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Nutrient Cycling in Terrestrial Ecosystems

With 55 Figures

Springer

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Preface

Food production will need to keep increasing substantially to meet the demands of the world's population, which is projected to increase to 8 billion people within the next two decades. Current levels of food production will require doubling by 2030, not only because of the sheer magnitude of the population increase, but also due to increased expectations in many countries as regards diet quality and quantity. This required increase in food production will place significant pressure on existing food-producing ecosystems as well as on their surrounding environments.

Environmental concerns, including conservation of natural ecosystems as well as sustainability of managed ecosystems in agriculture, horticulture, forestry and similar economic activities, have attracted increasing attention around the world in recent decades. A principle that is paramount in ensuring the health and sustainability of ecosystems is nutrient cycling in the soil–water–microbe–plant–animal continuum. Nutrient cycling in the majority of food- and fibre-producing ecosystems depends on the addition of fertilisers. However, most fertilisers are produced from natural minerals, which represent a finite resource. While predictions on how much time we have before such resources run out differ substantially depending on underlying assumptions, we can conclude that for some nutrients (e.g. phosphorus) estimates about longevity of economically viable mineral sources are in terms of decades rather than centuries. Hence, a knowledge of cycling of nutrients in the environment is essential in our attempts to efficiently utilise the finite resources of our planet.

Nutrient Cycling in Terrestrial Ecosystems covers important aspects of nutrient cycling at two different scales: (1) on a small scale and more fundamental scientific level, to present the current state of understanding of processes involved in cycling of nutrients from organic matter and other sources; and (2) at a large (whole-ecosystem) scale, describing cycling of nutrients and relevant impacts in situ as well as in the surrounding environment. The first part of the book covers cycling of carbon (Chapter 1), nitrogen (Chapter 2), phosphorus and sulphur (Chapter 3) and micronutrients (Chapter 4), paying particular attention to the role of root exudates (Chapter 5) and rhizosphere microorganisms (Chapter 6) in facilitating nutrient cycling. In the second part of the book, the authors cover nutrient cycling from the standpoint of the complexity of various ecosystems, emphasising cropping systems (Chapter 7), pastures (Chapter 8), natural grass-

lands (Chapter 9), arid lands (Chapter 10), tundras (Chapter 11) and forests (Chapter 12). Finally, Chapter 13, on modelling of nutrient cycling, integrates available knowledge on fundamental processes as well as on how these processes interact at the ecosystem level.

In covering a range of scales, and in emphasising the multidisciplinary approaches essential to increasing the understanding of the underlying processes and devising practical approaches for maintaining healthy nutrient cycling in native and sustainable managed ecosystems, this book will support scientists and practitioners alike, as well as demonstrating that improving sustainable economic output from managed ecosystems and conservation of natural ecosystems are inseperably linked.

All chapters have been reviewed according to the standards of international scientific journals. We would like to thank the authors for patiently revising the chapters, sometimes repeatedly, to meet these high standards. We would also like to express our thanks to the Editor-in-Chief, Prof. Ajit Varma, and to Jutta Lindenborn of Springer for their dedication, patience and diligence in the production of this book.

Adelaide and Perth
Australia August, 2006

Petra Marschner
and Zed Rengel

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Abbreviations

AM	arbuscular mycorrhiza
AM	arbuscular mycorrhizal fungi
ARA	acetylene reduction assay
BNF	biological N fixation
CEC	cation-exchange capacity
DNRA	dissimilatory reduction of NO_{3^-} to $NH4^+$
DOC	dissolved organic carbon
DON	dissolved organic N
DON	Dissolved organic nitrogen
DON	Dissolved organic nitrogen
DTPA	Diethylenetriaminepentaacetic acid
EDDHA	Ethylenediamine di(o-hydroxyphenylacetic acid)
EDTA	ethylene diaminetetraaminoacetate
FAME	Fatty Acid Methyl Ester
Ggt	*Gaeumannomyces graminis var. tritici*
HUM	humified organic materials
IBP	International Biological Programme
IHP	inositol hexakisphosphate
IOM	inert organic materials
IPCC	Intergovernmental Panel on Climate Change
LCO	lipo-chito-oligosacharide
LMW	low-molecular-weight
MAT	Mean Annual Temperature
MIT	mineralisation-immobilisation turnover
MIT	mineralisation-immobilisation turnover
MIT	mineralisation-immobilisation turnover
Mt	million tonnes
NA	nicotianamine
NAAT	nicotianamine-aminotransferase
NPP	net primary productivity
NUMALEC	Nutrient Management Legislation in European Countries
OM	organic matter
PGPR	Plant growth-promoting rhizosphere microorganism
PLFA	phospholipid fatty acids

PS	Phytosiderophores
PS	phytosiderophores
RPM	resistant plant materials
SIR	substrate induced respiration
SOC	Soil organic carbon
SOM	soil organic matter
SOM	soil organic matter
SON	soluble organic N
TNSC	total nonstructural carbohydrates
VA	vesicular arbuscular
VOC	volatile organic compounds
VOC	volatile organic compounds
XANES	X-ray absorption near-edge structure spectroscopy

1 Composition and Cycling of Organic Carbon in Soil

Jeffrey A. Baldock

1.1 Introduction

Soil organic carbon (SOC) represents a significant reservoir of carbon within the global carbon cycle that has been estimated to account for 1,200–1,550 Pg C to a depth of 1 m and for 2370–2450 Pg C to a depth of 2 m (Eswaran et al. 1995; Lal 2004a). Comparative estimates of organic C contained in living biomass (560 Pg) and atmospheric CO_2-C (760 Pg) (Lal 2004a) indicate that variations in the size of the SOC store could significantly alter atmospheric CO_2-C concentrations. A 5% shift in the amount of SOC stored in the 0–2 m soil profile has the potential to alter atmospheric CO_2-C by up to 16%.

Land-use change can induce emission or sequestration of carbon depending on a range of soil and environmental properties and land management practices. Carbon sequestration in soils is a slow process but may offer the most efficient natural strategy for offsetting increased atmospheric CO_2-C concentrations induced by fossil fuel burning and conversion of natural terrestrial systems to agriculture (Lal 2004a; Metting et al. 1999; Post et al. 1999). It has been suggested that, over the next century, improved land management strategies could sequester up to 150 Pg CO_2-C (Houghton 1995; Lal 2004b; Lal et al. 1998); however, considerable uncertainty exists in such estimates because of an inability to accurately predict the total carbon sequestration potential of soils. Improving our understanding of SOC cycling processes and how these are affected by land management practices will be important to defining future opportunities for carbon sequestration in soils.

In addition to its importance in the global carbon cycle, SOC contributes positively to a range of biological, physical and chemical properties important to defining the potential productivity of a soil (Baldock and Skjemstad 1999;

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Reeves 1997). SOC provides the energy essential to biological processes and, when considered in combination with its associated nutrients (N, P and S), can contribute to the resilience of soil/plant systems. Soil physical properties influenced by SOC content include soil structural form and stability, water retention, and thermal properties. SOC also contributes to defining the cation exchange and buffer capacities of soils. The amount and form of SOC required to make significant contributions to these soil properties varies with the property being considered and the soil type (Baldock and Skjemstad 1999). For example, more carbon may be required to maintain the structural stability of a sandy-loam soil than in a self-mulching clay, yet in terms of provision of energy or nutrient mineralisation, more SOC may be required in the clay-rich soil. Likewise, pieces of plant debris with a high C/N ratio (>40) are likely to have a different effect on net nutrient mineralisation during decomposition processes than well decomposed materials with a low C/N ratio (<40).

Understanding the dynamics of SOC, both in its entirety and its various components, and the influence of environmental and soil properties is essential to adequately characterise the effects of management and land use on fluxes of carbon and soil productivity. In this chapter, the composition of SOC and the factors that define the biological stability and cycling of SOC will be examined. Given this scope, it would not be possible to present an exhaustive review of all relevant studies. Instead, the objective of this chapter was to identify the major soil and environmental properties and processes that influence SOC cycling and provide references that can act as a starting point for further exploration of the concepts presented.

1.2 Composition of Soil Organic Carbon

SOC exists as a heterogeneous mixture of a wide range of organic materials, including individual simple molecules (amino acids, monomeric sugars, etc.), polymeric molecules (e.g. cellulose, protein, lignin, etc.), and pieces of plant and microbial residues composed of a mixture of simple and polymeric molecules bound together into recognisable cellular structures. Plant and microbial residues represent the major parent material from which SOC is formed. The chemical composition of these residues has been reviewed by Kögel-Knabner (2002). Each molecular form of SOC can exist along a continuum from fresh unaltered materials through to materials whose chemical composition has been significantly altered by decomposition processes. In this chapter the term SOC is hereafter used to refer to the entire organic fraction of soils, and various SOC components are defined as delineated by Baldock and Nelson (2000).

Given the compositional variability of SOC, different components of SOC will accumulate or be lost at different rates depending on their accessibility to

decomposition and/or biological stabilisation. Changes in SOC content with time therefore represent the weighted average change in contents of all SOC components. Radiocarbon dating (e.g. Anderson and Paul 1984) and isotopic labelling (e.g. Ladd et al. 1981) experiments clearly demonstrated that different components of SOC turn over at different rates. A variety of chemical and physical fractionation procedures has been developed in an attempt to isolate and characterise relatively "homogeneous" fractions of SOC that exhibit different biological stability.

1.2.1 Chemical Fractionation of SOC

Early attempts at fractionating SOC were chemically based and involved the use of alkaline extraction followed by acidic precipitation (Muller 1887). This fractionation scheme continues to be used to partition SOC into fractions referred to as humic acids, fulvic acids and humin on the basis of solubility in alkaline and then acidic solutions. Radiocarbon dating of SOC in a chernozem revealed that humin and humic acid fractions were older and the fulvic acid fraction was younger than intact SOC (Campbell et al. 1967). Given the mode of extraction and isolation of humic materials from soil and the potential for a variety of inter- and intra-molecular interactions to occur after acidifying alkaline extraction solutions, the probability of mixing older and younger organic species during extraction is high, and complete segregation on an age basis can not be expected.

A second form of chemical fractionation uses various extraction or degradative methodologies considered to be "selective" for given molecular components. Such methodologies are used to identify fractions of SOC with different susceptibilities towards mineralisation based on differences in chemical recalcitrance. Hydrolysis with 6 M HCl or methanesulfonic acid can be used to quantify the proportion of SOC associated with proteins, amino acids and amino sugars (Appuhn et al. 2004; Friedel and Scheller 2002; Martens and Loeffelmann 2003). Hydrolysis with sulphuric acid has been used to quantify the fraction of SOC attributable to carbohydrate structures (Martens and Loeffelmann 2002; Rovira and Vallejo 2000). The proportion of lignin in SOC has been quantified using a variety of methods that attempt to either isolate the intact lignin molecule (Tuomela et al. 2000) or quantify the monomeric species released (Chefetz et al. 2002; Leifeld and Kögel-Knabner 2005). A range of organic solvent extraction techniques have been developed to quantify the amount of lipid and lipid-like carbon in soils (Poulenard et al. 2004; Rumpel et al. 2004).

Although these molecular extraction or degradation methods are capable of identifying relative differences between different samples of SOC, due to incomplete extraction and non-selective action, absolute quantities should be considered as approximate. This issue is well exemplified by the work of Preston et

al. (1997), where a combination of extraction and degradation techniques were used in a "proximate" analysis procedure to fractionate carbon associated with various types of litter. ^{13}C NMR spectroscopy clearly demonstrated that the Klason lignin fraction contained significant amounts of non-lignin carbon.

Chemical fractionation procedures have also been used to allocate SOC to labile and recalcitrant fractions without attempting to define molecular composition. Two examples are the use of HCl hydrolysis and permanganate oxidation. In HCl hydrolysis, carbon retained in the residue after hydrolysis is considered recalcitrant, whilst carbon contained in the hydrolysate is considered labile. This was substantiated by radiocarbon dating HCl hydrolysis residues of 65 surface and subsurface soils (Leavitt et al. 1996). SOC in the hydrolysis residues was older than that present in the non-hydrolysed soils by an average of 1,800 years. A similar result was obtained by Paul et al. (2001), where hydrolysis residues were found to be 1,340 years older on average than total SOC in surface soils and 5,584 years older in subsoils. It is important to recognise that different biomolecules have different susceptibilities to acid hydrolysis, and the presence of acid hydrolysis resistant biomolecules, such as lignin, may lead to hydrolysis residues having younger radiocarbon ages.

Quantification of the proportion of SOC oxidised in permanganate solutions of increasing concentration has also been used to define fractions of SOC with different labilities (Blair et al. 1995). Permanganate concentrations of 0.033, 0.167 and 0.333 mM have typically been employed under the assumption that more labile fractions of SOC are oxidised at lower permanganate concentrations. The existence of strong correlations between the amounts of SOC oxidised at each permanganate concentration and between permanganate-oxidisable carbon and total SOC (Lefroy et al. 1993) question the selectivity of this approach towards identifying differentially labile SOC components (Blair et al. 1995; Mendham et al. 2002). It has also been shown that permanganate-oxidisable SOC had little relation to the labile pool of SOC respired over a 96-day incubation period (Mendham et al. 2002). These results, when considered with the absence of a clear definition of the chemical nature of SOC components attacked by each permanganate solution, limit the utility of this technique in helping to delineate biologically labile and recalcitrant fractions of SOC.

1.2.2 Physical Fractionation of SOC

The majority of organic carbon input to soils is in the form of plant residues. As these residues decompose and become mixed into mineral soil layers, particle size is reduced and the potential for interaction with soil minerals increases. Methods that fractionate SOC on the basis of particle size and density can therefore be used to isolate components of SOC that have different turnover times (Christensen 1996a, 2001). A prerequisite to separating SOC into primary parti-

cles with different sizes or densities is complete dispersion. To minimise chemical alteration, inclusion of strong acid, alkali or chemical oxidant pre-treatments is avoided, and a combination of sodium saturation and physical dispersion methods is used (Skjemstad et al. 2004). Initial approaches to SOC fractionation tended to complete the dispersion process first in the fractionation scheme (Baldock et al. 1992). However, Golchin et al. (1994a) and Amelung amd Zech (1999) showed that recovery of coarse particulate organic matter decreased with increasing sonification time or energy and resulted in a redistribution of carbon into finer particle size classes.

To avoid a redistribution of coarse SOC into finer size classes, it is now recommended that a two-step process be followed (Amelung and Zech 1999). In the first step, the free particulate SOC is removed either prior to dispersion or subsequent to minimal dispersion in which the integrity of soil aggregates is maintained. A second more vigorous dispersion treatment is then used to release pieces of SOC occluded within soil aggregates and SOC adsorbed onto mineral surfaces. In its simplest form this approach results in the isolation of three forms of SOC: (1) free pieces of organic residue found between soil particles and aggregates (inter-aggregate SOC), (2) occluded pieces of organic residue found within aggregations of soil particles (intra-aggregate SOC), and (3) organic matter strongly bound to mineral particle surfaces (mineral-associated SOC).

The rate of turnover of SOC found in different particle size classes has been examined using $\Delta^{14}C$ measurements. Trumbore and Zheng (1996) determined the $\Delta^{14}C$ content of 2,000–63 μm, 63–2 μm and <2 μm fractions of soils. After normalisation of the $\Delta^{14}C$ values to those measured for the 2,000–63 μm fraction (Fig. 1.1a), relative changes associated with decreases in particle size ranged from a depletion (in sample BS-7) through to an enrichment (in sample NS-13) of ^{14}C, suggesting that the age of SOC can either increase or decrease in progressing from coarse to fine particles. Schöning et al. (2005) measured the percentage of modern carbon in the Ah horizons of Luvisols, Leptosols and Phaeozems under a European beech (*Fagus silvatica* L.) forest and found a consistent trend of decreasing amounts of modern SOC with decreasing particle size (Fig. 1.1b).

Kahle et al. (2003) used $\Delta^{13}C$ and $\Delta^{14}C$ measurements to assess the extent of decomposition and turnover times of SOC associated with fine (<0.2 μm) and coarse (0.2–2 μm) clay fractions of illitic soils. Fine clay organic carbon was more enriched with ^{13}C and ^{14}C, suggesting a greater extent of microbial processing but a shorter turnover time than coarse clay organic carbon. Enrichments in ^{13}C and a decrease in C/N ratio with decreasing particle size were also observed by Amelung et al. (1999). The general lack of consistency with respect to changes in ^{13}C and ^{14}C enrichment with decreasing particle size suggests that different processes of SOC stabilisation operate in different soils and that relatively young SOC may be stabilised against mineralisation.

The application of density fractionation, either independently or combined with particle size fractionation methods, has also been used to isolate and characterise SOC fractions with different labilities. Trumbore and Zheng (1996)

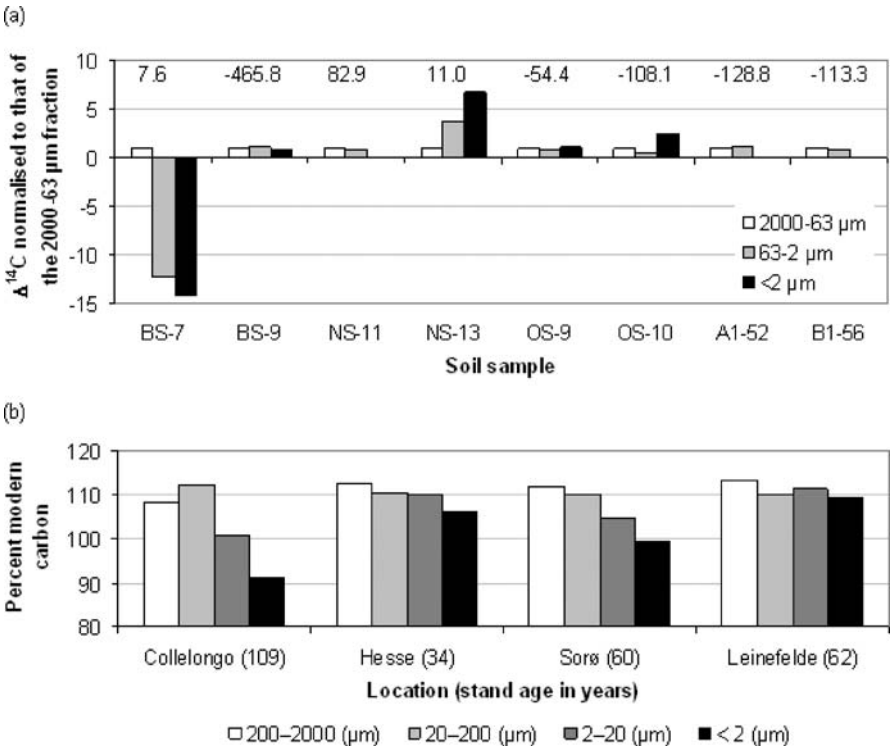

Fig. 1.1 **a** Relative change in $\Delta^{14}C$ value of organic carbon associated with 2,000-63 µm, 63-2 µm and <2 µm particle size fractions isolated from eight different soil samples after normalisation against the $\Delta^{14}C$ value of the 2,000-63 µm fraction (Trumbore and Zheng 1996). Values given above bars associated with each soil sample present the $\Delta^{14}C$ value obtained for the 2,000-63 µm fractions. **b** Changes in the percentage of modern soil organic carbon (SOC) associated with particle size fractions obtained from soil under beech (*Fagus sylvatica* L.) forests (Schöning et al. 2005)

found that SOC in dense soil fractions (>2.0 g cm^{-3}) was more depleted in ^{14}C and therefore older than that found in less dense fractions (<2.0 g cm^{-3}). John et al. (2005) determined the $\Delta^{13}C$ of four density fractions isolated from silty soils under maize: (1) free particulate organic matter <1.6 g cm^{-3} ($fSOM_{<1.6}$), (2) light occluded particulate organic matter <1.6 g cm^{-3} ($oSOM_{<1.6}$), (3) dense occluded particulate organic matter 1.6–2.0 g cm^{-3} ($oSOM_{1.6–2.0}$) and (4) mineral-associated soil organic matter >2 g cm^{-3} ($mSOM_{>2.0}$) and then calculated the mean age of the C in each pool (Table 1.1). The decreasing C/N ratio measured in progressing from the $fSOM_{<1.6}$ through to the $mSOM_{>2.0}$ fractions was suggested to indicate an increase in the degree of degradation and humification. The mean age of SOC in these fractions and the values obtained for percent modern carbon (Rethemeyer et al. 2005) did not follow the same trend, suggesting that the oldest carbon in a soil may not be the most decomposed.

Table 1.1 Properties of the organic matter associated with soil density fractions isolated from the surface soil of a maize trial at Rotthalmünster (John et al. 2005; Rethemeyer et al. 2005). *SOC* Soil organic carbon

Density fraction[a]	% of SOC	C/N ratio	$\Delta^{13}C$	Mean age[b]	Modern C[c]
			(‰)	(years)	(%)
$fSOM_{<1.6}$	4.1	19	−17.3	22	103
$oSOM_{<1.6}$	1.0	19	−23.9	83	98
$oSOM_{1.6–2.0}$	8.1	13	−22.0	49	103
$mSOM_{>2.0}$	86.8	7.5	−22.1	63	103

[a] $fPOM_{<1.6}$: free particulate organic matter <1.6 g cm^{-3}, $oPOM_{<1.6}$: light occluded particulate organic matter <1.6 g cm^{-3}, $oPOM_{1.6–2.0}$: dense occluded particulate organic matter 1.6–2.0 g cm^{-3}, $mOM_{>2.0}$: mineral-associated soil organic matter >2 g cm^{-3}

[b] Mean ages were calculated from changes in carbon content and $\Delta^{13}C$ (John et al. 2005)

[c] Percent modern carbon data was calculated from $^{14}C/^{12}C$ ratios with 100 pMC = 1950 AD (Rethemeyer et al. 2005)

Baisden et al. (2002) measured C/N ratios, $\Delta^{13}C$, $\Delta^{15}N$, and $^{14}C/^{12}C$ of soil organic matter isolated in free particulate organic matter ($fSOM_{<1.6}$), three density fractions of occluded organic matter ($oSOM_{<1.6}$, $oSOM_{1.6–1.85}$, $oSCO_{1.85–2.2}$) and mineral-associated organic matter ($mSOM_{>2.2}$) from soils of different ages. Generally, C/N ratios decreased and $\Delta^{13}C$ and $\Delta^{15}N$ values increased in progressing from the $fSOM_{<1.6}$ through to the $mSOM_{>2.2}$ fractions irrespective of soil age, indicating an increase in extent of decomposition with increasing density. In the young soil (<200,000 years), these changes were not associated with an increase in $\Delta^{14}C$-derived residence times other than for the $fSOM_{<1.6}$ fractions that were much younger. However, a progressive increase in $\Delta^{14}C$-derived residence times with increasing density and extent of decomposition was noted for the oldest soil (1–3 million years).

Swanston et al. (2005) used a simpler density fractionation scheme to isolate three types of SOC ($fSOM_{<1.7}$, $oSOM_{<1.7}$ and $mSOM_{>1.7}$) from a forest soil receiving vegetative residues inadvertently labelled with ^{14}C and an unlabelled near-background site. The occluded fraction of Swanston et al. (2005) represents the sum of the occluded fractions differentiated by John et al. (2005) and Baisden et al. (2002). Changes in C/N ratio and $\Delta^{14}C$ values at the unlabelled background site were consistent with those measured by Baisden et al. (2002), with the exception of a higher C/N ratio in the occluded SOC fraction. Differences in SOC content, C/N ratio and $\Delta^{14}C$ of the fractions isolated from the ^{14}C-labelled soil indicated that free particulate SOC was the most active fraction and also most responsive to C inputs subsequent to the labelling event. The occluded particulate SOC fraction appeared to be less dynamic with a minimal entry of ^{14}C since the labelling event. Based on ^{13}C NMR analyses (Golchin et al. 1994a; Poirier et al. 2005; Sohi et al. 2001, 2005), occluded SOC is more degraded compared to free

particulate SOC; however, this is not consistent with the higher C/N ratios measured by Swanston et al. (2005). Such high C/N ratios would be consistent with the presence of a significant amount of charcoal C, which could mask the entry of new labelled ^{14}C into this pool based on $\Delta^{14}C$ measurements alone. A significant movement of new labelled ^{14}C into the dense mineral-associated SOC fraction was also measured. The depleted ^{14}C signature of this dense fraction at the near-background control site suggested that, at the ^{14}C labelled site, the dense fraction consisted of at least two different pools of SOC: a fast cycling pool and an older, more stable, pool. The presence of a labile pool of carbon within the dense mineral-associated SOC fraction is supported by the lack of a difference in rate of carbon respiration from free particulate and dense mineral-associated SOC over the first 120 days of an incubation study (Swanston et al. 2002).

Irrespective of whether fractionations of SOC are completed on the basis of particle size, density, or a combination thereof, it is essential that any potential for redistribution of SOC amongst the fractions is minimised. It is evident that, although general trends of increasing extent of decomposition and age are associated with decreasing particle size and increasing density, significant perturbations to these sequences may occur. Protection of young chemically labile organic carbon against biological attack through interactions with soil mineral components, and the presence of relatively inert and potentially old charcoal may account for at least a portion of these perturbations. Combining assessments of chemical composition with measures of isotopic composition and SOC age would be most instructive in elucidating the mechanisms responsible for quantifying the cycling of organic carbon in soils.

1.3 Consistency between SOC Fractionation Methods and Pools of SOC in Simulation Models

SOC simulation models [e.g. Rothamsted (Jenkinson et al. 1987), Century (Parton et al. 1987) and APSIM (McCown et al. 1996)] are used to predict the influence of management and climate change on fluxes and stocks of soil carbon. Most SOC simulation models are based on a series of conceptual SOC pools with rapid (annual), moderate (decadal) and slow (millennial) rates of turnover. Although such models have been used successfully to simulate changes in total SOC contents, their ability to identify the underlying mechanism(s) accounting for SOC change is weak and difficult to test. Developing a capability to replace the conceptual pools of SOC found in models with measurable pools offers several advantages: (1) internal verification of appropriate allocations of SOC to pools, (2) greater mechanistic understanding of the implication of management and environment on the components of SOC most affected, and (3) improved confidence in simulation outcomes. Most attempts to define measurable frac-

tions of SOC that can be incorporated into simulation models have focused on the use of physical fractionation techniques. A suitable fractionation procedure should be capable of isolating and quantifying the allocation of SOC to pools that differ significantly in biological availability.

Christensen (1996b) proposed a revised model structure that included measurements of water-soluble SOC (readily decomposable), SOC associated with microbial biomass, light-fraction SOC (free pieces of plant residue not associated with mineral particles or aggregates), intra-aggregate SOC (particulate organic materials contained within aggregates), inert SOC (dominated by charcoal) and SOC associated with mineral surfaces. Sohi et al. (2001) proposed a simpler scheme that isolated only three fractions: free ($fSOM_{<1.7}$), intra-aggregate ($oSOM_{<1.7}$) and mineral-associated ($mSOM_{>1.7}$). In subsequent studies (Poirier et al. 2005; Sohi et al. 2005), the 1.7 g cm^{-3} density solution used in the fractionation process was replaced by a 1.8 g cm^{-3} solution. On the basis of differences in chemical composition defined by a range of spectroscopic and wet chemical oxidation techniques, Sohi et al. (2005) and Poirier et al. (2005) suggested that the biological reactivity of each SOC density fraction would differ and that the proposed method of density fractionation could form a basis for measurable SOC fractions in simulation models. However, biological availability of carbon in each fraction was not assessed. In addition, no attempt was made to substitute the measurable pools of C into a working carbon simulation model to demonstrate the utility of this proposal.

SOC simulation models often contain an "inert" pool of carbon that does not actively cycle. The cross polarisation ^{13}C NMR spectra presented for the occluded fractions of SOC isolated by density fractionation (Poirier et al. 2005; Sohi et al. 2001, 2005) all contained significant signal intensity in the aryl-C chemical shift region, especially the occluded intra-aggregate SOC fraction of the silty clay loam (Sohi et al. 2001). The distribution of aryl-C signal intensity in the occluded SOC fractions was consistent with that noted for charcoal derived from wood and for charcoal found in soils (Baldock and Smernik 2002; Skjemstad et al. 1999b, 2002), indicating a variable contribution of charcoal carbon to these fractions. It is also important to note that ^{13}C NMR spectra acquired using a cross polarisation analysis detect <50% of the total charcoal C present in a sample (Baldock and Smernik 2002). Actual contributions of charcoal C to the density fractions may therefore be much greater than indicated by the presented ^{13}C NMR spectra.

Skjemstad et al. (1999b) devised a method of estimating the charcoal carbon content of soils by correcting cross polarisation ^{13}C NMR spectra obtained after a photo-oxidation process for the presence of lignin and low cross polarisation NMR observability. A significant amount of charcoal found in soils has a small particle size (<53 μm) (Skjemstad et al. 1998). The potential therefore exists for charcoal to move vertically and accumulate at certain depths in the soil profile, and to move laterally and accumulate in zones of deposition within a landscape. Charcoal carbon has been found to account for 0–60% of the SOC found in Australian, German and American soils, and no relationship has been found to

exist between total SOC content and the proportion of charcoal carbon present (Schmidt et al. 1999, 2001; Skjemstad et al. 1996, 1998, 1999a, 1999b, 2002). Pieces of charcoal selectively removed from soil and not associated with soil minerals have radiocarbon ages equivalent to or greater than soil humin fractions (Pressenda et al. 1996). High recalcitrance of charcoal carbon to biological mineralisation has been demonstrated (Baldock and Smernik 2002), although priming with glucose has also enhanced mineralisation of a portion of charcoal carbon (Hamer et al. 2004). If variable quantities of charcoal exist in density fractions, as suggested by the NMR spectra presented by Sohi et al. (Poirier et al. 2005; Sohi et al. 2001, 2005), the usefulness of these fractions as measured surrogates for inclusion in carbon simulation models will be limited due to variation in the biological reactivity of the fractions.

Skjemstad et al. (1996) proposed a three-component fractionation scheme to identify measurable SOC fractions that avoids issues associated with redistribution of carbon during dispersion and fractionation and allocation of appropriate proportions of SOC to the most recalcitrant charcoal-rich pool (Fig. 1.2). The fractions isolated included: free particulate SOC (>53 μm particles), humus (<53 μm particles – charcoal carbon) and charcoal carbon (<53 μm particles from which non-charcoal carbon was removed using a photo-oxidation proce-

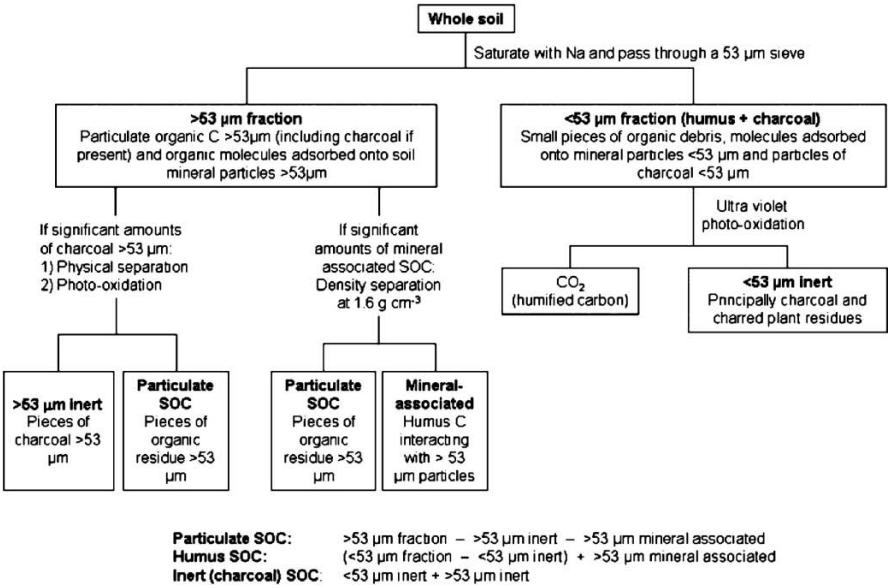

Fig. 1.2 Methodology used to isolate measurable SOC fractions that define the allocation of carbon to charcoal and minimise the potential for carbon redistribution during the fractionation process

dure). By first removing the large pieces of plant residue in the free particulate fraction and aggregating all soil particles <53 μm into one single fraction, any redistribution of C between soil particles <53 μm has no consequence on allocation of C to this fraction. Two issues that must be assessed when using this approach are the inclusion of large pieces of charcoal and organic carbon adsorbed to large mineral particles in the >53 μm fraction. The importance of both of these issues can be rapidly assessed by examining the >53 μm fraction under a light microscope. If a contribution from large particles of charcoal is present, this can be accounted for by physical removal or photo-oxidation. Where a significant amount of carbon is associated with >53 μm mineral particles, a density fractionation process using a solution of 1.6 g cm^{-3} can be used to separate the free particulate material from the mineral-associated humus material (Fig. 1.2).

Skjemstad et al. (2004) assessed the suitability of substituting the fractions identified in Fig. 1.2 for several of the conceptual pools included in version 26.3 of the Rothamsted soil carbon simulation model (RothC). A schematic representation of the pools and flows of carbon in the Rothamsted model is presented in Fig. 1.3. The resistant plant materials (RPM), humified organic materials (HUM) and inert organic materials (IOM) pools in the Rothamsted model were substituted with the >53 μm particulate SOC, humus SOC and inert SOC fractions, respectively. Changes in total SOC content and allocation to the pools were simulated for soils collected from two long-term field studies. Initial SOC content and allocation of C to the fractions was defined by applying the fractionation methodology to archived soil samples collected at the start of the studies. Model performance was assessed by comparing simulated changes in total

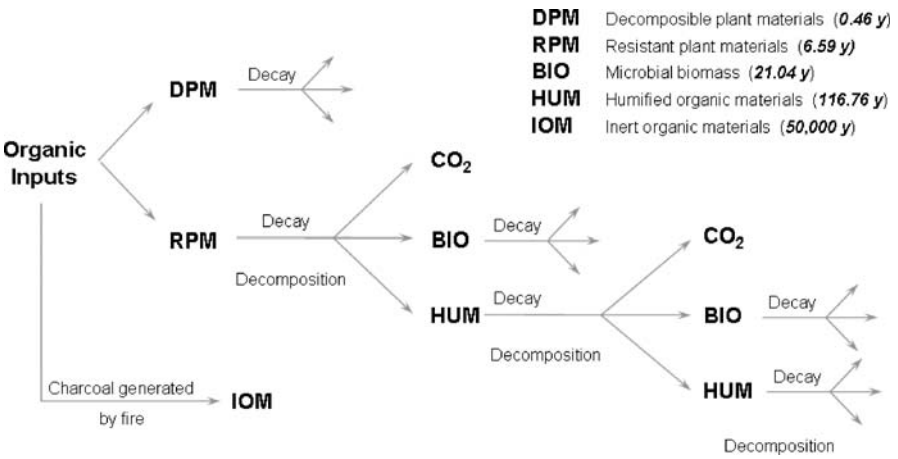

Fig. 1.3 Pool structure and flows of carbon in the Rothamsted SOC simulation model (modified from Jenkinson et al. (1987)

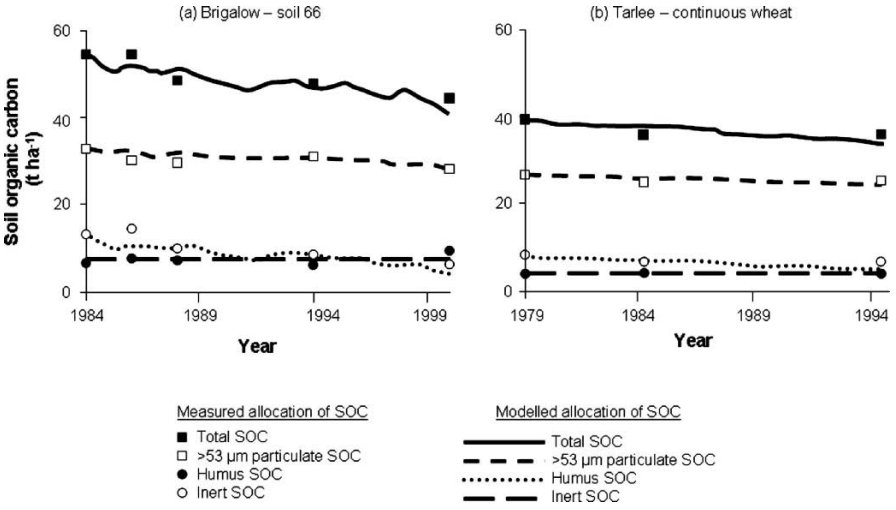

Fig. 1.4 Comparison of simulated (*lines*) and measured (*points*) total SOC contents and allocation of carbon to measurable SOC fractions at the (**a**) Brigalow and (**b**) Tarlee field sites (modified from Skjemstad et al. 2004)

SOC content and allocation of carbon to the pools with values measured on soils archived throughout the duration of the field studies. Without any modification to RothC, reasonable agreement was obtained for both total SOC and allocation of carbon to the fractions; however, improvements in agreement were obtained by decreasing the rate of decomposition of the particulate SOC pool (RPM in Rothamsted notation) from 0.30 year^{-1} to 0.15 year^{-1} (Fig. 1.4). Given the variation in environment, soil type, and rotation composition examined, it was concluded that, at least for Australian environmental conditions, the conceptual pools of carbon within the RothC soil carbon simulation model could be replaced with measurable fractions based on the methodology developed by Skjemstad et al. (1996). The potential for "modelling the measurable" (Christensen 1996b; Magid et al. 1996) appears to be a valid next step in simulating SOC dynamics. The challenge is to define the most appropriate set of fractions and, while several different procedures have been proposed, only that proposed by Skjemstad et al. (2004) has been successfully incorporated into a working SOC simulation model.