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Soil organic matter dynamics: a biological perspective derived from the use of compound-specific isotopes studies

Abstract Current attempts to explain the persistence of carbon in soils focuses on explanations such as the recalcitrant plant residues and the physical isolation of substrates from decomposers. A pool of organic matter that can persist for centuries to millennia is hypothesized because of the evidence provided by the persistence of pre-disturbance C in fallow or vegetation change experiments, and the radiocarbon age of soil carbon. However, new information, which became available through advances in the ability to measure the isotope signatures of specific compounds, favors a new picture of organic matter dynamics. Instead of persistence of plant-derived residues like lignin in the soil, the majority of mineral soil is in molecules derived from microbial synthesis. Carbon recycled multiple times through the microbial community can be old, decoupling the radiocarbon age of C atoms from the chemical or biological lability of the molecules they comprise. In consequence is soil microbiology, a major control on soil carbon dynamics, which highlights the potential vulnerability of soil organic matter to changing environmental conditions. Moreover, it emphasizes the need to devise new management options to restore, increase, and secure this valuable resource.

Keywords Compound-specific isotope ratios · ^{13}C · ^{14}C · Soil organic matter dynamics

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Introduction

Soils are the most important interfaces for life on earth. They provide the nutrients and water for plant growth, which in turn is the basis for all heterotrophic life on earth, including humans. Plants are also an important store of carbon, fixing carbon dioxide from the atmosphere and counteracting the human impact on climate change (Friedlingstein et al. 2006). However, human impacts on factors such as land use, which is considered to be the most import human impact on earth, and climate change, decreases the ability of soils to grow plants and to sequester carbon (Canadell et al. 2007; Lobell et al. 2011; van der Molen et al. 2011). The biggest climatic impacts on soils include extreme climate events (Jentsch et al. 2007; Garcia-Herrera et al. 2010), desertification (Lal 2010; Ravi et al. 2011) and soil erosion (Poesen and Hooke 1997; Nearing et al. 2004; Lal et al. 2011). Our knowledge on the reactivity of the fragile surface of our planet, however, is still very limited and soils remain the largest single uncertainty in the global carbon cycle (Canadell et al. 2007). Key to this uncertainty is a lack of basic understanding of the processes involved in stabilization and destabilization of the detrital organic matter added to soils, and how these are influenced by environmental parameters. This paper will briefly summarize how our current understanding of soil organic matter dynamics is evolving, especially through the advent of new results from compound-specific ^{13}C and ^{14}C measurements that can trace specific sources or processes. Overall, a new paradigm is emerging that soil organic matter dynamics and stocks are primarily under biological control, with implications for management of the valuable soil resource.

Soil organic matter

Organic matter, the major product of life, is mainly made from six chemical elements: carbon, hydrogen,

oxygen, nitrogen, sulphur, and phosphorus. Different types of organisms assimilate these elements in characteristic and distinct stoichiometric ratios, depending on the chemistry of structural components, like cell walls and tissues. The extracellular skeleton of plants for example is made from lingo-cellulose type material that mainly contains carbon, oxygen, and hydrogen. The low nitrogen content of lingo-cellulose widens the C/N ratio to characteristic values between 15 and 300 in higher plants. In contrast, microorganisms have a much narrower C/N ratio, i.e., between 5 and 12, as their cell walls are made from nitrogen containing mucopolysaccharides. Element ratios of organic matter are widely used to track the origin of organic matter (Martin and Haider 1971; Turchenek and Oades 1979; Guggenberger et al. 1999; Gleixner et al. 2001; Kogel-Knabner 2002).

Carbon, the backbone element of all organic matter, takes several forms in the Earth System. The most oxidized (CO_2) and reduced (CH_4) forms of carbon are important greenhouse gases that have relatively short lifetimes once they are in the atmosphere ($< 10^2$ years). For example, the amplitude of the seasonal cycle of atmospheric CO_2 indicates that the average CO_2 molecule is cycled about once every 6 years through the terrestrial biosphere. The dissolved forms of carbon, mainly dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), and solid forms of carbon, mainly carbonates and organic carbon in rocks including oil and coal, form larger overall reservoirs in the oceans (10^4 GtC) and sedimentary rocks (10^6 GtC) that influence atmospheric CO_2 on timescales of hundreds to millions of years, respectively. The terrestrial carbon cycle contains carbon primarily in the form of organic matter, although there is also an inorganic component of soil carbonates. The living terrestrial biosphere contains roughly the same (620 GtC) amount of C as the atmosphere (Fig. 1). Organic matter in soils, made up of dead and decomposing plant tissues as well as the living microbial decomposer community and its residues, contain more than twice as much carbon summing up to about 1,580 GtC (Gleixner et al. 2001). The combination of its relative large pool size in the terrestrial carbon cycle and its relatively fast response brings soil organic matter into the research focus (Amundson 2001; Sugden et al. 2004; Lal 2010). In order to predict the response of these large amounts of potentially reactive carbon to climate change, it is essential to understand the formation, decomposition, and storage of carbon in soils.

Plants use atmospheric CO_2 to synthesize the structural tissues that form the majority of organic matter in terrestrial ecosystems (Fig. 1). This organic matter is the basis for the formation of soil organic matter. Plants release litter from roots and leaves into and onto the soil. In addition they exude sugars, organic acids, and other low molecular weight compounds into the rhizosphere. High correlations observed at the global scale for carbon stocks in mineral soils with ecosystem net primary productivity (NPP) suggest that plant-derived inputs are driving the soil organic matter formation in
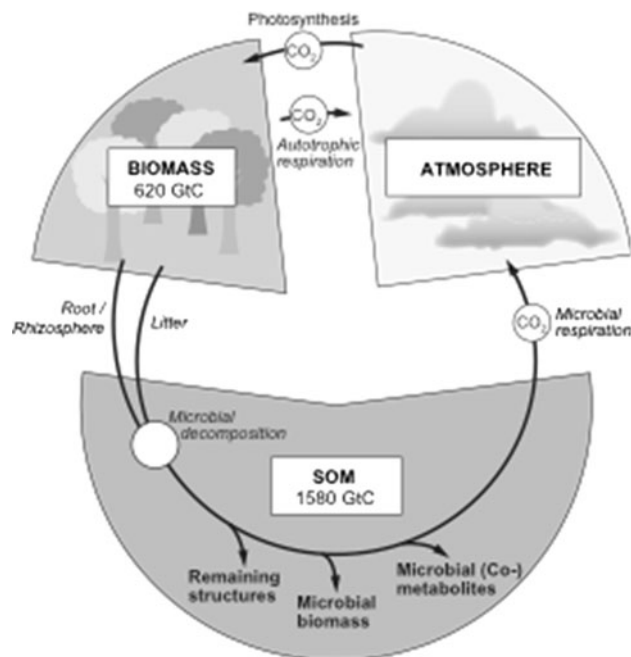

Fig. 1 Terrestrial carbon cycle

boreal, humid, and tropical forests (Fig. 2). Similar correlations, observed in regional studies from different forest stands in Oregon, also support this general relationship (Sun et al. 2004). However, the direct comparison of the vertical distribution of roots and soil carbon in soil depth profiles from a global dataset (Jobbagy and Jackson 2000) indicates that inputs of new plant materials alone cannot completely explain soil organic matter stocks. Both root and soil carbon distributions are highly correlated and decline exponentially with depth (Fig. 3), but overall declines are steeper than those for soil organic matter storage (Gleixner 2005). This suggests that carbon is stabilized, especially in lower soil horizons where the ratio of carbon inputs to carbon stocks are at a minimum.

Since all organic molecules are unstable with respect to decomposition to inorganic forms, it remains a mystery why organic molecules are present and not immediately decomposed in soil. Basically, organic matter persists because its breakdown is slowed by a variety of suggested mechanisms. On the one hand molecules can be stabilized in the soil by a range of processes, including (i) recalcitrance (molecules that require too much energy to decompose), (ii) inaccessibility to decomposition which includes the attachment of molecules to mineral surfaces and the spatial separation of decomposers and substrates (Sollins et al. 1996; Torn et al. 1997; Kaiser et al. 2002; Kogel-Knabner 2002; von Luetzow et al. 2006). On the other hand, molecules can be newly synthesized by soil organisms and mimic the stability of plant-derived molecules (Lichtfouse et al. 1995; Gleixner et al. 2001; Simpson et al. 2002; Kelleher and Simpson 2006; Kindler et al. 2006; Simpson et al. 2007; Miltner et al. 2009).
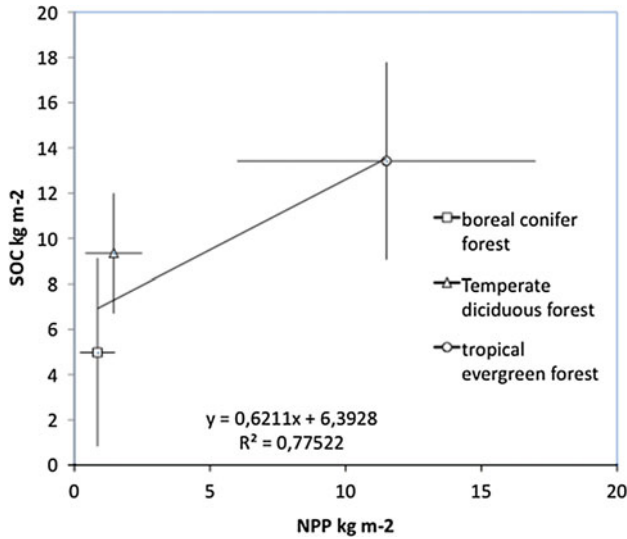
Fig. 2 Effect of net primary productivity (*NPP*) of forest in boreal (*rectangle*), temperate (*triangle*), and tropical ecosystems (*circle*) on soil carbon stocks (*SOC*) in the first meter of mineral soil excluding carbon from litter layers. Data source (Schulze et al. 2002; Gleixner et al. 2009)
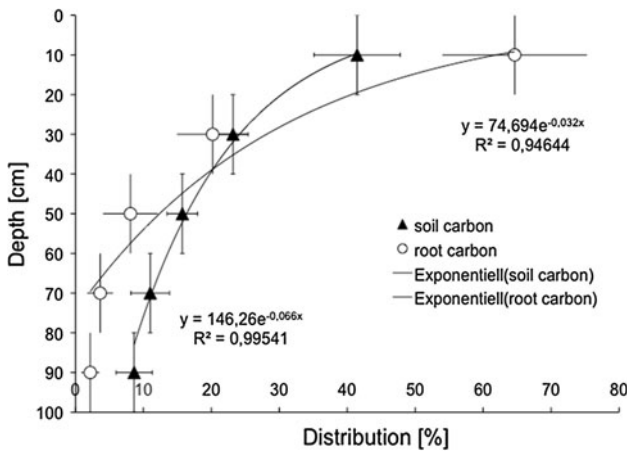
Fig. 3 Distribution of soil- (*triangles*) and root (*circles*)-derived carbon in soil depth profiles. Data source (Jobbagy and Jackson 2000), figure changed after (Gleixner 2005)

Recalcitrance of chemical compounds is very obvious from oil and coal that originate from plant material and consist of lipids like alkanes and polyaromatic structures like polyaromatic hydrocarbons (PAH), respectively (Engel and Macko 1993). Oil and coal deposits form and persist over millions of years. Carbohydrates, proteins, or cell membrane lipids like phospholipid fatty acids, decompose quickly in soil (Haider 1995). In recent years, however, the concept of recalcitrance has become less accepted (von Luetzow et al. 2006; Marschner et al. 2008). Oils (e.g., from oil spills) have been shown to be rapidly degradable by organisms, and kerogen from shales has been shown to be a substrate for microorganisms (Seifert et al. 2011). Instead, physical stabilization mechanisms, such as the binding of organic
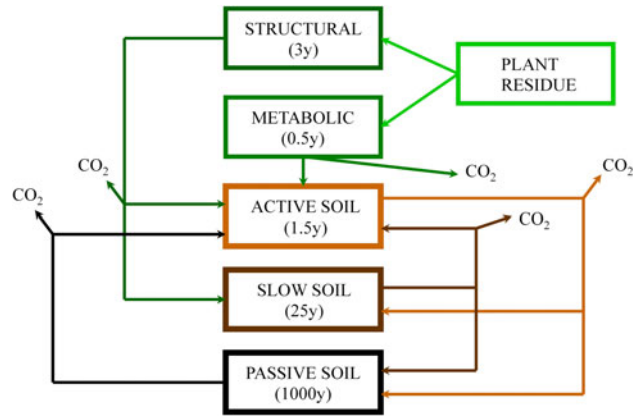
Fig. 4 Scheme of carbon pools and carbon flow used to model soil carbon [based on (Parton et al. 1987)]

molecules to mineral surfaces due to metal–ligand interactions, atomic bonds, and van der Waals forces, have been suggested to protect organic molecules from decomposition because enzymes cannot access these bound molecules (Kaiser et al. 2002; Mikutta et al. 2006; Kleber et al. 2007). This hypothesis is mainly supported by the general correlation between the global soil carbon content and soil clay content (Post et al. 1982; Amundson 2001) and the effect of soil mineralogy on carbon turnover (Torn et al. 1997). An additional hypothesis contends that carbon is persisting in soils over longer time scales because carbon atoms are constantly recycled through the resynthesis of new molecules. In other words, all organic matter in soil is in principle degradable, and that new and structural identical organic matter is formed from the breakdown and recycling of older molecules (Gleixner et al. 1999, 2002). Carbohydrates, lipids, and proteins are for example constantly synthesized in all organisms of the soil food chain and their continued presence in soil might not be related to their stabilization but simply due to the ongoing re-synthesis driven by their biological importance. This third, biologically dominated, mechanism provides a means to separate the age of carbon molecules from the lability of the organic compounds it comprises.

Current soil carbon models reflect the mechanisms of recalcitrance and physical stabilization in that they are based on pools, some of which are highly recalcitrant (Fig. 4) (Jenkinson et al. 1987; Parton et al. 1987). In such models, soil carbon is linked to the input of plant residues that are distributed and interchanged among three soil carbon pools with annual, decadal, and millennial carbon turnover. Carbon pools with very slow turnover times are necessary to model the carbon stocks in fallows. Without new carbon inputs, soil carbon stocks are interestingly stabilizing at a lower carbon level and are not decomposed completely. In the long-term fallow experiment at Utulna, Sweden, after 50 years of fallow, 60 % of the original carbon still remains in the soil (Gerzabek et al. 1997; Kirchmann et al. 2004). In

addition, long-term changes in vegetation (e.g., from C3 to C4 vegetation change) indicate that a portion of the organic C formed under the old synthetic pathway remains in the soil even after a century. As with the results from fallow, this finding is mainly interpreted as indicating the presence of a highly stabilized carbon pool with turnover times of centuries to millennia.

The final line of evidence for very stable soil carbon comes from ^{14}C ages of soil organic matter. [14]C is naturally produced in the upper atmosphere by solar radiation from ^{14}N and decays with a half lifetime of 5,568 years (Libby value). In the pre-industrial atmosphere, the amount of ^{14}C was almost constant, with relatively small variations due to solar and magnetic field activity. Newly synthesized plant biomass reflects the ^{14}C signature of atmospheric CO_2. After fixation, however, no further exchange with the atmospheric CO_2 pool is possible and the amount of ^{14}C in the biomass declines through radioactive decay. Using ^{14}C, ages up to 58–62 ky can be determined (note that changes in the atmospheric ^{14}C since the 1950s complicate this picture for very recently fixed organic matter). Published ^{14}C ages of carbon found in soil organic matter range from modern up to 20 ky (ESM Appendix 1). In general, carbon in topsoil is modern or up to 1 ky old, and carbon ages increase with depth in the mineral soil (Fig. 5). Here mean ages around 6 ky can be found, but the age in any given soil is a function of factors like mineralogy (Torn et al. 1997) and clay content. Only in desert soil was much older SOM found, but here environmental conditions like the missing water obviously prevents decomposition. The presence of very old carbon in soils based on ^{14}C ages of soil organic matter generally provides the strongest support that carbon can be highly stabilized in soil over millennial timescales.

In summary, the persistence of organic carbon in soils, sometimes for millennia, is well documented in the literature. However, the persistence of a carbon atom does not necessarily mean that the atom itself is still in the original molecule in which it was originally added to the soil. There is a need for additional information that allows us to distinguish between stability/lability of molecules and the carbon that might be recycled continuously into newly synthesized molecules. Here, compound-specific isotope ratios of biomarkers provide the information to better understand soil carbon dynamics.

Origin and turnover of organic matter found in soil

In principle, organic matter in soil can either be original plant biomass—i.e., the molecules added to the soil as fresh plant detritus—or transformed biomass, i.e., newly formed biomass after microbial decomposition of plant biomass (Fig. 1). Both origins can be easily distinguished by their chemical structure using fingerprint techniques (Schnitzer et al. 1994; Gregorich et al. 1996). For example, pyrolysis coupled to gas chromatography/mass spectrometry (Py-GC/MS) can resolve molecular fragments of biomass. In the pyrolysis process, organic matter is rapidly heated in the absence of oxygen to temperatures above 500 °C, producing volatile compounds like furanes and pyranes, and methoxyphenols, and nitriles, pyroles, and piperazines from non-volatile compounds like carbohydrates, lignins, and proteins, respectively (Gregorich et al. 1996). The main mechanisms in the pyrolysis process are intramolecular water abstraction and cyclization reactions. After coupling pyrolysis to compound-specific isotope ratio mass spectrometry (GC-IRMS), the isotopic content of individual pyrolysis products were measured (Gleixner and Schmidt 1998; Schulten and Gleixner 1999). Most interestingly, the ^{13}C isotope ratios of the volatile pyrolysis products mirror the isotopic content of their non-volatile precursors (Steinbeiss et al. 2006). In consequence, this technique can be used to determine the turnover and recycling of molecular fragments of soil organic matter using isotopic labeling.

Fig. 5 Distribution of ^{14}C ages against soil depth of published soil profiles. All depth intervals are grouped in four depth segments (*top*, 1st, 2nd and *bottom* segment), SE for depth and ^{14}C ages are given for each segment. Data are given in ESM Appendix 1
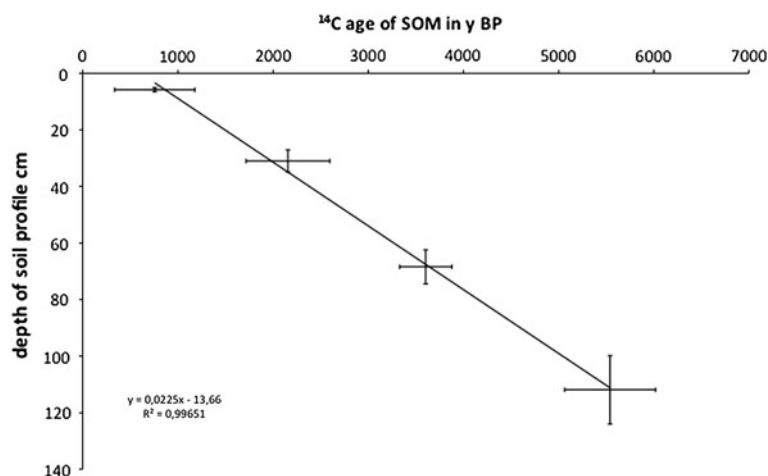
The most simple and straightforward way to introduce an isotope label into the plant–soil system is through vegetation change experiments (Balesdent and Mariotti 1996; Boutton and Yamasaki 1996). Here, typically C3 plants with a $\delta^{13}C$ value of −25 to −30 ‰ are replaced with C4 plants that have a naturally distinct isotopic signal close to −12 ‰ (O'Leary 1981). The time required for the isotopic shift of new plant material to appear in either bulk soil or individual compounds provides an estimate of their turnover rate (Balesdent et al. 1987; Balesdent and Mariotti 1996; Gleixner et al. 2001). Most interestingly, such analyses made on organic matter fractions indicate that plant litter residues do not form an important fraction of mineral soil organic matter (Fig. 6). Plant-derived signals from cellulose and lignin are typically lost quickly—within a few years—and are only found in particulate organic matter that forms a minor carbon fraction in mineral soil (Grandy and Neff 2008; Bol et al. 2009; Miltner et al. 2009). The calculated turnover for these plant-derived compounds is very rapid, suggesting that if the compounds are found in soils, they are not stabilized, but only not yet decomposed, probably due to separation of decomposers from their substrate. Most interestingly, molecular fragments of non-structural carbohydrates and proteins, which are chemically and biologically labile molecules thought to be rapidly metabolized in

soils demonstrate much slower incorporation of the isotope label and therefore lower turnover rates than structural components (Gleixner et al. 2002). Taken together, these findings argue against recalcitrance and stabilization of plant-derived carbon as the major mechanisms allowing organic matter to persist in soils. In contrast is organic matter found in soils not chemically identical to plant biomass. Moreover, point the observed slow turnover rates for non-structural carbohydrates and proteins in soils more to biological resynthesis of organic molecules as the reason for "apparently persistent" soil organic matter fractions. Evidently, these compounds (in spite of their low intrinsic stability) are newly made from recycled carbon that is not yet isotopically labeled. This implies that such compounds should also have a low ^{14}C content as they are formed from pre-aged soil carbon (DeNiro and Epstein 1978; Boschker and Middelburg 2002). In consequence, we have to understand that ^{14}C ages of soil carbon do not measure the stability of individual molecules. In contrast measure the ^{14}C ages of soil organic matter simply the time since the carbon atoms in the molecule were separated from equilibrium with the atmospheric carbon pool, e.g., old carbon does not necessarily imply chemical recalcitrance, and might just demonstrate repeated recycling of carbon atoms through more labile molecules.
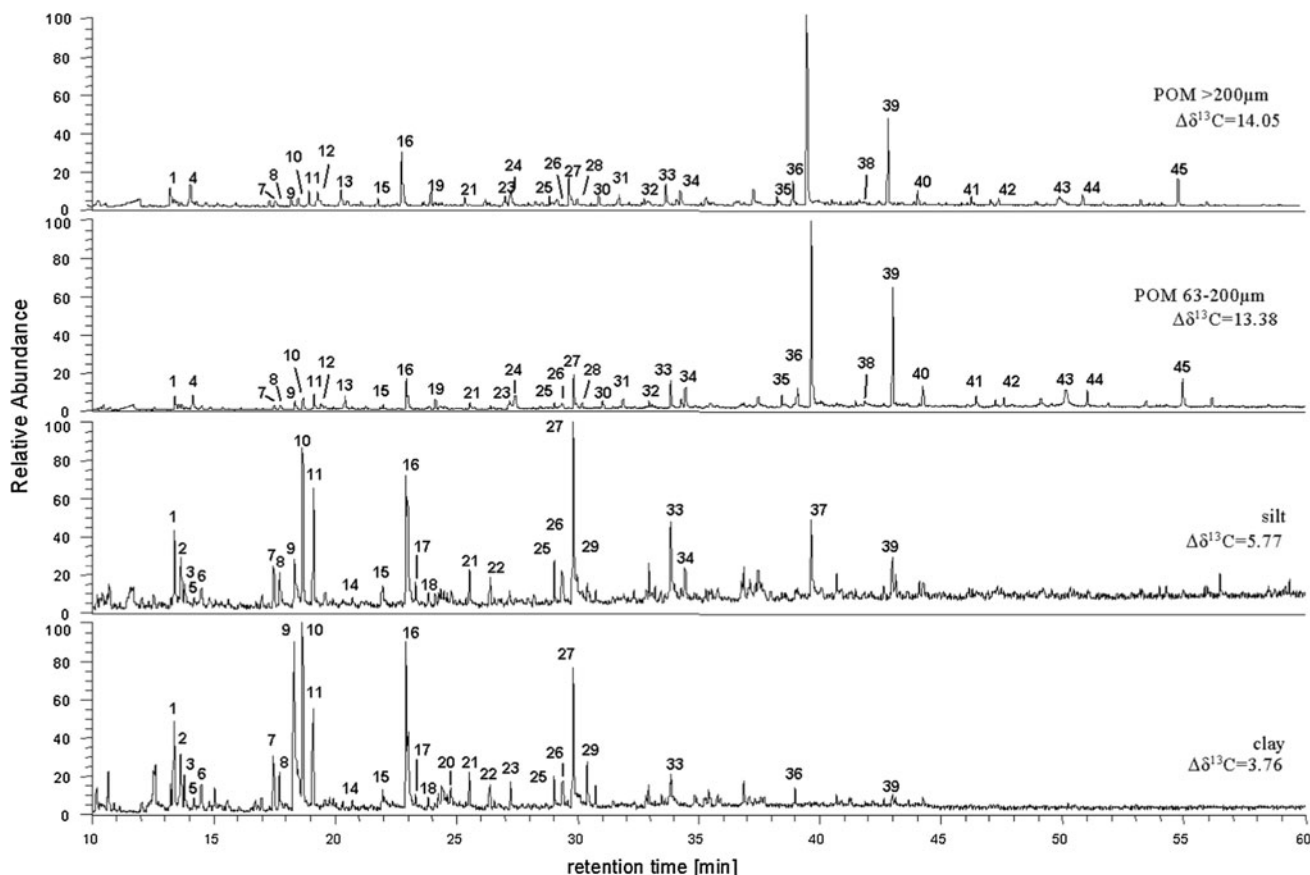

Fig. 6 Chemical composition of particle size fractions from soil organic matter (Bol et al. 2009)

Controls of organic matter storage and dynamics in soil

As stated earlier, carbon stocks in the mineral soil are related to the rate of above-ground organic matter production—or the rate of addition of new C to soils—on a global basis. However, the physical basis for this observation remains unclear, and it breaks down when applied to the vertical soil profile. We have to distinguish between the effects of root-related inputs into the soil like root growth and exudation and the effect of leaf and woody stem litter input onto the soil surface. This opens the question if only the amount of dead biomass matters or if there is a vital effect of living plants. Furthermore, if the main component of mineral soil organic carbon is derived from microorganisms decomposing plant residues rather than the residues themselves, as noted above, then organic matter storage may reflect the efficiency of the microbial community rather than the rate of fresh plant residue addition.

Role of plants

Detailed and highly replicated datasets on soil organic matter and plant parameters like root growth are unfortunately very sparse in the literature. Some of the best data sources are highly replicated biodiversity experiments like the Jena Experiment (Roscher et al. 2004). Here annual root growth was found to be in the same order of magnitude as the annual soil carbon stock changes in this aggrading grassland planted on a former agricultural field (Steinbeiss et al. 2008a, b). The implication is that carbon storage efficiency in this system, which is rapidly accumulating soil C, is very high. The storage efficiency is much lower in comparison to above-ground plant litter addition (Fig. 7). In some plots, C4 grasses were cultivated in order to trace the flow of C4 versus C3 carbon into soil organic matter. These plots were designed as split plots. In one half of the plot above-ground litter was removed after mowing, (zero litter input above-ground) while in the other half the cut grass litter remained on the field (about 500 g C m^{-2} y^{-1} litter added above-ground). Using the isotopic signal of C4 plants in comparison to C3 plants, it was possible to calculate the amount of carbon storage derived from the above-ground litter (Steinbeiss et al. 2008b). In the experiment with and without above-ground litter addition, total carbon storage (132 g C m^{-2} y^{-1} and 191 g C m^{-2} y^{-1}, respectively) was again more reflective of the root standing biomass (187–214 g C m^{-2} y^{-1}), rather than above-ground inputs (500 vs. 0 g C m^{-2} y^{-1}). Indeed, the plots with above-ground litter addition showed overall lower total C storage, although more of what they accumulated was shown to have the label associated with the new, C4 plant source (145 vs. 101 g C m^{-2} y^{-1}). Overall, for plots with above-ground litter inputs, only about 10 % of the 500 g C m^{-2} y^{-1} litter addition remained in the soil per year. This suggests that
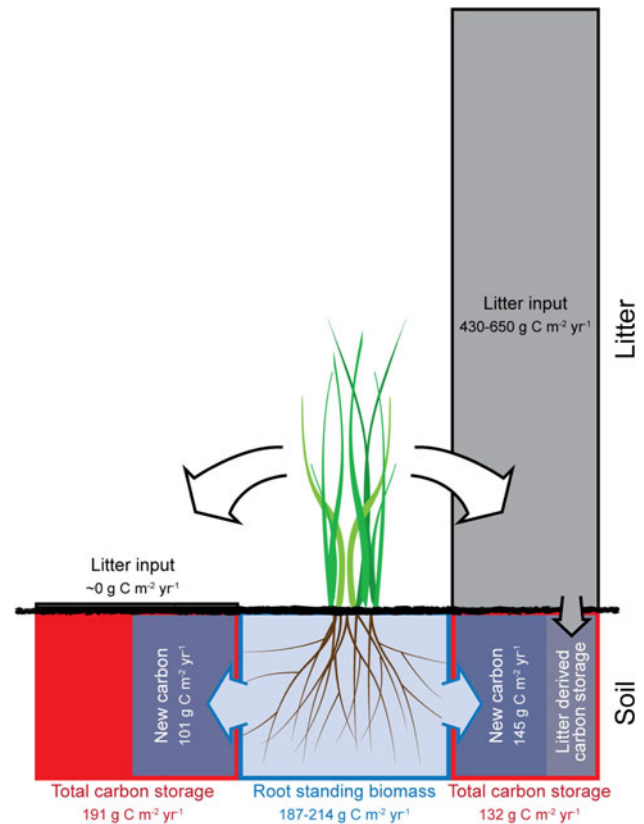

Fig. 7 Effect of litter addition on soil carbon storage and turnover [figure changed after (Steinbeiss et al. 2008a, b)]

added dead above-ground leaf litter is primarily decomposed by soil microorganisms, and that this additional energy source enables them to more effectively decompose existing soil organic matter. This effect is well known as priming (Dalenberg and Jager 1981; Jenkinson et al. 1985; Kuzyakov et al. 2000; Fontaine et al. 2011). This vital effect on soil carbon storage is further supported from studies investigating the positive effect of biodiversity on carbon storage. Here, carbon stock changes are significantly explained by carbon input but also by an additional effect related to plant communities (Steinbeiss et al. 2008a). This biodiversity effect might in turn be an effect of the microbial community, which is also related to plant community (Habekost et al. 2008). In summary might soil carbon storage be more a function of the root rhizosphere continuum than a simple mass relation to above-ground inputs. In order to understand this relationship better, we need to explore the food sources of soil microorganisms.

Role of soil microorganisms

Soil microorganisms are investigated on several levels of complexity because of the difficulty of measuring them directly. Indirect methods attempt to quantify the total amount of microorganisms in soil using either CO_2

respired following substrate additions or the amount of carbon leachable after cell disruption. Substrate-induced respiration indicates the portion of the total community decomposing the added substrate (Andersson et al. 2004). Usually, simple substrates such as glucose or sometimes organic acids and amino acids are added and the fast respiratory response is assumed to indicate the activity of the responding microbial community. This technique helps to compare communities from different sites and soil types. Information on the in situ substrate use can only be drawn from cell remains in combination with their isotopic content. The simplest method is chloroform fumigation extraction (CFE) (Vance et al. 1987). Here the cell walls of the microbial community are disrupted by fumigation with chloroform. The cell contents are extracted with salt solutions and are compared to non-fumigated controls. In combination with the prior addition of labeled complex substrates like plant biomass, cellulose, or after vegetation change from C3 to C4 or vice versa, the degree of label uptake into the microbial community can be calculated. Results from both methods are not necessarily comparable as the substrate use efficiency is not identical for different growth phases of the community and for different substrates.

A deeper insight into the community structure requires molecular-level techniques. DNA and RNA enable description of the total and active community, respectively (Ostle et al. 2000; Kreuzer-Martin 2007). The involvement in the decomposition process can only be traced with highly labeled substrates using stable isotope probing (Kreuzer-Martin 2007). At the natural abundance level, this information can be drawn from biomarkers of microbial cell walls, following an isotopic label derived from vegetation change (Boschker et al. 1998; Kramer and Gleixner 2006), though with less overall specificity. Phospholipids that are the integral part of all cell membranes are extracted using organic solvents. After trans-esterification to fatty acid methyl esters (FAME), they are isolated and identified using chromatographic techniques using mass spectrometric detection (Zelles 1999). PLFA analyses provide information on the overall size of the microbial community as well as information on members of different microbial groups having characteristically difference cell walls, including Gram-negative, Gram-positive bacteria, and mycorrhizal and decomposing fungi. Further, the uptake of substrate into parts or functional units of the microbial community can be inferred by tracing an isotopic label using compound-specific isotope measurements. However, for the latter, a complete separation of individual FAMEs is mandatory (Kramer and Gleixner 2008). Most interestingly, the PLFA technique has been successfully combined with ^{14}C measurements (Eglinton et al. 1996). Here individual FAMEs are isolated by preparative GC and after graphitization the ^{14}C content is measured by accelerator mass spectrometry (AMS).

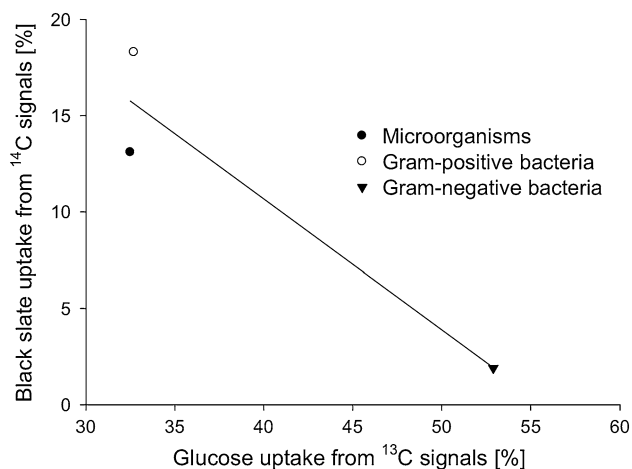Both techniques can be combined and two different sources can be identified. This was recently done using two field sites differing in the ^{14}C content of soil organic matter (Kramer and Gleixner 2006). Comparing the ^{14}C signal of individual PLFAs it is consequently possible to calculate the uptake of carbon from soil organic matter. Additionally, both sites had a plot that underwent vegetation change from C3 to C4 plants several years ago in addition to the corresponding control plots that differed only in bulk soil ^{14}C. Comparing the isotopic shift in ^{13}C for each site enables to calculate the uptake of carbon that is related to carbon directly derived to plant carbon (Fig. 8). Most interestingly, this investigation suggests that between 50 and 100 % of carbon used by the whole microbial community is derived from fresh plant material and between 0 and 40 % from soil organic matter. A difference in substrate use preference could be observed across the individual PLFA compounds. In the mean the PLFA associated with Gram-negative bacteria were slightly more influenced by plant carbon compared to soil carbon than Gram-positive bacteria (Kramer and Gleixner 2006). This meets our expectations as Gram-negative bacteria are more abundant in the rhizosphere than in the neighboring soil, whereas this preference is not found for Gram-positive bacteria (Waldrop et al. 2000).

In the mean only 80 % of carbon sources were explained by this experiment, suggesting that the microbial community uses carbon sources not represented in the "fresh plant" and "soil organic matter" end-members we used in the mass balance calculations. If we look through the literature we can find a range of processes that might be responsible for this. First of all, is the direct uptake of carbon from CO_2 observed in several soils (Miltner et al. 2005b; Stein et al. 2005). Most interestingly, this is also observed in the dark, which excludes photosynthetically active organisms like algae, so that heterotrophic CO_2 fixation is suggested (Miltner et al. 2005a). Several metabolic pathways of microorganisms are known for this heterotrophic carbon uptake (Preuss et al. 1989; Berg et al. 2007) and might be, in consequence, a missing process for carbon uptake. For soils on sedimentary substrates, carbon stored in rocks, i.e., kerogen and bitumen (Engel and Macko 1993), and
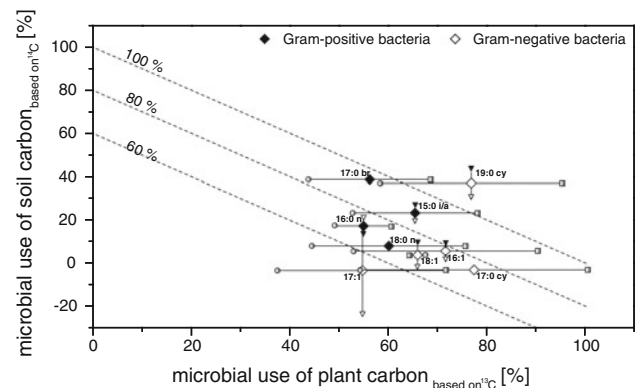
Fig. 8 Quantification of soil- and plant-derived carbon sources of soil microbial phospholipid fatty acids (Kramer and Gleixner 2006)

carbon found in coal and char is used for growth by soil microorganisms (Petsch et al. 2001; Steinbeiss et al. 2009; Seifert et al. 2011). Most interestingly, the uptake of carbon from rocks would strongly affect the age of the soil microorganisms and even if their biomass was instantaneously built, its ^{14}C content would be very low, indicating "dead living biomass" (Petsch et al. 2001). Mainly fungi and actinobacteria are able to use these unlikely carbon sources (Steinbeiss et al. 2009; Seifert et al. 2011). Both groups of organisms are able to "move" (grow) through the soil and might therefore better explore new sites where carbon can be found. The ability to use these unlikely carbon sources seems to be related to the availability of easily decomposable carbon

sources (Fig. 9). Both naturally available carbon as well as added glucose decreased the carbon uptake from kerogen. In summary use soil microorganisms every likely (plant and microbial biomass, and soil carbon recycling) and unlikely (carbon from parent material and direct CO_2 uptake) carbon source in soils (Fig. 10). The first choice is likely fresh organic matter, but if this organic matter is not available, every unlikely carbon source is used.

Results to date suggest future areas where research can test the above hypotheses. For example, tracing of CO_2 fixed non-photosynthetically in soils using isotope labeling would provide valuable information of the fate and kinetics of C fixed by this pathway. If the microbes involved in these processes have specific molecular biomarkers, the importance of this process with depth and in various soil environments could be assessed. The importance of sedimentary C could be established by comparing the ^{14}C age of organic matter in soils developed on different (igneous versus sedimentary) parent materials at sites where climatic factors are identical. Additionally, current studies following the fate of isotopically labeled biochar addition to soils and its incorporation into microbial biomarker molecules may provide further evidence of the ability of the microbial community to degrade these presumably "recalcitrant" substrates.

Fig. 9 Negative effect of labile carbon on the uptake of carbon from parent material, i.e., kerogen from Paleozoic slates (Seifert et al. 2011)

Biological control of soil carbon dynamics

New results from labeled litter additions and compound-specific isotope research clearly demonstrate that soil organic matter dynamics does not simply operate
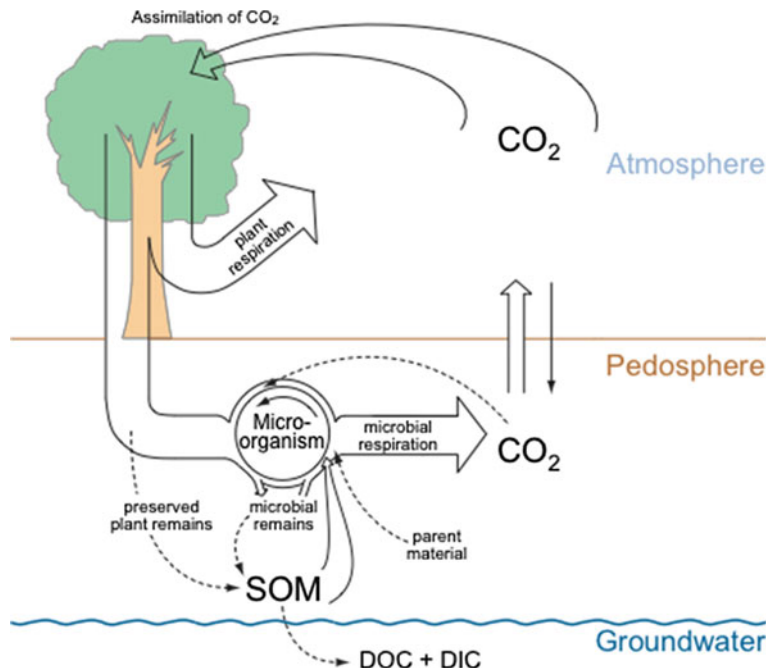
Fig. 10 Soil organic matter formation and carbon cycling in soil

according to the input-driven, pool-dominated approach used in current models of soil organic matter dynamics. The missing key player in our current understanding is the importance of the biological loop (Fig. 10). Our general established view of soil organic matter dynamics is related to exponential decay functions. It assumes that carbon added to the soil is decomposed with a constant decay rate (K) (Eq. 1).

$$C = C_0 e^{(-kt)}. \tag{1}$$

C is the carbon concentration at a given time point (t) in years and C_0 is the initial carbon concentration. For multiple pool models, there are different k's and the inputs can be either from fresh organic matter directly to each pool, or from transfers among pools. The decomposition rate constants are modified by environmental factors like temperature and moisture (Sierra 2012).

However, for biological reactions, namely enzyme catalyzed reaction, first-order kinetics no longer apply, as here a two-step kinetic is valid (Davidson and Janssens 2006; Davidson et al. 2012). In a first step, the substrate and decomposer have to meet and then the decomposition reaction takes place. This kinetics is described by the well-known Michaelis–Menten kinetics (Eq. 2).

$$v = v_{max}S/(k_M + S) \tag{2}$$

v and v_{max} are the actual and maximum speed of the reaction, respectively. K_M is the Michaelis–Menten constant of the reaction indicating the substrate concentration (S) when $v = v_{max}/2$. K_M represents the affinity of the substrate to the enzyme.

Using a Michaelis–Menten formulation, the rate constant depends on the substrate concentration, and decomposition tends (catalyst concentrations being equal) to be fast at high substrate concentration and slow at low substrate concentration. This reflects the lower probability of a substrate molecule to meet the catalyst when concentration is low. This has some fundamental consequences for how the time course of decomposition is predicted to proceed when compared to the first-order model (Fig. 11). With first-order kinetics (exponential decay), the remaining substrate is constantly decreasing, whereas the loss of substrate slows as concentration decreases under Michaelis–Menten kinetics. A substrate-dependent decomposition rate can explain the observation from bare ground plots that decomposition rates slow over time, without the need for invoking a stable carbon pools that somehow has different characteristics (either physical stabilization mechanism or chemical structure) that create slower decomposition rates.

In sensu stricto, however, Michaelis–Menten kinetics cannot be applied to soils, as this equation applies only for liquid solutions. However, the concept of a two-step kinetics can be also applied to organic matter decomposition. Conceptually, one can imagine a soil where all that is required for decomposition is that
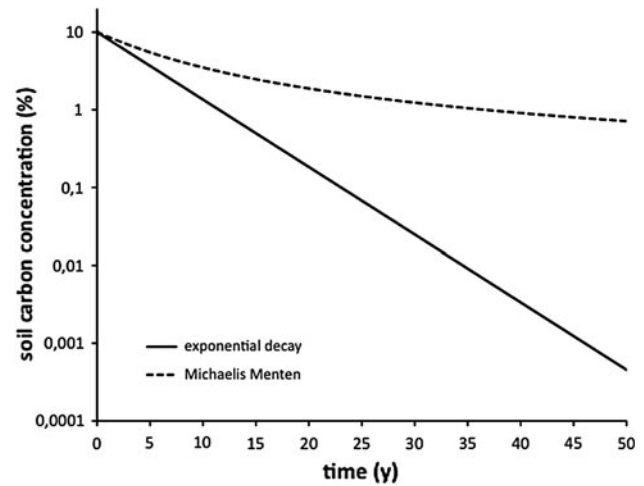

Fig. 11 Remaining soil carbon after exponential decay and Michaelis–Menten kinetics

an organism (or its exoenzyme) has to meet an appropriate substrate molecule—once the two meet, decomposition occurs. The overall age and depth distribution of carbon in such a case then depends on the spatial distribution of microbes and substrate inputs, including physical incorporation of substrates into soil (Fig. 12). As a thought experiment, consider a soil containing two types of particles. One type, called soil microorganisms, are randomly distributed in a 2D space. The other type of particle, called organic matter, is constantly added at the top of the profile. Both particles are allowed to random walk (mix) in the soil profile. Whenever the two types of particles meet, the organic matter is transformed to microbial biomass and respired with a constant rate. In such a case, second-order kinetics also applies. The first step is the probability of the two particles meeting in space, and the second the (first-order) decomposition reaction. Overall, the total rate of decomposition in the soil will depend on the substrate concentration; hence rates (and concentrations) will be high at the top and low at the bottom of the soil profile. Such models can interestingly yield a very realistic distribution of carbon, carbon age, and microbial biomass in soil profiles, again without a requirement for stipulation of separate organic matter pools (Fig. 12). Here, the age of the particle is not related to its stability (i.e., the reaction rate when the microbe and particle meet), which is the same for the particles in the topsoil. Instead, the C is on average older because the probability of mixing into contact with a microbe is low and this particle was not yet decomposed. This brings another new view on soil carbon. The age of soil organic matter is decoupled from the persistence of soil organic matter. Instead, it is telling us the overall mean time the carbon has resided in the soil since it was originally fixed from the atmosphere, and the particle itself could be recently synthesized by soil microorganisms from old carbon that was either not
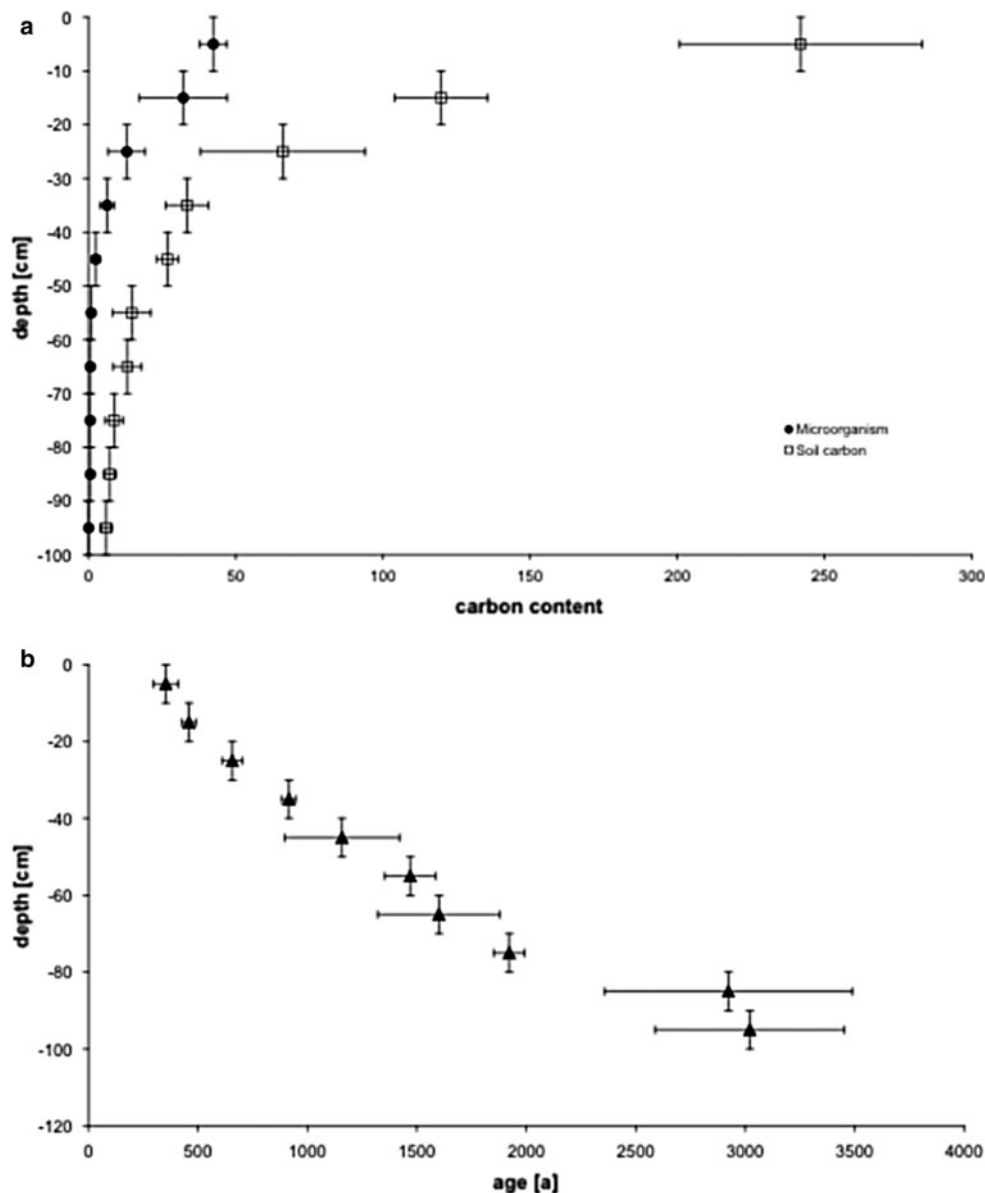
Fig. 12 Soil and microbial carbon (a) and carbon age (b) distribution in soil profiles modeled using two random-walk particles

decomposed yet or was already recycled by other soil microorganisms several times.

Future research should explore modeling soil organic matter dynamics using substrate and spatial limitations, perhaps as a simpler alternative to the current box model approaches, which likely reflect the portions of the soil that are substrate-limited, or the time required to degrade all plant inputs through the microbial "mill", and the relationship between microbial community composition and the efficiency of organic matter degradation versus retention as new microbially constructed compounds. Such models may ultimately also have to include processes like CO_2 fixation and parent material or char-derived C to fully explain both carbon and ^{14}C distributions in different kinds of soils.

Conclusions

The current view of soil organic matter dynamics, with its emphasis on identifying pools of organic matter that decompose at intrinsically different rates, does not fully explain observations of the chemical nature and age of organic carbon in soils. The idea that there is a stable "pool" of organic matter is driven by observations of old ^{14}C ages, relationships between the total age and amount of C and type and amount of mineral surfaces, and field experiments using fallows or long-term C3–C4 vegetation change. New results clearly show that the chemical nature of this old carbon is microbial—rather than plant-related material. New information from compound-specific investigations of the speed of incorporation of isotope

label into microbial communities clearly shows that the age of carbon in soils is decoupled from its lability, in that old carbon sources are used by microbes and made into chemically labile compounds that can be further recycled. Together, these results clearly demonstrate that soil carbon dynamics is strongly linked the role and function of soil (micro)organisms.

This review highlights that plant carbon input is completely decomposed by soil microorganisms and that soil organisms form structurally new carbon, which makes up the majority of mineral soil organic matter. Soil microorganisms use a mix of carbon sources besides fresh plant material, including microbial material, recycling of soil organic matter, fossil carbon from the parent material, and direct uptake of carbon from soil gases like CO_2 or CH_4. The influence of recycling on the age of soil C means that overall soil organic matter may be respond much more rapidly to a shift in climate or vegetation than one might predict based on the age of the carbon it contains, with consequences not yet incorporated into models of future global change (Schulze and Freibauer 2005). Soil organic matter models are based on a carbon flow that is derived from litter input. Additional processes of carbon input, like the direct carbon uptake of methane and CO_2 by soil microorganisms (see above), are all lumped into a stable carbon pool. Some of these processes, like carbon use from rocks or the heterotrophic carbon uptake yield in soil organic matter having low ^{14}C content that also mimic stable carbon pools. Especially the results from compound-specific ^{13}C and ^{14}C measurements of microbial membranes suggest that soil organic matter dynamic is mainly under biological control.

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