Radiocarbon Dating of Soil Organic Matter

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INTRODUCTION

Radiocarbon dating of organic matter in soils has been used to study the chronology of soil development (Paul et al., 1964; Jenkinson, 1969; Herrera and Tamers, 1971; Martel and Paul, 1974; Goh et al., 1977; Hammond et al., 1991). However, the significance of the measured dates or ages is a perplexing problem (Perrin et al., 1964; Campbell et al., 1967a,b; Goh and Stout, 1972; Goh et al., 1976, 1977; Gilet-Blein et al., 1980, 1992; Hammond et al., 1991; Goh and Stout, 1972; Scharpenseel and Becker-Heidmann, 1991) because soil organic matter is the product of an ongoing process. The apparent ages deduced from the $^{14}$C content of the bulk soil organic carbon have been recognized as too young because of "contamination" by recently introduced carbon. Historically, a solution to the problem has been to obtain, through chemical or physical means, portions of the soil organic matter which are presumed to be of greater age than the remaining fractions (Gerasimov and Chichagova, 1971; Scharpenseel, 1971a,b; Grant-Taylor, 1972; Tate, 1972; Martel and Paul, 1974; Jenkinson and Raynor, 1977; Gilet-Blein et al., 1980; Goh, 1991; Hass and Dalbey, 1991; Tornqvist, 1991; Martin and Johnson, 1995). Unfortunately no extraction technique has proved reliable and results for a given procedure can vary with different soils. Fresh carbon is continuously incorporated, but at varying rates, into any defined fraction (e.g., humin, humic acid, fulvic acid, lipids). Therefore, ages from $^{14}$C dating of any organic matter fraction from soils are interpreted as minimal ages for the length of soil formation (Perrin et al., 1964; Scharpenseel, 1971a,b, 1972, 1976; Cherkinsky and Brovkin, 1991). Alternatively, the age of the bulk soil organic carbon has been interpreted as the "mean residence time" (MRT) of the steady-state soil organic matter. However, there has been no clear definition of what MRT implies and its relationship to steady state (Paul et al., 1964; Campbell et al., 1967a,b; Goh and Stout, 1972; Scharpenseel, 1972; Sheppard et al., 1976).

Recently, a series of models has been developed to study the uptake of bomb $^{14}$C in soil organic matter pools with the purpose of understanding the dynamics of soil organic matter (O’Brien and Stout, 1977; Trumbore et al., 1989, 1990; Harrison et al., 1993; Trumbore, 1993). The difference in $^{14}$C in soil organic carbon between prebomb and postbomb soils has demonstrated differences in the amount, character, and steady-state turnover rate of carbon in organic matter (Trumbore, 1993). Here we modify the approach to use it to evaluate the evolution of $^{14}$C age of soil organic matter with increasing soil age.
TABLE 1
Soils Selected for the Study

<table>
<thead>
<tr>
<th>Soil ecosystem</th>
<th>Soil type</th>
<th>Location</th>
<th>Vegetation</th>
<th>Mean annual temperature (°C)</th>
<th>Mean annual precipitation (cm)</th>
<th>Parent material</th>
<th>Estimated age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest</td>
<td>Ultisol</td>
<td>Sierra Nevada, Fresno County, California</td>
<td>Coniferous and deciduous forest</td>
<td>8.9</td>
<td>102</td>
<td>Granodiorite</td>
<td></td>
</tr>
<tr>
<td>Prairie</td>
<td>Mollisol</td>
<td>Tama County, Iowa</td>
<td>Perennial grass</td>
<td>8.3</td>
<td>86</td>
<td>Till</td>
<td>~10,000 yr</td>
</tr>
<tr>
<td>Desert</td>
<td>Aridisol</td>
<td>Barstow, California</td>
<td>Desert scrub</td>
<td>19.4</td>
<td>12.7</td>
<td>Alluvium</td>
<td></td>
</tr>
</tbody>
</table>

SAMPLE SELECTION AND ANALYTICAL METHODS

We selected three soils from different climatic zones (Table 1) to reveal the effect of climate on soil C dynamics and on the 14C ages of soil organic matter: a forest soil from central California, a prairie soil from Iowa, and a desert soil from the Mojave Desert. The prairie soil was obtained from the archives at the U.S. National Soil Survey Laboratory. This soil, a Mollisol, was collected in 1959 from Tama County, Iowa. The 14C contents of three different organic fractions separated by physical and chemical means were analyzed and reported by Trumbore et al. (1990). In this paper, we calculated the bulk C and 14C contents of soil organic matter (Table 2) from the C and 14C measurements on different fractions (Trumbore et al., 1990) based on mass balance relationships. The calculated bulk C and 14C contents of soil organic matter were then used in the following model evaluation. The forest soil, a Musick loam, classified as Ultisol, was collected in 1958 from the Sierra Nevada (Fresno County) in central California. The desert soil, an Aridisol, was collected from Barstow area in the Mojave Desert in 1951. Both the forest soil and the desert soil were obtained from the archives at the Department of Environmental Science, Policy, and Management, University of California at Berkeley. We deliberately selected soil samples collected before the peak of nuclear weapons testing for this study to avoid any “bomb 14C” contamination.

Samples of the forest and desert soils were hand-picked of visible roots and plant material and ground into powder. The powder was treated with 1 M HCl overnight to remove carbonate, rinsed with deionized water six times, and dried. CO2 was produced by combustion of the treated sample with CuO and silver foil under vacuum at 875°C for 2 hr. The resulting CO2 was purified cryogenically and its stable carbon isotope ratio was measured on a mass spectrometer. For 14C analysis, purified CO2 was reduced to graphite with H2 over Co and its 14C/13C ratio was measured on an accelerator mass spectrometer (AMS) at Lawrence Livermore National Laboratory.

Stable C isotope data are reported in the standard permil notation relative to the PDB standard as

\[
\delta^{13}C = \left( \frac{R_{\text{sample}}}{R_{\text{PDB}}} - 1 \right) \times 1000
\]

14C data are expressed as (Stuiver and Polach, 1977)

TABLE 2
Organic Carbon and 14C Content of Three Prebomb Soils with Calculated Steady-State Input and Decay Rate

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Location</th>
<th>Depth (cm)</th>
<th>Organic C (10^-4 moles/cm³)</th>
<th>14C content (pMC)</th>
<th>φ steady state (10^-4 moles/cm²/yr)</th>
<th>k steady state (10^-4 yr^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desert soil</td>
<td>California</td>
<td>0–7.6</td>
<td>1.76</td>
<td>8.4</td>
<td>0.00202</td>
<td>0.1148</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.6–35.6</td>
<td>1.28</td>
<td>7.2</td>
<td>0.001232</td>
<td>0.0963</td>
</tr>
<tr>
<td>Prairie soil</td>
<td>Iowa</td>
<td>0–16.5</td>
<td>37.08</td>
<td>87.5</td>
<td>3.2465</td>
<td>8.7547</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.5–27.9</td>
<td>21.92</td>
<td>82.1</td>
<td>1.2475</td>
<td>5.6920</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.9–41.9</td>
<td>19.25</td>
<td>65.3</td>
<td>0.4503</td>
<td>2.3391</td>
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<tr>
<td></td>
<td></td>
<td>41.9–50.8</td>
<td>10.5</td>
<td>60.8</td>
<td>0.2029</td>
<td>1.9323</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.8–63.5</td>
<td>8.33</td>
<td>51.2</td>
<td>0.1088</td>
<td>1.3054</td>
</tr>
<tr>
<td></td>
<td></td>
<td>63.5–73.7</td>
<td>5.0</td>
<td>45.8</td>
<td>0.0525</td>
<td>1.0501</td>
</tr>
<tr>
<td>Forest soil</td>
<td>California</td>
<td>0–23</td>
<td>14.67</td>
<td>95.3</td>
<td>3.6754</td>
<td>25.0593</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23–51</td>
<td>6.42</td>
<td>88.7</td>
<td>0.629</td>
<td>9.799</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51–69</td>
<td>5.08</td>
<td>76.1</td>
<td>0.2018</td>
<td>3.9704</td>
</tr>
</tbody>
</table>
\[ \delta^{14}C = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000, \]

where \( \delta^{14}C \) is the permil value for \(^{14}C\) content (Stuiver and Polach, 1977), \( R_{\text{sample}} \) is the \(^{14}C/^{13}C\) ratio in the sample, and \( R_{\text{std}} \) is the absolute \(^{13}C/^{12}C\) ratio in the isotopic standard (NBS oxalic acid), or

\[ \text{pMC (percent modern carbon)} = \frac{A_{\text{SN}}}{A_{\text{abs}} \times 100}, \]

where \( A_{\text{SN}} \) is the \(^{14}C\) activity in the sample normalized to \( \delta^{13}C = -25\% \), and \( A_{\text{abs}} \) is the absolute \(^{14}C\) activity in the international isotopic standard (NBS oxalic acid).

The \(^{14}C\) age is calculated from the equation (Stuiver and Polach, 1977)

\[ \text{Radiocarbon age} = -8033 \ln \left( \frac{\text{pMC}}{100} \right) - \frac{y - 1950}{1.03}, \]

where \( y \) is the year of \(^{14}C\) measurement.

**A MODEL FOR INTERPRETING THE \(^{14}C\) AGE OF SOIL ORGANIC MATTER**

One of the criteria for accurate radiocarbon dating of a sample is that the system has to be closed with respect to \(^{14}C\). Soils, which form over long periods of time, represent open systems with respect to carbon and are in apparent violation of this criterion. Obviously, the standard \(^{14}C\) dating models are not applicable to soils. However, if we assume that organic matter decomposition is the only mechanism for carbon loss in soils, the variation in organic carbon with time for a soil or any of its horizons can be described by

\[ \frac{\partial C}{\partial t} = D_b \frac{\partial^2 C}{\partial \chi^2} + I - kC, \]

where \( C \) is the organic carbon content (moles/cm\(^3\)). The first term on the right side of the equation represents the transport of \( C \) by biodiffusion and the \( D_b \) is the biodiffusion coefficient (cm\(^2\)/sec). \( I \) is the *in situ* production of \( C \) by root growth and decay (moles/cm\(^3\)/yr). The third term represents loss of organic carbon by microbial decomposition and \( k \) is the decay constant (yr\(^{-1}\)). Diffusional transport of carbon is not well understood from a quantitative standpoint in any soil. In humid, coarse-textured soils downward transport of particulate \( C \) has been recognized (Chapelle, 1993). However, in arid and semi-arid soils (those examined here), downward movement of organic \( C \) is far less understood but is likely not as important. For example, the concentration of organic \( C \) in these soils is commonly strongly correlated with root distribution, suggesting that direct input from roots dominates the \( C \) input processes. For the simplicity of the modeling, we will combine the *in situ* production and diffusional transport of carbon into one “net production of organic carbon” term, \( \Phi \) (moles/cm\(^3\)/yr). Our purpose here is to demonstrate, at least semi-quantitatively, the effect of soil genesis on the \(^{14}C\) ages of soil organic matter.

Equation (1) can then be reduced to

\[ \frac{\partial C}{\partial t} = \Phi - kC. \]

Similarly, the \(^{12}C\) and \(^{14}C\) content of soil organic matter can be expressed by

\[ \frac{\partial C^{12}}{\partial t} = \Phi^{12} - kC^{12} \]

\[ \frac{\partial C^{14}}{\partial t} = \Phi^{14} - (k + \lambda)C^{14}, \]

where \( C^{12} \) and \( C^{14} \) are the soil organic \(^{12}C\) and \(^{14}C\) contents, respectively, and

\[ \Phi^{14} = \Phi^{12} \left( \frac{\delta^{14}C_{\text{input o.m.}}}{1000} + 1 \right) \frac{R_{\text{std}}}{R_ {\text{PDB}}} \]

\[ \Phi^{12} = \Phi (1 - \tilde{\delta}) \]

\[ \tilde{\delta} = \left( \frac{\delta^{13}C_{\text{input o.m.}}}{1000} + 1 \right) \frac{R_{\text{PDB}}}{1 + \left( \delta^{13}C_{\text{input o.m.}} + 1 \right) R_{\text{PDB}}} \]

and \( \lambda \) is the decay constant of \(^{14}C\) (0.0001245/yr), and \( \delta^{13}C_{\text{input o.m.}} \) and \( \delta^{14}C_{\text{input o.m.}} \) are the \(^{13}C\) and \(^{14}C\) contents of input organic matter in permil notation, respectively. If we assume that \( C = 0 \) at \( t = 0 \), and \( \Phi \) and \( k \) are constant with time but vary with depth, the solutions to Eqs. (2), (3), and (4) are

\[ C = \frac{\Phi}{k} (1 - e^{-kt}) \]

\[ C^{12} = \frac{\Phi^{12}}{k} (1 - e^{-kt}) \]

\[ C^{14} = \frac{\Phi^{14}}{k} [1 - e^{-(k + \lambda)t}]. \]

When a soil is at steady state, the steady-state input rate and decay rate can be calculated from Eqs. (8) to (10):
If the true age of a soil (i.e., the age since the initiation of a soil’s development) is known (or if a soil is at steady state), and $\delta^{14}C_{\text{in}}$, the organic carbon content, and $^{14}C$ content of organic matter at different depth intervals are measured, Eqs. (8) to (10) can be solved for $\phi$ and $k$ for the soil depth intervals of interest. The $\phi$ and $k$ can then be used to calculate the organic carbon, $^{14}C$ content, and $^{14}C$ ages of organic matter vs soil depth at different times of the soil’s development. We have made such calculations for the three prebomb soils described in the previous section (Table 2) using Eqs. (5) to (12). The evolution of the $^{14}C$ content of organic matter in these soils is discussed in relation to its implication for $^{14}C$ dating. Our model calculations simulate the way in which $^{14}C$ content or $^{14}C$ ages of soil organic matter might have evolved from time $t = 0$ to various “true ages.”

In our calculations, we assume that organic C input (\(\phi\)) and decay (\(k\)) are constant with time. This assumption is unlikely to be valid for real soils because soil organic matter is a heterogeneous mixture of compounds with differing decay rates (Trumbore et al., 1990; Trumbore, 1993) that are affected by seasonal/annual soil temperature and moisture variations. However, we have no ability to predict their behavior with time and have no data regarding the decay rates of various C pools. We, therefore, emphasize that the $\phi$ and $k$ in our model should be considered as representing long-term average behaviors of these soil C properties. Second, we assume that the $^{14}C$ content of input organic carbon, $\delta^{14}C_{\text{in}}$, is the same as the atmospheric $^{14}C$. This implies that most of the carbon input is from root growth and decay, and diffusional transport of carbon is not important except for recently added material. At present, we have no quantitative knowledge of the amount and $^{14}C$ content of C associated with biodiffusion. Our calculations, therefore, may not be entirely quantitative for soils in which biodiffusional transport of organic fractions, with lower $^{14}C$ contents than the atmosphere, is important. Nuclear weapons testing in the late 1950s and 1960s injected considerable $^{14}C$ into the atmosphere; this “bomb” $^{14}C$ is an ideal tracer for studying C cycling in soils. Plant materials added to a soil in the late 1950s to early 1990s had much higher than “normal” $^{14}C$ content. Studies (Goh and Stout, 1972; Stout and O’Brien, 1972) have shown that bomb $^{14}C$ enrichment of soil organic matter occurred mainly in the top soils. Since most organic matter input is from surface litter and root turnover at shallow depths, the mechanisms by which “new” C can be transported to deeper depths are vertical translocation of C by biodiffusion or solution and deep roots turnover. Minimum influence of bomb $^{14}C$ in subsoils may therefore suggest that biodiffusional transport of C is less important in subsoils. Goh and Stout (1972) suggested that the subsoil organic matter is subjected to a slow but continuous incorporation of $^{14}C$ from the atmosphere via plant residues, especially plant roots, and translocation of soluble organic compounds from the surface horizon. These processes, together with the slow but continuous decomposition of organic matter already formed in the subsoil, lead to interchanges between the various carbon isotopes not only within the different organic fractions but also between the organic matter in the different soil horizons. Further work is needed to study the biodiffusional transport and solution translocation of carbon in different soils and how they affect the $^{14}C$ content of soil organic matter.

**DISCUSSION**

The carbon inventory, $^{14}C$ content of bulk soil organic matter, and calculated steady-state input and decay rates of the three prebomb soils are shown in Table 2. Using the data in Table 2, we calculated the $^{14}C$ ages of soil organic matter vs soil depth at different times of the soils development, as shown in Figure 1. These diagrams show that (1) the $^{14}C$ age of soil organic matter decreases with soil depth, (2) the $^{14}C$ age of soil organic matter is always younger than the true age of the soil due to a continuous input of fresh organic matter, (3) the $^{14}C$ content/age of soil organic matter will eventually reach a steady state provided that no climatic or ecological perturbations occur, and (4) “steady-state $^{14}C$ age,” which is defined as the minimum time required for a soil horizon or a soil to reach steady state, increases with depth.

Once a soil or a soil horizon is at steady state, the $^{14}C$ age of organic matter becomes constant with respect to time and therefore cannot give any indication of the age of the soil. The time for this to occur varies greatly with climate (from less than 5000 yr in the temperate climate of California to more than 300,000 yr in the arid environment of the Mojave Desert) and also with depth in a soil profile (Fig. 1). It is evident from these diagrams that the measured $^{14}C$ ages at any time can be significantly different from the true ages of the soils. For example, soil samples taken from the 25-cm depth in a 40,000-year-old forest soil (similar to the Sierra Nevada soil) will have a measured $^{14}C$ age of about 5000 yr B.P. (Fig. 1a).

The most important factor affecting the measured $^{14}C$ ages of soil organic matter is the rate of organic carbon cycling in soils. The rate of C cycling in soils is affected by a number...
rates, has the oldest steady-state $^{14}$C age. The steady-state $^{14}$C ages for the three soils are ca. 15,000 yr below and <10,000 yr above 40-cm depth for the forest soil, >40,000 yr below and <40,000 yr above 50-cm depth for the prairie soil, and much greater than 50,000 yr (the current $^{14}$C dating limit) at 4–22-cm depth interval for the desert soil (Table 3). Clearly, it is not prudent to compare the ages of different soils by simply looking at the measured $^{14}$C dates of soil organic matter or its fractions. For the same type of soils, the measured $^{14}$C ages of soil organic matter from the same depth interval can give some indication of the relative ages of the soils. However, for different types of soils in different climates, differences in the dynamics of soil carbon can result in completely different $^{14}$C ages even when they do have the same true age.

Our modeling exercise demonstrates that $^{14}$C method of dating soil organic matter will be limited by the steady-state $^{14}$C age of a soil or a soil horizon. However, it is theoretically possible to estimate the age of a soil provided that the input and decay rates are known and the steady state has not yet established. In practice, this will involve a considerable amount of work: the availability of a prebomb soil similar to the soils to be dated from a nearby locality, $^{14}$C analysis of this soil, and modeling.

One possible way of applying this concept is the following. In areas where a series of terraces or geomorphic surfaces of different ages can be identified based on geomorphological and soil development evidence, the soil on the oldest terrace can be assumed to be at steady state, and the steady-state input and decay rate can be determined from its $^{14}$C and C content. Because of bomb $^{14}$C contamination, archived samples best serve this purpose. However, in environments such as deserts where C inputs are low, deep soil horizons may be effectively utilized. The calculated steady-state input and decay rate can be used to calculate the $^{14}$C ages of soil organic matter at time $t = 0$ to various true ages using the model described in the previous section. The ages of the other younger surfaces in the area can then be estimated by comparing measured $^{14}$C ages with model calculations. This

<table>
<thead>
<tr>
<th>TABLE 3</th>
<th>Steady-State Ages (yr) of Organic Matter for Three Soils Studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (cm)</td>
<td>Forest soil, California</td>
</tr>
<tr>
<td>10</td>
<td>&lt;5000</td>
</tr>
<tr>
<td>20</td>
<td>5000</td>
</tr>
<tr>
<td>30</td>
<td>8000</td>
</tr>
<tr>
<td>40</td>
<td>10,000</td>
</tr>
<tr>
<td>50</td>
<td>15,000</td>
</tr>
<tr>
<td>60</td>
<td>15,000</td>
</tr>
<tr>
<td>70</td>
<td>&gt;15,000</td>
</tr>
</tbody>
</table>

FIG. 1. Evolution of $^{14}$C age of soil organic matter for a forest soil (a), a prairie soil (b), and a desert soil (c). Different curves represent the calculated $^{14}$C ages of soil organic matter at different times of the soil’s development. Numbers along the curves indicate the true age of the soil.
method has been applied to date Holocene alluvial fan surfaces in the Providence Mountains area of the Mojave Desert. The model ages of soil formation based on measured 14C ages of soil organic matter were consistent with the relative ages suggested by geomorphologic evidence and were also compatible with 14C model ages derived from soil carbonate (Wang et al., in press).

The organic matter in buried soils is an obvious substrate for 14C dating. However, for buried soils, 14C dating of soil organic matter could overestimate the true age of the burial by as much as the steady-state age of the soil or soil horizon which is a function of climate and other factors (i.e., Table 3). An additional complication can occur in high rainfall/leaching environments. Studies (Hammond et al., 1991) have shown that in such environments, downward translocation of water-soluble fulvic acid could significantly lower the 14C ages of soil organic matter, adding additional uncertainty to these measurements.

CONCLUSIONS

Radiocarbon ages of organic matter or any organic fractions in a soil can be better understood by evaluating the evolution of 14C content of its organic matter. Measured 14C ages of soil organic matter or organic matter fractions are always more younger than the true age of soil formation. The most important factor controlling the measured 14C ages of soil organic matter is the rate of organic carbon cycling in soils. Differences in the dynamics of organic carbon in different soils or soil horizons will result in significantly different 14C signatures of soil organic matter even when the true ages of the soils are the same. Radiocarbon ages of soil organic matter increase with depth and time, but will eventually reach a steady state. When a soil or a soil horizon is at steady state, 14C dating of soil organic matter gives no indication of the age of a soil. However, the age of a soil can be estimated if the input and decay rates of organic matter are known and the soil is not at steady state. Radiocarbon dating of organic matter in a buried soil could overestimate the age of burial by as much as the steady-state age of the soil or soil horizon. Contamination of environmental 14C by various processes will confound these dates even more. Our approach provides a new perspective to the problems in using 14C to date soil organic matter. However, on a positive note, we believe that our simple model of soil organic matter dynamics may provide much more profitable interpretations of radiocarbon dates and soil ages than has hitherto been possible.

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REFERENCES


