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Radiocarbon Dating of Soil Organic Matter

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Radiocarbon ages of soil organic matter are evaluated with a model which incorporates the dynamics of the ^{14}C content of soil organic matter. Measured ^{14}C ages of soil organic matter or its fractions are always younger than the true ages of soils due to continuous input of organic matter into soils. Differences in soil C dynamics due to climate or soil depth will result in significantly different ^{14}C signatures of soil organic matter for soils of the same age. As a result, the deviation of the measured ^{14}C age from the true age of soil formation could differ significantly among different soils or soil horizons. Our model calculations also suggest that ^{14}C ages of soil organic matter will eventually reach a steady state provided that no climatic or ecological perturbations occur. Once a soil or a soil horizon has reached a steady state, ^{14}C dating of soil organic matter will provide no useful information regarding the age of the soil. However, for soils in which steady state has not been reached, it is possible to estimate the age of soil formation by modeling the measured ^{14}C contents of soil organic matter. Radiocarbon dating of buried soils could, in general, overestimate the true age of the burial by as much as the steady-state age of the soil or soil horizon. © 1996 University of Washington

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; Gerasimov and Chichagova, 1971; Scharpenseel, 1971a,b, 1972, 1976; Grant-Taylor, 1972; Gerasimov, 1974; Sheppard *et al.,* 1976; Goh *et al.,* 1976, 1977; Gilet-Blein *et al.,* 1980; Hammond *et al.,* 1991; 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.

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TABLE 1
Soils Selected for the Study

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

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 ^{14}C 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 ^{14}C 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 ^{14}C contents of soil organic matter (Table 2) from the C and ^{14}C measurements on different fractions (Trumbore *et al.,* 1990) based on mass balance relationships. The calculated bulk C and ^{14}C 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 ^{14}C'' 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. CO_2 was produced by combustion of the treated sample with CuO and silver foil under vacuum at 875°C for 2 hr. The resulting CO_2 was purified cryogenically and its stable carbon isotope ratio was measured on a mass spectrometer. For ^{14}C analysis, purified CO_2 was reduced to graphite with H_2 over Co and its $^{14}C/^{13}C$ 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

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

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

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

Soil type	Location	Depth (cm)	Organic C (10^{-4} moles/cm^3)	^{14}C content (pMC)	ϕ steady state (10^{-6} moles/cm^3/yr)	k steady state (10^{-4} yr^{-1})
Desert soil	California	0–7.6	1.76	8.4	0.00202	0.1148
		7.6–35.6	1.28	7.2	0.001232	0.0963
Prairie soil	Iowa	0–16.5	37.08	87.5	3.2465	8.7547
		16.5–27.9	21.92	82.1	1.2475	5.6920
		27.9–41.9	19.25	65.3	0.4503	2.3391
		41.9–50.8	10.5	60.8	0.2029	1.9323
		50.8–63.5	8.33	51.2	0.1088	1.3054
		63.5–73.7	5.0	45.8	0.0525	1.0501
Forest soil	California	0–23	14.67	95.3	3.6754	25.0593
		23–51	6.42	88.7	0.629	9.799
		51–69	5.08	76.1	0.2018	3.9704

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

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

$$pMC \text{ (percent modern carbon)} = A_{SN}/A_{abs}*100,$$

where A_{SN} is the ^{14}C activity in the sample normalized to $\delta^{13}C = -25\%$, and A_{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)

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

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

$$\frac{\partial C}{\partial t} = D_B \frac{\partial^2 C}{\partial x^2} + I - kC, \tag{1}$$

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 domi-

nates 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, Φ (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

$$\frac{\partial C}{\partial t} = \Phi - kC. \tag{2}$$

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

$$\frac{\partial C^{12}}{\partial t} = \Phi^{12} - kC^{12} \tag{3}$$

$$\frac{\partial C^{14}}{\partial t} = \Phi^{14} - (k + \lambda)C^{14}, \tag{4}$$

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

$$\Phi^{14} = \Phi^{12}\left(\left(\frac{\delta^{14}C_{input\ o.m.}}{1000} + 1\right)R_{std}\right) \tag{5}$$

$$\Phi^{12} = \Phi(1 - \hat{\delta}) \tag{6}$$

$$\hat{\delta} = \left(\frac{\left(\frac{\delta^{13}C_{input\ o.m.}}{1000} + 1\right)R_{PDB}}{1 + \left(\frac{\delta^{13}C_{input\ o.m.}}{1000} + 1\right)R_{PDB}}\right) \tag{7}$$

and λ is the decay constant of ^{14}C (0.0001245/yr), and $\delta^{13}C_{input\ o.m.}$ and $\delta^{14}C_{input\ o.m.}$ 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 ϕ and k are constant with time but vary with depth, the solutions to Eqs. (2), (3), and (4) are

$$C = \frac{\Phi}{k}(1 - e^{-kt}) \tag{8}$$

$$C^{12} = \frac{\Phi^{12}}{k}(1 - e^{-kt}) \tag{9}$$

$$C^{14} = \frac{\Phi^{14}}{k}[1 - e^{-(k+\lambda)t}]. \tag{10}$$

When a soil is at steady state, the steady-state input rate and decay rate can be calculated from Eqs. (8) to (10):

$$k_{\text{steady-state}} = \frac{\left(\dfrac{\delta^{14}\text{C}_{\text{o.m.}}}{1000} + 1\right)\left((R_{\text{atd}})(\lambda)\right)}{\left(\dfrac{\delta^{14}\text{C}_{\text{input o.m.}}}{1000} + 1\right)(R_{\text{std}}) - \left(\dfrac{\delta^{14}\text{C}_{\text{o.m.}}}{1000} + 1\right)(R_{\text{std}})}$$

(11)

$$\phi_{\text{steady-state}} = kC. \qquad (12)$$

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 $\delta^{14}\text{C}_{\text{input o.m.}}$, 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 ϕ and k for the soil depth intervals of interest. The ϕ 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 (ϕ) 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 ϕ 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, $\delta^{14}\text{C}_{\text{input o.m.}}$, is the same as the atmospheric CO_2. 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 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
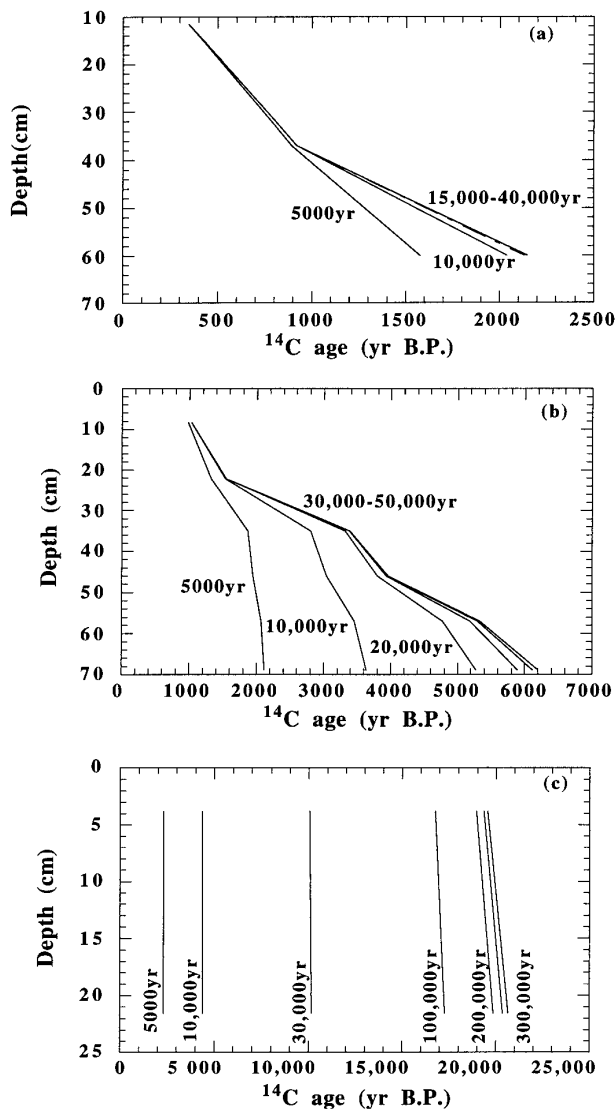
FIG. 1. Evolution of ^{14}C age of soil organic matter for a forest soil (a), a prairie soil (b), and a desert soil (c). Different curves represent the calculated ^{14}C ages of soil organic matter at different times of the soil's development. Numbers along the curves indicate the true age of the soil.

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

of variables including (a) climate, (b) biotic factors, such as plant community composition, productivity, resistance of organic detritus to decomposition, and (c) physical/chemical factors, e.g., the surface area and chemistry of minerals for stabilizing organic matter. These various factors vary with soil depth and soil age, and among different ecosystems, resulting in differences in organic C cycling rates in subsoils and among different soils. Differences in the dynamics of soil carbon among different soils or soil horizons will result in significantly different soil organic ^{14}C signatures. For the forest soil, higher input and decay rates result in higher steady-state ^{14}C contents and younger steady-state ^{14}C ages. In contrast, the desert soil, with the lowest input and decay

TABLE 3
Steady-State Ages (yr) of Organic Matter
for Three Soils Studied

Depth (cm)	Forest soil, California	Prairie soil, Iowa	Desert soil, California
10	<5000	<10,000	>300,000
20	5000	10,000	>300,000
30	8000	20,000	
40	10,000	30,000	
50	15,000	40,000	
60	15,000	50,000	
70	>15,000	>50,000	

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 ^{14}C ages of soil organic matter were consistent with the relative ages suggested by geomorphologic evidence and were also compatible with ^{14}C model ages derived from soil carbonate (Wang *et al.,* in press).

The organic matter in buried soils is an obvious substrate for ^{14}C dating. However, for buried soils, ^{14}C 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 ^{14}C dates of buried soils, 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 ^{14}C content of its organic matter. Measured ^{14}C ages of soil organic matter or organic matter fractions are always much younger than the true age of soil formation. The most important factor controlling the measured ^{14}C 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 ^{14}C 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, ^{14}C 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 ^{14}C by various processes will confound these dates even more. Our approach provides a new perspective to the problems in using ^{14}C 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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