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Radiocarbon and Soil Carbon Dynamics

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Key Words

^{14}C , soil organic matter, carbon cycle, state factor, radiocarbon, climate change

Abstract

Research over the past several decades has clarified the mechanisms and timescales involved in stabilizing organic matter in soils, but we still lack process-based understanding sufficient for predicting how vulnerable soil carbon (C) is, given climatic or environmental change across a range of soil types and landscapes. Part of the problem is the emphasis on short-term studies and processes that dominate C balance at the point or soil profile scale, whereas other processes that dominate over longer timescales and larger spatial scales may actually be more important for determining the carbon balance of soils in a region. Radiocarbon is one of the only tools to study the dynamics of C in soils on decadal to millennial timescales. It provides a means for directly testing models of organic matter dynamics in ecosystems and, when measured in respired CO_2 or dissolved organic carbon (DOC), provides evidence of shifts in microbial metabolism. This review explores the application of this underutilized tool, with an emphasis on conceptual advances made using the state-factor approach and on detecting processes causing abrupt change in soil C stores.

INTRODUCTION

Globally, soils and surface litter store 2–3 times the amount of carbon (C) present in atmospheric CO₂. Soil respiration, which integrates below-ground plant and microbially derived CO₂, is one of the largest annual transfers in the global C budget. Predictions of terrestrial feedbacks to climate warming differ dramatically in the magnitude and even the sign of soil C responses over the next century (Friedlingstein et al. 2006). These differences reflect uncertainties inherent in how models parameterize two key responses: the temperature dependence of decomposition rates and the rate of C accumulation given hypothesized increases in vegetation productivity due to CO₂ fertilization. Observations of change in soil C cycling, such as the loss of soil C (Bellamy et al. 2005) and increases in stream and lake dissolved organic carbon (Evans et al. 2006) over recent decades in the United Kingdom, underscore the need to understand the complex and interacting factors—physical and chemical as well as biological—that can allow organic matter to persist in and be lost from the soil environment.

Widely applied models of soil organic matter [e.g., CENTURY (Parton et al. 1987) and Rothamsted (Jenkinson & Rayner 1977)] recognize the requirement for soil organic matter to exist in pools with different intrinsic turnover times, and much effort over the past two decades has sought to link these conceptual pools with measurable components of soil organic matter (**Figure 1**). These efforts have been most successful in predicting the dynamics of C in the earlier stages of decomposition. Assumptions made in model parameterizations of stabilized C pools, which comprise the bulk of C in most soils, have been less rigorously tested (Falloon & Smith 2000). Further, commonly used models track carbon only in the upper ~20 cm, less than the rooting depth in many soils, and therefore may miss part of the active C cycle in soils.

Predicting changes in soil C over the next century requires knowledge of how rapidly C can be stabilized in soil, the vulnerability of soil C stores to changes in climate, nutrient deposition, and vegetation and land management, and it requires development of the ability to determine how mechanisms of C stabilization and destabilization scale across space and time. The ability to measure the age of carbon stored in and lost from soils is critical to unraveling the timescales on which stabilization mechanisms operate and for providing a means for detecting processes that accelerate losses of previously stabilized organic matter.

Figure 1

Pathways of carbon input, transformation, and loss from soils.

Mechanisms for Stabilizing Carbon

Carbon enters the soil system in the form of plant detritus, including dead leaves, roots, branches, and wood (**Figure 1**). The mass of that material decreases over time as it is metabolized and transformed by soil fauna. Microbial biomass represents a small fraction of total soil C, hence the overwhelming majority of detrital C gets respired as CO₂ or transformed into soluble metabolites and other microbial byproducts. Plant detritus and microbial byproducts may be stabilized (protected from decomposition) by one of several mechanisms, as reviewed by Six et al. 2004, Sollins et al. 1996, and Torn et al. 2009.

1. Climatic stabilization: Soil organic matter can be preserved due to freezing temperatures, low O₂ content, and/or high moisture content in a range of ecosystems. Examples of this type of preservation are found in high-latitude soils and water-saturated soils in temperate and tropical environments.
2. Intrinsic recalcitrance: While all organic carbon is ultimately thermodynamically unstable, soils contain a number of compounds that may be difficult to decompose owing to their specific chemical structure. Pyrolyzed carbon formed in fire can be one example (Krull et al. 2006b, Preston & Schmidt 2006); some lipid compounds are also extremely long-lived in soil (Mikutta et al. 2006).
3. Physical stabilization: There is clear evidence that the association of organic compounds with aggregates and mineral surfaces through a range of interactions (inclusion, sorption, etc.) slows their decomposition (Oades 1984, Jastrow 1996, Torn et al. 1997, Baldock & Skjemstad 2000, Masiello et al. 2004, Six et al. 2004, Rasmussen et al. 2005, Mikutta et al. 2006).
4. Inhibition of microbial activity/inaccessibility: Until recently, links between the microbial community and the amount and age distribution of SOM have received less attention than physical and chemical controls on SOM (Waldrop et al. 2000, Balser & Firestone 2005). Breakdown of organic molecules is, for the most part, mediated by microbial enzymes, and, if there are barriers to the interaction of extracellular enzymes with substrate, decomposition is slowed (Schimel & Weintraub 2003, Allison 2005, Ekschmitt et al. 2005).

These mechanisms are not necessarily independent and can operate on different timescales. For example, preservation of a specific organic compound in soils may reflect its intrinsic chemical recalcitrance or could result from the association of chemical properties and physical stabilization mechanisms (e.g., solubility, surface charge). Warming of high-latitude soils potentially thaws large stores of climatically stabilized (frozen) carbon, thereby accelerating decomposition rates. However, the magnitude of this response would be modulated by the nature of the organic matter that is thawed. For example, if the C preserved in frozen soils is in forms with low intrinsic decomposition rates, even doubling or tripling those rates means that the erosion of these C pools may be a minor feedback to warming over the next century (Czimeczik et al. 2006, Dutta et al. 2006).

Radiocarbon provides a direct measure of the time elapsed since C in organic matter was fixed from the atmosphere, which, in turn, integrates several factors: (*a*) how long C resides in living plant tissues, (*b*) the location (surface litter versus roots) and form (wood versus leaves) in which C is delivered to the soil system, (*c*) the nature and capabilities of the soil microbial community, (*d*) the kinds of stabilization mechanisms operating in the given soil, and (*e*) the rates of processes like leaching and erosion that can remove C from the soil. Each of these factors may be sensitive to changes in climate or in land cover on different timescales.

The State Factor Framework

Most studies of radiocarbon in soil organic matter have been carried out on individual soil profiles. Extrapolating from these points to landscapes requires a conceptual framework that can predict how factors that can influence C storage and dynamics vary at different spatial scales. One such framework is provided by the state-factor approach (Amundson & Jenny 1997, Jenny 1941, Torn et al. 2009), which relates measurable properties of soils, such as organic-matter content, to five state factors: climate, organisms, parent material, topographic position, and time. Amundson & Jenny (1997) added a sixth state factor, human activity, in recognition of the tremendous impact humans have in shaping the land surface. The value of the state-factor framework lies in the experimental approaches it suggests—isolation of the impact of one factor (e.g., parent material) by allowing minimal variability in the other factors in a sampling matrix.

Soil properties do not necessarily vary smoothly (linearly) across the range of state factors; there are pedogenic thresholds that, when crossed, can lead to dramatic shifts in soil properties and function over short time- or length-scales. One example of such a threshold is the ratio of annual precipitation to available soil pore space, which essentially determines whether weathering products remain in the soil profile or are leached out of it (Chadwick & Chorover 2001). Finally, soils have history, and the degree to which current soil conditions reflect past climatic regimes or even past land uses must be part of the overall view of soil development (Harden et al. 1991, Harden et al. 2002).

As noted by Amundson & Jenny (1997), the state-factor approach is a framework for study but by itself does not provide mechanistic understanding of how state factors translate into soil properties. Most of the processes stabilizing organic matter in soils have been studied at the soil profile and smaller scales. As models are applied to predict soil C dynamics over continents, it is appropriate to ask whether the processes and rates that are robust at the single profile or even the watershed scale are the best predictors across larger areas (Holmes et al. 2005, Rosenbloom et al. 2006).

Radiocarbon as a Measure of Soil C Dynamics

This review emphasizes studies where radiocarbon was used to study dynamics of soil C within the state-factor framework and allows improved conceptual description of the processes important for stabilization and destabilization of organic matter across landscapes. In cases in which there has been a documented shift in vegetation accompanied by a change in the ^{13}C of photosynthetic products (usually C3 to C4 vegetation), the rate of change of ^{13}C isotopes in soil organic matter to reflect new inputs also provides a tool for studying C dynamics on decadal timescales (e.g., Balesdent et al. 1987). This approach has provided a number of important insights into C dynamics; however, it requires a disturbance (vegetation change from C3 to C4 plants), which cannot occur in all ecosystems and cannot be reliably applied to study C dynamics on very long (e.g., millennial) timescales.

Radiocarbon (^{14}C) is a useful tool for studying C exchange between terrestrial ecosystems and the atmosphere on two timescales. It is a cosmogenic radionuclide, which means it is constantly being created by the interaction of cosmic rays with the atmosphere and Earth's surface. The ^{14}C nucleus is unstable and will spontaneously emit a β particle (electron), decaying to ^{14}N with a half-life of 5730 years. The balance of cosmogenic production, mixing of carbon among atmosphere, ocean, and land reservoirs, and radioactive decay are such that the natural abundance of ^{14}C in atmospheric CO_2 is roughly one in every trillion (10^{12}) carbon atoms. For C atoms removed from contact with the atmosphere and stored with no further exchange with other reservoirs, the

time elapsed since removal may be determined from the degree to which the $^{14}\text{C}/^{12}\text{C}$ ratio has been reduced (by radioactive decay) compared with the original atmospheric CO_2 from which it was derived. An example of such a material might be an intact seed or carbonate shell found buried in sediments. For C pools like soil organic matter, which constantly receive new C inputs from plants and lose C through decomposition, the $^{14}\text{C}/^{12}\text{C}$ ratio in a given organic matter pool reflects both the rate of decomposition and radioactive decay (Trumbore 2000, Torn et al. 2009).

Explosion of thermonuclear weapons in the atmosphere also produces radiocarbon. During the early 1960s, weapons testing nearly doubled the $^{14}\text{C}/^{12}\text{C}$ ratio in Northern Hemisphere atmospheric CO_2 . A subsequent moratorium on atmospheric testing to limit radioactive fallout meant that this bomb-produced ^{14}C serves as a global isotope tracer for C exchange among the atmosphere, ocean, and terrestrial C reservoirs over the subsequent five decades (Broecker & Peng 1982, Levin & Hesselshimer 2000). Since 1964, the amount of ^{14}C in atmospheric CO_2 has decreased, initially through dilution as bomb ^{14}C mixed from the atmosphere of the Northern to Southern Hemisphere and over subsequent decades as bomb ^{14}C was incorporated into ocean and terrestrial C pools (Randerson et al. 2002, Naegler & Levin 2006). Radioactive decay of ^{14}C is comparatively small on these timescales, and the current decrease in the atmospheric $^{14}\text{CO}_2$ signature from one year to the next is greater than the precision of the ^{14}C measurement. Since 1963, therefore, the record of radiocarbon allows us to infer the timescales for C exchange with the atmosphere in a given reservoir on annual to decadal timescales.

Radiocarbon data are reported compared with an accepted standard value of known ^{14}C content. The most common way to express radiocarbon content of a sample is the Fraction Modern:

$$\text{Fraction Modern (FM)} = \left[\frac{\frac{^{14}\text{C}}{^{12}\text{C}}_{\text{sample}, -25}}{0.95 \frac{^{14}\text{C}}{^{12}\text{C}}_{\text{OXI}, -19}} \right], \quad (1)$$

where the numerator is the ratio of ^{14}C to ^{12}C , corrected for mass-dependent isotope fractionation to a common $\delta^{13}\text{C}$ value of -25‰ , and the denominator refers to the primary standard for reporting radiocarbon data. The correction to a common $\delta^{13}\text{C}$ value is necessary because radiocarbon, like ^{13}C , is affected by mass-dependent fractionation in the environment. However, the fractionation factor for ^{14}C can be estimated from ^{13}C data for the same sample. It is important to realize that mass-dependent fractionation effects are removed in reporting nearly all ^{14}C data so that Fraction Modern values reflect time elapsed rather than the pathway taken by C in ecosystems.

For tracking bomb-produced radiocarbon in the decades since 1963, a second nomenclature is used that reports the $^{14}\text{C}/^{12}\text{C}$ ratio of the sample measured in year y to an absolute standard that does not change with time, that of the oxalic acid standard decay corrected to 1950:

$$\Delta^{14}\text{C} = \left[\frac{\frac{^{14}\text{C}}{^{12}\text{C}}_{\text{sample}, -25}}{0.95 \frac{^{14}\text{C}}{^{12}\text{C}}_{\text{OXI}, -19} e^{((y-1950)/8267)}} - 1 \right] 1000. \quad (2)$$

Prior to ~ 1990 , most radiocarbon measurements were made by decay counting, which detects the electron emitted during radioactive decay of ^{14}C in the sample. Since the 1990s, however, many more samples have been measured with the newer method of accelerator mass spectrometry (AMS), which detects individual ^{14}C atoms from the sample by accelerating them to high energy. Because it counts atoms rather than waits for them to decay, AMS requires $\sim 10,000$ – $100,000$ times

less material than decay counting and substantially less time for analysis. The expanded capacity for AMS measurement has permitted rapid growth in the available radiocarbon data from soils, and the small sample capability has enabled measurements of low-concentration constituents like dissolved organic carbon (DOC), operationally isolated fractions of soil with very low C content, and even single organic compounds isolated from soils.

Radiocarbon is used to quantify processes associated with the soil C cycle in several ways:

1. As a dating tool to determine the age of C in an object that has remained closed since addition to soil, e.g., one that is not exchanging C with the soil environment. For samples made from carbon fixed prior to 1960, radiocarbon ages need to be calibrated to correct for fluctuations in atmospheric ^{14}C ; these fluctuations combined with limitations on the precision of the ^{14}C measurement mean that radiocarbon is not a useful dating tool for distinguishing C fixed between ~ 1650 and 1950 AD. For samples made from C fixed since 1960, the year can be determined to ± 1 -2 years. Examples might be charred material (e.g., Pessenda et al. 2001) or recognizable pieces of undecomposed organic material (e.g., sphagnum moss leaves in peat deposits; Trumbore & Harden 1997).
2. As a source tracer—for example, comparing the isotopic values of respired CO_2 with those of potential substrates will determine which substrate contributes the most (reviewed in Trumbore 2006).
3. As an indicator of the rate of exchange of carbon in reservoirs that are continuously exchanging carbon with atmospheric CO_2 . Soil organic matter is an open system to which fresh material is continuously added and removed (**Figure 2, top**). The ^{14}C age of organic matter collected prior to the 1960s can be used to estimate the mean decomposition rate (Agnelli et al. 2002, Törn et al. 1997). However, the rate of incorporation of the bomb ^{14}C tracer provides a sensitive indicator of whether the majority of C in soils is derived from the atmosphere in the last few years, decades, or centuries (**Figure 2**). Radiocarbon reflects the time since the carbon atoms were fixed from the atmosphere by a plant, and thus does not necessarily provide a direct measure of decomposition rates (see **Figure 2b** versus **2c**). A more detailed discussion of how decomposition rates may be inferred from radiocarbon data, including equations used to produce **Figure 2**, may be found in Törn et al. (2009).
4. As a purposeful tracer of carbon allocation on timescales less than several years. Much of what is understood about C allocation comes from early studies using ^{14}C as a purposeful tracer (e.g., Isebrands & Dickson 1991, Hanson et al. 2000, Kuzyakov & Domanski 2000). However, regulation of the use of radioactivity in the environment meant that most of these studies were performed on seedlings and not under field conditions. Continuous labeling using ^{13}C and pulse labeling using highly enriched ^{13}C are used currently in field studies (e.g., Keel et al. 2006, 2007). More sensitive tracer studies are made possible using low levels of radiocarbon detectable by AMS (Czimczik et al. 2005, Hanson et al. 2005, Carbone et al. 2007).

Changes in the ^{14}C of C in soil organic matter since 1960 combined with observations of the rate of change of soil C stocks and ^{13}C signatures in disturbed soils show definitively that C in soils has several intrinsic timescales of accumulation and decomposition (Trumbore et al. 1989, Townsend et al. 1995). Modeling all soil organic matter as a homogeneous pool with a single turnover time clearly overestimates soil C response on decadal to century timescales. However, finding ways to separate organic matter into pools that cycle with different intrinsic timescales and to relate the quantity and turnover time of C in those pools with soil-forming factors is a major challenge. Ongoing work focuses on physical (density, aggregation), chemical (solubility, mineralogy), and biological (CO_2 respired in incubations, biomolecular markers) methods to

Figure 2

(a) Model used for calculating radiocarbon changes in SOM due to incorporation of bomb radiocarbon. I_L , I_R are rates of input of above- and belowground plant detritus; I_W and I_S are rates of input from microbial byproducts (M) to weakly (W) and strongly (S) stabilized OM pools. Rates of decomposition are assumed to be first order, with decay constants k_S and k_W . Turnover times for C in each pool are given in years and are the same for **Figures 2b** and **2c**. (b) The evolution of $\Delta^{14}C$ in litter inputs and soil pools (M, W, S) for annual plants (i.e., inputs reflect the atmospheric $\Delta^{14}CO_2$ for the year of growth). (c) The evolution of $\Delta^{14}C$ in litter inputs and soil pools when half of the carbon added to the soil is annual and half resides in the plant for 10 years before being added to the soil. In 2005, the $\Delta^{14}C$ predicted for the bulk soil carbon are 66‰ (b) versus 85‰ (c).

separate organic matter into pools with different C dynamics (Kleber et al. 2005, Mikutta et al. 2005, Olk & Gregorich 2006, von Lutzow et al. 2007; see **Figure 3**). Application of these and other operationally defined separation methods has met with limited success. Clearly, separation of less-decomposed plant detrital material by density or size isolates younger soil C. However, low-density carbon can contain material with distinct chemical properties and dynamics (Torn et al. 2005). Methods for isolating different fractions of mineral-associated organic matter are also problematic, and even the oldest chemically isolated fractions can contain a component of younger (postbomb) carbon (Paul et al. 2006). The most fruitful work in this area comes from combining radiocarbon information with observations of the chemical nature of organic matter or from studying the age of C associated with specific mineral phases or soil structural components (Krull et al. 2006a, Mikutta et al. 2006, Sollins et al. 2006, von Lutzow et al. 2007).

Recycling of stabilized C through microbial biomass (**Figure 2**) means that organic matter that is chemically labile (i.e., decomposes rapidly in soils) can be old in terms of its ^{14}C content (Gleixner et al. 2002). Radiocarbon measurements of phospholipid fatty acids (PLFA) extracted from living soil microbes demonstrate that C being utilized by microbes is derived from substrates with a range of ages, even including fossil organic matter (Rethemeyer et al. 2004). Similarly, the

Figure 3

Example of changes in the radiocarbon content of organic matter. Data are from Trumbore & Zheng (1996) for a mature forest Oxisol collected in 1992 from Paragominas, Brazil at 30–35 cm depth. The $\Delta^{14}\text{C}$ for atmospheric CO_2 in the year of sampling was $+143\text{‰}$, and fine roots ($<2\text{ mm}$) had $\Delta^{14}\text{C}$ signatures between $+170$ and $+230\text{‰}$ (Trumbore et al. 2006).

radiocarbon signature of CO_2 heterotrophically respired in incubations includes contributions of C substrates of different ages (Figure 1; Dioumaeva et al. 2002). Hence, we should not necessarily expect operationally defined separations based on chemical lability to isolate fractions of SOM that are homogeneous with respect to age. Alternatively, monitoring of radiocarbon in labile components can provide a sensitive method for detecting shifts in microbial substrates associated with destabilization of older C pools in soil (e.g., Ewing et al. 2006).

STATE FACTOR ANALYSIS OF SOIL C DYNAMICS

Climate and Vegetation Controls

Climate and vegetation controls are difficult to separate, as plant communities can respond rapidly to changes in climate or influence microclimates over decade to century timescales. The initial stages of decomposition are most clearly linked to climate and vegetation controls (see for example, Parton et al. 2007); links to longer timescales may be indirect and are not currently well understood. One study that directly compared climate and vegetation controls concluded that vegetation controls were more important (Quideau et al. 2001a), although the sites investigated were all to some extent limited by moisture availability for part of the year. Clearly, common garden experiments show large differences in soil C stocks and residence times due to interactions that develop between litter quality, soil fauna such as earthworms, and factors like soil acidity

(Quideau et al. 2001b, Reich et al. 2005). These studies also demonstrate that transformations in soil organic matter in response to vegetation change take place in decades.

Measurements documenting climate controls on the turnover of C along elevation gradients (Townsend et al. 1995, Trumbore et al. 1996) confirm that—where moisture is not limiting—cooler temperatures are associated with slower decomposition and increased age of C in low density and litter fractions. However, patterns of turnover for mineral-associated C fractions are complicated by elevation-based differences in mineralogy. For these pools, the outstanding question is how rapidly C stabilized on soil mineral surfaces, and the minerals themselves, can respond to climate change.

One factor that impacts the interpretation of radiocarbon measurements in terms of organic matter decomposition rates is the recent discovery of long lifetimes for woody roots in temperate and tropical ecosystems (Gaudinski et al. 2001, Trumbore et al. 2006). Given that fine (<1 mm) roots of forest trees can live for more than a decade and given the potential importance of roots as sources of soil organic matter in mineral soils, previous work that has implied decadal timescales for decomposition rates of some soil organic matter pools (e.g., Trumbore et al. 1996) may need to be re-assessed. Time lags for incorporation of organic matter from surface litter and roots need to be carefully considered when radiocarbon is used to infer dynamics (**Figure 2**).

Time and Parent-Material Controls

The term chronosequence refers to a series of soils, such as volcanic deposits or marine or river terraces of different ages, in which all state factors are constant except time for soil development. Studies of the evolution of carbon storage using the chronosequence approach often show initially rapid accumulation of organic matter, followed by slower rates of accumulation or even loss of C as soils became highly weathered. Schlesinger (1990) used C accumulation rates in young (3000–10,000-year-old soils) to set limits on the long-term C-sequestration potential of soils. However, it is clear that much more rapid rates of C stabilization can occur in response to disturbances or in response to vegetation/land-use change (**Table 1**).

It has long been known that stabilization of C in soils is related to the type of minerals present and is particularly related to properties such as surface area and surface charge (Oades 1984). Soil mineral composition, in turn, varies in predictable ways over time as soils develop (Harden et al. 1991, Chadwick & Chorover 2001, Baisden et al. 2002, Chorover et al. 2004). Torn et al. (1997) demonstrated very long (>50,000 years) residence times for the large amounts of C associated with allophane that are the initial weathering products in young soils with basalt parent material. Highly weathered, older soils dominated by secondary weathering products like kaolinite and iron and aluminum oxides had less and significantly younger (thousand to tens of thousands of years) C. Masiello et al. (2004) found a similar pattern of C age and mineral transformation in a chronosequence of soils developed on sedimentary parent material. The picture that emerges shows longest residence times (thousands to tens of thousands of years) for C associated with poorly crystalline or nanocrystalline primary weathering products (ferrihydrite, allophane, imogolite) and shorter residence times (thousands of years) for C associated with secondary weathering products such as crystalline clays (Chorover et al. 2004). Despite clear evidence for the role of minerals as a direct control on the age of associated carbon, fundamental questions remain concerning the relationships between the chemistry and structure of C compounds and the strength of their interactions with soil surfaces (Mikutta et al. 2006, Sollins et al. 2006). Soil mineral/organic matter interactions also influence the dynamics of C not associated with minerals through indirect controls on factors such as vegetation and hydrology (Torn et al. 2005, Reich et al. 2005).

Table 1 Rates of C stabilization and destabilization observed in soils

Process	Rate (MgC ha ⁻¹ year ⁻¹)	Duration	Reference
Increase in organic matter during soil development (young soils 3000–10,000 years old)	+0.02	Thousands of years	Schlesinger 1990
CO ₂ removal from atmosphere by organic-matter accumulation and silicate weathering	+0.085 (young soils) +0.007 (old soils)	Thousands of years	Chadwick et al. 1994
Soil development (first 50 years)	+0.11 (surface litter) –0.03 to +0.3 (soil)	~50 years	Quideau et al. 2000
C accumulation in surface litter after fire (boreal)	0.03 to 0.3	~100 years	Trumbore & Harden 1997
Loss of C from upper 15 cm on United Kingdom soils	–0.7 to –1.2 (low-C soils) –5.5 (peat soils)	1973–2003	Bellamy et al. 2005, Schulze & Freibauer 2005
Drainage of peatland (Sacramento Delta)	~ –11.0	Decades	Deverel & Rojstaker 1996
Conversion of tropical forest to pasture (tropical)	–0.4 to +1.7	~20 years	Trumbore et al. 1996
N amendment (tundra soil)	–1.0	20 years	Mack et al. 2004
Aggregate stabilization/destabilization	0.8	10 years	DeGryze et al. 2004

The coevolution of time, mineral weathering, and organic matter can also provide insight into patterns of dissolved organic carbon in streams (**Figure 4**). In temperate streams developed on young (postglacial) soils, weathering of primary minerals dominates the source of stream-dissolved load. Concentrations of base cations during baseflow conditions are high, while Ge/Si ratios (used as a measure of silicate weathering but also potentially influenced by vegetation) and dissolved organic carbon (DOC) concentrations are low (Markewitz et al. 2001, Derry et al. 2005). The ¹⁴C content of DOC leached from soils in low-flow conditions demonstrates contributions from older (pre-1950) carbon, reflecting interaction with weakly stabilized C associated with deeper soil horizons (Trumbore et al. 1992, Schiff et al. 1997, Evans et al. 2006). In such streams, increased rainfall tends to dilute the products of primary weathering (base cations) but increase DOC concentrations and ¹⁴C signatures, reflecting the influence of surface organic layers. Tropical streams draining highly weathered soils in which there are few secondary minerals show different trends (Markewitz et al. 2001). The soils contain almost no weatherable minerals, so the main

Figure 4

Conceptual relationships between the concentrations of base cations and dissolved organic carbon (DOC) (*left*) and the $\Delta^{14}\text{C}$ of DOC (*right*) in first-order streams draining catchments in soils developed on postglacial, largely granitic parent material (such as Hubbard Brook, NH) and a highly weathered Oxisol in a tropical forest (Paragominas, Brazil; Markewitz et al. 2001).

source of base cations (and Ge and Si) is leaching of organic matter at the surface. Similarly, DOC is mostly derived from young, rapidly decomposing surface pools, as demonstrated in the ^{14}C signature of DOC (Mayorga et al. 2005). The concentrations of both base cations and DOC increase with streamflow in these environments; the age of DOC reflects the dominant, young surface sources.

Topographic Controls

Soil properties are most often explored in one (vertical) dimension, but, on sloping landscapes, the vertical profiles are influenced by lateral movement of material (**Figure 5**). Carbon can be transported downslope along with soil minerals but is also continuously added in the form of new plant material and removed by decomposition and leaching. Both plant-production and decomposition rates, in turn, may vary with slope position (Yoo et al. 2006). The inventory of C in soils at the base of a slope like that in **Figure 5** is higher than on the eroding slope (Harden et al. 2002), which could be the result of accumulation of strongly stabilized C attached to soil minerals or stable aggregates that are eroded and transported downslope or to greater plant inputs (higher productivity) at the base of the slope and/or slower decomposition (more moisture, less oxygen) at the base of the slope.

Figure 5

Processes operating along a hillslope that will affect C and ^{14}C of soil organic matter. Bottom panels show predicted profiles for ^{10}Be added by precipitation to the surface, ^{10}Be produced in situ (actual amounts would be far smaller than those for precipitation-derived ^{10}Be), the percent of C, and ^{14}C with depth. Depth profiles reflect data published in Manies et al. 2001, Harden et al. 2002, Bierman 2004, and Yoo et al. 2006.

Quantifying how C storage and dynamics change with topography is aided by the use of physical tracers of particle movement, including precipitation-derived (or garden-variety) ^{10}Be and ^{137}Cs , which fall out of the atmosphere onto the soil surface and can track subsequent lateral redistribution of mineral particles (Harden et al. 1999; Harden et al. 2002; Van Oost et al. 2003, 2008; Yoo et al. 2006). Another useful tracer is in situ ^{10}Be produced within minerals like quartz by cosmic ray interactions (von Blanckenburg 2006). Increases in the inventory of these tracers downslope provide a measure of the soil mass flux independent of plant productivity and C inputs. However, radiocarbon measurements are required to distinguish whether C at the base of the slope represents passive accumulation of eroding material (older C) or whether it results from higher in situ productivity (younger C). Only a few studies are currently available (Harden et al. 2002; Van Oost et al. 2003, 2008; Rosenbloom et al. 2006; Yoo et al. 2006) but these demonstrate the importance of both mechanisms for explaining enhanced C stores at the base of a slope. Interpretations are complicated by the episodic nature of erosion events (Yoo et al. 2006) in which most of the mass movement may occur once a century or so, with much slower creep between major events. On century and longer timescales, the assumption of steady state often made in models of C and ^{14}C dynamics requires careful examination. More studies are needed in a variety of settings not only to improve estimates of C stores and dynamics but also to evaluate the role of increased erosion due to human land use on the current global land C balance (Stallard 1998, Berhe et al. 2007, Van Oost et al. 2008).

HOW FAST CAN SOIL C RESPOND?

Evidence for Active C at Depth

The overwhelming majority of studies and models of soil C dynamics focuses on only the upper 10–20 cm of mineral soil. In a wide range of ecosystems, a large fraction of total soil carbon is found deeper than 20 cm (Jobbagy & Jackson 2000) and, accordingly, it is important to assess whether all of this carbon is in highly stable forms. Carbon concentration decreases and C gets older with depth in most soils. Low-density C and microbial phospholipid fatty acids get older (Rethemeyer et al. 2005; Kramer & Gleixner 2008) and decomposition rates slow with depth. A number of factors contribute to these patterns, including the physical mechanisms for vertical and lateral C transport and changes in the spatial distribution of microbes and substrates with soil depth (Lindahl et al. 2007).

Although it is clear that the majority of roots, plant inputs, and microbial activity are in the upper 20 cm of most soils, there is clear evidence from radiocarbon changes observed in organic matter over the period 1960–2000 that an active carbon cycle continues as deep as plant roots extend (Trumbore et al. 1995, Richter et al. 1999, Baisden et al. 2002). Integrating even small concentrations of active C and microbial biomass (Fierer et al. 2003) over the large volumes of soil below 20 cm means that fluxes associated with these pools can be significant, particularly on decadal timescales (Trumbore et al. 1995). Hence, current models based on the top 20 cm of soil may significantly underpredict the response of soil C to climate or land-use change.

Evidence for Abrupt Changes in Soil Carbon

Typical rates for stabilization and destabilization of soil carbon are summarized in **Table 1**. Schlesinger (1990) used a chronosequence approach to demonstrate that the rates of change in C stocks averaged over millennial timescales are relatively small, on the order of

0.02 MgC ha⁻¹ year⁻¹, or ~100–500 times smaller than annual net primary production of most ecosystems. On long (e.g., glacial-interglacial) timescales, large stores of C are transferred between ocean and land; however, the millennially averaged fluxes are not large compared with ecosystem-atmosphere annual C exchange (Harden et al. 1992). For putting these fluxes in perspective, a 0.1 MgC ha⁻¹ year⁻¹ flux operating over a land area of 1 billion hectares (ha) (the tropical forest biome encompasses roughly 1.4 billion ha) would result in an annual net transfer of 0.1 PgC. Rates averaged over long timescales emphasize changes in the most slowly cycling C pools—those responsible for most of the soil C stock. It is clear that disturbance (fire, vegetation or land-use change, afforestation/deforestation) can result in temporarily faster rates of storage or loss of soil C that are sustained over decades and are averaged out or become responsible for spatial variability in the longer-term estimates. For example, Quideau et al. (2000, 2001a,b) found rates of accumulation of organic C in litter and soil following vegetation planting over bare soil ~10 times faster than millennially averaged rates in **Table 1**. Even higher rates can be observed when tropical forests are cleared and planted with productive grasses or when forest-floor C accumulates between fires in boreal forests (see examples in **Table 1**). Indeed, the most commonly cited cause of abrupt change is associated with agriculture-induced destabilization of soil carbon (Cole 1997, Lal 2003); reversal of this destabilization by improved management practices has been suggested as a C sequestration strategy (e.g., Lal 2003, Post et al. 2004). These changes integrate a number of important factors, including differences in the rate and quality of plant litter additions to soils, physical destabilization by breakup of aggregates during plowing, and changes resulting from fertilizer application. This aggregate-based and land-use change-based destabilization probably accounted for a 20–30% decline in the upper 20 cm of SOC in the United States in the early part of the 20th century (Harden et al. 1999). To be important fluxes at the global scale, however, disturbances have to occur over very large land areas (e.g., 1 MgC ha⁻¹ year⁻¹ over 1 billion ha for a 1Pg C yr⁻¹ flux).

Observations of C losses from soils reported in the United Kingdom (Bellamy et al. 2005) are 10 to 100 times higher than long-term rates found in chronosequence studies (**Table 1**). The amount of dissolved organic carbon in streams and lakes has increased over the same time period, and hypotheses have been advanced to explain both phenomena. Evans et al. (2006) use radiocarbon to demonstrate that the extra DOC is mostly postbomb and therefore points to a mechanism for destabilization related to recent reductions in acid deposition that might release C stabilized in previous decades. Hence, the mechanism for documented C loss is still a matter of debate (Roulet & Moore 2006).

Radiocarbon measurements in respired CO₂ or DOC leached from soils can provide evidence for processes that destabilize C that has remained in soils for hundreds to thousand of years. For example, Karlton et al. (2005) hypothesized that a change in the ¹⁴C signatures of DOC exported from soil following a vegetation change reflected destabilization of older, sorbed soil organic matter. Several additional processes have been demonstrated that can rapidly destabilize older organic carbon: breakup of soil structure (Ewing et al. 2006), sudden wetting of dry soil (Miller et al. 2005), changes in nutrient supply and vegetation/microbial community (Nowinski et al. 2008), and thawing of previously frozen soil (Czimczik et al. 2006, Dutta et al. 2006) or draining of previously waterlogged (**Table 1**) soil. At the ecosystem scale, however, observations must be interpreted in the context of normal seasonal variations (e.g., **Figure 4**). Several studies have demonstrated contributions of pre-1950 carbon to soil respiration and DOC loss from boreal and high-latitude soils associated with seasonal warming of deeper soil layers (Hirsch et al. 2002, Neff et al. 2006) or in soils warmed after stand-killing fire removes tree cover and insulating moss layers (Czimczik et al. 2006). Clear demonstration of a response to global change that involves

net destabilization of older C pools will require longer-term measurements coupled to models that estimate the rate of stabilization of C over the same landscapes on appropriate (decadal to century) timescales.

The largest potentially vulnerable stores of soil and litter C, with total inventory estimated at several hundred petagrams, are currently found in intermittently or permanently frozen soils and poorly drained wetlands at high northern latitudes. These regions have already experienced dramatic warming and are predicted to further warm and get wetter in the coming century. Warming will change decomposition rates directly by, for example, thawing previously frozen organic matter, but also inadvertently, by changing vegetation, litter quality, and nutrient availability, which, in turn, will influence soil microbial community and decomposition rates. Vulnerability of C to decomposition with warming has been explored using laboratory incubations (Bol et al. 2003, Biasi et al. 2005, Czimczik & Trumbore 2007, Dioumaeva et al. 2002, Dutta et al. 2006) and field observations (Czimczik et al. 2006, Neff et al. 2006). These studies clearly show that old, frozen organic carbon will decompose when thawed, though the intrinsic rates of decomposition indicate these pools are likely to erode relatively slowly, even given large increases in temperatures. Even more rapid destabilization of large stores of C can occur through fire (Harden et al. 2000). The current and future balance of C loss by fire versus decomposition mechanisms likely is the most important feedback to climate change in many ecosystems.

Very rapid destabilization of large, centuries-old, C stores has been observed in N-amended tundra soils (**Table 1**; Mack et al. 2004, Nowinski et al. 2008), though the reasons for destabilization—direct effects of N, or indirect effects associated with the accompanying vegetation change—are as yet unclear. Even when overall C inventories do not change, radiocarbon measurements have been used to show that the lack of change in bulk C stocks masks increases in rates of decomposition (of prefertilization) and accumulation (of postfertilization) of organic matter (Neff et al. 2002, Nowinski et al. 2008).

The Need for Synthesis Combined with Increased Radiocarbon Analysis

Over the past two decades, the analytical and experimental techniques available for studies of SOM have improved dramatically. In addition to the wider use of radiocarbon to determine the age of organic matter stored in or lost from soils, there have been major advances in applying methods such as NMR and pyrolysis-mass spectrometry to characterize the structure and composition of organic matter and insights into the role of organisms as controls of the kinetics of decomposition. However, these approaches are only rarely applied in concert and many of these studies have focused on single soil types with little replication and attention to the broader context of controls on SOM cycling across landscapes. Enough studies have been done to demonstrate the power in approaches that combine tracers like radiocarbon with measures of standing stocks or fluxes of carbon. It is time for concerted effort to apply them in manipulative studies and across the range of state-factor gradients available and to use the results to improve predictive understanding of the rates of C stabilization and destabilization. The continued decline in atmospheric radiocarbon associated with fossil-fuel burning will limit the utility of the radiocarbon tracer without the ability to reconstruct a time series for the past decades. This lends some urgency to accelerating the use of radiocarbon in studies of organic matter in all reservoirs, including soils. Although the costs of AMS sample measurement have been high, recent advances in low-energy AMS for radiocarbon should reduce the costs and increase global sample throughput substantially. At the minimum, researchers involved in time-series measurements or who have kept samples taken over the past several decades should be encouraged to maintain sample archives and explore the value of their samples for research into changing carbon dynamics.

SUMMARY POINTS

1. Radiocarbon provides an excellent, but underutilized tool to determine the age (and thereby infer the stability) of carbon in soil organic matter. The continued decline of ^{14}C in atmospheric CO_2 lends urgency to expansion of its use to study soil C dynamics.
2. Studies that have explored the variations of soil carbon storage and dynamics in the state-factor framework demonstrate a range of rates of stabilization and destabilization of C, ranging from years to decades for plant residues, to millennia for organic matter strongly attached to mineral surfaces.
3. Soil carbon pools that have been stabilized for centuries to millennia are susceptible to abrupt change when soils cross pedogenic thresholds associated with rapid changes in climate, fire frequency, nutrient input, or vegetation/land use. Of major concern is the potential for destabilization of the large stores of climatically stabilized carbon in frozen soils, but work is also needed to quantify the degree to which C below soil A horizons may be subject to abrupt change.

FUTURE ISSUES

1. Time lags between C assimilation and addition to soil organic matter require careful assessment not only because they influence interpretations of soil organic matter dynamics based on radiocarbon but also for understanding the role of C storage in plants.
2. Determining what mechanisms underlie abrupt changes in soil carbon storage will require combining manipulations with a concerted effort to combine measures of microbial community and activity, soil physics and chemistry, and the structure, age, and chemical nature of organic matter in and exiting soils.
3. Most detailed studies of soil age and chemistry are conducted at single points on the landscape; more work is needed to allow spatial extrapolation, especially in the role of lateral versus vertical processes in determining the distribution and age of C with soil depth.
4. To be important global C fluxes, areas of soil disturbance or management must cover large areas. More effort needs to go into efforts to detect large-area change in soil status that may be reflected in stream chemistry or the age of respired C or DOC.

DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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