3.84·10^{-12} s^{-1}). 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 dif-