Storage and Turnover of Natural Organic Matter in Soil

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1. INTRODUCTION

Historically, attention on soil organic matter (SOM) focused on the central role that it plays in ecosystem fertility and soil properties, but in the past two decades the role of soil organic carbon in moderating atmospheric CO₂ concentrations has emerged as a critical research area. This chapter will focus on the storage and turnover of natural organic matter in soil, in the context of the broader role of soil organic carbon in the global carbon cycle.

Natural organic matter in soils is the largest carbon reservoir in rapid exchange with atmospheric CO₂, and is thus important as a potential source and sink of greenhouse gases over time scales of human concern (Fischlin and Gyalistras, 1997). SOM is also an important human resource under active management in agricultural and range lands worldwide. Questions driving present research on the soil C cycle include: Are soils now acting as a net source or sink of carbon to the atmosphere? What role will soils play as a natural modulator or amplifier of climatic warming? How is C stabilized and sequestered, and what are effective management techniques to foster these processes? Answering these questions will require a mechanistic understanding of how and where C is stored in soils.

SOM quantity and composition reflect the long-term balance between plant carbon inputs and microbial decomposition. The processes underlying soil carbon storage and turnover are complex and dynamic, involving influences from global to molecular scales. At the broadest level, SOM cycling is influenced by factors such as climate and parent material, which affect plant productivity and soil development. At a more proximate level, factors such as plant species and soil mineralogy affect decomposition pathways and stabilization processes. The molecular characteristics of SOM play a fundamental role in all processes of its storage and stability.

We review here the most important controls on the distribution and dynamics of SOM at the field scale and across landscapes, and the methods used to study them. The concept of SOM turnover, or mean residence time, is used quite a bit herein, and so is described in some detail. The appendix details the use of a radiocarbon ($^{14}$C), a powerful isotopic tool for studying SOM dynamics. Much of the material here was originally presented at a NATO Advanced Study Institute on the global carbon cycle.

2. THE AMOUNT OF ORGANIC C STORED IN SOILS

2.1 EMPIRICAL ESTIMATES OF GLOBAL C STOCKS IN SOILS

Most assessments of global soil C stocks have limited their reporting to storage in the top meter of soil, but recent estimates have encompassed lower depths. Historical global estimates for the top meter of soil vary from 800 Pg C to 2,400 Pg C, converging on the range of 1,300–1,600 Pg C to 1 m. Batjes (1996) estimated that an additional 900 Pg C is stored between 1 and 2 m depth, and Jobbágy and Jackson (2000) revised that estimate to 500 Pg between 1 and 2 m and another 350 Pg between 2 and 3 m depth. Global organic carbon stocks to 3 m are currently estimated at 2,300 Pg, with an additional 1,000 Pg contained in permafrost and peatlands (Jobbaga and Jackson, 2000; Zimov et al., 2006). Their distribution with ecosystem type is shown in Fig IPCC.

Two general approaches have been taken to estimate the global soil C inventory from soil profile data. The first, used by Schlesinger (1977) and Post et al. (1982), relates C storage to climate and
vegetation (expressed as Holdridge life zone classifications). For example, Post et al. (1982), using climate/vegetation relationships to soil C developed from 2,700 soil profiles, calculated a global soil C inventory of 1,400 Pg C in the top 1 m. A second approach uses soil mapping units for extrapolation (Eswaran et al., 1993; Batjes, 1996). Eswaran (1993) determined the average C inventory for each soil order, based on data from ~1,000 pedons from FAO/UNESCO and 15,000 profiles from the U.S. Dept. of Agriculture databases. This soil map-based estimate of soil C inventory globally is 1,600 Pg C in the top 1 m. Batjes (1996), using a database of 4,353 soil profiles considered to be representative of soil units on the FAO map, estimated 1,500 Pg soil organic C to 1 m depth.

Regardless of approach, these global inventories underestimate the amount of dead organic matter in ecosystems because they do not include important reservoirs. All omit C stored in surface detritus, which adds an additional 50–200 Pg C (Matthews, 1997). Moreover, in some soils there is significant soil C even below 3 meters. For example, some tropical soils and many Histosols contain as much C below 1 m as they do above 1 m (Eswaran et al., 1993; Nepstad et al., 1994). Finally, most soil C estimates do not include organic C in permafrost or relic soils, a reservoir containing roughly 900 Pg C in the boreal and arctic alone (Figure 1).

Uncertainties in the global soil C inventory are large. Post et al. (1982) estimate an error of ±200 Pg C (14%), reflecting the variability in soil C inventory within each life zone category. Eswaran et al. (1993) show large coefficients of variation (from 28–70%) for soils within given soil classification categories. Profile data employed for these estimates often use bulk density values estimated from empirical relationships between C content and bulk density (described below), developed from profiles where both were measured (Zinke et al., 1984).

2.2 PREDICTING VARIATION IN C STORAGE ACROSS THE LANDSCAPE

Constructing estimates of the amount of C stored in soils requires extrapolating from individual soil profiles to larger regions. Likewise, simulating soil C stocks requires quantitative relationships with the factors controlling stocks. In other words, we need to link soil C to factors that are mapped, or otherwise modeled, globally.

Are there predictable ways in which C storage varies across the landscape? Jenny (1941), expanding on an approach by Dokuchaev (Glinka, 1927; Jenny, 1941) and Rizpólozhenski (Lapenis et al., 2000), suggested that soil properties—including C inventory—may be predicted from soil forming, or “state”, factors. This concept is expressed by the “clorpt” equation:

Soil property (in this case, SOM inventory) = f(cl,o,r,p,t),

where cl = climate, o = potential organisms (vegetation and fauna), r = relief (aspect and topography) p = parent material, and t = time. While this may seem to be only common sense, one of Jenny’s important contributions was to develop the experimental approach that derives from the clorpt relation (Amundson and Jenny, 1997). In this approach, sites are selected such that the variable (state factor) of interest varies and all other important factors are held relatively constant. For example, to understand the influence of temperature regimes, one can locate a series of sites with the same soil age (time), biota, parent material, and precipitation but with different temperature regimes. In contrast, interpreting the influence of temperature from gradient studies (e.g., elevation gradients) in which other state factors (such as vegetation or parent material) vary is difficult.
We note that each factor can influence soil carbon storage in two ways: by influencing plant inputs and/or by influencing the residence time of organic matter in the soil. Examples of the influence of three soil-forming factors on C storage are shown in Figures 2, 3, and 4. Many of the examples below hint at the important controls of soil organic matter stabilization, and these are discussed more explicitly in a following section.

2.2.1. Climate

Jenny (1930) measured Nitrogen (and Carbon) storage in soil sampled across the U.S. Great Plains (Figure 2), where the parent material consists largely of loess deposited during the last glacial period. In this region precipitation increases from west-to-east, while mean annual temperature varies from north (coldest) to south (warmest). By comparing soils at the same latitude but different longitude, the gradient in temperature is isolated from variation in mean precipitation, vegetation, and parent material. By comparing soils across latitude, one can isolate the effect of precipitation. Jenny used the variation in climate across the Great Plains to explore the controls of both temperature and moisture on SOM. Carbon stocks are largest toward the cooler and wetter northeast, and are smallest in the hotter and drier southwest (Jenny 1930, from Jenny, 1941).

2.2.2. Time

A chronosequence is a series of sites that vary in the period of time over which the soil has developed, or since significant disturbance, e.g., deforestation. In a state factor experiment, all the sites in the chronosequence would have the same climate history, parent material, and, unless specifically included in the study design, vegetation species. Such sequences have been constructed from terraces formed by coastal uplift or by rivers, by glacier retreat, and by lava or ash deposits of different ages. A chronosequence in Hawaiʻi, developed on ash deposits of different ages (Chadwick et al., 1999) illustrates a trend seen in other, similar studies (Jahn et al., 1992; Percival et al., 2000). Soil organic carbon accumulates for the first several-hundred-thousand years of soil development, then declines in very old soils (>several million years). The slow build up and subsequent decline of carbon has been linked to changes in the amount and type of soil minerals that can stabilize SOM (e.g., Oades, 1989) and also the very long time needed to build up substantial stocks of refractory organic matter (Schlesinger, 1990). In Hawaiʻi, changes in soil carbon are linked to changes in the amount of non-crystalline secondary minerals like allophane and imogolite, which have large reactive surface areas (Torn et al., 1997, Figure 3). In many places, estimates of carbon storage in highly weathered soils are complicated by the fact that they are often very deep (tens of meters) so that even very low C concentrations may add up to a large amount of stored carbon in the total profile (Sombroek et al., 1993).

2.2.3. Parent Material

Parent material—the mineral substrate at the inception of soil development—has a variety of influences over SOM stocks. It affects fertility and plant productivity (C inputs to soil); texture, which affects soil moisture retention and thus both productivity and decomposition; and clay content and mineralogy which affect SOM stabilization. For example, soils developed on volcanic ash or rocks of basic pH often contain more organic carbon than those formed on granitic or acidic parent material (e.g., Harradine and Jenny, 1958; Marti and Badia, 1995). In many cases, differences in C storage between soils developed on different parent materials
decrease as soils reach great age (millions of years). We speculate that over millions of years, the mineral and associated organic content of different soils tends to converge to a state predicted or constrained by climate (Torn et al., 1997).

An analysis of worldwide data shows differences in carbon storage among parent materials, in spite of the fact that it does not control for confounding factors such as soil age (Zinke et al., 1984) (Figure 4). Jenny (1980) showed that soils developed on postglacial till deposits with different amounts of loess exhibit increasing C density with more loess, a pattern he ascribed to finer texture (Figure 5). Indeed, soil texture (particularly clay content)—which is a product of parent material as well as climate and other soil forming factors—has been positively correlated with C storage in many sites and is used as the proxy for mineral control in ecosystem soil carbon models. The reliance on texture as a proxy for mineral stabilization is one area of understanding that is changing very rapidly, however. Recent studies show that storage and turnover may be much more closely related to mineral properties, in particular the poorly crystalline clay phases, than to texture per se (Kleber 2006, Torn 1997, (Basile et al., 2005; Masiello et al., 2004)). As a countervailing view, in some soils and in sediments, surface area and texture will remain a very useful predictor of soil carbon storage, as long as they are measured correctly (Aufdenkampe et al., 2001).

2.2.4. Organisms

In an analysis of more than 2700 soil profiles from three global databases, Jobbágy and Jackson (2000) found that vegetation type strongly influenced the amount of soil carbon and its distribution with depth. Vegetation controls C storage in several ways. First, net primary productivity, which depends on plant species and communities, determines C input rates to soil. As a result, for soils where decomposition rates of organic matter are similar, the soils with more productive vegetation will have higher organic C inventory. Soil carbon losses after forest conversion to pasture or agriculture are attributed least in part to decreases in primary productivity (Trumbore et al., 1995). Second, since a large fraction of soil C inputs comes from root turnover, and since soil C decomposition decreases with depth, the distribution of root inputs with depth, affects soil C storage. Third, vegetation type affects tissue chemistry, seasonality and depth of inputs, as well as the proportion of photosynthate allocated to roots, shoots, or woody structures—all of which have a large impact on the transformation and stabilization of organic matter (Bird and Torn, 2006; Steinmann et al., 2004; Zanelli et al., 2006). Tissue differences in macroscopic and molecular structure affect initial decomposability and possibly the decay products. For example, litter decomposition rates have been linked to the amounts of lignin, nitrogen, and non-structural carbohydrates in leaf and root litter (Berg et al., 2001; Melillo et al., 1982). While the long-term importance of tissue chemistry for decomposition is under debate. Quideau et al. (1998) found that soil C stocks differed several-fold among sites of the same parent material, age, and climate, depending on the type of vegetation—and aspects of the organic matter chemistry as determined by NMR also varied with vegetation type. Moreover, in a related study, differences among plant genera (this case Quercus, Arctostaphylos, and Pinus) had a bigger influence on the chemical composition of SOM than did climate (Quideau et al., 2001).
2.2.5. Relief

For landscape-scale studies, factors like local topography and soil drainage are important in determining soil C storage. C inventories are higher at the bottom of slopes, in part because erosion transports topsoil downward and because wetter conditions or burial in depositional areas promote plant productivity and/or inhibit decomposition rates (Berhe et al., 2007). These landscape-scale variations are particularly important when considering how representative a single soil profile is of regional soil C storage (Davidson and Lefebvre, 1993).

2.2.6. Opportunities and Drawbacks

These illustrations give us general rules for predicting how C inventory in soils will vary across large regions and over long time scales. The largest C inventory should be in cool, wet climates with high ecosystem productivity, on young volcanic surfaces (as in the Pacific Northwest of the USA). The smallest C stocks should be found in hot, arid regions of low productivity (as in desert soils). Another observation put forth by Jenny is that the major reservoirs of soil carbon change with latitude: at low latitudes, very little of the total soil C is stored in surface detritus, and most of the C is associated with the mineral soil. At high latitudes, slow decomposition rates lead to large accumulations of detrital organic material, and relatively little of the organic matter is associated with the mineral soil.

The approach of studying gradients is not without drawbacks. Clean environmental gradients, in other words, gradients with a minimum of confounding variability, can be challenging to locate. For example, one of the problems in climate-gradient studies is that climate and vegetation cannot always be separated as independent variables across landscapes. In Hawai’i, the same tree species dominates native forests in young to mature and mesic to wet sites, and thus Hawai’i has proven a rich location for gradient studies. Perhaps more fundamental for research on environmental change, the vegetation/climate/soil characteristics in the undisturbed ecosystems that are used for gradient studies represent linkages that have taken shape over relatively long time scales. The response to rapid environmental change may not be of the same magnitude or even in the same direction as the response predicted from a gradient. For example, the difference in carbon stored at two sites along an elevation gradient with a 3°C temperature difference may not adequately represent the change in carbon that would occur at the higher elevation site with a 3°C warming over the course of a century. This is a general weakness in using equilibrium conditions to predict rapid or transient responses (Dunne et al., 2004)

Experimental manipulations are important not only for controlling variables of concern but also for investigating short term responses to environmental change. On the other hand, field experiments may not run for long enough, or encompass a large enough area, to predict long term effects of environmental change. For example, the relationship of carbon stocks to soil temperature was negative during the first nine years of experimental warming in a montane meadow but positive along a local climate gradient. The C decline observed in the experiment appears to have been a transient response; concurrent changes in plant litter quality may lead to long term increases in soil storage (Saleska et al., 2002). Another limitation of ecological experiments is that they tend to use step changes in variables rather matching the gradual nature of expected changes (Shaver et al., 2000). Results from a suite of ecosystem warming manipulations in Europe and North America indicate that (1) the same temperature change can elicit different responses, depending on the initial climate and biogeochemical conditions of the system; (2) temperature affects ecosystems rapidly via process rates and more slowly via species...
composition and tissue chemistry; and, as a result (3) the magnitude and direction of the response can change over time.

2.3 SOIL BULK DENSITY AND CARBON INVENTORY ESTIMATION

The amount of organic carbon stored in a soil profile is calculated from measurements of the C density and bulk density (BD; the dry weight of a known volume of soil, including pore space) in the horizons, as shown in equation 1.

\[
C_{\text{inventory}} \left( \frac{g \, C}{cm^2} \right) = \sum_{\text{all horizons}} \text{Bulk Density} \left( \frac{g \, soil}{cm^3} \right) \times \left( \frac{g \, C}{g \, soil} \right) \times \text{depth (cm)} \times (1 - \text{fraction gravel})
\]

The last term is a correction for stones and gravel (greater than 2 mm in diameter; the coarse fraction). Bulk density values can vary by a factor of 4 depending, for example, on soil OM content, depth, and compaction. As a result, the largest uncertainties in determining C stock in a soil profile usually come from estimates of bulk density and the volume of soil that is gravel. It is difficult to reproducibly collect a precise volume of soil and in many studies bulk density simply has not been measured at all.

Large plant fragments and organic mats are often excluded from the estimates of C in soil, either by being excluded during sample collection or removed during sieving at 2 mm. This traditional focus on the ‘fine soil’ in soil science is not adequate in the context of carbon management, where a complete accounting of organic carbon is desirable. Researchers are actively adapting to this expanded perspective by developing new protocols and expectations in the customary reporting of soil characteristics.

There is a new soil carbon measurement technique, using a neutron generator and gamma ray detector, currently being field tested that would offer several benefits. The probe relies on inelastic scattering of 14 MeV neutrons by the carbon nucleus in soil and nearly simultaneous measurement of the carbon characteristic (4.4 MeV) gamma radiation. The measuring system is housed in a set of large boxes that can be wheeled over the soil. It measures total C atoms to 30 cm depth and as a result, it does not require a bulk density measurement. In addition, because it is in-situ and non-invasive, the same spot can be measured repeatedly. Potential drawbacks include that measurement depth is not readily adjustable and the system is very heavy and therefore is limited to sites with some kind of vehicle access. An on-going intercomparison between this approach (led by L. Wielopolski) and conventional methods in a range of temperate sites (e.g., U.S. Southern Great Plains, M. Torn data not shown) must be completed before applications can be recommended.

3. TURNOVER TIME AND DYNAMICS OF SOIL ORGANIC MATTER

Simply knowing the amount of organic carbon in soil provides little insight into its roles in ecosystem function or atmospheric feedbacks. For example, a large SOM reservoir that is extremely stable may provide little in the way of plant-available nutrients and may respond slowly to climate change. It is thus important to understand not only how much C is stored in a reservoir, but also how rapidly the C cycles. This is not a simple proposition, however, as SOM is a complex mixture of compounds that cycle along a continuum of time scales from minutes to tens of thousands of years (for mineral stabilized C in subsoil; Torn et al. 1977). Segregating SOM into discrete reservoirs with different turnover times, and understanding their relationship
to biotic and soil conditions, is an ongoing challenge. This section summarizes some approaches and observational constraints in characterizing C dynamics in soils.

To lay the foundation for the following section on metrics, consider that the decomposition flux from soil is a function of the stock of the soil C stock \((C)\) and its decays rate. More strictly speaking, decomposition of a homogeneous reservoir is treated as a linear, donor-controlled process—meaning that the amount of C decomposed is the product of the C stock \((C)\), a decomposition rate constant \((k)\), and the time interval \((\Delta t)\). The turnover time \((\tau)\) is simply the reciprocal of the decomposition rate \((\tau = 1/k)\), and thus the amount of C decomposed per time interval \(= C/\tau\). The change in soil C stock between one year and the next \((dC/dt)\) is the difference between the inputs and outputs over that year:

\[
\frac{d(Soil\ C)}{dt} = \text{Plant inputs} - \text{Decomposition losses}, \text{ or in the symbols of the Appendix:}
\]

\[
\frac{dC}{dt} = I - C/\tau
\]

and at steady state \(\tau = I/C\) (see Appendix 2 for further explanation and equation A2.1).

### 3.1 METRICS OF CARBON DYNAMICS

Several terms are used to describe the dynamic cycling of biogeochemical reservoirs. Rodhe (1992) identifies three key terms for expressing dynamics of cycling for a geochemical reservoir: turnover time, mean residence time, and average age. Although under the right conditions these terms may be equivalent, they often differ and it is important to understand the distinctions among them. The turnover time \((\tau_o)\) of a reservoir is a measuring of its mixing or refresh rate, and is the time it would take for the reservoir to completely empty if there were no further inputs. For soils, it is a measure of the first order kinetics for decay \((\tau_o = 1/k)\). At steady state (i.e., when gains equal losses) it is calculated as the inventory divided by the gross flux through the reservoir. To calculate the turnover time for a soil C reservoir at steady state, we would divide the mass \((M)\) of C in SOM by the total C flux \((S)\) from the SOM, including decomposition to CO₂ and leaching of dissolved organic or inorganic C:

\[
\tau_o = \frac{M}{S}.
\]

The average residence time (also, mean residence time; \(\tau_r\)) of C in the reservoir is the average time spent in the reservoir by individual C atoms before leaving:

\[
\tau_r = \int_{0}^{\infty} \tau \phi(\tau) d\tau, \quad \text{where } \phi(\tau) = \text{probability density function of residence times in the reservoir.}
\]

Finally, the average age \((\tau_a)\) of C atoms in the reservoir is the average time spent in the reservoir by all the atoms currently in the reservoir:

\[
\tau_a = \int_{0}^{\infty} \tau \psi(\tau) d\tau, \quad \text{where } \psi(\tau) = \text{probability density function of ages in the reservoir.}
\]

For a homogeneous reservoir (one for which the probability of every atom leaving is equal) at steady state, the turnover time, mean residence time, and average age of organic matter in the
reservoir are equal ($\tau_o = \tau_t = \tau_a$). While steady state is often a reasonable assumption for undisturbed ecosystems, it is almost never the case that a bulk soil sample will have a homogenous pool of soil C (i.e., all C turning over at the same rate).

Measurement of radiocarbon in SOM is often used to produce a radiocarbon-based age ($^{14}$C age), which is commonly used as a proxy for the average reservoir age, $\tau_a$, and turnover time. The ideal scenario ($\tau_o = \tau_t = \tau_a$) is seldom encountered, however, because SOM is a heterogeneous mix of compounds that decompose at different time scales, from hours to millennia and the carbon inputs come from sources with different ages (time since photosynthesis). The latter is important for linking the radiocarbon age to the time in the ecosystem. Unfortunately, the $^{14}$C-ages of inputs into SOM reservoirs are often greater than zero, so that using $^{14}$C-age as a direct proxy for $\tau_a$ will lead to an overestimate of $\tau_a$. Even when $^{14}$C-age $\approx \tau_a$, these averages may actually lead to a false impression of fluxes through a heterogeneous reservoir (e.g., $\tau_t < \tau_a$), as illustrated in Figure 6.

For example, Raich and Schlesinger (1992) calculated the turnover time for C in soils using C inventory (to 1 m depth, and including surface litter) divided by the CO$_2$ emission observed for the same ecosystem (corrected assuming ~30% was root respiration and ~70% from organic matter decomposition). The turnover times they calculate ranged from 10 y in tropical grasslands to ~500 y for tundra and wetland environments, with a global average of 32 y.

Yet, radiocarbon measurements of SOM made in the early 1960s, or on archived soils collected prior to the 1960s, showed the average age of soil C to be several hundreds to thousands of years in temperate and some tropical systems. The apparent contradiction with Raich and Schlesinger’s results may be explained if most of the flux of CO$_2$ from the soil is derived from decomposition of “young” carbon, whereas much of the C residing in the soil is stabilized and decomposing only very slowly. In other words, instead of a large C reservoir with 10-year turnover in tropical grasslands, there is likely a small reservoir of annual-cycling organic matter and a much larger one with cycling on time scales of several decades to a century. The distinction is important if we want to predict the response rate and magnitude of the grassland soil to disturbances like management or climate change.

One key area of work in understanding and modeling soil C is the study of relative decomposition rates and mean residence times for various organic substrates and organic matter byproducts. Although the compounds comprising organic matter form a continuum of decomposability, a continuous distribution of decomposition rates is difficult to constrain using field measurements. There is general agreement that the distribution of soil C mean residence times tend to cluster at three very different scales: < 1 year, years to centuries, and millennial. The terms used to describe the reservoirs (e.g., “active”, “slow”) vary, often according to frame of reference (e.g., microbial community dynamics, or soil genesis). Root exudates and components of fresh plant litter decompose on the time scales of hours to months (e.g., Norton, 1990) and are often referred to as the “active pool.” Stabilized organic matter persists in soils over several thousands of years and is often referred to as the “passive” or “millennial cycling” C pool. The remaining “intermediate” or “slow” C has turnover times in the range of years to centuries, and may consist of structural components of plants more resistant to decay, or organic compounds that have been weakly stabilized by their association with mineral surfaces or protection within aggregates. Figure 7 shows a three-pool conceptual model.
3.2 OBSERVATIONAL CONSTRAINTS FOR DETERMINING C DYNAMICS IN SOILS

No single satisfactory method yet exists by which to separate soil C from the complex soil matrix into discrete components with different turnover times. Instead, soil C distribution and dynamics are deduced using many constraints, including: physical and chemical fractionation of organic matter, field and laboratory decomposition studies, measures of C fluxes into and out of the soil, measurements of $^{14}$C in soils sampled at various times before and after the peak of atmospheric nuclear weapons testing, changes in the $^{13}$C content of SOM following a vegetation change from plants with C3 to C4 photosynthetic pathways, additions of $^{13}$C and $^{14}$C tracers, and measurements of changes in the total amount of C in soils of different age or following disturbance. Each of these tools is suitable for determining different time scales of soil C dynamics, and when two or more are combined they may form an especially powerful means of elucidating C dynamics. Here we discuss the use and constraints of some of the most common approaches.

3.2.1. Litter Decomposition Experiments

The rate of mass loss of fresh plant litter may be used to estimate litter decomposition rates, assuming first order kinetics:

$$\frac{dM}{dt} = -kM; \quad k = -t\ln\left(\frac{M_t}{M_0}\right),$$

where $M_0$ is the initial mass and $M_t$ is the mass at time $t$ after deployment. This method is complicated by the design of the containment system for the plant litter, which needs to allow soil fauna in but not transport of litter fragments out. Most field litter-bag experiments show relatively rapid initial rates of loss, followed by slower decomposition of the remaining recalcitrant compounds. Decomposition rates vary with climate (fastest decomposition in hot, moist climates, and slowest in cold, wet climates), the type of plant material (roots versus leaves, lignin versus cellulose), soil fauna, and soil texture. Isotopically-labeled C (enriched in $^{13}$C or $^{14}$C) may be added to the litter layer either as labeled plant material or as individual organic compounds to follow specific decomposition pathways. These studies have shown that, while much of the labeled material may decompose rapidly, a portion is incorporated into components that are more stable and persist for many years. It should not be assumed, then, that plants that produce litter with rapid rates of initial degradation will also produce SOM with rapid turnover rates. Indeed, C dynamics in aboveground litter vs. mineral soil may bear little resemblance, reflecting fundamental differences in substrate chemistry as well as biotic and abiotic conditions.

3.2.2. Laboratory Incubations

Laboratory incubations provide a controlled environment for characterizing and comparing C and nutrient dynamics in isolated soils. Most often, soils are incubated in jars (Hart et al., 1994; Stotzky, 1965) or microlysimeters (Nadelhoffer, 1990). Incubations have been used to estimate C mean residence times (Paul et al., 2006; Torn et al., 2005) and stability (Swanston et al., 2002; Whalen et al., 2000), interactions of SOM and various nutrients (Swanston et al., 2004; Torn et al., 2005; Zak et al., 1993), and the influence of temperature and moisture on SOM decomposition (Dutta et al., 2006; Reichstein et al., 2005). However, the very isolation that allows for controlled conditions also introduces artifacts. The lack of continued inputs, changes
in substrate quality and availability, and associated shifts in microbial communities such that they no longer resemble those in the field, all combine to reduce the ability to reliably extrapolate incubation results to dynamic ecological settings.

3.2.3. Soil Respiration

Soil respiration, or the efflux of CO$_2$ from soils to the atmosphere, is one of the fundamental flows in the terrestrial carbon cycle. It is the primary way that carbon moves from ecosystems back to the atmosphere. Globally, soil respiration is one of the largest fluxes, an estimated 50–80 Pg C year$^{-1}$ (Potter et al., 1993; Raich and Schlesinger, 1992; Schimel, 1995). Since the annual exchange of C between the soil and atmosphere is so large (by comparison, we add only ~8 Pg C year$^{-1}$ to the atmosphere by fossil fuel burning), interannual variability in soil respiration may potentially cause changes in the rate of increase in atmospheric CO$_2$ (Trumbore et al., 1995). Soil respiration makes up >50% of total ecosystem respiration (which in turn roughly equals gross photosynthesis in ecosystems). Soil respiration thus varies with latitude, from 80 g C m$^{-2}$ year$^{-1}$ in deserts to 800–2000 g C m$^{-2}$ y$^{-1}$ in a tropical forest (Raich and Potter, 1995; Raich and Schlesinger, 1992; Schlesinger, 1977; Trumbore et al., 1995)

Despite its importance in ecosystem C flux, soil respiration currently has substantial limitations as a constraint on the $\tau$ of SOM. This is primarily because of the difficulty in partitioning the sources of soil respiration. Soil respiration has two fundamental sources: (1) decomposition of SOM by microbes (heterotrophic respiration) and (2) respiration from live plant roots (autotrophic respiration). Potential changes in CO$_2$, temperature, and moisture regimes in the coming decades will likely influence autotrophic and heterotrophic respiration in different ways (Kuzyakov, 2006). If we are to use soil respiration measurements to help understand the effects of climate change on NPP and on the turnover of SOM, it is necessary to adequately partition soil respiration into at least the two basic components. There are numerous approaches to partitioning CO$_2$ efflux (Kuzyakov and Larionova, 2005), but each has drawbacks and a method able to partition soil respiration in situ remains elusive (Kuzyakov 2006). As a result, it has proven very difficult to observe the effect of soil temperature, moisture, and other factors such as elevated CO$_2$ on decomposition directly in the field. Without this essential ability, we are unable to confidently determine the relationship between ecosystem variables such as NPP, temperature, moisture, and SOM decomposition. Further, partitioning the sources of respiration from different SOM reservoirs, which may respond differently to climatic variables, is not currently attainable through soil respiration measurements alone.

The most common method of measuring soil respiration is to place a chamber over the soil and measure the change in CO$_2$ concentration in the headspace over time. For a continuous 24-hour measurement, the CO$_2$ is trapped in soda lime in the chamber. This soda lime method may be useful for determining relative soil respiration rates and for integrating over a diurnal cycle. The long incubation time (typically 24 h) for the soda lime method leads to large chamber effects that likely create substantial artifacts in the flux measurements. For more rapid and more accurate measurements, changes in the CO$_2$ concentration in the chamber headspace are monitored over time, using either syringe samples analyzed with a gas chromatograph or by circulating chamber air through an infra-red gas analyzer. Eddy covariance methods can measure net ecosystem carbon exchange (the difference between photosynthesis and respiration by the whole ecosystem), but, except where a below-canopy eddy flux system is employed, do not separate
soil respiration from aboveground respiration without using a model to predict aboveground respiration.

### 3.2.4. Isotopic Tracers

The use of enriched C isotopes can be an effective means of characterizing rapidly cycling C reservoirs, and if pursued long enough may also shed light on decadal reservoirs. Carbon has three relatively long-lived isotopes: 98.9% of earth’s C is $^{12}$C, ~1% is $^{13}$C (a stable isotope) and ~0.1% is $^{14}$C. By enriching or depleting the ratios of the rare isotopes and introducing them to plants, plant litter, or directly to soil, it is possible to follow the pulse of altered isotopic ratios as they diffuse through the system. Primarily because of the high cost of the enriched isotopes, these studies typically take place only on a small-plot basis. A notable exception is the series of Free-air CO$_2$ enrichment (FACE) experiments, which maintain elevated levels of atmospheric CO$_2$ in open-air sites that are up to 30m in diameter. The elevated CO$_2$ is also isotopically depleted, with a $\delta^{13}$C of -21 as compared to -8 at natural abundance. Jastrow et al. (2005) traced the depleted pulse into SOM and used meta-analysis to show net accumulation of SOM in elevated CO$_2$ treatments at several FACE sites. Another exception is the Enriched Background Isotope Study (EBIS) at Oak Ridge National Laboratory in Oak Ridge, Tennessee, USA. EBIS investigators used a combination of a stand-level radiocarbon enrichment and a reciprocal litter transplant from a forest stand with litter that had near-background $^{14}$C levels, to partition sources of soil respiration (Cisneros-Dozal et al., 2006) and investigate SOM dynamics (Hanson et al., 2005; Swanston et al., 2005).

### 3.2.5. Natural Abundance Stable C Isotopes

The $\delta^{13}$C of litter and particulate SOM are typically more similar to plant values, with mineral-associated SOM often 1-3‰ higher (more enriched). The $\delta^{13}$C of the bulk soil also generally increases by 1-3‰ with increasing depth and decreasing particulate SOM. There is ongoing and active discussion regarding whether the source of these trends primarily resides in microbial discrimination or selective preservation of plant compounds (Dijkstra et al., 2006; Mikutta et al., 2006), but the variability is too high and the range of values too narrow to clearly answer these questions using natural abundance stable isotopes in non-manipulated systems.

Plants with C$_3$ or C$_4$ photosynthesis pathways discriminate against $^{13}$C to different degrees, and thus accumulate biomass with differing $^{13}$C:$^{12}$C ratios (C$_3$:$\delta^{13}$C $\approx$ -27; C$_4$:$\delta^{13}$C $\approx$ -13). For the special case where a vegetation change from C$_3$ to C$_4$ plants (or vice-versa) has occurred, the rate of change of $^{13}$C:$^{12}$C ratios in SOM will give an idea of the turnover time of SOM. This method has been used frequently in tropical pastures where C$_4$ grasses have replaced C$_3$-dominated forest, and in the American Midwest where maize has replaced native forest. There are two drawbacks to this method: (1) it cannot be used to study soils that have not undergone a vegetation change; and (2) it requires careful measurement of C inventory changes in disturbed versus undisturbed soils. These attempts are complicated by plowing, discing, and/or erosion of the pasture soils, as well as the inherent uncertainty in bulk density determinations.

### 3.2.6. Radiocarbon

Radiocarbon ($^{14}$C) is unstable, with a half-life of 5,730 y, and decays by emission of an electron to form $^{14}$N. It is continuously produced in the upper atmosphere by interactions of high-energy cosmic rays with the upper atmosphere. The $^{14}$C is oxidized to $^{14}$CO$_2$ within a few weeks, and
mixed into the troposphere (the lower, well-mixed part of the atmosphere), where it is taken up by plants during photosynthesis and may dissolve in the surface waters of the ocean. If a C reservoir ceases to exchange \(^{14}\text{C}\) with the atmosphere, the \(^{14}\text{C}\) it contains will begin to decrease because of radioactive decay. This is useful for studying very stable C pools in soils, since they reside long enough for significant decay of \(^{14}\text{C}\) to occur. The longest time scales that can be addressed with \(^{14}\text{C}\) in this way are on the order of 60,000 y.

Atmospheric thermonuclear weapons testing, which peaked in 1963, approximately doubled the amount of \(^{14}\text{C}\) in the atmosphere (Figure 8). This “bomb” \(^{14}\text{C}\) provides a global isotopic tracer for the C cycle, although still several orders of magnitude below levels of \(^{14}\text{C}\) used in many most small scale \(^{14}\text{C}\)-tracer studies. The degree to which bomb \(^{14}\text{C}\) is found in SOM provides a direct measure of the amount of fast-cycling (active+slow) SOM. The most straightforward approach compares \(^{14}\text{C}\) measurements of SOM sampled prior to 1960 with contemporary samples from the same location (Torn et al., 2002). Where no archived soils are available, however, radiocarbon measurements must be combined with other observational constraints to separate the radiocarbon signature of rapidly cycling from very refractory organic matter. The time scales of C turnover that may be addressed using bomb \(^{14}\text{C}\) range from ~4 to ~100 y.

Direct measurement of the age of C atoms leaving the soil is possible using trapped air from the headspace of a chamber (Dörr and Münstich, 1986; Gaudinski et al., 2000). The degree to which \(^{14}\text{C}\) reflects recently fixed C versus C fixed several years to decades ago provides a potentially important tool for partitioning the sources of soil respiration (autotrophic plant respiration versus heterotrophic microbial respiration) and the turnover times of the decomposing organic matter that contributes the most to soil respiration (Torn et al., 2005). Working in temperate grassland and forest, Dörr and Münstich (1986) found significant seasonal differences in the \(^{14}\text{C}\) content of total soil respiration, with summer emissions dominated by recently fixed carbon, and winter fluxes by carbon fixed up to several decades previously (which likely indicates a higher proportion of autotrophic respiration in the growing season as well as changes in the substrate for decomposition).

Radiocarbon can also be a valuable tool in identifying the relative stability of long-term soil C reservoirs, if not necessarily their ages. The dynamic nature of SOM is such that even very stable C reservoirs within contemporary soils have likely incorporated some bomb \(^{14}\text{C}\), rendering the interpretation of \(^{14}\text{C}\)-age problematic. The depletion of \(^{14}\text{C}\) (i.e., \(\Delta^{14}\text{C} < 0\)) in different SOM reservoirs, however, is certainly indicative of stability and slow turnover, as it indicates radiocarbon decay and low incorporation of bomb \(^{14}\text{C}\) (Mikutta et al., 2006; Sollins et al., 2006). Under steady-state assumptions, the incorporation of bomb \(^{14}\text{C}\) into these reservoirs can be modeled, yielding mean residence times.

Appendices 1 and 2 contain more thorough discussion of radiocarbon methods and applications to SOM studies.

### 3.2.7. Fractionation of Soil Organic Matter

There are numerous approaches to separating SOM pools for analysis, with a corresponding number of underlying conceptual frameworks. The objective of fractionation is usually to reduce the chemical, physical, and/or age variation in the resulting fractions, as compared to the bulk soil. Ultimately, most isolated SOM pools are nonetheless operationally defined and remain a
mixture of heterogeneous compounds from multiple sources. The challenge is not to find a single method that will perfectly characterize all SOM pools, but instead to understand what kind of information is provided by a given method and how that relates to the scientific questions of interest. The most common methods of characterizing SOM include chemical (humic/fulvic separation, acid hydrolysis), density, size, and aggregate fractionations.

Humic and fulvic acids are isolated by extracting the soil with alkali, thus solubilizing the acids from the humin, and then treating the extract with acid to separate the humic and fulvic acids. Compounds are thus separated along a continuum of increasing degree of polymerization, molecular weight, and C and oxygen concentration, from fulvic to humic acids (e.g., Stevenson, 1994). These fractions may be useful in providing “signatures” for soils, perhaps varying with factors such as vegetation and management (Miglierina and Rosell, 1995). Another common chemical separation is acid hydrolysis, used to isolate N-rich compounds (including proteins and nucleic acids), polysaccharides, and other chemically labile SOM from acid resistant material such as aromatics and long-chain aliphatics (Paul et al., 2001). When simply applied to bulk soil, one may question how relevant these separated chemical fractions are to the decomposition environment (where the different fractions are intermixed together). For example, an organism may inhabit a discrete piece of organic matter, degrading carbohydrates and polyphenolic lignin structures simultaneously in a co-metabolic process (Chotte et al., 1998; Guggenberger et al., 1998). Extraction with NaOH may separate some lignin-derived aromatic C, depositing it into the humic acid while the remainder is left in the humin (Kögel-Knabner et al., 1991). Most polysaccharides would presumably reside in the fulvic fraction. Thus, although these C structures are related spatially and biologically in the soil, chemical fractionation procedures may separate them into several fractions, potentially obscuring their connected roles in soil C cycling.

Physical soil fractionation methods such as density, size, and aggregate separations aim to isolate pools of SOM based upon their degree of organomineral interaction, the extent of protection within aggregates, and the size and location of the aggregates. Density fractionation takes advantage of the differences in density between particulate organic matter and mineral-associated organic matter. In the simplest, 2-pool density approach, a light fraction is floated on a dense liquid after soil disruption, and the denser, or heavy fraction, sinks (Strickland, 1987; Sollins et al., 1999). The light fraction is typically less degraded and more plant-like than the C in the mineral-associated heavy fraction (Gregorich et al., 1996). Radiocarbon measurements (see Appendix 1) confirm that light fraction organic matter contains more recent carbon than organic matter in the dense fraction (Trumbore and Zheng, 1996). This technique has the drawback of mixing unprotected light fraction with aggregate-protected light fraction, which may cycle at a much slower rate. Golchin et al. (1994a) modified this technique to separate the ‘free’, unprotected light fraction first, then disrupting aggregation to separate the “occluded”, aggregate-protected light fraction. Recent work using $^{13}$C has confirmed that the occluded light fraction has a slower turnover rate than the heavy fraction (Rasmussen et al., 2005; Swanston et al., 2005). The heavy fraction can be further separated by increasing density, generally yielding older, but smaller, organomineral pools (Golchin et al., 1994b; Sollins et al., 2006). There is evidence that initial or repeated aggregate dispersion may redistribute C and N between fractions (Baisden et al., 2002; Cambardella, 1994). However, density separation will often capture the major trends of mineral-associated SOM, and trends related to the protection of particulate organic matter in macro- and some microaggregates if the Golchin et al. (1994a,b) method is used.
Particle size fractionation is founded on the concept that increasing degradation and strength of organomineral associations and increasing are associated with decreasing particle size (increasing reactive surface area) (Christensen, 1992; Tiessen and Stewart, 1983a). Numerous variations in the methodology exist (e.g., Christensen, 1992), but soils are typically dispersed sonically, by shaking with glass beads, or chemically with hexametaphosphate, and the resulting soil slurry is passed through a series of decreasing sieve sizes and centrifuged to isolate fine fractions. Although there are general differences related to particle size, it is also evident that C pools differentiated by size class are composed of multiple chemically protected or biochemically recalcitrant pools with differing residence times that may be classified as a function of origin, chemical composition, and mineralogical interactions (Kiem and Kogel-Knabner, 2003; Schmidt and Kogel-Knabner, 2002).

The goal of aggregate-based soil fractionations is to isolate functional pools tied to the cycling and stabilization of SOC within the context of soil structural organization. To the extent possible, aggregate-based separation avoids mixing C pools that are spatially separated in the soil matrix, a problem with simple density and size fractionation approaches. Conceptual models of the interactions between soil aggregate cycling and the conversion of detrital inputs to SOM are the basis for this approach (e.g., (Oades, 1984); Golchin et al., 1994b; (Jastrow et al., 1998); Six et al., 2000). New inputs (particularly plant detritus) enter the soil as POM which is relatively unprotected until it is stabilized within microaggregates. Physical isolation of intact microaggregates, including those located within macroaggregates, followed by their dispersion provides quantitative information for several process steps related to SOC cycling. Based in part on earlier work by Golchin et al. (1994b) and Cambardella and Elliot (1994), Six et al. (2000) developed a complex fractionation scheme designed to maintain the spatially explicit relationships of SOM existing within and between aggregates of different sizes and stabilities.

4. IMPORTANT CONTROLS ON C DYNAMICS

We hope to facilitate this discussion by first defining terms that are commonly used interchangeably but nonetheless have distinct meanings. These definitions aid us in describing the context of C dynamics, and we hope they will be helpful to others, as well. In the most general sense, a process is a series of steps leading to a result; in the context of carbon cycling, the result is the stabilization or destabilization of carbon. A mechanism is the crucial 'step' in the process, or the physicochemical condition that most distinctly results in carbon stabilization or destabilization. A control is something that exerts an exceptionally strong influence on a process, often rendering mechanisms more or less effective.

Soil C dynamics reflect the concurrent activity of the myriad processes leading to stabilization or destabilization of SOM. Sollins et al. (1996) discuss SOM cycling within the context of proximal and distal influences; that is, mechanisms that have an immediate influence on C stability and flux (e.g., molecular recalcitrance, mineral and organic interactions, and accessibility) ranging to controls with a distinct but more general influence (e.g., state factors, such as climate). This conceptual hierarchy is a useful framework under which to chart the interrelationships of the numerous influences on soil C turnover. An important concept, however, is that a proximal influence (mechanism) is not necessarily the dominant factor in C stabilization, nor is distal influence necessarily a minor factor. We suggest that there is no universally dominant mechanism or control on SOM dynamics. Instead, we consider different controls, and what factors make a particular mechanism more important or effective in one place but not another.
4.1 MECHANISMS OF STABILIZATION

A physical or chemical condition that renders SOM less susceptible to alteration or transport (i.e., more stable) is a mechanism of stabilization. A great deal of careful thought has gone into defining and comparing the mechanisms that control C stability, and organizing them into a limited number of broad categories (Sollins et al. 1996; Baldock and Skjemstad, 2000; Krull et al., 2003; Lützow et al., 2006). Additionally, researchers have sought to identify a dominant mechanism of long-term stabilization, leading some to focus on the inherent molecular recalcitrance of organic molecules (Krull et al., 2003), and others concluding that mineral interaction and protection are the fundamental controls (Lützow et al., 2006; Van Veen and Kuikman, 1990). Here we discuss several categories of stabilization mechanisms, largely adapted from Sollins et al. (1996), and place them within the context of climate, ecology, and management.

4.1.1. Recalcitrance

We use the term ‘recalcitrance’ to specifically refer to the inherent molecular characteristics of SOM that contribute to resistance to degradation (Sollins et al. 1996). Aliphatic (e.g., lipids, waxes) and aryl (e.g., charcoal) compounds tend to have the longest turnover times in many soils (Hamer et al., 2004; Preston and Schmidt, 2006). Krull et al. (2006) studied a grassland, woodland, and subtropical rainforest in Australia. They concluded that, although the woodland and rainforest had greater aggregate and mineral protective capacity respectively, the grassland supported a larger reservoir of more stable carbon due to frequent inputs of charcoal from regular fires. In this case, the fire ecology of the grassland acted as a dominant control, leading to increased initial and long-term recalcitrance of the SOM.

4.1.2. Mineral associations

Direct association between organic C and primary and secondary minerals in soil includes H-bonding, van der Waals forces, ligand exchange, cation bridging, and metal complexation (e.g., v. Lützow et al. 2006). Multiple layers of organic C may range outward from the mineral surface with decreasing strength of association, and the outer layers may thus be the most actively cycling of the mineral-stabilized C (Sollins et al., 2006). The cleavage of the innermost bonds may often prove energetically unfavorable, raising the possibility that it is actually mineral dissolution or evolution that results in destabilization of the SOM at the mineral surface instead of direct degradation. Torn et al. (1997) characterized soil carbon stability along a chronosequence in Hawaii and suggested that as metastable non-crystalline minerals evolve into crystalline clays that have lower surface area and charge density, their ability to directly stabilize SOM is reduced. This idea is reflected in their data, which show the C content and radiocarbon abundance changing proportionately to the nature of the soil mineralogy. In this warm, humid system, with very low fire frequency and rapid turnover rates in the upper soil, mineral association appears to be the dominant control on long-term SOM stability.

4.1.3. Accessibility

Physical protection that precludes microbial access to SOM may preserve a substrate that would otherwise be rapidly degraded. This type of protection is largely a function of soil structure, occurring primarily within microaggregates or micropores too small for soil organisms to enter...
In soils that undergo frequent disturbance, such as agroecosystems, the disruption of these aggregates can be the foremost cause of C loss from the system (e.g. Six et al., 2002). Yet soil structure is intimately related to soil texture and mineralogy. Denef et al. (2004) looked at conventional tillage (CT) and no-tillage (NT) cropping systems across several soils with differing clay mineralogies. While total SOM storage and aggregate stability appeared to be associated with mineralogy, >90% of the SOM loss related to CT in all soils was associated with a single size class of microaggregates that were isolated from water-stable macroaggregates. Direct mineral association appeared to be a dominant mechanism of long-term stabilization, but a shorter-term mechanism of stabilization was the limitation of accessibility. In these intensively managed ecosystems, the method of soil preparation can thus become a major control on C stabilization by influencing accessibility to occluded SOM.

### 4.1.4. Biotic suppression and climatic stabilization

In the midst of a discussion on C dynamics, it behooves us to recall that C does not simply cycle; rather, C is cycled. The mechanisms discussed earlier ultimately relate to the ability of soil organisms to access and degrade SOM. However, if the organisms themselves are in some way suppressed, the low activity of the soil microbiota becomes the effective mechanism of stabilization. In these cases, distal influences on C stability become dominant controls through severe conditions. Biotic suppression, and consequent C stabilization, may thus occur through conditions such as O$_2$ limitation (e.g., flooding), desiccation (e.g., desert environments), extreme or prolonged cold (e.g., boreal systems), nutrient conditions (e.g. N concentration; Waldrop and Zak, 2006), and excessively high or low pH (e.g., mine spoils). Some of these ecosystems may nonetheless have a high enough NPP to result in significant SOM accumulation, such as in peat bogs (Smith et al., 2004) and boreal forests (Harden et al., 2000). An increasing concern when considering changing global and regional climate is that conditions may become more favorable to microbial activity, possibly leading to vast quantities of SOM destabilization (Freeman et al., 2001) and positive feedbacks to global warming (Chapin et al., 2000; Davidson and Janssens, 2006; Davidson, 2006; Kirschbaum, 2000).

### 4.2 MECHANISMS OF DESTABILIZATION

Just as mechanisms of stabilization cause greater SOM stability, mechanisms of destabilization render SOM more susceptible to alteration or transport (i.e., less stable). In the most general sense, these mechanisms in some way reduce or eliminate the efficacy of the mechanisms of stabilization (e.g., Sollins et al. 1996). The controls on destabilization typically promote disturbances that expose SOM, or otherwise foster a physical environment more advantageous to microbial or faunal degradation of SOM. There are numerous examples of natural and anthropogenic soil disturbance, including direct disturbances such as tilling (Six et al., 1999), freeze/thaw and shrink/swell cycles (Denef et al., 2001), erosion and mass wasting (Harden et al., 1999), bioturbation (Stork and Eggleton, 1992), windthrow (Kramer et al., 2004), and fire (Harden et al., 2000). The actual degradation of a substrate can also be considered a mechanism for further destabilization through the production of more labile byproducts or otherwise increasing their susceptibility to further alteration or transport. Degradation can be from biotic or abiotic sources, such as faunal degradation (Verhoeof and Brussaard, 1990), microbial degradation and extracellular enzymatic alteration (Cairney and Burke, 1998), and photo-degradation (Zepp et al., 2003). It’s important to remember, however, that destabilization often
happens concurrently with stabilization. Even as a compound is degraded, some byproducts may be generated that are more stable than the original compound (e.g., (Wolters, 2000)).

4.3 TEMPORAL AND SPATIAL SCALES

As the scale of analysis moves from centuries to years and hours, and regions are reduced to meters and microns, the context of controls, processes, and mechanisms also changes. That is, a dominant control at a millennial scale may be largely irrelevant at an hourly scale, just as a mechanism at the scale of a field plot may be an irrelevant process when considered from the perspective of the edge of a clay micelle. It is beyond the scope of this chapter to consider the entire continuum, although a few truisms can be offered. Over large spatial scales or among biomes, climate tends to dominate at the extremes of temperature and moisture—for example for tundra and deserts—due to direct effects on microbial processes. Within most temperate biomes, a more complex and varied relationship between state factors, processes, mechanisms, and scale exists that is not easily generalized. At the field scale within these zones, vegetation and topography heavily influence hydrology and C cycling. At the fine scale of the plant-soil interface, accessibility and recalcitrance driving stabilization reflect the dynamic nature of the inputs and soil moisture. The relationship among these mechanisms, in turn, will vary greatly with ecology and management. Recalcitrance will play a principle role with high fire frequency and charcoal inputs, otherwise accessibility will typically dominate decadal dynamics. Direct mineral interactions, especially the ‘inner layer’ molecules, tend to stabilize C for much longer time spans, 100s to 1000s of years. These mechanisms are associated with the most stable C throughout the profile in low-fire ecosystems, but generally decide the fate of a much larger proportion of the C below the rooting zone. At the mineral surface itself, many of the mechanisms we have discussed take on the nature of processes, and it is the charge density of the mineral, polarity and structure of the molecule, and the density of the pore water that most distinctly results in C stabilization. More specific discussions of mechanisms at this scale are provided by Kleber et al. (2007) and Rillig et al. (2007).

5. RESPONSES OF SOIL ORGANIC MATTER TO GLOBAL ENVIRONMENTAL CHANGE

Human activities can have profound consequences for soil carbon cycling. Climate change, nitrogen deposition, elevated atmospheric CO₂ concentrations and other atmospheric changes, land use and land cover change, and altered disturbance regimes are all having increasing influence on plant productivity, soil decomposition rates, and soil carbon storage.

5.1 PRODUCTIVITY AND SOIL C STORAGE

Plant productivity is determined by many factors, mainly plant species composition, temperature, moisture, soil fertility, growing season length, and radiation—all of which are affected by human activities. All else equal, increases in productivity will lead to increases in soil C stock, while decreases will lead to decreases in soil C stock, at a rate determined by the difference between C inputs and outputs. The quantitative time-course of change depends on the turnover times of the soil C pools receiving the input, which is often not known. Here we review briefly how some environmental factors are expected to alter productivity and explore how the effects on stock depend on the number of soil carbon pools and their turnover times.

Elevated CO₂ enhances plant growth, albeit with uncertain efficacy, while the accompanying suite of climate changes have variable effects on NPP. Most coupled climate carbon-cycle models predict that terrestrial ecosystem productivity increases in the first half of this century
due to CO₂ fertilization and moderate increases in temperature, but has moderate declines after that due to more severe change in climate (Fischlin et al., 2007; Friedlingstein, 2006; Gerten, 2004; Sitch, 2003). For example, observed increases in the productivity of intact tropical forests over recent decades has been linked to CO₂ fertilization, modest warming, reduced tropical cloud cover, and increased radiation (Baker, 2004; Boisvenue and Running, 2006; Lewis, 2004; Malhi and Phillips, 2004; Nemani, 2003). These gains are predicted to be transient, however, due to losses associated with escalating heating and drying trends (Malhi & Phillips 2004). More generally, in the long term, it is unlikely that plant productivity will continually continue to increase with increasing atmospheric CO₂, due to widespread limitation of NPP by water or nutrients, and because of acclimation of plants to higher CO₂ conditions.

By increasing plant N availability, nitrogen deposition can contribute to carbon uptake in N-limited (e.g., temperate) ecosystems (Melillo et al., 1995; Schimel, 1995; Trumbore, 2000) but can also lead to changes in plant species composition and soil pH (Boggs, 2005; Silvertown, 2006). Any benefits of N-deposition are expected to reach a saturation point, after which productivity levels off, and eventually diminishes due to other nutrient limitations or increased susceptibility to stresses such as pollution, frost damage, or disease (Aber et al 1989; Agren and Bosatta 1988). Other atmospheric pollution, such as acid rain, increased tropospheric ozone, and stratospheric ozone depletion, are all predicted to decrease NPP.

In addition to productivity, plant species composition and abundance affect soil C cycling through tissue chemistry and surface energy balance. The latter influences soil microclimate, while the former helps determine decomposition pathways and products as described in section 4. Global warming is projected to lead to large-scale vegetation shifts, such as expansion of boreal forests as growing season lengthens, transition from temperate evergreen to deciduous forests due to warming, and from tropical evergreen forest to seasonal forest or to grassland due to drought stress (Fischlin et al. 2007).

If plant productivity increases without a commensurate increase in decomposition rates, more carbon will be sequestered in soil. Since decomposition is proportional to the stock of SOM, stock will build up until the efflux from decomposition reaches a level roughly equal to the higher rate of inputs. Although faster-cycling C pools will adjust more rapidly to reach a new steady state, slower cycling pools will build up to a higher stock of C for the same increase in NPP. As an illustrative example, consider the world’s shallow carbon stocks (1500 Pg) in equilibrium with global NPP (60 Pg year⁻¹). The average turnover time of this C is estimated as 25 years (y) for fast cycling C (Harrison, 1993) or 32 y for all soil C to 1 m (Raich and Schlesinger, 1992). Now consider that CO₂ fertilization and other factors increase NPP by 10 percent worldwide. The predicted change in global soil stocks will depend on number of C pools and the turnover times of each pool. For this example, we compare the one-pool scenario considered by Harrison or by Raich and Schlesinger with a two-pool scenario illustrated in Figure 9. The initial C inventory, NPP, and bulk turnover time are the same in either case. For the single soil C pool, with τ = 25 y, increased inputs to soils from CO₂ fertilization would result in a build up of soil C inventory to 1600 Pg in less than 100 y. However, if 30 percent of C inputs have a 2-year turnover (τ = 2 y) and 70 percent of C inputs have a 35-year turnover (τ = 35 y) then the new C stock would – over the course of ~150 y – build up to 2500 Pg C! More generally, treating soil as one pool for global change predictions will lead to an underestimate for the short term and an overestimate for the long term.
Detecting whether soil stocks have increases in the past decades—in which terrestrial ecosystems have acted as a sink of atmospheric CO$_2$ due to CO$_2$ fertilization effect and other processes—is very difficult due to spatial heterogeneity in soils, relatively large analytical uncertainties (especially in bulk density), and the fact that even changes of a small fraction of standing stock are environmentally important. In fact, Post et al. (1995) conclude that a change of global or regional soil C inventory on the order of 1 Pg C would be impossible to measure directly. Even a 1 Pg C y$^{-1}$ sink continuously for 30 y would increase the global soil C inventory by only 2 percent. One of the first studies to document a regional change in carbon stock found that the top 15 cm of soils in Great Britain have lost two percent of its C stocks over the past 25 y (Bellamy, 2005). Because the soil C loss occurred fairly evenly over soils of all land uses, they conclude that the observed warming in Great Britain is the most likely explanation for the loss.

5.2 CLIMATE CHANGE

One of the most important questions regarding SOM is whether future climate change will cause soils to release more CO$_2$ to the atmosphere and thus form positive feedback with climate change. This can be evaluated by land surface models coupled to global climate models. In a recent inter-comparison of coupled climate carbon-cycle models (C$^4$MIP), all but one of eleven models predicted faster decomposition rates with climate change to 2100 (Figure 10, Friedlingstein et al. 2006). Because NPP did not increase commensurately, most of these models predicted decreases or no change in soil carbon stocks. Currently, terrestrial ecosystems act as a significant sink for the atmospheric CO$_2$ released by human activities. However, all of the models predicted that terrestrial ecosystems will be a less effective sink, and in many simulations become a net C source by the latter third of the 21st century (IPCC 2007; Friedlingstein et al. 2006).

The large variation in decomposition response in the C$^4$MIP arises due to differences in the number of C pools with different turnover times, the ways C is partitioned into them, and the climate-dependence of those turnover times. The current generation of models differ in how they handle temperature and moisture interactions. Decomposition is highly sensitive to these interactions but their representation in models is poorly constrained by data or theoretical understanding.

Most land surface models used in global predictions are missing nitrogen transformations in soil and plants, and thus are likely missing an important modulator of CO$_2$ and climate impacts. None of the eleven soil modules in the C$^4$MIP takes into account the release of nitrogen through increased decomposition, which can stimulate plant growth. Including this nitrogen feedback in the CENTURY biogeochemical model reduced the loss of soil organic C due to increasing temperature by half compared to simulations without the nitrogen processes (Schimel et al 1994). The new nitrogen cycling module in the land surface model CN, which is coupled to the CCSM general circulation model (but was not included in the C$^4$MIP) had a similar effect (Thornton and Rosenbloom 2005). Coupling between the N and C cycles may, therefore, act to buffer the impacts of climate change. The main reason is that stimulation of decomposition in relatively undisturbed ecosystems may cause ecosystem C sequestration as nutrients are transferred from soils (low C/N ratio) to plant reservoirs with higher C/N ratios.

As was described above for soil organic matter pools with slower or faster turnover times, the rate and duration of ecosystem response to environmental changes depends on the rates at which
the carbon cycles. Per unit area, wet and moist tropical forests tend to have more C and faster rates of C turnover times than dry tropical forests (Raich and Schlesinger 1992). And across a gradient of mean annual temperature in intact mature tropical forest, NPP increased, but soil C stocks decreased more steeply, implying a net loss in ecosystem C from faster SOM decomposition (Raich et al., 2006). Modeling and radiocarbon work show that per unit area soil CO2 fluxes from tropical forest soils are an order of magnitude greater than from temperate or boreal forest soils (Trumbore 2000). These large fast-cycling C stocks are therefore predicted to dominate short-term, interannual, response to climate variations (Townsend et al., 1995; Trumbore et al., 1996).

In contrast, the extremely large stocks of organic matter in the soils of high latitude tundra, forests, and peatlands cycle very slowly because they are mostly climatically stabilized. If these soils are warmed and dried, decomposition will proceed rapidly, leading to a large positive feedback to CO2-induced climate change. Indeed, year to year differences in decomposition of old stores of humic materials in some boreal forest soils may determine the status of the entire stand as a net source or sink of C (Goulden et al., 1998). Because gross C fluxes at boreal and artic latitudes are small compared to those in the tropics, it is unlikely that even large interannual variability in those fluxes could be as important in affecting the short term (years and shorter) C balance of the atmosphere. However, the potential for a large, longer-term (years-to-decades) response of soil C to climate change is greatest at higher latitudes, because more C is stored there in potentially decomposable forms.

In addition to the large soil stocks, high latitude permafrost holds close to 900 Pg C, about half of which is contained in relict deep loess soils from the last glacial period. The radiocarbon content of these gases indicates that in many sites this carbon was fixed in the last glacial period (Zimov et al., 2006). As the permafrost thaws, C from grass roots trapped in the ancient soil is being released to the atmosphere, thereby acting as a positive feedback to global warming. In a contrasting view, Bockheim (Bockheim, 2007) speculates that (1) by increasing cryoturbation, warming will lead to a redistribution of soil carbon deeper into the soil where temperatures are cooler and furthermore that (2) in the long term, higher arctic temperatures will lead to higher SOM stores (presumably due to increased NPP).

The land areas of earth have warmed 0.27 °C per decade since 1979 and almost 1 °C since 1850 (IPCC 2007). On the basis of temperature alone, soils should be a growing source of atmospheric CO2. However, trends in soil moisture and forest growth influence carbon flows in ways that may reverse this pattern in some places. Looking to the future, in many regions the interaction of temperature and moisture on plant growth and decomposition, as well as changes in plant litter quality (from changes in species composition and allocation) may swamp the direct effects of the predicted 2-6 °C warming over the next century.

5.3 LAND USE AND LAND COVER CHANGE

5.3.1. Disturbance

Disturbances that affect soil C cycling include fires and floods, deforestation, cultivation, and drainage. All of these alter C inputs and losses to soil by changing vegetation, soil structure, temperature, water balance, and nutrient availability. Rates of change in organic C stocks in response to disturbance can be an order of magnitude larger than those associated with response
to increased productivity or climate variability, because the changes in ecosystem inputs and decomposition rates are more extreme for disturbance.

Wildfires are predicted to get more frequent and severe in many regions due to climate change, particularly in regions that do not practice active fires suppression. Fire will alter ecosystem C cycling by removing biomass and litter, and creating black (pyrolyzing) carbon. In boreal forests and Mediterranean chaparral, decomposition is slow enough to be less important than periodic removal of biomass by fire for returning CO₂ to the atmosphere. In Boreal forests, fire is often controlled by permafrost; increasing drought could drive these ecosystems to become net C sources (Harden et al. 2000). Across a series of Australian sites, Krull et al (2006) determined that systems where fire occurs regularly on a decadal cycle have the largest relative stocks chemically recalcitrant carbon. Thus, changes in fire frequency linked to climate or to land use (such as fire suppression) may ultimately control a region’s status as a C source or sink.

Rapid rates of C accumulation and loss may occur over relatively short time scales as the large component of fast-cycling soil C responds to disturbance. As alluded to previously, warming of a subalpine meadow caused a shift in NPP from forbs, with labile inputs, to shrubs, with recalcitrant inputs. The loss of inputs to the faster cycling C pool resulted in warming-induced losses of ~200 g C m⁻², 5-10 y after the warming was initiated. As the more recalcitrant shrub-derived litter accumulates in the soil, a reversal of this trend is predicted trend over the next few decades. (Saleska et al 2002).

5.3.1.1 Eroding landscapes
Soil erosion by wind and water is a widespread global phenomenon, currently affecting more than 16 trillion m² of land (Jacinthe and Lal, 2001). This erosion moves 3-5 Pg C per year (Berhe et al., 2007), with more than 70% deposited terrestrially (rather than in ocean margins) (Stallard, 1998). Soil erosion affects carbon cycling through its effects on soil C inputs from plant growth and outputs from decomposition of organic matter. Usually, erosion reduces the input of C from plant production in eroding hillslope environments; while deposition of eroded topsoil promotes higher rates of plant productivity. The effect of erosion on soil organic matter decomposition is more complicated, and not yet fully understood. Transport of particles likely breaks down aggregates and increases SOM accessibility; while lower carbon content of subsoil material in the eroding settings and burial of eroded carbon on depositional settings might result in lower rates of C available for decomposition. Consequently, several studies have suggested that overall, erosion results in a terrestrial carbon sink with a strength of up to 1 Pg C per year (Berhe et al., 2007; Smith et al., 2005; Stallard, 1998)

5.3.2. Land management
During the past two centuries, cultivation has led to large losses of soil C as native ecosystems are replaced by less productive ones; these changes represent a loss of fast-cycling C rather than passive C pools (Davidson and Ackerman, 1993; Harrison et al., 1993; Stallard, 1998; Trumbore et al., 1995). Tillage leads to substantial losses of old soil carbon due physical disruption of naturally occurring soil aggregates that formed over long time scales and due to enhanced aeration of the soil. Upon disruption of the soil structure, organic matter occluded within aggregates is exposed to microbes and subsequently oxidized (e.g. Baisden et al., 2002; Ewing et al., 2006; Tiessen and Stewart, 1983b; Tisdall and Oades, 1982). Based on a careful assessment of soil C stocks in pairs of uncultivated and cultivated fields (Davidson and Ackerman, 1993),
cultivation reduces C stocks by 25-30% within five years temperate regions and faster (within two years) in the tropics. The fraction of C lost is even higher in the A horizon.

Agricultural management options that do not rely on tillage, such as bare-fallow and stubble-mulch practices, can greatly reduce carbon losses (Cambardella and Elliott, 1992). Moreover, converting tilled land to no-till agriculture typically leads to rapid increases in soil C stocks (Lal and Bruce, 1999). Consequently, management of cropping systems may have potential for C-sequestration and has been promoted as a way to offset anthropogenic C emissions (e.g., Kong et al., 2005; Paustian et al., 2000). Soil carbon is a resource that is potentially manageable, particularly in agricultural lands, although it is important to understand that soils have a finite capacity for C-sequestration (Six et al., 2002), and to be able to predict these limits.

Globally, the highest rates of land conversion occur in the tropics and a significant proportion of this region is some state of recovery from past disturbance, mainly as forests re-colonize former pasture and croplands. Because the current climate is conducive to high plant productivity, soils under re-growing forests have been identified as a potential C-sink to help offset anthropogenic CO₂ emissions. Soil C sequestration capacity is, however, highly contingent on site history and climate. It may be more favorable in wetter sites where soil decomposition rates are lower (Guo and Gifford, 2002; Silver et al., 2000), and in sites that have not been degraded, for example by intensive use of pasture and subsequent compaction, and where pre-existing forest root systems were not heavily damaged.

5.4 ARE SOILS NET SOURCES OR SINKS OF CARBON?

5.4.1. Temporal scales of soil C dynamics

As soils and ecosystems develop, they gain and lose C. For example, approximately 25% of the world’s SOM is stored in soils that began developing after the last major deglaciation (Harden et al., 1992). Based on chronosequence studies, these soils are now functioning as long-term sinks for atmospheric CO₂. Similarly, we predict that older soils may be acting as long-term net sources of CO₂ to the atmosphere because of declines in NPP and in weathering of minerals to more stable forms. In the pre-1850 world, it is unclear whether soils could have been assumed to be at steady state. However, net fluxes between soils and the atmosphere have been accelerated by large-scale land-cover changes over the past century.

On decadal to century time scales, the net C balance of soils may be dominated by disturbance regime and frequency. At the stand level, ecosystems recover from events such as large storms (blow-downs), fire, insect mortality, or floods. Disturbance-dominated regimes are characterized by short periods of rapid C loss (e.g., through burning in fires), followed by longer periods of C sequestration. Net C accumulation between disturbances may be rapid compared to the long-term rates associated with the formation and loss of soil minerals. However, when averaged over long times or large spatial scales (many stages of disturbance), the long-term rates should dominate.

Superimposed on the decadal to century timescales associated with disturbance and recovery are the interannual changes in C storage in soils. The lag time between C uptake by photosynthesis and respiration, together with the amount of C uptake and loss, will determine the magnitude of interannual variability. For example, if most organic C is respired within a year of when it is fixed by plants, enhanced plant productivity in a given year will be offset by increased decomposition in the same year. However, if lag times are significantly longer than 1 year on
average, higher than average productivity in one year would lead to net C sequestration, with net C loss in following years, as the pulse of high productivity is decomposed slowly over time. These effects are expected to be largest in regions where C fluxes are greatest into plants and out of soils, and where a significant time lag exists.

6. CONCLUSIONS AND FUTURE PROSPECTS

As the focus on soil organic matter has grown to encompass its pivotal role in the global carbon cycle and climate, the study of organic matter in soil has taken on a new importance. Climatic change will cause ecosystems to experience novel and rapidly changing conditions, as well as putting new demands on land management for carbon sequestration. Accurately predicting future atmospheric CO$_2$ concentrations and better managing soil resources will require a clear understanding of the processes and mechanisms controlling SOM storage and turnover.

The numerical models used to simulate soil carbon cycling largely share the same rules governing allocation of plant inputs, structure (pools), and controls of turnover time. They incorporate multiple soil carbon pools, detailed plant growth modules, and temperature response functions (e.g., the CENTURY family, RothC, CASA, IBIS, Orchidee, LPJ, CN). Yet there is much room for improvement, in at least three important ways. First, while temperature and moisture interact to control decomposition and are predicted to change in novel combinations in future, most models treat their effects as independent. Second, models rely on clay content as a proxy for the host of physical stabilization mechanisms in soil. Finally, plant tissue chemistry drives model partitioning of inputs into pools of different turnover time, yet intrinsic plant compound recalcitrance is much less important than previously thought. These simplifications exist in large part because the growing understanding of the processes that influence turnover time has yet to be translated into mathematical functions of variables that are regionally-to-globally available and operate on area (i.e., per m$^2$) basis.

We have in hand sufficient understanding and data to begin development of much-improved model parameterizations, including the influence of plant allocation, soil mineralogy, and climate conditions. However, fundamental research targeting these areas, in parallel with model development, is still needed. There are many fruitful areas for future research, we suggest that priority be given to those processes and ecosystems that are vulnerable to global change, are potentially manageable, represent a large stock of carbon, and could influence atmospheric CO$_2$ concentrations significantly within the next several decade.

In the last decade, exciting new molecular, genomic, and imaging techniques have emerged for probing soil organic matter at atomic and molecular scales, such as the Advanced Light Source (ALS, soft-energy x-ray); Secondary ion mass spectrometry (SIMS, nano-SIMS) and Pyrolysis-gas chromatography-mass spectrometry-isotope ratio mass spectrometry (Py-GC-MS-IRMS), and gene-based microarrays. These techniques can be used in combination with isotopic analysis ($^{13}$C, $^{14}$C) to link to detailed characterizations to turnover times. The vanguard, then, is utilizing these techniques in the context of experiments and controlled environmental gradients to gain insight at the landscape scale.

In terms of improving our ability to predict soil C turnover, we identify five priorities for research: (1) The interactive effects of changes in temperature and moisture on microbial decomposition rates, because soils will experience novel and transient conditions. (2) The
mechanisms governing protection of OM through interactions with mineral surfaces and due to spatial structure. (3) The mechanisms leading to slower OM turnover times with depth. (4) The potential for and importance of non-linear responses of decomposition to C availability; for examples, the role of labile C inputs in stimulating decomposition of less labile OM (i.e., priming) and density-dependent microbial behavior. (5) Finally, how the chemical characteristics of organic compounds, as inputs from different plant species or charred (black) carbon, or microbial cell walls and byproducts, influence mechanisms of stabilization and turnover.
References


Davidson, K.C., 2006. The woes of Kilimanjaro: The fabled glaciers on Tanzania's majestic mountain will soon be gone. Its forests are disappearing too. For local farmers, this could mean disaster. For the rest of us, it's another unbearable loss on an overheating planet., Salon.com.


7. APPENDIX 1. METHODS OF RADIOCARBON ANALYSIS AND REPORTING OF $^{14}$C DATA

7.1 BACKGROUND INFORMATION

In this Appendix we briefly describe sample preparation and radiocarbon analysis, and in more depth the notoriously complex conventions on the reporting of $^{14}$C data. We have tried to strike a balance between brevity and explanation while providing the most important information and addressing common questions and misperceptions we’ve encountered. Additionally, we strongly urge those interested in using $^{14}$C as a tool to read Stuiver and Polach (1977), the paper that largely established $^{14}$C reporting conventions, and from which most of the equations in this appendix were acquired.

There are two general methods for measuring radiocarbon: decay counting and accelerator mass spectrometry (AMS). Decay counting measures electrical pulses (gas counting) or light pulses (scintillation counting) emitted through the decay of $^{14}$C to $^{14}$N. In samples containing a high proportion of ancient C, much of the $^{14}$C has already decayed (the half-life of $^{14}$C is 5,730 y), so using decay counting might require several grams of material and take days to count enough decay events for a reasonable estimate of the $^{14}$C concentration. AMS directly counts the $^{14}$C atoms (and measures the ratio of $^{14}$C to $^{13}$C and $^{12}$C) and thus requires far less sample, only enough to provide between 100 µg to 1 mg of C. Additionally, the measurement only takes minutes compared to days with decay counting, so a much larger number of samples can be measured in a given amount of time when using AMS. The key characteristics of $^{14}$C-AMS are the electron stripping and ion acceleration, which allow $^{14}$C to be distinguished from isobars and molecules that would confuse a standard mass spectrometer.

7.2 SAMPLE PREPARATION

Organic matter must first be completely combusted to CO$_2$ for all $^{14}$C measurements in soils. For AMS analysis, enough homogenized sample to provide ~1 mg C is added to a quartz glass tube with CuO and Ag. The tube is then evacuated, sealed, and combusted at ~900°C (Buchanan and Corcoran, 1959). The CO$_2$ produced is purified cryogenically and then reduced to graphite using a zinc- or iron-catalyzed reduction method described in Vogel (1984). The graphite is pounded or pressed into a small sample holder, which is later targeted by a Cs beam in the AMS and thereby delivers a stream of C ions. Samples for decay counting are combusted at similar temperatures in a large vacuum line (Goh, 1991). The resulting CO$_2$ is cryogenically purified, then counted directly (gas counting) or converted to acetylene or benzene (scintillation counting). For more details on experimental methods, see Goh (1991) and Trumbore (1996).

7.3 REPORTING OF $^{14}$C DATA

Both AMS and conventional counting facilities report $^{14}$C data as the ratio of $^{14}$C activity in the sample to a known standard. By convention (Broecker and Olson, 1959; Stuiver and Polach, 1977), the standard is corrected to 0.95 times the activity of an oxalic acid standard (OX1), which is normalized to a δ$^{13}$C of -19‰. The unknown sample, in turn, is also normalized:
\[
A_{SN} = A_{S(\delta)} \frac{(1 - 25/1000)}{(1 + \delta /1000)},
\]

where the activity of each sample \(A_s\) with a \(\delta^{13}C\) of \(\delta\) is corrected to a constant \(^{13}C\) abundance \(N\) (-25‰). These \(^{13}C\) corrections account for isotopic fractionation effects (Stuiver and Polach, 1977), and are a crucial part of the analysis. For example, the \(\delta^{13}C\) difference between atmospheric \(\text{CO}_2\) and carbon fixed during photosynthesis by \(C_3\) plants is approximately 20‰. Assuming the fractionation of \(^{14}C\) will be roughly twice that of \(^{13}C\) (since the mass difference between 12 and 14 is twice that between 12 and 13), the \(^{14}C\) abundance of photosynthates and the atmospheric \(\text{CO}_2\) being used will differ by approximately 40‰, even though both \(\text{CO}_2\) and photosynthates are the same “age.”

A common term used in relation to \(^{14}C\) data is “fraction Modern.” The OX1 standard was originally prepared in 1950 by the U.S. National Bureau of Standards (NBS), now called the U.S. National Institute of Standards and Technology (NIST). ‘Modern’ is by definition 1950 and represented by the OX1 standard. The sample/OX1 ratio is thus referred to as fraction Modern (\(F^{14}C;\) Reimer et al., 2004):

\[
F^{14}C = \frac{A_{SN}}{A_{ON}} = \frac{\left(\frac{^{14}C}{^{12}C + ^{13}C}\right)_{\text{sample}(-25)}}{\left(\frac{^{14}C}{^{12}C + ^{13}C}\right)_{\text{OX1}(-19)}},
\]

where \(A_{SN}\) is the activity of the sample normalized to a \(\delta^{13}C\) of -25‰ (described in Eq. (A1.1)), and \(A_{ON}\) is the activity of the OX1 standard normalized to a \(\delta^{13}C\) of -19‰. In addition to \(F^{14}C\), other terms used to represent fraction Modern (\(A_{SN}/A_{ON}\)) are \(F\) and \(F_m\) (Donahue et al., 1990), and \(^{14}a_n\) (van der Plicht and Hogg, 2006). Although van der Plicht and Hogg (2006) suggest the term \(^{14}a_n\) is most appropriate due to the historical use of \(A\) to represent radioactivity, they acknowledge the intuitive appeal of \(F^{14}C\) and use it to represent fraction Modern in their discussion of \(^{14}C\) reporting.

The conventional radiocarbon age is then:

\[
^{14}C\text{ age} = -8,033 \ln F^{14}C,
\]

using fraction Modern and the Libby mean life of radiocarbon, 8,033 y.

When considering an open and dynamic system, such as soil, the need arises for a standard that represents a constant value. The activity of the OX1 changes through time as \(^{14}C\) in the standard decays (i.e., \(A_{ON}\) decreases). Stuiver and Polach (1977) thus proposed an absolute international standard activity (\(A_{abs}\)) that would incorporate a yearly correction for the decay in the OX1 standard:

\[
A_{abs} = A_{ON} \exp^{\lambda(y-1950)}, \quad \text{where } \lambda = \frac{1}{8267} \text{ yr}^{-1},
\]

where \(\lambda\) is the decay constant for \(^{14}C\).
and y is the year of sample collection. Using $A_{abs}$ to calculate fraction Modern ($A_{SN}/A_{abs}$) will lead to a different value than when using $A_{ON}$. Reimer et al. (2004) explicitly addressed this potential source of confusion when they proposed the relationship $F^{14}C = A_{SN}/A_{ON}$. We suggest that when fraction Modern is calculated using $A_{abs}$, the term $F'$ be used:

$$F' = \frac{A_{SN}}{A_{abs}} = \left(\frac{^{14}C}{^{12}C+^{13}C}\right)_{\text{sample} (-25)}.$$  \hspace{1cm} (A1.5)

This value can also be represented as ‘percent Modern’ (Stuiver and Polach, 1977):

$$pM = (F' \times 100) \quad \text{(A1.6)}$$

Once again, after 1950 the values for $F^{14}C$ and F’ will not be equal, and authors should be clear about which relationship they are reporting. Another commonly reported parameter in biogeochemical studies is $\Delta^{14}C$. This parameter is the deviation in parts per thousand (per mil, ‰) from the absolute standard ($A_{abs}$):

$$\Delta^{14}C = (F' - 1) \times 1000 = \left[F^{14}C \times \exp\left(\frac{-(y-1950)}{8267}\right) - 1\right] \times 1000.$$  \hspace{1cm} (A1.7)

Using the geochemical notation, positive values of $\Delta^{14}C$, or $F' > 1$, indicate the presence of bomb-produced $^{14}C$. Conversely, negative values of $\Delta^{14}C$, or $F' < 1$, indicate the predominance of C fixed from the atmosphere long enough ago for significant radioactive decay of $^{14}C$ (half-life = 5,730 y) to have occurred. The analytical precision for determination of $^{14}C$ for typical graphite targets averages ± 5‰ (AMS analysis) for samples containing bomb $^{14}C$, and ± 2‰ for high-precision analyses.

Most radiocarbon measurement facilities provide the analysis results in different formats, depending on the needs of the researchers. The geochemistry format is most useful to biogeochemists and ecologists, and includes $F^{14}C$ (not F’), $\Delta^{14}C$, and $^{14}C$ age. If it is unclear which fraction Modern is used ($F^{14}C$ or F’), one can quickly plug the fraction Modern values into equation (A1.7) and compare the results to $\Delta^{14}C$.

8. APPENDIX 2. MODELING C DYNAMICS USING RADIOCARBON MEASUREMENTS

8.1 BACKGROUND INFORMATION

Soil organic matter (SOM) is a heterogeneous reservoir with a variety of turnover times, to which carbon is continuously added (as new plant matter) and lost (as leached organic carbon or CO$_2$). These dynamics preclude using radiocarbon to meaningfully “date” SOM, and at best the
14C-based age of SOM represents the average 14C age of a carbon atom in the soil reservoir. This tells us relatively little about the distribution of C into reservoirs with different turnover times, and can be actively misleading when the SOM has incorporated ‘bomb 14C’ created through atmospheric nuclear weapons testing. In this Appendix we describe methods of using 14C inputs into SOM to estimate turnover times of soil C. These methods differ somewhat when the source is natural radiocarbon (‘pre-bomb’) or bomb 14C, and when the system is assumed to be at steady-state or otherwise.

8.2 STEADY-STATE SYSTEMS

8.2.1. Natural Radiocarbon

For a homogeneous carbon-containing reservoir, i, with input rate $I_i$, first-order decomposition constant $k_i$, and carbon content $C_i$, the balance of carbon is:

$$\frac{dC_i}{dt} = I_i - k_i C_i$$  \hspace{1cm} (A2.1)

For a steady-state reservoir, $k_i = I_i / C_i$. The turnover time ($\tau$) is defined as $1/k_i$. At steady state, this equals the inventory of carbon divided by the input rate, $C_i/I_i$. The balance of 14C atoms in the same reservoir ($^{14}\text{C}_i = F_i' C_i$, where $F_i'$ is the decay-corrected fraction Modern) will reflect the rate of decomposition, $k_i$, the rate constant for radioactive decay of 14C, $\lambda$ ($\lambda = 1.210 \times 10^{-4}$ y$^{-1}$), and the rate of inputs (in this case, from the atmosphere):

$$\frac{dF_i'}{dt} = \left( \frac{1}{C_i} \right) (I_i F_i' - (k_i + \lambda) F_i' C_i)$$  \hspace{1cm} (A2.2)

At steady state,

$$F_i' = \left( \frac{I_i}{C_i} \right) \left( \frac{1}{(k_i + \lambda)} \right)$$  \hspace{1cm} (A2.3)

Since at steady state, $C_i = I_i/k_i$, Equation (A2.3) may be rewritten as:

$$F_i' = \left( \frac{k_i}{(k_i + \lambda)} \right)$$  \hspace{1cm} (A2.4)

For components with short turnover times ($k_i >> \lambda$), a calculated 14C age will approximate the turnover time, $\tau$ ($1/k_i$). For components with $k_i$ equal to or less than the decay constant for radiocarbon, the age will be less than the turnover time. For example, the 14C age calculated for a steady-state reservoir with $k_i = 0.01$ y$^{-1}$ ($\tau = 100$ y) would be 100 y, while that for a component with $k_i = 0.0002$ y$^{-1}$ ($\tau = 5000$ y) would be 3,910 y.

8.2.2. Bomb Radiocarbon

For a steady state system, a time-dependent model is used because of the irregular shape of the atmospheric 14CO2 record.

$$F_{C,t}' = \left[ I F_{\text{atm},t} + C_{i-1} F_{C,i-1}' (1 - k - \lambda) \right] / C_i$$  \hspace{1cm} (A2.5)
Since the reservoir is at steady state, \( C(t-1) = C(t) = I/k \), so Equation (A2.5) reduces to:

\[
F'_{C,t} = kF'_{atm,t} + F'_{C,t-1}(1 - k - \lambda)
\]  
(A2.6)

Figure 8 shows the 1996 predicted values of \(^{14}\text{C}\) for a homogeneous, steady state reservoir with different turnover times. For turnover times <50 y, it is clear that two different turnover times may yield the same \( \Delta^{14}\text{C} \) value. To distinguish which of these two turnover times is correct, we use one of two methods. First, if an archived sample from the same soil is available, radiocarbon measurements may distinguish between the two possibilities. Organic matter with shorter turnover times will have decreased \(^{14}\text{C}\) over the past several decades, while those with longer turnover times will have increased in \(^{14}\text{C}\). If no archived soil is available, knowledge of the \( C \) fluxes into and out of the soil may be used to determine the correct turnover time.

The \( \Delta^{14}\text{C} \) values measured in low-density organic matter isolated from the A horizon of a soil sample in 1956 and 1992 in the Sierra Nevada mountains were -31 %o and +127 %o, respectively (Trumbore et al., 1995). This \(^{14}\text{C}\) increase is consistent with either a turnover time of 5 or 57 y. The total amount of low-density carbon in the A horizon was 6.5 kg C m\(^{-2}\), with low-density carbon accounting for nearly 90% of the carbon in this layer. The 5-year turnover time implies annual C inputs from litter of ~1,300 g C m\(^{-2}\) yr\(^{-1}\), while the 57-year turnover time implies inputs of only 114 g C m\(^{-2}\) yr\(^{-1}\). The measured aboveground litterfall at a nearby site was ~100 g C m\(^{-2}\) yr\(^{-1}\). Hence, the most reasonable turnover time is 57 y for the low-density organic matter in the A horizon.

A potential problem with this approach is the uncertainty as to whether the reservoir under consideration is homogeneous. Bulk SOM is almost certainly heterogeneous, and the bulk \(^{14}\text{C}\) value does not give a good idea of SOM dynamics. Even low-density organic matter is made up of relatively fresh litter material (small roots and pieces of leaves) as well as more humified materials that likely have slower turnover. Normally, the soil must be split into components with different turnover times using fractionation methods outlined in the text. For each component, a new measurement constraint (such as total C flux into and out of the soil) must be added to arrive at a unique solution. A second problem is that carbon entering the soil as litter may not have the \(^{14}\text{C}\) signature of that year’s atmospheric CO\(_2\) (\( F'_{atm} \) in the equations above). For example, conifer needles often reside on trees for several years before they fall and are incorporated into soils. Failure to account for these time lags in living vegetation may result in an overestimate of the time required for decomposition (since the turnover time will reflect the time spent in the plant plus soil, rather than the soil alone).

**Systems That Are Accumulating Carbon**

Again, net change in \( C \) storage (d\( C \)/dt) represents the balance between annual C inputs (I; kg C m\(^{-2}\) yr\(^{-1}\)) and decomposition (k\( C \), where k is a first-order decomposition rate constant (yr\(^{-1}\)), and \( C_t \) is the organic layer C inventory kg C m\(^{-2}\)) in year t. The solution to this (integrating A2.1 above) is:

\[
C(t) = I/k - \left( I/k - C_0 \right) e^{-kt}
\]  
(A2.7)
Using radiocarbon data to determine time, t, we can determine the history of C accumulation at a site. A plot of accumulated carbon inventory (C_t) versus the time it took to accumulate (t, from radiocarbon) may then be fit with Equation (A2.7) to derive estimates of I and k describing either decadal (bomb radiocarbon) or millennial (natural radiocarbon) C dynamics (Trumbore and Harden, 1997). An example is shown in Figure 10. Alternatively for a known-age disturbance or soil age, the amount of C accumulated, and the amount of radiocarbon accumulated, will uniquely determine I and k.

8.2.2.1 Natural Radiocarbon

Prior to 1950, the 14C content of atmospheric CO_2 was approximately constant. For constant atmospheric 14C content (F'_{atm} = 1.0 pre-1960), F'_{C,t} may be expressed as:

\[ F'_{C,t} = \frac{I}{(k + \lambda)} \left[ 1 - e^{-(k+\lambda)t} \right] \]

where t is the time since soil began to form. Substituting for C_t,

\[ F'_{C,t} = \frac{k}{(k + \lambda)} \left[ 1 - e^{-(k+\lambda)t} \right] \left[ 1 - e^{-\lambda t} \right] \]

In their study of how different minerals affect the long-term turnover rates of carbon in soils of Hawaii, Torn et al. (1997) used measurements of F'_{C,t}, and the known age of the ash deposit on which the soil was developed (t), together with Equation (A2.8) to estimate the turnover time, 1/k.

8.2.2.2 Bomb Radiocarbon

To determine the inventory-weighted mean \Delta^{14}C value in 1996, we assume annual C additions are labeled with the \Delta^{14}C of that year’s atmospheric CO_2, and track the loss of C and 14C with time for each year’s C input. Isotopes are assumed not to fractionate during decay (i.e., respired C is assumed to have the same 14C content as the organic matter in each annual layer). The equation expressing the inventory-weighted mean 14C content of the soil profile in year t after initiation of accumulation is:

\[ F'_{C,t} = \frac{\sum_{i=0}^{t-T} C_{i,t} F'_{atm,i}}{\sum_{i=0}^{t-T} C_{i,t}} \]

where T is the total number of years carbon has been accumulating (years since disturbance), and F'_{atm,i} is the fraction Modern of C fixed in the year i (assumed to equal that year’s atmospheric 14CO_2), and C_{i,t} = I/k (1 - exp^{(k)t}) is the carbon remaining t years after it was fixed in year i (t = T – i). For example, consider a layer of moss and detritus sampled in 1994 that began to...
accumulate 120 years ago following a fire in a boreal forest. If the rate of C inputs is 120 g C m$^{-2}$ yr$^{-1}$, and the decomposition rate is 0.02 yr$^{-1}$ (turnover time of 50 years), the total amount of carbon accumulated in 120 years will be 5.5 kg C m$^{-2}$, and the bulk $\Delta^{14}$C of the moss layer will be +183 ‰. For the same input rate, but with faster decomposition (0.04 yr$^{-1}$, or turnover time of 25 years), only 3.0 kg C m$^{-2}$ will have accumulated, with $\Delta^{14}$C of +231 ‰. Knowing the bulk amount of C and its inventory-weighted $\Delta^{14}$C value for a known period of accumulation will uniquely define I and k. Again, complications arise because of the assumption of zero time lag for C storage in vegetation (especially woody biomass that may represent a significant portion of the litter carbon in fire-dominated forest systems).
Figure Legends

Figure 1. (Copied from (Fischlin et al., 2007)). Major ecosystems with their global areal extent (lower panel, Mkm$^2$), transformed by land use in yellow, untransformed in purple, from Hassan et al. (2005), except for mediterranean-climate ecosystems, where transformation impact is from Myers et al. (2000), and total carbon stores (upper panel, PgC) in plant biomass (green), soil (brown), yedoma/permafrost (light blue). D = deserts, G&S(tr) = tropical grasslands and savannas, G(te) = temperate grasslands, ME = mediterranean ecosystems, F(tr) = tropical forests, F(te) = temperate forests, F(b) = boreal forests, T = tundra, FW = freshwater lakes and wetlands, C = croplands, O = oceans. Data are from Sabine et al. ((2004), Table 2.2, p. 23), except for carbon content of yedoma permafrost and permafrost (light blue columns, left and right, respectively, Zimov et al., 2006), ocean organic carbon content (dissolved plus particulate organic; (Denman et al., 2007), Section 7.3.4.1), and ocean surface area from Hassan et al. (2005, Summary, Table C2, p. 15, inserted as a number). Figures here update the TAR (Prentice et al., 2001), especially through considering soil C to 3 m depth (Jobbágy and Jackson, 2000), as opposed to 1 m. Approximate carbon content of the atmosphere (PgC) is indicated by the dotted lines for last glacial maximum (LGM), pre-industrial (P-IND) and current (about 2000).

Figure 2. (A) Variations in percent nitrogen (proportional to C content) with precipitation along the 11°C isotherm in the Great Plain. The humidity factor (NSQ, or Meyer's quotient), is the total annual precipitation (mm) divided by the absolute saturation deficit of air (mm mercury). Soils are all developed on loess deposits. (B) Change in %N with precipitation along the 19°C isotherm. Note that C density (as estimated from %N) is lower at higher mean annual temperature (Jenny 1941)

Figure 3. Changes in soil organic C storage and mineral content along a chronosequence in Hawaii (Torn et al., 1997). The parent material is basaltic ash deposits of known age. Climate and vegetation are constant across the sites. (A) Soil organic C inventory versus ash substrate age. The solid line is the whole mineral soil to the C horizon, the dashed line is the top 20 cm. The increase and subsequent decrease in SOM is mostly due to changes in the sub surface mineral soil. (B) The distribution of C with depth for the same sites. (C) The correlation of soil carbon in mineral horizons with the amount of non-crystalline minerals.

Figure 4. Soil organic carbon inventory by parent material category. Zinke et al (1984) worldwide data (n=2995) include the California Soil-Vegetation Survey data (Allardice et al., 1984; Allardice et al., 1983; Begg et al., 1985), that in this case are for well-drained soils only (n=568).

Figure 5. Variation of organic carbon density with texture, in surface soils developed on glacial till and loess in Iowa, where finer textured soils have more loess (data are from Brown, 1936, as reported in Jenny, 1941).

Figure 6. Illustration of how age and turnover time may be confused using radiocarbon data. Case 1 is interpreted as a single, homogeneous reservoir, with a $^{14}$C content equivalent to a turnover time of 2,770 years (0.78 fraction Modern, F$^{14}$C; see Appendix 1). If there are ten kilograms of carbon in the reservoir, the annual flux in or out of the reservoir at steady state, Flux = 10,000 g/2,770 y = 4 g y$^{-1}$. In Case 2, the soil organic matter is assumed to be a two-component mixture, with two thirds of the carbon having a turnover time of 20 years, and one
third with a turnover time of 10,000 years. The overall $^{14}$C content is the same as in Case 1, but the annual flux is now $\text{Flux} = (6,670 \text{ g/20 y}) + (3330 \text{ g/10,000 y}) = 334 \text{ g y}^{-1}$. So the bulk turnover in case 1 provides little indication of how fast the system will respond to changes in inputs or decomposition rates associated with land use or climate change.

Figure 7. Simplified Soil Carbon Cycling Scheme. Major inputs (plant litter) to and outputs (respiration and erosion) from to the soil carbon reservoir. The observed flux of C out of the soil can be modeled by assuming three pools of carbon - an active pool with a turnover time on the order of years, an intermediate pool with a turnover time on the order of decades to centuries, and a passive pool with a turnover time on the order of centuries to millenia. The decomposition constant, $k=1/\tau$. Subscripts $a$, $i$, and $p$ refer to the active, intermediate, and passive C pools, respectively. Adapted from Amundson (2001)

Figure 8. Change in atmospheric $^{14}$C with time in the northern hemisphere (heavy solid line) since 1955. Radiocarbon values are expressed as the per mil variation in $^{14}$C/$^{12}$C ratio relative to a standard (see Appendix for definition of units). The other lines show the evolution of $^{14}$C for homogeneous, steady-state reservoirs with turnover times of 5, 15, 30, and 60 years.

Figure 9. Modeled time series of global C stocks assumed to start at 1,500 Pg C, following a one-time 10 percent increase in NPP from 60 to 66 Pg C y$^{-1}$. The blue line represents a single pool scenario (as proposed, for example, by Raich and Schlesinger (1992) and Harrison (1993)) in which all soil C has a residence time, $\tau$ of 25 years. This residence time is derived from the mass balance equation, $\frac{dC}{dt} = \text{NPP} - \frac{C}{\tau}$, and assuming steady state (such that inputs equal outputs). The blue line represents a two-pool scenario in which 70 percent of the incoming C has a residence time, $\tau = 35$ years and 30 percent has a $\tau = 2$ years, such that the overall residence or “bulk” $\tau = 25$ years. Because it contains a slower cycling pool, the two pool model accumulates C faster and takes longer to reach a new steady state equilibrium, with much higher C stocks than the single pool model.

Figure 10. Turnover time of soil organic carbon as a function of land surface temperature change. Results for the soil submodel response of coupled climate-carbon cycle models. Copied from Friedlingstein et al. 2006.
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
Case 1. Bulk radiocarbon age is 2770 years; interpreted as a homogeneous pool at steady state.

Case 2. Same bulk age, but interpreted as having two components each with different turnover times.

Figure 6
Plant and root litter 

Active ($\tau = 10^0$ year)

Intermediate ($\tau = 10^{1-2}$ year)

Passive ($\tau = 10^{3-4}$ year)

CO$_2$ from microbial decomposition

$C_t/\tau_t = C_a/\tau_a + C_i/\tau_i + C_p/\tau_p$

$C_a/\tau_a > C_i/\tau_i > C_p/\tau_p$
Figure 8.
Figure 9.