

INVITED REVIEW

Soil organic matter turnover is governed by accessibility not recalcitrance

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Abstract

Mechanisms to mitigate global climate change by sequestering carbon (C) in different ‘sinks’ have been proposed as at least temporary measures. Of the major global C pools, terrestrial ecosystems hold the potential to capture and store substantially increased volumes of C in soil organic matter (SOM) through changes in management that are also of benefit to the multitude of ecosystem services that soils provide. This potential can only be realized by determining the amount of SOM stored in soils now, with subsequent quantification of how this is affected by management strategies intended to increase SOM concentrations, and used in soil C models for the prediction of the roles of soils in future climate change. An apparently obvious method to increase C stocks in soils is to augment the soil C pools with the longest mean residence times (MRT). Computer simulation models of soil C dynamics, e.g. RothC and Century, partition these refractory constituents into slow and passive pools with MRTs of centuries to millennia. This partitioning is assumed to reflect: (i) the average biomolecular properties of SOM in the pools with reference to their source in plant litter, (ii) the accessibility of the SOM to decomposer organisms or catalytic enzymes, or (iii) constraints imposed on decomposition by environmental conditions, including soil moisture and temperature. However, contemporary analytical approaches suggest that the chemical composition of these pools is not necessarily predictable because, despite considerable progress with understanding decomposition processes and the role of decomposer organisms, along with refinements in simulation models, little progress has been made in reconciling biochemical properties with the kinetically defined pools. In this review, we will explore how advances in quantitative analytical techniques have redefined the new understanding of SOM dynamics and how this is affecting the development and application of new modelling approaches to soil C.

Keywords: C isotopes, decomposition, recalcitrance, soil C models, soil microorganisms, soil organic matter

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Introduction

By the end of the current century, global mean temperature is predicted to increase by 2–7 °C, and the amount and distribution of precipitation is predicted to change, due to increases in atmospheric greenhouse gas concentrations, especially carbon dioxide (CO₂; Wu *et al.*, 2011). Soils represent a massive stock of potentially volatile carbon (C) and act as both a buffer against atmospheric CO₂ increase and as a potential sink for additional C depending on the balance between photosynthesis, the respiration of decomposer organisms and the stabilization of C in soils. The total global stock of C in soil is estimated at approximately 2500 Pg C distrib-

uted between soil organic C (1550 Pg C) and soil inorganic C (i.e. carbonates, 950 Pg C). The total terrestrial biota contains about 560 Pg C and is the major source of C inputs to the soil organic matter (SOM) pool (Lal, 2008; Fig. 1). Organic carbon is the largest single component of SOM which encompasses not only the continuum from fresh to progressively decaying plant, microbial and soil faunal debris and exudates but also contains the other elements vital for life, i.e. nitrogen (N), phosphorus (P) and sulphur (S). Hereafter, the term SOM will be used to cover all references to SOM and soil organic C. Terrestrial ecosystems offer significant potential to capture and hold substantially increased volumes of C within SOM (Smith & Fang, 2010), mainly through the recovery of soil C lost due to land-use change (Smith, 2008; Powlson *et al.*, 2011) and by enhancing the ‘missing C sink’ proposed to exist in soils (Canadell *et al.*, 2007). There are indications that

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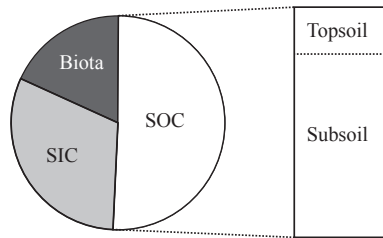


Fig. 1 The global distribution of C between soil biota (flora and fauna; 560 Pg), soil inorganic C (SIC; 950 Pg) and soil organic C (SOC; 1550 Pg) in the terrestrial C pool (Lal, 2008), showing division of soil organic C between top-soils (i.e. A horizon ~25%) and subsoils (i.e. below A horizon ~75%; Jobbágy & Jackson, 2000).

plants and soils combined annually absorb 1 Pg C more than they emit, but the reasons are unclear (Janzen, 2004). It has been postulated that increasing SOM concentrations in soils up to 2 m depth by 5–15% could decrease atmospheric CO₂ concentrations by 16–30% (Baldock, 2007; Kell, 2011). These ideas have led to substantial attention being paid to quantifying the stocks of C in soils, and the mechanisms of stabilizing C in soils, including by land management options, to increase SOM stocks (Lal, 2002; Smith, 2008). Despite the fundamental importance of reliable estimates of C stocks in soils, estimating them at the global or even a regional scale, and more importantly detecting changes in these stocks, is remarkably difficult for the following reasons: (i) mismatches between the temporal and spatial resolution of the survey and analytical data, (ii) the natural temporal and spatial variability in soils, (iii) the relative paucity of data on the variations in soil depth and distribution of C with depth, and (iv) the fact that key parameters, such as soil depth (particularly for the subsoils) and bulk density have often not been recorded, which compromises the conversion of concentration data into amounts of SOM (Hopkins *et al.*, 2009). Added to these compounded operational difficulties is the fact that accurate assessments of SOM change are bedevilled by all the problems of determining a very small difference between two very large values.

Soil organic matter is critical to ensure secure food production; the process of decomposition is key to the recycling of macronutrients, i.e. N, P and S, into plant-available forms, and its effective management can reduce the need for fossil fuel consumption to supply N fertilizer. A wide range of soil properties, including soil structure, water and nutrient holding capacity and biodiversity, are improved by maintaining optimal quantities of SOM (Watts *et al.*, 2006; Powlson *et al.*, 2011). A SOM concentration of less than 2% is considered to be the threshold value below which soil function is impaired (Greenland *et al.*, 1975; Lal, 2004;

Huber *et al.*, 2008), although there is little quantitative evidence for such a threshold (Loveland & Webb, 2003), and Janzen (2006) proposed that it is the bioavailability of SOM that is the major influence on soil properties. Importantly, the general responses of C stocks in terrestrial ecosystems to changes in environmental conditions, especially temperature and precipitation, and their combined effects, remain unclear (Wu *et al.*, 2011).

Three sets of interacting factors, substrate quality, organisms (including implicitly their combined enzymatic repertoire) and environment (which includes a relatively poorly understood and frequently overlooked set of abiotic decomposition processes), are the main controlling decomposition of organic materials (Swift *et al.*, 1979). Substrate quality is an abstract term used to describe the ability of SOM: (i) to supply organic molecules for both catabolic (energy conversion) and anabolic (biosynthetic) metabolism, (ii) to supply other nutrient elements to decomposer organisms, and (iii) the extent to which properties of the substrate retard its exploitation. These retarding factors include, for example, being hydrophobic or physically impenetrable, or containing compounds that inhibit enzyme activity, such as tannins or polyphenol contents that complex with and inhibit enzymes (Freeman *et al.*, 2004; Sinsabaugh, 2010). The ability to assess substrate quality is not easy and the bulk of this review addresses the biochemical dimensions of this question and its importance relative to physical accessibility of the SOM to decomposer organisms or extracellular (exo-) enzymes as a constraint on decomposition.

The response of different ecosystems to changes in temperature has attracted much attention and obtaining definitive evidence of its effects on SOM decomposition has proved remarkably difficult to obtain, yet the response of decomposition to temperature change is intimately linked to the recalcitrance of SOM. It is bizarre but true that, depending on the experimental approach used and the particular aspect of decomposition being investigated, it is possible to find reports demonstrating that increases in temperature have a strong positive effect (Fang *et al.*, 1998; Knorr *et al.*, 1998) or no effect on decomposition (Liski *et al.*, 1999; Giardina & Ryan, 2000), or even a negative effect on long-term decomposition (Dalias *et al.*, 2001). The main reason given for these paradoxical observations is that SOM is not a single pool of biochemically or kinetically uniform molecules (Knorr *et al.* 1998). Traditional kinetic theory predicts that while more 'chemically recalcitrant' compounds will decompose more slowly, their decomposition should also be more temperature sensitive (Ågren & Bosatta, 2002). Although apparently a simple concept governed by the van'tHoff principle, the effects of changes in temperature on the decomposition

of SOM and nutrient mineralization in soils have proven remarkably difficult to quantify (Kirschbaum, 2006). Although it is well established that, within reasonable limits, the biological processes which drive decomposition will be more rapid at greater temperatures, being able to assign a thermal coefficient or set of coefficients to decomposition and nutrient mineralization has proved remarkably difficult (Davidson & Janssens, 2006). **It is a widely held concept that 'recalcitrant' SOM is more sensitive to changes in temperature than 'labile' SOM (Bauer *et al.*, 2008) on the grounds that a higher resistance to decomposition (Ea, activation energy) is associated with the energetics of decomposition. The warmer the environment, the more likely the critical value of Ea is to be exceeded.** Such effects are taken up in models but it is difficult to infer both differences in rate of decomposition and rate of change with temperature for multiple pools or qualities of SOM from data which are necessarily sparse because it is long term. Experiments which removed 'labile' SOM (Conant *et al.*, 2008a,b) support increased temperature sensitivity of the remainder. However, there are three more significant remaining challenges in understanding and modelling the effects of climate change on SOM turnover. First, there is the practical difficulty of disentangling the effects on the decomposer communities of relative depletion of the most accessible components of the SOM, from the direct effects of temperature on the metabolism of soil microorganisms (Hartley *et al.*, 2007). Second, there are conflicting reports about whether soil microorganisms adapt to increased temperatures by down-regulating respiration (Bradford *et al.*, 2008; Hartley *et al.*, 2008, 2009). Third, plants will

also respond to altered environmental conditions which may change C inputs to soil (Dungait *et al.*, 2010). The quantity and quality of SOM entering soils may be substantially altered depending on how the combination of changes in temperature and moisture regime affect primary production, and the regulatory cascades that affect other ecosystem processes, such as nutrient availability and herbivore abundance, which regulate production indirectly (Wookey *et al.*, 2009).

Can pools in soil C models be defined according to molecular structure?

The most widely applied SOM simulation models, e.g. Century and RothC, divide SOM into pools (Table 1) with varying intrinsic decomposition rates that are rationalized by assuming that a combination of biochemical and physical properties control decay (Adair *et al.*, 2008; Kleber, 2010). However, the relative contributions of the biochemical and physical controls on decay are rarely tested empirically and the pools are usually only defined kinetically. Assumed mean residence times (MRTs) of different SOM pools are used to partition the highly complex, dynamic process of SOM turnover into a series of soil C fluxes from the pools. This partitioning is supposed to reflect the average biochemical and physical properties of SOM in the pools (e.g. metabolic, structural and recalcitrant) or the accessibility of the SOM to decomposer organisms or catalytic enzymes, or constraints imposed on decomposition by environmental conditions. However, perceptions of the stability of particular plant compounds often appear to reflect the roles that the different molec-

Table 1 The pools of SOM defined according to their mean residence times (MRTs; Jenkinson & Rayner, 1977; Paustian *et al.*, 1992) and corresponding compound classes (Brady & Weil, 2002)

Residue type	Century	RothC	Residence time (years)	C : N	Compounds
Litter	Metabolic	DPM	0.1–0.5	10–25	Simple sugars Amino acids Starch
	Structural		2–4	100–200	Polysaccharides
SOM	Active	BIO DPM	1–2	15–30	Living biomass POM Polysaccharides
	Slow	RPM	15–100	10–25	Lignified tissues Waxes Polyphenols
	Passive	HUM IOM	500–5000	7–10	Humic substances Clay: OM complexes Biochar

DPM, decomposable plant material; BIO, microbial biomass; RPM, resistant plant material; HUM, humified organic matter; IOM, inert organic matter; POM, particulate organic matter; OM, organic matter.

ular structures perform within the plant, and how humans manipulate them for their benefit, i.e. glucose in energy drinks, lignin in wooden structures and waxes as preservatives. Thus, strategies for increasing C stocks in soil suggest the enhancement of inputs of biochemically recalcitrant 'biomacromolecules' as a management tool to augment stable SOM stocks (Lorenz *et al.*, 2007), although an overall dilemma associated with soil management for C sequestration is presented by Janzen (2006): 'Shall we hoard [soil C] or use it?', since SOM is also the source of fertility. However, the stability of plant compounds outside the soil does not necessarily imply stability within the soil. Microorganisms are in a constant state of 'starvation' in the soil environment where substrate supply is sporadic both in time and space (Dungait *et al.*, 2011), and highly adapted, complex decomposer communities have evolved in soils to tackle any SOM that is encountered.

Empirical evidence is building against the notion of intrinsic molecular recalcitrance as a concept in understanding the stability of SOM (see recent reviews by Kögel Knabner *et al.*, 2008; Marschner *et al.*, 2008; Kleber, 2010; Schmidt *et al.*, 2011) although this attitude is not new (Jenkinson & Rayner, 1977; Sollins *et al.*, 1996), with opinion turning away from the idea that the very old SOM in soils is inherently resistant to biological attack (Jenkinson *et al.*, 2008). Recent biogeochemical analyses of organic compounds assigned to the pools in soil C models have revealed that SOM does not comprise pools of biochemically or kinetically uniform molecules (Davidson & Janssens, 2006; Kirschbaum, 2006). Evidence from the diversity of compound-specific responses to experimental manipulation in different soils suggests that **recalcitrance cannot be intrinsic to specific compounds** (Amelung *et al.*, 2008). For example, SOM in fast cycling fractions comprises a mixture of plant compounds including plant lignins ('recalcitrant' compounds; Table 1) as well as carbohydrates ('metabolic' or 'structural' compounds; Table 1; Derrien & Amelung, 2011). Thus, Kleber (2010) argued that 'recalcitrance' is a semantic term without a mechanistic foundation, even though it has empirically derived meaning. Von Lütow & Kögel-Knabner (2010) contended that the value of the concept of recalcitrance is the ability to differentiate between the decomposability of organic molecules, although Von Lütow *et al.* (2006) concluded earlier that recalcitrance appears to be a property of SOM that allows it to resist decomposition for years rather than centuries. Overall, the diverse mechanisms for explaining this difference begs for a more quantitative understanding of the relative importance of the mechanisms involved (Kleber, 2010). This is being pro-

vided through analytical advances in tracking the fate of specific organic compounds which are associated with pools in soil C models, reported as the outcomes of experiments that have explored the fate of metabolic, structural and recalcitrant compounds from plant litter in soils (Amelung *et al.*, 2008).

Metabolic compounds

Metabolic compounds are usually low molecular weight, highly labile compounds, such as simple sugars, organic acids including amino acids, which may derive directly from plants, e.g. photosynthate and rhizoxudates, proteins and storage carbohydrates, e.g. starch and fructans (Hopkins & Dungait, 2010). They may also derive secondarily from microbes as a result of exudation and excretion, cell death and decay (Hofman & Dusek, 2003). Metabolic compounds that are been applied to soils *in vitro* can decompose very quickly, presumably because they are rich in energy, readily accessible to organisms and rapidly assimilated; the half-life of amino acids and simple sugars can be less than 1 h in surface soil horizons (Boddy *et al.*, 2007; Hill *et al.*, 2008). These compounds are therefore associated with the 'active' and 'metabolic' pools in the Century model, and the DPM (decomposing plant material) and BIO (biomass) pools in the RothC model (Table 1). Paradoxically, although easily biodegradable metabolic compounds actually constitute a substantial component of SOM (Derrien *et al.*, 2007), the BIO and DPM compartments are small in RothC model. Recent evidence also shows that apparently easily biodegradable metabolic compounds may be older than bulk SOM (Gleixner *et al.*, 2002; Derrien *et al.*, 2006) and become stabilized for millennia in the 'passive' SOM pool (Paustian *et al.*, 1992).

Structural compounds

Polysaccharides are described as 'structural' compounds in plant litter presumed to enter the 'active' pools in the Century model, and DPM in RothC (Brady & Weil, 2002). Cellulose and hemicellulose polysaccharides are the most abundant substrates in plant litter (Dungait *et al.*, 2005; Jia *et al.*, 2008), and aminopolysaccharides, including N-acetylglucosamine and muramic acid, are abundant in the peptidoglycan of the bacterial cell envelope and the chitin of fungal cell walls. It is perhaps surprising that there is little empirical evidence for their specific decomposition dynamics, although it is their very ubiquity and relatively simple chemistry which confers challenges in determining their turnover dynamics in soils. Strong acid hydrolysis is widely used to extract total sugars from soils making

it difficult to distinguish between the monomers of 'structural' polymers of plant or microbial origin, and alternative sources including 'metabolic' compounds (see *Metabolic compounds* above), even if the plant or polysaccharide is ^{13}C or ^{14}C (radiocarbon) labelled (Cheshire & Mundie, 1990; Derrien *et al.*, 2006; Dungait *et al.*, 2009). Many bacteria and fungi degrade plant polysaccharides through the hydrolysis of the glycosidic links using exo-enzymes, e.g. cellulase and xylanase. It has been determined that 60% of cellulose is mineralized in soil after 1 month, with an additional 7% decomposed within 3 months (Derrien *et al.*, 2007), and the remainder persisting in soils long-term (Gleixner *et al.*, 2002; Quenea *et al.*, 2005). Because of the wide range of generalist and specialist soil microorganisms that use polysaccharides as a substrate (Fontaine & Barot, 2005), it is unlikely that 'structural' compounds persist intact in surface soil horizons unless they become protected from decomposition. Cheshire (1977) pointed out more than 30 years ago that **it is the inaccessibility to enzymes, not recalcitrance, which is responsible for the slow degradation of polysaccharides in soil**. For example, it has been suggested that soil polysaccharides play a key role in the stabilization of soil microaggregates (<250 μm) as their length and linear structure allow them to bridge the space between soil particles (Martens, 2000), and intact polysaccharides may become occluded within soil aggregates as components of intra-aggregate particulate SOM (iPOM; Six *et al.*, 2000). Physical protection of SOM is discussed further in 3.1.

'Recalcitrant' compounds

Lignin. The breakdown of lignin and its derivatives is often regarded as the rate limiting step in biological C cycling (Adair *et al.*, 2008; Zhang *et al.*, 2008; St. John *et al.*, 2011). The observed degradation of lignin above-ground may also lead to the perception of recalcitrance, e.g. 'leaf skeletons' that remain after the other components of leaf litter have degraded. Its unique macromolecular, heteropolymeric structure with variable bonding patterns is thought to lead to the relative enrichment of lignin-derived molecules in SOM. **However, unmodified lignin is rarely detected in surface soil horizons, except in recognizable fragments of plant material, leading to the proposal that it is actually preferentially degraded relative to the bulk SOM** (Van Bergen *et al.*, 1997; Dignac & Rumpel, 2006). Compound-specific ^{13}C stable isotope analyses of lignin monomers extracted from soils have determined that most lignin decomposes within 1 year (Rasse *et al.*, 2006; Dungait *et al.*, 2010) with the remainder decomposing within decades (Dignac *et al.*, 2005; Heim &

Schmidt, 2007). Indeed a recent review concluded that the literature is contradictory with regard to lignin decomposition rates but supported the idea that most decomposed within 5 years (Thevenot *et al.*, 2010). **Basidiomycetes are the major biotic decomposers of lignin, of which only the white rot fungi are capable of its complete mineralization to CO_2 and H_2O , and then only in aerobic environments** (Robertson *et al.*, 2008). However, other soil organisms are important in partial lignin breakdown and modification, and may operate even under anaerobic conditions (Chen *et al.*, 1985). **Actinobacteria** are considered to be responsible for up to 15% of lignin degradation in soil; although they cannot completely mineralize lignin they solubilize the polymer to gain access to the associated polysaccharides (Dignac *et al.*, 2005). Xylanases disrupt hemicellulose-lignin associations, without mineralization of the lignin *per se*, subsequently making the lignin more readily available to direct digestion, and Vane *et al.* (2001) proposed that hemicellulose degradation is required for efficient lignin degradation. New insights into the structure of the lignin macromolecule also suggest that lignin biosynthesis is not random (Reale *et al.*, 2004). Well-defined chain configurations identified in lignin macromolecules (Chen & Sarkanen, 2010) and characteristic decomposition rates of individual lignin monomers (Bahri *et al.*, 2006, 2008; Dungait *et al.*, 2008a) point to mechanisms for rapid turnover. Overall, the perception of lignin as a recalcitrant compound is being questioned, as its selective preservation (if any) is only pertinent during initial decomposition with subsequent degradation being more rapid than bulk SOM (Marschner *et al.*, 2008).

Long chain n-alkanes. The *n*-alkanes containing odd-numbered chains with 25–35 C atoms per molecule originate exclusively from the epicuticular wax layers on the leaves and roots of terrestrial higher plants (Jansen *et al.*, 2010) and are the major free lipids in many soils (Bull *et al.*, 2000a; Otto & Simpson, 2005). They are considered to be resistant to degradation due to their apolar chemistry (Derenne & Largeau, 2001). However, like lignin, recent evidence from SOM degradation studies using compound-specific ^{13}C stable isotope analyses has suggested that very long chain *n*-alkanes may turn over more rapidly in soil than total SOM (Quenea *et al.*, 2004; Wiesenberger *et al.*, 2004; Otto & Simpson, 2005). The microbially mediated degradation of *n*-alkanes in soil is well studied (e.g. Wentzel *et al.*, 2007). Environmental conditions that affect the activity of the soil microorganisms, i.e. pH, soil moisture and anaerobicity, influence the stability of lipids and have been observed to reduce the turnover rate of *n*-alkanes (Bull *et al.*, 2000b). However, there is

no doubt that a proportion of *n*-alkanes are stabilized in soil long-term: Bol *et al.* (1996) determined that the aliphatic hydrocarbon fraction from a peaty soil was around 14 000 years old, confirming the potential for *n*-alkanes to be sequestered for millennia in soils under particular conditions. This has been independently confirmed by a wide range of solid-state ¹³C-nuclear magnetic resonance (NMR) studies (Baldock *et al.*, 1991).

Humic substances. Humic substances are obtained from soil as humic acids and fulvic acids by simple extraction with strong alkalis and acids, with the residue 'humin' as the non-hydrolysable fraction assumed to equate to the most refractory SOM. However, these are operationally defined chemical fractions with no real relevance in ecological terms (Wander, 2004), and it is well documented that such preparations contain artefacts from sample preparation and are entirely non-selective with respect to biological entities in soils (Baldock *et al.*, 1991). For a long time the formation of recalcitrant humic substances created through spontaneous reactions between small reactive metabolites, or oxidative cross-linking with biomacromolecules resulting in new condensation products or restructured compounds, has been considered as the major pathway for SOM stabilization (Piccolo, 2001). Heterogeneity in size and chemistry is assumed to make such amorphous polymers resistant to enzyme attack (Marschner *et al.*, 2008). Thus, humic substances are assigned to the 'passive' (Century) and 'HUM' (RothC) pools, with MRTs of 500–5000 years (Table 1). Stevenson (1982) recognized much earlier that humic substances are readily degradable when extracted from soils, which leads one to assume that another mechanism must be responsible for the stability of their molecular constituents within the soil. Thus, the view that novel macromolecules arise from random condensation reactions in soils has given way to the point of view that 'humic substances' are in fact mixtures of partially decomposed plant and microbial biomass that are inaccessible to soil microorganisms (Kelleher *et al.*, 2006; Von Lützow *et al.*, 2008).

Black C and biochar. 'Black C' is the charred remains of plant material which appears in soils as a result of human activity and natural fires. Biochar is a similar material produced by oxygen-limited pyrolysis of biomass, organic waste or other feedstock which is proposed as a soil amendment that is sufficiently recalcitrant to aid C storage in soils, as well as conferring potential chemical and physical benefits on soil functions (Krull *et al.*, 2009). Black C and biochar are assigned to the 'passive' and 'inert organic matter' (IOM) pools of the Century and RothC models respec-

tively (Table 1). Biomass-derived black C comprises a substantial component (5–50%) of organic C in some soils, and is assumed to decompose at a much slower rate than SOM due to its highly condensed aromatic structure (Schmidt *et al.*, 2001). Large charcoal particles originating from forest wildfires can remain in soils for thousands of years (Major *et al.*, 2010), although smaller particles derived from grassland burning can hardly be detected in steppe and prairie soils (Forbes *et al.*, 2006). Lehmann *et al.* (2006) suggested that conversion of biomass C to biochar leads to sequestration of about 50% of the initial C yielding more stable soil C than burning or direct land application of biomass. However, biochar can be used as a substrate by soil microorganisms (Wengel *et al.*, 2006) and is therefore not completely inert. However, it is difficult to evaluate the factors controlling its breakdown because there are significant variations in the physicochemical structure and composition of biochar that arise due to differences in starting material and pyrolysis conditions (Li *et al.*, 2006; Krull *et al.*, 2009; Asadullah *et al.*, 2010; Smith *et al.*, 2010b). After application to soils, biochar decomposition rates vary under different soil conditions, e.g. water regime (Nguyen & Lehmann, 2009), native SOM concentrations (Kimetu & Lehmann, 2010) and pH (Luo *et al.*, 2011). Clearly, any increase in C sequestration due to biochar incorporation would be further diminished if there were a positive priming effect on SOM caused by biochar addition, or if there were an increased mineralization of biochar following the introduction of a substrate (Luo *et al.*, 2011). Indeed, stimulation of biochar mineralization in soil by the addition of glucose to a biochar amended soil has been reported (Hamer *et al.*, 2004; Kuzyakov *et al.*, 2009), although no effect was observed following the addition of cellulose (Nocentini *et al.*, 2010). Losses of native SOM have also been determined after addition of biochar (Wardle *et al.*, 2008; Zimmerman *et al.*, 2011). Overall, the use of biochar as a robust strategy to increase soil C stocks as described by Lovelock (2009) requires additional investigation.

The role of soil organisms in SOM dynamics

Carbon dioxide emissions from autotrophic (root) and heterotrophic (microorganisms and fauna) soil respiration are an order of magnitude greater than those from human activities, such as fossil fuel burning (Nielsen *et al.*, 2011). Soil microorganisms, and implicitly their combined enzymatic repertoire, demonstrate massive physiological and biochemical capacity and are present in vast numbers. These factors have led to two pieces of environmental microbiological dogma: (i) that the soil microbial community is collectively infallible in terms of the range of organic molecules it can degrade, and

(ii) the capacity to degrade any substrate exists in almost any soil. These ideas owe much to the early work of Baas-Becking and Beijerinck: 'everything is everywhere, but the environment selects' (de & Bouvier, 2006), coupled with the diverse range of enzymes of both bacteria and fungi. Although probably not strictly accurate, they are good enough working assumptions because microorganisms or microbial consortia capable of degrading any natural compound and many xenobiotic compounds can be enriched from soil communities. The diversity of microorganisms in a soil at Rothamsted starved of inputs for 50 years appears no different from an adjacent SOM-rich pasture (Hirsch *et al.*, 2009). The large diversity and abundance of soil microorganisms is undoubtedly a result of a long evolutionary history and the vast number of spatial and environmentally distinct niches in soils. Moderating factors such as plant diversity will interact with microbial diversity through factors such as the timing, composition and abundance of residue and exudate supply (Scherber *et al.*, 2010), and the opportunities for symbioses, such as mycorrhizas. Most models assume that changes in the microbial community have limited effects on soil processes (Condrón *et al.*, 2010), and consequently the role of the soil microbial community that is acknowledged overtly in the BIO pool of the RothC is a pool with short MRT (Table 1). However, C from SOM incorporation into soil microorganisms can be C being repeatedly recycled through, and conserved within, the microbial biomass (Rinnan & Bååth, 2009).

The activity of soil microorganisms, and therefore the potential to decompose SOM, is often facilitated by soil meso- and macroinvertebrates (nematodes, enchytraeids, collembola and lumbricids). This is done by physical conditioning of the substrate by comminution (which increases the surface to volume ratio), wetting and the application of surfactants, mixing with soil components leading to incorporation (thereby removing SOM from the extremes of temperature and desiccation at the surface), and by inoculation with soil microorganisms (Wolters, 2000). Conversely, they can also process labile compounds into more stable entities (Fox *et al.*, 2006; Rawlins *et al.*, 2006, 2007). Earthworms are particularly important agents of SOM decomposition in most terrestrial ecosystems, accelerating rates of comminution and dispersal through feeding activities, although whether their activity is a net sink or source of C is under debate (Oyedele *et al.*, 2006; Don *et al.*, 2008; Ekschmitt *et al.*, 2008; Hong *et al.*, 2011). ¹³C stable isotope analyses of soil invertebrates have revealed that different species exhibit dietary preference and trophic niche exploitation of the same SOM resource (Dungait *et al.*, 2008b; Murray *et al.*, 2009; Pollierer *et al.*, 2009; Crotty *et al.*, 2011). Despite these observations, there

has been relatively little attempt to integrate models of food webs with more general models of C turnover (De Ruiter *et al.*, 1994; Fitter *et al.*, 2005). Brussaard *et al.* (2007) suggest a conceptual framework for doing this, acknowledging that the issue of the different scales of macrofaunal and microbial action must be taken into account, and Blanchart *et al.* (2009) describe how an 'agent-based' modelling approach can simulate the effects of earthworms on soil structure. A similar approach might be able to reconcile the many different scales at which soil biota act on SOM.

If all SOM is decomposable, what preserves it?

Some degree of chemical recalcitrance as a stabilization factor of SOM in soils cannot be ruled out (Von Lützow & Kögel-Knabner, 2010). The concentrations of aromatic and double-bond hydrocarbons increase with depth whereas other compounds, such as single-bond alkyl C hydrocarbons, tend to decrease (Eusterhues *et al.*, 2007; Spielvogel *et al.*, 2008). Ellerbrock & Gerke (2004) found that coatings of C on aggregates in the subsoil contained hydrophobic substances which contributed to aggregate stability. However, overall it appears that if soil microorganisms can access SOM, they are able to degrade it relatively rapidly, i.e. within years or decades. The major C stabilization mechanisms in soils are now recognized to be 'biologically non-preferred soil spaces' (Ekschmitt *et al.*, 2008) where SOM is physically protected from microbial activity regardless of its initial chemical structure (Kleber *et al.*, 2011). Van Veen & Kuikman (1990) and Von Lützow *et al.* (2006) listed the mechanisms involved in physical preservation of SOM as (i) occlusion within aggregates, and (ii) adsorption onto minerals, but also a third mechanism has been postulated: (i) substrate-driven 'biological rate limitation' (e.g. Ekschmitt *et al.*, 2005).

Physical protection – aggregates and organomineral complexes

The mechanisms involved in physical preservation of SOM are occlusion within aggregates and adsorption onto minerals (Six *et al.*, 2000). The literature associated with these mechanisms is particularly rich, and we offer a summary herein, and refer the reader to the many excellent references cited in this section.

Adsorption onto minerals is a much more intimate association between SOM and other soil components than the occlusion mechanisms. Sorption between SOM and clay minerals and both amorphous iron and amorphous aluminium colloids plays a major role in preservation due to their large, charged surface areas (Kiem & Kögel Knabner, 2002; Six *et al.*, 2002). Such

organomineral associations render SOM protection because the adsorption affinity to the mineral exceeds that of the enzyme active site. Organomineral complexes are likely to be the primary mechanism whereby SOM is stored for millennia, and their assignment to the 'passive' pool in the Century model (Table 1) appears to be well deserved. Large amounts of C with old radiocarbon ages are found in association with size fractions <20 μm (Marschner *et al.*, 2008). It is generally accepted that the protection of SOM is proportional to the increasing density and decreasing size of the soil fractions (Poirier *et al.*, 2005; Sohi *et al.*, 2005; Zimmermann *et al.*, 2007), however, Baldock (2007) cites a range of studies that showed no obvious relationship between C age and mineral particle size. The fact that clay and silt fractions further combine to form soil aggregates enhances protection because a combination of adsorption and occlusion operate together (Martens *et al.*, 2003). The source of the majority of low molecular weight compounds found in soils is likely to be bacteria that are also associated with mineral surfaces (Hopkins *et al.*, 1992a,b). Correlations have been found between mineral-bound microbial-derived sugars such as galactose and mannose with iron and aluminium oxide content in subsoil fractions, and that such C was highly stable and old (Spielvogel *et al.*, 2008; Rumpel *et al.*, 2010). Studies using ^{14}C -labelled glucose suggest that *in situ* microbial growth associated with clay particles is likely to be responsible for the persistent sugars, peptides and amino acids in mineral soils (Saggar *et al.*, 1999). There is of course a paradox here – both microorganisms and SOM are associated with mineral surfaces presumably in close proximity. However, the forces holding both in place effectively restrict accessibility of the microorganisms to SOM which may be only a small distance away. Extracellular enzymes can potentially contribute to the breakdown and release of sorbed SOM, but they may also become sorbed and, in any case, their activity is compromised outside the optimized intracellular environment.

Occlusion within aggregates may confer protection because the SOM is inaccessible to enzymatic attack, or because the activity of microorganisms is limited by environmental constraints such as the rate of oxygen diffusion to the site of microbial activity, so that even in the presence of a competent microbial community decomposition is limited. The size of soil aggregates is usually inversely proportional to the amount of energy needed to disrupt them; thus, microaggregates afford the most protection to associated SOM (Ashman *et al.*, 2009; Stewart *et al.*, 2009). The importance of SOM in soil aggregate formation has been indicated in several studies that have tried to determine the specific components of SOM which might act as key drivers in aggregate

formation (Krull *et al.*, 2004). Aoyama *et al.* (2000) added ^{13}C -labelled glucose to soil and found that the majority of the ^{13}C was assimilated by soil microorganisms in soil macroaggregates after 14 days. Polysaccharides exuded from fungal hyphae, bacteria and roots adsorb strongly to negatively charged soil particles through cation bridging, binding together individual soil particles and microaggregates into macroaggregates, contributing to aggregated stabilization (Wander, 2004). There is another paradox herein: although stable aggregates contribute to the stabilization of SOM, the biological contributions to aggregate stability are dependent on a supply and turnover of SOM by microorganisms (Watts *et al.*, 2001, 2005). If the supply of SOM is restricted, the aggregate stability declines and the contribution to SOM protection by occlusion diminishes (Hirsch *et al.*, 2009). Thus, the occlusion mechanism of protection relies on SOM turnover and is a prime example of Janzen's (2006) 'use it or hoard it' argument. It is unlikely that all ancient C in soils can be physically protected because there must be a threshold at which the available C storage niches are filled, referred to as C saturation by Hassink & Whitmore (1997) and Six *et al.* (2002), which is defined by the physicochemical properties of the soil. In addition, the presence of inorganic competitors for sorption sites is an important consideration (Lima *et al.*, 2010), and the maintenance of stable aggregates depends at least in part on the turnover of SOM in aggregates to sustain soil microorganisms.

Regulation of microbial activity by substrate supply

Ekschmitt *et al.* (2005) proposed that under the starvation conditions prevalent in soil, it may cost organisms as much to acquire energy from SOM as they gain from it, so energetically limiting their capacity to decompose SOM. This complements the idea previously developed by De Nobili *et al.* (2001) who proposed the 'Trigger Molecule Hypothesis' to explain the survival of soil microorganisms physically isolated from SOM for the majority of the time, via the maintenance of a 'metabolically alert' state supported by endogenous energy reserves accumulated under intermittent conditions of C excess (Rinnan & Bååth, 2009). The proposed 'Trigger Molecules' are low molecular weight compounds that signal the potential proximity of larger concentrations of utilizable substrates. It is hypothesized that some microorganisms have the ability to respond to this signal by upshifting from a 'metabolically alert' state to a fully functional and metabolically active state, observed as a quick increase in respiratory activity promoted by trace amounts of substrate (De Nobili *et al.*, 2001; Blagodatskaya & Kuzyakov, 2008). Despite expending

scarce energy reserves to remain 'metabolically alert', this strategy enables some microorganisms to respond rapidly to fresh substrate when it becomes available, conferring a competitive advantage over microorganisms the survival strategy of which is based upon true dormancy (Dungait *et al.*, 2011). The need for a slow trickle of organic molecules from SOM to maintain the survival of soil microorganisms has subsequently led to the suggestion that there is an abiotic bottleneck (the 'Regulatory Gate') that regulates a sustained, but limited supply of SOM to soil microorganisms (Kemmitt *et al.*, 2008).

Soil structure and aggregation may control the supply of water, nutrients and oxygen, and the connectivity between C and potential decomposers (Eusterhues *et al.*, 2007; Kuka *et al.*, 2007; Bachmann *et al.*, 2008). Sinsabaugh & Follstad Shah (2011) proposed a conceptual model in which the recalcitrance of SOM is a function of its relative susceptibility to a succession of exo-enzymes, the activity of which is limited by the movement of substrate, enzyme and organism. Kuka *et al.* (2007) modelled SOM decomposition in terms of the pore-space in soil, arguing that decomposition can only be achieved when water, oxygen, substrate and organism/enzyme come together, and the organisms can only benefit if there is a transport connection to enable metabolites to travel back to the same organism from the site of enzyme action. These ideas marry well with the Regulatory Gate Hypothesis (Kemmitt *et al.*, 2008) where decomposition is thought to be limited by factors other than the activity of microorganisms. One key substrate-enzyme interaction has attracted much attention. Tannins and polyphenols complex with proteins and inhibit the activity of soil enzymes, except polyphenol oxidase, which is limited by low pH and low oxygen status (Freeman *et al.*, 2001, 2004). Based on the behaviour of polyphenolic compounds and the enzymes that catalyze their oxidation, Sinsabaugh (2010) proposed that cool, wet, anaerobic soils should accumulate C and that warm, dry, aerobic soils should lose it. Although observations generally bear out this proposal the key intervention would be to remove phenols from peat or preserve them in arid soils.

If all soil SOM is degradable in principle, the constraints on microbial decomposition of SOM in soil probably depend on the co-occurrence of water, air, substrate and microbe at the same point in space and time. Van Haastert & Bosgraaf (2009) described the food-searching strategy of starving organisms in heterogeneous environments, as progressively longer 'random walks', probably because there is no information about substrate availability (Hénaut *et al.*, 2002; Edwards *et al.*, 2007; Reynolds *et al.*, 2011). Thus, in the absence of physical disturbances caused by, for exam-

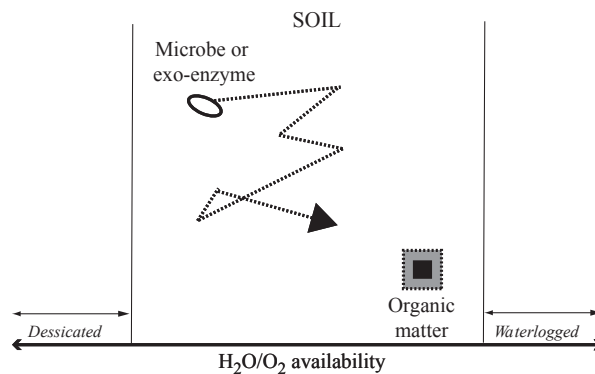


Fig. 2 The 'random walk' theory representing the controls of decomposition of soil organic matter (SOM) as a function of accessibility by microorganisms in the soil matrix. The probability of access of microbe to organic matter in the soil matrix is controlled by a combination of biological, physical and chemical variables. The pathway (indicated by dotted lines) connecting the decomposer microorganism or exo-enzyme with the organic matter is the 'route' that has to be 'navigated' multi-dimensionally before the organic matter decomposes. Examples of the dimensions that have to be navigated include the metabolic energy level of the microorganism, the motility of the microorganism or the movement by the exo-enzyme, the spatial separation of the microorganism or the exo-enzyme and the organic matter, pH, temperature, soil pore size, length, connectivity and tortuosity, strength of SOM sorption to soil particles, occlusion between clay layers and within aggregates, efficiency of enzyme activity, steric hindrance, and the requirement for synergy with other enzymes. The shading around the substrate indicates the abiotic release of components of organic matter (after Kemmitt *et al.*, 2008).

ple, freeze-thaw and wet-dry cycles, or bioturbation, the potential for decomposition is likely to depend on the mean length of a 'random walk' by the decomposer organisms through tortuous soil pore space (Fig. 2). Physical variables include the distance between microorganisms and substrate; soil pore size, length, connectivity and tortuosity (Kuka *et al.*, 2007); and, physical protection of the substrate, i.e. strength of sorption to soil particles and occlusion between clay layers and within aggregates. Once within the vicinity of substrate, exo-enzymes might accelerate decomposition, but this will be metabolically uneconomic if the pathway of the digested substrate back to the microorganism is equally long and tortuous. The efficiency of enzyme activity will be compromised by steric hindrance, the requirement for synergy with other enzymes, pH and temperature. If the Regulatory Gate hypothesis of Kemmitt *et al.* (2008) is correct, a small but sustained abiotic release of SOM (indicated by the shadow around the substrate source in Fig. 2) may also contribute to the likelihood of an encounter between soil microorganisms and SOM.

C sequestration in subsoils

If accessibility by microbes and exo-enzymes is the key factor in controlling C turnover in soils, then deeper soil horizons may provide an opportunity to enhance C sequestration. Up to 75% of the C in the soil resides below the surface horizon (Fig. 1; Jobbágy & Jackson, 2000). The deeper SOM is assumed to be very stable, with radiocarbon ages of more than 4000 years reported (Jenkinson *et al.*, 2008), and ascribed in part to more mineral association and protection at greater depths (Spielvogel *et al.*, 2008; Chabbi *et al.*, 2009). Deep soils are more likely to be colder, waterlogged, anoxic and nutrient-limited compared with surface horizons, leading to smaller and less active microbial communities. The restricted connectivity between microorganisms and the substrate mentioned above (see *Regulation of microbial activity by substrate supply*) will be more severe in the subsoil (Ekschmitt *et al.*, 2008; Salomé *et al.*, 2010). However, environmental conditions in subsoils are typically more stable because they are buffered from rapid changes in moisture and temperature, and therefore provide a nutritionally and energetically impoverished but stable set of niches for microorganisms, compared with surface soils (Sanaullah *et al.*, 2011).

Kell (2011) recently suggested the potential to enhance C storage through the development of deep-rooted plants that would incorporate C directly into the subsoil. Rasse *et al.* (2005) described the preferential stabilization of root C compared to shoot C in soils. However, the principal obstacles to C incorporation to subsoils by deep rooting plants is the mechanical impedance offered by the soil, and the facts subsoils are not usually environmentally favourable for root growth and sometimes offer only limited resources to the plants. Deep root penetration may also contribute to priming the decomposition of otherwise stable subsoil C (Fontaine *et al.*, 2007; Marschner *et al.*, 2008; Xiang *et al.*, 2008; Chabbi *et al.*, 2009; Salomé *et al.*, 2010). Despite this interest there is remarkably little data that trace the dynamics of carbon in subsoil (Gregory *et al.*, 2011) and the mechanisms that would stabilize carbon or release it require investigation before the potential to store carbon can be exploited.

Linking soil biogeochemical understanding with soil C modelling

To date, the new and emerging ideas on C turnover in soils expressed above have had mixed uptake in quantitative or predictive computer simulation models, although complex models can work well with results from controlled experimental systems. Models that

have found wide use for predictive purposes have tended to be simple and robust (RothC, Coleman *et al.*, 1997; Q model, Ågren & Bosatta, 1987) or versatile (Century, Parton *et al.*, 1987). It is widely accepted that models can only be expected to operate effectively when applied to soil systems for which they were designed and when applied within the parameter ranges for which they have been validated (Manzoni & Porporato, 2009). This leads to obvious difficulties when the models are pushed to the edge of, or beyond, their validation, such as may occur when they are applied to rapid environmental change or 'unusual' soils. For example, reductive models, based on long-term agricultural experimental data from mineral-dominated, low SOM content soils, have their downfalls and critiques when applied to peats. Although soils with restricted drainage such as peats contain about one-third of the world's store of soil C, the RothC and Century models handle mineral soils only (Chimner *et al.*, 2002; Falloon *et al.*, 2006), yet the models are widely used in global studies of soil C dynamics. ECOSE (Smith *et al.*, 2010a), based on RothC, and MILLENNIA (Heinemeyer *et al.*, 2010), which uses a cohort approach similar to that in the Q model (see below) are recent attempts to rectify this failing.

Models of C turnover are the only reasonable approach available for the prediction of the roles of soils in future climate change. To date, Global Ecosystem Models vary in the way they treat differences in the decomposition of soil C. As an illustration of some of the difficulties, Jenkinson & Coleman (2008) suggested that emission of CO₂ from soils as a result of global warming by modelling subsoil C in the same way as surface C may have been over-estimated, and proposed a 'layered' approach which requires additional development. Friedlingstein *et al.* (2006) found that between one and nine soil organic C pools were used in different modes, but that all the models considered adopted a pool approach rather than that of quality continuum. Both the Van Veen & Paul (1981) and Century models conceive fresh plant material as an intimate mixture of components that differ in decomposability, such that the decomposition of two easily decomposable components is restricted by the remaining skeleton of a third, which is identified with lignin. Total decomposition is thus retarded in this scheme because the lignin gradually becomes a greater and greater proportion of the remaining substrate and its structure impedes the ability of microorganisms to find the easily decomposable substrates. Whitmore & Matus (1996) have suggested a simpler function that traces the ratio of two components only to achieve the same effect. Alternatively, the Q model uses a 'continuous-quality theory' approach that dispenses with artificial

pool classification and attempts to take account of the complete biochemical spectrum of compounds in the SOM from labile to stable, and SOM quality as a measure of substrate availability to decomposers (Ågren & Bosatta, 1987). This may be particularly advantageous when modelling soil C under changing climatic conditions, because of the likely alterations in substrate quality, above and below-ground allocation, and ecological and physiological responses by the both plants and decomposer organisms.

The RothC model simulates physical protection by means of clay, which diverts a greater proportion of C turn over to the slowly turning over HUM fraction rather than CO₂. The Van Veen (1981) model models protection explicitly with factors that increase protection with clay content. Both models include a very stable fraction similar to the Century model, but whereas this may itself decompose in the Century and Van Veen models, stable SOM is inert in RothC. These inert or passive pools are necessary to simulate the very old radiocarbon age of soils (Jenkinson & Rayner, 1977). Hassink & Whitmore (1997) took the concept of physical protection of a portion of the SOM further and modelled the physical protection in a dynamic way. In their model, protected SOM does not decompose but must become free before it can do so. Protection and release were modelled in analogy to a sorption isotherm with the assumption that soils' ability to protect C can become saturated. The success of these models (especially Century and RothC), especially their use in simulating Global Environmental Change and national inventories of C stocks and emission of CO₂, is support for the mechanisms they contain and that physical protection in particular better describes the stability of organic C in soil than long-term chemical recalcitrance. Nevertheless, the need for inert organic C in the RothC model points to the existence of small amounts of long-lived C in soil, which is presumed to derive from black C.

The relative recalcitrance or lack of decomposability of SOM can sometimes be more apparent than real. There is often an assumption among modellers that decomposition of SOM is proportional to the amount present, i.e. first-order kinetics. Even Michaelis–Menten kinetics describing the activity of enzymes approximate first-order if the substrate is abundant relative to the enzyme. However, Schimel & Weintraub (2003) have suggested that conditions in soil are such that the enzymatic capacity concentration may be greater than the substrate concentration, and Whitmore (1996) has shown how second or partial order kinetics can explain observations better than first-order. Data on the turnover of the soil microbial biomass (Dalenberg & Jager, 1989) or the reduction in the inducibility of enzymes

decomposing low concentrations of starch in soil (German *et al.*, 2011) are examples of kinetic behaviour other than first-order in soils. In short, if the kinetics differs from assumption, SOM can appear more or less decomposable than expected. Given the hard-won and rare nature of long-term SOM decomposition data, it would be surprising if the kinetics of turnover were not subject to considerable uncertainty. Reliable means to infer mechanisms conclusively from sparse data are lacking and it is probably for this reason that relatively simple, robust models of soil processes such as RothC and Century have found wide application in modelling the turnover of C in soils.

Conclusion

After the geological and marine C pools, the terrestrial pool is the largest global store of C, and has the potential to increase thus improving soil quality as well as C storage. However, the size of the pool changes in time as a result of environmental change and can only be estimated with limited accuracy, especially for subsoils. The evidence against mechanisms for C stabilization based on initial molecular structures has grown, particularly in the past decade, with advances in analytical technologies for tracking the fate of specific labelled organic compounds in soils. Inconsistencies between predicted and measured SOM values have been identified indicating that soil C dynamics are more complex than previously thought and that our models need to be improved. Specifically, the concept of biochemical recalcitrance, wherein molecular structures are inherently resistant to microbial decomposition, has been widely accepted because it has empirical meaning but it is now called into question because of the lack of an adequate molecular and mechanistic definition. If the probability for SOM decomposition is low in most soils, because of the requirement for a suite of biological, physical and chemical conditions to be met, this might explain the paradox that soils contain very large amounts of ancient but apparently decomposable SOM. This new understanding suggests that the search for the 'holy grail' of inherently stable C in soils may be a hopeless quest, and our attention should be diverted to the proper management of SOM, including the rejuvenation of the many degraded soils worldwide, particularly those resulting from inappropriate land management.

There is a critical need to develop a chain of related hypotheses that express current understanding and point to critical experiments to calibrate and validate these ideas. Some questions that could be used to frame such hypotheses are given below. The list is certainly not definitive, but is intended to highlight some of the major areas of uncertainty within known mechanisms,

and open questions where new conceptual thinking may be required to link understanding of the biological, chemical and physical mechanisms with modelling to improve predictive capacity particularly in a global change context

1. If decomposition requires the combination of substrate, enzymes (microorganisms), oxygen, water and heat, explicit modelling of all these factors in space and time should improve the predictability of SOM turnover.

- How can the distribution of each factor in space and time in the soil be determined? What is the probability of the 'perfect encounter' between these factors leading to decomposition?
- Is the concept of C saturation valid? If so, can it be defined in terms of sites or microsites in the soil that lack one or more of the enzyme (microorganism), oxygen, water and heat factors? Is there unused C sorption capacity?
- Can C be introduced to deep soils without priming the decomposition of existing stocks?
- Are explicitly hybridized SOM turnover models needed (e.g. 'layered' models) that operate on different principles for different sub-layers?

2. Models that explicitly take account of the effects of the impediments and accessories to movement of all factors required for decomposition through soils should improve prediction.

- Is explicit modelling of the movement of exoenzymes and dissolved organic carbon required?
- Can the fine-scale connectivity of pores be accurately assessed/inferred?
- Does the activity of soil animals provide a source or sink for SOM?

3. Are all the enzymatic controls over decomposition adequately characterized?

- Can enzyme or microorganism dynamics be controlled to regulate decomposition?
- What is the relative significance of biochemistry vs. inorganic chemistry in determining the potential of SOM to be decomposed?
- How can the quality continuum for SOM as a substrate approach to SOM modelling be developed?
- How significant are abiotic decomposition processes?
- Is 'Trigger Molecule' hypothesis valid? If so, what is the source of the organic molecules? Could they be derived from fresh inputs of plant litter and rhizodeposits, metabolites from decomposing microorganisms, or released during abiotic transformation of SOM (the 'Regulatory Gate')?

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References

- Adair EC, Parton WJ, Del Grosso SJ *et al.* (2008) Simple three pool model accurately describes patterns of long term litter decomposition in diverse climates. *Global Change Biology*, **14**, 2636–2660.
- Ågren GI, Bosatta N (1987) Theoretical analysis of the long-term dynamics of C and nitrogen in soils. *Ecology*, **68**, 1181–1189.
- Ågren GI, Bosatta E (2002) Reconciling differences in predictions of temperature response of soil organic matter. *Soil Biology and Biochemistry*, **34**, 129–132.
- Amelung W, Brodowski S, Sandhage-Hofmann A, Bol R (2008) Combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. *Advances in Agronomy*, **100**, 155–250.
- Aoyama M, Angers DA, N'dayegamiye A, Bissonnette N (2000) Metabolism of ¹³C-labeled glucose in aggregates from soils with manure application. *Soil Biology and Biochemistry*, **32**, 295–300.
- Asadullah M, Zhang S, Li C-Z (2010) Evaluation of structural features of chars from pyrolysis of biomass of different particle sizes. *Fuel Processing Technology*, **91**, 877–881.
- Ashman MR, Hallett PD, Brookes PC, Allen J (2009) Evaluating soil stabilisation by biological processes using step-wise aggregate fractionation. *Soil and Tillage Research*, **102**, 209–215.
- Bachmann J, Guggenberger G, Baumgartl T *et al.* (2008) Physical carbon sequestration mechanisms under special consideration of soil wettability. *Journal of Plant Nutrition and Soil Science*, **171**, 14–26.
- Bahri H, Dignac MF, Rumpel C, Rasse DP, Chenu C, Mariotti A (2006) Lignin turnover kinetics in an agricultural soil is monomer specific. *Soil Biology and Biochemistry*, **38**, 1977–1988.
- Bahri H, Rasse DP, Rumpel C, Dignac MF, Bardoux G, Mariotti A (2008) Lignin degradation during a laboratory incubation followed by ¹³C isotope analysis. *Soil Biology and Biochemistry*, **40**, 1916–1922.
- Baldock J (2007) Composition and cycling of organic C in soil. In: *Nutrient Cycling in Terrestrial Ecosystems* (eds Marschner P, Rengel Z), pp. 1–35. Springer, Berlin, Heidelberg.
- Baldock J, Currie G, Oades J (1991) Organic matter as seen by solid state ¹³C NMR and pyrolysis tandem mass spectrometry. In: *Advances in Soil Organic Matter Research: The Impact on Agriculture and the Environment*, (ed Wilson WS) pp. 45–60. The Royal Society of Chemistry, Cambridge.
- Bauer J, Kirschbaum MUF, Weihermüller L, Huisman JA, Herbst M, Vereecken H (2008) Temperature response of wheat decomposition is more complex than the common approaches of most multi-pool models. *Soil Biology and Biochemistry*, **40**, 2780–2786.
- Blagodatskaya E, Kuzyakov Y (2008) Mechanisms of real and apparent priming effects and their dependence on soil microbial biomass and community structure: critical review. *Biology and Fertility of Soils*, **45**, 115–131.
- Blanchart E, Marilieu N, Chotte JL, Drogoul A, Perrier E, Cambier C (2009) SWORM: an agent-based model to simulate the effect of earthworms on soil structure. *European Journal of Soil Science*, **60**, 13–21.
- Boddy E, Hill PW, Farrar J, Jones DL (2007) Fast turnover of low molecular weight components of the dissolved organic C pool of temperate grassland field soils. *Soil Biology and Biochemistry*, **39**, 827–835.
- Bol R, Huang Y, Meridith JA, Eglinton G, Harkness DD, Ineson P (1996) The ¹⁴C age and residence time of organic matter and its lipid constituents in a stagnohumic gley soil. *European Journal of Soil Science*, **47**, 215–222.
- de Wit R, Bouvier T (2006) 'Everything is everywhere, but, the environment selects'; what did Baas Becking and Beijerinck really say? *Environmental Microbiology*, **8**, 755–758.
- Bradford MA, Davies CA, Frey SD *et al.* (2008) Thermal adaptation of soil microbial respiration to elevated temperature. *Ecology Letters*, **11**, 1316–1327.
- Brady NC, Weil RR (2002) Soil organic matter. In: *The Nature and Properties of Soils*, pp. 501–522. Prentice Hall, Upper Saddle River, New Jersey.

- Brussaard L, De Ruiter PC, Brown GG (2007) Soil biodiversity for agricultural sustainability. *Agriculture, Ecosystems & Environment*, **121**, 233–244.
- Bull ID, Nott CJ, Van Bergen PF, Poulton PR, Evershed RP (2000a) Organic geochemical studies of soils from the Rothamsted classical experiments-VI. The occurrence and source of organic acids in an experimental grassland soil. *Soil Biology and Biochemistry*, **32**, 1367–1376.
- Bull ID, Bergen PFV, Nott CJ, Poulton PR, Evershed RP (2000b) Organic geochemical studies of soils from the Rothamsted classical experiments-V. The fate of lipids in different long-term experiments. *Organic Geochemistry*, **31**, 389–408.
- Canadell JG, Kirschbaum MUF, Kurz WA, Sanz M-J, Schlamadinger B, Yamagata Y (2007) Factoring out natural and indirect human effects on terrestrial C sources and sinks. *Environmental Science & Policy*, **10**, 370–384.
- Chabbi A, Kögel-Knabner I, Rumpel C (2009) Stabilised carbon in subsoil horizons is located in spatially distinct parts of the soil profile. *Soil Biology and Biochemistry*, **41**, 256–261.
- Chen Y-R, Sarkanen S (2010) Macromolecular replication during lignin biosynthesis. *Phytochemistry*, **71**, 453–462.
- Chen W, Supanwong K, Ohmiya K, Shimizu S, Kawakami H (1985) Anaerobic degradation of veratrylglycerol-beta-guaiaicyl ether and guaiaacoxycetic acid by mixed rumen bacteria. *Applied and Environmental Microbiology*, **50**, 1451–1456.
- Cheshire MV (1977) Origins and stability of soil polysaccharide. *Journal of Soil Science*, **28**, 1–10.
- Cheshire MV, Mundie CM (1990) Organic matter contributed to soil by plant roots during the growth and decomposition of maize. *Plant and Soil*, **121**, 107–114.
- Chimner RA, Cooper DJ, Parton WJ (2002) Modeling carbon accumulation in Rocky Mountain fens. *Wetlands*, **22**, 100–110.
- Coleman K, Jenkinson D, Crocker G *et al.* (1997) Simulating trends in soil organic carbon in long-term experiments using RothC-26.3. *Geoderma*, **81**, 29–44.
- Conant RT, Drijber RA, Haddix ML *et al.* (2008a) Sensitivity of organic matter decomposition to warming varies with its quality. *Global Change Biology*, **14**, 868–877.
- Conant RT, Steinweg JM, Haddix ML, Paul EA, Plante AF, Six J (2008b) Experimental warming shows that decomposition temperature sensitivity increases with soil organic matter recalcitrance. *Ecology*, **89**, 2384–2391.
- Condron L, Stark C, O'Callaghan M, Clinton P, Huang Z (2010) The role of microbial communities in the formation and decomposition of soil organic matter. In: *Soil Microbiology and Sustainable Crop Production* (eds Dixon GR, Tilston EL), pp. 81–118, Springer, Heidelberg.
- Crotty F, Blackshaw R, Murray P (2011) Tracking the flow of bacterially derived ^{13}C and ^{15}N through soil faunal feeding channels. *Rapid Communications in Mass Spectrometry*, **25**, 1503–1513.
- Dalenberg J, Jager G (1989) Priming effect of some organic additions to ^{14}C -labelled soil. *Soil Biology and Biochemistry*, **21**, 443–448.
- Dalias P, Anderson JM, Bottner P, Cousteaux MM (2001) Temperature responses of carbon mineralization in conifer forest soils from different regional climates incubated under standard laboratory conditions. *Global Change Biology*, **7**, 181–192.
- Davidson EA, Janssens IA (2006) Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, **440**, 165–173.
- De Nobili M, Contini M, Mondini C, Brookes PC (2001) Soil microbial biomass is triggered into activity by trace amounts of substrate. *Soil Biology and Biochemistry*, **33**, 1163–1170.
- De Ruiter PC, Neutel A-M, Moore JC (1994) Modelling food webs and nutrient cycling in agro-ecosystems. *Trends in Ecology and Evolution*, **9**, 378–383.
- Derenne S, Largeau C (2001) A review of some important families of refractory macromolecules: composition, origin, and fate in soils and sediments. *Soil Science*, **166**, 833.
- Derrien D, Amelung W (2011) Computing the mean residence time of soil carbon fractions using stable isotopes: impacts of the model framework. *European Journal of Soil Science*, **62**, 237–252.
- Derrien D, Marol C, Balabane M, Balesdent J (2006) The turnover of carbohydrate carbon in a cultivated soil estimated by ^{13}C natural abundances. *European Journal of Soil Science*, **57**, 547–557.
- Derrien D, Marol C, Balesdent J (2007) Microbial biosyntheses of individual neutral sugars among sets of substrates and soils. *Geoderma*, **139**, 190–198.
- Dignac MF, Rumpel C (2006) Relative distributions of phenol dimers and hydroxy acids in a cultivated soil and above ground maize tissue. *Organic Geochemistry*, **37**, 1634–1638.
- Dignac MF, Bahri H, Rumpel C *et al.* (2005) ^{13}C natural abundance as a tool to study the dynamics of lignin monomers in soil: an appraisal at the Closeaux experimental field (France). *Geoderma*, **128**, 3–17.
- Docherty G, Straker V, Evershed RP (2010a) Seasonal variations in bulk tissue, fatty acid and monosaccharide $\delta^{13}\text{C}$ values of leaves from mesotrophic grassland plant communities under different grazing managements. *Phytochemistry*, **71**, 415–428.
- Don A, Steinberg B, Schöning I, Pritsch K, Joschko M, Gleixner G, Schulze E-D (2008) Organic C sequestration in earthworm burrows. *Soil Biology and Biochemistry*, **40**, 1803–1812.
- Dungait JAJ, Bol R, Evershed RP (2005) Quantification of dung C incorporation in a temperate grassland soil following spring application using bulk stable C isotope determinations. *Isotopes in Environmental and Health Studies*, **41**, 3–11.
- Dungait JAJ, Stear NA, Van Dongen BE, Bol R, Evershed RP (2008a) Off-line pyrolysis and compound-specific stable carbon isotope analysis of lignin moieties: a new method for determining the fate of lignin residues in soil. *Rapid Communications in Mass Spectrometry*, **22**, 1631–1639.
- Dungait JAJ, Briones MJI, Bol R, Evershed RP (2008b) Enhancing the understanding of earthworm feeding behaviour via the use of fatty acid $\delta^{13}\text{C}$ values determined by gas chromatography-combustion-isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry*, **22**, 1643–1652.
- Dungait JAJ, Bol R, Bull ID, Evershed RP (2009) Tracking the fate of dung-derived carbohydrates in a temperate grassland soil using compound-specific stable isotope analysis. *Organic Geochemistry*, **40**, 1210–1218.
- Dungait JAJ, Bol R, Lopez-Capel *et al.* (2010) Applications of stable isotope ratio mass spectrometry in cattle dung C cycling studies. *Rapid Communications in Mass Spectrometry*, **24**, 495–500.
- Dungait JAJ, Kemmitt SJ, Michallon L, Guo S, Wen Q, Brookes PC, Evershed RP (2011) Variable responses of the soil microbial biomass to trace concentrations of ^{13}C -labelled glucose, using ^{13}C -PLFA analysis. *European Journal of Soil Science*, **62**, 117–126.
- Edwards AM, Phillips RA, Watkins NW *et al.* (2007) Revisiting Levy flight search patterns of wandering albatrosses, bumblebees and deer. *Nature*, **449**, 1044–1048.
- Ekschmitt K, Liu M, Vetter S, Fox O, Wolters V (2005) Strategies used by soil biota to overcome soil organic matter stability – why is dead organic matter left over in the soil? *Geoderma*, **128**, 167–176.
- Ekschmitt K, Kandeler E, Poll C *et al.* (2008) Soil carbon preservation through habitat constraints and biological limitations on decomposer activity. *Journal of Plant Nutrition and Soil Science*, **171**, 27–35.
- Ellerbrock R, Gerke H (2004) Characterizing organic matter of soil aggregate coatings and biopores by Fourier transform infrared spectroscopy. *European Journal of Soil Science*, **55**, 219–228.
- Eusterhues K, Rumpel C, Kögel-Knabner I (2007) Composition and radioC age of HF-resistant soil organic matter in a Podzol and a Cambisol. *Organic Geochemistry*, **38**, 1356–1372.
- Falloon P, Smith P, Bradley RI *et al.* (2006) RothC-UK – a dynamic modelling system for estimating changes in soil C from mineral soils at 1 km resolution in the UK. *Soil Use and Management*, **22**, 274–288.
- Fang C, Smith P, Moncrieff JB, Smith JU (2005) Similar response of labile and resistant soil organic matter pools to changes in temperature. *Nature*, **433**, 57–59.
- Fitter AH, Gilligan CA, Hollingworth K *et al.* (2005) Biodiversity and ecosystem function in soil. *Functional Ecology*, **19**, 369–377.
- Fontaine S, Barot S (2005) Size and functional diversity of microbe populations control plant persistence and long term soil C accumulation. *Ecology Letters*, **8**, 1075–1087.
- Fontaine S, Barot S, Barre P, Bdioui N, Mary B, Rumpel C (2007) Stability of organic C in deep soil layers controlled by fresh C supply. *Nature*, **450**, 277–280.
- Forbes MS, Raison RJ, Skjemstad JO (2006) Formation, transformation and transport of black C (charcoal) in terrestrial and aquatic ecosystems. *Science of the Total Environment*, **370**, 190–206.
- Fox O, Vetter S, Ekschmitt K, Wolters V (2006) Soil fauna modifies the recalcitrance-persistence relationship of soil C pools. *Soil Biology and Biochemistry*, **38**, 1353–1363.
- Freeman C, Ostle N, Kang H (2001) An enzymic 'latch' on a global C store. *Nature*, **409**, 149.
- Freeman C, Ostle N, Fenner N, Kang H (2004) A regulatory role for phenol oxidase during decomposition in peatlands. *Soil Biology and Biochemistry*, **36**, 1663–1667.
- Friedlingstein P, Cox P, Betts R *et al.* (2006) Climate-C cycle feedback analysis: results from the C4MIP model intercomparison. *Journal of Climate*, **19**, 3337–3353.
- German DP, Chacon SS, Allison SD (2011) Substrate concentration and enzyme allocation can affect rates of microbial decomposition. *Ecology*, **92**, 1471–1480.
- Giardina CP, Ryan MG (2000) Evidence that decomposition rates of organic carbon in mineral soil do not vary with temperature. *Nature*, **404**, 858–861.
- Gleixner G, Poirier N, Bol R, Balesdent J (2002) Molecular dynamics of organic matter in a cultivated soil. *Organic Geochemistry*, **33**, 357–366.

- Greenland D, Rimmer D, Payne D. (1975) Determination of the structural stability class of English and Welsh soils, using a water coherence test. *European Journal of Soil Science*, **26**, 294–303.
- Gregory AS, Whitmore AP, Kirk GJD, Rawlins BG, Ritz K, Wallace P. (2011) Review of the evidence base for the status and change of soil carbon below 15 cm from the soil surface in England and Wales. Defra Project SP1106: Soil carbon: studies to explore greenhouse gas emissions and mitigation. Research Project Final Report. 46 p, Department for Environment, Food and Rural Affairs, London.
- Hamer U, Marschner B, Brodowski S, Amelung W (2004) Interactive priming of black C and glucose mineralisation. *Organic Geochemistry*, **35**, 823–830.
- Hartley IP, Heinemeyer A, Evans SP, Ineson P (2007) The effect of soil warming on bulk soil vs. rhizosphere respiration. *Global Change Biology*, **13**, 2654–2667.
- Hartley IP, Hopkins DW, Garnett MH, Sommerkorn M, Wookey PA (2008) Soil microbial respiration in arctic soil does not acclimate to temperature. *Ecology Letters*, **11**, 1092–1100.
- Hartley IP, Hopkins DW, Garnett MH, Sommerkorn M, Wookey PA (2009) No evidence for compensatory thermal adaptation of soil microbial adaptation of soil microbial respiration in the study of Bradford *et al.* *Ecology Letters*, **12**, E12–E14.
- Hassink J, Whitmore AP (1997) A model of the physical protection of organic matter in soils. *Soil Science Society of America Journal*, **61**, 131–139.
- Heim A, Schmidt MWI (2007) Lignin turnover in arable soil and grassland analysed with two different labelling approaches. *European Journal of Soil Science*, **58**, 599–608.
- Heinemeyer A, Croft S, Garnett MH, Gloor E, Holden J, Lomas MR, Ineson P (2010) The MILLENNIA peat cohort model: predicting past, present and future soil C budgets and fluxes under changing climates in peatlands. *Climate Research*, **45**, 207–226.
- Hénaut Y, Alauzet C, Lambin M (2002) Effects of starvation on the search path characteristics of *Orius majusculus* (Reuter) (Het., Anthoridae). *Journal of Applied Entomology*, **126**, 501–503.
- Hill PW, Farrar JF, Jones DL (2008) Decoupling of microbial glucose uptake and mineralization in soil. *Soil Biology and Biochemistry*, **40**, 616–624.
- Hirsch PR, Gilliam LM, Sohi SP, Williams JK, Clark IM, Murray PJ (2009) Starving the soil of plant inputs for 50 years reduces abundance but not diversity of soil bacterial communities. *Soil Biology and Biochemistry*, **41**, 2021–2024.
- Hofman J, Dusek L (2003) Biochemical analysis of soil organic matter and microbial biomass composition – a pilot study. *European Journal of Soil Biology*, **39**, 217–224.
- Hong HN, Rumpel C, Henry Des Tureaux T, Bardoux G, Billou D, Tran Duc T, Jouquet P (2011) How do earthworms influence organic matter quantity and quality in tropical soils? *Soil Biology and Biochemistry*, **43**, 223–230.
- Hopkins DW, Dungait JAJ (2010) Soil microbiology and nutrient cycling. In: *Soil Microbiology and Sustainable Crop Production* (eds Dixon GR, Tilston EL), pp. 59–80, Springer, Heidelberg.
- Hopkins DW, Macnaughton SJ, O'Donnell AG (1992a) A dispersion and differential centrifugation technique for representatively sampling microorganisms from soil. *Soil Biology and Biochemistry*, **23**, 217–225.
- Hopkins DW, Macnaughton SJ, O'Donnell AG (1992b) Evaluation of a dispersion and elutriation techniques for sampling microorganisms from soil. *Soil Biology and Biochemistry*, **23**, 227–232.
- Hopkins DW, Waite IS, McNicol JW, Poulton PR, Macdonald AJ, O'Donnell AG (2009) Soil organic C contents in long-term experimental grassland plots in the UK (Palace Leas and Park Grass) have not changed consistently in recent decades. *Global Change Biology*, **15**, 1739–1754.
- Huber S, Prokop G, Arrouays D *et al.* (2008) *Environmental Assessment of Soil for Monitoring: Volume I, Indicators & Criteria*. Office for the Official Publications of the European Communities, Luxembourg.
- Jansen B, Van Loon EE, Hooghiemstra H, Verstraten JM (2010) Improved reconstruction of palaeo-environments through unravelling of preserved vegetation biomarker patterns. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **285**, 119–130.
- Janzen H (2004) C cycling in earth systems – a soil science perspective. *Agriculture, Ecosystems and Environment*, **104**, 399–417.
- Janzen H (2006) The soil C dilemma: shall we hoard it or use it? *Soil Biology and Biochemistry*, **38**, 419–424.
- Jenkinson DS, Coleman K (2008) The turnover of organic carbon in subsoils. Part 2. Modelling carbon turnover. *European Journal of Soil Science*, **59**, 400–413.
- Jenkinson DS, Rayner JH (1977) The turnover of soil organic matter in some of the Rothamsted classical experiments. *Soil Science*, **123**, 298–305.
- Jenkinson DS, Poulton PR, Bryant C (2008) The turnover of organic C in subsoils. Part 1. Natural and bomb radioC in soil profiles from the Rothamsted long-term field experiments. *European Journal of Soil Science*, **59**, 391–399.
- Jia GD, Dungait JAJ, Bingham EM, Valiranta M, Korhola A, Evershed RP (2008) Neutral monosaccharides as biomarker proxies for bog-forming plants for application to palaeovegetation reconstruction in ombrotrophic peat deposits. *Organic Geochemistry*, **39**, 1790–1799.
- Jobbágy EG, Jackson RB (2000) The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications*, **10**, 423–436.
- Kell DB (2011) Breeding crop plants with deep roots: their role in sustainable carbon nutrient and water sequestration. *Annals of Botany*, **108**, 407–418.
- Kelleher BP, Simpson MJ, Simpson AJ (2006) Assessing the fate and transformation of plant residues in the terrestrial environment using HR-MAS NMR spectroscopy. *Geochimica et Cosmochimica Acta*, **70**, 4080–4094.
- Kemmitt SJ, Lanyon CV, Waite IS *et al.* (2008) Mineralization of native soil organic matter is not regulated by the size, activity or composition of the soil microbial biomass – a new perspective. *Soil Biology and Biochemistry*, **40**, 61–73.
- Kiem R, Kögel Knabner I (2002) Refractory organic carbon in particle-size fractions of arable soils II: organic C in relation to mineral surface area and iron oxides in fractions <6 µm. *Organic Geochemistry*, **33**, 1699–1713.
- Kimetu JM, Lehmann J (2010) Stability and stabilisation of biochar and green manure in soil with different organic carbon contents. *Soil Research*, **48**, 577–585.
- Kirschbaum MUF (2006) The temperature dependence of organic-matter decomposition – still a topic of debate. *Soil Biology and Biochemistry*, **38**, 2510–2518.
- Kleber M (2010) What is recalcitrant soil organic matter? *Environmental Chemistry*, **7**, 320–332.
- Kleber M, Nico PS, Plante AF, Filley T, Kramer M, Swanston C, Sollins P (2011) Old and stable soil organic matter is not necessarily chemically recalcitrant: implications for modeling concepts and temperature sensitivity. *Global Change Biology*, **17**, 1097–1107.
- Knorr W, Prentice IC, House JI, Holland EA (1998) Long-term sensitivity of soil carbon turnover to warming. *Paleoceanography*, **13**, 150–160.
- Kögel Knabner I, Guggenberger G, Kleber M *et al.* (2008) Organo-mineral associations in temperate soils: integrating biology, mineralogy, and organic matter chemistry. *Journal of Plant Nutrition and Soil Science*, **171**, 61–82.
- Krull E, Sachse D, Mugler I, Thiele A, Gleixner G (2004) *Compound-specific δ¹³C and δ²H Analyses of Plant and Soil Organic Matter: A Preliminary Assessment of the Effects of Vegetation Change on Ecosystem Hydrology*, pp. 3211–3221. Fall Meeting of the American-Geophysical-Union, San Francisco, CA.
- Krull ES, Baldock J, Skjemstad JO, Smernik RJ (2009) Characteristics of biochar: organo-chemical properties. In: *Biochar for Environmental Management: Science and Technology* (eds J Lehmann, S Joseph), pp. 53–66. Earthscan, London.
- Kuka K, Franko U, Rühlmann J (2007) Modelling the impact of pore space distribution on C turnover. *Ecological Modelling*, **208**, 295–306.
- Kuzyakov Y, Subbotina I, Chen H, Bogomolova I, Xu X (2009) Black C decomposition and incorporation into soil microbial biomass estimated by ¹⁴C labeling. *Soil Biology and Biochemistry*, **41**, 210–219.
- Lal R (2002) The potential of soils of the tropics to sequester C and mitigate the greenhouse effect. *Advances in Agronomy*, **76**, 1–30.
- Lal R (2004) Soil C sequestration impacts on global climate change and food security. *Science*, **304**, 1623–1627.
- Lal R (2008) Carbon sequestration. *Philosophical Transactions of the Royal Society B: Biological Sciences*, **363**, 815–830.
- Lehmann J, Gaunt J, Rondon M (2006) Bio-char sequestration in terrestrial ecosystems – a review. *Mitigation and Adaptation Strategies for Global Change*, **11**, 395–419.
- Li X, Hayashi J-I, Li C-Z (2006) FT-Raman spectroscopic study of the evolution of char structure during the pyrolysis of a Victorian brown coal. *Fuel*, **85**, 1700–1707.
- Lima DLD, Schneider RJ, Scherer HW, Duarte AC, Santos EBH, Esteves VI (2010) Sorption-desorption behavior of atrazine on soils subjected to different organic long-term amendments. *Journal of Agricultural and Food Chemistry*, **58**, 3101–3106.
- Liski J, Ilvesniemi H, Mäkelä A, Westman CJ (1999) CO₂ emissions from soil in response to climatic warming are overestimated: the decomposition of old soil organic matter is tolerant of temperature. *Ambio*, **28**, 171–174.
- Lorenz K, Lal R, Preston CM, Nierop K GJ (2007) Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio(macro)molecules. *Geoderma*, **142**, 1–10.
- Loveland P, Webb J (2003) Is there a critical level of organic matter in the agricultural soils of temperate regions: a review. *Soil and Tillage Research*, **70**, 1–18.
- Lovelock J (2009) James Lovelock on Biochar: Let the Earth Remove CO₂ for Us. *The Guardian*, 24 March 2009, London.
- Luo Y, Durenkamp M, De Nobili M, Lin Q, Brookes PC (2011) Short term soil priming effects and the mineralisation of biochar following its incorporation to soils of different pH. *Soil Biology and Biochemistry*, **43**, 2304–2314.

- Major J, Lehmann J, Rondon M, Goodale C (2010) Fate of soil-applied black carbon: downward migration, leaching and soil respiration. *Global Change Biology*, **16**, 1366–1379.
- Manzoni S, Porporato A (2009) Soil C and nitrogen mineralization: theory and models across scales. *Soil Biology and Biochemistry*, **41**, 1355–1379.
- Marschner B, Brodowski S, Dreves A *et al.* (2008) How relevant is recalcitrance for the stabilization of organic matter in soils? *Journal of Plant Nutrition and Soil Science*, **171**, 91–110.
- Martens DA (2000) Plant residue biochemistry regulates soil C cycling and C sequestration. *Soil Biology and Biochemistry*, **32**, 361–369.
- Martens DA, Reedy TE, Lewis DT (2003) Soil organic C content and composition of 130-year crop, pasture and forest land-use managements. *Global Change Biology*, **10**, 65–78.
- Murray PJ, Clegg CD, Crotty FV, De La Fuente Martinez N, Williams JK, Blackshaw RP (2009) Dissipation of bacterially derived C and N through the meso- and macrofauna of a grassland soil. *Soil Biology and Biochemistry*, **41**, 1146–1150.
- Nguyen BT, Lehmann J (2009) Black carbon decomposition under varying water regimes. *Organic Geochemistry*, **40**, 846–853.
- Nielsen UN, Ayres E, Wall DH, Bardgett RD (2011) Soil biodiversity and carbon cycling: a review and synthesis of studies examining diversity-function relationships. *European Journal of Soil Science*, **62**, 105–116.
- Nocentini C, Guenet B, Di Mattia E, Certini G, Bardoux G, Rumpel C (2010) Charcoal mineralisation potential of microbial inocula from burned and unburned forest soil with and without substrate addition. *Soil Biology and Biochemistry*, **42**, 1472–1478.
- Otto A, Simpson MJ (2005) Degradation and preservation of vascular plant-derived biomarkers in grassland and forest soils from Western Canada. *Biogeochemistry*, **74**, 377–409.
- Oyedele DJ, Schjønning P, Amusan AA (2006) Physicochemical properties of earthworm casts and uningested parent soil from selected sites in southwestern Nigeria. *Ecological Engineering*, **28**, 106–113.
- Parton W, Schimel DS, Cole C, Ojima D (1987) Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Science Society of America Journal*, **51**, 1173–1179.
- Paustian K, Parton WJ, Persson J (1992) Modeling soil organic matter in organic-amended and nitrogen-fertilized long-term plots. *Soil Science Society of America Journal*, **56**, 476–488.
- Piccolo A (2001) The supramolecular structure of humic substances. *Soil Science*, **166**, 810–832.
- Poirier N, Sohi SP, Gaunt JL, Mahieu N, Randall EW, Powlson DS, Evershed RP (2005) The chemical composition of measurable soil organic matter pools. *Organic Geochemistry*, **36**, 1174–1189.
- Pollierer MM, Langel R, Scheu S, Maraun M (2009) Compartmentalization of the soil animal food web as indicated by dual analysis of stable isotope ratios ($^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$). *Soil Biology and Biochemistry*, **41**, 1221–1226.
- Powlson D, Gregory P, Whalley W *et al.* (2011) Soil management in relation to sustainable agriculture and ecosystem services. *Food Policy*, **36**, S72–S87.
- Queena K, Derenne S, Largeau C, Rumpel C, Mariotti A (2004) Variation in lipid relative abundance and composition among different particle size fractions of a forest soil. *Organic Geochemistry*, **35**, 1355–1370.
- Queena K, Derenne S, Largeau C, Rumpel C, Mariotti A (2005) Spectroscopic and pyrolytic features and abundance of the macromolecular refractory fraction in a sandy acid forest soil (Landes de Gascogne, France). *Organic Geochemistry*, **36**, 349–362.
- Rasse DP, Rumpel C, Dignac MF (2005) Is soil carbon mostly root carbon? Mechanisms for a specific stabilisation. *Plant and Soil*, **269**, 341–356.
- Rasse DP, Dignac MF, Bahri H, Rumpel C, Mariotti A, Chenu C (2006) Lignin turnover in an agricultural field: from plant residues to soil-protected fractions. *European Journal of Soil Science*, **57**, 530–538.
- Rawlins AJ, Bull ID, Poirier N, Ineson P, Evershed RP (2006) The biochemical transformation of oak (*Quercus robur*) leaf litter consumed by the pill millipede (*Glomeris marginata*). *Soil Biology and Biochemistry*, **38**, 1063–1076.
- Rawlins AJ, Bull ID, Ineson P, Evershed RP (2007) Stabilisation of soil organic matter in invertebrate faecal pellets through leaf litter grazing. *Soil Biology and Biochemistry*, **39**, 1202–1205.
- Reale S, Di Tullio A, Spreti N, De Angelis F (2004) Mass spectrometry in the biosynthetic and structural investigation of lignins. *Mass Spectrometry Reviews*, **23**, 87–126.
- Reynolds AM, Dutta TK, Curtis RHC, Powers SJ, Gaur HS, Kerry BR (2011) Chemotaxis can take plant-parasitic nematodes to the source of a chemo-attractant via the shortest possible routes. *Journal of the Royal Society Interface*, **8**, 568–577.
- Rinnan R, Bååth E (2009) Differential utilization of C substrates by bacteria and fungi in tundra soil. *Applied and Environmental Microbiology*, **75**, 3611–3620.
- Robertson SA, Mason SL, Hack E, Abbott GD (2008) A comparison of lignin oxidation, enzymatic activity and fungal growth during white-rot decay of wheat straw. *Organic Geochemistry*, **39**, 945–951.
- Rumpel C, Eusterhues K, Kögel-Knabner I (2010) Non-cellulosic neutral sugar contribution to mineral associated organic matter in top- and subsoil horizons of two acid forest soils. *Soil Biology and Biochemistry*, **42**, 379–382.
- Rumpel C, Chabbi A (2010) Response of bulk chemical composition, lignin and carbohydrate signature to grassland conversion in a ley-arable cropping system. *Nutrient Cycling in Agroecosystems*, **88**, 173–182.
- Saggar S, Parshotam A, Hedley C, Salt G (1999) ^{14}C -labelled glucose turnover in New Zealand soils. *Soil Biology and Biochemistry*, **31**, 2025–2037.
- Salomé C, Nunan N, Pouteau V, Lerch TZ, Chenu C (2010) C dynamics in topsoil and in subsoil may be controlled by different regulatory mechanisms. *Global Change Biology*, **16**, 416–426.
- Sanaullah M, Chabbi A, Leifeld J, Bardoux G, Billou D, Rumpel C (2011) Decomposition and stabilization of root litter in top- and subsoil horizons: what is the difference? *Plant and Soil*, **338**, 127–141.
- Scherber C, Eisenhauer N, Weisser WW *et al.* (2010) Bottom-up effects of plant diversity on multitrophic interactions in a biodiversity experiment. *Nature*, **468**, 553–556.
- Schimel JP, Weintraub MN (2003) The implications of exoenzyme activity on microbial C and nitrogen limitation in soil: a theoretical model. *Soil Biology and Biochemistry*, **35**, 549–563.
- Schmidt MWI, Skjemstad JO, Czimczik CI, Glaser B, Prentice KM, Gelinas Y, Kuhlbusch TAJ (2001) Comparative analysis of black C in soils. *Global Biogeochemical Cycles*, **15**, 163–168.
- Schmidt MWI, Torn MS, Abiven S *et al.* (2011) Persistence of soil organic matter as an ecosystem property. *Nature*, **478**, 49–56.
- Sinsabaugh RL (2010) Phenol oxidase, peroxidase and organic matter dynamics of soil. *Soil Biology and Biochemistry*, **42**, 391–404.
- Sinsabaugh R, Follstad Shah J (2011) Eoenzymatic stoichiometry of recalcitrant organic matter decomposition: the growth rate hypothesis in reverse. *Biogeochemistry*, **102**, 31–43.
- Six J, Elliott E, Paustian K (2000) Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. *Soil Biology and Biochemistry*, **32**, 2099–2103.
- Six J, Conant R, Paul E, Paustian K (2002) Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. *Plant and Soil*, **241**, 155–176.
- Smith P (2008) Land use change and soil organic carbon dynamics. *Nutrient Cycling in Agroecosystems*, **81**, 169–178.
- Smith P, Fang C (2010) C cycle: a warm response by soils. *Nature*, **464**, 499–500.
- Smith J, Gottschalk P, Bellarby J *et al.* (2010a) Estimating changes in Scottish soil carbon stocks using ECOSSE. I. Model description and uncertainties. *Climate Research*, **45**, 179–192.
- Smith JL, Collins HP, Bailey VL (2010b) The effect of young biochar on soil respiration. *Soil Biology and Biochemistry*, **42**, 2345–2347.
- Sohi SP, Mahieu N, Powlson DS, Madari B, Smittenberg RH, Gaunt JL (2005) Investigating the chemical characteristics of soil organic matter fractions suitable for modeling. *Soil Science Society of America Journal*, **69**, 1248–1255.
- Sollins P, Homann P, Caldwell BA (1996) Stabilization and destabilization of soil organic matter: mechanisms and controls. *Geoderma*, **74**, 65–105.
- Spielvogel S, Prietzel J, Kögel Knabner I (2008) Soil organic matter stabilization in acidic forest soils is preferential and soil type specific. *European Journal of Soil Science*, **59**, 674–692.
- St. John MG, Orwin KH, Dickie IA (2011) No 'home' versus 'away' effects of decomposition found in a grassland-forest reciprocal litter transplant study. *Soil Biology and Biochemistry*, **43**, 1482–1489.
- Stevenson FJ (1982) *Humus Chemistry, Genesis, Composition, Reactions*. John Wiley, New York.
- Stewart CE, Paustian K, Conant RT, Plante AF, Six J (2009) Soil C saturation: implications for measurable C pool dynamics in long-term incubations. *Soil Biology and Biochemistry*, **41**, 357–366.
- Swift MJ, Heal OW, Anderson JM (1979) *Decomposition in Terrestrial Ecosystems*. Blackwell Scientific Publications, Oxford.
- Thevenot M, Dignac M-F, Rumpel C (2010) Fate of lignins in soil: a review. *Soil Biology and Biochemistry*, **42**, 1200–1211.
- Van Bergen PF, Nott CJ, Bull ID, Poulton PR, Evershed RP (1997) Organic geochemical studies of soils from the Rothamsted classical experiments-IV. Preliminary

- results from a study of the effect of soil pH on organic matter decay. *Organic Geochemistry*, **29**, 1779–1795.
- Van Haastert PJM, Bosgraaf L (2009) Food searching strategy of amoeboid cells by starvation induced run length extension. *PLoS ONE*, **4**, e6814.
- Van Veen J, Kuikman P (1990) Soil structural aspects of decomposition of organic matter by micro-organisms. *Biogeochemistry*, **11**, 213–233.
- Van Veen J, Paul E (1981) Organic carbon dynamics in grassland soils. 1. Background information and computer simulation. *Canadian Journal of Soil Science*, **61**, 185–201.
- Vane CH, Martin SC, Snape CE, Abbott GD (2001) Degradation of lignin in wheat straw during growth of the oyster mushroom (*Pleurotus ostreatus*) using off-line thermochemolysis with tetramethylammonium hydroxide and solid-state ¹³C NMR. *Journal of Agricultural and Food Chemistry*, **49**, 2709–2716.
- Von Lütow M, Kögel-Knabner I (2010) Response to the Concept paper: 'What is recalcitrant soil organic matter?' by Markus Kleber. *Environmental Chemistry*, **7**, 333–335.
- Von Lütow M, Kögel Knabner I, Ekschmitt K, Matzner E, Guggenberger G, Marschner B, Flessa H (2006) Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review. *European Journal of Soil Science*, **57**, 426–445.
- Von Lütow M, Kögel-Knabner I, Ekschmitt K, Flessa H, Guggenberger G, Matzner E, Marschner B (2007) SOM fractionation methods: relevance to functional pools and to stabilization mechanisms. *Soil Biology and Biochemistry*, **39**, 2183–2207.
- Von Lütow M, Kögel Knabner I, Ludwig B *et al.* (2008) Stabilization mechanisms of organic matter in four temperate soils: development and application of a conceptual model. *Journal of Plant Nutrition and Soil Science*, **171**, 111–124.
- Wander MM (2004) Soil organic matter fractions and their relevance to soil function. In: *Advances in Agroecology* (eds Magdoff F, Weil R), pp. 67–102. CRC Press, Boca Raton.
- Wardle DA, Nilsson M-C, Zackrisson O (2008) Fire-derived charcoal causes loss of forest humus. *Science*, **320**, 629.
- Watts C, Whalley W, Longstaff D, White R, Brook P, Whitmore A (2001) Aggregation of a soil with different cropping histories following the addition of organic materials. *Soil Use and Management*, **17**, 263–268.
- Watts CW, Whalley WR, Brookes PC, Devonshire BJ, Whitmore AP (2005) Biological and physical processes that mediate micro-aggregation of clays. *Soil Science*, **170**, 573.
- Watts C, Clark L, Poulton P, Powelson D, Whitmore A (2006) The role of clay, organic C and long-term management on mouldboard plough draught measured on the Broadbalk wheat experiment at Rothamsted. *Soil Use and Management*, **22**, 334–341.
- Wengel M, Kothe E, Schmidt CM, Heide K, Gleixner G (2006) Degradation of organic matter from black shales and charcoal by the wood-rotting fungus *Schizophyllum commune* and release of DOC and heavy metals in the aqueous phase. *Science of the Total Environment*, **367**, 383–393.
- Wentzel A, Ellingsen TE, Kotlar HK, Zotchev SB, Throne-Holst M (2007) Bacterial metabolism of long-chain *n*-alkanes. *Applied Microbiology and Biotechnology*, **76**, 1209–1221.
- Whitmore A (1996) Alternative kinetic laws to describe the turnover of the microbial biomass. *Plant and Soil*, **181**, 169–173.
- Whitmore AP, Matus FJ (1996) The decomposition of wheat and clover residues in soil: measurements and modelling. In: *Progress in Nitrogen Cycling Studies* (eds Van Cleemput O, Hofman G, Vermoesen A), pp. 465–469. Kluwer Academic Publishers, Dordrecht, Developments in Plant and Soil Sciences, 68.
- Wiesenberg GLB, Schwarzbauer J, Schmidt MWI, Schwark L (2004) Source and turnover of organic matter in agricultural soils derived from *n*-alkane/*n*-carboxylic acid compositions and C-isotope signatures. *Organic Geochemistry*, **35**, 1371–1393.
- Wolters V (2000) Invertebrate control of soil organic matter stability. *Biology and Fertility of Soils*, **31**, 1–19.
- Wookey PA, Aerts R, Bardgett RD *et al.* (2009) Ecosystem feedbacks and cascade processes: understanding their role in the responses of Arctic and alpine ecosystems to environmental change. *Global Change Biology*, **15**, 1153–1172.
- Wu Z, Dijkstra P, Koch GW, Peñuelas J, Hungate BA (2011) Responses of terrestrial ecosystems to temperature and precipitation change: a meta-analysis of experimental manipulation. *Global Change Biology*, **17**, 927–942.
- Xiang S-R, Doyle A, Holden PA, Schimel JP (2008) Drying and rewetting effects on C and N mineralization and microbial activity in surface and subsurface California grassland soils. *Soil Biology and Biochemistry*, **40**, 2281–2289.
- Zhang D, Hui D, Luo Y, Zhou G (2008) Rates of litter decomposition in terrestrial ecosystems: global patterns and controlling factors. *Journal of Plant Ecology*, **1**, 85–93.
- Zimmerman AR, Gao B, Ahn M-Y (2011) Positive and negative C mineralization priming effects among a variety of biochar-amended soils. *Soil Biology and Biochemistry*, **43**, 1169–1179.
- Zimmermann M, Leifeld J, Schmidt M, Smith P, Fuhrer J (2007) Measured soil organic matter fractions can be related to pools in the RothC model. *European Journal of Soil Science*, **58**, 658–667.