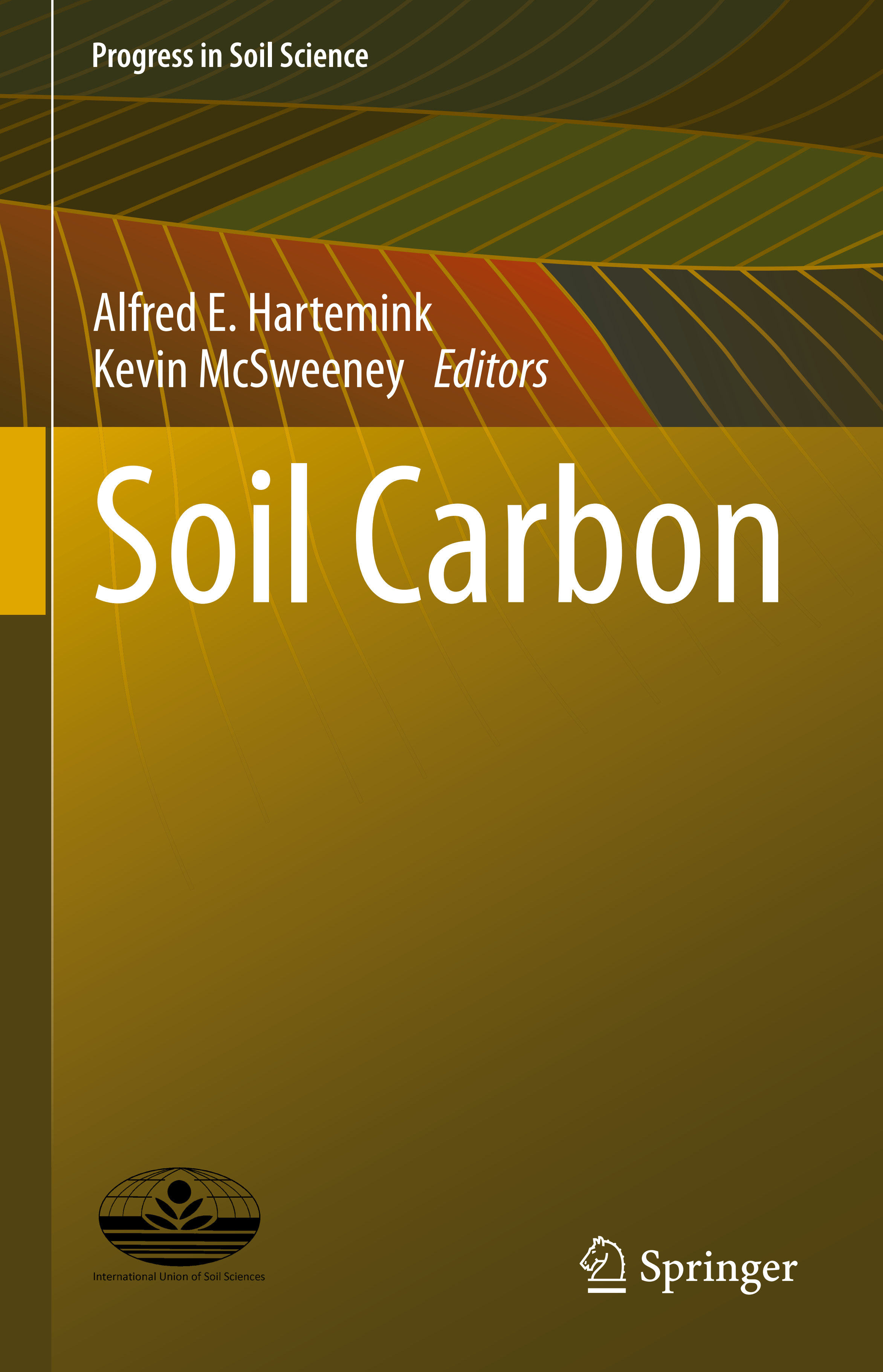

Progress in Soil Science

Alfred E. Hartemink
Kevin McSweeney *Editors*

Soil Carbon

International Union of Soil Sciences

Springer

Soil Carbon

Progress in Soil Science

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Progress in Soil Science series aims to publish books that contain novel approaches in soil science in its broadest sense – books should focus on true progress in a particular area of the soil science discipline. The scope of the series is to publish books that enhance the understanding of the functioning and diversity of soils in all parts of the globe. The series includes multidisciplinary approaches to soil studies and welcomes contributions of all soil science subdisciplines such as: soil genesis, geography and classification, soil chemistry, soil physics, soil biology, soil mineralogy, soil fertility and plant nutrition, soil and water conservation, pedometrics, digital soil mapping, proximal soil sensing, soils and land use change, global soil change, natural resources and the environment.

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International Union of Soil Sciences

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Foreword

We live in the carbon era. Carbons are ubiquitous in soil, water, atmosphere, and minerals of all ages and in all places. The carbon of million years ago is still the same as that of today. However, carbon is more important than ever before not only to scientists but also to politicians, tax payers, consumers, and producers. Low carbon and green growth becomes the main theme of the research and policy agenda across the globe.

Carbon is a simple chemical element with atomic number 6 and an atomic weight of 12; it is nonmetallic and tetravalent. However, carbon is a somewhat mysterious element since it can camouflage into various compounds and materials depending upon where it exists or what it reacts with. The properties of carbon vary widely with the allotropic forms such as graphite, diamond, and amorphous carbon. It can also exist in inorganic and organic forms. There is a chemistry joke on carbon. Why did carbon marry hydrogen? They bonded well from the minute they met.

Carbon is the 15th most abundant element in the Earth's crust and the fourth most abundant element in the universe by mass after hydrogen, helium, and oxygen. In the human body, carbon is the second most abundant element by mass after oxygen. This abundance, together with a diversity of organic compounds and polymer-forming ability, makes carbon the chemical basis of all known life.

Carbon in the soil is crucial for sustaining human life and ecosystem health and functions. Soil is the most important reservoir of carbon, and thus changes in soil carbon levels can have a large impact on life and the ecosystem. Soil carbon can be described as the motherhood of life, since it is the basis of life, energy, fiber, food, and shelter. However, with mismanagement, carbon can trigger irreversible and catastrophic changes to the conditions of life on our planet with devastating ecological and economic consequences.

Assessment of soil carbon cycle and dynamics is at the frontier of soil science, and the International Union of Soil Sciences (IUSS) as a global union of soil scientists is fostering soil carbon research. Soil carbon is important in space and time (IUSS Division 1), properties and processes (IUSS Division 2), use and management (IUSS Division 3), and sustaining society and the environment (IUSS Division 4). Thus, having the IUSS Global Soil C Conference in June 2013 in Madison, Wisconsin, USA, with over 100 presentations from 30 countries across the globe was timely.

This book contains a selection of papers presented at the conference. I truly believe that this book serves all country members and public with all ingredients of soil carbon.

Jae E. Yang
IUSS President

Preface

In the past two decades, an increasing number of soil studies have focused on soil carbon (C). Most of these studies were related to stock assessment, monitoring, microbial dynamics, loss of C, tillage effects, soil management, economics, or policy issues – to name a few topical areas that have been widely researched and discussed. The driving force for much of soil C research is related to climate change or the maintenance of soil quality and fertility. Few topics cut across the whole soil science discipline wider than research on soil C.

In 2009, the International Union of Soil Sciences (IUSS) recognized the need for a conference that focused on a single topic that is of interest to all IUSS Divisions, Commissions, and Working Groups. Naturally, it was decided that the conference topic should be soil C and that the conference should have an interdivisional and intercommissional approach. To achieve this goal, it was decided that there should be no concurrent sessions and that the conference should consist of sessions with several short presentations followed by ample discussions. The IUSS Global Soil C Conference was held in June 2013 in Madison, USA, and consisted of 3 days of presentations and discussions, followed by a 1-day field trip. There were 140 participants from over 30 countries.

This book contains selected papers from the IUSS Global Soil C Conference. The conference presentations were structured by IUSS Commissions and Working Group under each of the four Divisions. We have more or less kept this structure for the book and loosely grouped papers in four sections: Soil Carbon in Space and Time; Soil Carbon Properties and Processes; Soil Use and Carbon Management; and Soil C and the Environment. We have selected papers that focus on novel and exciting aspects of soil C research, and a few review papers.

We are greatly indebted to all IUSS officers, all conference participants, and authors who helped shape the conference and made excellent contributions to discussions and papers in this book. We acknowledge the financial support from the College of Agriculture and Life Science (CALS) and the Department of Soil Science at the University of Wisconsin—Madison. Special thanks go to Bill Bland and

Birl Lowery and to CALS Conference Services (Leah Leighty) for assistance in the organization of this global conference.

It is our hope that the carbon that was needed to bring these soil scientists together be counterbalanced by the knowledge gained to manage it wisely.

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Part I
Soil Carbon in Space and Time

Chapter 1
Challenges for Soil Organic Carbon Research

Alex B. McBratney, Uta Stockmann, Denis A. Angers, Budiman Minasny, and Damien J. Field

Abstract The soil body is the largest terrestrial pool of organic carbon globally. Lately, research related to soil organic carbon has been a main focus worldwide, motivated by the potential the soil inhabits to become a manageable sink for atmospheric carbon dioxide and thus to mitigate climate change and the known benefits of increased soil organic carbon for the functioning of soils. Here, challenges are highlighted for soil organic carbon research that we are currently facing. Knowledge on soil organic carbon dynamics in the soil system is briefly reviewed, followed by an elaboration on how soil organic carbon dynamics and soil organic carbon stocks have been modelled in space and time and where modelling needs to go.

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Introduction

There is currently a wide and deep interest in the science of soil carbon, which motivated the IUSS Global Soil C conference and the consequent book. This is largely driven by the potential of soil carbon to mitigating climate change, i.e. soil as a potential sink for greenhouse gases (GHG); but also by the effect of enhanced or decreased carbon on soil function, i.e. SOC as one of the main indicators for the soil's condition or quality.

This chapter briefly documents the growth in interest, reviews the consequences of increased or decreased soil carbon concentrations and stocks, and then focuses on key scientific challenges around soil carbon that must be taken up to help meet societal demands for climate and food security into the foreseeable future.

Motivation Behind the Interest in SOC Globally

Over the years, the interest in soil organic carbon (SOC) has risen significantly in the science community. The number of publications on SOC over time, for example, has increased steadily since the early 2000s (refer to Fig. 1.1 which shows the number of publications on SOC per year from 1960 to 2012 listed in the scientific search engines

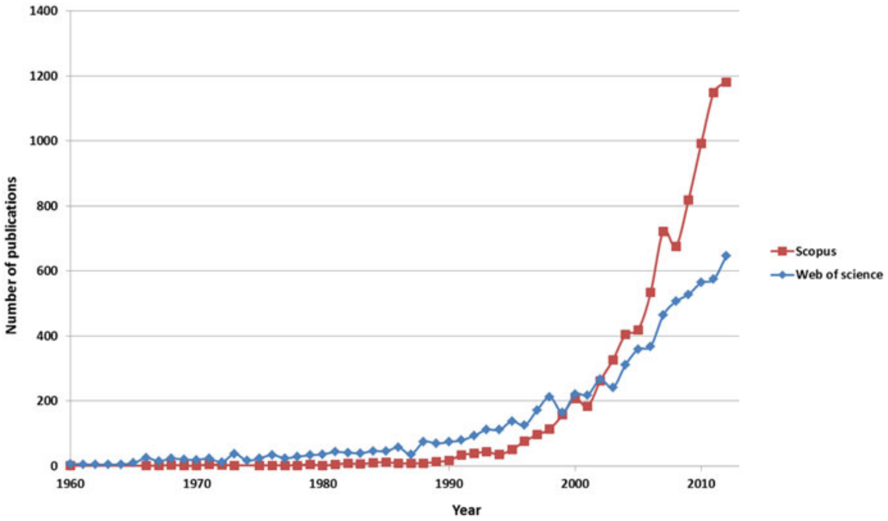

Fig. 1.1 Number of papers on soil carbon each year over time listed in the scientific search engines 'Scopus' and 'Web of Science' (from 1960 to 2012). The lower amount of publications each year found in the 'Web of Science' search engine is due to the selected consideration of journals which is based on the journal's impact factors. In addition, conference papers and book chapters are not included here

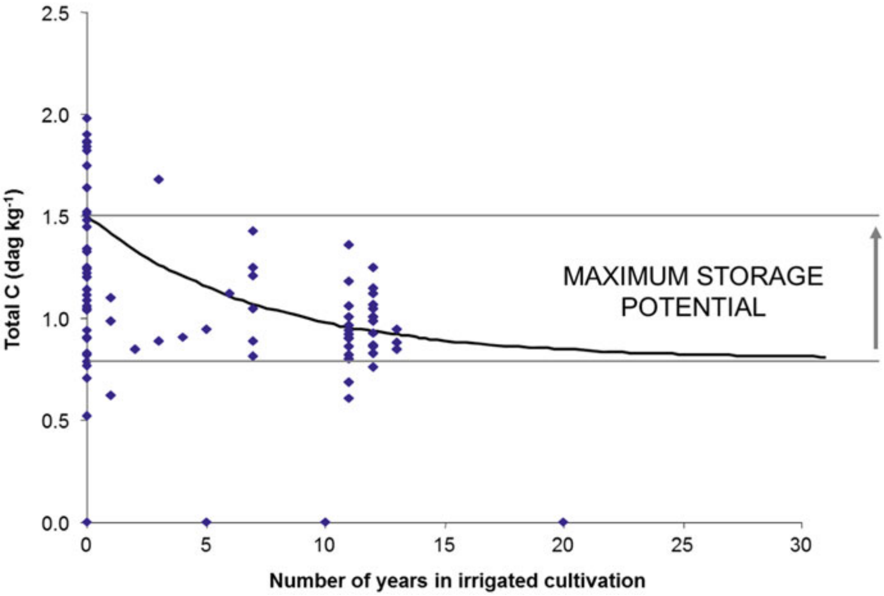

Fig. 1.2 An example of changes in C storage with time since land clearance, induced by management practices (Cotton production, Lower Namoi Valley, Australia) (Based on Minasny et al. 2006, used with permission http://www.publish.csiro.au/nid/84/paper/SR05136.htm)

'Scopus' and 'Web of Science'.). In broad terms, most of these publications tackle research related to the forms of SOC and their organisation in the soil architecture, the role of SOC in nutrient cycling, soil fertility and yield production as well as SOC dynamics in relation to climate change, management practices and modelling.

The steady increase in publications on SOC, however, is more or less due to two aspects.

Soil as a Potential Sink for Greenhouse Gases (GHG)

First, the increase stems from the attention that SOC has received globally due to its potential to play a role in mitigating GHG through Soil Carbon Sequestration (SCS). SCS can be defined as the net removal of atmospheric carbon dioxide (CO_2), i.e. the transfer into long-lived pools such as soil organic matter (SOM), so that the build-up of CO_2 concentration in the atmosphere is reduced or slowed. As such, SCS can be a recognised offset in a market-based carbon pollution reduction scheme (Lal 2004). This is mainly owing to the size of the soil C pool (estimated at 2,344 Gt of OC) compared to the terrestrial biotic C pool (estimated at 560 Gt of OC) (Jobbágy and Jackson 2000). In addition, this is due to anthropogenic influences – mainly management induced changes in C on agricultural land – that have resulted in an estimated loss of SOC of up to 78 Gt per annum (Lal 2004). The soil body may therefore have significant C storage potential. This possibility is demonstrated in Fig. 1.2 which shows the decrease in C storage with time, induced by the establishment of irrigated cotton production in the Lower Namoi Valley, Australia, and subsequently highlights the maximum C storage potential of the local soil to 30 cm (~1.5–1.0 dag kg^{-1} which represents the original average value of SOC under native vegetation). Studies such as this consider trends in C storage with time, starting with a reference value, employing long-term field experiments as well as soil legacy data. These are necessary to help with the assessment of maximum C storage potential for a range of soil types and agricultural regions. On the other hand, rates of SCS have been measured globally for principal biomes by adoption of 'best' management practices and have been synthesized by Stockmann et al. (2013, Table 8, p. 93). Based on this selection of actual measured SCS rates, we can assume a rounded average of half a tonne of carbon per hectare per year can be sequestered globally under best management cropping practice.

Soil Function

Secondly, the interest in SOC stems from the known benefits of SOC for soil fertility, plant growth and production (Janzen 2006). SOC also plays an important role in soil and water conservation. SOC is associated with aggregate stability which in turn determines erodibility. Increased SOC has also been linked to increased available water holding capacity (AWC) which may provide greater landscape resilience under climate change. Moreover, SOC is known to increase the soil's nutrient cycling capability.

The notion that higher SOC contents result in an improvement of the soil's condition has been discussed widely within the *soil quality* concept (Andrews et al. 2004) and has been addressed more recently as part of the *Soil Security* framework (Bouma and McBratney 2013). In both concepts, soil C is considered one of the key indicators of soil function (e.g. in regards to agricultural production or mitigation of climate change).

Scientific Challenge 1: Critical Levels of SOC and the Concept of SOC Saturation

Together with the benefits of SOC for a soil to function, the existence of a critical texture-dependent concentration of SOC as well as the possibility of SOC saturation in agricultural soil, has been widely discussed (Hassink 1997; Six et al. 2002). A critical concentration of SOC is referring to a SOC level below which a soil's function is reduced significantly, whereas the concept of SOC saturation relates to the limiting capacity of a soil to accumulate carbon in dependence on the amount of fine particles in the soil (e.g. clay and the fine silt content).

Critical Levels of SOC for Soil Function

Zvomuya et al. (2008), for example, identified total SOC content as one of the key *soil quality* indicators associated with differing yield of spring wheat in southern

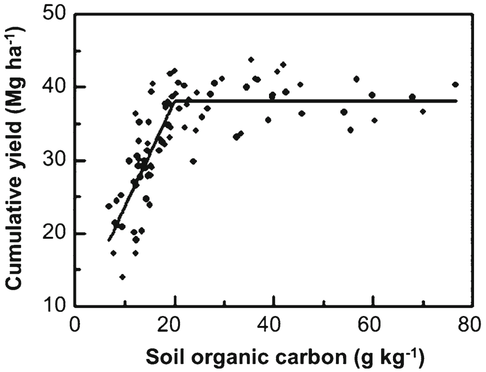

Fig. 1.3 Critical concentration of SOC in relation to biomass yield response – an example from Lethbridge, Alberta, Canada (Zvomuya et al. 2008, used with permission)

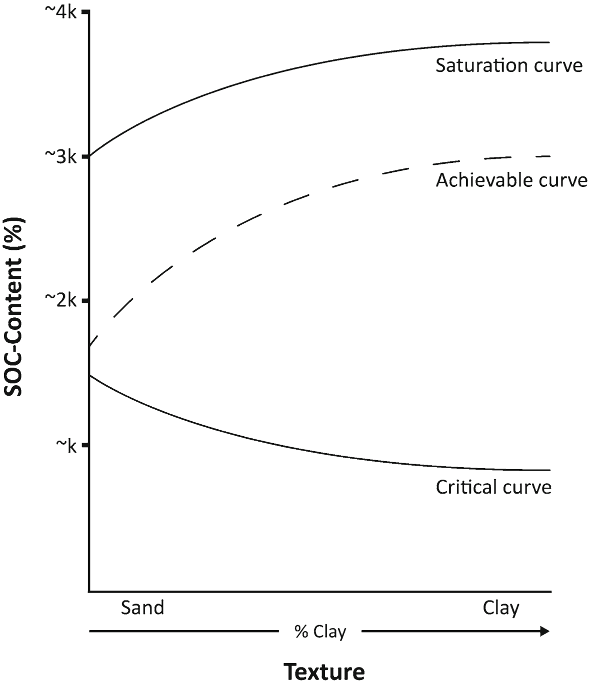

Fig. 1.4 Notional saturation, achievable and critical curve of SOC accumulation as a function of soil texture. Here, k is a site- or region-specific proportionality constant that depends on a variety of interacting factors (e.g. climate, soil material and topographic position) (Stockmann et al. 2013, used with permission)

Canada. A critical concentration of 20 g SOC kg^{-1} (2 % SOC) was found fitting a 'broken-stick' regression model above which no change in yield response was expected and below which the productivity of the soil was reduced notably (Fig. 1.3). Similarly, Yan et al. (2000) identified a critical level of 1.76 % SOC above which soil microbial diversity remained constant and did not increase further. Stockmann et al. (2013) proposed a notional critical as well as saturation curve of SOC accumulation as a function of soil texture as well as climate, soil material and topographic position (Fig. 1.4) which is intended to be used as a conceptual guide for land managers to identify critical concentrations of SOC.

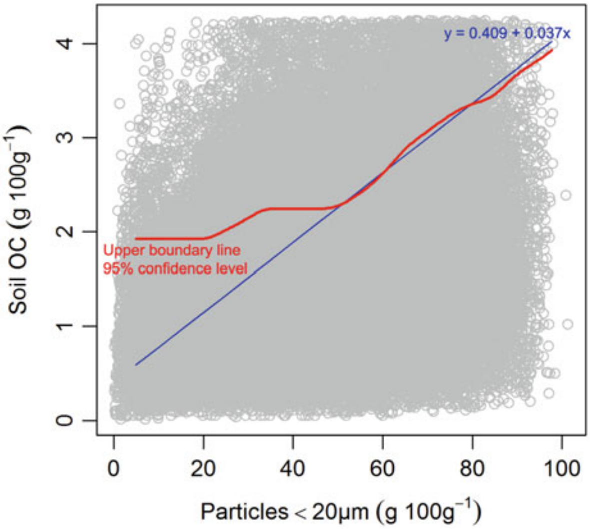

Fig. 1.5 Fit of the upper boundary line (95 % confidence level) for the data set of French agricultural soils (Based on Angers et al. 2011, used with permission from Unité Infosol INRA, Orléans)

SOC Saturation Concept

Angers et al. (2011) estimated the soil carbon saturation deficit for French agricultural soils which was assumed to be largely dependent on the amount and type of the soil's fine fractions (clay plus fine silt content). Here, a saturation deficit represents C that may be stored in the soil in a stable form and represents the difference between the theoretical SOC saturation value (Hassink 1997) and the present SOC content. This study found that most of the agricultural soils in France are below their SOC saturation potential. We used this data set to fit an upper boundary level to the distribution (Shatar and McBratney 2004), which represents the maximum SOC storage potential in dependence on the soil's clay and fine silt content (Fig. 1.5).

Scientific Challenge 2: Influence of Management Practices on SOC Storage

Over decades, research has clearly shown that agricultural management practices significantly influence the soil C content and associated soil properties. A study comparing bio-dynamic to conventionally managed dairy pastures, for example, demonstrated the vital relationship of SOC and soil structure and its dependence on management strategies (Lytton-Hitchins et al. 1994). Results showed that 18 years of bio-dynamic farming resulted in more favourable physical and chemical soil conditions with greater macro-porosity, smaller bulk density values and a larger soil organic matter content (Fig. 1.6). However, we must note here that even so organic farming does result in an increase of SOC at a local scale; it does not necessarily

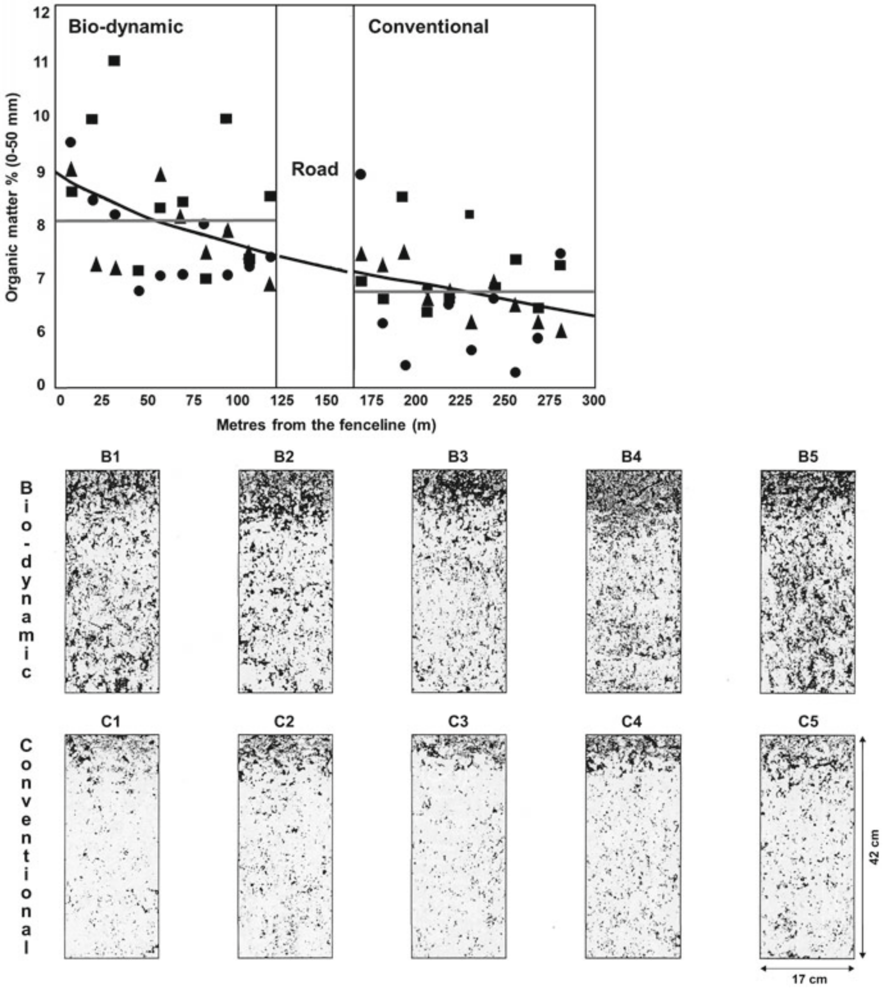

Fig. 1.6 An example of management effects on SOC content and soil structure. Conventionally managed versus bio-dynamically managed dairy pastures (Redrawn, based on Lytton-Hitchins et al. 1994)

translate to SCS, i.e. a net removal of CO_2 from the atmosphere (Leifeld et al. 2013). Often it is simply a transfer of one terrestrial C pool to another and has no impact on climate change *per se*.

In general, research suggests that the adoption of ‘best management’ practices will increase the amount of SOC accumulated in agricultural soil (Lal 2008). However, the influence of management practices on crop residue and SOC decomposition as well as the distribution with depth is still poorly understood and under discussion. Meta-data analysis, for example, has shown that the SOC content in the surface layers increased under no-till (NT) when compared to full-inversion tillage

(FIT) and that this tendency increases with time (Angers and Eriksen-Hamel 2008; Luo et al. 2010; Virto et al. 2012). Limiting effects of NT on SOC stocks have been found when the whole soil profile is considered (Angers and Eriksen-Hamel 2008; Luo et al. 2010). Cases have also been published where NT does not increase SOC contents (e.g. Loke et al. 2012) or where NT resulted in SOC increase at great depth when NT has been used with legume cover crops (e.g. Boddey et al. 2010).

Scientific Challenge 3: The Nature of Soil Carbon

Soil organic C has been described as a continuum of materials in varying states of decomposition with differing residence times (Table 1.1: Forms of (soil) organic C presented in the scientific literature) that are located within the soil's architecture (Jastrow and Miller 1998). Within the soil matrix, SOC is stabilized through physico-chemical processes, i.e. SOC is protected within aggregates which translates to its spatial inaccessibility for the soil microbes and limited oxygen availability. In addition, SOC is stabilized within the soil's architecture through interactions with mineral surfaces as well as metal ions (Six et al. 2004). These stabilization processes can provide *a priori* limits to the soil's capacity to store or sequester C which has been discussed previously.

Traditionally, SOC dynamics have been explained by the *Humus Concept* where composition is assumed to be at least partly controlled by the molecular structure of C inputs. Chemical extractions (alkaline/acid) result in unextractable residues with complex polymeric macrostructures that are believed to be inherently chemically stable (humins and humic acids). However, *chemical recalcitrance* of SOC as

Table 1.1 Forms of (soil) organic carbon found in the scientific literature (Adapted from Baldock 2007)

Form	Composition	Pool category
Surface plant residue	Plant material residing on the surface of the soil, including leaf litter and crop/pasture material	**Fast (or labile) pool** Decomposition occurs at a timescale of days to years
Buried plant residue	Plant material greater than 2 mm in size residing within the soil	**Fast (or labile) pool** Decomposition occurs at a timescale of days to years
Particulate organic matter (POC)	Semi-decomposed organic material smaller than 2 mm and greater than 50 μm in size	**Fast (or labile) pool** Decomposition occurs at a timescale of days to years
Mineral-associated OC ('Humus')	Well decomposed organic material smaller than 50 μm in size that is associated with soil particles	**Slow (or stable) pool** Decomposition occurs at a timescale of years to decades
Resistant organic carbon (ROC)	Charcoal or charred materials that results from the burning of organic matter (resistant to biological decomposition)	**Passive (or recalcitrant) pool** Decomposition occurs at a timescale of decades to thousands of years

determined through the solubility of SOM in response to chemical extractions has now been questioned (Kleber and Johnson 2010), and it is believed that some extracted humic substances are only a product of the extraction procedure itself rather than a real component of SOM. This change in view of SOC dynamics arrived in response to advances in physics, material sciences, genomics and computation which led to new technologies to investigate soil (Schmidt et al. 2011). For example, it became possible to investigate undisturbed soil with the use of NMR (nuclear magnetic resonance), synchrotron based near-edge X-ray fine structure spectroscopy. Using this technology, no clear evidence of discrete humic molecules was found in undisturbed soil (Lehmann et al. 2008). Furthermore, stable isotope-based research resulted in findings that residence times of SOM are not correlated to its chemical composition; therefore, chemical complexity can only be used to explain the short-term decomposition of litter or added OM but not the decomposition of SOM in the long-term (Amelung et al. 2008). Moreover, studies using Curie point pyrolysis-gas chromatography coupled on-line to mass spectrometry (Py-GC/MS) and isotope ratio mass spectrometry (Py-GC IRMS) have related that substances with low molecular weight (proteins or peptides) are more likely to be preserved in soil after decomposition of SOM (Gleixner et al. 2002).

According to these findings current understanding is that decomposition of SOM is predominantly controlled by biological as well as environmental conditions (synthesized in Schmidt et al. 2011). The chemical composition of SOM is then dependent on the interplay of site conditions and biological limitations. More explicitly, the persistence of SOM does not occur because of its intrinsic properties but due to physicochemical and biological influences that reduce the probability of SOM decomposition (Schmidt et al. 2011).

Scientific Challenge 4: Modelling SOC Dynamics in Space and Time

SOC varies in space and time, and modelling approaches are needed to predict SOC dynamics in both dimensions. Here, we attempt to classify modelling approaches in relation to how these address SOC dynamics in space (x, y, z) and time (t) and subsequently present some examples (Table 1.2), including some attempting to couple spatial and temporal variations.

There has been more effort devoted to modelling SOC dynamics over time (t) with the help of *non-spatial process-oriented* models in a 1D dimension (Smith et al. 1998). These are reliably facilitating the prediction of SOC stocks for a variety of natural and agricultural systems. Details on several of these process-oriented models have been given comprehensively in Stockmann et al. (2013). These process-oriented models are also becoming more powerful in predicting the soil's biological activity (e.g. Lawrence et al. 2009; Wutzler and Reichstein 2008). Tentative steps have also been taken to represent the response of SOC dynamics to a changing environment below the usual modelling depth of the top 30 cm of soil (e.g. Jenkinson and

Table 1.2 An approach of classifying the modelling of SOC dynamics in space (*x*, *y*, *z*) and time (*t*)

Dimension	Space	Time	Examples
1D	x, (z)	Yes *Process-based*	Jenkinson and Coleman (2008) Lawrence et al. (2009) Malamoud et al. (2009) Wutzler and Reichstein (2008)
2D	x, y *Empirical*	No	
3D	x, y, z *Empirical*	No	Malone et al. (2009) Malone et al. (2011)
3D	x, y *Empirical*	Yes *Empirical*	Minasny et al. (2011)
2D/3D	x, y, (z) *Empirical*	Yes *Process-based*	Minasny et al. (2013)
3D	x, y, z *Process-based*	Yes *Process-based*	Viaud et al. (2010) Vanwalleghem et al. (2013)

Coleman 2008). Attempts have also been made to incorporate soil structure hierarchies and physical protection mechanisms of SOC through soil aggregates into models of SOC dynamics (e.g. Malamoud et al. 2009).

Lately, there has also been increased interest to map the spatial distribution of soil C including its distribution with depth (*z*), employing methods of digital soil mapping (DSM) (Minasny et al. 2013). There is demand for the accurate assessment of the soil C pool in space and time, globally, using *empirical spatio-temporal* models in a 2D (*x*, *y*), but preferably 3D dimension (*x*, *y*, *z*). The mapping of SOC variation with depth is difficult to achieve with accuracy and the prediction accuracy generally decreases with depth and the environmental covariates used may only explain the variation of SOC in the top 50 cm of the soil profile. Malone et al. (2009) attempted a *pseudo* 3D more or less 2½ D mapping of soil C storage and variation with depth by employing equal-area spline functions. They predicted the vertical and lateral variations of SOC storage for the whole soil-profile up to 1 m depth. They also estimated the uncertainty of the predictions (Malone et al. 2011) which is crucial in DSM. Attempts have also been made to map SOC change over time (3D; *x*, *y*, *t*) in response to land use change employing soil legacy data (e.g. Minasny et al. 2011).

The need to move towards *spatio-temporal process-oriented* models (*x*, *y*, *z*, *t*) and therefore landscape-scale modelling of SOM dynamics has been expressed, to fully represent the transfer of C between the terrestrial pools. This representation is difficult to model and has been conceptually presented by Viaud et al. (2010). Models that operate at the landscape scale have been developed in the fields of hydrology and geomorphology as well as in pedology. Recently, Vanwalleghem et al. (2013) succeeded in combining soil formation modelling with landscape evolution for the first time. Relevant to SOC modelling is that they also included rudimentary mechanistic modelling of SOC dynamics in the soil landscape. Their model represents processes of pedogenesis starting from bedrock in conjunction with vertical and horizontal soil redistribution in the landscape over millennial time scales. This model allows investigating the effect of soil formation and soil erosion on the distribution of soil profiles (including soil horizons) as well as soil properties such as SOC content in the landscape. It can be seen as a first step towards assessing SOC dynamics in the landscape.

Ultimately, there is the need to focus on and to work towards combining SOC predictions in time (t) and space (x, y, z) with mechanistic models of SOC dynamics. A first, effort has been made by Minasny et al. (2013) who employed the so-called *dynamic-mechanistic-simulation-modelling* approach to simulate future SOC change (for the next 10 years) in a sub-catchment of the Hunter Valley, NSW, Australia.

Discussion and Conclusions

Here, we summarize important issues associated with SOC research that arise from this chapter:

1. *Sequestration potential versus soil function or both*
   The soil's C sequestration potential refers to the capacity of soil to sequester C sourced from the atmosphere in the long-term to mitigate climate change. On the other hand, soil C is also related to the soil's condition through its capacity to function (e.g. water holding, nutrient cycling). Both of these contribute to *Soil Security*.

2. *Management and modelling*
   Soil C variability with depth (>30 cm) needs to be better represented in process-oriented models to estimate SOC dynamics accurately based on the whole soil profile. In addition, the factors controlling SOC and residue decomposition at depth are still poorly understood and modelled. SOC models are currently using reduction factors in one direction only and there is the need now to separate processes with depth, i.e. C allocation (roots, dissolved organic carbon (DOC), tillage) as well as factors (e.g. nitrogen (N), water (H_2O), oxygen (O_2), tillage, soil pH) that are controlling the decomposition and stabilization of initial SOC. The main question here is what kind of models we need to fully represent changes in C stocks in relation to management practices for the whole soil profile up to 1 m depth.

3. *Compounds of SOC versus Model pools versus Operational separates*
   The representation of SOC in relation to 'real chemical compounds', 'SOC pools used in modelling' and 'operational separates as determined by fractionation methods in the laboratory' is summarized briefly in Table 1.3.

   The subject of measuring the modellable versus modelling the measureable has been discussed in the literature (Post et al. 2007; Von Lützow et al. 2007). There may be discordance between the conceptual pools and the measureable pools of SOC. In this regard, it may be worthwhile to implement a shift towards measureable pools of SOC to improve the validation of SOC models with measured data.

Table 1.3 Representation of SOC – compounds versus model pools versus operational separates (Adapted from Stockmann et al. 2013 (Table 4, p. 87; Table 5, p. 90))

'Real' chemical compounds of SOC	Representation of SOC in process-oriented models	Operational separates as determined by fractionation methods	Representation of SOC in organism-oriented models
Polysaccharides (e.g. amino sugars) Lignin Lipids	*Active pool* Fresh plant material, root exudates, microbial biomass MRT: 1 year	Macroaggregates (>250 μm) and microaggregates DOC (dissolved organic carbon, <0.45 μm in solution)	Pools of soil biota represented by functional groups: Microorganisms (e.g. bacteria, mycorrhizal and saprotrophic fungi)
Protein molecules (e.g. amino acids), all associated with the elements of C, H, O, N, S, plus P	*Slow pool* SOC that decomposes at intermediate rate MRT: 100 years	Clay-sized particles Silt-sized particles Sand-sized particles	SOM and litter (e.g. roots, detritus)
In addition metals such as Ca, Mg, as well as Cu, Mn, Zn, Al, Fe	*Passive pool* SOC with physical or chemical stability, including charcoal MRT: 1,000 years	Heavy fraction (organo-mineral complexes) Light fraction Particulate organic carbon (POC)	

MRT mean residence time

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Chapter 2
Micromorphology Techniques for Soil Organic Carbon Studies

Rosa M. Poch and Iñigo Virto

Abstract Most research about soil organic C (SOC) has dealt with its composition, fractionation, degree of stability and turnover time, through analyses that involve the complete or partial destruction of the soil structure. Different fractionation techniques on soil aggregates have produced information about the relationships between SOC, minerals and soil structure. There is still a gap between aggregates or organo-mineral associations isolated from the soil matrix and the soil structure and organic matter distribution in the field. Micromorphology and micromorphometry can be very useful to fill this gap. Classical micromorphology is capable of producing true-scale images of the 2D porosity of undisturbed soils. The study of soil organic matter (SOM) through light microscopy is however limited by the isotropic nature of most soil organic components. A set of new techniques developed more or less recently exist that can complement the information obtained using classical micromorphology. Fluorescence microscopy, SEM and microanalyses applied to undisturbed samples provide a more detailed information on the arrangement of soil components, although the results do not fully provide information about the distribution of SOM types. TOF-SIMS, NanoSIMS, FTIR microscopy and XANES through synchrotron facilities are able to yield information about the location of SOM functional groups and microorganisms in relation to soil structure, and thus are promising for associating specific microsites and SOM characteristics with different degrees of activity or stability. In this work the fundamentals and usefulness of these techniques for SOM studies are described.

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Introduction

An intrinsic soil characteristic is its spatial variability. This variation is not continuous across the scales, but occurs at abrupt transitions (Burrough 2006), forming the soil cover pattern where the main scale steps are the individual compounds, the materials (intrapedal associations and pedality), the horizon volumes, and the soilscapes (Targulian and Goryarchkin 2004; Ruellan 2000; ISSS, ISRIC, FAO 1998). These hierarchy levels, structurally organised, have been proposed by Lin (2003) to soil hydrology, and by Hoosbeek and Bryant (1992) to the study of pedogenetic processes.

In the last two decades progress has been made in the knowledge of SOM composition, stability and reactivity (e.g. Lopez-Capel et al. 2005; Hernández-Soriano et al. 2013; Semenov et al. 2013) and in soil carbon mapping (e.g. Chen et al. 2000; Mueller and Pierce 2003; Simbahan and Dobermann 2006). The soil carbon spatial variability at the scale of horizons and landscapes is taken into account when mapping soil carbon stocks or determining carbon distribution in horizons (e.g. Liu et al. 2012), but most of the methods looking at SOC at the level of material or individual compounds are disruptional, i.e. they disturb the original soil structure by fractionation procedures (von Lützow et al. 2007; Sohi et al. 2010).

While the fractionation of the soil organic fraction (SOM) by isolation of different SOM moieties based on chemical characteristics can render useful information on the SOM characteristics, the functional representativeness of these fractions has been questioned (Wander 2004). Extraction procedures based on the reactivity of SOM can affect stabilization mechanisms that are of different relevance in different soils (von Lützow et al. 2007). Physical (size, density) soil fractionation techniques have the advantage of recovering relatively unaltered primary and secondary organo-mineral complexes (Christensen 1996). Physical fractionation techniques designed to isolate soil aggregates (e.g. Elliott 1986; Six et al. 2002) usually obtain different size fractions of aggregates from one horizon, but the original pore structure, aggregate hierarchy and organisation are not preserved. When studying SOM, however, this pore structure can be relevant, e.g. the behavior of similar materials with different c/f related distributions or different structures after fractionation (Stoops 2003) (Fig. 2.1). Recent research has shown that the accessibility of SOM, rather than its chemical characteristics, is the major factor governing SOM turnover in the soil (Dungait et al. 2012).

Few researchers have studied SOM in its original structure and its relation to soil porosity and pedality at detailed scales (Descheemaeker et al. 2009; Kooijman et al. 2009) and soil micromorphology is available to characterize SOM variability at the scale of materials. The spatial variability of SOM at a nanoscale, however, is being satisfactorily developed in synchrotron facilities, which improve the precision of measurements (X-ray, IR) and produces SOM maps of microaggregates (Lehmann and Solomon 2010).

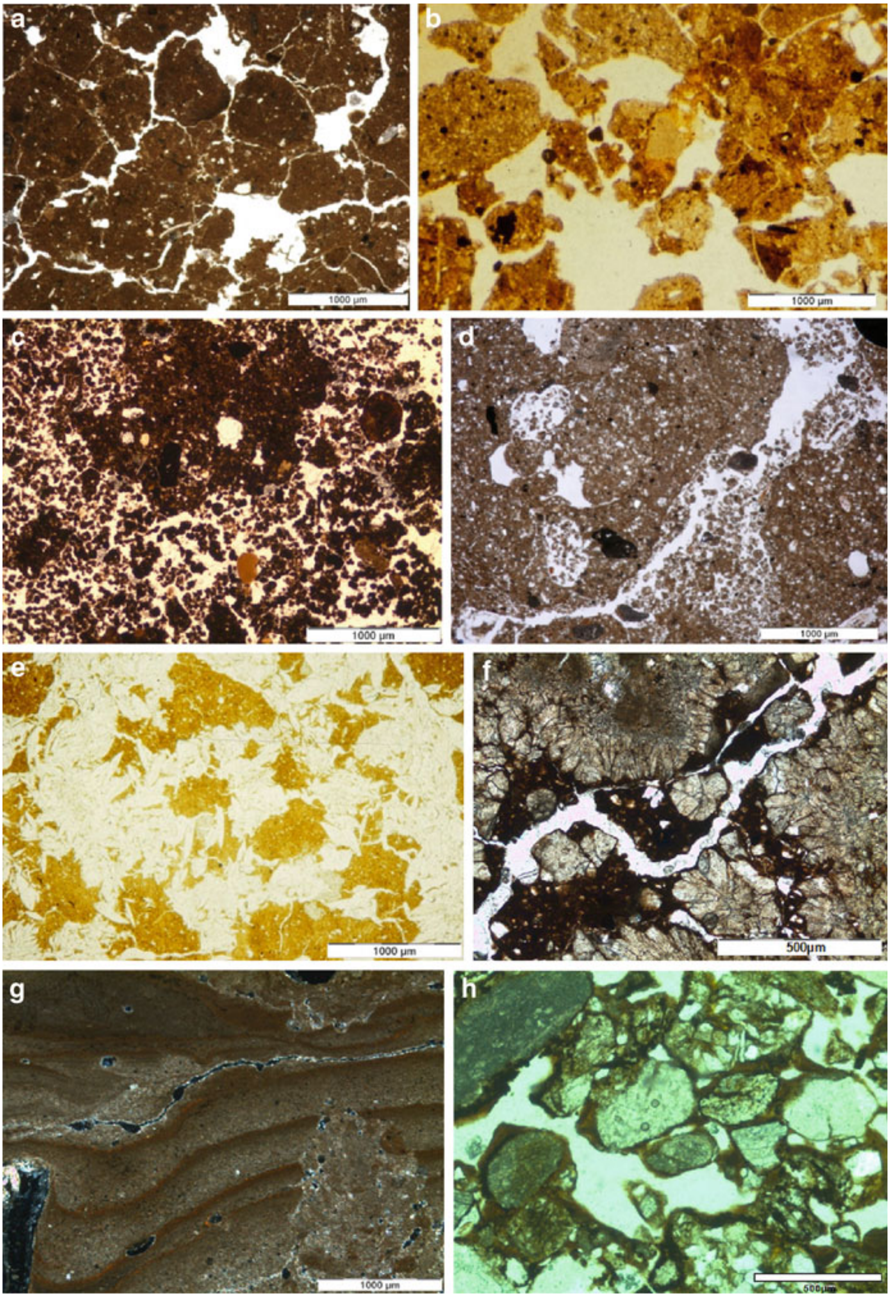

Fig. 2.1 Examples of soil fabrics and the meaning of the associated aggregates produced by physical fractionation. Only microphotograph (**g**) is under XPL, the rest is under PPL. (**a**) and (**b**) Classical well-separated microstructure. Its physical fractionation produces aggregates with a fairly straightforward interpretation. (**c**) and (**d**) Hierarchical and juxtaposed structures. Their physical fractionation produces aggregates with different functionalities regarding C storage (inside the pore infillings/in the groundmass). (**e**) and (**f**) Structures produced by fissuration caused by gypsum and calcite accumulation respectively. The aggregates produced by a physical fractionation have a very different meaning than in (**a**) and (**b**). (**g**) and (**h**) Laminated fabrics (**g**) or chitonic g/f distributions (**h**) warrant the study of SOM distribution; these fabrics yield meaningless results through physical fractionation

The objective of this chapter is to review the potential and limitations of classical micromorphology in the study of SOM, to explain why we think it has not been more widely used when studying SOM in relation to porosity and microsites, and to make some recommendations in order to fill in this methodological gap in the continuum of observation from landscape to submicroscopy.

Optical Microscopy of SOM

Micromorphology of SOM is largely influenced by Babel's work, whose "Micromorphology of Soil Organic Matter" (Babel 1975) has been the basis for the current system of soil thin section description (Bullock et al. 1985; Stoops 2003). He presented a comprehensive review of the knowledge of SOM micromorphology and its relation to SOM chemical composition and biology including information about fabric, structure, position related to pores and minerals, genesis and evolution.

The works of Babel and of other micromorphologists (e.g. Bal 1973; Fox and Parent 1993; Kooistra 1991) address the basis of some of the SOM sequestration principles (e.g. degree of decomposition, processes of incorporation into the soil matrix, protection in aggregates), therefore they should be considered in present-day soil carbon studies. The most recent reviews on SOM (Stockmann et al. 2013), soil biochemistry (Totsche et al. 2010), SOM micromorphology (Stolt and Lindbo 2010), and some studies on SOM dynamics (e.g. Nannipieri and Eldor 2009) stress the need of properly addressing the relationship between SOM and the soil (micro)structure, which would assist in understanding SOM and CO_2 responses to global changes.

The guidelines by Stoops (2003) classify SOM according to the extent to which its origin can be recognized. This can yield information about the position, fabric, and degree of decomposition of SOM higher than microscope resolution (about 20 μm), the general composition (origin of organic residues, presence of some components like phlobaphene, cellulose, lignine), the spatial relation with structure and mineral components; quantitative data by image analyses, and therefore the frame or location for further investigations. SOM micromorphology gives no information about detailed composition of SOM, nor about SOM particles smaller than the microscope resolution and the thickness of a thin section (about 20 μm). Other problems using classical micromorphology for the study of SOM are found in Table 2.1. Although most of the information is descriptive, SOM quantification for particulate organic matter is also possible through point counting (e.g. Davidson 2002) or image analyses (Poch and Antúnez 2010; Marks et al. 2012).

Fluorescence Microscopy

Babel (1972, 1997) used fluorescence microscopy through UV transmitted light for the study of organic matter, because some organic components (cell walls of fungi hyphae) are autofluorescent, whereas colloidal organic matter, such as found in

Table 2.1 Problems and their solutions when studying SOM with the optical microscope

Problem	Solution
Distinguishing SOM from other opaque soil components	Staining or dissolution techniques; fluorescence microscopy (references in Stolt and Lindbo 2010)
Identifying different types of particulate organic materials	Combinations of different images obtained with optical and fluorescence microscopy (e.g. biochar identification; Marks et al. 2012)
Distinguishing organic impregnations from other soil components or the soil matrix e.g. Fe or Mn compounds	Thin section pre-treatments with acids (selective dissolution; Bullock et al. 1975)
Drying of samples creating artifact cracks	Acetone or dioxane drying; alternative drying (references in Stolt and Lindbo 2010)
Sampling difficulties due to lack of coherence of organic matter	Encasing techniques: plaster, polymers (see Murphy 1986; Benyarku and Stoops 2005)
Inferring 3D features from 2D images	Binocular observations, adequate number of replicates, making vertical and horizontal sections, use of Computer Tomography Imaging
Lack of information about micromorphology of soil organic components	Build-up knowledge starting from existing SOM micromorphology

spodic horizons, is not. Special stains may be used to cause specific secondary fluorescence in components such as plant tissue or bacteria (Altemüller and Van Vliet-Lanoë 1990; Bruneau et al. 2005). The resulting images provide information about the type and distribution of organic matter and soil biota in relation to the mineral, aggregate and soil processes such as migration of organic matter or clays (Eickhorst and Tippkötter 2008; Tippköter et al. 1986; Hall 1996; Wierzchos and Ascaso 1998; Driese and McKay 2004).

SEM and Microanalyses

Scanning Electron Microscopy (SEM) and the associated Energy Dispersive X-Ray (EDX) analysis is the first submicroscopic technique to provide maps of element distribution, and relative atomic mass when viewed through Back Scattering Electron Mode. Its application to the study of SOM is indirect since the detection of SOM may be masked by the impregnating resin and also because of the ubiquity of its elemental components (C, H, O) in soils. The technique has been used to trace specific elements in the soil-root interphase (Adamo et al. 1998; van Breemen et al. 2000), and in polluted or mined soils where SOM can be marked by a specific element (Tomlin et al. 1993; Arocena et al. 2010; Sort and Alcañiz 2001). Some others (e.g. Miltner et al. 2011) have used SEM-EDX micrographs to identify and differentiate organic components (e.g. microbial cells) from other soil elements.

NanoSIMS

Nano-scale Secondary Ion Mass Spectrometry (NanoSIMS) consists of a combination of high-resolution microscopy and isotopic probing, providing spatially-referred information on the isotopic composition of materials. It can be used to produce high-definition 2D maps (some nm) of isotopic abundance in the upper layers of a soil sample. Initial studies (Herrmann et al. 2007a, b) focused on the location and activity of microorganisms in the soil matrix using ^{15}N labeling of SOM, with the aim of characterizing the biophysical interface in soils. Recent studies using isotopic labeling (^{13}C and/or ^{15}N) of substrates added to the soil (Mueller et al. 2012), observed the distribution of fresh SOM (particulate and dissolved) in soil aggregates. Advances in sample preparation (avoiding embedding and therefore the interferences of resin in the analysis), have added to the potential of this technique to identify sorption sites of SOM (Heister et al. 2012), and organo-mineral associations (Hatton et al. 2012). These authors have also combined NanoSIMS with SEM, and Elemental Analysis and Isotope Ratio Mass Spectrometry (EA-IRMS) on soil fractions in a multi-scale approach that allows for some quantification and a better identification of SOM forms within the soil matrix. Remusat et al. (2012) have shown how the combination of NanoSIMS, Scanning Transmission X-ray Microscopy (STXM) and Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS) allowed relating the presence of metabolites in intact soil aggregates, and indicates the potential of this technique for in-situ SOM analysis. As outlined above, classical SEM and micromorphological studies are however still necessary in combination with this new technology for an accurate assessment of SOM distribution in the soil and its relationship to ecological processes and SOM stabilization.

DRIFT-FTIR

Fourier Transformed Infrared Spectroscopy (FTIR) is an Absorption Spectroscopy where the sample is subjected to a range of wavelengths in the IR, and the obtained interferograms are decomposed by Fourier transforms. Its application to surfaces is called DRIFT: Diffuse Reflectance Infrared Fourier Transform Spectroscopy, whereby areas occupied by specific functional groups of a given element can be located on a surface. One of the first applications of FTIR to SOM studies was point analysis of C functional groups on intact aggregates and soil peels (Arocena et al. 1995). Examples of SOM types mapping through FTIR and DRIFT can be found in Ellerbrock and Gerke (2004), Ellerbrock et al. (2010) and Leue et al. (2010), where it is concluded that differences of meso- and microsites in soils, as those affected by faunal activity or other structural mechanisms result in different SOM qualities and properties.

Synchrotron-Based NEXAFS and FTIR

Synchrotron-assisted imaging through NEXAFS and FTIR (Lehmann and Solomon 2010) is a promising technique that allows a detailed mapping of soil carbon (Kinyangi et al. 2006) and sulphur (Prietzel et al. 2009) organic chemistry at a nanoscale. The main problems are the preparation of 200–800 nm thick sections, and the analysis of the results through PCA and background-effect removal, dependent on sample thickness and preparation. Upscaling is another issue.

Challenges and Recommendations

Micromorphology can give information on SOM location and quantification that cannot be obtained with other techniques. Some of the main difficulties arise from deriving 3D from 2D observations, and, in some cases, from the lack of representativeness. This can be overcome by a sound sampling from detailed field observations, and by an appropriate number of replications. The relationship to soil functioning has also to be taken into consideration, especially water movement, since all techniques use dried samples. It implies that in some cases specific drying techniques need to be applied in order to avoid artifacts. The combination of micromorphology with recent techniques for the SOM analyses of micro- and nanosites is promising, since it can give answer to functional relationships among SOM components and between SOM and the mineral phases of the soil.

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Chapter 3

Soils as Generators and Sinks of Inorganic Carbon in Geologic Time

H. Curtis Monger

Abstract Soil is a continuum in geologic time. Like today, pedogenesis in the geologic past altered soils by transformations, translocations, additions, and losses as continents drifted and collided across global climatic zones. One of the major biogeochemical systems operating in soils across geologic time is the carbonic acid system, which includes gaseous $CO_{2(g)}$, dissolved $CO_{2(aq)}$, carbonic acid $H_2CO_{3(aq)}$, bicarbonate $HCO_3^{-}{}_{(aq)}$, carbonate $CO_3^{2-}{}_{(aq)}$, and solid-phase calcium carbonate (mainly calcite). These chemical species, collectively referred to as inorganic carbon, increased in the Silurian when vascular plants colonized the continents and began pumping atmospheric CO_2 into soils via photosynthesis and root respiration, which accelerated mineral weathering and made soils "generators" of bicarbonate. In humid regions soils are "flushing" and bicarbonate enters groundwater, streams, and is transported to the oceans. In arid regions soils are "non-flushing" and bicarbonate is not linked to the hydrological system, but precipitates in soil as pedogenic carbonate, making arid soils sinks of inorganic carbon. Pedogenic carbonate is documented in paleosols throughout the Cenozoic, Mesozoic, and back into the Silurian of mid-Paleozoic time. Paleogeographic maps from Present to Precambrian are useful for revealing where arid regions were located in geologic time and how they expanded and contracted; thus, propounding the question of how (and if) a currently expanding "Aridosphere" will impact the global carbon cycle.

Keywords Pedogenic carbonate • Paleosols • Carbon sequestration • Deserts

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Introduction

Why is soil organic carbon studied more than soil inorganic carbon? A word-search of the IUSS Global Soil Carbon Conference Program & Abstracts (Madison, Wisconsin 2013), for example, found six abstracts that mentioned inorganic carbon in contrast to 65 abstracts that mentioned organic carbon. The Intergovernmental Panel on Climate Change chapter on biogeochemistry does not mention soil inorganic carbon, in contrast to soil organic carbon which is mentioned 18 times (Denman et al. 2007). Perhaps because soil inorganic carbon is restricted to sparsely populated arid and semiarid climates, in contrast to humid regions where soil organic carbon covers every continent in varying amounts and is important for agriculture. Perhaps soil inorganic carbon is studied less, especially as a method of carbon sequestration, because it is viewed as mineralogy, unresponsive to management, in contrast to soil organic carbon which is dynamic and capable of being manipulated.

Soil inorganic carbon is, however, widely recognized as being a large pool (940 PgC), exceeded only by the amount of carbon in oceans (38,000 PgC) and soil organic matter (1,530 PgC) (Eswaran et al. 2000; Sarmiento and Gruber 2002). It is less widely recognized that inorganic carbon is biological, at least in part, and therefore might be more dynamic than previously thought (Phillips et al. 1987; Monger et al. 2009). It is least widely recognized that, unlike organic carbon which has a concentration level controlled by its vegetative community, inorganic carbon can continue to accumulate to highly concentrated levels, such as those in petrocalcic horizons (Fig. 3.1).

Overall, the role of inorganic carbon as a method for carbon sequestration is viewed as being insignificant (Schlesinger 2000). This view is the result of at least three reasons. First, in order for soil carbonate to actively sequester atmospheric carbon the source of calcium must be from silicate minerals, not pre-existing carbonate, and tracing calcium to its silicate or carbonate source is difficult. Second, quantifying sequestration by soil carbonate is also difficult because many soils contain both pedogenic carbonate and lithogenic carbonate, which cannot be differentiated using routine measurements of "calcium-carbonate equivalents" (Rabenhorst et al. 1984). Third, carbonate accumulation rates are on times scales of thousands of years (Monger and Gallegos 2000). Such low influx values give rise to long mean residence times, such as 85,000 years (Schlesinger 1985).

However, progress has been made to track the source of Ca by using Sr isotopes as a proxy indicator (Capo and Chadwick 1999; Naiman et al. 2000). Progress has also been made to differentiate pedogenic from lithogenic carbonate using carbon isotopes and micromorphology (Nordt et al. 1998; Kraimer and Monger 2009). Likewise, progress has been made to refine mean residence times using artifacts and meteorites of known age to refine accumulation rates (Barrat et al. 1998; Pustovoytov 2003; Monger and Cooke 2013).

The objective of this paper is to construct a broad-scale context—both spatially and temporally—for viewing the generation, loss, and accumulation of inorganic carbon in soils. It focuses on the major pathways along which carbon moves through the inorganic system and makes inferences about pedogenic carbonate

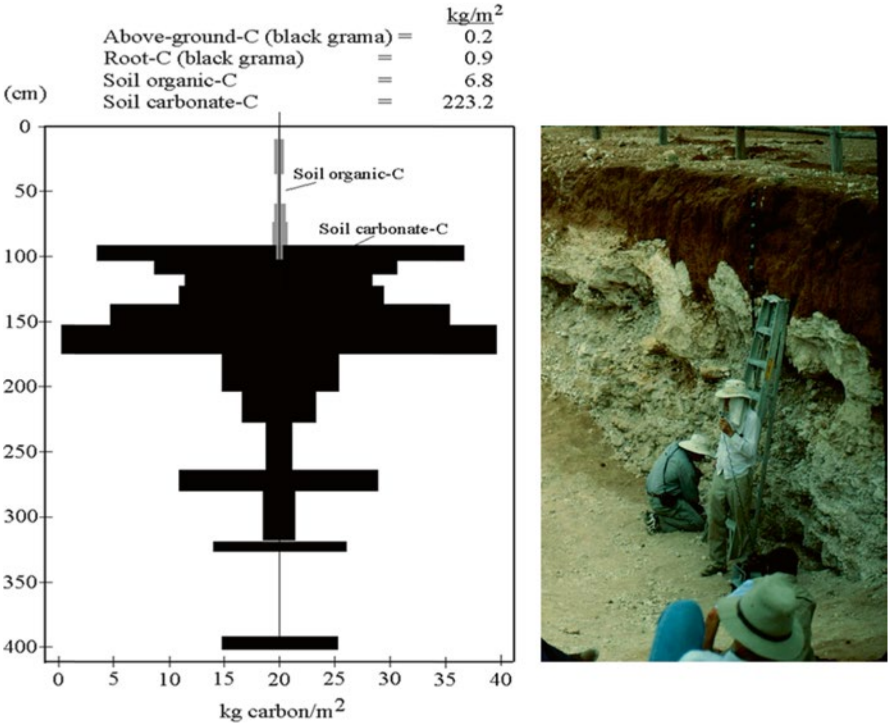

Fig. 3.1 Comparison of amounts of carbon stored as inorganic carbon versus organic carbon in a desert soil with a petrocalcic horizon at the USDA-ARS Jornada Experimental Range in the northern Chihuahuan Desert in New Mexico. The site illustrates the huge amount of carbon that can reside in some desert soils. The soil is an Argic Petrocalcic (USDA-NRCS soil survey number S95NM-013-004). Black grama data are from Xing (2002) (Picture was taken in May 2000 during a tour of the Desert Soil-Geomorphology Project (Gile et al. 1981))

through geologic time. The purpose for this broad-scale context is to help us conceptualize how the global carbon cycle might be impacted if the "Aridosphere" expands as the result of global warming.

Inorganic Carbon Generators and Sinks

There are two end-members for soils as generators and sinks of inorganic carbon—humid soils in which profiles are "flushing" (Rode 1962) and arid soils in which profiles are "non-flushing" (Fig. 3.2). Between these end-members is a continuum of sub-humid through semiarid soils whose profiles are periodically flushing. Humid soils are linked to groundwater and rivers. This hydrological connection provides a conduit whereby bicarbonate, which is generated in soil, travels to the oceans. In contrast, arid non-flushing soils lack the moisture required to leach bicarbonate downward out of the profile and into the phreatic groundwater-river-ocean system.

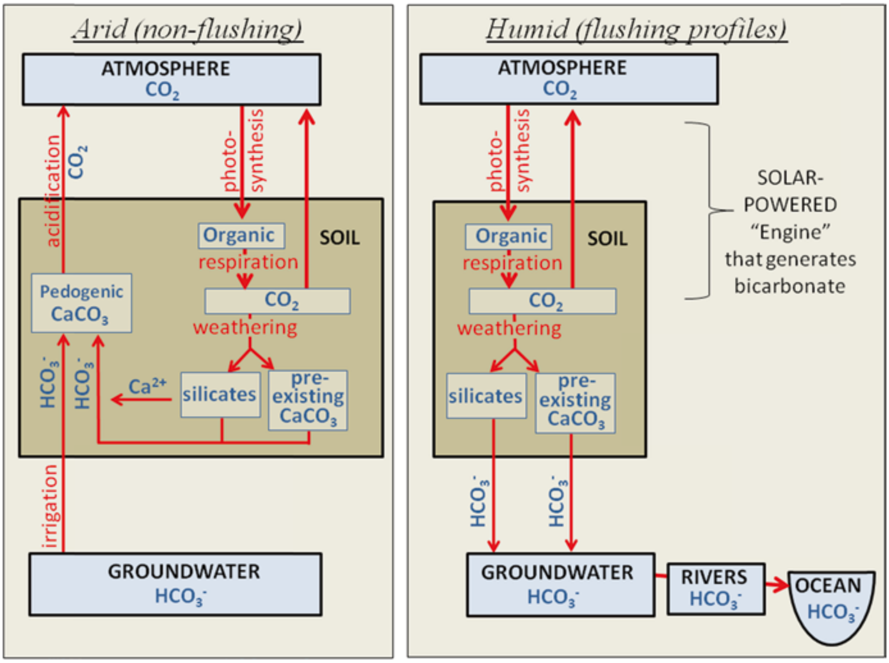

Fig. 3.2 Pathways of modern inorganic carbon arid versus humid climates illustrating how inorganic carbon enters and exits soils, how it is transformed while in soils, and how it is hydrologically connected to groundwater, rivers, and oceans

Humid soils, and to a lesser extent arid soils, generate bicarbonate during the weathering of silicates and pre-existing carbonates. Silicate minerals are chemically weathered via their reaction with carbonic acid (Reaction 3.1). This results in the production of one mole of Ca and the consumption of two moles of carbon dioxide (Berner 2004).

$$2CO_2 + 3H_2O + CaSiO_3 \rightarrow Ca^{2+} + 2HCO_3^- + H_4SiO_4 \tag{3.1}$$

When Ca and bicarbonate from silicate minerals precipitate as calcite, one mole of carbon is sequestered and one mole is released as CO_2 (Reaction 3.2).

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \tag{3.2}$$

Thus, there is a net sequestration of one mole of carbon. Pre-existing carbonates in soil are also chemically weathered via carbonic acid (Reaction 3.3). In this case, however, one of the two moles of carbon in bicarbonate is from the pre-existing carbonate, and the other mole is from carbon dioxide (Krauskopf and Bird 1995). Thus, the carbon dioxide consumed during the formation of carbonic acid ($H_2O + CO_2 \leftrightarrow H_2CO_3$) is released upon the re-precipitation of calcium carbonate. Therefore, no sequestration has occurred.

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{3.3}$$

On the global scale, bicarbonate generated in humid "flushing" soils travels to oceans, precipitates as calcium carbonate, and sequesters one mole of atmospheric CO_2—if the Ca is derived from silicates. If, however, the Ca is derived from pre-existing carbonates, no carbon is sequestered. Similarly, in "non-flushing" soils atmospheric carbon is sequestered in pedogenic carbonate if Ca is derived from silicates. On the other hand, if Ca is derived from pre-existing carbonate, then no carbon is sequestered. The same stoichiometry would apply to irrigated agricultural soils—sequestration depends on the source of Ca (Fig. 3.2).

Throughout geologic time high concentrations of carbon dioxide in soil air have been a consequence of root and microbial respiration made possible by photosynthesis. Without plants and photosynthesis soils would contain less carbon dioxide, which was the case in pre-Silurian time before the evolution of land plants (Berner 1992). Post-Silurian soils, however, are *generators* of inorganic carbon because of the bicarbonate-mineral-respiration-photosynthesis system that is driven by the sun's energy (Fig. 3.2). The amount of bicarbonate-C generated in soils is at least 0.40 Pg per year, which is the amount of carbon as HCO_3^- in the world's rivers (Schlesinger and Bernhardt 2013). Of this, about 37 % is from silicate weathering (Reaction 3.1) and 61 % from pre-existing carbonate weathering (Reaction 3.3) (Berner and Berner 1996). In addition to being generators of bicarbonate, soils are also *sinks* of inorganic carbon in the form of pedogenic carbonates in arid, semiarid, and subhumid soils.

Geologic Time and the Formation of Inorganic Carbon

Figure 3.3, in a single view, provides a broad-scale temporal and spatial framework for thinking about how inorganic carbon has changed in geologic time. This figure compares modern soil carbonate (USDA-NRCS 2000) with paleogeographic maps showing deserts and semiarid regions as tan to light brown, in contrast to humid vegetated regions that are shown as green and dark green. The upper two maps in Fig. 3.3 show the correlation of soil carbonate with deserts and semiarid regions of the present.

Assuming uniformitarianism, deserts and semiarid regions in the geologic past would have resulted from the following three conditions that create modern deserts and semiarid regions (Dick-Peddie 1991). First, they are located between 25° and 35° latitude where dry air from the Hadley cells, as viewed in cross-section, descends on the continents. Second, deserts and semiarid regions result from rain shadows on the leeward side of mountain ranges that scavenge precipitation from air cooled as it rises over lofty terrain. Third, deserts and semiarid regions form because they are located great distances from oceans, such as the drylands of central Asia. In addition to these hot and warm drylands, cold deserts also exist in polar zones (e.g., Antarctica) and in high elevation terrain (e.g., Tibetan Plateau).

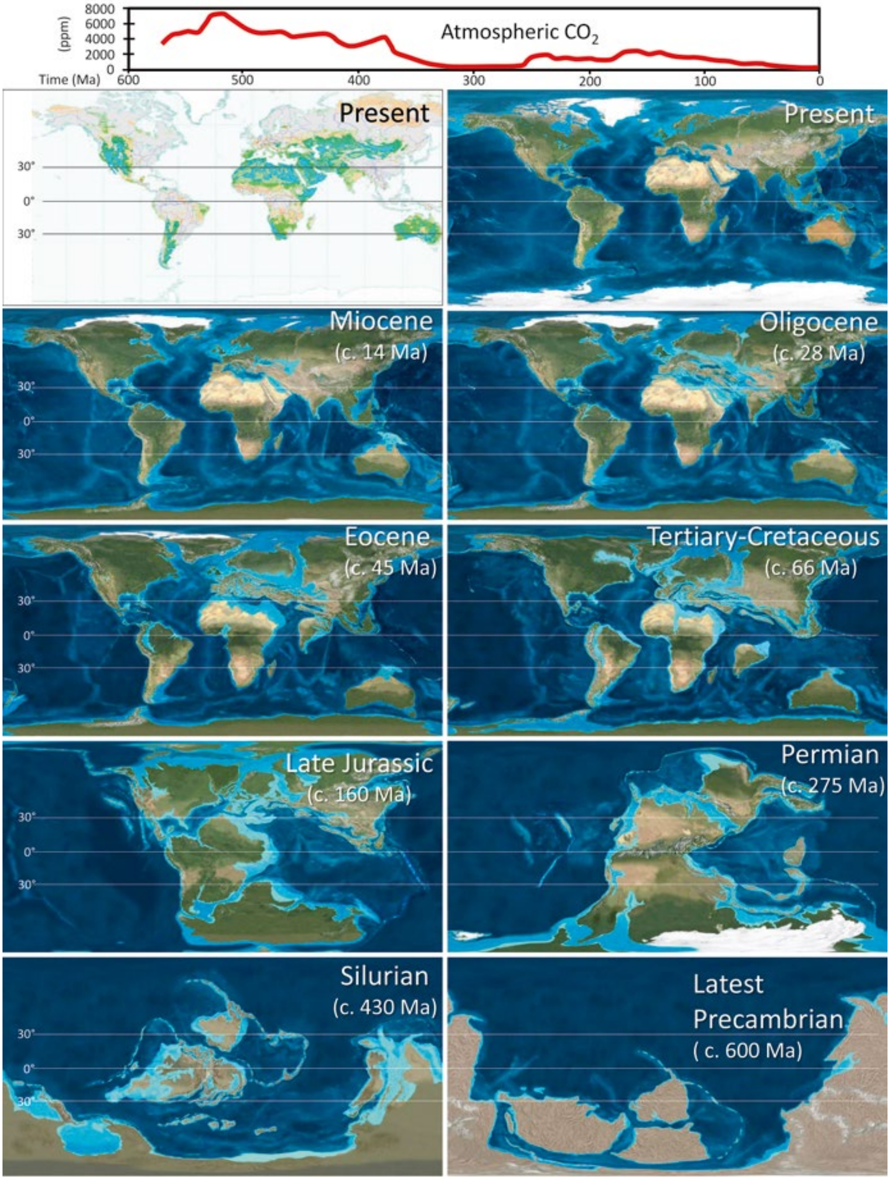

Fig. 3.3 Paleogeographic maps in which tan and brown colors correspond to zones with pedogenic carbonate, thus illustrating how pedogenic carbonate might have changed across geologic time. Dates are approximate mid-points of each era. Images courtesy of Colorado Plateau Geosystem, Inc. (http://cpgeosystems.com/paleomaps.html) (Images used with permission)

For pedogenic carbonate to be generated in modern soils (and presumably ancient soils) four conditions must be met. (1) The soil must have an alkaline pH. (2) There must be an active source of CO_2, namely root and microbial respiration, which is necessary for HCO_3^- production. (3) There must be available Ca^{2+}.

(4) The soil must occasionally contain moisture; but not too much moisture. That is, the formation of calcium carbonate is an aqueous phenomenon. Some deserts, like the driest zones of the Atacama, are too dry for pedogenic carbonate (Ewing et al. 2006). On the other hand, when rainfall increases above 500–760 mm, pedogenic carbonate does not typically form in soil profiles (Birkeland 1999; Royer 1999).

By starting with the oldest and working toward the youngest, we can see in Fig. 3.3 that the Precambrian map is unlike the younger paleogeographic maps because it lacks green colors on any continent, despite latitude, since land plants had yet to evolve—a phenomenon that occurred during the Late Silurian and Devonian (Kenrick and Crane 1997). The Precambrian landscape, therefore, was likely barren and gullied with abundant rock outcrops. On gentle slopes a chemically-weathered regolith, in some areas with an argillic horizon, probably resided atop bedrock. The landscape was probably not totally devoid of life based on carbon isotopes in pedogenic goethite (Yapp and Poths 1993). A cyanobacterial crust similar to certain types of modern soil biological crusts might have covered the soil surface.

By Silurian time when the continents were being progressively covered by vascular plants the conditions became increasingly suited for pedogenic carbonate formation. Carbon dioxide would have been pumped into soils by plants and soil air would have reached higher CO_2 concentrations than those in the atmosphere. Calcium would have been increasingly controlled by vascular land plants, as it is today (Yanai et al. 2005), in contrast to pre-plant times when it would have traveled with water controlled exclusively by gravity and evaporation. By late Silurian and Devonian time, pedogenic carbonates were forming in soils based on paleosol evidence (Mora et al. 1991, 1996). Several studies show that later in Paleozoic and Mesozoic time, pedogenic carbonates were widespread and provide evidence for climate change and concentrations of atmospheric CO_2 (e.g., Mack et al. 1991; Ekart et al. 1999; Lee and Hisada 1999; Tanner et al. 2001; Ziegler et al. 2002; Cleveland et al. 2008).

By late Cretaceous-early Tertiary time, continents began taking on their recognizable shapes including the formation of major deserts in Africa, North and South America, and central Asia (Fig. 3.3). Australia began its slow drift northward into the arid 30° latitude zone in the Cretaceous which continued through the Eocene, Oligocene, Miocene, and to the Present. Thus, the major deserts of today have generally existed for at least 60 million years. Pedogenic carbonates preserved in paleosols of these deserts and semiarid lands have provided important clues about paleoecology, especially the rise of C_4-photosynthesis (e.g., Quade et al. 1989; Cerling et al. 1993; Magioncalda et al. 2004).

Currently Earth is experiencing an abrupt rise in atmospheric CO_2 caused by fossil fuel burning and land use that is unprecedented during human evolution and modern ecosystems (Schlesinger and Bernhardt 2013). During the Phanerozoic, however, carbon dioxide in Earth's atmosphere was generally more concentrated than today's levels (Fig. 3.3). How did such high concentrations impact the formation of pedogenic carbonate? During the Cambrian, for example, atmospheric CO_2 levels were likely to have been almost 8,000 ppm (Berner 2004). Therefore, diffusion into soils would have caused those plant-free soils to also have been 8,000 ppm. Pedogenic carbonate, however, does not appear in Cambrian paleosols (based on literature searches by the author). Is the lack of Cambrian pedogenic carbonate the result of high CO_2 levels of that era? Probably not since CO_2 concentrations of 8,000 ppm are within the range of soil CO_2 in which modern pedogenic carbonate forms (e.g., Parada et al. 1983). Instead, the absence of pedogenic carbonate might be the result of an absence of land plants and their associated microorganisms. In the dries zones of deserts today, where there is an absence of plants, there is an absence of pedogenic carbonate (e.g., Bespalov 1964).

Conclusions

Vast amounts of research are being focused on understanding the consequences of higher levels of atmospheric carbon dioxide. Paleosols, both lithified (i.e., petrosols, McSweeney and Fastovsky 1987) and unlithified, provide a means to study the ecology and biogeochemistry in a higher-CO_2 world. Based on the paleosol record, inorganic carbon has been an important component of the global carbon cycle throughout the Phanerozoic, especially the weathering of Ca silicates that have resulted in massive amounts of carbon being stored as marine limestone (Berner 1999). Likewise, pedogenic carbonate that began forming after land plants evolved must have played a significant role in the global carbon cycle.

Carbon sequestration by inorganic carbon requires that the source of Ca be derived from silicates. However, carbon can also be sequestered as bicarbonate via the dissolution of pre-existing carbonate until it re-precipitates and releases CO_2 back into the atmosphere. There may be great potential for promoting carbon sequestration as inorganic carbon. It requires a manipulation of Ca from silicates, water, alkaline pH, and CO_2 (i.e. root respiration). In addition, because soil fungi and bacteria are agents of calcite biomineralization, they might also be manipulated to enhance inorganic sequestration. Inorganic carbon, unlike organic carbon which reaches an equilibrium with crops or native vegetation, can, in theory, be made to accumulate carbon up to the petrocalcic horizon stage. Another important aspect of inorganic carbon is its role in future climate change. That is, given the importance of a shrinking Cryosphere to the global carbon cycle, how would an expanding Aridosphere impact the global carbon cycle?

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Chapter 4
Organic Carbon as a Major Differentiation Criterion in Soil Classification Systems

Erika Michéli, Phillip R. Owens, Vince Láng, Márta Fuchs, and Jon Hempel

Abstract Soil is the largest terrestrial pool of organic carbon (OC), however the spatial distribution of the estimated 1.5–2.3 Tt organic carbon content of the soil cover has great variation horizontally and vertically. As organic carbon is one of the most important soil constituents, governing important functions and properties of soils, it is one of the major differentiation criteria in internationally used soil classification systems, such as Soil Taxonomy (ST) and the World reference base for soil resources (WRB), and most national systems. Several soil units at the highest level of the systems, such as surface and subsurface horizons, modifiers and qualifiers are defined on the basis of presence and amount of OC and/or depth and thickness of OC rich soil layers. As a result of the evaluation of current definitions of ST and the WRB, and analyses of international soil data sets (US NASIS and the ISRIC WISE) it was concluded that there are sufficient number of categories for expression of the amount, kind and vertical distribution of OC, however several of the definitions are very complicated, and not always consistent throughout the systems. This makes interpretation and also computation of categories difficult. With globally available data and mathematical tools, there is an opportunity to improve definitions

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and adjust arbitrarily set limits. An improved set of organic carbon related diagnostics could serve the needs of a future global classification system, mapping and monitoring OC, and also modeling of related estimations and processes.

Keywords Soil organic carbon • Soil classification • Diagnostics • Soil data • Numerical methods

Introduction

Topsoil properties, including OC content, are influenced by different factors such as climate, vegetation, topography and physiography, mineral soil constituents, surface processes, biological and human activity (Post et al. 1990; Lal 2004). Variability of OC in space and time makes it difficult to classify them. Perhaps that is one of the reasons that more attention is given to the subsoil in most soil taxonomic classifications. At the same time the top soil is the most important part for food production, and also is considered to be the most impacted by degradation processes and climate change. There is a need expressed for more detailed characterization of top soil and humus forms (Spaargaren and Nachtergaele 1998; Broll et al. 2006). The objective of this paper is to review the definitions related to OC of the two most commonly used international classification systems, how they approach the content, the composition, thickness or depth of organic matter as differentiation criteria?

Materials and Methods

OC related definitions of taxonomic and diagnostic units (horizons, materials, properties) as well as modifiers or qualifiers of Soil Taxonomy (Soil Survey Staff 2010) and the World reference base for soil resources (IUSS WG WRB 2006) were reviewed. The soil Characterization Data and the National Soil Information System of the US (USDA, NRCS, NCSS 2012), the ISRIC-WISE Harmonized Global Soil Profile Dataset (Ver. 3.1) (Batjes 2008) served to support the evaluations and study taxonomic relationships.

Taxonomic relationship studies were performed using a concept based approach, where selected ST units and WRB Reference soil groups (RSGs) were coded against selected identifiers (Minasny et al. 2009; Láng et al. 2013). These identifiers represented the soil moisture and temperature regimes, the presence and absence of diagnostic horizons, properties and materials. Identifiers were matched and coded against 47 selected soil units. On the basis of the matrix, Euclidean distances were calculated.

Results

In both systems **organic soils** (**Histosols**) are differentiated from **mineral soils** (all other soils) based on the presence or lack of a minimum amount and thickness of diagnostic "**organic soil material**" (OSM) (Table 4.1). These soils occur mostly in cold areas, and less attention was given to them than to those that have been more important for food production. Since the impact and consequences of climate change has become better understood on these soils, it became more important to know where they are, how deep they are and to what extent they are decomposed. As soils with 10 cm tick organic layer over hard rock or ice may qualify as Histosols, just as soils with a meter or several meters of organic material, current soil maps do not provide much information on the stock of OC stored in "organic" called soils. Thus it is suggested to review the depth criteria of the OSM for the taxonomic units.

In the studied soil classification systems we examined the OC content limit is set in function of the clay content for the OSM. However the determination of the clay content of organic layers is seldom done, creating unnecessary complication in establishing the diagnostic material. It is suggested to set only the OC limit.

The degree of decomposition of OSM is well defined based on the proportion recognizable plant fragments, such as: **fibric** having 75 % or more, **hemic** having between 15 and 75 %, and **sapric** properties having less than 15 % recognizable plant materials.

Among the mineral soils ST differentiates **Mollisols** at the highest (order) level based on the presence of high base organic matter rich epipedons (Mollic epipedon). The WRB differentiates four RSGs, the **Chernozems, Phaeozems, Kastanozems** similarly, and the **Umbrisols** without the base saturation requirement (Table 4.1). In other soils classified in ST and the WRB, the presence, composition and thickness and/or depth of organic carbon containing layers are recognized on lower levels of the systems.

Diagnostics

Both ST and the WRB define a great number of diagnostic units with OC as a major criteria. These diagnostics serve not only to differentiate soil taxa, but carry important information on properties that can be interpreted or mapped for different purposes. The OC related diagnostics are summarized in Table 4.2. In Soil Taxonomy there

Table 4.1 Soil units differentiated on the highest level of classification: order in Soil Taxonomy (ST); Reference Soil Group (RSG) in the World reference base (WRB) based on major criteria related to organic carbon (content and/or composition)

ST order	WRB RSGs	Criteria
Histosols	Histosols	Presence of organic soil material
Mollisols	Chernozems Kastanozems Phaeozems	Presence of mollic epipedon (horizon), and high base saturation
	Umbrisols	Presence of mollic or umbric (horizon)

Table 4.2 Diagnostic units (horizons, materials, properties) Soil Taxonomy (ST); Reference Soil Group (RSG) in the World reference base (WRB) with strong criteria related to organic carbon (OC)

ST order	WRB RSG	Organic carbon related criteria (not all criteria are listed)
Organic soil material	Organic material	Minimum organic carbon content (18 %)
Histic epipedon	Histic horizon	Presence and minimum thickness of organic soil material (wet conditions)
Folistic epipedon	Folic horizon	Presence and minimum thickness of organic soil material (aerated conditions)
Mollic epipedon	Mollic horizon	Minimum organic carbon content (0.6 %) and thickness of the horizon (high base)
	Voronic horizon	Minimum organic carbon content (0.6 %) and thickness of the horizon (high base)
Melanic epipedon	Melanic horizon	Specific organic matter nature[a] higher minimum organic carbon content (6 % weight average), and thickness of the horizon
	Fulvic horizon	Specific organic matter nature[a] minimum organic carbon content (6 % weight average), and thickness of the horizon
Umbric epipedon	Umbric horizon	Minimum organic carbon content (0.6 %) and thickness of the horizon (low base)
Anthropic epipedon	Anthric horizon	Minimum organic carbon content (0.6 %) and thickness of the horizon (mollic like with anthropogenic influence)
Plaggen epipedon	Plaggic horizon	Minimum organic carbon content (0.6 %) and thickness of the horizon (mollic like with anthropogenic influence and artefacts)
	Hortic horizon	Minimum organic carbon content (1 %) and thickness of the horizon (anthropogenic influence, high phosphate content)
	Irragric horizon	Minimum organic carbon content (0.5 % weight average) and thickness of the horizon (with anthropogenic influence)
Spodic materials	Spodic horizon	Minimum organic carbon content (0.6 %) (subsurface accumulation)
Sombric horizon	Sombric horizon	More organic carbon than the overlaying horizon (subsurface accumulation)
	Fulvic material	Minimum organic carbon content (0.2 %) at 1 m depth

[a] Higher humic acids ratio compared to fulvic acids in the melanic horizon than in the fulvic horizon, determined by the melanic index (Soil Survey Staff 2010; IUSS WG WRB 2006)

are 9 diagnostic horizons and 1 diagnostic material, while the WRB defines 13 diagnostic horizons and 2 diagnostic materials with OC criteria. It seems that there are a great number of diagnostic horizons that are interpreted as organic matter rich mineral horizons with a minimum OC content of 0.6 %, and there are few with 2 or 4 % OC criteria. After reviewing the OC content of soils with mollic or umbric horizons it was found that the majority of them contain more than 1 % OC. In the WISE database 92 % of the studied Chernozems, Phaeozems, Kastanozems and the Umbrisols (all together 860) profiles, and in the NASIS bases 89 % of the Mollisoll (6557) profiles, we examined, have more than 1 % OC content. Those that have less than 1 % OC, belong mostly to the Natrixeroll, Natrudoll, Duraquoll, Durixeroll great groups. We suggested adopting a minimum criterion of 1 % OC criteria for the mollic and umbric horizons.

The OC content has been a problem with degraded agricultural soils. Many that lost the OC% for the current mollic diagnostic designation would satisfy only the ochric epipedon (horizon) criteria. Beside the need for stronger criteria for the mollic horizons an "intermediate" horizon between the mollic and the ochric is proposed, for better differentiation between agricultural soils and to provide useful information for regional and global carbon calculations.

Table 4.2 gives a summary of OC related criteria from definitions of the ST and WRB diagnostics. Unfortunately in both systems, most of the definitions are long, complicated and include some criteria that are difficult to establish or measure and often missing in national databases, making it difficult to derive or compute the diagnostic units. As an example, the definition of the Mollic epipedon in Soil Taxonomy includes 9 major diagnostic requirements, 6 sub requirements, 2 have 3rd level sub requirements, it includes 10 *"or"*s and 12 *"and"*s.

Modifiers, Qualifiers

Modifiers and qualifiers are applied to indicate the presence of diagnostics that reflect important properties of other "intergrading" classes, or to express the presence, composition or distribution of OC in the classified soil (Table 4.3). In the WRB the definitions are used consequently throughout the system, however in ST there is a great inconsistency in the application of the same modifiers. The mollic and umbric is applied in 5, the humic in 9 and pachic in 7 alternative definitions for different taxonomic levels or units of ST. Beside confusion in differentiation it makes interpretation, teaching and property mapping difficult.

It is suggested to simplify and apply single, harmonized definitions in both systems.

The Results of the Numerical Studies

Mollisols are differentiated from other soils based on the presence of the mollic or similar horizons. Numerical studies were performed to study the taxonomic relationships between Mollisols greatgroups. The distance matrix resulted from the calculations

Table 4.3 Modifiers and qualifiers applied in Soil Taxonomy (ST) and the World reference base (WRB) to indicate the presence of humified OC accumulation

ST	WRB	Criteria
Mollic (Umbric)	Mollic (Umbric)	Refers to the presence of mollic epipedon or umbric horizon in soils that are not classified on the highest level based on those horizons (ST, WRB), or refer to similar horizons not fully satisfying the criteria of those horizons (ST)
	Rendzic	Presence of mollic horizon that overlies calcaric material containing certain amount of $CaCO_3$
Humic	Humic	Indicate OM accumulation to certain depth
Pachic	Pachic	Indicate thick mollic (umbric) horizons
Cummulic	Cummulic	Indicate OM accumulation through sedimentation to certain depth

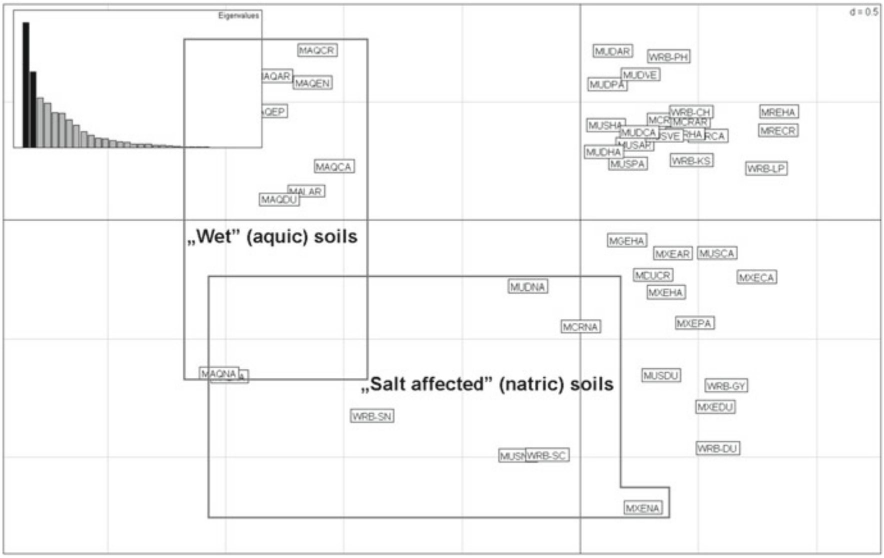

Fig. 4.1 Selected soil units plotted on their first two principal coordinates based on a concept based distance matrix. Codes were created according to the SSURGO nomenclature: "M" in the beginning represents Mollisol order, next four letters are a combination of the followings: AL-Albic, AQ-Aquic, AR-Argic, CA-Calcic, CR-Cryic, DU-Duric, EN-Endo, EP-Epi, GE-Gelic, HA-Haplic, NA-Natric, PA-Pale, RE-Rendzic, UD-Udic, US-Ustic, VE-Vertic, XE-Xeric. WRB RSGs were coded as follows: WRB-SN-Slonetz, WRB-SC-Solonchak, WRB-LP-Leptosols, WRB-DU-Durisols, WRB-GY-Gypsisols, WRB-CH-Chernozems, WRB-KS-Kastanozems, WRB-PH-Phaeozems

was transformed into principal coordinate axes and soil groups were plotted on their first two principal coordinates (Fig. 4.1). Calculation plotted the "wet" (aquic) and "salt affected" (natric) great groups to separate them from the rest of the Mollisol great groups. This suggests that the OC rich mollic horizon may not be the best differentiation criteria for those soils.

Conclusions

The systems we examined have great number of units to express the presence, content, thickness, and composition of OC. Introduction of new units should be limited. The current definitions of the existing diagnostic and taxonomic units are often complicated and have arbitrary set limits. Simplification of definitions and revision of limits is recommended. The accumulated data and numerical tools proved to be useful for improving our current systems and support the development of a universal soil classification system.

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Chapter 5
Quantitatively Predicting Soil Carbon Across Landscapes

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Abstract Quantitative prediction of soil carbon (C) in the landscape can be achieved by empirical or mechanistic models, or a combination of both. The empirical approach called digital soil mapping, usually involves: collection of a database of soil carbon observations over an area of interest; compilation of relevant covariates for the area; calibration or training of a spatial prediction function based on the observed dataset; interpolation and/or- extrapolation of the prediction function over the whole area; and finally validation using existing or independent datasets. The resulting digital maps of C can be used in landscape mechanistic models simulating soil organic C evolution laterally and vertically (within the profile). Here we

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demonstrate the two approaches in predicting C stock evolution in a landscape in Northwest of France. We introduce the pedogeomorphometry approach which can combine the two approaches to map soil carbon dynamics at the landscape scale.

Keywords Soil maps • Clorpt model • Spatial prediction • Dynamic soil carbon model

Introduction

Climate change, which is manifested in change of temperature, elevated CO_2 concentrations, increased rainfall variability, and extreme weather events, will have a great impact on soils. It will create a feedback between soil and the environment, and understanding the biological, chemical, and physical processes governing soil functions is related to many of the grand challenges in environmental science. As soil systems are a significant terrestrial sink of carbon, predicting the spatial distribution of soil carbon has been of interest as exemplified by the increasing number of publications in mapping soil carbon stock globally and nationally (Minasny et al. 2013).

At a global scale, the variation in soil organic carbon (SOC) and inorganic carbon (SIC) is large. SOC content is greater at higher latitudes, decreases in the mid-latitudes, and increases in the tropics (Fig. 5.1). This pattern follows the global mean annual precipitation, where the tropics have a maximum precipitation, and a peak around 50°N. The high C content at high latitudes corresponds to the low temperature

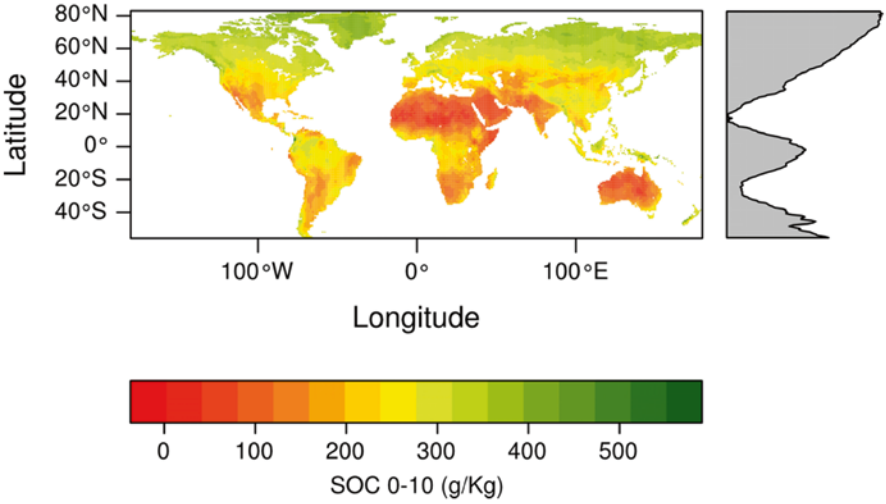

Fig. 5.1 A global map of soil organic carbon content 0–0.1 m. The map was generated using an empirical model relating the soil carbon data from the ISRIC-WISE global profile database to climate (mean annual temperature, precipitation, radiation, evapotranspiration) and a topographic variables (topographic wetness index)

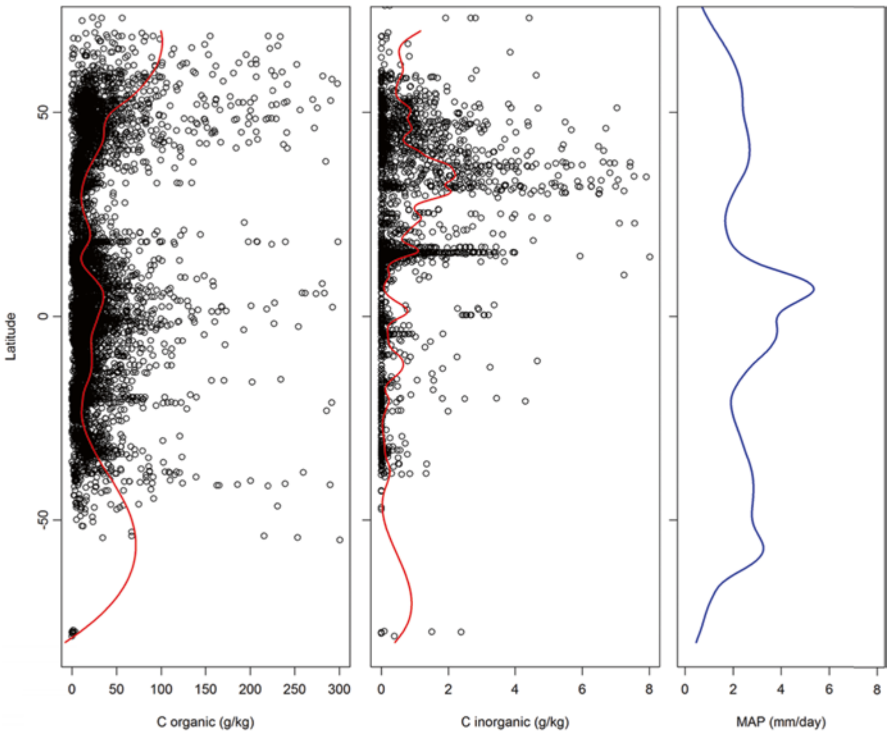

Fig. 5.2 The average soil organic (0–0.1 m) and inorganic carbon (0–1 m) content and mean annual precipitation as a function of Latitude. The *dots* are data from the ISRIC-WISE global profile database (Batjes 2008), the *red lines* are smoothed spline fitted to the data. MAP is the zonally averaged mean annual precipitation rate from Adler et al. (2003) (Color figure online)

regimes and reduced decomposition. Conversely, SIC occurs in areas with low rainfall (30° N), and has an inverse relationship with SOC between −40 and 50°N (Fig. 5.2).

The need of information on soil carbon distribution has made research in Digital Soil Mapping (DSM) progress rapidly in the past decade, making it operational for routine mapping over large areas to landscapes (Bui et al. 2009). A review on digital mapping of soil carbon at various spatial scales was presented in Minasny et al. (2013). This chapter will review some early work on DSM and SOC and then will focus on the aspects of predicting soil carbon in space and time in the landscapes using empirical and mechanistic modelling approaches.

Early Work on Digital Mapping of Soil Carbon

Jenny's (1941) *clorpt* model is mostly used where a factor is varied, while the other is held constant (*ceteris paribus*, e.g. chronofunctions, topofunctions), where 'the clorpt formula was taken apart and explicit factor sequences were secured'. In a presentation at the "Study Week on Organic Matter and Soil Fertility" (April 22–27, 1968) organised by the Pontificia Academia Scientiarum (one of the early global soil organic matter conferences), Jenny et al. (1968) presented an "integrated clorpt" model, where all clorpt factors were simultaneously modelled in the form of a multivariate linear regression:

$$\begin{gathered} \mathrm{C} = \mathrm{a} + \mathrm{k}_1\,\mathrm{MAP} + \mathrm{k}_2\,\mathrm{MAT} + \mathrm{k}_3\,\mathrm{Parent\,Material} \\ + \mathrm{k}_4\,\mathrm{slope} + \mathrm{k}_5\,\mathrm{Vegetation} + \mathrm{k}_6\,\mathrm{Latitude}, \end{gathered}$$

where C is the soil organic carbon content, and k are empirical constants. This model was calibrated based on 97 topsoil samples (0–20 cm depth) collected along a moisture transect from deserts in 35°N latitude to high rainfall of 41°N. In the model, Jenny realised there were correlations among the factors, which was addressed using principal component analysis (PCA). This paper is one of the early papers that used PCA for soil data, and one of the first attempts to model soil carbon as several factors of soil formation. He found that for soil carbon, precipitation was the strongest exploratory variable ($R^2 = 0.45$), followed by temperature ($R^2 = 0.09$), parent material ($R^2 = 0.06$). In this regional dataset, the influence of slope was minimal ($R^2 = 0.01$). The model is mostly used to explain the factors that control the distribution of soil carbon (and nitrogen, and acidity), not as a prediction function.

Research from the Laboratory for Applications of Remote Sensing in Purdue (Al-Abbas et al. 1972; Kristof et al. 1973) proposed 'Spectral Mapping of Soil Organic Matter' using soil reflectance from the visible and near infrared signal of an airborne scanner. Here a numerical classification procedure was used to group the data into classes that represent the distribution of soil organic matter (SOM). This type of work is still being continued, as exemplified by Frazier and Cheng (1989) who devised a linear relationship between with organic carbon content and Landsat TM Band ratio 5/4 (SWIR/NIR) for mapping SOM in a landscape extent.

Soil spatial models for carbon mapping started to appear with the advent of digital elevation models (DEM) in the early 1990s. Simple linear models have been developed for spatial prediction of soil properties in a field, notably by the studies of Moore et al. (1993) and Gessler et al. (1995) which related soil carbon (among other properties) to topographic indices. Arrouays and Pelissier (1994) made a spatial prediction model specifically for surface soil carbon pools in forest soils in France using climatic, geomorphological, and pedological data in the form of a multiple linear model. McKenzie and Ryan (1999) introduced the use of a regression tree approach to model soil carbon and other soil properties in the Bago and Maragle State Forests in south-eastern Australia. On the continental scale, Henderson et al. (2005) were among the first to employ a data-mining approach (regression rules) for spatial prediction of soil properties over Australia. This approach is different from conventional methods used at a continental scale, where soil carbon is derived by linking soil mapping units (soil classes) with look-up tables (Batjes 1996).

These approaches were then formalised as Digital Soil Mapping by McBratney et al. (2003):

$$C_{\mathrm{x}} = f\left(s,c,o,r,p,a,n\right) + e$$

where soil carbon *C* at spatial position *x* is a function of soil factors (*s*), climate (*c*), organisms which include landuse, human effects, and management (*o*), relief (*r*), parent materials (*p*), age or time (*a*), spatial position (*n*), and *e* is the spatially correlated errors. Except for the "time" or "age" factor, most digital soil mapping examples have either explicitly or implicitly used these factors for prediction of soil carbon. The digital soil mapping approach usually involved: collection of a database of soil carbon observations over the area of interest; compilation of relevant covariates (*scorpan* factors); calibration or training of a spatial prediction function based on the observed dataset; interpolation and/or extrapolation of the prediction function over the whole area.

Spatial Model

The *f* model has evolved from multiple linear regression and PCA to geostatistics, linear mixed modelling (considering spatial correlation of the residuals), and data mining techniques. In linear (mixed) models, the model can be explicitly written out and explained (Rawlins et al. 2009). Figure 5.1 is an example of a map based on Jenny et al. (1968)'s multilinear approach. While this type of model is still being developed (Gray et al. 2012) much of the research on digital soil mapping now employs the data-mining approach (Grimm et al. 2008; Wiesmeier et al. 2011). In data mining, the models are usually treated as a black box. While some models can be explicitly written out, it is usually complex and difficult to interpret. Instead, the results (expressed as significant predictors) are interpreted as 'knowledge discovery' from databases which were *a posteriori* justified by principles of soil genesis (Bui et al. 2009). As opposed to a mechanistic model which firstly defines the process, the empirical approach learns the process mechanisms through the data. The model thinking is reversed (which can have opposite effects), where some new knowledge can be discovered through the data, or the results can became a self-confirming theory.

While the model complexities have increased, the number of soil observations per unit area has not increased much as soil data are still expensive to collect. The complexity of the model should be balanced with the number of observations, and most often, users do not realise that there are more parameters in their models than available soil data. As an example, the Random Forests technique has been used widely in digital soil mapping as it was claimed that "Random Forests does not overfit. You can run as many trees as you want" (Breiman and Cutler 2004). Many DSM practitioners recite this mantra without questioning its rationality. It can be shown easily with soil carbon data, where the relationship between soil properties and covariates can be weak, yet Random Forests model can fit the data perfectly (Minasny and McBratney 2013). Often explicit linear models are useful as a starting point for exploratory data analysis. Recent popular models in pattern recognition and artificial intelligence such as "deep-learning" may be too rich to be applied to soil data that are scarce and sparse (Bengio et al. 2012). But in the future such models could be useful.

Resolution and Uncertainty

An important output of digital soil mapping is the availability of an uncertainty or measure of confidence in prediction. Most studies do not show the uncertainty of prediction even though they are critical in determining the prediction confidence (Minasny et al. 2013). Soil carbon has been mapped using digital soil mapping technology at the field, regional, national and continental scale with sampling densities ranging from 0.001 to 1,000 samples per km^2. Generally, the grid spacing (resolution) of the digital maps increases logarithmically with extent, and the grid spacing decreases logarithmically with sampling density. Although there is no strict rule for sample density and grid spacing in digital soil mapping, it does not mean that we can confidently generate maps at a fine resolution with low data densities. In conventional soil maps, a finer scale map implies a greater accuracy (Leenhardt et al. 1994) as more field work was conducted and more samples were analysed. There is a misconception that finer resolution digital maps are more accurate (Kim et al. 2012). This is not necessary true, as it depends on the data density and pedodiversity of the area. The uncertainty of prediction should reflect the observation density in the maps. If a digital map was made at a 100 m resolution with a low data density (e.g. 1 sample per 1,000 km^2), the uncertainty of this map should be higher compared to a map that was made at resolution of 1 km. Simply because the observations cannot capture the whole variability at 100 m, and there is more extrapolation in the 100 m covariates, compared to using 1 km covariates. There are no general guidelines but some suggested data densities are given in Table 5.1. It needs to be stressed that larger data densities are required for regions with larger intrinsic pedodiversity and where the legacy sampling is clustered in space or with respect to other covariates. The lower limit of the suggested density should cover most of the covariates space.

Table 5.1 Suggested grid spacing and data density for digital soil mapping

Grid spacing	Suggested data density (n/km^2)	Equivalent soil mapping scale	No. sites required for conventional maps (n/km^2)
10 m	0.01–1	1: 20,000	5–20
100 m	0.001–0.01	1: 200,000	0.05–0.20
1,000 m	0.0001–0.001	1: 2000,000	0.0005–0.002

Predicting Soil Carbon in the Landscapes

While the *scorpan* model has been successfully used to predict the spatial distribution of soil carbon, the empirical relationships are non-transferrable. The dynamics of SOC with time means that the time dimension should be considered in the mapping. From empirical geostatistical approach, SOC data can be interpolated using spatio-temporal kriging (Van Meirvenne et al. 1996), but this approach is not dynamic, and cannot be extrapolated for scenario modelling. Moreover there are very few datasets that have complete space-time coverage.

Mechanistic models of SOC have been used to predict the state of change in SOC (Jenkinson and Coleman 2008). Most mechanistic models represent only the topsoil and have no spatial component – it needs calibration, and the state or initial condition of the soil needs to be known. SOC at a landscape extent is usually simulated using existing models by running the model individually at each pixel, based on the likely scenario, e.g. climate change or changes in land management. However, the structure of the model is usually left unaltered, without considering vertical and lateral fluxes of soil organic matter (SOM). While landscape evolution models have progressed rapidly in the field of geomorphology (Willgoose 2005), SOC modelling at the whole landscape extent is still in its infancy. The need to explicitly model soil carbon at the landscape extent was highlighted by Viaud et al. (2010), and they proposed that a mechanistic soil carbon model that operates on a landscape scale should consider: the relevant features of the landscape (patterns of soil-landscape heterogeneity), SOM transfers within the soil in both the lateral and vertical dimensions, and patterns of SOM input should also be modelled accurately. They concluded that relevant procedures for model calibration, validation, and uncertainty assessment should be developed.

Here we will demonstrate the integration of digital soil carbon mapping and landscape SOC modelling. Lacoste et al. (2012) produced a high resolution 3-D map of soil carbon stocks from the soil surface to a depth up to 105 cm, at a spatial resolution of 5 m in a heterogeneous agricultural landscape in North-Western France. Under the digital soil mapping framework, a data mining tool was used to build rule-based regression models to predict SOC content and bulk density at a resolution of 2 m at 8 standard layers for the whole area of 10 km^2 (0–7.5, 7.5–15, 15–30, 30–45, 45–60, 60–75, 75–90 and 90–105 cm). The detailed maps (Fig. 5.3) showed the variation of SOC stocks within fields, which is mainly in relation to distance to the hedges and local topography. An independent validation dataset showed that the prediction of SOC content has an R^2 value of 0.33 and a root mean square error (RMSE) of 7.47 g kg^{-1} for all the layers. The best predictions were obtained for layers between 15 and 60 cm of depth.

The digital soil map was used as input in a mechanistic landscape SOC model (Lacoste 2012). This model had two modules: a soil redistribution model, which simulated soil erosion and deposition induced by rainfall and tillage (Ciampalini et al. 2012). The model used an initial topography (DEM) as the input data. At each time step (described by a rainfall or tillage operation), LandSoil produces an updated DEM,

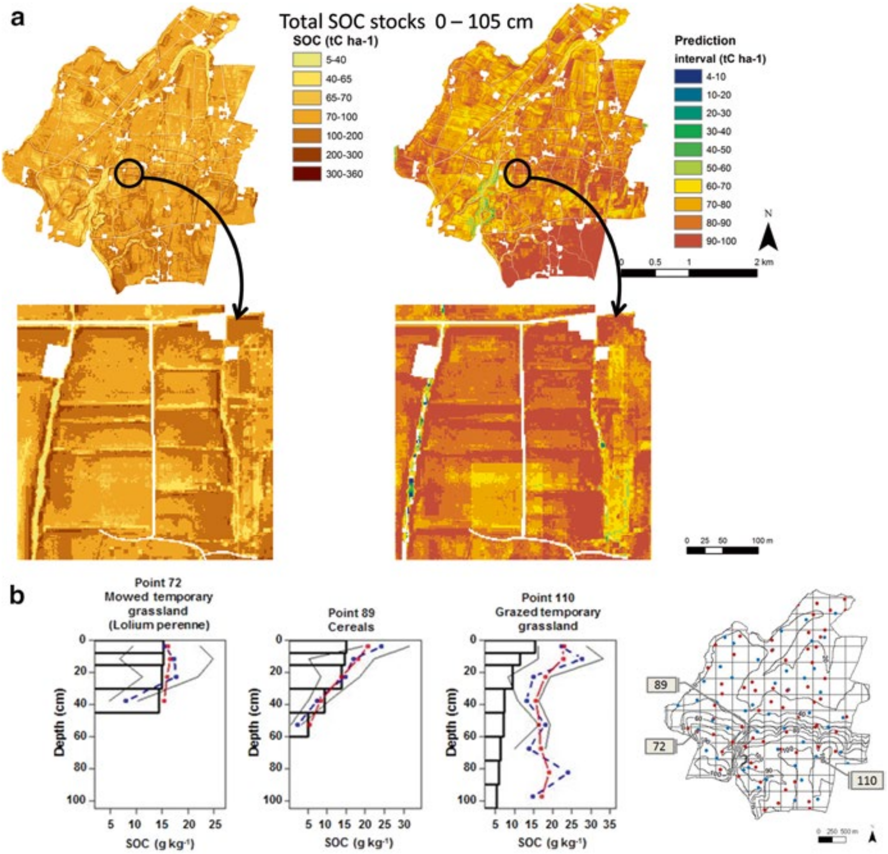

Fig. 5.3 (**a**) Maps of SOC stocks (0–105 cm) (*left*) and its 95 % prediction interval (*right*), over the 10 km^2 study area in North-West France, with a local zoom on a 60 ha area (*bottom*). (**b**) Examples of soil profiles reconstruction on three randomly selected points on an independent validation dataset (*box-plot*: measured data, *blue dashed line*: predicted values, *red line*: reconstructed of soil profile using the mass preserving splines, and *thin black lines* are the upper and lower 95 % prediction interval) (Color figure online)

which is used as input in the SOC dynamic model. The SOC model is an adaptation of the RothC model which simulates SOC dynamics laterally and vertically within a profile (Viaud et al. 2011). The simulation was conducted in an area of 1 km^2 within the mapped region (Fig. 5.4a) over the period from 2010 to 2100 with two climate change scenarios: Business as Usual (BAU), which showed the same trends as those observed in the past, and the A1B climate, which simulated a global warming (increase in mean annual temperature and decrease but more intense mean annual precipitation). Different landscape management scenarios were also simulated, taking into account land use (crop rotation) and land management (presence or absence of hedges). Thus, the interaction between land use and climate change were modelled.

The BAU landscape scenario was simulated using BAU crop rotations for each field and the hedges network as observed in 2010. Figure 5.4b shows the variation of SOC stocks during the simulation period for the BAU scenario. Although there is an average of 25 % loss of SOC over the whole farm (from 2010 to 2100), there is a strong spatial differentiation, some areas are less or more sensitive to climate or landscape change. The erosional areas has a mean loss of 3 t C/ha, while depositional areas gained 4 t C/ha. Figure 5.4c demonstrates the different climate and landscape change scenarios on SOC stocks. While climate change induced a loss of SOC for all the scenarios, land use has the greatest impact on SOC dynamics at the landscape scale (Lacoste 2012).

Pedogeomorphometry

The study demonstrated that SOC can be mapped in great detail and that a landscape simulation model can be used to predict changes in SOC. However, we can reverse the role: to use process-based understanding in the mechanistic model for better predictions of the SOC spatial distribution. The next step is to integrate soil and landscape modelling in space and time under the pedogeomorphometry concept. This concept attempts to combine pedometrics, digital soil mapping, and soil dynamic modelling for a better representation of soil properties, processes and entities. The process-based model has advantages over the empirical *scorpan* approach, where the processes of C distribution are modelled explicitly. The process-based model will still use environmental covariates as drivers and the boundary conditions:

- *s*oil, which will affect the soil-carbon protection and stability of carbon;
- *c*limate, affecting decomposition;
- *o*rganism, or landuse, affecting both input and stability;
- *r*elief, affecting the lateral distribution of carbon, and moisture distribution through its landscape attributes: slope, aspect, wetness index;
- *p*arent material, affecting clay mineralogy thus the carbon-clay association;
- *a*ge, explicitly modelled as time;
- spatial positio*n*, affecting the lateral distribution and transport.

Another leap in the modelling is that the process-based model can be combined with an empirical statistical model. This fits in with the Bayesian Hierarchical Modelling approach (Cressie and Wikle 2011), which enables a coherent use of all observed data, allows the incorporation of process-based relationships, and accounts for the uncertainty in the processes that generated the data. There is a self-correcting mechanism when there is little known about the process-based relationships, or when there are data is limited or of poor quality. The resulting uncertainty would be large. When the process-based model has low precision, it allows to look for unexplained or missing processes that need to be modelled. When the data are limited or dated, it allows for identifying areas of future investment.

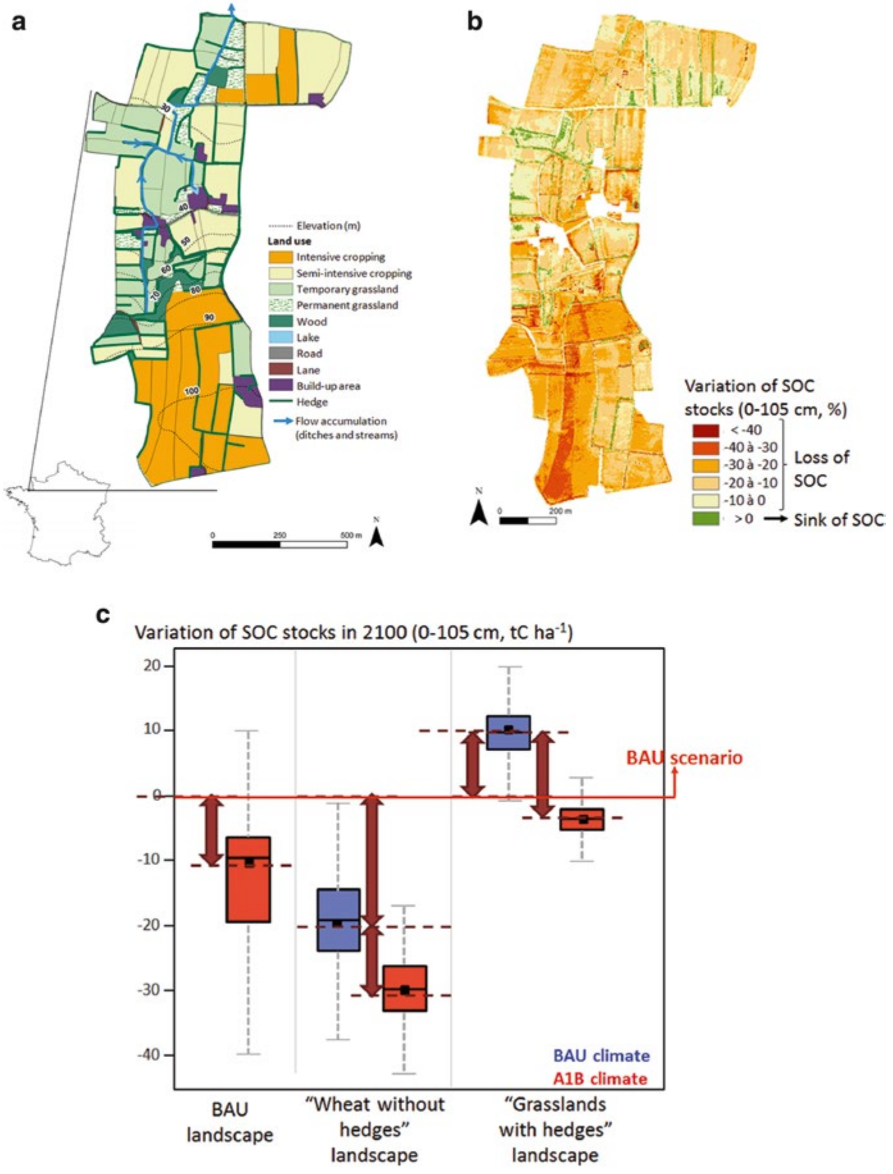

Fig. 5.4 (**a**) A map of the study area and its current land use, (**b**) the predicted change of SOC stocks from year 2010 to 2100 for the BAU (landscape and climate) scenario, (**c**) the differences in SOC stocks (0–105 cm) at the end of the simulation period in 2100 under different landscape-climate scenarios with those simulated in 2100 under the reference (BAU) scenario

Conclusions

Advances in computing, spatial databases management and numerical modelling has accelerated the development of digital soil mapping and it has moved from a research stage to operational. This chapter emphasised several issues that need to be considered to advance the art and science of mapping soil carbon at the landscape scale:

- Obtaining representative soil samples for spatial modelling is important. The soil-landscape relationships using the *scorpan* model only describes the empirical correlation found from the data.
- Model parsimony should be considered when building spatial prediction models. We need a more disciplined approach solidly grounded in soil science and statistical theory. At the same time we do need to exploit the power of the computer to search for structure in large data sets.
- Optimal resolution and uncertainty need to be carefully thought through. The balance between sample densities and resolution of the map need to be balanced. The rapid increase in the use of digital soil mapping has not been accompanied by an associated increase in the use of uncertainty assessment.
- The dynamics of soil carbon with time means that we need to consider the time dimension in our maps. A soil landscape carbon model provides a better digital soil assessment of soil carbon. Modelling SOC stocks evolution at the landscape scale, required the lateral process (soil redistribution by tillage and water processes), and also vertical process (bioturbation). Soil redistribution by tillage and tillage can be an important contribution of SOC loss.
- Pedogeomorphometry unites the mechanistic simulation model and empirical data to deepen the knowledge of soil carbon distribution in space and time. As was learnt from empirical studies, the covariates used by data mining models can infer the biophysical drivers of soil carbon distribution. However, we can also use our dynamic understanding of the soil-landscape system to better understand and predict the distribution and changes. This approach will present a dynamic representation of soil carbon where digital soil assessment can be easily incorporated.

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Chapter 6
On Soil Carbon Monitoring Networks

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Abstract The design of a Soil Monitoring Network (SMN) poses numerous scientific challenges, especially for the assessment of national or continental areas. The task is particularly challenging because soil carbon content and stocks are driven by controlling factors of disparate origins and scales. Various approaches to the establishment of SMNs are reviewed here. Frameworks for soil monitoring exist in numerous countries, especially in Europe. Although some countries work using standard monitoring methodologies and coverage, there is considerable variation in approaches to the monitoring of soil carbon even within a country. In addition to achieving harmonization, there are generic issues which must be addressed when SMNs are established and operated: the SMN should be effective for different soils, and it must enable the detection of change in soil carbon at relevant spatial and temporal scales with adequate precision and statistical power. We present examples which address these issues and summarize previous reviews on this topic. It is essential to establish an adequate sampling protocol which can be applied at each sampling location and time. The design must address the questions that the user of

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data has and provide information with accuracy and precision at the spatial and temporal scales that match the users' needs. Furthermore, the design must match the methods of analysis so that statistical assumptions can be justified. At the global scale, the question of harmonizing sampling and analytical methods is difficult. Here, we propose the establishment of benchmark sites devoted to harmonization and inter-calibration. We present a case study from France which addresses scientific issues such as how many calibration sites are necessary and how they should be selected.

Keywords Soil • Carbon • Monitoring

Introduction

Worldwide, soils contain about 2,000 gigatons of organic carbon. A small relative change in soil organic carbon (SOC) stocks has significant effect on the net flux of greenhouse gases between the soil and the atmosphere. Climate change and changes in land use and agricultural production practices could contribute to this, notably by changing the magnitude and the duration of organic carbon storage in soils. The residence time of carbon in the soil organic matter is variable and depends on the rate of carbon mineralisation, through which organic carbon is returned to the atmosphere. The uncertainty of predictions in soil organic carbon stocks obtained with process models is large. It is therefore important to monitor the status of the soil organic carbon pool and its variation between soil types, their uses and associated practices, and over time. In order to comply with the Kyoto Protocol, it is also necessary to know how and with what precision the soil organic carbon pool can be measured and monitored. The monitoring of SOC is also important for issues other than climate change. Sustainable intensification (SI) is a strategy to achieve food security (Foley et al. 2011). The principle of SI is to achieve larger crop yields by management to optimize the effects on the agricultural system of natural processes such as nutrient cycling, and to minimize negative impacts on natural resources from intensification. Soil organic matter concentrations and dynamics are crucial to the management of agricultural soils and SOC is a key indicator of whether soils are being degraded. It is therefore important to monitor SOC so that the success or otherwise of SI can be evaluated.

In this chapter, we review some issues of soil carbon monitoring networks (SCMN), including the design and implementation of sampling in space and time, the development of statistical techniques which can be used to describe the patterns of spatial and temporal variations of soil carbon, and harmonisation issues. We also review some major results from SCMN, including demonstrated changes, minimum detectable changes and recommended time-steps for monitoring.

Several reviews of soil monitoring networks (SMN) which measure SOC have been published recently (e.g., Morvan et al. 2008; Saby et al. 2008a; van Wesemael et al. 2011; Arrouays et al. 2012). Morvan et al. (2008) reviewed the

SMNs of 27 European countries. They defined a SMN as “a set of sites/areas where changes in soil characteristics are documented through periodic assessment of soil parameters”, and they pointed out that official frameworks for comprehensive soil monitoring exist in most European countries. Although some countries work to common standards of monitoring methodology and coverage, there is often variation in approaches to the monitoring of soil carbon, even within a country. Geographical coverage by SMNs differs between and even within countries. Most of the SMNs have been sampled only once, so they are inventories. Saby et al. (2008a) used the data collected by Morvan et al. (2008) to calculate the time necessary to prove a significant change in SOC. They showed that in most countries, it will take at least 10 years to detect a significant change in SOC. The ability to detect changes mainly depends on their rates, the accuracy of measurements, the number of sites or replicates, the analytical method and the spatial variability of C. Van Wesemael et al. (2011) reviewed the SMNs of ten different countries. They distinguished two kinds of SMN: those that aim to characterize the SOC response to changes of land use or land management or both, and those designed for national or regional SOC monitoring. Arrouays et al. (2012) distinguished three broad approaches to the establishment of SMNs: (i) the design and construction of purpose-built SMNs, (ii) re-sampling of the soil at sites where measurements have previously been made for other purposes, and (iii) compilation and analysis of soil data which have previously been collected for other soil analysis purposes or experiments. The review mainly focused on sampling design and statistical aspects. All these reviews raised some generic issues which we summarize here.

How Many Sites and Where?

The locations for the installation of SMN sites may be influenced by various factors: (i) the use of a particular design (e.g. grid-based or independent random site selection), (ii) the intention to obtain a sample which is representative (landform, soil types, land use, specific site-related situations), which should be achieved by the selection of an appropriate design, (iii) the objective to monitor soils under specific land uses or unusual conditions, (iv) an associated objective to record and/or control land use and practices, (v) the availability of soil legacy data, (vi) design considerations to investigate particular effects, such as the pairing of sample sites to compare management effects between similar soils, (vii) the integration of sites into other currently-established ecological observation areas. There are extensive discussions about the choice of sample design (Brus and de Gruijter 1997; de Gruijter et al. 2006; Arrouays et al. 2012). For a single-date survey, Brus and de Gruijter (1997) distinguished three types of questions: the first is “how much?”: the user requires a quantitative estimate of some variable, typically its spatial mean (which may be a status or a change) across some region. The second question is ‘where?’: the user wants to know how the target variable varies in space, typically to be presented as a map. The third question is a combination ‘how much and where?’: estimates of global means are required, and associated maps of the corresponding spatial variation. Brus and de Gruijter (1997) proposed a decision tree for choosing between design-based and model-based sampling strategies to answer such questions from responses to a series of questions. The sampling design should take into account the questions that we want to answer, the spatial and time scale to be addressed, and the precision that the users require. For example, if the objective is to demonstrate the effect of management practices on changes in SOC, then sampling at paired locations, detailed recording of practices and a sufficient number of replicates to detect a particular difference may suffice. If the objective is to detect a mean change over a domain then stratified random sampling may be the most cost-effective. Logistical factors may constrain sampling; some terrain may be difficult to access because of its remoteness, physical conditions and hazards such as conflicts. If the objective is to produce maps, then dense grids or stratified random sampling using a large number of sites is needed. However, we must be aware that cost constraints will also have to be taken into account. This is one of the reasons why some countries choose to use legacy data and to return to sites that were sampled previously. Resampling such sites has the advantage of providing information over longer periods. Some limits of the approach are that the locations of the sites have not necessarily been designed for monitoring, that historical data from practices may be difficult to reconstruct, and that the within-site sampling of the first inventory is often a single core or a single profile. Another way to reduce costs is to run a compilation and analysis of soil data which have previously been collected in other soil analysis exercises or experiments, instead of carrying out specific field campaigns. This approach has been exemplified for soil carbon in France (Saby et al. 2008b; Orton et al. 2012), in The Netherlands (Reijneveld et al. 2009), in South Korea and Java (Minasny et al. 2012) and in New-Zealand (Wheeler et al. 2004).

What Time Step?

A major challenge of the design of SMNs is the selection of the time interval between measurements. Lark (2009) pointed out that the current status of a variable and its rate of change are different quantities and so their variability may differ. Since the task of monitoring the soil is therefore different from the task of forming repeated inventories, we rarely have statistical information on which to base the design of a monitoring scheme since most available SOC data, particularly at national scale, is for a single time step. He showed that the design of a SMN might be improved if one uses knowledge of soil processes encapsulated in a process model. One option is to select a time interval to make sure that the observed changes will be significantly larger than the differences which might be expected from sampling and other methodological issues (e.g., Smith 2004; Bellamy et al. 2005; Saby et al. 2008a). This will tend to increase the time interval that is chosen, but this reduces the scope of a monitoring scheme to detect short-term changes, some of

Table 6.1 Soil depth increments used in some international programmes

Program	Coverage	Soil depth increments
GlobalSoilMap	World (planned)	0–5; 5–15; 15–30; 30–60; 60–100; 100–200 cm
BioSoil	European forest soils	0–10; 10–20; 20–40; 40–60; 40–80 cm
LUCAS Soil	Europe	0–20 cm

which might reflect important trends (e.g. Desaules et al. 2010). Most studies show that, unless there are drastic changes in land-use or major erosion events, the time-step required to demonstrate a change is at least 5–10 years (e.g., Conen et al. 2003, 2004; Smith 2004; Bellamy et al. 2005; Saby et al. 2008a, b; van Wesemael et al. 2011).

What Sampling Depth?

There are several reasons to focus on topsoil layers and to adopt fixed increments (Kibblewhite et al. 2008; Morvan et al. 2008; van Wesemael et al. 2011) rather than pedogenic horizons in order to avoid subjectivity and to allow comparison between sites.

In their review of European SMNs, Morvan et al. (2008) showed that fixed-depth increments are predominantly used for core sampling (in more than 70 % of the SMNs). As there is commonly a marked decline in SOC with depth, and because changes in SOC are expected to occur mainly in the topsoil (e.g., Arrouays and Pélissier 1994a, b; Bernoux et al. 1998), it is advisable to sample over smaller increments in the topsoil layers and larger increments in the subsoil. However, the sampling variability of SOC data on a thin depth increment is greater than that for a larger sampling depth increment; therefore, inferences may be subject to a larger uncertainty if the sampling increments are too thin. It would be sensible to use increments which are widely-used in soil monitoring networks or in other international programmes e.g. (Table 6.1).

Statistical Issues

Statistical analyses are required to estimate the status and change of soil properties, to quantify the uncertainty of these estimates and to determine when observed trends and patterns in soil properties are significant or whether they might have arisen by chance given the sampling error of estimates. All statistical methods make assumptions about the observed data or the manner in which they have been collected. When deciding upon which statistical method one should confirm that the assumptions are appropriate for the particular data being investigated.

Design-based analyses (de Gruijter et al. 2006) are often used to estimate the mean of a property (or the change in a property) across a region. They require that the sampling has been conducted according to a probability design. However, they make few assumptions about the variation of the property and the estimates that result are therefore considered to be reliable, provided that they are obtained by an analysis compatible with the original design.

Model-based methods and in particular geostatistics can be used to produce maps of the status and change in soil properties and to quantify the uncertainty of these mapped properties. In contrast to design-based methods, model-based methods do not require that sampling locations are selected at random. Instead they assume that the observed data have been generated by a particular statistical model. The challenge, therefore, is to ensure that the assumptions of these models are consistent with the observed variation of the soil properties. In their simplest form, geostatistical models might assume that the property results from a Gaussian process and that the mean, variance and spatial correlation of this distribution are the same throughout the study region. In reality these assumptions are rarely appropriate and the models must be generalized to account for inconsistent features such as variations in the mean (e.g. Lark et al. 2006b); variation in the variance (e.g. Marchant et al. 2009); extreme values (e.g. Marchant et al. 2010) and below detection limit values (e.g. Orton et al. 2009).

Examples of Proved Changes

Probably one of the most cited studies on measured SOC changes using a SMN is that by Bellamy et al. (2005; times cited: 418 in Web of Knowledge® on 21 June 2013). Using repeated measurements from 1978 to 2003, they showed large losses in nearly all soils of England and Wales. Possible causes of these changes have been widely discussed (e.g., Lark et al. 2006a; Smith et al. 2007; Kirk and Bellamy 2010), but without a precise recording of management practices, they still remain difficult to interpret. Evidence from other surveys (Reynolds et al. 2013) has not corroborated the findings of Bellamy et al. (2005). Numerous examples of detection of changes over large areas and time frames exist in the literature (e.g., Sleutel et al. 2007; Saby et al. 2008b; Goidts et al. 2009a, b; Meersmans et al. 2009, 2011; Reijneveld et al. 2009; Pan et al. 2010; Orton et al. 2012; Minasny et al. 2012). These show that the time interval over which a detectable change in SOC might occur is at least 5–10 years, and support the suggestion by Smith (2004) and Conen et al. (2004) that it would be very difficult to detect changes in soil organic carbon stock over a 5-year period (e.g. for Kyoto verification). However, these studies helped to demonstrate the magnitude of changes, even if the effect of various controlling factors on these changes in SOC remained often difficult to assess. This explains why a comprehensive SMN should include, in addition to sample sites selected to estimate global changes, sites which allow direct estimation of the response of SOC to specific changes of land use or land management.

Predicting or Explaining Changes with Models

Models can be used to explain or predict changes in SOC. In support of this, SMNs are needed to provide input data and baseline values. Observed changes of SOC at SMN sites can be extrapolated to particular classes of soil or land use or climate. However, most reported modelling exercises showed large uncertainties in predictions (e.g., Parton et al. 1993; Friedlingstein et al. 2006). These arise from uncertainties in the baseline values, in the model itself, and in the magnitude of the changes of future controlling factors (land-use changes, climate change, lack of enough soil data, etc.).

Harmonization Issues

The harmonization of methods for soil monitoring is difficult for many soil properties (Jolivet et al. 1998; Kibblewhite et al. 2008). One way to tackle this is by the establishment of benchmark sites to compare methods and to estimate statistical functions for adjusting estimates from one monitoring scheme, so that they can be compared with those from another. We call these: cross-calibration functions. To our knowledge, no study has investigated how many calibration sites are necessary for this purpose and how to select them. A recent study in France used paired sites from two different SMNs to estimate the number of benchmark sites necessary to allow a statistical comparison between results from the two networks (Louis et al. 2014). The availability of data from two SMNs at sites which are common to two SMNs and so which have been sampled to yield material analysed under the protocols of both has allowed the authors to investigate the impact of sample design on the quality of cross-calibration functions. They showed that, even with powerful sampling designs (e.g., various Latin hypercube sampling methods) in order to estimate cross-calibration functions of adequate precision it was necessary for the number of sites common to the two SMNs to be large. In fact, in this case where the two SMNs were of the same density, some 20–30 % of the sites had to be common to the two. Given this, it would be more efficient for common protocols to be accepted across countries or supranational regions for future monitoring activities. In the early phases of monitoring on such a common protocol, a proportion of sites could also be sampled, and material analysed, according to previous protocols used. Cross-calibration functions from the resulting data could be used to allow comparisons with previously-collected information.

Archiving Samples

The establishment of a network would require long-term commitment from researchers and from funding agencies. In numerous countries, soils are monitored on the basis of particular national schemes, but surprisingly, despite the large effort involved, not all programmes retain archived soil material after sampling and analysis. There are several reasons not to throw away the samples once they are analysed.

We do not know what new scientific questions and policy challenges connected to soil change will arise in the future. We do not know what new analytical techniques will be developed, but we can expect that they will be more precise and will allow the use of new tracers of environmental and biogeochemical processes. Various substances which today cannot be detected or measured will be measurable with precision in the future. Techniques and standards for soil analyses are evolving. If this is not apparent as a matter of common sense, then those who have responsibility for the design of soil monitoring schemes should reflect on the prescience of Rothamsted Experimental Station in archiving soil material from long-term experiments. The oldest samples were collected in the middle of the nineteenth century, and this material allowed researchers to quantify and model soil change by processes which the originators of the experiment would neither have known nor foreseen (Peterson et al. 2012).

Conclusions

There is a need for harmonized SOC SMNs all over the world. We need appropriately designed sampling schemes in space and time, with minimal constraining prior assumptions (because we do not know what will happen and we do not know all the driving factors of possible future changes). We also need monitoring sites selected to focus on particular processes and management effects so as better to understand how the soil retains carbon and how to promote this.

Early investment in the development of a design for a global SOC SMN is required and a common protocol is needed. The establishment of a global SMN will take several years and information on trends in SOC will become available only following re-sampling. Realistically, unless enough prior legacy data exist, it will be at least a decade and possibly two decades before a global SOC SMN can start to report. Given the increasing pressure on soil resources for food production, the need for urgent action to establish this system is clear. Reliable, agreed methods are now available for estimating SOC changes. Thus there is an existing technical basis for establishing a global SOC monitoring system and investment in this should be an urgent priority for the international community. Current international projects, such as GlobalSoilMap, could help to design the sampling strategy of such an international network. Other international initiatives, such as the GlobalSoilPartnership, could provide a political framework to raise awareness and to get funds. Finally, the soil monitoring working group from the International Union of Soil Sciences could act as a group of scientific advisers to develop a set of methodological recommendations.

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Chapter 7
A Novel Method for Measurement of Carbon on Whole Soil Cores

Robert Pallasser, Budiman Minasny, and Alex B. McBratney

Abstract Dry combustion is a reliable method of determining soil C but like all methods has been challenged by the required scale. Several methods for measuring soil carbon stocks have been promoted in recent years as a way of dealing with the current soil C data crisis but techniques such as spectroscopy depend on standardisation by dry combustion. A new robust approach has been developed where the contents of whole soil cores are analysed by dry combustion to yield C data for full depth intervals. The system has a configuration which is based on extracting all C from a 50 cm long soil plug. The method relies on direct quantitative detection and minimising any interference from water. Apart from pre-drying to remove excess moisture, the flow-on benefits have been reduced time and associated costs in soil processing. The advantage is that this methodology captures the natural variability in all dimensions and can directly produce results on a volumetric (kg/m^3) or gravimetric basis (g/kg). Determinations on cores have been reproduced within 0.1 % C (mass basis) which is the level of sensitivity required. The technique, which can be deployed on cores set out according to an appropriate sampling design, facilitates fast and cost effective determination of soil C stocks to support mapping, modeling and management.

Keywords Dry combustion • LECO • Soil carbon measurement • Carbon sequestration

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Introduction

The reliable assessment and monitoring of soil carbon stocks is of key importance for soil conservation and in mitigation strategies for increased atmospheric carbon (Gehl and Rice 2007; Schrumpf et al. 2011). Carbon credits are the heart of a cap-and-trade scheme, by offering a way to quantify carbon sequestered from the atmosphere (IPCC 2006). The agricultural sector has the potential to capture and store carbon emissions in soil. However, there is no guarantee that the industry can benefit from the offsets in the current and future carbon economy because there is no efficient way of measuring soil carbon storage with appropriate statistical confidence for large areas. A successful method should deliver: reliable C data with requisite levels of precision, ease of application, cost effectiveness, and readily verified soil C data.

Technologies such as remote sensing and proximal sensing have been proposed for estimating surface soil carbon content over large areas (Gehl and Rice 2007). Such approaches only provides measurement on or near the soil surface, moreover the high cost of acquiring such data and the need for laboratory calibration limits its application in a routine auditing process. Field near infrared spectroscopy can give estimates of carbon, but the estimation is based on calibration to standard analytical techniques (error usually 1–8 g C/kg soil) (Bellon-Maurel and McBratney 2011).

Dry combustion of soils has been the benchmark method for soil C determination (Merry and Spouncer 1988; Wang and Anderson 1998; Conyers et al. 2011). It extracts C by converting it to CO_2. Conventional methods for soil analysis are based on analysing an aliquot of the bulk soil sample, which means only one or a few grams of the soil core will be analysed. The dry combustion method on samples much larger than a few grams has generally been regarded as difficult to carry out due to incomplete conversion and in particular the huge volumes of gas that are generated. The issue surrounding small amounts necessitates greater sample handling and pre-processing e.g. selection, grinding, bulking and sub-sampling (added cost and labour) which can lead to deviations from the true composition and a loss of representativeness.

Here we demonstrate the possibility of analysing whole soil core by using a direct combustion technique that analyses the bulk soil gas composition. This has the potential to eliminate bias and error in sub-sampling for laboratory analysis and thus reduces the cost of sample preparation. Large aliquots in this study refer to amounts of 300–600 g, which is hundreds of times the mass of soil that is currently analysed for the determination of soil C stocks.

The Soil Carbon Bench

Classically, carbon is determined in a range of materials by combustion at temperatures usually over 800 °C and then determining the product by mass (gravimetric), titration or some other means (Rayment and Lyons 2011; Pallasser et al. 2013).

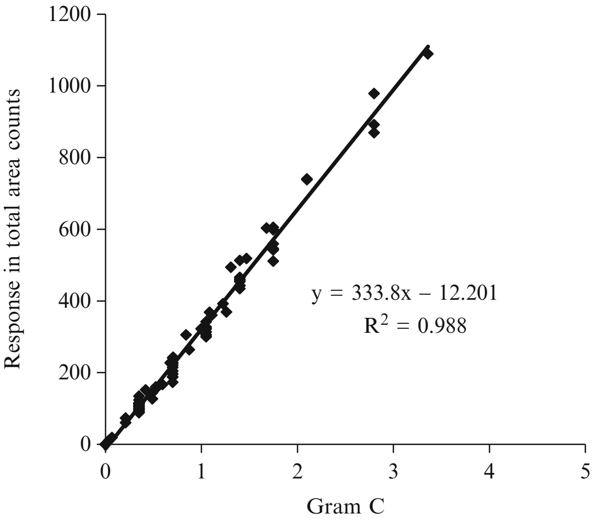


Fig. 7.1 Calibration chart for the SCB correlating instrument output with the amount of C

Combustion is carried out in O_2 rich atmospheres to achieve complete oxidation and any minor CO formed can be further converted catalytically. Anaerobic atmospheres produce pyrolysis products.

We designed and built an instrument which provides a novel way of measuring the soil carbon for a soil core of 300–500 cm^3 or 300–600 g soil. The instrument called the soil carbon bench (SCB) was designed around these four main modules:

1. Enclosed and refractory flow-through reactor tube with gas supply,
2. Furnace mounted on rolling stock (mobile heat source),
3. Split flow arrangement leading to measurement systems (e.g. gas chromatograph detector) and
4. Data acquisition system and computer

To assist in monitoring combustions and devising the most effective methodology for determining C from soil cores, the SCB system was connected to a gas chromatograph (GC) fitted with a thermal conductivity detector. The SCB is a bulk C system that operates at over 800 °C and transfers heat into the 300 g+ soil mass to degrade and extract carbonaceous material including black carbon. Elemental analysers run at the same temperatures but transfer product gases in stages and remove water with hydrophilic traps.

The calibration for our Soil Carbon Bench instrument was based on the combustion of known amounts of pure carbonaceous materials. These became the internal standards and were primarily sugar (42 % C) and charcoal (70 %C) which were readily available. Combustion initially of neat (pure carbonaceous) material was replaced by synthetically prepared (i.e. organic bearing) soils, providing C in a soil matrix. The calibration summarised in Fig. 7.1, spans from 0.1 to 3.5 g C to cover the typical soil contents expected in field trials. While most attention was given to lower-end calibration, an upper limit for the system has not been reached.

Performance Parameters

This calibration function (Fig. 7.1) was linear with a standard error of prediction (SEP) (Fig. 7.1) of 0.17 g C. The limit of detection of the instrument is derived from the smallest measure that can be detected with reasonable certainty. There are a number of different “detection limits” that are commonly used, one of them being the method detection limit (MDL). The method detection limit (MDL) is a statistical approach based on replicate analyses at one particular concentration (Childress et al. 1999). This parameter quantifies the amount of signal unrelated to the analyte which is then used to determine LLD:

$$\text{MDL} = \text{Std deviation}\left(\text{replicate analyses}\right) \times \text{student's } t\text{-coefficient},$$

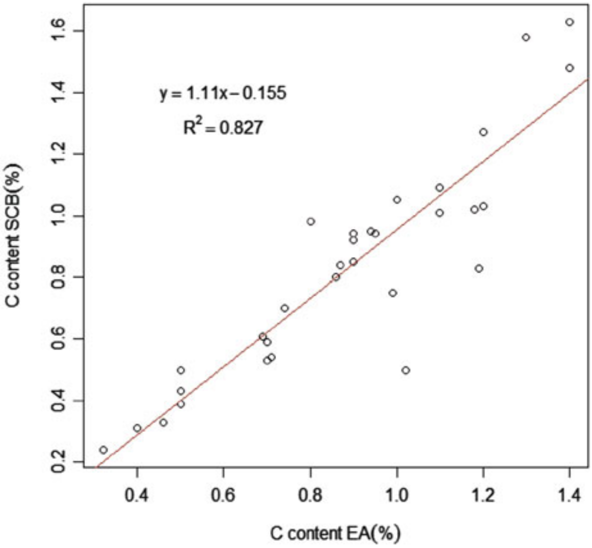
where the replicate analyses are carried out on the same (low) concentration over several days to capture all possible variables and the student’s coefficient (*t-distribution*, $P=0.01$) given by the number of replicates. Accordingly, the MDL and LLD were determined for the SCB based on repeated aliquots of soil containing 0.35 g C (representing low end of scale) analysed over different days. The standard deviation for the test values was 0.03 with the *t*-test value for $n=9$ at 99 % confidence level, yielding the MDL of 0.085 g C.

Laboratory Testing

In order to demonstrate how accurately and reproducibly the SCB system could deliver results in comparison to the industry standard it was necessary to conduct conventional soil carbon analyses. These were carried out on the small amounts of soil necessary for the elemental analyser (EA) (Elementar vario Max, Hanau Germany). Soil samples (mainly from Lansdowne, NSW) were air-dried, and well homogenised. SCB takes about 200–300 g of soil, while the elemental analyser takes approximately 0.5 g of soil materials. The results on the comparison of the two methods are presented in Fig. 7.2.

Elemental analysers are precise instruments capable of replicating results below 0.1 % C when using similar masses of homogenous soil. All soils were dried prior to analysis so that values could be expressed on a standard oven-dried basis. The mean difference between the two determination methods was 0.12 % C. It must be noted these were not measures of precision which are closer for individual instruments. These variations rather than being due to calibration can probably be attributed to

Fig. 7.2 A comparison of C content (in percent mass) as measured by elemental analysis using the vario Max CNS analyser (EA) and the soil carbon bench (SCB)



heterogeneity of C within the sample. Heterogeneity has an impact using standard C analyses but not with the SCB because it analyses the whole soil mass.

Field Testing

The SCB was tested from soil samples collected in a field at Lansdowne Farm, near Cobbitty, NSW, Australia. Soil texture varied from sandy loams to sandy clay loams along a North to South transect. The area consisted of a good grading of particle-sizes and carbon content ranging from a proven 0.2 % in the sandier parts up to 1–2 % in surface clay loams close to the river.

In order to develop a method that allowed C data to be expressed on a volumetric basis a method of obtaining reliable soil cores was an important requirement. Obtaining soils from known volumes avoids the issues of bulk density correction as described by Lee et al. (2009), which include the complicated calculation of equivalent soil mass. Several soil recovery tools including 50 cm vibracore were tested for the most suitable soil plugs in terms of uniformity and a volume of soil that could be processed in the SCB. The samplers (Fig. 7.3) were drawn down at the cutting end from the standard 38 mm tubes so that a volume/mass of soil appropriate for the SCB (~450 cm^3 or 600 g) could be recovered up to 1 m depth. Each core results in one C value.

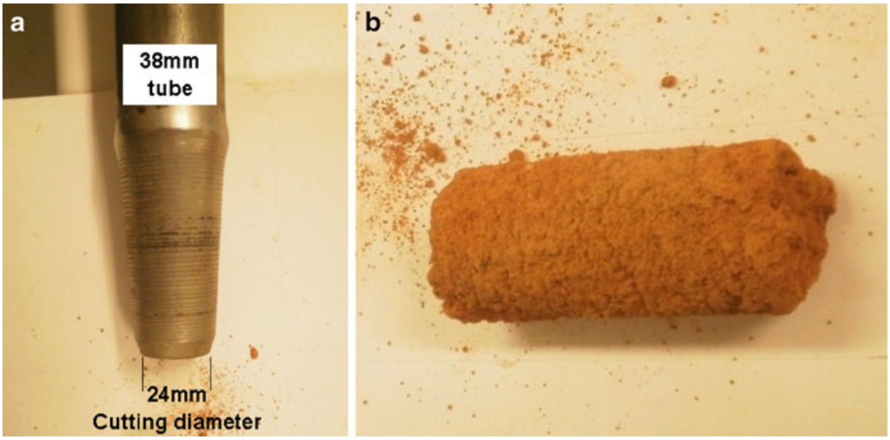


Fig. 7.3 Close-up of the corer cutting edge (**a**) used to recover soil plugs (**b**) with dimensions 24 mm across and lengths to usually 500 mm were suitable for the SCB

The processing requirement for this analysis is breaking up the soil and pre-drying (at 90 °C for a minimum of 12 h) to remove excess moisture. The replicate results for whole core analyses from each sampling location over the study area are shown in Fig. 7.4. The results can be expressed as g C per whole core interval (50 cm), % C of total dry mass or C stock (in kg/m^2). The soil C values from the cores were coherent (per site and trend down transect) and varied less compared to measurements using elemental analysis. Total C per core was within 0.2 g of their mean for each site where the totals ranged from 0.7 to 4.7 g C per 50 cm core for the sampled positions over the transect. On a gravimetric basis (the ranges are 0.2–1.09 % C per 50 cm core) the site reproducibility was around 0.0003 kg/kg. Both EA and SCB produce similar mean values across the transect (mean = 4.2, median = 4.1 kg/m^2), however the values obtained by SCB has smaller variance (std. deviation = 0.97, interquartile range = 1.08 kg/m^2) when compared to values obtained by EA (std. deviation = 1.36, interquartile range = 2.71 kg/m^2).

Conclusions

This methodology for sampling and analyzing soil C captures the natural variability and can directly produce results on a volumetric (kg/m^3) or gravimetric basis (g/kg), making it amenable to protocols proposed under IPCC. Determinations on cores have been reproduced within 0.1 % C (mass basis) which is the level of sensitivity required. Apart from pre-drying to remove excess moisture, the flow-on benefits have been reduced time and associated costs in soil sample preparation. Based on our initial trial work, time savings have been estimated to be over 60 % resulting in lower analysis costs which could become as low as 20 % that of conventional methods.

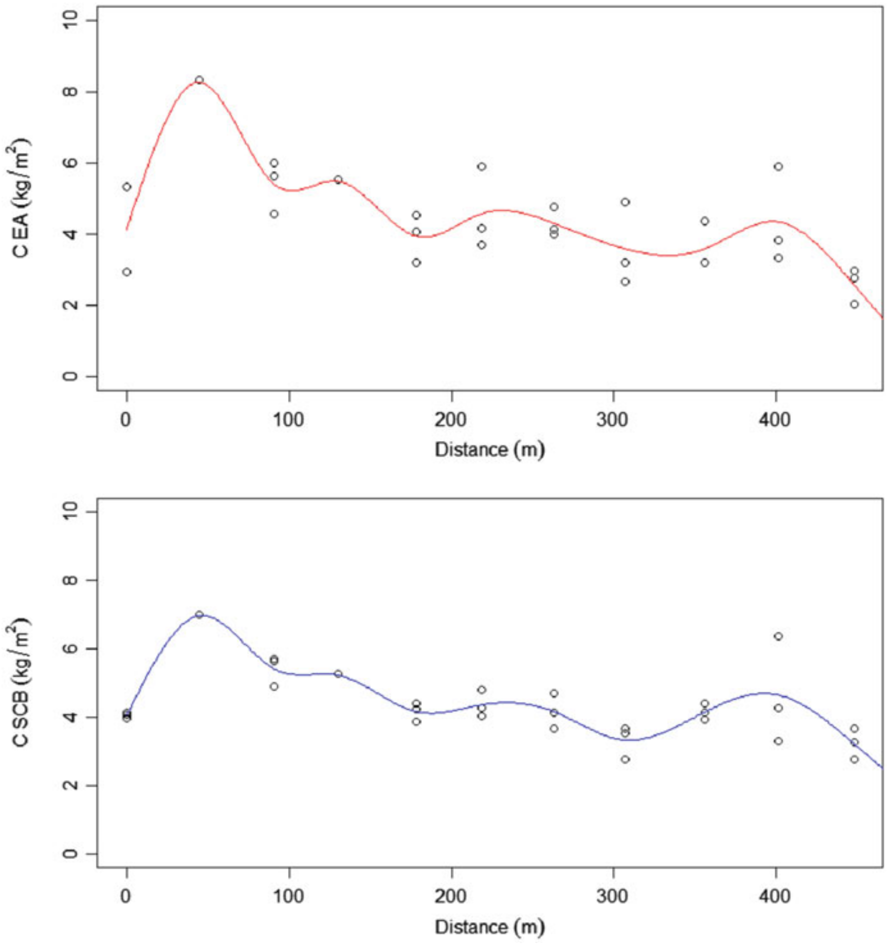


Fig. 7.4 Soil C stock (kg/m^2) 0–50 cm along a transect (from South to North) in Lansdowne as measured by the conventional Elemental Analysis (EA, *top figure*) and Soil Carbon Bench (SCB, *bottom figure*) shown as points, the curves are smooth splines fitted through the data

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Chapter 8
Evolutionary Optimization of Spatial Sampling Networks Designed for the Monitoring of Soil Organic Carbon

Alí Santacruz, Yolanda Rubiano, and Carlos Melo

Abstract In this research, optimal spatial networks designed for second-phase sampling of soil organic carbon were found based on the spatial information obtained during a first-phase sampling. The study was carried out in soils of tropical crops, forests and pastures in an area of about 1,310 ha located in the foothills situated to the east of the Colombian Andes mountains. Mean soil organic carbon content in the upper 1 m in the study area was 18.9 t ha^{-1}. Additional points supplementing the existing initial sampling set were allocated, in random and regular configurations, following two different approaches: sequential and simultaneous addition. The search for the optimal set of additional points was performed using an evolutionary optimization technique known as genetic algorithms. Results showed that random schemes allocated following the simultaneous addition approach were more efficient than regular schemes. Besides, the sequential addition produced suboptimal solutions, becoming less efficient than the simultaneous addition when the number of additional points to be allocated was increased. The optimization technique used in the study, the genetic algorithms, proved to be effective to find optimal spatial networks designed for second-phase sampling of the variable of interest.

Keywords Soil carbon • Spatial sampling • Geostatistics • Kriging • Genetic algorithms • Optimization

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Introduction

Soil organic carbon is one of the most important pools in the global carbon cycle. The total quantity of organic carbon in 100 cm depth ranges from 1,220 Gigatons (Gt) to 1,550 Gt (Kirschbaum 2000). It is equivalent to about twice the carbon stored in the biomass (Sommer et al. 2000), and the organic carbon stored in soils is more than twice the amount stored in the atmosphere (Lal 2004; Townsend et al. 1997).

Given its relevance, appropriate methods for measuring and monitoring soil organic carbon stocks are important. However, estimation of the organic carbon stored in soils, when regional or national estimates are required, is a difficult task, as finding optimal sample locations can be challenging.

Geostatistical techniques have proved to be well suited for the design of sampling networks (van Groenigen 2000). In a geostatistical model-based approach, a first-phase sampling seeks to collect spatial samples at short distances to estimate the variogram. Observations are usually evenly distributed following triangular or square sampling configurations, which makes sure that unvisited locations are not localized too far from a sampling point. Once initial observations have been sampled, the variable of interest (e.g. a soil property such as soil organic carbon) can be estimated at unvisited locations using interpolation techniques such as kriging (Delmelle and Goovaerts 2009).

The second-phase sampling looks for allocating additional sampling (i.e. augmenting the initial sampling set) based on the variogram structure, especially in cases when the interpolation estimates have not been satisfactory or when the number of initial samples is considered not sufficient (Delmelle and Goovaerts 2009).

An efficient second-phase sampling searches for the optimum location of the additional sampling sites that minimize the kriging variance, which depends on the sample pattern, the sample density and intensity, and the covariance structure (Cressie 1993). The problem of defining a suitable network design also demands the selection of an efficient sampling configuration, i.e. the researcher must decide whether the information will be collected in regular or in random sampling configurations.

For augmenting an existing initial sampling set, there are two different approaches: the sequential method and the simultaneous method. In the first one, one point at a time is added, n-times, while in the second one, a total of n points supplement the existing set (Delmelle 2005).

Given that choosing the set of additional samples from a set of candidate locations can be computationally intensive (Borgoni et al. 2013), the search for an optimal sample set requires the implementation of heuristic methods. One of the search techniques that have demonstrated a potential for solving such problems are genetic algorithms, which have been successfully applied to a wide range of issues (Fleming and Purshouse 2002), but have not yet been used for the design of spatial sampling networks as extensively as other techniques (Lin et al. 2008; Reed et al. 2007).

In this chapter, we present the results of a model-based methodology aimed to design optimal networks for second-phase sampling of soil organic carbon. The procedure is illustrated using data from a case study in a tropical savanna in

Colombia. The optimal sets of additional observations are allocated in regular and random configurations according to the sequential and simultaneous methods, through the implementation of a genetic algorithm.

Materials and Methods

The study was carried out at La Libertad Research Center, located in Villavicencio, department of Meta, Colombia. The average annual rainfall in the study area is approximately 2,700 mm, with a dry season from December to March. The average elevation is 336 m above sea level, where the estimated average temperature is 27 °C. The predominant soils in this region are Oxisols characterized by acidity, low fertility and high levels of Al, Fe and Mn (Vanegas et al. 2013; CORPOICA 1995; Malagón 1995).

Soil Sampling and Analysis

Soil samples were collected in September 2007 under different types of land cover: grasses, rice crops, citrus crops, forest plantations, natural forests, annual crops and oil palm. A total of 150 soil samples at a 0–10 cm depth were collected and bulk density and organic carbon were measured. Organic carbon was determined by the Walkley-Black method and bulk density by the core method. The samples were taken following a rectangular grid, at points separated by approximately 270 m. A complete database and description can be found in Santacruz (2011).

Total soil organic carbon stock (SOC, in t ha^{-1}) was calculated as the product of soil bulk density (g cm^{-3}), soil organic carbon concentration (%) and sampling depth in cm (Guo and Gifford 2002). The depth of the soil layers was adjusted to avoid errors due to differences in bulk density produced by compaction (Solomon et al. 2002). The bulk density and depth of the cultivated and pasture soils were assumed to be originally the same as those of the corresponding forest soils.

Spatial Variability Analysis of Soil Organic Carbon

Exploratory spatial data analysis, along with tests for assessing the presence of outliers, trends and normality, were performed on the observed values of SOC, using GeoDa, ArcGIS and R software. Subsequently, an analysis of the sample variogram was performed and different theoretical variogram models were fitted by maximum likelihood, which were evaluated by cross validation to find the best-fitting model. Given that neither first nor second order trends were detected on the data, ordinary kriging was used to predict the SOC values at unsampled locations in the study area.

Design of Optimal Spatial Sampling Networks

For the design of optimal networks for SOC monitoring, two methods were tested: the sequential addition method and the simultaneous addition method (Delmelle 2005). In the first case, only random sampling networks were evaluated, while in the second method, both random networks and regular sampling grids were tested. In the sequential addition method, one new randomly-located point was added to the initial network (which corresponds to the sites of the field sampling carried out at the study area). In this case, the genetic algorithm was used to find the optimal random location for the addition of a new point to the network with the original sampling sites. The original network plus the optimal point were used as the new initial network and, then, the genetic algorithm was used again to find a new optimal point. The process continued iteratively until finding 25 new additional points.

In the simultaneous addition method, a genetic algorithm was used to determine the optimum locations of *n* points (found simultaneously) to be added to the initial network. It was found that the optimal location of one additional sampling site as if we wanted to include a new point to the original network (for a total of $n + 1$ points). Optimum locations were found to include two new points to the original network, discarding the locations found in the previous optimization (for a total of $n + 2$ points). The process continued until finding optimal locations for 150 additional sampling sites to the original network. In this method, we evaluated random sampling designs, as well as rectangular and triangular configurations.

For finding the optimal network designs, we developed a software package in the free and open source R language named *geospt* (currently available in CRAN, the official R-project repository) that optimizes the location of the additional sampling sites based on the minimization of an objective function. Based on the implementation of a genetic algorithm, the optimal solution corresponds to the chromosome, i.e. the new sampling network, which minimizes the value of the average standard error (ASE) obtained in the kriging interpolation. ASE is calculated as:

$$ASE = \frac{\sum_{i=1}^{n} \sigma_i}{n} \tag{8.1}$$

where σ_i corresponds to the square root of kriging variance and *n* is the number of sample points.

For the execution of the algorithm, the population size was defined to be 30 individuals, which means that for each one of the *n* points in the network, there were 30 possible values (pairs of coordinates) in each iteration.

The results obtained with the two methods evaluated in this research (sequential addition and simultaneous addition) were compared, as well as the results of the different sampling configurations (random and regular grids).

Results and Discussion

Total organic carbon stock at a 0–10 cm depth ranged from 8.5 to 57.9 t ha^{-1}, with a mean value of 18.9 t ha^{-1}. The vegetation covers in which soils showed the highest total carbon stock corresponded to natural forests and pastures (24.7 and 19.1 t ha^{-1}, respectively). The lowest carbon stock corresponded to soils in rice crops (14.2 t ha^{-1}). Organic carbon stock in natural forests also had the highest coefficient of variation (47.5 %). Besides, results of the Duncan's multiple range test (95 % confidence level) showed that the mean total organic carbon stock in forest soils was significantly higher than other land cover types, with the exception of pastures.

The spatial variability of soil organic carbon was modeled satisfactorily using spherical models, which showed a strong spatial dependence and enabled a consistent spatial prediction of the variable. The best-fitting model was a spherical model with a lag value equal to 230.4 m and a range equal to 433.7 m. The values obtained for the nugget effect and the partial sill were 0.00014 and 0.00083 respectively, obtaining a nugget effect corresponding to 14.43 % of sill. The selected model had good values for the cross-validation statistics, showing an appropriate range according to the expected behavior of the spatial variability of SOC at a 0–10 cm depth in the study area.

According to the map generated with this model, values of total organic carbon stock between 15 and 20 t ha^{-1} predominate in most parts of the study area. The kriging variances map showed that the lower values of variance are concentrated around the sampled sites.

In the design of networks for soil organic carbon sampling, when the results between different sampling configurations were compared, we found that optimized random networks had a lower average standard error than regular networks (Fig. 8.1a). The results showed that random sampling networks provided an advantage over regular schemes. This could be explained by a lower flexibility of regular configurations, which would be somewhat more limited than random schemes to reduce uncertainty. Some have argued that systematic selection can be inflexible to irregular features of the space, such as stratification, unhomogeneous variances and anisotropy (Banjevic 2004). On the other hand, random selection of units can be inefficient, since it does not take into consideration spatial nature of the locations which can be strongly correlated (Banjevic 2004; van Groenigen 2000).

We found that the relative efficiency of triangular networks compared to that of rectangular grids depended on the size of the additional network. The rectangular networks designed for soil organic carbon sampling were more efficient than triangular schemes for network sizes between 5 and 8 points, between 20 and 70, and between 120 and 150 additional points (Fig. 8.1a).

Previous studies evaluating the efficiency of square, hexagonal and triangular sampling designs for predicting the mean over a region have shown that the triangular grid may be marginally more efficient than the square grid, and that the square grid could be slightly improved by moving the sample points of every other row by

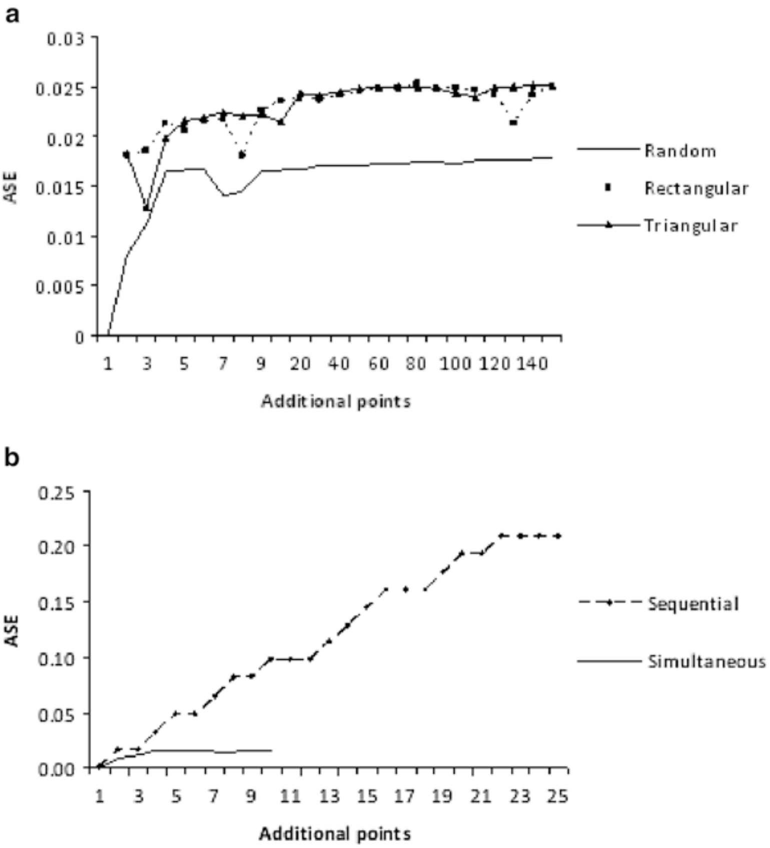

Fig. 8.1 (**a**) Comparison of average standard error (*ASE*) obtained for *n* additional points for different sampling configurations generated through the simultaneous addition method. (**b**) Comparison of ASE obtained for *n* new random points generated through the sequential method and the simultaneous method

one-half the side of the square. Besides, the equilateral triangular grid may yield the most reliable estimation of the variogram (Delmelle 2005).

Networks created with the simultaneous method were more efficient than the networks created through the sequential method, even for the smaller network sizes (Fig. 8.1b). The results showed that the sequential method did not always lead to the optimal solution for soil organic carbon sampling in the study area. Besides, when more new points were included sequentially, the relative improvement in reducing the uncertainty was less than the improvement obtained by the simultaneous method.

The results of our research indicate that genetic algorithms can be efficient to find optimal locations sampling. One of the main advantages found in this study was that the processing time of the genetic algorithm was more affected by the population size and by the number of iterations, than by the number of variables, which are related to the number of new sampling points. For this reason, genetic algorithms are preferred against other optimization techniques when a search in a very large parameter space is required.

Conclusions

Minimization of the kriging average standard error using genetic algorithms resulted in sampling schemes that took into account the nature of spatial dependence, based on preliminary data from a first-phase sampling. The results showed that a model-based approach joint with an optimization technique is able to provide a useful tool for soil surveyors in future studies of soil organic carbon.

The simultaneous addition method showed to be a more efficient approach for augmenting the existing initial sampling set for soil organic carbon in the study area. The sequential addition method did not always lead to the optimal solution. When the number of new sampling points to be added was increased, the sequential method became less efficient than the simultaneous addition method.

This research considered a univariate problem, where an isotropic variogram and temporal stationarity were assumed for the variable of interest. As a methodological improvement, future research should address multivariate prediction where, once defined a model of co-regionalisation, the co-kriging variance might be minimized using a stochastic optimization method. Additional improvements are recommended in addressing also anisotropy and the prediction of time-dependent variables.

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Chapter 9
Distribution of Soil Organic Carbon in the Conterminous United States

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Abstract The U.S. Soil Survey Geographic (SSURGO) database provides detailed soil mapping for most of the conterminous United States (CONUS). These data have been used to formulate estimates of soil carbon stocks, and have been useful for environmental models, including plant productivity models, hydrologic models, and ecological models for studies of greenhouse gas exchange. The data were compiled by the U.S. Department of Agriculture Natural Resources Conservation Service (NRCS) from 1:24,000-scale or 1:12,000-scale maps. It was found that the total soil organic carbon stock in CONUS to 1 m depth is 57 Pg C and for the total profile is 73 Pg C, as estimated from SSURGO with data gaps filled from the 1:250,000-scale Digital General Soil Map. We explore the non-linear distribution of soil carbon on the landscape and with depth in the soil, and the implications for sampling strategies that result from the observed soil carbon variability.

Keywords Soil organic carbon • Conterminous United States • Soil survey

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Introduction

Soil organic carbon (SOC) is of considerable scientific interest because it is part of the carbon cycle. The carbon cycle includes the atmosphere, the oceans, sediments, rocks, and soil. The buildup of carbon dioxide (CO_2) and methane (CH_4) in the atmosphere are major causes of climatic warming and global changes. Soils interact with the atmosphere by absorbing or releasing CO_2 and CH_4 in processes that include plant growth (photosynthesis) and decomposition by microorganisms. Processes that increase or decrease soil carbon can happen simultaneously, so separating the effects and making recommendations for strategies that will increase carbon storage and contribute to mitigating climate change requires understanding processes at many time scales and spatial scales (Sundquist et al. 2009).

Soil organic carbon is also important in agriculture and forestry because organic matter contributes to soil fertility by helping to retain soil moisture and supply plant nutrients (UNEP 2012). SOC is among the soil properties used by hydrologic modelers to predict how precipitation is processed by the land surface and contributes to stream flow, and surface water and groundwater quantity and quality (Saxton and Rawls 2006). Our objectives are to quantify stocks of SOC, to understand relationships with land use and land cover to guide land management decisions, to advise sampling protocols for improving estimates of SOC stocks, and to make data easily available to scientists and the public through the U.S. Department of Agriculture's (USDA) Natural Resources Conservation Service (NRCS) and the U.S. Environmental Protection Agency (USEPA).

Materials and Methods

A single database model is used to organize information in both the Soil Survey Geographic database (SSURGO) and the Digital General Soil Map of the United States (also called STATSGO2). Analyses in this chapter are based on a 30 m resolution version of the SSURGO data, with gaps (unmapped areas) filled with the more generalized STATSGO2 data. The NRCS is responsible for the leadership of soil survey activities and coordination of the National Cooperative Soil Survey (NCSS). There are two primary types of data in a soil geographic database: spatial data and attribute data. Spatial data represent the location of soil map units, and may be in either vector (as digitized from traditional soil maps) or raster (grid cell) format. The attribute data contain information on the soil properties for each map unit, and are represented by a hierarchy of tables in a relational database structure. At the top of the hierarchy is information about map units, and each of the lower levels represent increasing spatial and attribute detail. The SSURGO data were most often compiled at map scales from 1:12,000 to 1:24,000, and the STATSGO2 data were compiled at the 1:250,000 map scale. We used data obtained on December 30, 2009 from the NRCS Geospatial Research Unit (USDA-NRCS 2009).

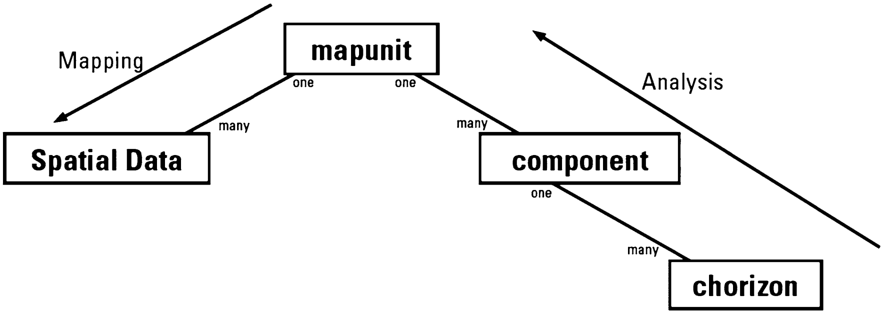

Fig. 9.1 A simplified diagram of the relational data structure for SSURGO and STATSGO2 data. The **mapunit** table is critical for linking attribute data to the spatial data. The relational key variable **mukey** occurs in all of the top level tables (the Spatial Data, the **mapunit** table, and the **component** table). Together, the **mapunit** and **component** tables represent the two-dimensional land surface. The component horizon table (**chorizon**) represents soil properties that change with depth into the ground. The "analysis" process proceeds from the lowest level tables on the right side of the diagram and summarizes results to the map unit level. The "mapping" process copies these results to the spatial data, either adding an attribute or making a new version

Figure 9.1 shows a diagram of a small portion of the relational data structure. On the left side, spatial data represent each map unit. On the right side, attribute tables have information on soil properties and relationships. An analysis proceeds from the right side, summarizing information to define a result at the map unit level. The result is transferred to the spatial data, creating a new spatial data set with the results of the analysis.

Map units are conceptually subdivided into components to retain information on how soils and miscellaneous land types change on the landscape for areas too small to be map units. Map units and components represent the two-dimensions of the surface of the landscape. Horizons represent how soil changes with depth from the surface to complete a three-dimensional view. For each component, the percentage of the map unit area represented by the component (**comppct_r**) is in the database. The horizons have detailed information on how soil properties change with depth. Taken together, all the soil horizons for a soil component represent the soil profile.

Components of map units can represent non-soil areas, such as water, bedrock at the surface, paved areas, gravel pits, fill, and dumps. If some components represent non-soils, the soil properties of interest (such as SOC) are given zero values for the soil property, and these zeros would be included in the averages computed at the map unit level. By including zero for the areas without component information then the quantities of interest are appropriately scaled for multiplying by the total area of the map unit and accumulating sums for the study area.

The SSURGO and STATSGO2 databases do not have a separate attribute for soil organic carbon. Although SOC is measured in the laboratory, it is reported in the soil geographic databases as soil organic matter (e.g., **om_r**) on the component horizon (chorizon) table. The organic matter was calculated as SOC divided by 0.58, reflecting an assumption that soil organic matter is 58 % carbon (USDA-NRCS 2004, p. 347). We reverse this calculation to convert organic matter back to soil organic carbon by multiplying by 0.58. The **om_r** attribute is defined as "The amount by weight of decomposed plant and animal residue expressed as a weight percentage of the less than 2 mm soil material," and thus excludes large roots, surface duff, and decaying trees.

At the horizon level, the SOC (g C) is calculated using the mass fraction soil fines (M_f) on a unit surface area basis (cm^{-2} is implicit), where the M_f is computed from the soil bulk density and three other variables that define the rock content:

$$^{h}SOC = {}^{h}Mf * 0.58 * \mathbf{om\_r} * 0.01 \tag{9.1}$$

where the 0.01 converts **om_r** from a percentage to a ratio.

The horizon (h) level SOC values are summarized to the component (c) level as a sum:

$$^{c}SOC = \sum_{h} {}^{h}SOC \tag{9.2}$$

The component level SOC values are summarized to the map unit (m) level as a weighted sum, with a corrected component percentage (*comppct_r_fix*) as the weighting factor:

$$^{m}SOC = \frac{\sum_{c} {}^{c}SOC * comppct\_r\_fix}{\sum_{c} comppct\_r\_fix} \tag{9.3}$$

Total carbon stocks for the conterminous United States are summed from the product of the unit area estimates of SOC for a map unit (Eq. 9.3) and the area of the map unit.

Results

A map of SOC is shown in Fig. 9.2, representing the total depth of profile and with gaps in SSURGO filled from STATSGO2. Areas of high SOC include areas with substantial wetlands along the border with Canada, in the Northeast, and along the Atlantic and Gulf coasts. There are prominent glacial influences that created areas of poorly drained soils from North Dakota to central Iowa. In the Pacific Northwest, the high rainfall and volcanic soils contribute to the retention of SOC, whereas in Texas, bands of high SOC soils are apparent where organic matter is tightly bound in soils with a high clay content.

The non-linear distribution of SOC with land area is illustrated in Fig. 9.3. On the left half of the figure, the low-carbon half of land area (3,866,000 km^2) has about 20 % of the SOC, whereas on the right side of the figure, the high-carbon half of the land area has about 80 % of the SOC. By splitting the vertical axis into top and bottom

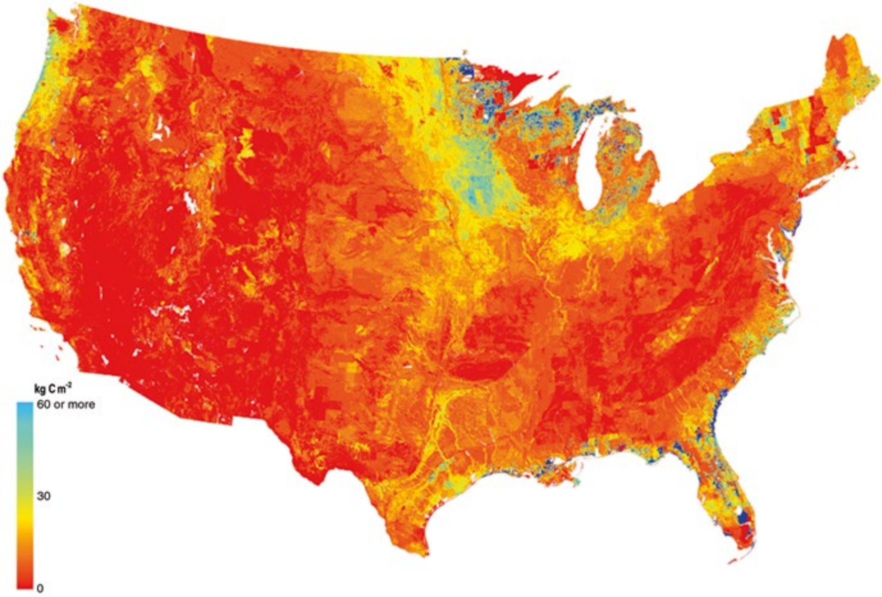

Fig. 9.2 Map of soil organic carbon in the conterminous United States for the total depth of the profile (which is variable). Gaps in the SSURGO data were filled using STATSGO2 data. Note that colors are scaled to show extreme patterns, so interpolation along the color scale is approximate. Abrupt changes in SOC along county or state boundaries often reflect the age of the survey (old versus recent) or the scale (SSURGO versus STATSGO2), and are being addressed by the NRCS with a major re-correlation effort

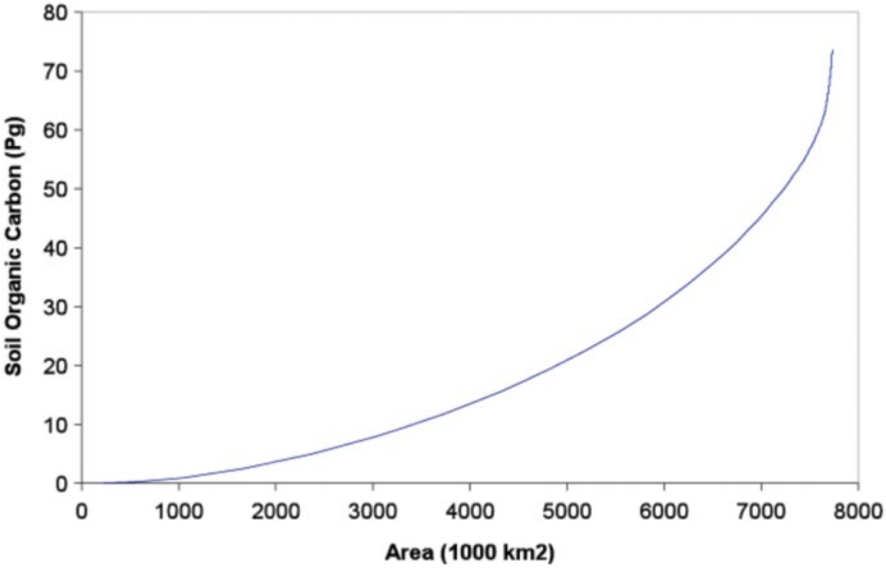

Fig. 9.3 Cumulative SOC by cumulative land area. The non-linear distribution indicates that small areas of high carbon soils are important contributors to the total SOC. The curve is based on SOC in the total profile for all land areas, so it is not directly comparable to Table 9.1

halves, 84 % of the land area is needed to reach the 36.7 Pg SOC point on the curve, and the high-carbon land portion of the curve (between the 36.7 Pg C and the total 73.4 Pg C) represents just 16 % of the total land area.

Table 9.1 shows soil carbon stocks by groups of land cover class from the National Land Cover Database of 2001 (Homer et al. 2007). This table represents another view of the non-linear distribution of SOC by land area. The largest quantities of SOC are in the forest, grassland, and cropland areas, reflecting both large land areas in those groups and moderately high carbon stocks per unit area. Although wetlands have smaller land area (327,271 km^2), they have much larger SOC per unit land area (27.28 kg C m^{-2}), and so they have the fourth highest contribution to total SOC (8,929 Tg C in the 0–100 cm zone) in this table. The vertical distribution of carbon in the profile is also non-linear. Although the 0–30 cm depth zone has only 30 % of the soil volume compared to the 0–100 cm depth zone, it has more than half the SOC. Values in this table were calculated with an algorithm that compared the land cover class of a pixel to the dominant land cover class for the soil map unit. For pixels where the land cover matched the dominant land cover, the representative value of carbon content was used, reflecting the practice to map soil properties for the dominant land cover type. Where a pixel had a different land cover type than the dominant one, expert rules were used to select lower or higher organic matter content values as appropriate for the minority land cover classes (West et al. 2010).

Discussion

The spatial patterns of SOC as seen in Fig. 9.2 can be used as a guide for sampling to improve estimates of SOC stocks. Much of the data collection used to develop SSURGO and related databases was intended to describe many soil properties, and soil carbon was not necessarily the focus of the sample selection. When future surveys are designed to sample soil carbon, careful attention should be given to the "population" which is being sampled. One way to think of this is that the "population" is the total set of organically bound soil carbon atoms present in the study area (here the conterminous United States). An ideal sampling scheme would give equal probability for each of the carbon atoms to be included in the sample. Viewing the non-linear distribution of organic carbon on the landscape (as shown in Fig. 9.3), this scheme would imply that the sampling should be based on equal intervals of the vertical axis (cumulative carbon) rather than equal intervals of the horizontal axis (cumulative land area). When differences in carbon content, as known from soil mapping, are used to stratify the sampling, then an inverse transformation would need to be used to scale the new carbon measurements back to land area and study-area totals. In practice, a sampling strategy will be based on a partitioning of the land surface. Some approaches, such as stratified random sampling are likely to be impractical to obtain accurate estimates. Cluster sampling approaches, and strategies that account for rare populations (Lohr 2010) would be desirable for characterizing the distribution of soil carbon. A second consideration for sampling strategy

Table 9.1 Area (km^2), stocks of soil organic carbon (SOC, Tg C), and SOC per unit land area (SOC, kg C m^{-2}) by soil depth zone and by land cover group (generalized from the 2001 National Land Cover Database) for SSURGO data only

	Depth range (cm)	Water[a]	Developed[b]	Barren[c]	Forest[d]	Shrub/scrub[e]	Grass/pasture/hay[f]	Crop[g]	Wetland[h]	Total[i]
Area (km$^{2)}$		22,920	383,375	54,563	1,710,633	1,295,304	1,645,238	1,248,295	327,271	6,687,612
SOC (Tg C)	**0–30**	170	1,715	97	7,400	3,048	6,340	6,786	3,717	29,273
	0–100	377	3,273	197	13,144	5,612	12,330	13,361	8,929	57,224
SOC (kg C m^{-2})	**0–30**	7.43	4.47	1.77	4.33	2.35	3.85	5.44	11.36	4.38
	0–100	16.46	8.54	3.60	7.68	4.33	7.49	10.70	27.28	8.56

[a] Combines NLCD 2001 classes 11 Open Water and 12 Permanent Ice/Snow (carbon contents are not applicable (NA)). SOC values are given in the Water class because the land cover classes were mapped at a more detailed scale than the soil classes, so sometimes generalized soil information was associated with water pixels

[b] Combines NLCD 2001 classes 21 Low Intensity Residential, 22 High Intensity Residential, 23 Commercial/Industrial/Transportation, and 24 Developed High Intensity (usually insufficient data for carbon calculations, so the values may not properly reflect national totals)

[c] Consists of NLCD 2001 class 31 Bare Rock/Sand/Clay

[d] Combines NLCD 2001 classes 41 Deciduous Forest, 42 Evergreen Forest, and 43 Mixed Forest

[e] Consists of NLCD 2001 class 52 Shrub/Scrub

[f] Combines NLCD 2001 classes 71 Grassland/Herbaceous and 81 Pasture/Hay

[g] Consists of NLCD 2001 class 82 Row Crops

[h] Combines NLCD 2001 classes 90 Woody Wetlands and 95 Emergent Herbaceous Wetlands

[i] The total area of the conterminous United States is approximately 7,700,000 km^2, whereas this table only includes the areas mapped with SSURGO (USDA-NRCS 2009)

would be the potential rate of change of the carbon stocks with anticipated changes in land management, climate change, or other forcing factors. Areas with a high potential for carbon sequestration or release may need special emphasis in the sampling design.

Models of the distribution and changes of carbon on the landscape may be empirical (as driven by remotely sensed data and flux tower data) (Wylie et al. 2007) or use process-based biogeochemical relationships to simulate how various carbon pools and driving forces will change carbon through time (Liu et al. 2003, 2011). The empirical models have the advantage that they can be more easily spatially validated. The process models have advantages for simulating future conditions. Each type of model may need inputs of soil data, including the water storage capacity of the soil, the soil carbon content, measures of infiltration, ease of water movement (permeability), and fertility (as rates of plant growth are often a control for the net sequestration or release of carbon at a location).

To make soil data easier for modelers to use, the gridded SSURGO (gSSURGO) has been recently developed. The original SSURGO vector map layer was reformatted into a grid cell (raster) format at 10-m resolution using an equal area projection for the United States. The gSSURGO data allow rapid visualization and use of soil properties for modeling for large land areas, and are available to the public for each state of the United States (USDA-NRCS 2013).

Many soil attributes, including SOC, will be available to scientists and the public through the USEPA's EnviroAtlas. The EnviroAtlas is a collection of tools and resources that provides geospatial data, maps, research, and analysis on the relationships between nature, people, health, and the economy. The atlas allows exploration of environmental services that humans receive from nature, such as clean air, clean and plentiful water, natural hazard mitigation, biodiversity conservation, food, fuel, and materials, recreational opportunities, and cultural and aesthetic value. Soil organic carbon data are one of the foundations for modeling and interpreting these ecosystem services (USEPA 2013).

Conclusions

The SOC total for the conterminous United States is approximately 73.4 Pg C in the total soil profile, as computed with SSURGO data with gaps filled with STATSGO2. This value compares to a prior estimate of 68 Pg C from STATSGO alone (Bliss 2003), however the differences are attributable to the data sources, and are not an estimate of SOC change. The quantity in the top 100 cm of soil is 57.2 Pg C, and in the top 30 cm of soil is 29.3 Pg C, as computed with SSURGO data. The SSURGO data represent most of the high value land, so the gaps in SSURGO generally represent mountainous and desert areas with much lower carbon contents.

The non-linear distribution of SOC stocks has implications for future sampling and modeling of carbon stocks and the interactions of soil carbon with the atmosphere and ground water. Land cover classes with high SOC stocks include forests, grasslands, and cropland, with wetlands representing a smaller total quantity but a much larger carbon stock per unit land area.

Soil organic carbon stocks form a starting point and calibration check for models that estimate changes in carbon stocks through time. Such models can guide management and policy decisions that will need to take into account changing land use and land cover patterns, climate change, changes in vegetation productivity, and conditions affecting microorganisms that decompose soil organic matter.

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Chapter 10
Overview of the U.S. Rapid Carbon Assessment Project: Sampling Design, Initial Summary and Uncertainty Estimates

Skye Wills, Terrance Loecke, Cleiton Sequeira, George Teachman, Sabine Grunwald, and Larry T. West

Abstract The Rapid Carbon Assessment (RaCA) project was undertaken by the Soil Science Division of the Natural Resource Conservation Service (NRCS) to capture baseline soil carbon stocks across the conterminous US (CONUS). A multilevel hierarchical design was used to ensure that samples were distributed across regions, soils and land use/land cover classes (LULC). Within those strata, sites were selected at random locations where five pedons were described and sampled at 0–5 cm and by genetic horizon from 5 to 100 cm. A total of 6,148 sites, 32,084 pedons and 144,833 samples were described. Bulk density was calculated for samples from the upper 50 cm and predicted for deeper samples using pedon and horizon information in a regression tree developed with random forests. Soil organic carbon (SOC) concentration was predicted for each sample using processed Visible-Near Infrared spectra and a random forest model. Pedon SOC stocks were calculated by fixed depth to 100 cm. Expected variance was introduced into the stock calculations using analytical and modeling prediction errors (e.g., SOC concentration and bulk density measurements) and the stratified sampling design was partitioned using a hierarchical Bayesian modeling approach. Pedons were averaged by site. The mean of all RaCA site SOC stocks to 100 cm was 321.1, with a median

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of 173.3 and range of 2 to over 5,000 Mg ha^{-1}. Geometric means of soil groups and LULC classes were used to extrapolate results to all assessed areas. Further work is needed to properly weight averages by areal extent and assess the cause of higher than expected site SOC stock values.

Keywords Soil organic carbon • Carbon stocks • Uncertainty

Introduction

Understanding soil C stocks and the uncertainty around these stocks is necessary for national C inventories (IPCC 2007), inputs to earth system models (Todd-Brown et al. 2013), and to determine soil organic carbon (SOC) temporal changes (Kravchenko and Robertson 2011). Current assessments of national scale carbon stocks rely on a variety of methods. Most efforts use published maps of ecosystem, climate and soils (e.g. Eswaran et al. 1993; Post et al. 1982; Guo et al. 2006), sometimes legacy pedons are used (e.g. Kern 1994; Wu et al. 2003) and some supplement those with additional sampling (e.g. Bellamy et al. 2005; Bradley et al. 2005). Recent estimates of SOC for the conterminous US (CONUS) (Guo et al. 2006) are based on the STATSGO database which provides an upper and lower range for SOC for each map unit. No probability distributions are assigned to the STATSGO ranges, thus it is unknown what these uncertainty estimates represent or if they are narrow or broad relative to reality. Soil C stocks in temperate regions are dynamic (Bellamy et al. 2005); however, the underlying soil data for the STATSGO database were collected over several decades (1950s–2000s, L. T. West personal communication) and thus the STATSGO SOC estimates may not represent a static inventory. The Rapid Carbon Assessment (RaCA) project was undertaken by the Soil Science Division of the Natural Resource Conservation Service (NRCS) to capture baseline soil carbon stocks across the CONUS at a single point in time using a robust sampling design.

Project Sampling Design

The initial RaCA project emphasis was on soil organic carbon (SOC) stocks, or the amount of SOC in a certain volume (area and depth of soil). The effort was conceptualized by staff at the National Soil Survey Center (NSSC) and carried out by Natural Resource Conservation Service (NRCS) soil scientists. A multi-level stratified random sampling scheme was created to both maximize geographical/spatial sample coverage with a maximum of conditions represented while giving a framework for aggregating information into regional areas. The first level of strata were RaCA regions based on major land resource area (MLRA) regional offices (USDA 2010). Within each region, samples were further stratified by a combination of soil groups and land use/land cover classes.

Table 10.1 National Land Cover Dataset (NLCD) codes and corresponding RaCA land use – land cover (LULC) classes

NLCD code	NLCD class	RaCA LULC class
11	Open water	
12	Perennial ice/snow	
21	Developed – open space	
22	Developed – low intensity	
23	Developed – medium intensity	
24	Developed – high intensity	
31	Barren land	
41	Deciduous forest	Forestland
42	Evergreen forest	Forestland
43	Mixed forest	Forestland
51	Dwarf scrub	Rangeland
52	Shrub/scrub	Rangeland
71	Grassland/herbaceous	Rangeland[a]
81	Pasture hay	Pastureland
82	Cultivated crop	Cropland
90	Woody wetlands	Wetland
95	Emergent herbaceous wetlands	Wetland

RaCA classes reflect NRI classes and definitions

[a] In the Eastern CONUS (regions 11, 12, 14, and 18), the Grassland/herbaceous NLCD class was assigned to pasture land instead of rangeland to better match NRI assessments

Soil groups were created using a statistical algorithm as described by Wills et al. (2013). Soil information from official series descriptions (Soil Survey Staff 2010a) and the soil data access (SDA) portal (Soil Survey Staff 2010b) was translated into scores that related to the amount of SOC the soil was expected to contain. The scores were then used in a statistical clustering algorithm to create 8–20 groups for each RaCA region.

Land use-land cover (LULC) information was assigned in order to align with NRCS National Resource Inventory (NRI) classes and definitions (USDA 2007). In order to obtain complete spatial coverage of LULC, the national land cover dataset (NLCD) was used (Fry et al. 2011). NLCD classes were relabeled as RaCA land use/cover (LULC) classes to correspond with the classes used in NRI (Table 10.1). There was some geographic variation in the correspondence of NRI and NLCD classes. In the Eastern CONUS (regions 11, 12, 14, and 18), the Grassland/herbaceous NLCD class was assigned to pasture land instead of rangeland to better match NRI assessments.

The pool of potential RaCA sites was created using the NRI sampling framework (Nusser et al. 1998). The primary sampling units of NRI are arranged randomly within geographic strata in a way that provides complete coverage of CONUS. One point was randomly generated within each primary sampling unit. The soil group was assigned by performing a spatial join with SSURGO (Soil Survey Staff 2010b). The land use/cover of the nearest NRI point was used to assign LULC. In cases where that was not possible (within areas of federal lands that are not assessed for NRI), a spatial join with the NLCD coverage was used to assign a LULC class.

The number of points in each soil group and LULC strata was determined using their relative extent within each region. Soil group and LULC strata were attached to a raster that combined SSURGO (Soil Survey Staff 2010b) as of October 2010 – current versions available as gSSURGO (Soil Survey Staff 2013a) – and NLCD on a 10 m grid.

A target number of sites to sample per soil group and LULC along with a randomized list of potential sites were supplied to each region. An excess of sites was supplied so that as sites were rejected (due to lack of access, safety or unexpected land use/cover) they could be replaced by the next random site on the list.

RaCA Site Data Collection and Pedon Sampling

Five pedons were sampled at each site: one at the plot center and one 30 m away in each cardinal direction (unless the arrangement was altered due to obstructions such as fences or roads). Each pedon was described according to the Field Book for Describing and Sampling Soils v.2 (Schoeneberger et al. 2002) and assigned to the most likely soil series given the information available. Minimum required information for each horizon included: horizon nomenclature, depths, color, texture, rock fragment modifier (% volumetric coarse fragments), redox features, and structure (where possible). Small pits were excavated to 50 cm or a root limiting layer such as bedrock or cemented soil. Samples were collected from 0 to 5 cm and from 5 to 50 cm by genetic horizon. Probes or augers were used to sample genetic horizons from 50 to 100 cm. Volumetric samples were collected for samples from 0 to 50 cm in the most appropriate manner . Samples were labeled, sealed in air-tight bags and transported to the regional office for processing. Complete sampling instructions can be found at the RaCA website (Soil Survey Staff 2013b).

Samples were air dried and sieved to a size of <2 mm. A sub-sample was oven dried to calculate bulk density as given in the Soil Survey Lab. Manual (Burt 2004). A LabSpec® 2500 spectrometer (Analytical Spectral Devices, Boulder, CO), which we refer to as VNIR, was used to scan all mineral samples. Each region had an identical VNIR and measured both reference and high/low QC sample checks in order to maintain consistency and comparability across regions. Organic horizon samples and 3 % of mineral samples were sent the Kellogg Soil Survey Laboratory. Those samples were scanned with another VNIR and carbon was measured according to the Soil Survey Laboratory Methods Manual (Burt 2004). Total carbon was measured with dry combustion and inorganic carbon content was measured by manometer after HCl treatment.

For samples that were not collected volumetrically (including all samples collected below 50 cm), a suite of pedotransfer function (PTFs) were developed to predict bulk density (Sequeira et al. 2014a). Twelve PTFs were developed using 2,680 pedons (20,045 horizons) from the National Cooperative Soil Survey characterization database (NCSS 2011). All bulk density measurements in the NCSS database were determined at −33 kPa matric potential using the clod method (Burt 2004). The PTFs used information known to be available for samples collected using the RaCA protocols. The PTFs had 9 input variables (regressors): 4 from the horizon for which bulk density would be predicted [designation, textural class, depth (at the middle of the horizon), and thickness] and 5 from a neighbor horizon (bulk density, horizon designation, textural class, depth, and thickness). The Random Forest algorithm (Breiman 2001) was used to develop the PTFs. The accuracy of these models was good, with predictions errors of 0.10–0.15 g cm^{-3} (Sequeira et al. 2014a). Huang et al. (2003) reported that the prediction error should be below 20 % to be declared acceptable for bulk density prediction. The measured bulk density data were used when available with outliers removed if the measured bulk density was outside of the 1st and 99th percentiles of samples from the NCSS database by simplified horizon nomenclature. The bulk density of all other samples was estimated with the PTFs described above.

Similarly, the NCSS characterization data were used to create carbon prediction models using the spectra of each sample's VNIR scan. The VNIR scans were taken on air-dry, <2 mm samples using the LabSpec® 2500 spectrometer (Analytical Spectral Devices, Boulder, CO) with spectral range of 350–2,500 nm, acquired at 1 nm increments. Preprocessing methods were applied to the spectra to reduce non-constituent-related interferences (e.g., light scattering, light path-length, spectrum baseline drift) that decrease the signal-to-noise ratio. Additionally, the artifact bands generated around the edge of the three detectors built-in the spectrometer were also removed to improve model performance (Duckworth 2004). Two multi-variate techniques, partial least squares regression and random forest regression trees were used to model SOC from VNIR scans modified with a variety of pre-processing techniques.18 VNIR-based SOC prediction models were tested. The best performing models used random forest with VNIR spectra that had been preprocessed by clipping out artifact bands and smoothing with using a Savitzky-Golay first derivative (Sequeira et al. 2014b).

No satisfactory model was developed for predicting SOC with VNIR spectra in organic horizons. Therefore, all O horizons were sent to the Kellogg Soil Survey lab for SOC determination by combustion (Burt 2004). When samples were collected from multiple segments of a horizon (e.g. 0–5 cm and 5–25 cm samples for a Horizon described from 0 to 25 cm) but no other volume or description information was provided to differentiate them, the average SOC content was recorded.

SOC Stock Calculations

Soil organic carbon stocks were calculated by multiplying horizon bulk density and SOC concentration, adjusting for coarse fragments and then summing the horizons stocks to a fixed depth of 100 cm for each pedon (Ellert et al. 2008). Where horizon depth did not match the fixed depth increment, the within horizon bulk density and C concentration was assumed to be constant. Variance introduced into the stock calculations by analytical and modeling prediction errors (e.g., SOC concentration and bulk density measurements) and the stratified sampling design was partitioned using a hierarchical Bayesian modeling approach implemented in WinBUGS (Clark 2005; Gelman and Hill 2007; Cressie et al. 2009) and R (Sturtz et al. 2005; R Development Core Team 2011). Specifically, measurement and model prediction errors were used as informative priors and hyperpriors whereas the hierarchical levels of the sampling design (e.g., region, soil group, and LULC) were given uninformative priors. Stock model parameters were estimated with three Markov Chain Monte Carlo (MCMC) chains each with 5,000 updates, a 100 update burn in, and a 50 % thinning rate to reduce auto-correlation within the chains. Convergence of the three MCMCs was determined using the Rhat parameter (Gelman and Hill 2007). This approach allows for complete error propagation and is a flexible method for estimating uncertainty in complex environmental data and models (Clark 2005).

All GIS manipulations were done using ArcGIS (ESRI Inc. Redlands, CA). All prediction and error assessment were conducted using R (R Development Core Team 2011).

Initial SOC Stocks and Uncertainties

A total of 6,148 sites, 32,084 pedons and 144,833 samples were described for the RaCA project. In order to summarize SOC stocks, pedons were averaged by site. Site averages are displayed by GPS coordinates taken at the time of sampling (Fig. 10.1). Summary statistics for site SOC stocks are given in Table 10.2. The mean of all RaCA site SOC stocks to 100 cm was 345.4 Mg ha^{-1}, with a median of 183.2 Mg ha^{-1}. These values are much higher than previous estimates based on SSURGO data, but only slightly higher than reported in the NCSS database by Wills et al. (2013). They report that NCSS SOC stocks to 100 cm ranged from 0 to more than 8,000 Mg C ha^{-1}; with an average of 136.5 and median of 152.3 Mg C ha^{-1}. The NCSS database and SSURGO do not have a full range of LULC classes present and likely include 'typical' or 'representative' conditions. The RaCA project was designed to capture a range of LULC classes, soil groups and expected SOC stocks. Specifically, we found that within and nested-among site variation account for 34 and 60 % of the total variation in SOC stocks to 1 m, respectively, while the remaining variation was attributable to LULC within soil groups and regions (5 %), soil groups within regions (0.5 %), and regional differences (0.04 %).

To extrapolate to all sampled strata, pedon stocks were first natural log transformed, to better approach normality and avoid the skew of extremely large values. Transformed values were averaged by site and site averages were further averaged by soil group and LULC. The average SOC stock value for each soil group and

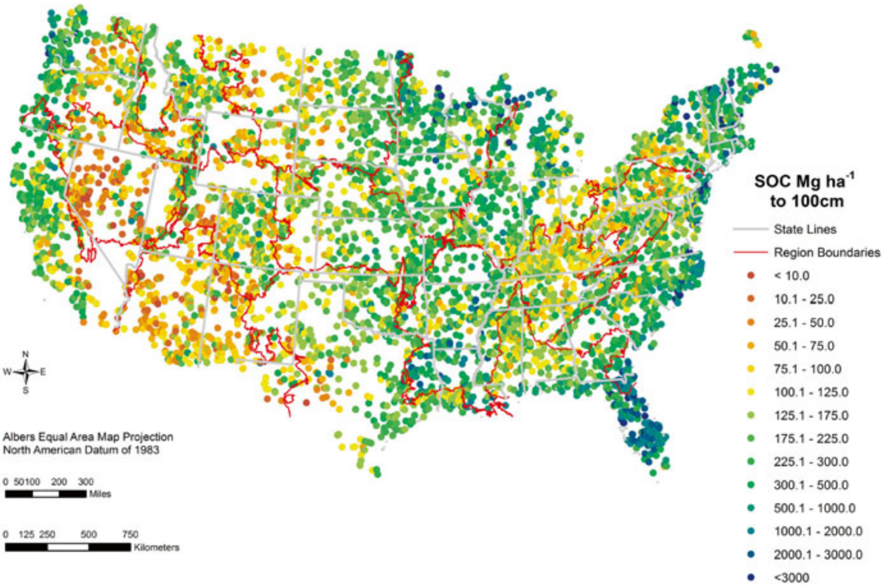

Fig. 10.1 Soil organic carbon stocks to 100 cm for each RaCA site

Table 10.2 Soil organic carbon stocks (Mg C ha^{-1} to 100 cm) summary for original values (stock), log normal transformed values (ln(stock)), and back-transformed values exp$^{(\ln(\text{stock}))}$

	Stock	ln(stock)	Exp$^{(\ln(\text{stock}))}$
Minimum	2.2	0.7	2.1
25th quartile	111.9	4.7	106.5
Median	183.2	5.2	174.3
Mean	345.4	5.2	321.8
75th quartile	317.2	5.7	300.1
Maximum	5,567.0	8.6	5,560.0

LULC combination is displayed on the Jan 2012 SSURGO-NLCD raster grid (Fig. 10.2). Only assessed areas were considered (pixels with both an assigned soil group and a relevant NLCD class). Values were back transformed from natural log to whole stock values before being reported and mapped. Thus, reported means represent geometric means as described by Crawley (2013). Soil group and LULC class geometric means ranged from 14.9 to 3366.7 Mg C ha^{-1}, with an overall mean of 284.6 Mg C ha^{-1}.

Given that this study is the first comprehensive one-time sampling of the CONUS, no studies are available to directly compare with our uncertainty estimates. Whole country comparable uncertainty assessments of SOC stocks have been conducted elsewhere (e.g., Bellamy et al. 2005; Heikkinen et al. 2013) and serve as a basis for comparison upon further analysis of the RaCA data.

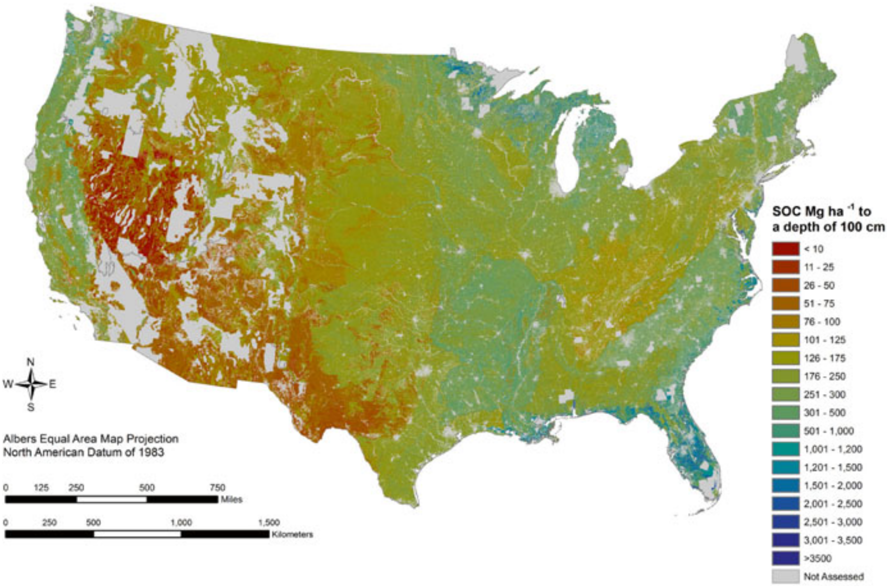

Fig. 10.2 Geometric mean of SOC stocks by soil groups and LULC

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Part II
Soil Carbon Properties and Processes

Chapter 11
Molecular Models of Cation and Water Molecule Bridges in Humic Substances

Daniel Tunega, Adelia J.A. Aquino, Georg Haberhauer, Hans Lischka, Gabriele E. Schaumann, and Martin H. Gerzabek

Abstract The molecular basis for many properties of humic substances (HS) still has to be investigated. Besides advanced analytical methods, molecular modelling offers the opportunity to investigate various features of HS. We investigated the wetting process of model nanopore segments in humic substances as a function of distance between two trimeric chains of polyacrylic acid. At shorter distances an outer solvation was most stable. With increasing distance, the water molecules penetrated into the formed free space connecting both chains by means of a hydrogen-bonded network, which had a significant stabilization effect. Similar stabilization was observed when two aliphatic chains terminated by carboxyl groups were overbridged by a chain of water molecules. Another setting with four undecanoic fatty acids served as a model for spatially fixed aliphatic chains in HS terminated by carboxyl group. The rigidity of the model is significantly enhanced as soon as the water cluster is large enough to comprise all four carboxyl groups. These simulations strongly support the hypothesized bridging function of water molecules in humic substances. The interactions of Na^+, Ca^{2+}, and Al^{3+} with carboxylate and

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carboxyl groups and the concomitant proton transfer reactions induced by these interactions were investigated. The strongest effect on the local environment was observed for Al^{3+} cation. The calculations reflect the amphoteric character of the hydrated Al^{3+} complex showing in most cases its acidic character via proton transfer from the water molecules of the hydration shell to the carboxylate group.

Keywords Humic substances • Molecular modelling • Cation bridges • Water bridges

Introduction

Humic substances (HS) represent complex and heterogeneous organic compounds and, as the main constituent of the Soil Organic Matter (SOM), are the most ubiquitous and common natural non-living organic materials found in soils and in all terrestrial and aquatic environments. They are formed in the environment during microbial decay of biological material and manifold chemical reactions of diverse organic molecules appearing in soils. They have a significant impact on soil properties contributing to soil fertility, water acidity, and mineral weathering (Stevenson 1994; Aiken et al. 1985). Based on solubility under acidic or alkaline conditions HS are operationally categorized to three fractions: fulvic acids (FA), humic acids (HA), and humin. The structure of HS is ambiguous and reflects the history of its formation (e.g. location, parent material, conditions, external influences). In spite of that categorization and intensive experimental research HS are extremely complex colloidal supermixtures practically non-separable into individual components and with no existence of some standard (reference) material. Therefore, no complete (full atomic) structure of HS has been determined so far. Earlier concepts of molecular structure of HS supposed polymer-like structure of randomly coiled macromolecules with high molecular mass in a size of tenths kDa (Swift 1999; Ghosh and Schnitzer 1980). However, later concept of HS structure as supramolecular associates of less weighted chemically diverse organic molecules becomes more accepted, mainly due to results obtained by advanced experimental techniques (Piccolo 2001, 2002; Schaumann 2006). Chemically, those association molecules resemble to known natural organic substances such as oligosaccharides, fatty acids, peptides, aliphatic chains and aromatic rings. Owing to this miscellaneous chemistry of the supramolecular structures with alternating polar (hydrophilic) and nonpolar (hydrophobic) domains, a large variety of intermolecular interaction types are involved in the stabilization of the HS supramolecular associates. These interactions account for dispersion forces (van der Waals, π-π, and CH-π), hydrogen bonds, and electrostatic forces. As HS coexist in soil with soil solutions containing numerous solvated natural ions (e.g. released from dissolved minerals), in the formation and stability of HS associates water molecule bridges (WaMB) and cation cross-linking bridges (CaB) play an important role (Schaumann and Bertmer 2008; Kunhi Mouvenchery et al. 2012, 2013; Schaumann et al. 2013).

Cations take part in various interactions with HS such as cation complexation, ion-exchange, adsorption, or organo-mineral aggregation. Typical cations in HS complexes are monovalent Na^+ and K^+ or multivalent Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, and Al^{3+}. As HS are weak acids, mainly polar groups such as carboxyl, hydroxyl, and phenolic are involved in interactions with cations and water. The strength of these interactions and the impact on the HS stability depend on various factors including concentration and spatial distribution of functional groups in HS matrix, water content, p*H*, and ionic strength of soil solution (Wilson et al. 2008). For example, p*H* significantly affects a formation and concentration of negatively charged (deprotonated) sites acting as strong sorption attractors. The interplay between water and cation bridges as a response to varying external conditions contributes to rearranging and restructuring of HS (i.e. aging). In spite of the intensive experimental investigation of cation and water molecule bridges in HS (see e.g. review by Kunhi Mouvenchery et al. 2012), there are still open questions, e.g. if cations form inner sphere complexes, direct outer sphere complexes, or indirect complexes combined with the water molecule bridges. In such situation methods of molecular modelling represent an effective tool for understanding such phenomena at a true atomistic level both in spatial and temporal (nano)scales (Schaumann and Thiele-Bruhn 2011). Wider application of molecular simulation methods in the study of complexation of HS has been hampered mainly due to extraordinary structural and chemical diversity of HS and incomplete information on their atomistic structure. From available atomistic simulation methods mainly classical molecular mechanics simulations were applied in several studies of cation-HS complexation. The interactions of hydrated Na^+ and Ca^{2+} cations with the HS structural models proposed by Schulten and Schnitzer (1993, 1997) have been modelled by Sutton and Sposito (2005). Classical molecular dynamics simulations on the HS complexation with several mono- and divalent cations have been performed (Kalinichev and Kirkpatrick 2007; Iskrenova-Tchoukova et al. 2010; Kalinichev et al. 2011) on the Temple-Northeastern-Birmingham (TNB) structural model of HS derived by Davies et al. (1997). However, modelling of such complex and large HS aggregates based on high-level quantum chemical methods is not available in the literature so far as such calculations are very expensive and unpractical. As an alternative approach, calculations on specific functionalities have been performed at the level of density functional theory (DFT) and the results are presented in this comprehensive overview.

Molecular Simulation Methods

During the last decades the methods of molecular simulations expanded to various areas of research and became an important tool in characterization of various physical chemical properties and chemical processes (Leach 2001). This rapid increase of molecular simulations is mainly due to a continuous progress in computational power and performance and in developing of new approaches and effective codes.

The atomistic-based simulations include two main groups of methods outgoing from classical molecular mechanics (or "force-field", FF) and quantum mechanics (QM) principles. FF-based methods are usually combined with molecular dynamics (MD) or Monte Carlo (MC) simulations providing thermodynamic characteristics of the modelled systems. The advantage of the FF methods, which are based on empirical interatomic potentials, is their efficiency and speed. Currently very large systems ($>10^6$ atoms) and microsecond MD simulations are manageable in a realistic computational time. The main problem of the FF methods regards the quality of FF parameters or missing parameters for a specific chemical bonding. In the latter case a set of new parameters needs to be determined. The examples referred in the introduction section were obtained at the FF-MD level.

The second group of methods (QM) is based on an approximate solution of the Schrödinger equation and comprises several classes of approaches differing in accuracy and computational cost – ranging from very accurate but time consuming *ab initio* to very effective semi-empirical methods. In the QM calculations, molecular systems contain interacting electrons and nuclei and the output is given by the calculated electronic structure in a form of electron density distribution and molecular orbitals (Hehre et al. 1986; Cook 1998). The QM methods provide a broad scale of properties such as electronic structure, energy-minimized molecular structures, spectroscopic parameters (e.g. NMR, EPR, IR/Raman), or thermodynamic quantities. Chemical reactions can also be explained by QM including reaction mechanism and reaction energies. Among available QM methods the approach based on density functional theory (DFT) became very popular and found a lot of successful applications. The standard DFT scales with N^3 (where N is the number of electrons) and can provide cost-effective results, which quality and reliability depend on used DFT functional and atomic basis set. Considerable progress in the development of the DFT methods has been achieved in recent years. For example, weak dispersion interactions represented a serious problem for the standard DFT functionals. The inclusion of the dispersion corrections to DFT (DFT-D) improved the quality of the results for weakly bound systems enormously (Grimme 2004, 2006). The DFT can be also combined with molecular dynamics for the treatment of systems scaling up several hundred atoms and 10^3 ps. From semi-empirical methods, DFTB (density functional tight-binding) approach (Frauenheim et al. 2002) is a promising method approaching the quality of DFT results with a speed of several orders of magnitude faster than DFT.

Despite the progress in the DFT methods, their application on HS associates in their full structural complexity is computationally extremely difficult. However, HS can be modelled at several levels of complexity as it is shown in Fig. 11.1. Supramolecular and macromolecular models can be simulated only at the FF level but functional groups, oligomeric fragments, and polymer-like models are manageable also at the QM level. The results for various HS models presented in this work were achieved using Turbomole (Ahlrichs et al. 1989) (DFT code) and DFTB+ (Aradi et al. 2007) program suites.

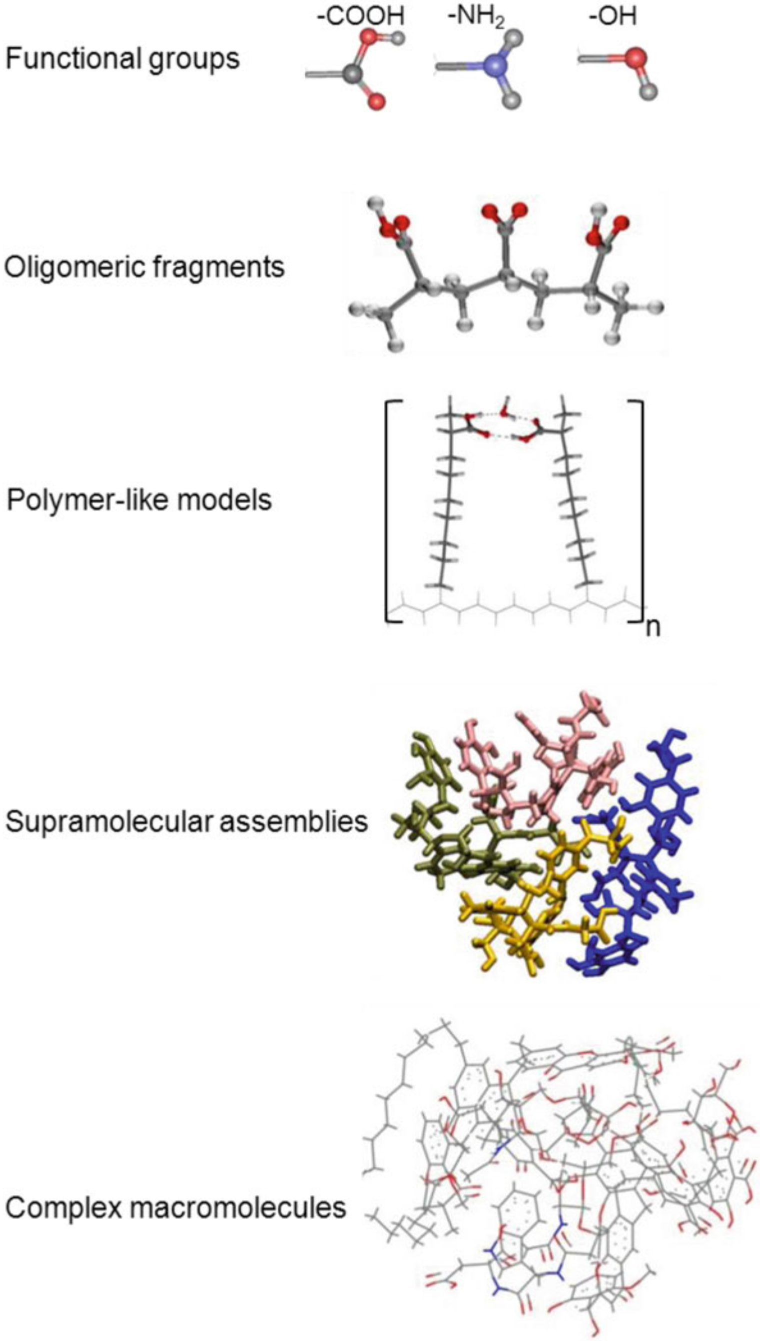

Fig. 11.1 Structural models of humic substances

Results and Discussion

The models of HS used in our simulations of water and cation bridges are amphiphilic segments mimicking a coexistence of hydrophilic and hydrophobic domains in HS. They consist of polar sections (represented by the most active carboxyl group) and nonpolar regions, usually represented by aliphatic chain(s). The models have a different spatial arrangement and the aliphatic end is fixed in order to mimic a linkage of the segment to the HS backbone (Fig. 11.2).

Water Molecule Bridges

DFT and DFTB methods were used in the study of wetting process of nanopore segment models in the HS associates (Aquino et al. 2009). A structural complex of two poly(acrylic acid) trimers was constructed as an example for a supramolecular

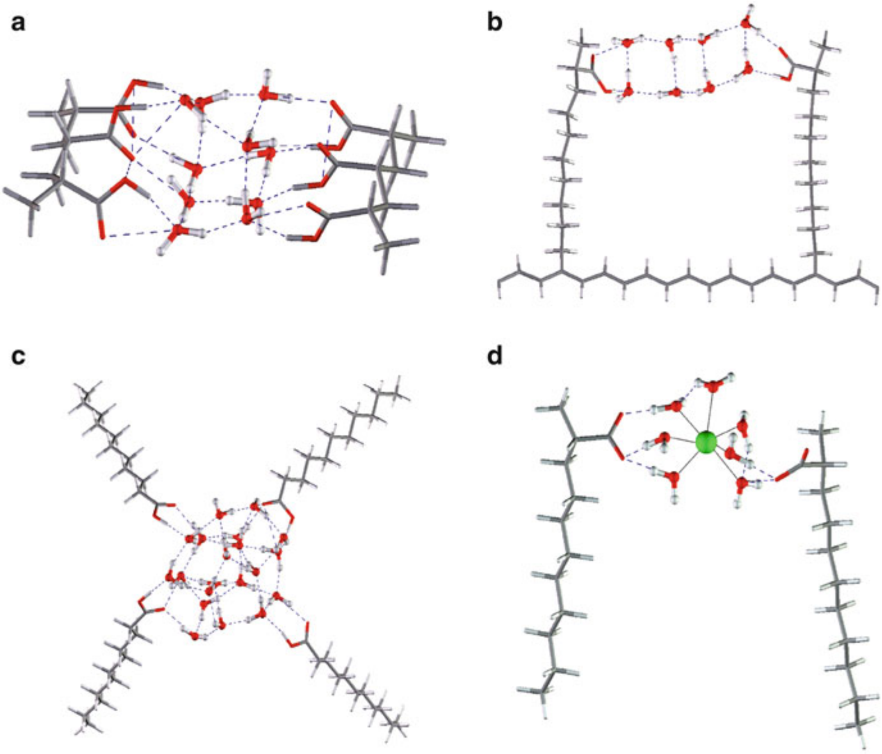

Fig. 11.2 Structural fragment models of water molecule (**a**, **b**, and **c**) and cation (**d**) bridges used in quantum mechanical simulations (Aquino et al. 2009, 2011a, b, c, 2014)

contact of two polar domains in HS mediated by hydrogen bonds (Fig. 11.2a). The effect of water content and a spatial arrangement on the stability of the complex was investigated. At shorter distances between two chains and lower water content outer solvation complexes are stable. However, with the increasing distance between trimers the water molecules penetrate into the created free space, keeping the two chains together by means of a hydrogen-bonded network. At higher water contents an optimal range of distances between the trimers exists resulting in a stabilization effect of 10–20 kcal/mol with respect to the outer solvation. This model, therefore, strongly supports the hypothesized bridging function of water molecules in HS provided that a local distribution of appropriate functional groups is available in the HS matrix.

Another model of water bridges in the HS associates was used in the DFTB-MD simulations (Aquino et al. 2011a). The model was composed of two parallel aliphatic chains geometrically restrained on one end and terminated with a carboxyl group on the other to supply the structural pattern for the supramolecular contact of two HS chains through hydrogen bonds (Fig. 11.2b). For the particular spatial arrangement it was observed that five water molecules form a stable water bridge between the two carboxylic groups located at each aliphatic chain. The effect of the environment through three solvents of different polarities (n-hexane, acetonitrile and water) was investigated. It was found that the solvent with moderate polarity (acetonitrile) is most efficient in exerting an ordering effect on the water bridge.

A system consisting of a tetramer of undecanoic fatty acid molecules connected to a bunch of water molecules (Fig. 11.2c) was used as a model of humic substances in DFTB-MD and FF-MD simulations to describe the stabilizing effect of water molecule bridges for cross-linking distant locations of the hydrophilic groups in polar domains of the HS associates (Aquino et al. 2011b). The effect of environmental polarity was modeled by embedding the system into solvents of low (n-hexane) and moderate polarity (acetonitrile). It was shown that the rigidity of the oligomer chains increases considerably once the water nano-cluster is sufficiently large to encompass all carboxyl groups in the model. Upon increasing temperature the rigidity of the tetramer-water cluster is lowered. Nonpolar environment enhances stiffness of the water cage what drastically obstructs releasing of water molecules from the cluster region. On the other hand, polar environment facilitates diffusion of water molecules away from the cluster.

Cation Bridges

Geometric and energetic properties of the cation bridges in the HS associates were studied by DFT calculations performed for nonpolar (isolated structures) and polar (water as continuum polarization model) environment (Aquino et al. 2011c, 2014). The model consists of two aliphatic oligomer chains terminated with carboxyl/carboxylate groups connected via hydrated cation bridges (Fig. 11.2d). In particular, Na^+, Ca^{2+}, and Al^{3+} cations were modeled in order to compare the effect of the cation charge on the stability of the complexes. Wetting/drying conditions were modeled by a different hydration degree of the cations (starting with a bare model). It was found that direct (–COOH/COO⁻ groups coordinate directly the cation) and indirect (water molecules from the coordination shell are bound to –COOH/COO⁻ groups) complexes have a different stability. Drying (stepwise reduction of water molecules) affected the predicted mobility of Al^{3+}, Ca^{2+}, and Na^+ cation specifically. The calculations reflect the amphoteric character of the hydrated Al^{3+} complex showing in most cases its acidic character via proton transfer from the water molecules of the hydration shell to the carboxylate group, but in some cases also deprotonation of the carboxyl group. The Al^{3+} cation has an extremely strong polarization effect and bridging capacity that significantly reduces the exchange capacity and increases the rigidity of the HS associates.

Conclusions

Molecular modelling tools are found to be useful in investigating basic interactions of water and cations with humic substances. It has been shown that even water molecule bridges alone lead to a significant stabilization of HS agglomerations, underlining the important role of drying and wetting of soils as well as temperature in HS stability and rigidity. Cation bridges have been even more efficient in connecting polar functional groups and negatively charged sites of HS, Al^{3+} showing the strongest bridging capacity.

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Chapter 12
Rapid Evaluation of Soil Quality Based on Soil Carbon Reflectance

Mohammad Sadegh Askari and Nicholas M. Holden

Abstract Many studies have considered spectroscopy for measurement of soil carbon (SC), and there is potential for spectroscopy to be used as a cost and time effective approach to assess soil quality (SQ). In this research, the relationship between SC and SQ in Irish grassland soils was studied; particularly the efficiency of spectroscopy and chemometric techniques for assessing SC and its contribution to SQ. The study was conducted using 20 sites with 5 replicates per site ($n = 100$ soil samples). Twenty soil properties were measured using standard methods as soil quality indicators. Management intensity was classified using K-means clustering, and the results reflected a trend in soil properties indicative of poorer SQ under more intensive management. Soil porosity, CN ratio and SC were selected as a minimum data set using principal component analysis and SC was the most discriminating indicator of the impact of management intensity on SQ. Soil visible and near-infrared spectra showed a good efficiency ($R^2 = 0.91$, $RMSE = 0.4$, $RPD = 2.94$) for prediction of SC. Spectroscopy and chemometric analysis allowed rapid evaluation of SC, and because of the strong relationship with management intensity, can provide a rapid, low cost, quantitative method for evaluating SQ under grassland management.

Keywords Spectroscopy • Soil carbon • Soil quality • Grassland

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Introduction

Soil carbon (SC) plays an important role in sustainable soil and land management (McBratney et al. 2000; Florinsky et al. 2002) and was reported as one of the most important indicators for evaluating soil quality (SQ) because it is associated with most ecosystems and productivity functions (Jarecki and Lal 2005; Reynolds et al. 2007). SC is positively correlated with SQ and is sensitive to ecosystem management (Moreno et al. 2006; Spargo et al. 2008). Therefore, increasing and maintaining SC is crucial for sustainable use of soil resources and crop production (Ghosh et al. 2012). Pastures have the potential to transform large amounts of carbon to soil organic carbon (SOC) (Wright et al. 2004). More than 90 % of organic carbon in pasture is located underground as root biomass or SOC (Schuman et al. 1999; Silveira et al. 2013). It can enhance the activity of soil microorganisms, soil C mineralization, rhizosphere production and SQ (Schuman et al. 1990; Frank and Groffman 1998; Wright et al. 2004). Grasslands, found in most regions of the world are considered a globally significant carbon resource, and are the main land use in Ireland, supporting very productive livestock enterprises and carbon-rich soils (Lafferty et al. 1999). Assessing the effect of current management systems on grassland soil is of particular interest because of the need to monitor and manage recognized threats to soils (Semikolennykh 2008) and for national carbon inventory reporting (Kiely et al. 2010).

Management practices affect the quantity of SC through biomass production, product extraction (e.g. milk, meat, silage) and inputs such as organic fertilizers (Lal et al. 1999; West and Marland 2002; Arshad et al. 2004) and erosion (Eynard et al. 2005). The aim of increasing management intensity is to maximize animal production by “sustainable intensification” (Pretty 1997; Garnett et al. 2012), thus the carbon balance in the soil can be changed (Conant et al. 2001; Lal 2002; Silveira et al. 2013). A sustainable management intensity will increase, or maintain at a high level, the quantity of SC and contribute to the sustainability of agricultural systems and SQ improvement (Guo and Gifford 2002). SC is regarded as a key indicator of soil health in the UK (Anon 2006; Bhogan et al. 2009).

Visible (VIS) and Near inferred (NIR) spectroscopy and chemometric analysis have been used for SC analysis, offering potential cost and time effective analysis (Chang et al. 2001; O’Rourke and Holden 2011) compared to methods such as chromate oxidation (Walkley and Black 1934), loss-on-ignition (Ball 1964) and combustion (Allison et al. 1965). Prediction of SC by NIR in the laboratory produces accurate models ($R^2 > 0.9$) and reasonable standard error (Chang et al. 2001; Brunet et al. 2007; Grinand et al. 2012). The efficiency of spectroscopic techniques offers potential for SQ assessment (Brown et al. 2005; Cécillon et al. 2009), Accurate SC estimation linked with SQ using visible (VIS) and NIR spectra could be a rapid and cost effective method for SQ monitoring. This research examined the potential of SC as an indicator of SQ in Irish grassland using spectroscopic techniques. The objectives were to evaluate the impact of management intensity on SC and SQ, and to assess the efficiency of spectroscopy for prediction of SC as an indicator of SQ.

Materials and Methods

The study was conducted at 20 grassland sites in Ireland (latitude 52°8′N and 54°20′N; longitude: 6°32′W and 8°19′W; mean daily temperature winter: 4.0–7.6 °C, and summer: 12.3–15.7 °C; average annual precipitation in eastern Ireland: 750 and 1,000 mm; www.met.ie). Soil and crop management practices were recorded through individual semi-structured interviews with each farmer. Field measurements were taken from September to December 2011. At each site within a representative 30 m^2 plot, with random orientation relative to the field boundaries and avoiding atypical areas such as gateways, unusually dry or wet areas, headlands and highly trafficked areas, 5 points equal distance apart were sampled from 0 to 10 cm depth across the central diagonal of the plot for laboratory analysis. Twenty soil properties were measured using standard methods as SQ indicators (Table 12.2). Soil total carbon (TC), and soil inorganic carbon (IC) were measured using a dry combustion carbon and nitrogen analyser (LECO Tru-Spec CHN analyser and Skalar-Primacs SLC-IC analyzer) that was described by Matejovic (1997) and Wright and Bailey (2001). All samples had low inorganic carbon content and therefore total carbon was approximately equal to SOC. For this paper, the term SC is used to avoid confusing with the more exact term total carbon. Samples were also analysed by spectroscopy by first crushing and passed through a 200 μm sieve, re-drying at 30 °C for 14 h in an oven to eliminate the effects of moisture content and acquisition of reflectance spectra using a Foss VIS-NIR Systems 6500 (Foss NIRSystems, Denmark) in the wavelength range 400–2,498 nm, with 2-nm intervals. Noise regions (400–450 and 950–1,000 nm in VIS and 1,000–1,050 and 2,450–2,498 nm in NIR) were cropped. In order to improve the linearity of spectra, reflectance data were converted to absorbance using the log (1/Reflectance). Samples were selected randomly for calibration (70 %) and validation (30 %) sets, and partial least-squares regression was used to develop a total carbon model using Unscambler software (version X10; CAMO software, Oslo, Norway). The calibration model was evaluated based on a combination of the coefficient of determination (R^2), root mean squared error (RMSE), and ratio of predicted deviation (RPD). The normality of all data sets was tested using the Kolmogorov-Smirnov test and visual examination of histograms.

Management was initially categorized by farm type (dairy, beef, beef plus dairy, mix sheep and other cattle), frequency of reseeding (less than 10 years, 10–20 years, more than 20 years and no reseeding), stocking rate which was categorized in low (less that 2.51 cow per hectare), medium (2.51–3) and high (more than three cow per hectare) based on McCarthy et al. (2012), grazing and silage management system, as typically used to characterize grassland systems, e.g. Macdonald et al. (2008), O'Donnell et al. (2008), Baudracco et al. (2010) and McCarthy et al. (2012). However, because of the relatively small number of sample sites (20), a more robust approach was deployed using K-means cluster analysis (Hartigan and Wong 1979) to identify three major clusters of management intensity using the management data for each site. Multivariate analysis of variance (MANOVA) and univariate analysis of variance (ANOVA) were then performed on soil variables to explore the effect of management intensity on SQ indicators, and only those attributes that were significantly different ($P < 0.05$) by management intensity were considered further. Principal component analysis (PCA) was applied to determine a minimum data set (MDS) for evaluating the effect of management intensity on SQ based on the method described in detail by Rezaei et al. (2006) and Li et al. (2013). The first three principal components (PC) with eigenvalues >1 that explained around 73 % of variation of all variables were selected, and the indicators with loading values within 10 % of the highest weighted loading factor were considered for the correlation test to determine the MDS. Stepwise discriminant analysis was used to select the SQ indicator that was most discriminating between the three levels of management intensity according to the method describes by Brejda et al. (2000) and Nosrati (2013). All statistical analyses were performed using SPSS v. 18.0 (SPSS Inc).

Results and Discussion

Conventional classification of management intensity using descriptive properties of the farm systems was not suitable for analyzing the data because membership of each class was very small. Based on the K-mean clustering, 25 % of fields were classified high intensity, 45 % percent medium intensity and 30 % low intensity (Table 12.1). The 20 SQ indicators (Table 12.2) had ranges consistent with previous studies (Diamond and Shanley 2003; Kurz et al. 2006; Curtin and Mullen 2007), which indicated that the study sites were representative of the range of grassland soil in Ireland. Of the 20 properties, only 13 were significantly different ($p < 0.05$) by management intensity, and thus used as the total dataset (TDS) for assessing SQ (Table 12.2). The K means clustering reflected a trend in soil properties indicative of poorer SQ under more intensive management.

The MDS derived from PCA was SC from PC1, soil porosity (SP) from PC2 and CN ratio from PC3. From the stepwise discriminant analysis the first discriminant function explained 85.3 % of the total variance and the second 14.7 %. SC had the greatest discriminating power between the management intensity classes:

$$\text{Function1} = \mathbf{13.964\,(SC)} + 0.934\ (\text{CN}) - 0.073\ (\text{SP}) \tag{12.1}$$

$$\text{Function2} = \mathbf{20.241\,(SC)} + 0.255\ (\text{CN})0.144\ (\text{SP}) \tag{12.2}$$

The application of PCA and discriminant analysis reduced data redundancy by identifying the most relevant soil properties for detecting the impact of management intensity on SQ (Rezaei et al. 2006; Li et al. 2013). For the Irish grassland soils studied, intensification of management resulted in lower SC, which was associated with poorer SQ. These trends are consistent with previous research on management intensity (e.g. Potter et al. 2001; Leifeld and Fuhrer 2009), and perhaps reflect an increase of carbon mineralization and residue quality leading to SC losses (Silveira et al. 2013). Improving

Table 12.1 Management practices and intensity classification in each site

Sites	Farm type	Reseeding frequency (years)	Management	Stocking rate	K mean clustering		
					Cluster	Distance	Intensity class
1	D	10–20	S+G	L	1	0.894	High
2	D	10–20	S+G	H	1	1.265	High
3	M	NO	G	M	3	0.943	Low
4	D+B	10–20	G	M	2	0.981	Mid
5	D	<10	S+G	L	1	1.000	High
6	D+B	10–20	G	M	2	0.981	Mid
7	D+B	>20	G	L	2	1.515	Mid
8	B	10–20	S+G	M	2	0.720	Mid
9	B	10–20	S+G	M	2	0.720	Mid
10	M	NO	G	L	3	0.745	Low
11	D	<10	S+G	M	1	0.632	High
12	D	10–20	S+G	M	1	0.447	High
13	B	NO	G	L	3	0.471	Low
14	B	<10	S+G	L	2	1.186	Mid
15	B	<10	G	L	2	1.232	Mid
16	B	10–20	S+G	L	2	0.793	Mid
17	B	NO	G	L	3	0.471	Low
18	B	NO	G	M	3	0.745	Low
19	B	NO	G	L	3	0.471	Low
20	B	10–20	S+G	M	2	0.720	Mid

D dairy farm, *B* beef farm, *M* mix sheep and cattle farm, *D+B* mix dairy and beef farm, *G* only grazing, *S+G* both silage and grazing, Stocking rate: *H* high (>3 cows/ha), *M* medium (2.51–3 cows/ha), *L* Low (<2.51 cow/ha), *High* high intensive pasture, *Mid* medium intensive pasture, *Low* low intensive pasture

grassland management can have an impact on the carbon sequestration, which is associated with SC accumulation (Conant et al. 2001; Lal 2008), but there is little research to indicate the best intensification management for sustainable soil quality. Increasing SC improves SQ because it is reflected in porosity, bulk density (Miralles et al. 2009), promotion of infiltration, reduction of soil erosion and compaction (Islam and Weil 2000; Miralles et al. 2009), structure stability (Stevens 2008), water storage, nutrient cycling and other soil attributes which are related with soil productivity and environmental protection (Gilley et al. 1997; Miralles et al. 2009).

Accurate prediction of SC using VIS-NIR spectroscopy is required to facilitate research to find the best management options for sustainable livestock production from grasslands, and high resolution monitoring for SQ. Prior to calibration, the homogeneity of variance of SC in the calibration and validation sets ($p > 0.85$) was confirmed by Levene's test, and the mean comparison (T test) indicated there was no significant difference between validation and calibration mean values ($P > 0.46$). The random selection of the validation set reliably represented the samples distribution. The best SC prediction was achieved from the NIR region (Table 12.3) in both calibration ($R^2 = 0.95$, RMSE = 0.34) and validation ($R^2 = 0.94$, RMSE = 0.34,

Table 12.2 Soil properties measured as potential indicators of Soil Quality

SQ indicator	Mean	Std	TDS	TDS range High	TDS range Mid	TDS range Low	Measurement method
Aggregate size distribution (MWD)	2.44	0.64	✗				Nimmo and Perkins (2002)
Bulk density (g/cm^3)	0.81	0.12	✓	0.85–1.03	0.51–0.99	0.6–0.96	Grossman and Reinsch (2002)
Bulk density <2 mm (g cm^{-3})	0.80	0.12	✓	0.81–0.99	0.51–0.97	0.6–0.92	Grossman and Reinsch (2002)
Porosity (%)	64.20	6.51	✓	49.9–67.4	50.3–82.3	46.6–78.3	Flint and Flint (2002)
pH	5.61	0.64	✓	5.0–6.7	4.9–7.1	4.3–7.0	pH meter 1:1 (Thomas 1996)
Total Nitrogen (%)	0.54	0.13	✓	0.4–0.7	0.3–0.8	0.4–0.8	Matejovic (1997), Wright and Bailey (2001)
Total Carbon (%)	5.88	1.45	✓	4.3–7.2	3.3–10.2	4.9–9.5	Matejovic (1997), Wright and Bailey (2001)
SOC (%)	5.85	1.44	✓	4.3–7.2	3.25–10.16	4.89–9.40	Matejovic (1997), Wright and Bailey (2001)
CN ratio	11.00	0.91	✓	9.9–13.1	10–12.6	8.9–11.4	
Calcium (PPM)	2,624	1,896.6	✗				Soltanpour et al. (1996)
Magnesium (PPM)	205.26	92.12	✗				Soltanpour et al. (1996)
Potassium (PPM)	179.87	159.45	✗				Soltanpour et al. (1996)
Phosphate (PPM)	10.94	10.35	✗				Kuo (1996)
Sorbtivity (cm s$^{-0.5}$)	0.06	0.05	✓	0.10–0.40	0.03–0.11	0.03–0.08	Philip (1957)
Penetration resistance (Kpa)	1,265	509.54	✓	632–2,695	397–1,951	491–2,944	Penetrometer (FIELDSCOUT SC900)
Water content (%)	50.31	14.14	✗				Topp and Ferre (2002)
Sand (%)	40.56	12.87	✗				Gee and Or (2002)
Silt (%)	34.33	7.80	✓	17–40	20–50	20–43	Gee and Or (2002)
Clay (%)	25.11	6.62	✓	13–35	13–34	16–40	Gee and Or (2002)
Soil respiration (mg C kg^{-1} day^{-1})	23.50	5.98	✓	15.8–31.5	10.8–39.0	6.7–29.3	Horwath and Paul (1994)

From these a total dataset (TDS) (properties that differed by management intensity) and a minimum dataset (MDS) (the most discriminating properties) were identified

High high intensive pasture, *Mid* medium intensive pasture, *Low* low intensive pasture, *TDS* total data sets, *Std* standard deviation

Table 12.3 Spectral analyses results by wavelength range and pre-processing

	Wavelength range	Latent variables	RPD	Model	R^2	RMSE
Prediction models	NIR+VIS	10	2.94	Calibration	0.93	0.39
				Validation	0.91	0.40
	VIS	7	2.06	Calibration	0.82	0.62
				Validation	0.83	0.57
	NIR	11	3.42	Calibration	0.95	0.34
				Validation	0.94	0.34
Optimum preprocessing						
Max Normalization	NIR+VIS	13	3.20	Calibration	0.93	0.38
				Validation	0.92	0.38
Mean center Std Scale	NIR+VIS	10	2.97	Calibration	0.93	0.39
				Validation	0.92	0.38

NIR near infrared, *VIS* visible

RPD = 3.42) models, but the VIS–NIR region also showed a robust model in calibration ($R^2 = 0.93$, RMSE = 0.39) and validation ($R^2 = 0.91$, RMSE = 0.4, RPD = 2.94) sets. Preprocessing transformations did not improve the accuracy of the models (Table 12.3). The results were similar to O'Rourke and Holden (2011, 2012), and confirm the capability of VIS-NIR spectroscopy for quantitative assessment of SC especially in NIR regions without applying particular preprocessing methods. Therefore, this approach is likely to provide time and cost effective for assessing the impact of management systems on the quality of Irish grassland soils.

Conclusion

The relationship between management intensity, and SQ indicated that for current management practices, increased intensity, typified by sward management and stocking rate, resulted in a decrease in SQ. The most powerful discriminating property was SC, thus it could be used for rapid assessment and monitoring of SQ change with changes to grassland management. While SC alone will not be suitable for a full SQ assessment, it does reflect a range of biological, chemical and physical properties of the soil so is a good integrating variable.

Spectroscopy proved to be a reliable technique for rapid, low cost analysis of SC. This means that high sampling resolution (spatial and temporal) can be deployed for monitoring grassland SQ with a robust spectroscopic analysis. The study indicated a promising future for the application of spectral data sets for quantitative and direct evaluation of SQ based on integrating indices and discrimination of multiple facets of SQ.

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Chapter 13
Characterization of Soil Organic Substances by UV-Vis Spectrophotometry in Some Soils of Hungary

Klaudia Kiss, Zoltán Szalai, Gergely Jakab, Balázs Madarász, and Nóra Zboray

Abstract UV-Vis spectrometry methods are widely used to characterize soil organic matter, especially humic substances from different extracts of soils. Our aims were to investigate organic characteristics of soils, as part of a project focusing on relationships between solute mineral components and organic matter quality. The study was performed using UV-Vis spectrophotometry on six Hungarian soils. For the characterization of humic substances we used several visible and UV methods. Humic materials were extracted from soils using a variety of extractants. We found that a decrease in pH and an increase in dissolved electrolyte concentration supported coagulation in preferance to dissolution in almost every case. The highest absorbance values was given by extractants which contained sodium-pyrophosphate. In our experience double extraction methods (E_{NaF}/E_{NaOH} according to Hargitai, A talaj szerves anyagának meghatározása és jellemzése. In: Buzás I (ed) Talaj- és agrokémiai vizsgálati módszerkönyv II. Mezőgazdasági Kiadó, Budapest, 1988, $E400_{NaOH+Na4P2O7}/E400_{PBS}$) and E4/E6 are suitable for analysing humic substances. Comparing these three visible methods there are only slight differences between them. The results do not show strong correlation between visible and UV methods as these techniques analyse different properties of soil humic substances.

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Introduction

UV-Vis spectrometric methods are widely used to characterize soil organic matter, especially humic substances from different extracts of soils, because UV-Vis spectrophotometry is a rapid and – compared with isolation of different fractions – relatively simple technique to estimate humic properties (Hautala et al. 2000; Spiegel et al. 2007).

The dissolution of humic substances is mainly governed by their particle size (or molecular weight) (Chen et al. 1977), acidity, aromaticity or aliphatic character and is influenced by some external conditions. The absorbance in the UV-Vis range is influenced by some properties of organic compounds, e.g. absorbance increases with total C-content, molecular weight and quantity of aromatic rings within the molecules (Chen et al. 1977). Absorbance might also change due to vibration and rotation of the molecules and intermolecular interactions as well (Korshin et al. 1997).

When applying spectrophotometrical techniques several methodological problems and external conditions have to be taken into account. The main problem is that spectrometry is non-specific for analysing humic substances and does not give a band that is very characteristic of humic compounds (Schnitzer and Kahn 1972). In the UV-Vis range of the spectrum, broad absorption bands can be observed and this smoothness implies that different components (organic and inorganic components as well) might be present in the samples (Pansu and Gautheyrou 2006). The spectra are influenced by chromophore groups of humic substances, ions dissolving out from the soil (e.g. Fe^{3+}) and also by the presence of solid particles.

Our aim was to investigate the organic characteristics of soils, as part of a project focusing on the relationship between solute mineral components and organic matter quality. The study was performed by UV-Vis spectrophotometry on the humic horizon of six Hungarian soils.

Methods

Soil samples were extracted in solutions which had different pH and ionic strength (0.05 M $NaHCO_3$, pH = 8.0 (Chen et al. 1977); 1 % NaF; 0.5 % NaOH (Hargitai 1988), pH = 13.1; and 0.5 M NaOH, pH = 13.7) in 1:10 m:V ratio. We used buffer solutions (Fujitake et al. 1999) (e.g. 0.05 M phosphate BS, pH = 4.0; 0.05 M NaOH with 0.05 M $Na_4P_2O_7$, pH = 12.1) (after Kumada 1985) to enhance stability. However, use of buffers poses a potential disadvantage, namely that sodium-pyrophosphate solution selectively extracts Fe- and Al-ions complexed to organic matter (Blakemore et al. 1987) and consequently the chemical properties of the soil surface could change significantly (Tombácz 2003).

Extraction of the organic compounds involved 16 h of shaking, followed by 12 h of settling and 20 min centrifuging at 5,000 rpm.

Absorbance measurements were made on a double-beam Shimadzu 3600 UV-Vis-NIR spectrophotometer in quartz cuvettes. Path length (1-cm or 2-mm) of the cuvettes depended on the concentration of the soil extracts. As a blank we used the solution in which the samples were solved. For every sample continuous spectra (shift: 1 nm) were scanned from 800 to 180 nm.

For the characterization of humic substances we applied the following methods:

For UV methods we used 0.05 M $NaHCO_3$ to extract humic substances from the soils.

- The proportion of the specific UV absorbance value on 254 nm and the SOC content (E254/SOC) is in strong correlation with the number of aromatic groups. The absorbance at 272 and 280 nm (Chin et al. 1994) refer to the aromaticity and molecular weight, respectively.
- The ratio of the absorption value at two different wavelengths is a widely used parameter to determine the aromatic characteristic of humic substances. In this work we used and compared two methods: the E2/E3 (E250/E365) and URI (E210/E254) (Her et al. 2008).

In visible range the E4/E6 ratio (the absorbance at 465 nm divided by the absorbance at 665 nm) was used. In this case the visible spectrum is measured in 0.05 M $NaHCO_3$ solution (after Kumada 1985 and Chen et al. 1977). It shows the degree of humification. The lower E4/E6 values refer to a higher degree of condensation within the molecules and low aliphatic chain content. Ratios lower than 5 are characteristic of humic acids (3–5), while fulvic acids have higher ratios (higher than 7 and 5 according to Chen et al. 1977 and Kononova 1966, respectively).

Besides this we applied visible methods in which we used two types of solutions for the extractions.

- According to a Hungarian method called Hargitai (1988) the absorbance of the solution extracted by 1 % NaF divided by that extracted with 0.5 % NaOH at different wavelengths (this is called Q-value) provides qualitative information of humic and fulvic acids (Hargitai 1988). The humic substances are bound to clay and carbonate minerals through Ca^{2+} and Al^{3+} ions. NaF can abrupt these strong complexes. NaOH splits these organomineral complexes by alkaline hydrolysis. NaF dissolves well-decomposed humic fractions with higher molecular size while raw humic materials are better dissolved by NaOH.
- The proportion of the absorbance for the solutions extracted by 0.05 M NaOH – 0.05 M $Na_4P_2O_7$ (pH 12.1) and 0.05 M phosphate buffer solution (pH 4.0), respectively, was calculated at 400 nm wavelength. In our experience this ratio gives information about the relative amount of humic and fulvic acid material too.

Materials

We measured the upper horizon for each soil described below. Depth and selected soil chemical properties of the horizons are presented in Table 13.1. Short descriptions of each soil is shown below.

– Calcic Mollic Gleysol (Humic, Arenic) (CMG):

The soil was developed from a marshland Histosol near Gerje stream (geographic coordinates: WGS84 N47°12′31.8″ E019°40′42.5″). The main properties are the results of hydromorphic features including dark colour, Fe-, Mn- and carbonate concretions and gleyic colour pattern.

– Calcic Phaeozem (Arenic) (CP):

This soil profile was exposed on a former floodplain near Gerje stream (N47°12′29.7″ E019°40′42.6″). The site is on a plateau. The soil is a weekly developed Calcic Phaeozem as it has only a thin B horizon developed in carbonatic sand.

– Rendzic Leptosol (humic) (RL):

Samples of RL originate from a soil profile, located on a karstic plateau in Gerecse Mts (N47°42′15.0″ E018°30′31.6″). The vegetation of the area is dominated by closer forest. The Munsell color of the soil shows that the soil was developed from the thin red clay that covers limestone. Clay minerals occurring in the soil can be bound with humic materials and produce organomineral complexes.

– Haplic Luvisol (HAL):

The soil profile was excavated in a closed deciduous forest on a 3° slope in Sopron Mts (N47°40′14.8″ E016°33′53.1″). The parent material is carbonatic Pleistocene loess, but there is no carbonate in the solum, the pH is strongly acidic. In the analysed A1 horizon located at 5–20 cm depth the soil particles are coated by humic concretions.

Table 13.1 Depth and soil chemical properties of the investigated soil horizons

Sample	Measured horizon	Depth (cm)	Munsell color	$pH_{(H2O)}$	$CaCO_3$ %(m/m)	SOC %(m/m)	C/N
CMG	A_h	0–30	2.5Y 2.5/1	7.18	51.3	5.53	41.85
CP	A_l	0–10	2.5Y 2.5/1	7.17	5.88	1.61	19.51
RL	AC	0–16	5YR 4/3	6.6	0.82	8.35	123.74
HAL	A_l	5–20	10YR 5/3	5.6	0.00	1.07	50.99
CC	A_p	0–20	10YR 3/1	8.6	5.41	2.22	45.80
PS		230–300	10YR 3/3	7.0	0.42	1.12	48.58

Legend: *CMG* Calcic Mollic Gleysol, *CP* Calcic Phaeozem, *RL* Rendzic Leptosol, *HAL* Haplic Luvisol, *CC* Calcic Chernozem, *PS* Paleosol

– Calcic Chernozem (Mollic) (CC):

Samples of CC came from a typical Pleistocene loess covered area near Martonvásár (N47°20′17.7″ E018°49′04.2″). The soil is in an arable field on a plateau. The soil organic substances are bound to carbonate minerals through Ca^{2+} ions forming Ca-humate complexes.

– Paleosol (PS):

It is a well-developed doline filling soil in Börzsöny Mts (N47°49′04.0″ E019°04′13.7″), presumably originating from the last interglacial (according to luminescent data). It has sharply separated genetic horizons. Micromorphology shows it has moderately developed texture and the soil aggregates can be separated. The analyzed horizon contains significant amount of organic matter that appears as humic film or as crack fillings.

Results and Discussion

Various quality and quantity of humic materials were diluted by different extraction methods (Fig 13.1a). It depended on several external conditions, firstly the pH. When pH decreased the amount of extracted humic compounds decreased in parallel. The quantity of the extracts is influenced by the ionic strength of dilution and its ion content. The highest amount of humic material is mobilized not by NaOH alone but by a solution made of $Na_4P_2O_7$ or $Na_4P_2O_7$ with NaOH. Similar results were reported by Kumada (1985).

Organic compounds of the analysed six soils are very different (Fig. 13.2b, c). When the humic matter was dissolved in 0.05 M NaOH along with 0.05 M $Na_4P_2O_7$ (pH = 12.1), the CMG and RL samples had the highest absorbance value on a specific wavelength ($E400_{NaOH+Na4P2O7}$). Using pH = 4 PBS buffer, the RL and HAL (which had the lower intensity by extraction of NaOH-$Na_4P_2O_7$) had the highest intensity values. Soil types such as chernozem had low extinction values (CC, PS). The $E400_{NaOH+Na4P2O7}/E400_{PBS}$ ratio of the intensities measured at 400 nm well featured the characteristic of the soils: we identified rather acidic, low molecular weight humic substances in the HAL, RL and CP samples, which dissolved relatively well in the acidic range (so they are predominantly fulvic acids). Samples which have high carbonate or iron content are probably more abundant in humates that form weak complexes with Ca- and Fe-ions and do not dissolve in acidic pH. The high ratio of the PS may caused by not only organic complexes but also inorganic components that are dispersed by sodium-pyrophosphate.

According to the E4/E6 ratio (Table 13.2) we classified the soil samples into three groups. Samples with highest rate – that means more abundant fulvic acids – are HAL (7.65) and RL (6.47), which have low pH and base saturation. The CC (3.85), CMG (4.08) and PS (4.05) basically consist of humic acids according to E4/E6 rate, while the weakly developed soil CP (4.72) is composed of circa similar amount of humic and fulvic acids.

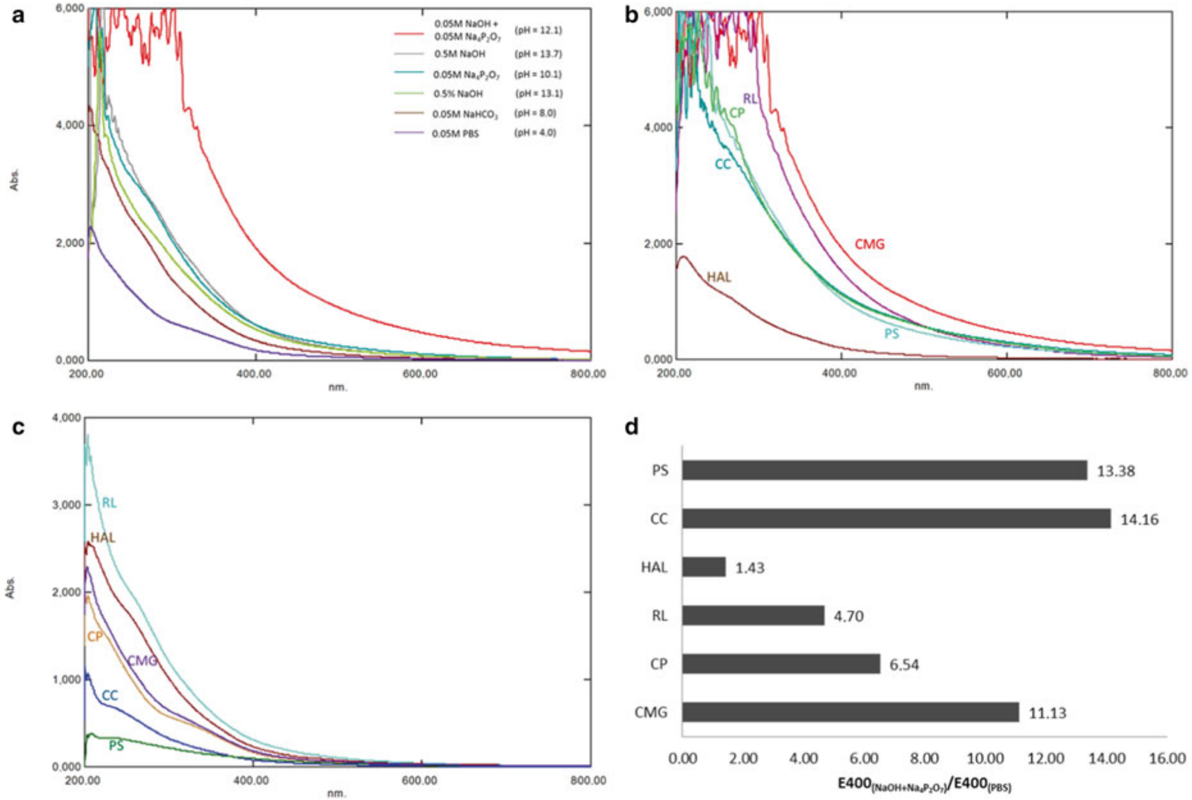

Fig. 13.1 (**a**) UV-Vis spectra of CMG diluted by different extraction methods; (**b**) Spectra of soils extracted by 0.05 M NaOH and 0.05 M $Na_4P_2O_7$ (pH 12.1); (**c**) Spectra of soils extracted by 0.05 M Phosphate buffer solution (PBS) (pH 4.0); (**d**) E400$_{NaOH+Na4P2O7}$/E400$_{PBS}$: ratio of the absorbance on 400 nm for the solutions extracted by 0.05 M NaOH – 0.05 M $Na_4P_2O_7$ and 0.05 M PBS

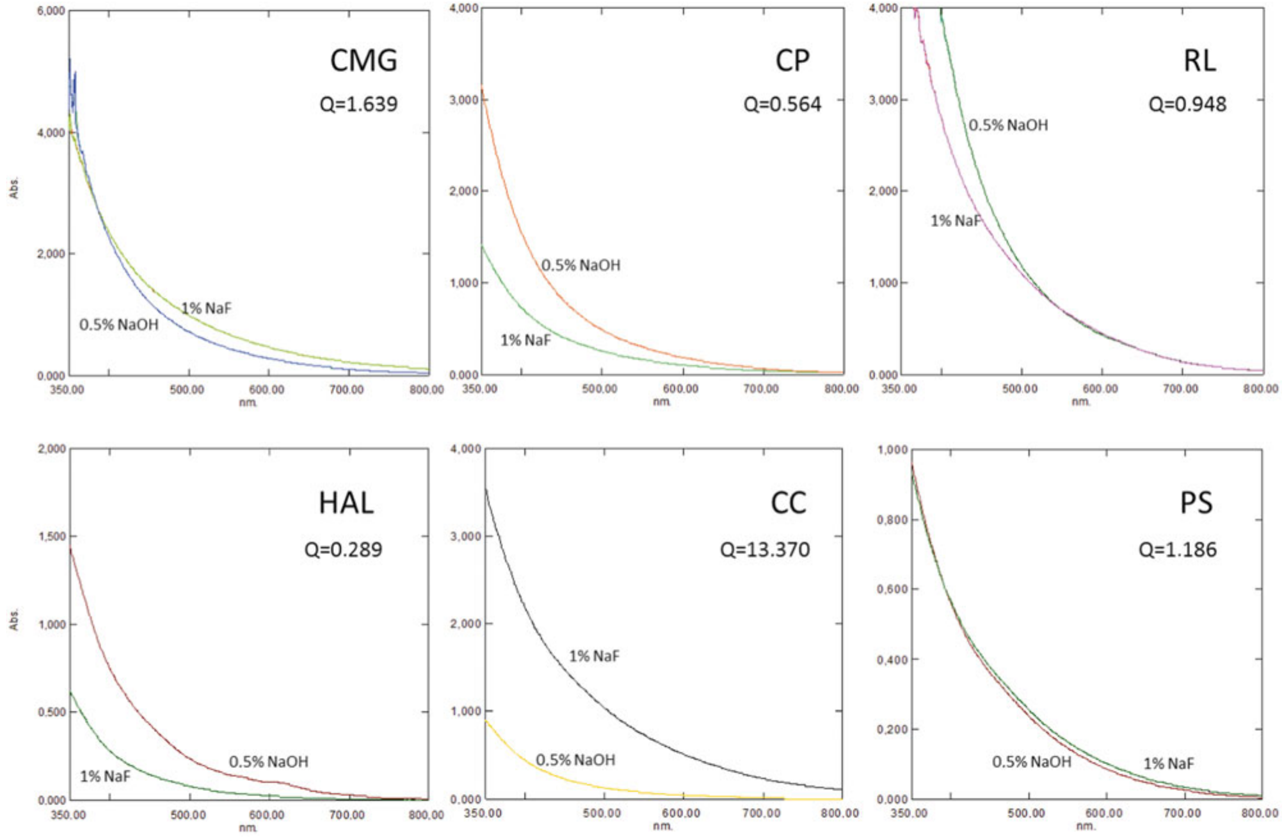

Fig. 13.2 Vis spectra and Q value (E_{NaF}/E_{NaOH}) of soils extracted by 1 % NaF and 0.05 % NaOH

Table 13.2 Specific ratios from UV-Vis spectra

Sample	E4/E6	Q (E_{NaF}/E_{NaOH})	$E400_{NaOH+Na4P2O7}/E400_{PBS}$	E2/E3	E210/E254	E254/SOC
CMG	4.08	1.64	11.13	4.27	1.63	1.322
CP	4.72	0.56	6.54	3.99	1.61	1.544
RL	6.48	0.95	4.70	4.35	1.74	1.661
HAL	7.65	0.29	1.43	4.52	1.54	1.449
CC	3.85	13.37	14.16	3.91	1.66	1.335
PS	4.05	1.19	13.38	3.19	0.75	1.55

According to the Q value of Hargitai method CC is distinct among the soils we examined, as it has a higher degree of humification than the others. Besides CMG also has a humic stability number higher than 1. We interpret that in these two soils, well-decomposed, higher molecular size humic materials (they are probably bound to Ca-ions) dominate. Q-value for HAL and CP is much less than 1, which shows that in these soils the acidic, less polycondensated and low molecular-weighted humic substances prevail. The Q-value of PS and RL is around 1. It suggests that in the case of these paleo- and fossil soils there was enough time for humic material with larger humic stability number to develop.

Soils with higher SUVA/TOC content have higher aromaticity. In our case the aromaticity decreased in the following order: CC > CP > PS > CMG > HAL > RL.

The lower E2/E3 ratio of the PS, CC and CP soils means higher aromaticity. According to Takács and Füleky (2010) the aromatic features decrease in a Soil HA > Soil FA > NOM (natural organic matter) order. Based on this it is not surprising that the humic acid rich chernozem-type soils and a well-developed, several times (probably quarternary) re-humified PS have higher aromaticity. HAL has got less aromatic features. It is an acidic soil which has <50 % base saturation and mainly contains fulvic acids.

The low E210/E254 ratio refers to a higher content of aromatic groups and lower content of non-aromatic function groups (Her et al. 2008). According to this, the order of decreasing aromaticity corresponds with increasing the amount of functional groups (e.g. carboxylic, phenolic -OH groups) was the following: PS > CMG > CC > HAL > CP > RL.

The results do not show strong correlation between visible and UV methods as these techniques analyse different properties of the soil humic substances. Relationships exist only in a narrower range between the Hargitai and E2/E3 methods ($r = 0{,}949$). It is an expected result that the E254, E272 and E280 data and E2/E3 ratio are in good correlation (e.g. E254 – E2/E3: $r = 0{,}908$), however, we could not show relationship between E2/E3 and E210/E254.

Conclusion

Humic materials from the soils were extracted using different methods. We observed that a decrease in pH and an increase in dissolved electrolyte concentration supported coagulation as opposed to dissolution almost in every case.

The highest absorbance values was given by extractants which contained Sodium-pyrophosphate, but a part of the intensity was likely augmented by inorganic components (e.g. Fe^{3+}, Al^{3+}, clay minerals) in these cases.

Our results show that double extraction methods (E_{NaF}/E_{NaOH} according to Hargitai 1988, $E400_{NaOH+Na4P2O7}/E400_{PBS}$) and E4/E6 are suitable for analysing humic substances. Comparing these three visible methods there are only slight differences between them. We observed that CC and CMG soils contain higher molecular-weighted humic materials (mainly humic acids) according to the three applied visible methods. Acidic, less polycondensated and low molecular-weighted humic substances (mainly fulvic acids) dominate in HAL and CP. We obtained similar results for PS and RL according to E4/E6 and $E400_{NaOH+Na4P2O7}/E400_{PBS}$ methods, but we did not get unambiguous results for humic stability by the Hargitai method.

The results do not show strong correlation between visible and UV methods as these techniques analyse different properties of soil humic substances.

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Chapter 14
Hot-Water-Soluble Organic Compounds Related to Hydrophobicity in Sandy Soils

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Abstract Soil water repellency (WR) reduces mineralization of soil organic matter (SOM) and has the potential to sequester soil carbon. However, predicted climate change events such as decreased rainfall and droughts can cause changes in WR influencing water storage and plant productivity. Hot-water-soluble carbon (HWSC) is a sensitive indicator of ecosystem changes. It contains binding agents influencing soil aggregate stability, which is mainly controlled by soil WR levels. Here we characterize the link between WR and the organic compounds composition in hot water extracts from accelerated solvent extraction (ASE) of sandy soils. Extracts were lyophilized, fractionated and measured by GC/MS. Dominant compounds were phenolic acids, short chain dicarboxylic acids (C_4–C_9), saccharides, glycosides, (C_8–C_{18}) fatty acids, and esters of oleic, stearic and palmitic acids. We speculate that the complete elimination of WR by hot water was due to: (i) critical quantity of HWSC extracted, necessary to disaggregate soil particles; (ii) removal of sugars and aromatics; (iii) removal of hydrophobic fatty acid esters (C_{16} and C_{18}); (iv) enhanced desorption of complex DOC fractions in water at high T and pressure; (v) exposure of greater proportion of hydrophilic sites. The polarity and aromaticity of HWSC can play a critical role in stabilization and destabilization of soil organic matter (SOM), particle wettability and C dynamics in soils.

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Introduction

The stabilization of soil organic carbon (SOC) by hydrophobic protection mechanisms enhances carbon sequestration through reduced microbial activity, soil organic matter (SOM) decomposition and CO_2 emissions. These short term benefits could be outweighed in the longer term by reduced plant productivity and photosynthesis which diminish the potential of soils to act as a carbon sink. The hot water soluble carbon (HWSC) has been suggested as a sensitive indicator of the effect of soil management practices on overall C stock change, carbon sequestration potential and environmental performance monitoring. HWSC was found to be positively correlated with soil aggregation, soil microbial biomass, microbial nitrogen, mineralisable N, total carbohydrates and total C (Ghani et al. 2003). Nearly half of the C pool in the HWSC extract is present as carbohydrates (Ghani et al. 2003; Simoneit et al. 2004). Dissolved organic matter (DOM) and water soluble organic matter (WSOM) have been studied by Py-GC/MS, Py-MS, Py-FIMS, UV/VIS and fluorescence spectroscopy (Leinweber et al. 1995; Huang et al. 1998; Nierop and Buurman 1998; Kalbitz et al. 2003; Nkhili et al. 2012) and ^{1}H, ^{13}C NMR (Guggenberger and Zech 1994; Leinweber et al. 1995) and were found to be dominated by sugars, aromatics (0-alkyl-C dominating), as well as N-containing compounds indicating origin from soil microbial biomass, root exudates and lysates. It is widely accepted that WR in soils is associated with the formation of coatings of hydrophobic compounds of aliphatic and aromatic nature on soil surfaces and/or the presence of interstitial particulate organic matter. It has been shown that not only lipophilic and amphiphilic, but also polar compounds such as LMW phenolic acids, short-chain diacids, and saccharides play an important role in soil WR development, therefore sequestering soil carbon through stabilizing hydrophobic interactions (Atanassova and Doerr 2010). To our knowledge, no studies to date have been concerned with the molecular composition of solvent soluble fractions of hot aqueous extracts of water repellent soils obtained under conditions of ASE. The aim is to unravel the molecular composition of free solvent soluble compounds in water repellent sandy soils and the mechanism behind the expression of soil water repellency.

Materials and Methods

Soil samples with different levels of soil WR were taken from sandy soils (Arenosols, FAO 2001, Table 14.1). Soils were subjected to accelerated solvent extraction (*ASE*) with water as a solvent using the following conditions: heating

Table 14.1 Main properties of the experimental soils

Soil code and texture	Fe_{cd} %	SSA $m^2 \cdot g^{-1}$	TOC before HWE wt %	TOC after HWE wt %	pH	WDPT[a] before HWE (s)	WDPT[a] after HWE (s)
GP[a] sand	0.07	0.32	3.9	3.5	4.5	993	<5
NT[a] sand	0.16	0.41	3.4	3.1	3.6	287	<5
ML[a] sandy loam	0.58	4.41	9.0	7.9	4.4	10	<5
UK[a, b] sand	0.19	0.42	1.3	1.2	7.5	205	<5

[a] TOC by dry combustion, SSA N_2 BET, Fe_{cd} citrate-dithionite extraction (Atanassova and Doerr 2010) and WDPT as median of three measurements (Doerr et al. 2002) for Australian soils under eucalypt vegetation

[b] UK soil under herbs and grass (this study)

phase 5 min., static extraction time 20 min and pressure 10.3×10^6 Pa at 100 °C. Soils after extraction were dried and tested for water repellency levels as described above. Hot water ASE extraction led to a lasting elimination of soil water repellency (Table 14.1). Soil water extracts (<1.3 μ) were lyophilized at (−50 °C) and subjected to fractionation in DCM, DCM/*iso*-propanol and methanol. Sample preparation and measurement was carried out similarly to our previous methodology (Atanassova and Doerr 2010).

Results and Discussion

The extracts from the Australian soils were dark brown coloured due to water soluble humic substances and hydrolysable tannins. Due to their polyphenolic nature tannins bind and precipitate proteins and amino acids and are controllers of SOM decomposition and C and N cycling in soils. Under the condition of ASE pressurized hot water also extracts additional amounts of non-microbial organic C. The compounds with higher relative intensity in the total ion chromatograms (TIC) were phenolic acids, aldehydes and their derivatives, short chain dicarboxylic acids, saccharides, glycosides and other polar compounds with complex nature (Figs. 14.1, 14.2, 14.3, and 14.4). Aromatics and their derivatives were detected with high intensity in the water repellent GP and NT soils (DCM fraction), the most abundant being benzoic, hydroxy-, dihydroxybenzoic and methoxy-hydroxybenzoic acids (Fig. 14.1a, b). However, organic carbon saturation with aromatics was highest in the UK sandy soil possessing the least organic matter (Fig. 14.4). Aromatic acids are depolymerisation products of lignin and can also originate from phenol oxidation (Young and Frazer 1987). Hot water extraction can liberate aromatic acids bound to polysaccharides from lignocellulose-degradation products present in the hydrophobic acid fraction of DOM (Guggenberger and Zech 1994). Aromatic acids similarly to dicarboxylic acids exhibit strong complexing abilities with Al and Fe sesquioxides through a mechanism of ligand exchange (Guggenberger and Zech 1994; Kaiser et al. 1996). Hot water extraction

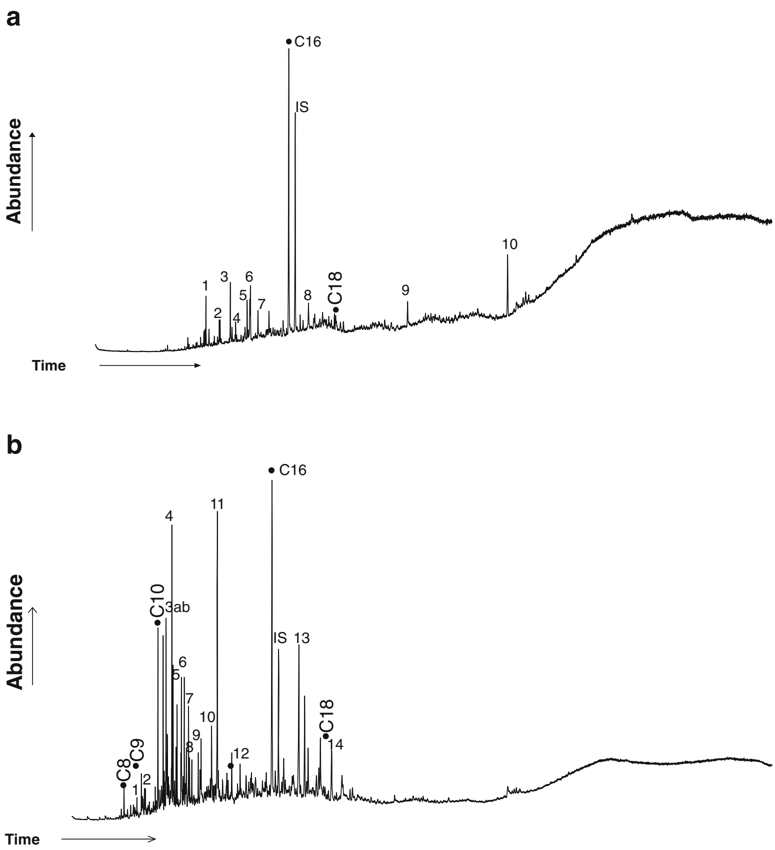

Fig. 14.1 Gas chromatogram of hot-water-soluble extracts (DCM fraction) obtained from GP soil (a) and ML soil (b). (**a**) • *n*-alkanoic acid; IS = internal standard 10-nonadecanone; *1* hydroxybenzoic acid, *2* 3,5-dimethoxy-4-hydroxybenzaldehyde, *3* 3-methoxy-4-hydroxybenzoic acid, *4* azelaic acid, *5* 3,4-dimethoxyphenyl, hydroxymethyl acetate, *6* unidentified m/z 73, 311, 339, *7* 3,5-dimethoxy-4-hydroxybenzoic acid, *8* Octadecenol, *9* unidentified m/z 57, 71, 95, 113, 149, 167, 255, 279, 382, 396, *10* stigmast-5-en-3-ol, oleate; (**b**) *1* 2-isopropyl-5-methylphenol (thymol), *2* 4-hydroxybenzaldehyde, *3a, b* isoxazolo[2,3-b]benz[1,2]oxazine, perhydro-2-methoxycarbonyl-10-methyl-5a-hydroxy- (suspected), *4* unidentified m/z 55, 73, 93, 127, 141, 155, 170, 183, 198, 223, 280, *5* 2-butendioic acid, *6* 4-hydroxybenzoic acid, *7* Glycoside, *8* octandioic acid, *9* 3,5-dimethoxy-4-hydroxybenzaldehyde, *10* 3-methoxy-4-hydroxybenzoic acid, *11* azelaic acid, *12* 3,5-dimethoxy-4-hydroxybenzoic acid, *13* suspected glycoside m/z 73, 107, 122, 147, 203, 239, 263, 278, 329, *14* unidentified m/z 73, 91, 109, 129, 151, 187, 233, 248, 341, 396

can hardly cause disruption of ester bonds in plant biopolyesters, but autohydrolysis can make possible some hemicellulose depolymerization. The reaction is catalyzed by H_3O^+ ions and leads to formation of acetic, uronic and phenolic acids (Liu 2010). The DCM fraction of the sandy loam soil of heavier texture is dominated by polar heterocyclic compounds of complex structure in combination with

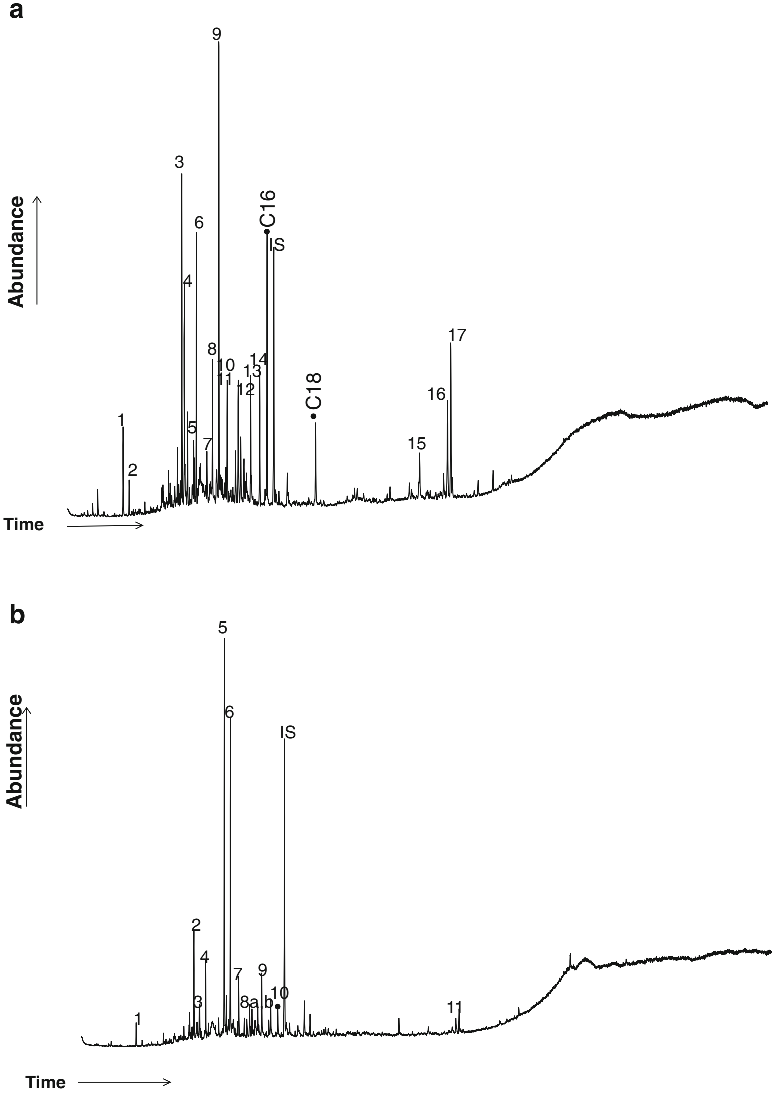

Fig. 14.2 Gas chromatogram of hot-water-soluble extracts (DCM/IPA fraction) from GP soil (**a**) and ML soil (**b**). IS = internal standard 10-nonadecanone (**a**) *1* Phosphate, *2* butandioic acid, *3* 4-hydroxybenzoic acid, *4* Hexose, *5* heptandioic acid, *6* Hexose, *7* 3-methoxy-4-hydroxybenzoic acid, *8* azelaic acid, *9* 3,4-dihydroxybenzoic acid, *10* Glycoside, *11* 3,5-dimethoxy-4-hydroxybenzoic acid, *12* Hexose, *13* 3,4,5-trihydroxybenzoic acid, *14* Hexose, *15* Disaccharide, *16* disaccharide (D-turanose), *17* glycoside. (**b**) Gas chromatogram of water soluble extracts obtained from ML soil. (DCM/IPA fraction). *1* Phosphate, *2* 3-hydroxybenzoic acid, *3* 3a,9b-dimethyl-1,2,3a,4,5,9b-hexahydrocyclopenta[a]naphthalen-3-one, *4* octanedioic acid, *5* azelaic acid, *6* 3,4-dihydroxybenzoic acid, *7* Pyranose, *8a* pyranose (pentose), *8b* tetrahydroxy-N-acetyl glucosamine methoxime, *9* 3,4,5-trihydroxybenzoic acid, *10* Hexose, 11 disaccharide

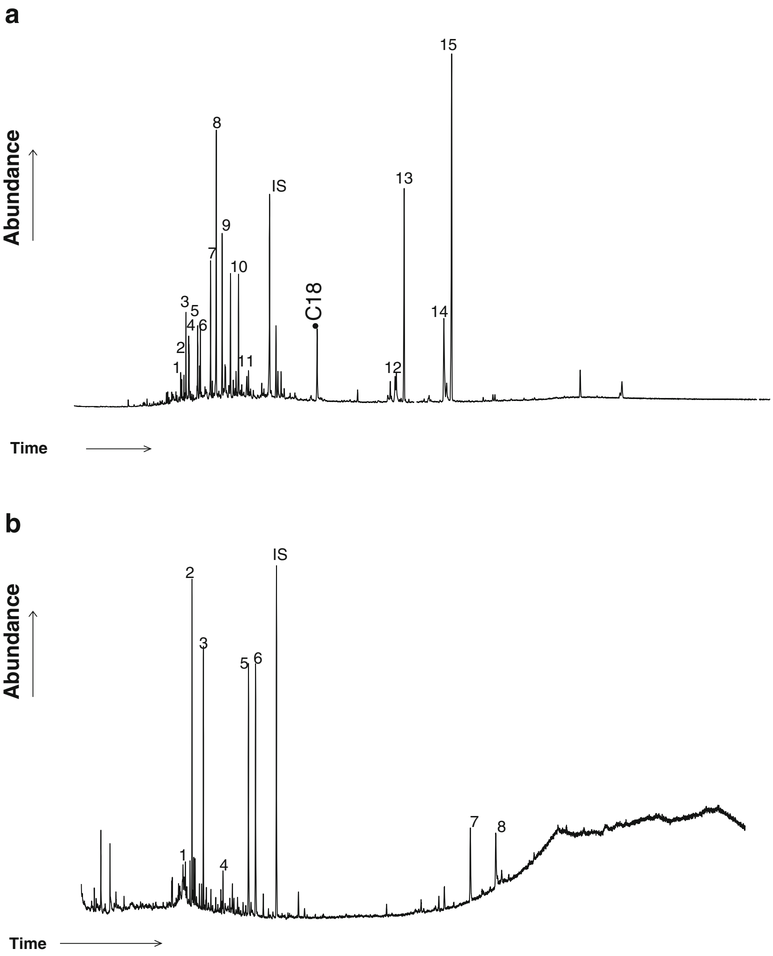

Fig. 14.3 Gas chromatogram of hot-water-soluble extracts (MeOH fraction) obtained from UK soil (**a**) and GP soil (**b**). IS= internal standard 10-nonadecanone; (**a**) *1* Glycoside, *2* hydroxyoctanoic acid, *3* hydroxybenzoic acid, *4* 2,3,4,5-tetrahydroxypentanoic acid, *5* octandioic acid, *6* 3,5-dimethoxy-4-hydroxybenzaldehyde, *7* 3-methoxy-4-hydroxybenzoic acid, *8* azelaic acid, *9* 3,4-dihydroxybenzoic acid, *10* 3,5-dimethoxy-4-hydroxy benzoic acid, *11* 5β-Cholestane-3α,7α,12α,24α,25-pentol, *12* 2-hydroxy-1-hydroxymethylethylpalmitate, *13* 2,3-dihydroxypripyl palmitate, *14* 2-hydroxy-1-hydroxymethylethyl stearate, *15* 2,3-dihydroxypropyl stearate; (**b**) GP soil. *1* Sugar (pentose), *2* Sugar (pentose), *3* Pentose, *4* Glycoside, *5* Pentose, *6* Pentose, *7* D-turanose, *8* stigmast-5-en-3-ol, oleate

short chain diacids (Fig. 14.1b). Sorption of aromatics to soil minerals and co-precipitation with Al and Fe-oxyhydroxides results in C stabilization. Aromatic acids will interact weakly with sand grains (composed mainly of quartz with a negative surface charge, pH_{zpc}~2–3) in the case of the sandy NT, GP and UK soils

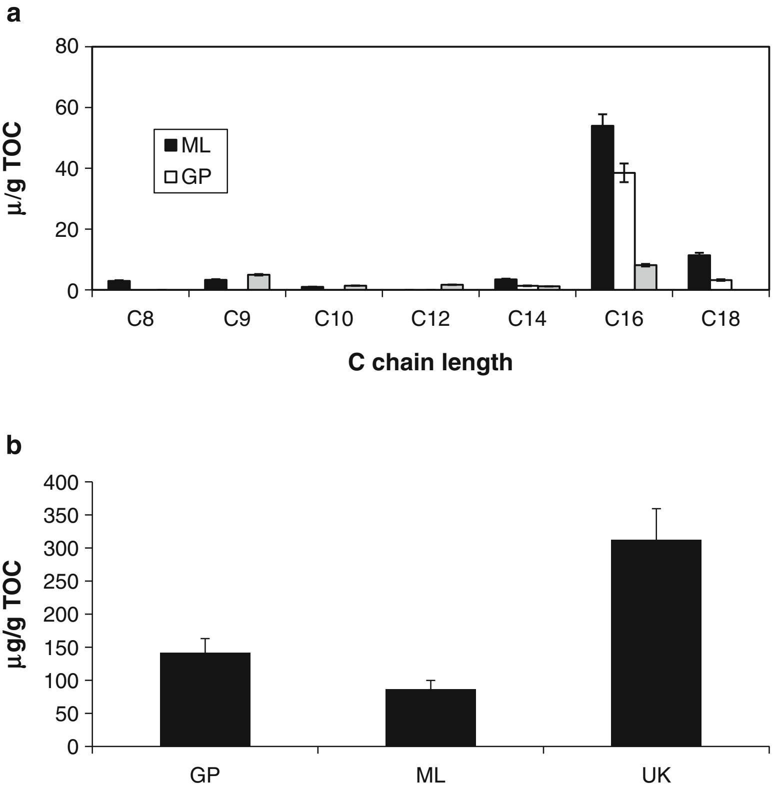

Fig. 14.4 Contents of fatty acids (**a**) and aromatics (**b**) in hot water soluble extracts (HWSE) from three WR soils in the DCM, DCM/IPA and methanol fractions based on the GC-MS data (only identified compounds of relative abundance >0.1 % of total peak area were computed and included in the group)

(Table 14.1) but will adsorb strongly to sesquioxides coating these grains and contributing to higher pH_{pzc} in the case of the sandy loam ML soil (Fe_{cd} 0.58 %). Low molecular weight (LMW) aromatic DOC components are preferentially adsorbed on the mineral surfaces, followed by adsorption of higher molecular weight aliphatic humic components (Pitois et al. 2008). Hot water desorption seems to detach the polar components from particles surfaces, as well as micelle like colloidal material. Sugars were detected at high abundance in the more polar dichloromethane/*iso*-propanol fraction in the four soils studied (>65 % of TIC traces) similarly to our previous results using *iso*-propanol/ammonia as a solvent (95:5). Of highest intensity were hexoses (mannose), (Fig. 14.2a, b) and disaccharides (turanose). The neutral sugars represent a major portion of the labile pool of SOC and provide energy for soil microbial processes. Pentoses (C_5), e.g. xylose and arabinose are important constituents of plants, while hexoses, e.g. mannose, ramnose and galactose are considered to be products of microbial synthesis

(Cheshire 1979; Clapp et al. 2005). The ratio C_6/C_5 (mannose + galactose)/(xylose + arabinose) has been used as a criterion for sugar origin. If this ratio is <0.5 a plant source is suspected, while values >2 show microbial sources. In the NT, GP and ML soils from Australia, the $C_6/C_5 = 2.6$ in the DCM/*iso*-propanol fraction and $C_6/C_5 = 2$ in the methanol fraction implying microbial contribution to HWSC. Soil carbohydrates are major binding agents in soil particle aggregation (Cheshire 1979) and play a critical role in the manifestation of soil water repellency (Atanassova and Doerr 2010). The association between soil saccharides and the mineral and organic soil components includes hydrogen and covalent bonds, e.g. anionic polysaccharides are adsorbed to soil colloids through complexation with polyvalent metal (Al, Fe) or cation bridges neutralizing the charges on clay minerals. Short chain C_4, C_7, C_8 and C_9 dicarboxylic acids were detected in the DCM and DCM/IPA fractions of the HWSC but dominated the TIC trace in the ML non-repellent sandy loam soil (DCM fraction). It is considered that short chain fatty acids are products from the enzymatic oxidation of Δ^9- unsaturated lipids (Grasset and Ambles 1998; Naafs et al. 2004). It's also suspected that short chain dicarboxylic acids together with short chain ω-hydroxy acids result from microbial metabolism (Naafs and Van Bergen 2002). Adsorption of these acids takes place through incorporation polymeric H-bonds, cation bridges in the organic matrix or inner sphere complexation with the inorganic soil components e.g. sesquioxides, favoured in dry conditions. The sandy loam ML soil of heavier texture contributes to a larger extent to the sorption of these acids. Palmitic acid (C_{16}) was detected with the highest intensity accompanied by stearic acid (C_{18}) in the sandy loam ML soil (Fig. 14.4). Long chain esters were detected in the DCM fraction of the soils studied (Figs. 14.1a, b and 14.3a, b), i.e. stigma-5-en-3-ol oleate, 2-hydroxy-1-hydroxymethylethyl palmitate and 2-hydroxy-1-hydroxymethylethyl stearate. The 2-monoacylglycerols are produced in eukaryotes by lipoprotein lipase hydrolysis of triacylgycerols. Also detected were 2,3-dihydroxypropyl palmitate, and 2,3-dihydroxypropyl stearate in the UK dune sand. Obviously, the solubility enhancement of these non-polar compounds in hot water has been caused by thermal desorption and extraction in the aqueous phase. Their presence in the water extracts might be explained through solubilisation from micelle-like colloidal and microparticles (<1.3 μ) of DOC similarly to the occurrence of hydrocarbons in aliphatic biopolymers of WSOC as observed in Py-GC/MS traces by Nierop and Buurnman (1998). Similarly, aliphatic C has been also found to augment in ^{13}C NMR and DRIFT spectra following sorption of DOM to soil and mineral samples (Kaiser et al. 2005). The polyfunctional macromolecules in the humic substances are involved in interactions with carboxyl, phenol, hydroxyl and other functional groups which are perturbed through extraction with water at high pressure and temperature. Extraction/desorption of low and high molecular weight polar compounds or colloids reveals hydrophilic sites on soil surfaces, i.e. wettable soil. The pressurized hot water also caused extraction (desorption) of labile hydrophobic compounds such as esters of oleic, palmitic and stearic acid, and solubilized from micelle-like micro-particle and colloidal DOC.

Conclusions

Soil water repellency is an important mechanism to reduce mineralization of SOM and sequester soil carbon. Climate change-induced long dry spells and water scarcity may exacerbate the negative outcomes of SWR such as a long-term reduction of soil water availability and low plant productivity. In this study we analyze the link between SWR and the molecular structure of HWSC (including DOC), which represents the bioavailable carbon fraction by making use of GC/MS analysis. Dominant compounds in the sandy soils were hydroxy- and methoxy- benzoic acids, short chain dicarboxylic acids C_4, C_7, C_8 C_9, mono- and di-saccharides, glycosides, fatty acids (C_8–C_{18}) and esters of oleic, stearic and palmitic acids. These low molecular weight (LMW) compounds released into the soil solution through root exudation, litter leaching and solubilization of microbial biomass components and products can influence in long- and short-term the C mineralization and fluxes in soil. We speculate that complete elimination of WR by hot water was due to: (i) critical quantity of HWSC extracted and removal of amphiphilic aromatics and polar sugars present in DOC; (ii) removal of hydrophobic compounds (C_{16} and C_{18} fatty acid esters) or HMW tannins in the non-solvent extractable fraction not amenable to GC/MS analysis (in the case of the Australian soils under eucalypt vegetation); (iii) quantity, temperature and pressure of water applied which relates to hydration of the soil particle surfaces and enhanced desorption of complex DOC; (iv) reorganization of hydrophobic material on particle surfaces and exposure of more polar hydrophilic sites; (v) extraction of HWSC seems to be a sufficient method to eliminate hydrophobicity in the sandy soils studied. HWSC is a heterogeneous group of compounds and molecular-level techniques are necessary to differentiate the mechanisms that are operative for the different compounds responsible for water repellency in soils differing in physico-chemical properties. As a labile SOM pool, HWSC is subject to temperature-sensitive decomposition. The LMW compounds identified in the extracts have functional significance in regulating ecosystem productivity as their rapid turnover may contribute substantially to the total CO_2 efflux from the soil. Changes are expected to occur also in their molecular composition and dynamics in response to microbial activity due to climate warming-induced soil hydrophobicity.

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Chapter 15
The Contribution of Soil Aggregates to Carbon Sequestration in Restored Urban Grasslands

Jenifer L. Yost, Corey E. Palmer, and Louise M. Egerton-Warburton

Abstract As urban development continues to replace or transform native grasslands, restoration has become increasingly critical for maintaining soil organic matter accrual. We asked if C-depleted urban soils could be restored to C accruing grasslands. Aggregate C content increased significantly between early- (<5 years) and later-stage (>10 years) model restorations (those resembling pristine prairies), and aggregate C levels in model restorations approached those in prairie remnants; more C was incorporated into the macroaggregate (>250 μm) than microaggregate fractions (53–250 μm). However, lower quality late-stage sites showed little evidence of macroaggregate C accrual. Stable isotope δ^{13}C signatures indicated that C_3 forbs were increasingly significant contributors to micro- and macroaggregate C accrual in restored grasslands and macroaggregates in pristine prairies whereas microaggregates in the pristine prairie showed δ^{13}C signature typical of C_4 plants. Our findings suggest that: C accrual occurs with urban grassland restoration; markers of restoration success and perception of a high quality restoration are reflected in C accrual; and management type rather than simply the duration of management are important in promoting C accrual.

Keywords Restoration • Prairie • Urbanization • Stable isotope • Aggregate fractionation

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Introduction

As urban development continues to replace or transform native grasslands, restoration has become increasingly critical for maintaining soil organic matter (SOM) accrual. Land use change coupled with disturbances, such as tillage and erosion, can reduce SOM accrual by up to 50 % by altering the physicochemical protection of SOM within aggregates. A key question is whether SOM accrual can be reinvigorated when disturbed soils are restored to grasslands. The beneficial effect of grassland restoration on SOM accrual in agricultural fields is well established: SOM can accumulate linearly for at least the first 40 years after conversion, and recover to near pre-cultivation levels (e.g., Jastrow et al. 1998; Post and Kwon 2000; McLauchlan et al. 2006; O'Brien and Jastrow 2013). Conversely, the comparison of a 65-year old grassland restoration versus a remnant prairie showed that soil C levels in the restored site were significantly lower than those in the remnant, and that it was unclear if the restored soils were functioning as a net C source or sink (Kucharik et al. 2006). Such divergent outcomes underscore the uncertainties in soil C accrual processes in grassland restorations, and confirm the need to understand more broadly the role of restored grasslands in C budgets. Few studies have examined the practice of grassland restoration on degraded urban sites as a means for SOM accretion. In this study, we evaluated the potential for SOM accrual and C stabilization in urban grassland restorations.

Terrestrial C sequestration is achieved through SOM stabilization by physical occlusion within aggregates, chemical interactions with clay minerals, and biochemical recalcitrance. Of these, the spatially hierarchical organization of soil aggregate structure is considered a major factor controlling SOM dynamics (Six et al. 2004, and references therein). In the hierarchical organization, primary particles and plant residues are cemented together by organic binding agents, such as aromatic humic compounds, to form microaggregates (53–250 μm diameter) that, in turn, are bound together and stabilized by microbial exudates, fungal hyphae, and labile organic matter into macroaggregates (≥250 μm; Tisdall and Oades 1982). This structural complexity allows plant residues to be incorporated into aggregates with a range of residence times, and produces fundamental differences in SOM content, stability, and turnover between aggregate size classes. Microaggregates are more stable and have slower rates of C turnover than macroaggregates, and persist following the breakdown of macroaggregates to form a pool of physically protected C with much-reduced turnover rates relative to free SOM (Six et al. 2004). In contrast, macroaggregates contain more organic C than microaggregates, but are more susceptible to rapid decomposition with disturbance (Six et al. 2000).

The shift from C loss due to agriculture to C replenishment with grassland restoration is well documented. We ask: Could similar mechanisms occur in C-depleted urban soils that are restored to grasslands? To answer this question, we investigated aggregate C content from a sequence of grasslands established on urban sites in Chicago. The Chicago region provides an excellent opportunity to study C cycling processes. The region is characterized by a mosaic of land use including urbanization, old fields, abandoned industries, restorations, and native prairie remnants. This urban fabric provides unique historical, land-use, and anthropogenic factors that are likely to impact SOM accrual. We examined whether: (1) the distribution of SOM in micro- and macroaggregates in restored sites returned to levels in remnant prairies; and (2) the duration of management influenced SOM accrual. To address these objectives, we isolated and analyzed micro- and macroaggregates from 15 sites that comprised a replicated sequence of unmanaged lands (old fields), restored and managed grasslands, and remnant (pristine) prairies in the Midwestern United States.

Materials and Methods

We selected 15 mesic prairie sites in northwestern Illinois that represented five categories of restoration and management ($n = 3$ sites per category; Table 15.1). These included unmanaged old fields (R1), early (R1) and intermediate (R2) restoration and management, as well as a high quality restorations (R3), and pristine prairie remnants that have never been farmed or developed and thus represent pre-settlement prairie conditions (P3). The restored sites (R1–R3) were previously corn-soybean fields farmed by conventional agriculture (tillage) and then abandoned. Prior to restoration, they were dominated by invasive, non-native species. Current management includes burning, seeding, mowing, and removal of invasive species by target herbicide spraying. The plant community in all sites comprises C_3 and C_4 grasses (26–40 %) and annual and perennial forbs (23–38 %). The soils are loamy, and texture and fertility are influenced by the percentages of sand (30–52 %) and silt (14–36 %). The R3 and P3 soils also contain appreciable levels of muck (Table 15.1). Annual precipitation in the area averages 995 mm, and mean annual temperatures range from −4 °C (minimum) to 24 °C (maximum). At each site, we collected five soil

Table 15.1 Management categories and associated plant community composition and soil texture

	Plant community composition				Soil texture			
Management (abbreviation)	Grasses (%)	Forbs (%)	Shrubs (%)	Detritus (%)	Sand (%)	Silt (%)	Clay (%)	Muck
Unmanaged (R0)	26	33	2	32	41	23	36	None
Early restoration, 1–5 year management (R1)	27	38	1	16	33	36	32	None
Intermediate restoration, >10 years of management (R2)	40	23	1	28	30	34	36	None
High quality model restoration, >10 year management (R3)	32	30	6	15	45	24	32	High
Prairie remnant (P3)	30	29	10	15	52	14	34	High

cores (each 7 cm diameter, 15 cm deep) from a 1-ha plot. Soil samples were pooled, sieved to remove any coarse debris, and then air-dried.

We determined the aggregate size distribution by wet sieving and separated the aggregates into four aggregate-size classes using the methods outlined by Robertson et al. (1999). Aggregates were classified as large (≥2 mm) or small macroaggregates (250–2,000 μm), or microaggregates (≤250 μm). Aggregate samples were dried to constant weight and ground to a fine powder using a VQ-N Desktop High Speed Vibrating Ball Mill, and analyzed for C content using a LECO TruSpec CN elemental analyzer. Sub-samples were tested for carbonate content using HCl. Since no carbonates were detected, the total C is considered to represent organic C. To estimate C stored in soil (C_s), we calculated Cs for each aggregate fraction on an area basis using the formula $C_s = f_C * f_A * b * z$, where f_C is C content of the aggregate fraction (g $C.g^{-1}$ aggregate); f_A is the aggregate fraction within the soil sample (g $aggregate.g^{-1}$ soil); b is the soil bulk density ($g.cm^{-3}$), and z is the soil sample depth (cm).

Sub-samples of ground aggregates were also analyzed for the natural abundance ^{13}C on a Costech CE Elemental Analyzer interfaced to a Thermo Delta V Plus Isotope Ratio Mass Spectrometer at the Northwestern University Stable Isotope Laboratory. The ^{13}C isotope composition was expressed in standard notation ($\delta^{13}C$) in parts per thousand (‰) relative to Vienna-Pee Dee Belemnite (VPDB), where $\delta = 1,000[(R_{sample}/R_{standard}) - 1]$, and R is the molar ratio $^{13}C/^{12}C$. Precision was better than 0.1 %.

Results

Overall, macroaggregates contained significantly greater levels of C than microaggregates (Fig. 15.1). Management also significantly influenced aggregate-associated C. Pristine prairie remnants (P3) and model restorations (R3) showed significantly higher aggregate C content than other management categories (Fig. 15.1). Interestingly, old fields (R0) showed higher aggregate C levels than early or intermediate restoration (R1, R2). No differences were detected in aggregate-associated C between R1 and R2. The total mass of C in aggregate fractions (C_s) followed similar patterns: soil C was significantly larger in pristine remnants and model restorations than the other management categories. There was no significant difference in total C mass between early and intermediate restorations and old fields.

Distinctive aggregate $\delta^{13}C$ shifts were detected across management categories (Fig. 15.2). The restoration sites exhibited a shift in aggregate $\delta^{13}C$ signatures from near constant values in the R1 sites (−18.5 ± 0.1 ‰) to more depleted values in R3 (−22.1 ± 0.1 ‰); values in both categories did not differ significantly between macro- and microaggregates. On the basis of mass balance, source partitioning indicated that C_4-derived SOM contributed, on average, to 50 and 28 % of aggregate SOM in R1 and R3 respectively. In contrast, the macroaggregate $\delta^{13}C$ signature was significantly depleted in comparison to $\delta^{13}C$ for microaggregates in pristine remnants, and C_4-derived SOM contributed to 56 % of SOM in microaggregates versus 24 % in macroaggregates.

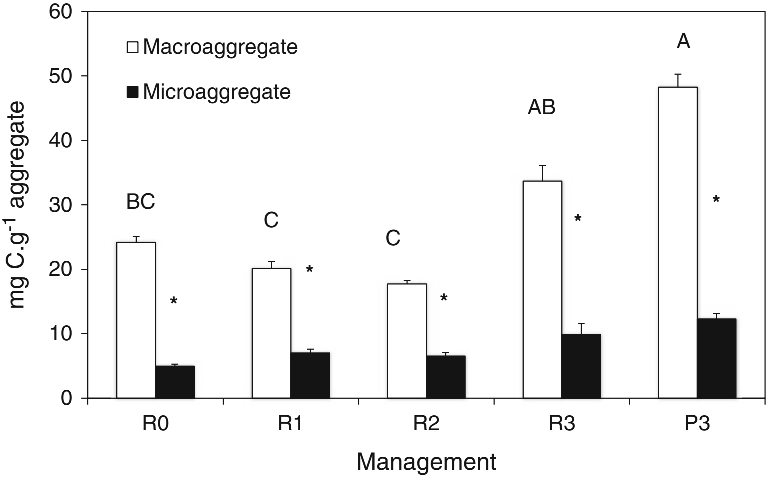

Fig. 15.1 Distribution of aggregate-associated C in restored sites and pristine prairie remnants. Management codes correspond to those listed in Table 15.1. *Vertical bars* indicate the standard error of the mean. Within each site, micro- and macroaggregate C denoted * differ significantly at $P < 0.05$; across management categories, sites with the same capital letter do not differ significantly at $P < 0.05$

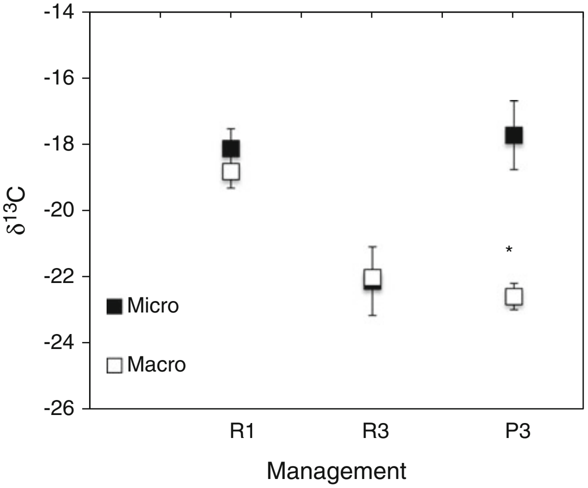

Fig. 15.2 Stable isotope C signatures for micro- and macroaggregates in early and late model restorations, and a pristine prairie remnant. Management codes correspond to those listed in Table 15.1. *Vertical bars* indicate the standard error of the mean. * Denotes $\delta^{13}C$ differs significantly between micro- and macroaggregate fractions ($P < 0.05$)

Discussion

Our study was designed to measure and compare SOM accrual in urban old fields, grassland restorations, and prairie remnants to test the underlying assumption that grassland restorations may increase SOM accrual in urban sites as they do in agricultural to grassland conversions. This expectation was partially supported by the data. The distribution of soil C among measured pools changed substantially following the establishment of tallgrass prairie. Notably, aggregate C increased between early (1–5 year; R1) and model restorations (>10 year; R3) to approach levels in the prairie remnants. However, soil C declined during the transition from old fields (R0) to early (R1) and intermediate restorations (R2), which is consistent with the observed loss of soil C in other long-term grassland restorations (Kucharik 2007). A larger proportion of soil C also occurred within macro- than microaggregates in the restorations and prairie remnants, which is consistent with the concept of hierarchical aggregate development (Tisdall and Oades 1982) and the patterns of aggregate C abundance in other restored sites (e.g., Jastrow et al. 1998). Further, macroaggregate formation implies the rapid incorporation and protection of C and that SOM is a major binding agent along with fine roots and mycorrhizal hyphae (Six et al. 2004).

Unexpectedly, we found no substantial increase in macroaggregate C between early and intermediate restoration sites. This pattern is more consistent with aggregate dynamics in tilled fields than restorations (Six et al. 2004), and suggests a faster macroaggregate turnover rate in intermediate sites than in model restorations, even though both types of sites have been restored and managed for similar lengths of time (>10 years). The addition of new residues (litter) into the soil matrix, litter decomposability, and fungal activity are key factors in macroaggregation. As a result, we can hypothesize that the rapid turnover of macroaggregates may be due to the limited input of root residues, the reduced availability of high quality litter (low C: N), or that the degradation of litter by fungal communities is reduced or suppressed (Helfrich et al. 2008; Gentile et al. 2011). The presence of muck (humus, black soil) in model restorations and remnant prairies, but not restored sites (Table 15.1), provides support for some of these processes. Studies elsewhere also indicate that the accumulating C may fill the pores within the microaggregates (McCarthy et al. 2008) or form silt- and clay-sized aggregates (Chenu and Plante 2006). The larger amounts of silt and clay in early and intermediate sites support these possibilities (Table 15.1). Thus, the management regime or intensity of management (Kucharik 2007), rather than simply the duration of management, are critical for the stabilization of SOM.

The observed trend of increasing SOM and ^{13}C depletion with restoration age (R1 to R3) indicates that C_3 forbs were increasingly significant contributors to SOM accrual. In addition, the increasing input of C_3–C into microaggregates was equal to those for macroaggregates indicating that aggregate turnover in restored systems was dynamic. In the pristine prairie site, however, the two-end member isotope mass balance approach using *Andropogon gerardii* (−15.3‰) as the C_4 end member and grassland forbs as C_3 end member (mean −26.1‰), shows that the average input of C_4–C shifted from 56 % in microaggregates to 24 % in macroaggregates. This pattern parallels aggregate $\delta^{13}C$ signature patterns in croplands converted to tallgrass prairie (Jastrow et al. 1998) and in reclaimed mining soils after restoration (Wick et al. 2009). In addition, these findings indicate that a significant portion of the microaggregate C is older and possibly stabilized with mineral particles in pristine prairies. Thus, the model restoration and remnant prairies may share similar structural components and functional attributes, including aggregate C accrual, but the source and patterns of C input into aggregate fractions are quite different.

Conclusions

We asked if C-depleted urban soils could be restored to C accruing grasslands. Our findings show that: (1) C accrual occurs with urban grassland restoration; (2) those markers of restoration success and perception of a high quality restoration are reflected in C accrual; and (3) management type rather than simply the duration of management are important in promoting C accrual. Notably, there was C accrual between early (<5 years) and model restorations (>10 years), with aggregate C levels in model restorations approaching those in pristine prairie remnants. However, the marked lack of macroaggregate C accrual in intermediate restoration sites (>10 years) raises a number of questions about the type of management rather than simply the duration. Management strategies that enhance litter inputs, the decomposition rate of organic matter, and the active root-associated belowground C cycle may be important in promoting C accrual.

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Chapter 16
Contribution of Fungal Macromolecules to Soil Carbon Sequestration

Kathryn M. Schreiner, Neal E. Blair, William Levinson, and Louise M. Egerton-Warburton

Abstract Saprotrophic fungi are key moderators in the global carbon cycle because of their ability to degrade the three most abundant biopolymers: cellulose, lignin, and chitin. Fungi are a significant contributor to soil microbial biomass but little is known about the contributions of fungal biomass to diagenetically altered soil organic carbon. Here we show that a portion of fungal necromass is resistant to decay by a natural soil microbial community over a month-long degradation study. The results of FTIR analysis indicate that this resistant portion is likely composed mainly of fungal chitin.

Keywords Chitin • Soil organic matter • Soil fungi • FTIR

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Introduction

Saprotrophic fungi have the ability to enzymatically degrade the three most important biopolymers: cellulose, lignin, and chitin (Baldrian et al. 2011). A globally important flow of carbon is therefore processed by fungi, but little is known about how that carbon is transformed, metabolized, or perhaps stored in soil organic matter (SOM), defined here as the total belowground organic matter without plant pieces and roots. Additionally, the contributions of fungal biomass and necromass to SOM, and their impact on the potential carbon sequestration abilities of soil remain poorly understood.

Fungi have been shown to constitute a major portion of belowground biomass (Six et al. 2006) but the amount varies widely with land use and ecosystem function (Joergensen and Wichern 2008). Fungal hyphal tissue is more resistant to biodegradation than bacterial polymers (Guggenberger et al. 1999). Fungi have been shown to contribute to soil aggregate formation (Hu et al. 1995) and are likely important to soil carbon sequestration (Jastrow et al. 2007; Clemmensen et al. 2013). It is known that the ratio of fungi to bacteria in soils is affected by a variety of environmental factors including cultivation intensity, grazing intensity, and C–N ratios or substrate quality (Six et al. 2006).

It is likely that fungal production of a variety of biopolymers, including cell exudates and cell wall materials, contributes to diagenetically altered SOM. As fungal hyphae are known to be important to the formation of soil aggregates (Bossuyt et al. 2001; Tisdall and Oades 1982), fungi actively work to stabilize SOM originating from other sources, including plants and bacteria. Fungal biomass itself has a greater chance for stabilization compared to other microbial biomass because of their association with aggregates (Six et al. 2006).

Here we first briefly summarize the chemistry of the most important fungal biopolymers, and then describe the results of a degradation study of fungal cell wall material. The degradation of ectomycorrhizal fungal tissue has been described previously (Koide and Malcom 2009; Wilkinson et al. 2011; Drigo et al. 2012), but to the best of our knowledge this is the first time fungal necromass degradation has been studied in a saprotrophic fungal species. This study provides results and insights into the biochemical stabilization (or chemical recalcitrance) of fungal biopolymers, and in the last section we summarize questions that remain to be addressed.

Fungal Biopolymers

Fungal cell walls contain a variety of biopolymers, with chitin and glucan being the most abundant for most species. Chitin is a polymer composed of *N*-acetyl-*D*-glucosamine in β-(1–4)-glycosidic bonds. Glucans are matrix polysaccharides that are part of fungal cell walls (Kogel-Knabner 2002). In general, structural polysaccharides like chitin and β-glucan are non-water-soluble crystalline substances whereas matrix polysaccharides like α-glucan are amorphous and water soluble. Fungal cell wall material is the main source of glucosamine to SOM (Parsons 1981), and amino sugar compounds like chitin in general contribute between 5 and 12 % of total soil organic nitrogen (Stevensen 1982).

Sporopollenin forms the outer wall of fungal spores as well as plant pollen and is another structural biopolymer synthesized by fungi. It is a polymer consisting predominantly of unbranched aliphatics and a varying amount of aromatics with a high degree of crosslinking, and is derived from the polymerization of unsaturated fatty acids. The complex polyether polymer contains no nitrogen and is composed of only carbon, oxygen, and hydrogen atoms (Bubert et al. 2002).

Melanin, another important fungal product, has long been hypothesized to be a precursor to humic materials in SOM (Linhares and Martin 1978; Six et al. 2006), but the exact mechanism of the formation of SOM from melanin is unclear as fungi contain melanin with many different structures (Knicker et al. 1995). However, fungal hyphae rich in melanin decay more slowly than hyphae low in melanin (Six et al. 2006), indicating that overall, melanin is relatively recalcitrant and may act to protect other hyphal organic matter from degradation.

Fungi have also been shown to contribute other, potentially recalcitrant, polymer-like materials to SOM through exudates. One example is glomalin-like soil protein (GLSP), which is thought to be a mucus-like substance produced by fungi, and has been estimated to contribute up to 5 % of soil C and N (Treseder and Turner 2007). However, because of the unspecific nature of the extraction procedure commonly used for GLSP analysis, it is likely that humic matter is extracted and analyzed along with GLSP and these numbers are an overestimate (Schindler et al. 2007). Soil fungi produce a range of extracellular polysaccharides that contribute to SOM and are important in soil aggregate formation, the mechanism for physical protection and slower decomposition of organic matter in soils (Wright and Upadhyaya 1998; Six et al. 2006).

The work described here is meant as a first estimate of the contribution of saprotrophic fungal necromass to diagenetically altered SOM. Only the contribution of the fungal cell wall material was studied, although fungal exudates are certainly also important contributors to SOM.

Degradation of *Fusarium avenaceum* Necromass

In order to determine the contributions of saprotrophic fungal necromass to diagenetically altered SOM, a degradation sequence of organic matter from the saprotrophic fungus *Fusarium avenaceum*, a member of the phylum Ascomycota, was studied. Fungal necromass was subjected to degradation by a natural soil microbial consortium over a period of 36 days. Fungal tissue was grown aseptically in liquid nutrient media for 14 days and at harvest was well-rinsed to remove traces of nutrient media and soluble organics from fungi, and oven-dried. It is assumed that after the rinsing steps the main source of organic carbon remaining was cell wall tissue. Fungal tissue was placed in mesh bags (100 μm pore size) and buried in the soil in pots containing a sterile 50:50 soil:sand mixture that was inoculated with a natural microbial community extracted from soil samples collected in a tallgrass prairie site at the Chicago Botanic Garden. The pots were watered periodically and kept under relatively constant temperature and photosynthetically active radiation. *Eruca sativa* (arugala) seeds were planted in each microcosm at Day 0 and again just before the Day 24 harvest in an effort to replicate a natural environment. Four samples were harvested at each of four time points: 5, 12, 24, and 36 days. At each harvest, the mesh bags were opened, fungal tissue was identified and separated from soil particles via handpicking, and then oven-dried and weighed. Samples from each harvest were ground to powder with mortar and pestle and analyzed via Fourier Transform Infrared (FTIR) spectroscopy.

The majority of fungal biomass was found to turn over on a time period of days, but a portion appears to survive this initial phase of degradation. When compared to fungal packets not subjected to degradation, over 75 % of the original fungal mass was lost within the first 5 days of incubation (data not shown). Between Day 5 and Day 12 an additional 5 % of mass was lost, on average (though this change is not significant), and after Day 12 the amount of fungal tissue remaining in the mesh bags stayed relatively constant at approximately 10–15 % of the original biomass. This relatively recalcitrant portion, resistant to microbial degradation over a period of weeks, is hypothesized to be a contributor to diagenetically altered SOM.

FTIR (Fig. 16.1) analysis further indicates that the residual relatively recalcitrant fungal tissue is biochemically distinct from the original tissue. FTIR data specifically shows two areas of significant chemical change over the month-long experiment: the ester (C═O stretch), amide I (C═O stretch), and amide II (C–N bend) region (approximately 1840 to 1490 cm^{-1}, Fig. 16.1a Box 1) and the carbohydrate (C–O stretch) region (approximately 1190 to 950 cm^{-1}, Fig. 16.1a Box 2). The component absorption peaks were resolved in each region using the PeakFit software package (SyStat). Data are shown in Fig. 16.1b–d, showing curve fits from raw fungal material and Day 36 of degradation as an example. Chitin, a glucosamine polysaccharide synthesized by *Fusarium* and other fungi, should be reflected structurally in both of the ranges analyzed, though other fungal polymers, like β-1, 4-glucan and melanins, are likely also represented in these spectral regions.

Striking differences are apparent between the raw fungal tissue and the Day 36 degraded tissue. First, ester functionality (represented by a peak at approximately 1745 cm^{-1} and shown as a red line in Fig. 16.1b) is present in raw fungal tissue (Fig. 16.1b) but is absent in degraded tissue (Fig. 16.1d). The carbohydrate region of the spectrum (between 1175 and 925 cm^{-1}, Fig. 16.1a Box 2, c, e) also shows significant changes after degradation. The raw fungal tissue has a mixture of absorbances in this region that is dominated by a doublet. By 36 days of degradation, however, the doublet is less pronounced as a result of the selective loss of at least one carbohydrate component. A similar phenomenon occurred in the carbonyl region between 1700 and 1580 cm^{-1} (Fig. 16.1a Box 1, b, d) that is dominated by amide I absorbances. These are likely from both protein and chitin. A loss of a non-amide carbonyl moiety at ~1715 cm^{-1} occurs. The relative intensities and absorption maxima of the various carbonyl stretches in the amide I range change over time. Curiously, the C–N absorbances in the amide II region are unchanged throughout the degradation sequence.

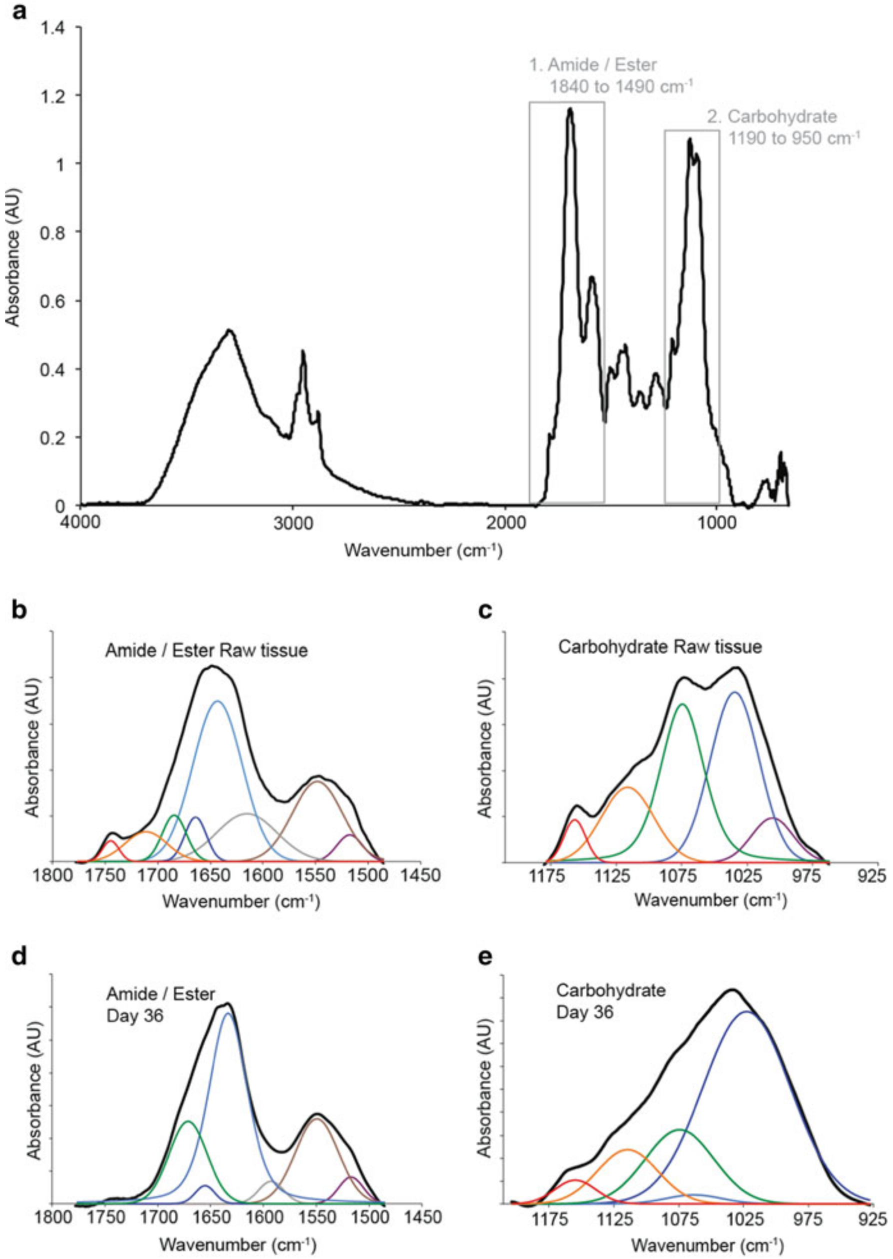

Fig. 16.1 FTIR spectra from fungal degradation experiment. Complete spectrum of raw fungal tissue with Amide/Ester and Carbohydrate regions indicated (**a**), Amide/Ester region from raw tissue (**b**), and Carbohydrate region from raw tissue (**c**), amide/ester region from day 36 tissue (**d**), and carbohydrate region from day 36 tissue (**e**). Colors correspond to the same peak in **b** and **d** and in **c** and **e**. *Thick black lines* in **b**–**e** correspond to the original spectrum

These data support the hypothesis that a portion of fungal biomass is relatively recalcitrant in these soils, as recently shown for arbuscular mycorrhizal fungi (Clemmensen et al. 2013) and ectomycorrhizal fungi (Drigo et al. 2012). The recalcitrant fraction contains polysaccharide and amide-linked functional groups, which is consistent with chitin. The breakdown of more labile organic carbon, including proteins (indicated by the changing amide I region), polysaccharides (indicated by the changing C–O stretch region assigned to carbohydrates), and esters (primarily associated with glycol- and phospholipids) occurs on a more rapid time scale than that of what we hypothesize to be fungal chitin. These results illustrate the potential contribution of fungal necromass to diagenetically altered SOM.

Future Research

The research summarized here sheds light on the role that fungal biomass plays in the formation and stabilization of diagenetically altered SOM. However, there is much that remains to be determined. The existence of fungal chitin after the degradation will be confirmed with additional analytical methods such as pyrolysis-gas chromatography analysis. Extending these analyses to the natural environment through *in situ* studies, examining the decomposition profiles of different species of fungi, and in different ecosystems are among our goals, as it is unknown whether the data summarized here can be broadly generalized to other soils and to fungal necromass from other species. Additionally, the microbial communities involved in the degradation of fungal tissue has been studied for only one species of ectomycorrhizal fungus (Drigo et al. 2012), and therefore are largely unknown. Physical protection of fungal biomass inside soil aggregates is likely also important for its stabilization in soils, and may actually be more important than the inherent biochemical stabilization of these biopolymers (Six et al. 2006), but this has yet to be systematically studied.

Further research may also focus on fungal extracellular polysaccharide exudates, of which there is even less information available than for fungal chitin. GLSP is still only operationally defined, and its exact function as well as the function of other fungal exudates, and how they may contribute to the protection and stabilization of SOM, is still not known.

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Chapter 17
Carbon Storage and DNA Adsorption in Allophanic Soils and Paleosols

**Yu-Tuan Huang, David J. Lowe, G. Jock Churchman, Louis A. Schipper,
Nicolas J. Rawlence, and Alan Cooper**

Abstract Andisols and andic paleosols dominated by the nanocrystalline mineral allophane sequester large amounts of carbon (C), attributable mainly to its chemical bonding with charged hydroxyl groups on the surface of allophane together with its physical protection in nanopores within and between allophane nanoaggregates. C near-edge X-ray absorption fine structure (NEXAFS) spectra for a New Zealand Andisol (Tirau series) showed that the organic matter (OM) mainly comprises quinonic, aromatic, aliphatic, and carboxylic C. In different buried horizons from several other Andisols, C contents varied but the C species were similar, attributable to pedogenic processes operating during developmental upbuilding, downward leaching, or both. The presence of OM in natural allophanic soils weakened the adsorption of DNA on clay; an adsorption isotherm experiment involving humic acid (HA) showed that HA-free synthetic allophane adsorbed seven times more DNA than HA-rich synthetic allophane. Phosphorus X-ray absorption near-edge structure (XANES) spectra for salmon-sperm DNA and DNA-clay complexes indicated that DNA was bound to the allophane clay

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through the phosphate group, but it is not clear if DNA was chemically bound to the surface of the allophane or to OM, or both. We plan more experiments to investigate interactions among DNA, allophane (natural and synthetic), and OM. Because DNA shows a high affinity to allophane, we are studying the potential to reconstruct late Quaternary palaeoenvironments by attempting to extract and characterise ancient DNA from allophanic paleosols.

Keywords Andisols • Allophane • Carbon sequestration • C NEXAFS • P XANES • Ancient DNA

Introduction

Carbon Storage in Soils

Soils are the largest reservoir of terrestrial organic carbon (Batjes 1996; Blanco-Canqui and Lal 2004), and soil organic matter (SOM) has become subjected to many diverse investigations because C is an important contributor to soil quality and because of its role as a potential store of CO_2. Nanocrystalline clay minerals including allophane and ferrihydrite have a greater affinity than crystalline clay minerals for organic functional groups, hence soil organic carbon (SOC), due to ligand exchange with their charged hydroxyl groups (Basile-Doelsch et al. 2005; Kleber et al. 2005; Churchman and Lowe 2012). Soils developed mainly on free-draining, explosively erupted, fragmental volcanic material (collectively, 'tephra'), typically classed as Andisols, 'hold' more C than other mineral soils (Batjes 1996; McDaniel et al. 2012) because of their constituent allophane (Chevallier et al. 2010; Calabi-Floody et al. 2011). Andisols occupy ~1 % of the world's land area, but contain 5 % of global C (Dahlgren et al. 2004; McDaniel et al. 2012). Sequestration of organic materials in soils is an important research area, and we are specifically interested in DNA adsorption and storage by allophanic soils because preserved DNA or ancient DNA (aDNA) from buried paleosols could in turn provide a way of reconstructing past environments.

Allophane and Carbon Sequestration

Allophane comprises tiny (3.5–5 nm in diameter), Al-rich nanocrystalline hollow spherules ($(1\text{–}2)SiO_2 \cdot Al_2O_3 \cdot (2\text{–}3)H_2O$) (Fig. 17.1a) with extremely large surface areas (up to 1,500 m^2 g^{-1}) (Parfitt 2009; Calabi-Floody et al. 2011). Broken-bond defects in the spherules, also called perforations, are ~0.3 nm in diameter (Fig. 17.1a) and it is the protonation and deprotonation of $(OH)Al(H_2O)$ groups exposed at these sites that give rise to allophane's variable (pH-dependent) charge (Parfitt et al. 1977; Yuan and Theng 2012), and thus its anion exchange capacity. The adsorption of negatively charged humic substances on allophane through ligand exchange is

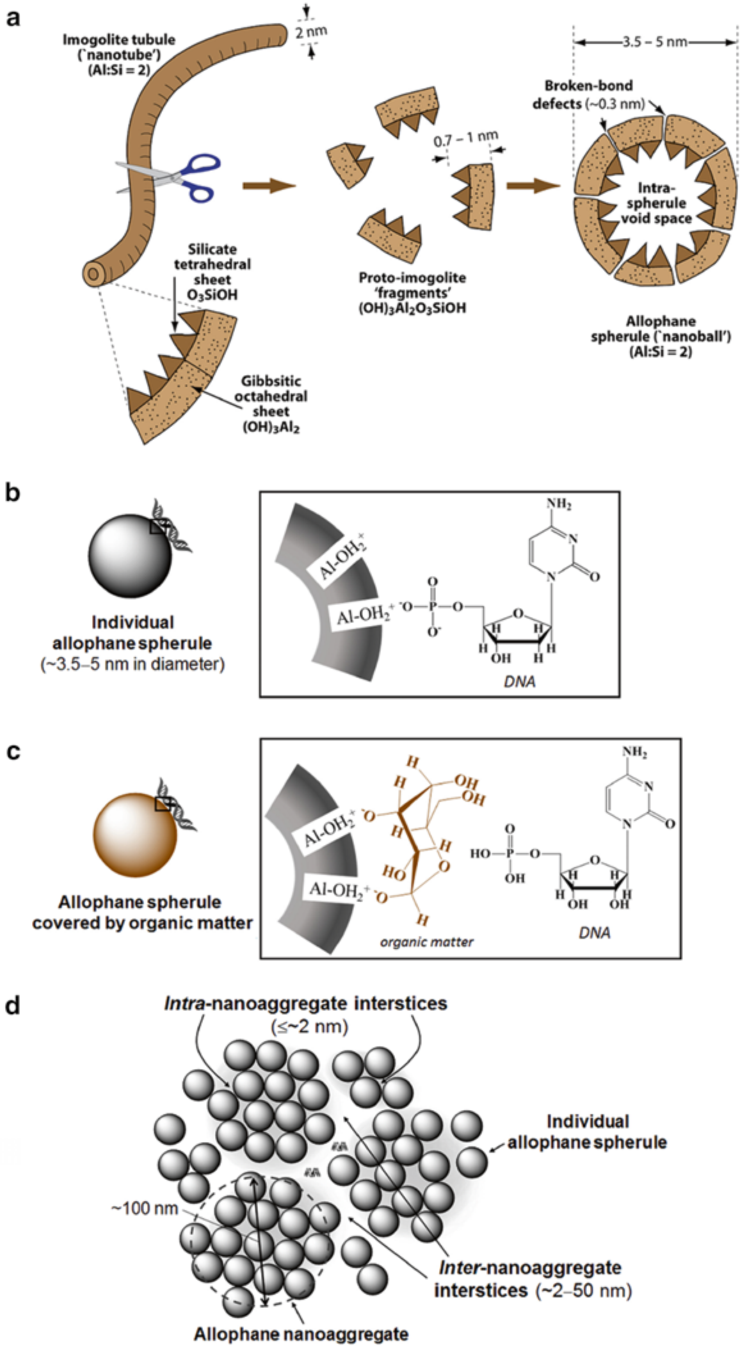

Fig. 17.1 Illustration of (**a**) nanoscale dimensions and composition of imogolite tubules and allophane spherules (from McDaniel et al. 2012), (**b**) direct chemical adsorption of DNA on allophane, (**c**) indirect chemical adsorption of DNA on organic matter-rich allophane, and (**d**) physical adsorption of DNA in the interstices of allophane nanoaggregates

represented by Eq. (17.1) (from Yuan and Theng 2012). $[\mathrm{R.COO}]^{n-}$ denotes a humic molecule containing n carboxylate functional groups.

$$\begin{aligned}&\left[\text{allophane}-\text{Al}(\text{H}_2\text{O})(\text{OH})\right]^0+\left[\text{R.COO}\right]^{\text{n}-}\\&\Rightarrow\left[\text{allophane}-\text{Al}(\text{H}_2\text{O})(\text{COO.R})\right]^{(\text{n}-1)-}+\text{OH}^-\end{aligned}\tag{17.1}$$

These high specific surface areas and surface properties help govern the strong association between allophane and SOM (Fig. 17.1b, c) (Buurman et al. 2007; Calabi-Floody et al. 2011; Yuan and Theng 2012). In addition, allophane spherules tend to form nanoaggregates up to about 100 nm in diameter (Fig. 17.1d) (Chevallier et al. 2010; Calabi-Floody et al. 2011). We suggest that the interstices (nanopores) both within and between such nanoaggregates (Fig. 17.1d) provide a haven for SOM so that a portion of SOC is poorly accessible to microbes or enzymes and thus protected. Calabi-Floody et al. (2011) showed that significant SOC, which resisted the treatment of hydrogen peroxide, was strongly held by allophane and imogolite in Andisols, a finding consistent with studies of the physical protection and stabilisation of SOM within larger micro- and macro-aggregates (Elliott 1986; Strong et al. 2004). It is possible that SOC is protected against the attack of enzymes in the narrowest interstices, such as in nanoaggregates, because the diffusion pathway for the passage of enzymes is constrained (McCarthy et al. 2008; Chevallier et al. 2010).

DNA Adsorption on Allophane

The adsorption of DNA on soil particles plays a major role in protecting extracellular DNA from degradation in soils (Paget and Simonet 1994), and the interactions between DNA and common clay minerals have been investigated using FTIR spectroscopy (Cai et al. 2006a). Allophane adsorbs more DNA than other minerals in soils (Saeki et al. 2010; Harsh 2012), and may be capable of preserving DNA as well. Greaves and Wilson (1970) suggested that nucleic acids in the centre of expandable montmorillonite crystal structures may be protected from attack by microbial enzymes, and hence we hypothesise that aDNA may also be physically protected and preserved within intra- and inter-nanoaggregate interstices of allophane in Andisols and andic paleosols. However, Cai et al. (2006b) revealed that DNA is more tightly adsorbed by organic matter-free clay than by clay containing organic matter, indicating that the abundant SOM in allophanic soils might hamper DNA adsorption on allophane. SOM is expected to increase the negative charge on minerals (Eq. 17.1), leading to a mutual exclusion between SOM-rich allophane and negatively-charged phosphate groups of DNA. In contrast to Cai et al. (2006b), Saeki et al. (2011) showed that humic acid had a high affinity for DNA, hence the influence of SOM on DNA (and potentially aDNA) adsorption in Andisol is still debatable.

A DNA strand comprises heterocyclic bases and a pentose-phosphodiester backbone, and it was suggested that DNA binds to clays through the phosphate group (Cai et al. 2006a) but there has been no direct evidence. We propose three main mechanisms for DNA adsorption on allophane: (1) direct chemical adsorption on the organic matter-free and protonated surface of allophane, (2) indirect chemical adsorption/dissolution on/into the SOM-rich allophane, and (3) physical adsorption in interstices/nanopores of allophane nanoaggregates (Fig. 17.1b–d). A clearer understanding of DNA adsorption on allophanic materials would help inform ways to extract preserved DNA or aDNA from buried paleosols.

Materials and Methods

Application of Synchrotron Radiation

Traditionally SOM was extracted chemically from soils, leading to possible artifacts of the treatment (e.g. see Schmidt et al. 2011; Churchman and Lowe 2012). Synchrotron radiation has been developed for several decades for studying materials (Sutton et al. 2006) including the chemical composition of soil components such as ‘resistant’ C (Wan et al. 2007; Lehmann and Solomon 2010). It allows the analysis of C at low concentrations and within bulk soil samples. C near-edge X-ray absorption fine structure analysis (NEXAFS) enables examination of speciation and structures of SOM (Lehmann 2005; Lehmann et al. 2007). Phosphorus X-ray absorption near-edge structure (XANES) reveals the configuration for phosphorus bonding to Fe(III)- or Al(III)-rich minerals (Kizewski et al. 2011).

Carbon NEXAFS

We used the Beamline 24A1 at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, for our C NEXAFS study of the C compositions of SOM associated with allophane through the electron yield mode. Contaminant C contributions from the beamline have been eliminated by a golden mesh anterior to the sample chamber.

Allophanic materials were collected in northern New Zealand from an Andisol of the Tirau series (a medial, mesic Typic Hapludand: Bakker et al. 1996) at Tapapa and from buried andic paleosols at two sites at Lake Rerewhakaaitu (near Mt Tarawera) and one near Lake Rotoaira (adjoining Tongariro National Park). Clay fractions (<2 μm) were pressed into indium foil to enable them to be conductive, and analysis was accomplished under 10^{-9} torr using a chemical pump.

DNA Adsorption Studies

Salmon-sperm DNA from Sigma-Aldrich Co. LLC that ranged from 0 to 300 μg was added to the natural clays from all sites and to a 1 mL suspension of pure synthetic allophane (synthesized following the method of Ohashi et al. 2002), and the mixture was gently rotated at room temperature for 3 h. DNA in the supernatant was analyzed at 260 and 280 nm spectrophotometrically.

Phosphorus XANES

P XANES spectra were obtained for pressed pellets of clays from Tirau soil, pure salmon-sperm DNA, and salmon-sperm DNA-clay complexes, at the Beamline 16A1 at NSRRC.

Results and Discussion

Carbon NEXAFS

The clay fraction of the upper subsoil of the Tirau soil contains about 10 % total C, and C NEXAFS spectra showed its SOM comprises quinonic, aromatic, aliphatic, and carboxylic C (Fig. 17.2a). Although C contents varied between horizons and sites, the compositions of SOM were similar in all horizons of the andic paleosols (data not shown). We attribute this compositional similarity to either (1) the downward leaching of dissolved SOM through the profiles vertically, effectively homogenising the composition of organic matter in each horizon, or (2) integrative developmental upbuilding pedogenesis whereby the profiles have formed by incremental additions of thin distal tephra over the past ~25,000 years that have interacted with the soil organic cycle whilst temporarily at the land surface, the land/soil surface slowly rising at an average rate of ~5 mm per century (Lowe et al. 2012; McDaniel et al. 2012), or both (1) and (2).

DNA Adsorption Studies

There was a negative relationship between total C and DNA uptake by all soil samples. However, at pH 6.5, humic-acid-free synthetic allophane adsorbed salmon-sperm DNA at the rate of up to 26 μg/mg allophane, which is about seven times more than that for humic-acid-rich allophane (Fig. 17.3). Hence humic acid (or SOM) occupied the active sites on allophane spherules, limiting their capacity for DNA adsorption.

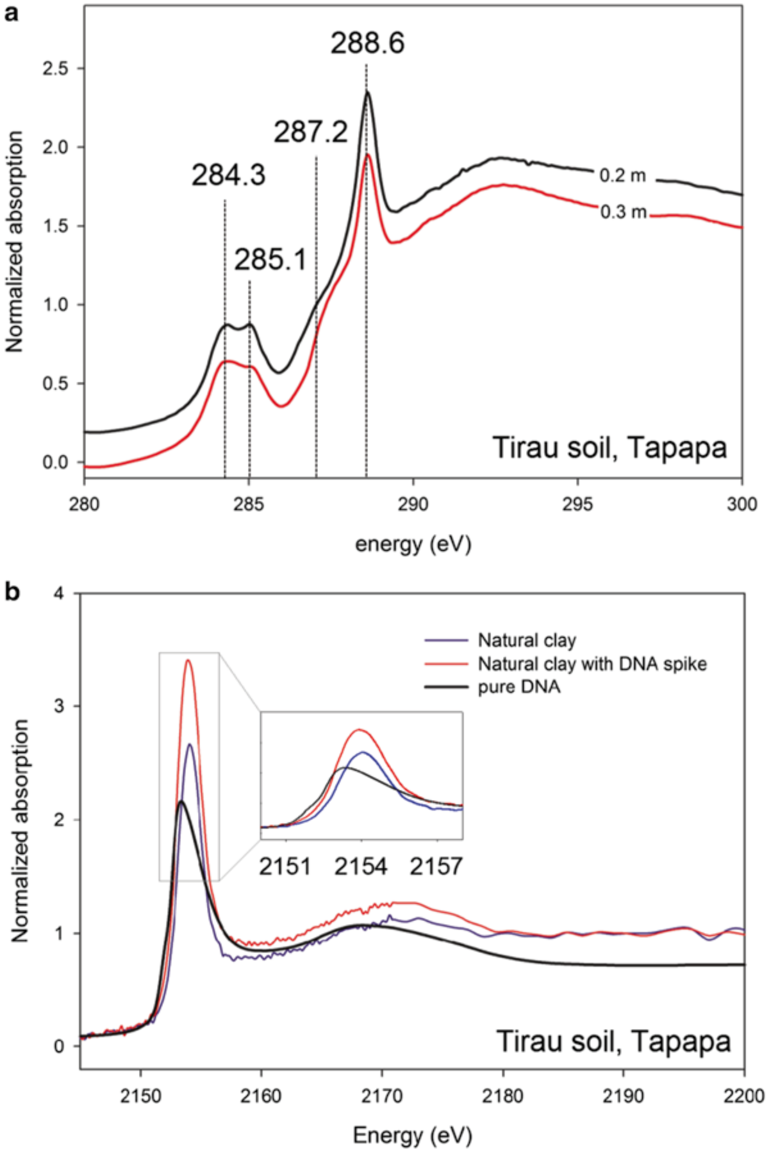

Fig. 17.2 Normalized (**a**) C NEXAFS spectra for organic matter in clays from the upper subsoil (~20–40 cm depth) of the Tirau soil, an Andisol at Tapapa in New Zealand (37° 59′ 41″ S, 175° 52′ 59″ E: Lowe et al. 2012), and (**b**) phosphorus XANES spectra for salmon-sperm DNA, for natural allophanic clay from the Tirau soil at Tapapa, and for allophanic clay with a salmon-sperm DNA spike. Peaks at 284.3, 285.1, 287.2, and 288.6 eV represent quinonic, aromatic, aliphatic, and carboxylic C, respectively

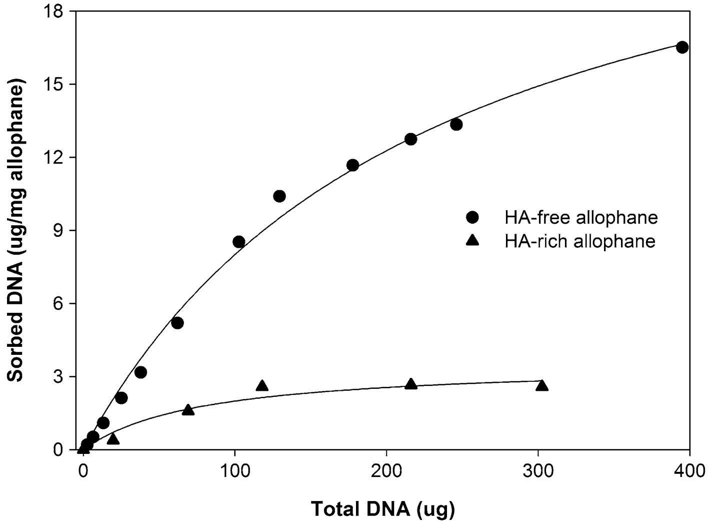

Fig. 17.3 Salmon-sperm DNA adsorption isotherm for humic-acid (HA)-free and for HA-rich synthetic allophane. This experiment was based on work by Saeki et al. (2010), and DNA in the supernatant was measured by UV spectrophotometry at 260 and 280 nm

Phosphorus XANES

The spectra showed that the absorption edge (absorption energy, the sharply rising peak of the spectrum) of phosphorus for pure DNA was 2,153 eV, and that binding of DNA and clay had induced a shift of the absorption edge to 2,514 eV (Fig. 17.2b). This shift indicates that the phosphate group of DNA has changed chemically after binding to natural clay. However, it is unclear whether DNA was bound to clay or to SOM, which is apparently pervasive in clay fractions from andic materials, and further experiments are needed to evaluate how DNA reacts to SOM and to organic-matter-free allophane. An improved understanding of DNA adsorption in Andisols should indicate how we can best potentially extract aDNA from allophanic paleosols that date back through time.

Conclusions

1. C NEXAFS spectra for an Andisol showed that OM comprises quinonic, aromatic, aliphatic, and carboxylic C. In other Andisols, C contents varied but C species were similar, attributable to pedogenic processes operating during developmental upbuilding, downward leaching, or both.
2. The presence of OM in natural allophanic soils weakened adsorption of DNA on clay: HA-free synthetic allophane adsorbed seven times more DNA than HA-rich synthetic allophane.

3. P XANES spectra for salmon-sperm DNA and DNA-clay complexes showed that DNA was bound to allophane clay through the phosphate group, either to the surface of allophane or to OM, or both.

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Chapter 18
Soil Microbial Biomass and C Storage of an Andosol

Kazuyuki Inubushi and Yuhua Kong

Abstract Volcanic soils (Andosols) cover about half of the arable upland in Japan, and these soils generally have a high amount of soil carbon. Soil microbial biomass C (MBC) and soil organic C (SOC) was compared in an Andosol and non-Andosol (Sand-dune Regosol) from Japan. Significant linear correlations were observed for Japanese Andosols but the slope of the correlation (MBC/SOC) was significantly lower for Andosol compared to such published relationships for non-Andosols. MBC was relatively lower at the same SOC level in the Andosol than non-Andosol. Subsurface Andosol had higher MBC indicating that cumulated soil C may be substrate for microorganisms even after thousand years of eruption and surface horizon formation. These finding indicate unique features of microbial biomass and C turnover in Andosols.

Keywords Andosol • Microbial biomass • Subsurface soil

Introduction

Soils are well recognized as large stock of carbon that is largely controlled by microbial biomass (Jenkinson et al. 2004). Changes in land use and management practices (e.g. tillage, use of fertilizers, organic residues, and pesticides) are responsible for the increase or decrease of soil C. Microbial biomass is pool of nutrients and the motor for soil C turnover (Jenkinson and Ladd 1981). Globally, soil C and microbial biomass are also controlled by the soil parent material, such as clay contents and mineralogy (Jenkinson and Powlson 1976). Increasing temperature can increase the decomposition rate of soil organic carbon (SOC) (Powlson 2005).

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SOC is returned to the atmosphere as CO_2 via respiration, as soil microorganisms use organic materials as a source of energy and nutrients (Baldock et al. 2012). Soil microbial biomass C (MBC) is an indicator of changes in soil properties (Brookes 1995). Moreover, MBC is the main driving force in the decomposition of organic materials, albeit MBC account for 1–3 % of soil total C (TC) (Jenkinson and Ladd 1981). Thus, MBC can provide useful understanding of the dynamics of soil C pool.

Andosols are the dominant soils in Japan covering about half of the arable uplands, with large amounts of soil carbon (Otowa 1986). Andosols are mainly derived from volcanic ash deposition. The soils have high P fixing characteristics as well as high active Al concentrations, which can cause toxicity. Detailed examinations of microbial biomass distribution in Andosol profile are limited (Goyal et al. 2000). In this paper, we compare soil MBC contents and its correlation with soil TC in the topsoil of Andosols in Japan, under different land-use and data in literatures taken from the Broadbalk experiment, Rothamsted, UK (Jenkinson and Powlson 1976; Jenkinson et al. 1979; Vance et al. 1987). We examined the concentration of soil MBC and TC in both surface and subsurface soil layers of two Andosol profiles.

Materials and Methods

Soil Sampling and Study Area

To compare the effects of climate and land-use on the relationship between soil MBC and TC, seven soil sampling sites in central Japan (34°49′–36°36′ N, 139°00′–54′ E) under different land-use (two sites for forest, orchard and cropland and one site for grassland) were selected. Soils (0–15 cm) were taken after removing litter and roots in October 2010. Most Japanese soils were Andosols, except cropland for paddy which is a Sand-dune Regosol (Table 18.1). To examine vertical distribution of the microbial biomass and its turnover in Andosol, soil samples were collected from deciduous forest and an adjacent apple orchard in Numata Farm of Chiba University, Gunma prefecture, Japan at a depth of 100 cm (Inubushi et al. 2004).

Soil Properties Analysis

Fresh soil samples were sieved (2 mm), and then stored in a dark refrigerator at 4 °C, prior to incubation. Soil moisture content was measured by drying them at 105 °C for 24 h. Air-dried soil (10 g) was mixed with 25 and 50 mL distilled water to measure soil pH and electrical conductivity (EC). Soil TC contents content was measured using a CN corder (MT-700 with an auto sampler, Yanaco, Kyoto, Japan).

Soil MBC was measured using the chloroform fumigation-extraction method (Brookes et al. 1985; Vance et al. 1987). Before analysis, the soil moisture content

Table 18.1 Characteristics of soil sampling sites in Japan

Location	Land use	Sampling code[a]	Latitude/ Longitude	Soil classes (FAO UNESCO)	Mean temperature (°C)[b]	Mean precipitation (mm)[b]
Atagawa	Forest	A-F	N34°50′ E139°04′	Andosols	16.5	2,726
	Orchard (orange)	A-O				
Kujuukuri	Cropland (rice)	K-C	N35°33′ E140°26′	Sand-dune Regosols	16.2	1,904
Matsudo	Cropland (soybean)	M-C	N35°47′ E139°54′	Light-colored Andosols	15.7	1,687
Numata	Forest	N-F	N36°36′ E139°00′	Humic Andosols	12.7	1,479
	Grassland	N-G				
	Orchard (apple)	N-O				

[a] The selected sites are: Atagawa evergreen broad leaf forest (A-F), Atagawa orange orchard (A-O), Kujuukuri rice croplands (K-C), Matsudo soybean croplands (M-C), Numata mixed forest (N-F), Numata grassland (N-G), and Numata apple orchard (N-O)

[b] Data come from Japanese Meteorological Agencies of 2010

was adjusted to the range of 40–50 % of water-holding capacity, and then the soils were pre-incubated at 25 °C for 48 h in an incubator to stabilize microbial activities (Vance et al. 1987). Finally, the soils were fumigated with alcohol free chloroform at 25 °C for 24 h in sealed desiccators. Fumigated and unfumigated soil samples were extracted with 50 mL 0.5 M potassium sulfate by shaking for 30 min, and the extracts were filtered. SOC in the K_2SO_4 extracts was measured by a TOC analyzer (TOC-5000, Shimadzu, Kyoto, Japan). MBC levels were calculated using the equation: $\text{MBC} = 2.22 \times E_C$, where E_C = organic C extracted from fumigated soils-organic C extracted from unfumigated soils (Vance et al. 1987; Watanabe et al. 2010).

Statistical Analysis

One-way analysis of variance (ANOVA) analysis and Tukey's honestly significant difference (HSD) test for multiple comparisons were used.

Results and Discussion

Relationships Between Soil MBC and Soil TC

Most soils had high concentrations of soil moisture content, TC, SOC and MBC (Table 18.2). A positive correlation with soil TC and MBC was observed in Japanese

Table 18.2 Chemical and microbiological properties of Japanese soils

Sampling code[a]	Soil moisture (%)	pH	EC (d S m^{-1})	TC (mg g^{-1} D.S.)	SOC (μg g^{-1} D.S.)	MBC (μg g^{-1} D.S.)	MBC/TC (%)
A-F	50.4	5.6	0.13	133 a	454 b	1862 a	1.4
N-F	38.5	5.8	0.08	94 b	371 c	625 c	1.2
N-G	34.0	5.8	0.10	91 c	125 e	594 c	3.2
A-O	36.6	5.9	0.11	70 d	206 d	807 b	0.6
N-O	34.6	5.4	0.08	63 e	228 d	207 ef	0.7
K-C	25.5	5.9	0.07	9 i	49 f	291 de	0.7
M-C	35.4	5.2	0.13	40 f	697 a	252 de	0.3

Means within a column followed by the same letter do not differ significantly by the Tukey's HSD test ($p<0.05$, n=3)

[a]Sampling code are the same as for Table 18.1

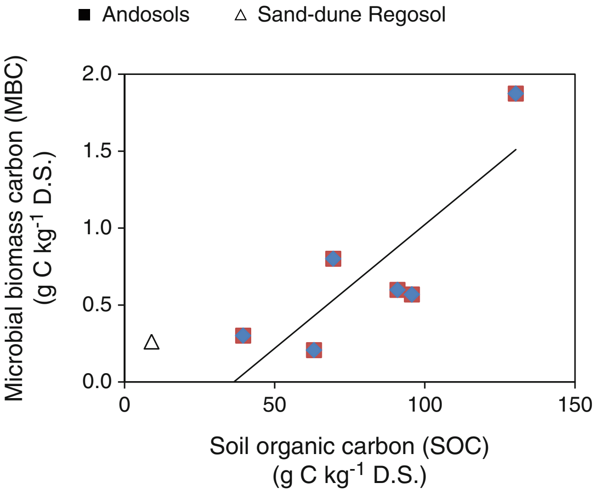

Fig. 18.1 Relationships between soil MBC and SOC in Japanese soils

soils (Fig. 18.1) as MBC/SOC=0.0161, being similar as reported by Inubushi et al. (2005) for Andosols in Japan but much lower than the Broadbalk soils in the UK. It suggests that stabilization and decomposition processes are different in Andosols which is affected by soil physicochemical properties, soil parent materials and climatic conditions.

Soil Microbial Biomass C and Soil Total C

Soil MBC concentrations in Andosol were generally greater in the surface soil layer than in deeper soil layers. The soils under forest showed higher MBC contents than in the soils under orchards. Higher MBC contents in the soil under forest was

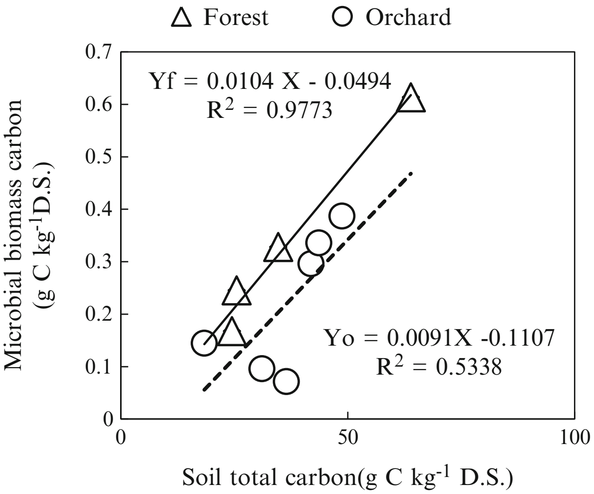

Fig. 18.2 Relationships between soil MBC and TC in surface and subsurface soils under apple orchard and forest, Numata Farm, Japan

probably due to large amount of organic matter inputs as litterfall while lower input in orchards was probably due to monthly weeding during the growing season. For surface and subsurface soils, positive correlations in both soils under apple orchard and forest between soil TC and MBC were also observed and the correlations were comparable to the Andosol samples (Fig. 18.2). However, there was a higher amount of MBC in deeper soil layers near the buried humic horizons. Originally, there was a buried surface layer with a larger humus content that was covered by volcanic ash depositions. Subsurface Andosol in the buried horizons had higher MBC amount than upper subsoil layer, indicating that cumulated soil C may be substrate for micro-organisms even after thousand years of eruption and surface horizon formation.

Conclusions

Land-use types and soil types had relatively large impacts on MBC and TC. In Andosols significant positive correlations between MBC and TC were observed. However, Andosol showed different correlation curve compared to soils from the UK. Buried topsoils had higher MBC than upper subsoil layer, indicating that cumulated soil C may be a substrate for micro-organisms.

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Chapter 19
Estimating Fine Resolution Carbon Concentration in an Intact Soil Profile by X-Ray Fluorescence Scanning

Sharon M. O'Rourke, Jonathan N. Turner, and Nicholas M. Holden

Abstract The link between the small (<mm) scale spatial organisation of soil carbon (C) and the long-term security of the abiotic C store is not well understood. Here we present a methodology that is being developed to map carbon concentration in an intact soil profile of a Cambisol by adapting X-ray fluorescence (XRF) scanning for soils. The main objective was to identify candidate indicators for the estimation of soil C using XRF with intact soil cores 1 m long. Following multiple correlation and regression of XRF elemental counts with carbon concentrations, sulphur emerged as the strongest candidate for the estimation of soil C but a loss of XRF spatial resolution from 200 μm to 1 cm was required for sulphur to achieve a strong relationship with C ($R^2 = 0.77$). It was concluded that XRF measurements using a Cr target tube may increase count rates for lighter elements and improve the accuracy with which elemental counts can predict soil C at the higher spatial scale.

Keywords Soil carbon • X-ray fluorescence scanning • Intact soil core

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Introduction

The vertical distribution of organic carbon is not well understood (Lorenz and Lal 2005). The deeper sub soil is assumed to be a carbon reservoir although some proportion has a relatively fast turnover and might act as a carbon source if temperatures increase (Smith et al. 2008; Jobbágy and Jackson 2000). Carbon security (permanence and residence time) needs to be addressed before carbon sequestration programmes can be advanced and deployed with confidence. Major carbon stabilization mechanisms are: (i) selective preservation due to recalcitrance of organic matter, (ii) stabilization by interaction with mineral surfaces and (iii) spatial inaccessibility to decomposer organisms which is most important during decomposition in the subsoil (Lützow et al. 2006).

Techniques such as transmission electron microscopy and X-ray microtomography have been employed at the microscopic scale to image soil organic carbon in situ within peds. Profile sampling has been used with conventional analytical methods to map carbon at the field to national scale (Martin et al. 2011) and more recently digital mapping methods have been used (Minasny et al. 2013). There is little work published that assesses the spatial arrangement of carbon in the soil from ped to horizon scale, and how this relates to soil structure and profile. Study of the specific location of carbon can only provide part of the picture (Stockmann et al. 2013), but this gap in our knowledge is a key impediment to understanding carbon security defined as the permanence and residence time of soil C pools.

Here we present a methodology to map carbon concentration in an intact soil profile by adapting X-ray fluorescence (XRF) scanning for soils. The objective is to develop a better understanding of the role of small-scale spatial organisation of soil organic carbon with respect to the long-term security of the abiotic carbon store.

X-ray fluorescence scanning has been employed as a semi-quantitative tool in sedimentology for paleoclimate reconstruction in marine and lacustrine environments. Organic carbon is of interest in reconstruction studies to determine sea surface productivity (Ziegler et al. 2008) and organic carbon burial in marine sediments (Mayer et al. 2007). Elements from aluminium (atomic mass 27) to uranium (atomic mass 238) can be quantified by XRF, but direct measurement of carbon (atomic mass 12) is not possible. A number of proxies have been tested for their ability to predict organic carbon. For example, bromine is exclusively associated with marine organic carbon, having been fixed in the water column, and can be used as a direct estimate except in intervals of the core where terrestrial organic matter is enhanced (Ziegler et al. 2008). The objective of the research was to identify candidate indicators for estimation of soil carbon using XRF at the millimetre scale.

Materials and Methods

The instrument used was an Itrax Core Scanner (Cox Analytical Systems, Mölndal, Sweden). It integrates an X-ray source, an x-ray focusing mechanism, and a number of sensors: (i) a laser triangulation system, (ii) an optical camera, (iii) an x-ray

Fig. 19.1 The ITRAX core scanner used for this study

line camera, and (iv) an XRF detection system (Croudace et al. 2006) with a mechanism for presenting a sample core (Fig. 19.1). The standard set-up used was a 3 kW X-ray generator and molybdenum target tube with a maximum capacity of 60 kV and 55 mA. Data were acquired sequential as topography profile, photographic image (50 μm pixel^{-1}), radiographic scan (20 μm pixel^{-1}) and XRF matrix (200 μm pixel^{-1}). The topography was recorded to ensure a constant path length for the XRF detector and to identify surface cracks. Such areas were excluded from analysis as being unreliable.

Soil cores (Cambisols) were collected from UCD Lyon's Research Farm, Co Kildare, Ireland (53°17′52″N 6°32′08″W). A percussion drill (Eijkelkamp, Giesbeek, The Netherlands) was used to collect intact soil cores of 7 mm diameter and 1,000 mm long. Conventionally sediment cores are sawn open and split with fishing wire into half cores and scraped clean with the side of a glass slide for presentation to the scanner. Due to the stones and roots found in most mineral soils a wire does not work. A fine toothed single-handed saw was used to cut the soil. No 'cleaning' of split soil cores was performed to minimise smearing of the soil surface. The surface presented to the scanner was therefore not as smooth as that envisaged for sediments and some parts of the core would not be useable due to cracks and empty stone cavities and thus were excluded. The threshold for exclusion based on surface topography was tested by adjustment from 0.5 to 2.0 mm standard deviation about the mean surface height.

In order to preserve time sequence from sedimentary layers, sediment cores are scanned under field moist condition (Haschke 2006). The moisture content of cores is unknown, and they are occasionally rewetted prior to scanning and a polypropylene film (6–1.5 μm) is applied to the core surface to reduce drying and build-up of condensation around the instrument. Considering the total time (approx. 24 h) and ambient temperature (ca. 20 °C) when scanning it was decided for these preliminary studies that slow drying during scanning could cause spatial artefacts in the data. Therefore, the soil cores were dried at 30 °C for 24 h in a forced draft oven prior to

XRF scanning. The impact of this pre-treatment may affect soil mineralogy and other constituents, but it is likely to be consistent throughout the sampling period rather than being temporally variable.

The core scanner was operated at 30 kV and 50 mA. Count times were tested for 5, 10, 15, 20 and 30 s to find the optimal balance between count and total scan time. Generally larger counts yield more accurate data. Scanning X-ray florescence data were collected for a central track 22 mm wide at a resolution of 200 μm. This corresponds to an elemental matrix of 37 elements by 5,000 data points for a 1000 mm sediment core. Elemental count data (counts s^{-1}) were collected for each data point for correlation with total carbon at the 1 cm scale. Macro samples were incrementally collected for each 1 cm length of the opposite half of the split core and analysed for total C by dry combustion.

Results and Discussion

Surface Exclusion Threshold

The XRF detector uses topographic information collected from a single location in the middle of the core and assumes this is equal across the core width. This is applicable to sediment cores, but causes positioning difficulties for the XRF detector on soils. Increasing the standard deviation threshold about the mean surface height from 0.5 to 2.0 mm (Fig. 19.2) allowed more data to be collected from the core, but poor relationships observed for 2.0 mm data for individual elements (i.e., Al = −0.11, Mn = 0.13, Fe = 0.05; NS) indicated that XRF data collected over an uneven path were of poor quality. Removal of some protruding stones was necessary to ensure the range tested was well within the maximum height restriction of 3.5 cm imposed to protect the sensors from damage, resulting in a loss of continuous structural feature data with soil depth in the cores. Increasing the standard deviation did not overcome the inability of XRF scanning to collect data from areas with heterogeneous topography which meant that data collected in some regions of the core was deemed invalid.

Count Times

Total scan time (*ST*, h) increased from 7 h at 5 s count time (*CT*, s) to 42 h at 30 s count ($ST = 1.38CT$). The correlation coefficient between elemental intensity observed over 5 s *CT* compared to 30 s *CT* was 0.83, increasing to 0.90 at 10 s, 0.95 at 15 s and 0.95 at 20 s. The results indicated that a 30 s *CT* was not justified as the additional 14 h for scanning added little additional information. The 15 s *CT* would be sufficient in a time limited situation, but the 20 s count rate was selected for XRF

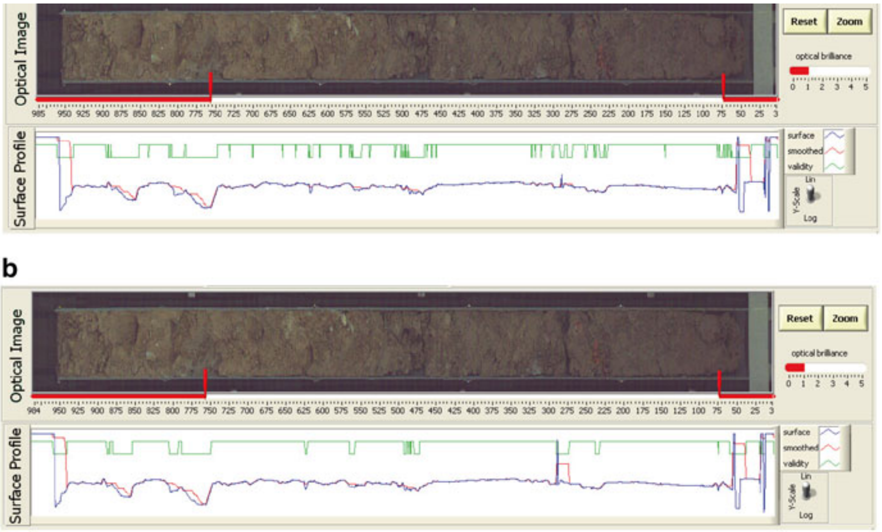


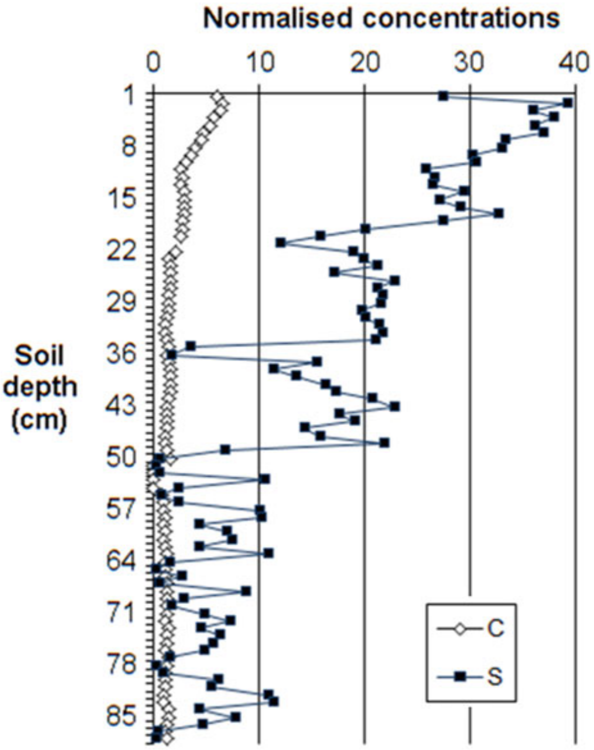
Fig. 19.2 Optical image and corresponding surface topography profile (*blue line*) for a soil core showing the validity data (*green line*) at (**a**) 0.5 mm and (**b**) 2.0 mm standard deviation (Color figure online)

measurement because the *CT* required is proportional to the element concentration in the sample. While 15 s may be sufficient for common elements (i.e., Si, K, Ca), 20 s is more likely to yield valid data for less common elements that may be useful for predicting organic carbon concentration from XRF data.

XRF Calibration

Elemental count values were not converted to concentrations. Calibration requires matrix matched standards, which have not yet been established. Two main issues require further research to allow calibration: Firstly, variable geometry in terms of texture and variable water content make calibration difficult for sediment cores, and this is much more problematic with the secondary pedal structure and mineralogical variation found in soils. Secondly, conventional bulk and wet chemistry methods that can be applied at the same scale as the XRF sampling (i.e., 200 μm^3) do not exist. Conventional XRF analysis on macro samples (Liang et al. 2012) has been successful, but peak concentrations in soil cores are likely to be averaged out compared to the Itrax sampling resolution. A log-ratio calibration model (Weltje and Tjallingii 2008) has been employed that captures the non-linearity between relative intensity and concentration. When tested for eight elements (Al, Si, Cl, K, Ca, Ti, Mn, Fe) in marine sediments, the relative standard deviation of predicted

Fig. 19.3 Normalised concentrations of soil carbon and sulphur in 0.89 m soil core



concentration was <2 % (Weltje and Tjallingii 2008). This problem will need solving only if strong evidence emerges that there are candidate elements that can be use singly or in combination as surrogates to reliably predict soil organic carbon content.

Candidate Indicators for Estimating Soil Carbon

The reported detection limits for Al (22,000 ppm), Si (9,000 ppm), K (500 ppm), Ca (100 ppm), Ti (60 ppm), Mn (25 ppm), Fe (25 ppm), Rb (5 ppm) and Sr (5 ppm) for geochemical reference samples measured at a count time of 100 s (Croudace et al. 2006) were generally less than reported ranges for the soils of Ireland (Fay et al. 2007). Limits for lighter elements are not certain and it is possible that the total counts of light elements may have been underestimated. There were low (<1,000) total counts for S, Cu, V, P, Cd, Br, Al, Se, Mg and Sc. Total carbon ranged from 9.4 to 1.2 % throughout the soil profile (Fig. 19.3) and all elements recorded were significantly correlated ($P < 0.05$) with carbon except Co (−0.02). The strongest relationships were found for S (0.61), Zn (0.50), Ta (0.41) and Ba (0.4) (Table 19.1). While S had the strongest correlation, the low count means its

Table 19.1 The correlation between total carbon and element counts from XRF, and the significance of each element in a multiple linear regression model to predict soil C

Spatial resolution		200 μm			1 cm		
Element	Atomic mass	Element intensity[a]	Pearsons coefficient	Multiple regression	Element	Pearsons coefficient	Multiple regression
S	32	100	0.61	**	S	0.77	**
Zn	65	10,000	0.50	**	Cu	0.56	
Ta	181	1,000,000	0.41	**	Br	0.54	
Ba	137	1,000,000	0.40		Zn	0.54	
Mn	55	100,000	0.39		Ta	0.54	
Fe	56	1,000,000	0.38		Mn	0.51	
Rb	85	10,000	0.36		Ce	0.49	
Cu	64	750	0.36	**	Ba	0.49	
W	184	2,000,000	0.34	**	Pb	0.48	
Ga	70	10,000	0.33	**	Rb	0.43	
Zr	91	10,000	0.32	*	Zr	0.43	
Ti	48	10,000	0.32	**	Fe	0.43	
Ce	140	1,000,000	0.32	**	W	0.40	
V	51	500	0.31		Ga	0.40	
Pb	207	1,000,000	0.28	**	Cr	0.39	
Ni	59	1,000	0.25	**	Ti	0.37	
Si	28	10,000	0.24	**	Ni	0.31	
P	31	250	0.24	**	U	0.29	
Cr	52	10,000	0.21		Si	0.29	
Cd	112	250	0.20	**	Cl	0.28	
Br	80	250	0.20	**	As	0.28	
K	39	10,000	0.20	**	K	0.25	
U	238	2,000,000	0.16		Se	0.23	*
As	75	1,000	0.14		Mg	0.22	
La	139	100,000	0.11		La	0.18	
Y	89	1,000	0.10		Ge	0.16	
Al	27	250	0.09	**	V	0.14	*
Cl	35	10,000	0.08		Y	0.14	*
Ge	73	1,000	0.07		Al	0.13	*
Se	79	500	0.07	**	Bi	0.11	
Bi	209	100,000	0.03		Cd	0.11	
Mg	24	50	0.03		P	0.01	
Co	59	10,000	−0.02	**	Co	−0.03	
Sr	88	10,000	−0.11	**	Sc	−0.07	
Sc	45	500	−0.14		Sr	−0.17	*
Sn	119	1,000,000	−0.15		Sn	−0.20	
Ca	40	1,000,000	−0.24	**	Ca	−0.29	

*$P<0.05$; **$P<0.01$

[a]< maximum element intensity stated

reliability is questionable. Multiple linear regression ($R^2=0.58$) indicated that 21 elements were significant ($P<0.01$) predictors of carbon and of these, Zn and Ta were also associated with high counts and significant linear correlations greater than or equal to 0.4. There were much stronger correlations between elements, e.g. S with Zn, Fe, Ba, Ti, Mn (all > 0.60), Zn with Fe, Ti, Si, Ba, Ni (all > 0.84) and Ta with W, Zn, Fe, Ti, Si (all > 0.74).

Superficial zero counts can occur in the XRF matrix for areas where measurements are made in soil cavities, so mean counts for elements were considered at the same spatial scale as soil C (1 cm) to determine if better correlations could be found. Over half of the elements recorded were significantly correlated with soil C ($P < 0.05$), and the relationship with S was stronger (0.77). Multiple linear regression ($R^2 = 0.968$) indicated 6 elements combined as significant predictors of C, and S had the strongest contribution ($P < 0.01$).

Theoretically the majority of S in well drained mineral topsoil (>90 %) is in organic forms, being a constituent of soil organic matter (Williams and Steinbergs 1958). The two main fractions of organic S are organic sulfates (S that is not directly bonded to C but linked to C via O or N atoms; sulphur esters, thioglucosides and sulfamates) and C-bonded sulphur (S that is directly bond to C as S containing amino acids and proteins, sulfonic acids and complex heterocyclic compounds). Carbon bonded S is thought to be reasonably resistant to decomposition due to its presence in high molecular weight forms (Schoenau and Malhi 2008). Early work on the distribution of S in soils (Tabatabai and Bremner 1972) found that organic S significantly accounted for 95–99 % of total S in topsoils (0–15 cm) and 84–99 % in subsoils (15–120 cm), thus highlighting its suitability to act as a indicator for the estimation of soil C throughout the profile using XRF techniques.

Conclusions

Sulphur emerged as the strongest candidate for the estimation of soil C using XRF, but at the cost of some loss of spatial resolution to achieve a highly significant relationship. Further method development will employ image analysis to isolate soil matrix material and repeat the X-ray fluorescence scanning using a Cr target tube to determine if higher counts can be produced for the lighter elements found to be significantly related to C distribution.

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Chapter 20
Probing Temperature-Dependent Organo-mineral Interactions with Molecular Spectroscopy and Quartz Crystal Microgravimetry

Michael Nguyen, William Hockaday, and Boris L.T. Lau

Abstract The global-scale cycling of carbon and mechanisms of carbon storage are important in climate change issues. It is uncertain as to whether climate change will turn soil into a carbon source or change its ability to serve as a sink. In fact, 50–75 % of all natural organic matter (NOM) in soils and sediments is associated with mineral surfaces. These organo-mineral associations can protect NOM from decomposition for timescales of centuries to millennia and serve as a mechanism by which carbon is stored in soils. The stability of organo-mineral complexes, defined as the degree of resistance to decomposition, could affect carbon storage as temperatures increase. The temperature-dependence of the kinetics and mechanisms of carbon stabilization need to be studied for the purpose of developing models to predict how soil carbon reservoirs respond to changes in temperature. Several techniques are proposed to be used in organo-mineral interaction studies. Nuclear magnetic resonance spectroscopy, x-ray photoelectron spectroscopy, and quartz crystal microgravimetry are discussed as potential tools to identify chemical bonding environment and adsorption/desorption dynamics.

Keywords Sorption • Temperature • Organo-mineral • Nuclear magnetic resonance spectroscopy • X-ray photoelectron spectroscopy • Quartz crystal microgravimetry

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Introduction

The importance of studying the soil carbon reservoir has become increasingly evident as climate changes occur. Various methods used to estimate the size of the global pool of soil organic carbon (SOC) indicate 1,000–1,500 gigatons of carbon in the upper 100 cm of the soil profile (Amundson 2001; Jones et al. 2005; Raich and Schlesinger 1992). Approximately, 50–75 % of SOC is associated with mineral surfaces (Arnarson and Keil 2007; Christensen 2002). The associations between organic matter and mineral surfaces are often referred to as organo-mineral interactions. Organo-mineral interactions protect SOC from decomposition for timescales of centuries to millennia and serve as a mechanism by which carbon is stored in soils (Guggenberger and Kaiser 2003; Kögel-Knabner et al. 2008; Mikutta et al. 2007; Schimel et al. 1994). This suggests quantitative descriptions of the temperature-dependence of organo-mineral interactions are needed to predict responses of the soil carbon budget to changes in the climate.

Empirical studies on the response of SOC to variations in temperature have mostly been conducted at the macro- or meso-scale perspective. For example, early temperature studies examined soils from various biomes such as temperate and tropical forests to investigate current effects of temperature on other soil properties. These early studies showed that (1) the SOC stocks in regions with lower soil temperatures were more sensitive to variations in temperature (Lloyd and Taylor 1994) (2) organic matter was more degraded (faster turnover rates) in tropical forest soils than in temperate forest soils (Grisi et al. 1998) and (3) an increase in temperature resulted in a loss of soil organic carbon (Kirschbaum 1995). Kirschbaum (1995) quantified the percent of soil organic carbon loss based on mean annual temperature (MAT). According to the study, a 1 °C increase could lead to a loss of 10 % of soil organic carbon in regions with MAT of 5 °C while the same temperature increase would result in a loss of 3 % soil organic carbon for regions with MAT of 30 °C (Kirschbaum 1995). Several other studies have reached similar conclusions. Melillo et al. (2002) examined the effects of soil temperature on soil organic matter decay and carbon dioxide flux and found both to be accelerated by warming (Melillo et al. 2002). Kaiser et al. (2001) investigated the effects of temperature changes to dissolved organic matter (DOM) sorption dynamics and concluded that DOM release from soil (due to enhanced solubility of hydrophilic DOM components) was accelerated by warming (Kaiser et al. 2001).

Despite the conclusions from these studies, a general consensus has not been reached about the effects of temperature on soil organic carbon. Giardina and Ryan (2000), Davidson and Janssens (2006), and Kirschbaum (2006) challenged the accuracy of previous temperature soil studies. Giardina and Ryan (2000) questioned the accuracy of decay constants derived from short-term laboratory and in-situ incubations. They argued that soil microbial activity may have a large influence that has not been understood. Through an intensive data search, they also found soil carbon decomposition rates to be constant across a global scale gradient (Giardina and Ryan 2000). Davidson and Janssens (2006) and Kirschbaum (2006) concluded in their studies that (1) due to the wide range of experimental conditions used on previous studies and (2) due to the temperature sensitivity of organic carbon compounds with varying activation energies and molecular structures, a general consensus cannot be reached yet.

The lack of a general consensus on the effects of soil warming has led to many studies focusing on individual components in soil systems to differentiate the causes of the apparent changes in soil carbon dynamics. Thornely and Cannell (2001) proposed that variations in temperature dependencies may be attributed to the fact that although warming could accelerate decomposition, it could also increase the rate of protection from decomposition (Thornley and Cannell 2001).

Using kinetic theory, Conant et al. (2008a) suggested that the heterogeneity of SOC: the two primary carbon fractions in soils, labile and recalcitrant, would have different sensitivities to temperature changes (Conant et al. 2008a). Labile soil organic carbon is the fraction of soil organic carbon that is the most active and has higher turnover rates (Harrison et al. 1993). Recalcitrant soil organic carbon, on the other hand, is the fraction of soil organic carbon that is inherently resistant to decomposition (Kleber 2010). The relationship between temperature sensitivity and the two organic matter fractions are disputed (Plante et al. 2010). Two separate studies conducted by Conant (2008a, b) have shown different responses of each fraction to temperature changes (Conant et al. 2008a, b). Plante et al. (2010) reported results that agreed with published experiments for the labile fraction but conflicting results for the recalcitrant fraction. They attributed the mixed results to the difficulty in isolating the different SOC pools as well as processes that may have masked responses to temperature changes such as microbial influences (Plante et al. 2010). Fang et al. (2005) found that temperature did not affect SOC decomposition which meant the temperature dependence of the two pools, recalcitrant and labile, respond similarly to warming (Fang et al. 2005).

Davidson and Janssens (2006) suggested that the key to elucidating the temperature-dependencies of SOC decomposition and stabilization is to examine the processes at a finer scale. They noted that SOC sorption onto mineral surfaces affects decomposition rates and warrants further investigations (Davidson and Janssens 2006). The effects of temperature on sorption have been studied by several authors. Tremblay et al. (2005) and Zhang et al. (2009) studying sorption of polycyclic aromatic hydrocarbons to estuarine particles (Tremblay et al. 2005) and naphthalene and phenanthrene sorption by soil (Zhang et al. 2009), respectively, found overall sorption of aromatic compounds to decrease with warming. This conclusion was supported by separate adsorption and desorption studies by Kaiser et al. (2001), Wang et al. (2010, 2011) who examined sorption of DOM to soils, the sorption of tetracycline onto clays and marine sediment, and the sorption of polycyclic aromatic hydrocarbons to sediments, respectively (Kaiser et al. 2001; Wang et al. 2010, 2011). These studies examined the temperature dependence of organo-mineral complexes from the thermodynamic perspective by calculating enthalpy changes for the sorption reaction. Negative enthalpy values indicated that sorption was an exothermic process and therefore an input of energy in the form of temperature would hinder the process. The results of Arnarson and Keil (2000) are consistent with this assessment, and they further concluded that a decrease in adsorption of DOM to montmorillonite clay upon warming indicates that entropy-driven sorption processes, such as hydrophobic interactions, are not an important driver of organic matter sorption (Arnarson and Keil 2000).

Few studies have attempted to approach the temperature dependence of organo-mineral interactions from the kinetic perspective by providing changes in the rate (mass/area/time) and extent of sorption (mass/area) associated with warming. Additionally, previous studies examined sediments and soils with a wide range of physical and chemical variability which may differentially affect sorption processes. Several techniques are proposed in the following section to investigate the kinetic aspect as well as finer scale chemical characterization of organo-mineral interactions.

Analytical Techniques

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) provides structural information on organic matter in aqueous solution. This technique can indicate whether bonding between organic matter and mineral is covalent or non-covalent by documenting the chemical shift (covalent) and spin-lattice relaxation times (T_1) (non-covalent of the reactive functional group(s)). The T_1 value is characteristic of overall molecular motion, including translation, rotation, and vibration, and has been used to examine non-covalent interactions of contaminants with NOM (Cardoza et al. 2004; Lau et al. 2012). Non-covalent interactions with specific functional groups in NOM may be identified by the shortened T_1 (reduced mobility) of protons in the reactive functional group(s). NMR has also been used to study the preferential arrangement of aliphatic components of humic and fulvic substances as well as determining the relative orientation of domains in proteins (Conte et al. 1997; Skrynnikov et al. 2000).

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) provides information about the elemental composition, chemical bonds, and oxidation state in the top ~10 nm of a surface. XPS has been used to study organo-mineral interactions such as: time-dependent chemical alteration of sorbed OM by quantifying the abundance of carbon in different chemical bonding environments (e.g., aromatic, aliphatic, and amide), the destruction of organo-mineral aggregates as function of oxygen exposure time, and determination of chemisorption by detecting strong interaction of carboxylate groups with the goethite surface (Arnarson and Keil 2007; Kaiser and Guggenberger 2007; Mikutta et al. 2009). Previous XPS studies have revealed that most redox reactions are restricted to the topmost 30 Å of mineral surfaces and do not involve the bulk of the mineral (Hersman et al. 1995; Kalinowski et al. 2000). In addition to composition information from the surface, XPS can measure the uniformity of elemental composition in a depth profile, which is important to examine whether a zonal structure of sorbed OM is present as a function of distance from mineral surfaces (Mikutta et al. 2009).

Quartz Crystal Microgravimetry

Quartz crystal microgravimetry (QCM) is an analytical technique that makes real-time measurements of the extent and kinetics of adsorption and desorption. QCM resolves mass differences using the piezoelectric oscillation frequency (f) of quartz. Mass changes (Δm) are calculated according to the Sauerbrey equation: $\Delta f = -S\Delta m$, where Δf is the change of frequency and S is the Sauerbrey constant. A solution with dissolved organic matter can be passed through a flow module (with programmable temperature setting) that contains a QCM sensor where changes in resonance frequency (Δf) are monitored as organics adsorb to the surface. QCM has been used to obtain sorption isotherms and measure the mass of adsorbed gold and cadmium sulfide nanoparticles, polymer films, metals, water, and natural organic matter and polymers such as S-propanolol (Brust et al. 1996; Buttry and Ward 1992; Furman et al. 2013; Haupt et al. 1999; Krtil et al. 2001; Marx 2003).

Conclusion

The soil carbon reservoir plays an important role in regulating climate as it represents one of the greatest fluxes of carbon dioxide to the atmosphere. Changes such as warming have the potential to create an imbalance between carbon loss and gain. The response of soil to temperature changes is heavily debated. Finer scale studies are required to elucidate the effects of temperature that may be masked at greater scales. Nuclear magnetic resonance spectroscopy, x-ray photoelectron spectroscopy, and quartz crystal microgravimetry are proposed as potential tools to investigate the temperature-dependencies of organo-mineral interaction (sorption and desorption) rates and mechanisms.

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Chapter 21
Storage of Total and Labile Soil Carbon Fractions Under Different Land-Use Types: A Laboratory Incubation Study

Shade J. Akinsete and Stephen Nortcliff

Abstract We studied the effect of different land uses (woodland, grassland and arable land) in two depths of a temperate silt-rich Typic Hapludalf on the storage of total organic C (TOC), readily oxidizable C (ROC), hot water-Extractable C (HWC), and cold water-Extractable C (CWC) fractions in bulk soil (<2 mm) and macroaggregates fractionated into small (1–2 mm), medium (2–4 mm) and large (5–8 mm) classes. A 120-day incubation was conducted to measure depletion of all C fractions. The highest C concentrations were associated with the macroaggregate-size classes but stored within the 1–2 mm aggregates for each of the soils. TOC and ROC concentrations depletion ranged from 1 to 14 % across the land uses throughout the incubation period. However, the concentrations of labile fractions (HWC; CWC) declined significantly during the incubation by 40–59 % and 3–35 % for the topsoil and subsoil respectively. This suggests that C fluxes are largely controlled by the highly bio-reactive labile fractions. Consequently, labile C is a promising measure for detecting changes in TOC following land use change. Woodland contained three to four times more TOC than grassland and arable land soils. Cultivation reduced C storage of this soil by >70 %.

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Keywords Total organic carbon • Readily oxidizable carbon • Hot water-extractable carbon • Cold water-extractable • Land use

Introduction

Soil organic carbon (SOC) and aggregation are vital component of soil science, especially in relation to the mitigation of carbon dioxide (CO_2) emissions into the atmosphere, which affects the global climate. Several anthropogenic activities such as land use change have profound impact on the accumulation and the loss of SOC (John et al. 2005; Spohn and Giani 2011). Therefore, land use changes on SOC storage is of concern in the context of greenhouse gas (GHG) emissions mitigation. Several studies have reported the impact of land use conversion on the depletion of SOC and destruction of stable aggregates (John et al. 2005; Lal 2005; Spohn and Giani 2011).

Most previous studies on SOC accumulation have been restricted to surface soils, and our understanding of subsurface SOC is limited (Gal et al. 2007; Rumpel and Kögel-Knabner 2011). Some studies found that subsurface soils contain a large fraction of total OC and are sensitive to land use changes (Don et al. 2009; Rumpel and Kögel-Knabner 2011; Schrumpf et al. 2013). In order to quantify SOC stocks and fluxes, a better understanding of land use changes on the storage of SOC in deeper depths is needed (Gal et al. 2007; Schrumpf et al. 2013). Relatively small changes in the amounts of SOC may bring about substantial effects on atmospheric concentrations and on global C cycling at large (Belay-Tedla et al. 2009), and the storage and stability of SOC with reference to different land use changes becomes important. However, the analysis of total organic C does not normally permit detection of small changes because of the high background levels and natural soil variability (Ghani et al. 2003; Belay-Tedla et al. 2009). Several studies have shown that soluble labile carbon extractable with water at varying temperatures serve as a revelatory measure for detecting changes in SOC following land use change (Ghani et al. 2003; Belay-Tedla et al. 2009; Adisa and Nortcliff 2011; Spohn and Giani 2011; Sarkhot et al. 2012).

Macroaggregates (>0.25 mm) are particular sensitive to land use changes (Tisdall and Oades 1982), and loss of SOC with cultivation is often connected to the destruction of macroaggregate (Elliot 1986; Madari et al. 2005). Some studies have reported higher concentrations of C in macroaggregates than in microaggregates (Mikha and Rice 2004; Kong et al. 2005). Macroaggregates house microaggregates and provide physical protection for labile OC which is a primary source of nutrient often loss during cultivation (Mikha and Rice 2004).

In this study, we examined macroaggregate-associated SOC fractions in a temperate top- and subsoils, under different land uses (woodland, grassland and arable land), seeking to provide better understanding of C accumulation (Adisa and Nortcliff 2011). Laboratory incubation was performed to monitor and detect the effect of land use change on the different SOC fractions.

Materials and Methods

Sites and Soils

The soil C fractions were studied under three land uses: conventional arable land grown to wheat (*Triticum aestivum* L.), grassland, and woodland (*Quercus* sp.). The site originates from similar parent material: the Hamble soil series (a Typic Hapludalf) with a silt loam texture, located in the Englefield Farm Estate (grid reference SU 628724), west of Reading, Berkshire, UK. These soils have been under arable agriculture for over 50 year, with areas converted to grassland and woodland 25 year ago. The mean annual precipitation in the area is about 650 mm. The Hamble soil series occurs on the silty Pleistocene drift (Brickearth) parent material (Jarvis 1968). Detailed general soil characteristics are described in Adisa and Nortcliff (2011).

Soil Sampling

Soil samples were collected in November 2004 from two soil depths—topsoil (0–25 cm) and subsoil (25–55 cm). The soil samples were passed through an 8-mm sieve prior to air drying. One part of the air-dried soil was sieved to obtain the bulk soil (<2 mm) and the remaining soil was sieved through different stacked sieves (1, 2, 4, 5, and 8 mm) to obtain the different aggregate sizes. Finely ground samples were used for all C determination.

Carbon Fraction Determinations

Total C was determined by dry combustion on a Leco SC 444 analyzer (Leco Corp., Logan, UT), while the ROC was determined using a modified acid-dichromate oxidation of the soil organic matter in the wet-oxidation reaction method (Rowell 1994). The labile C fractions (HWC and CWC) were determined on a sequential basis using the method outlined by Ghani et al. (2003). Total OC in both extractions was determined on a Shimadzu TOC 5000 analyzer (Shimadzu Corp., Kyoto, Japan).

Soil Incubation

Air-dried 2–4-mm soil aggregates were aerobically incubated in the dark at 20 °C (±1 °C) for 120 day at 65 % water-holding capacity (Rowell 1994). The moisture content was checked weekly and replenished as required. At 30-day intervals, the incubated aggregates were harvested, weighed, air dried, and stored until analyzed.

Statistical Analysis

Differences among means for the different soil C fractions were conducted using one-way ANOVA, and the Duncan's multiple range test was used to test for significance. Differences between treatment means were considered statistically significant at $P \leq 0.05$. All statistical analyses were performed using the SPSS for Windows statistical package (versions 15.0).

Results and Discussion

Aggregate-Associated Carbon Fractions Under Different Land Uses

Mean total concentrations of macroaggregate-associated C fractions varied from 5,456 to 91,666 mg kg^{-1} for TOC, from 4,998 to 75,255 mg kg^{-1} for ROC, from 36 to 250 mg kg^{-1} for HWC, and from 9 to 63 mg kg^{-1} for CWC, across the different land uses (Fig. 21.1). In general, the aggregate classes 1–2 and 2–4 mm contained significantly more C fractions than the 5–8 mm aggregate class. Other studies (Mikha and Rice 2004; Yang et al. 2007) reported that SOC concentrations peaked in the macroaggregate class size. The difference in macroaggregate-associated C concentrations in the different land uses shows the effect of land use change, which could be attributed to the differences in C input. These soils were found to accumulate varying concentrations of C fractions as follows: woodland > grassland > arable land for topsoil. The trend was similar for the subsoil except for grassland and arable land which showed similar C concentrations within the aggregate classes.

The topsoil of the woodland contained over three times more TOC and ROC, and twice more HWC and CWC compared to the soils under grassland or arable farming. For all C fractions, the C content decreased with increasing depth (Fig. 21.1), which was more pronounced in the grassland and arable land. Soils under woodland had more than eight times higher TOC and ROC and over three times more HWC and CWC than in the grassland and arable land in the subsoils. The woodland subsoil had higher concentrations in all C fractions compared to grassland and arable land thus revealing the effect of land use on C storage with depth. Our results corroborated other studies (John et al. 2005; Gal et al. 2007; Rumpel and Kögel-Knabner 2011) that showed that our understanding and conclusions on SOC storage studies can be improved by sampling subsoils. Cultivation reduced C storage of this soil by

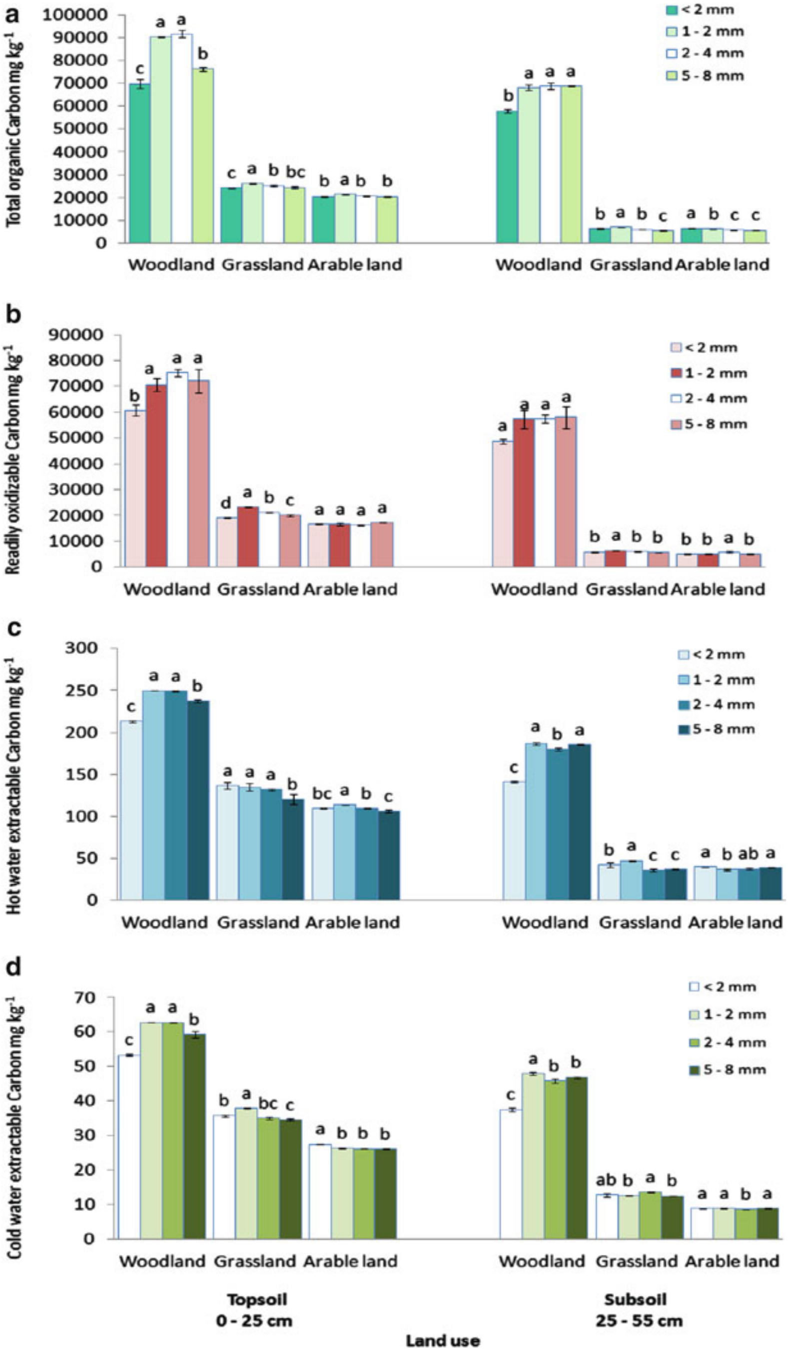

Fig. 21.1 Bulk soil and macroaggregate-associated carbon fractions (mg kg^{-1}) as affected by different land use: (**a**) Total organic carbon; (**b**) readily oxidizable carbon; (**c**) Hot water extractable carbon; (**d**) Cold water extractable carbon. Means (n = 3). *Different letter* on top of bars (standard error) indicates statistically significance ($P \leq 0.05$)

over 70 %. This is in agreement with Davidson and Ackerman (1993) that reported >40 % SOC loss following cultivation.

Soil Carbon Fractions Depletion: Incubation Study

Total Organic Carbon

There was little or no significant depletion in the total carbon (TOC) concentrations throughout the incubation period (Table 21.1). A small change was observed within the first 30 days of incubation in the soils under woodland use, which may indicate the heterogeneous state of the components of the TOC fraction under woodland.

Averaged over the incubation periods across the different land uses, the largest depletion occurred in the topsoil of the woodland, which was 14 % (Table 21.1) of TOC by the first 30 days of incubation. Depletion of TOC concentrations in the topsoil of the arable land and grassland, revealed that the highest depletion (7 %; 9 %) occurred at the 120-day and 90- and 120-day incubation periods respectively (Table 21.1). The TOC depletion in the subsoils of the arable land (11 and 10 %) and grassland (9 %) occurred at both 90- and 120-day and 30-day incubation periods respectively. The subsoil of the woodland responded differently with no specific pattern for TOC depletion (Table 21.1). Although, it is difficult to explain the inconsistent pattern of TOC depletion exhibited by the woodland subsoil, we suggest the presence of different C fractions with different turnover rates resulting from C input under woodland use might explain this irregular pattern.

Readily Oxidizable Carbon

In general, there was progressive depletion in the (ROC) concentrations during the incubation for the different land uses, which were mostly significantly different between the initial concentrations and the 60-, 90- or 120-day (Table 21.1). The depletion of the ROC concentrations in the topsoil of the woodland, grassland and arable land was 4 %, 8 % and 9 % respectively. The subsoil of the woodland revealed an inconsistent pattern of depletion, while in the grassland and arable land, the highest depletion by the 120-day incubation amounted to 15 % and 12 % respectively.

Hot-Water Carbon

The depletion of the HWC fraction revealed that about one-third to about a half of the HWC is depleted within the first 30 days of the incubation; no difference was found between the different land uses (Table 21.2). The depletion progressed significantly during the incubation, until the 90-day period, when a sudden increase was observed (Table 21.2), suggesting the occurrence of a release of a certain part

Table 21.1 Depletion of TOC and ROC concentrations during incubation

Incubation period (days)	Land use					
	Topsoil (0–25 cm)			Subsoil (25–55 cm)		
	Woodland	Grassland	Arable land	Woodland	Grassland	Arable land
Total organic carbon (TOC) mg kg^{-1} soil						
0	86067a (706)	26467a (176)	19433a (67)	64967a (133)	6697a (39)	6297a (33)
30	74300b (1300)	25933a (426)	18633ab (437)	61767b (203)	6107c (98)	5830bc (136)
60	77367b (968)	25633a (371)	18867a (203)	64133a (219)	6463ab (87)	5997b (85)
90	77533b (1690)	24233b (186)	18600ab (231)	63633a (902)	6243bc (101)	5620c (75)
120	76733b (463)	24067b (644)	17933b (273)	61433b (145)	6293bc (142)	5677c (81)
Readily oxidizable carbon (ROC) mg kg^{-1} soil						
0	69809a (945)	22253a (112)	17161a (96)	51080b (331)	6040a (92)	5514a (46)
30	67184b (1302)	22494a (149)	16750a (138)	52591ab (281)	5842ab (66)	5126b (134)
60	67120b (705)	21673b (253)	16180b (71)	53434a (1085)	5767b (7)	5015b (92)
90	66912b (187)	21390b (219)	15821bc (131)	54424a (661)	5694b ()98	4704c (56)
120	65068b (291)	20420c (125)	15579c (224)	53469a (291)	5344c (48)	4919bc (57)

Values followed by different lower case letters in the same column are significantly different for incubation period at $P \leq 0.05$. Values in parentheses are ± Standard error

Table 21.2 Depletion of HWC and CWC concentrations during incubation

Incubation	Land use					
	Topsoil (0–25 cm)			Subsoil (25–55 cm)		
Period (days)	Woodland	Grassland	Arable land	Woodland	Grassland	Arable land
Hot-water carbon (HWC) mg kg^{-1} soil						
0	249.28a (0.2)	131.47a (0.7)	109.78a (0.8)	179.98a (1.6)	36.21a (1.4)	37.38a (1.0)
30	158.97b (0.3)	77.96b (0.9)	53.34b (0.9)	129.91b (2.4)	24.32b (0.2)	21.61b (0.2)
60	125.89c (2.9)	62.30d (0.3)	45.73c (0.3)	106.62c (4.8)	22.38bc (0.9)	18.40c (0.4)
90	130.57c (1.5)	69.72c (1.9)	46.29c (1.4)	123.42b (1.6)	20.68c (0.5)	18.47c (0.9)
120	119.01d (1.4)	59.62d (0.1)	45.24c (0.6)	96.33d (1.2)	21.00c (0.8)	16.69c (0.5)
Cold-water carbon (CWC) mg kg^{-1} soil						
0	62.82a (0.1)	35.33a (0.2)	26.19a (0.2)	45.88a (0.7)	13.70a (0.1)	8.62a (0.0)
30	35.97b (0.8)	18.19b (0.3)	15.72b (0.5)	37.45b (1.1)	11.08b (0.1)	8.36a (0.1)
60	31.57c (0.4)	16.49c (0.2)	13.92c (0.4)	31.63c (0.1)	10.05c (0.1)	7.71b (0.0)
90	27.53d (0.2)	15.36d (0.1)	12.64d (0.1)	31.47c (0.9)	9.74c (0.1)	7.64b (0.2)
120	27.85d (0.5)	14.74d (0.2)	11.74d (0.3)	29.68c (0.7)	10.07c (0.1)	8.13ab (0.4)

Values followed by different lower case letters in the same column are significantly different for incubation period at $P \leq 0.05$. Values in parentheses are ± Standard error of this C fraction (pool). This agrees with other studies, where HWC is suggested to consist of two pools; very labile and slowly labile pools (Gregorich et al. 2003). By the end of the incubation period, nearly 42–60 % of the initial HWC concentrations was depleted, most of which occurred within the first 60-days of this incubation (Table 21.2).

Cold-Water Carbon

The progressive depletion of the CWC during incubation followed a different pattern from the other carbon fractions. For the topsoils, CWC concentrations depletion reached approximately nearly half of the initial concentration by the 30-day incubation period (Table 21.2), amounting to relative changes of 43, 49 and 40 % in the topsoils of the woodland, grassland and arable land respectively. In the topsoils, between 40 and 58 % CWC fraction was depleted throughout the incubation period. However, the subsoils revealed relatively lower depletion rates compared to the topsoils (Table 21.2). The depletion of the CWC concentrations in the subsoil, ranged from 3 to 35 % throughout the incubation periods. The relatively small size of the CWC depleted is suggested to result from the relatively small quantity of the total CWC fraction associated with the subsoils, except the woodland.

The results from this study revealed the dynamics of four different carbon fractions in the top- (0–25 cm) and sub- (25–55 cm) soils under different land uses, which showed distinctions between the TOC, ROC and labile fractions (HWC and CWC). Several studies have reported difficulties in identifying changes in soil TOC over a short-term (Ghani et al. 2003; Marriott and Wander 2006). In this study, TOC as well as the ROC fractions changed little throughout the incubation period. The labile carbon (HWC and CWC) fractions on the other hand demonstrated significant changes revealed by the depletion in C concentrations throughout the incubation period. The results of our study support previous work showing that HWC is a more sensitive and revelatory indicator for detecting changes in SOC than TOC and ROC (Ghani et al. 2003; Adisa and Nortcliff 2011; Spohn and Giani 2011; Sarkhot et al. 2012)

Apart from the woodland soils, where the depletion of CWC continued significantly throughout the incubation (Table 21.2), the arable land and grassland soils revealed major significant depletion within the first 30-days of the incubation period, due to higher CWC concentrations in the woodland soils when compared with the other land uses. High lability of the CWC has been attributed to ease of solubility in water and it been a readily available substrate energy source for soil microorganisms (McGill et al. 1986; Zhang et al. 2006)

The dynamics of the HWC fraction was different from that exhibited for the CWC and there was a relatively consistent depletion of this C fraction with increasing incubation period until the first 60 day. This may indicate that the hot-water carbon fraction is a larger fraction (Zhang et al. 2006) with a longer turnover rate in soils. Our results support other studies (Ahn et al. 2009) that found that 59 % of the variability in potential C mineralization was explained by changes in HWC concentration, implying that HWC is an useful indicator of changes in soil C.

The increased concentration of the HWC measured at 90-day of the incubation suggests that a less rapid labile portion of this labile C fraction might be the cause for this sudden increase. Thus implying that the HWC fraction in these soils might comprise of more than one carbon fraction, possibly, a rapidly labile fraction and a slowly labile fraction as suggested in other studies (Gregorich et al. 2003).

The labile C fractions (HWC and CWC) supports evidence of the high responsiveness of labile C fractions to changes in total carbon over a relatively short-term. Ghani et al. (2003) showed that the measurement of labile carbon fractions would readily identify early warnings and subtle changes in total soil carbon. In addition, Ahn et al. (2009) in their study reported responsiveness of HWC to land use.

Conclusions

This study provides information on the capacity of a silt-rich soil under different land uses to store C in macroaggregate class fractions. This study has provided a better understanding of land use changes on the storage of SOC in deeper depths.

Differential patterns of depletion were demonstrated for the different C fractions measured. TOC and ROC remained relatively steady throughout the incubation period, and these C fractions did not reveal changes in soil carbon. Conversely, the significant depletion of the labile C fractions (HWC and CWC) was demonstrated throughout the incubation periods, thus revealing the sensitivity of these labile C fractions to detect and reveal small and subtle changes in the soil carbon. This study further shows that partitioning between C fractions is essential to detect small changes otherwise masked when only the relatively Stable C fractions are considered.

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Chapter 22
Could Soil Acidity Enhance Sequestration of Organic Carbon in Soils?

Shinya Funakawa, Kazumichi Fujii, Atsunobu Kadono, Tetsuhiro Watanabe, and Takashi Kosaki

Abstract On the basis of field and laboratory measurements of the dynamics of soil organic matter (SOM) in Japan, Thailand, Indonesia, Kazakhstan, and Ukraine having different soil pH levels, we postulate that soil acidity plays an important role in the accumulation of SOM through two processes. Firstly, the amount of potentially mineralizable C (C_0) in the acid soils of Kalimantan or light-fraction C in the Japanese acid soils often increased drastically. Hence, it seems that high soil acidity can enhance the accumulation of organic materials in surface soils by decreasing the soil microbial activities for SOM decomposition. Secondly, field measurements of C flux in various soils under forest showed that the internal leaching of dissolved organic carbon (DOC) from litter layers or surface soils increased under low pH conditions, typically for Humods in Japan and Udults in Kalimantan. This indicates a downward movement of DOC in acid soils that increases the tendency of the subsoils to accumulate SOM as organo-mineral complexes. It is concluded that high soil acidity can enhance the storage level of

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soil organic materials in the form of readily mineralizable organic materials in the surface soils and by organo-mineral complexes formed in subsoils as a result of accelerated leaching of DOC from the O horizon.

Keywords Decomposition • Dissolved organic carbon • Organic matter • Soil acidity

Introduction

Soil organic matter (SOM) has traditionally been regarded as one of the vital components for maintaining the fertility of agricultural soils. Soils high in SOM have better soil physical properties (moisture retention, water drainage, aggregation, etc.) as well as chemical or biological properties (high nutrient retention or energy sources for microbial activities) (Paul and Collins 1998). Therefore, researchers have repeatedly warned about the decline of SOM due to inappropriate land uses as one of the serious land degradation problems (e.g. Craswell and Lefroy 2001; Lal 2004).

Recently, in relation to the problem of global climate change, considerable attention has been focused on SOM dynamics as possibly both a source and sink of carbon dioxide. In this context, many attempts have been made to simulate SOM dynamics quantitatively using models such as CENTURY (Parton et al. 1987) and RothC (Jenkinson 1990), which have proved successful under certain environmental conditions. These models use limited numbers of input parameters relating to the quality of substrates, the environmental conditions (i.e. temperature and moisture), and some of the soil properties (i.e. soil texture). The soil parameters that are used in the simulation models are rather simple, and neither acidity-related nor fertility-related parameters are included, though many biological processes can be affected by such parameters.

In the present work, we tested the influence of soil acidity on SOM dynamics by different approaches based on field and laboratory measurements of the dynamics of soil organic matter (SOM) in different regions of Asia (Japan, Thailand, Indonesia, and Eurasian steppes) having different soil pH levels.

Materials and Methods

Determination of Readily Mineralizable Pools of Soil Organic Matter

In total, 147 surface soils were collected from Japan, Indonesia (the islands of Kalimantan, Java, and Sumatra), Thailand, and Eurasian steppes (Kazakhstan and Ukraine). The larger part of the Eurasian steppe soils were classified as Mollisols according to the USDA Soil Taxonomy (Soil Survey Staff 2006), with loess deposits as the predominant parent materials. Such dark-colored steppe soils are formed in a relatively dry climate with annual precipitation of less than 500 mm; thus, the soil pH is close to neutral (6.86 ± 0.19 (SE)). The soils collected from Japan and Kalimantan were usually classified as Ultisols or Inceptisols. Owing to high annual precipitation (mostly > 1,500 mm) and their parent material, these forest soils have low pH values (4.24 ± 0.13 and 4.79 ± 0.06 for the Japanese and Kalimantan soils, respectively) with high values of exchangeable Al. The pH values of the soils from Java, Sumatra, and Thailand were intermediate: 5.20 ± 0.19 for Java or Sumatra and 5.71 ± 0.12 for Thailand.

Fresh soil samples were passed through a 2-mm mesh sieve and their moisture contents was adjusted to 60 % of the field moisture capacity. The mineralized C was determined at least six times during a period of more than 90 days of aerobic incubation at a constant temperature of 30 °C. The C mineralization pattern was fitted to equations by the least squares method using SigmaPlot 8.0 (SPSS Inc. 2002). As the function to describe C mineralization, a first-order kinetic model was used:

$$C_{\mathrm{m}} = C_0\left(1 - \mathrm{e}^{-kt}\right)$$

where C_{m} is the amount of mineralized C (mg kg^{-1}) at time t (d); C_0 is the pool of potentially mineralizable C (mg kg^{-1}); and k is the rate constant (d^{-1}).

The organic matter in light and heavy fractions (LF and HF) was determined, and LF and HF were separated on the basis of differences in specific gravity by using NaI solution (1.6 g cm^{-3}) followed by centrifugation at 3,000 rpm (Kadono et al. 2009; modified from Spycher et al. 1983). Materials remaining in the supernatant were collected and regarded as LF (partially decomposed plant residues mostly), whereas those included in the sediment were regarded as HF (more highly decomposed organic material, possibly fixed by soil mineral fractions). The C content of the LF was determined by dry combustion with an NC analyzer (NC–800–13N, Sumika), while the C content of the HF was determined by subtracting the C content of the LF from the total organic C content.

Field Measurements of C Fluxes in Different Forest Ecosystems

In total, nine experimental plots were installed in natural or secondary forests in Japan, East Kalimantan (Indonesia), and northern Thailand (Table 22.1). Hence, the soils from TG, KT, BS, BB, and KR3 were strongly acidic with pH values of less than 4.5, whereas those from NG, KR1, KR2, and RP were moderately acidic with higher pH values.

All the experiments were conducted throughout 1 year at these nine plots. Soil respiration rates were quantified once or twice per month in five replicates using a closed-chamber method. The soil temperature at a depth of 5 cm and the volumetric water content of soils at depths of 5, 15, and 30 cm were monitored using data

Table 22.1 Description of the experimental plots

Plots	Annual precipitation (mm)	Mean annual temperature (°C)	Soil classification (US Soil Taxonomy)	Surface soil pH
Japan				
NG	1,422	6.9	Acrudoxic Melanudands	4.6
TG	1,782	10.7	Andic Haplohumods	3.8
KT	1,490	15.9	Typic Dystrudepts	4.2
East Kalimantan, Indonesia				
BS	2,187	27	Typic Paleudults	4.0
BB	2,427	27	Typic Paleudults	4.2
KR1	2,256	27	Rhodic Eutrudox	6.3
KR2	2,256	27	Typic Paleudults	5.6
KR3	2,256	27	Typic Paleudults	4.5
Northern Thailand				
RP	2,084	25	Typic Haplustults	5.0

loggers. Soil solutions were collected in five replicates using tension-free lysimeters beneath the O, A, and B1 horizons (depths of 0, 5, and 30 cm, respectively). Throughfall was collected in five replicates using a precipitation collector. These samples were collected at each plot once or twice per month for 1 year. Fluxes of DOC from each horizon were calculated by multiplying the water fluxes with the DOC concentrations of throughfall and soil solutions as determined using a total organic carbon analyzer (TOC-V_{CSH}, Shimadzu). The water fluxes of throughfall were measured using precipitation collectors, whereas those of soil water percolating at depths of 5, 15, and 30 cm were estimated by applying Darcy's law to the unsaturated hydraulic conductivity and the gradient of the hydraulic head at each depth. Circular litter traps of 60 cm in diameter were used to collect litterfall in five replicates for estimation of the input of organic matter to the soils, followed by determination of the total C content in the litter samples. Detailed procedures for these experiments are given in Fujii et al. (2009).

Results and Discussion

Mineralizable Organic Matter and Decomposition Rates

Figure 22.1 shows the relationships between soil pH and the amount of readily mineralizable fractions of SOM; that is, (a) the potentially mineralizable C (C_0) determined by the aerobic incubation experiment and (c) the light-fraction C determined by density fractionation. The former fraction was often extremely high in the acidic soils from Kalimantan, whereas the latter fraction was increasing in the acidic soils from Kalimantan and Japan. The decreasing trend in the rate constant, *k*, under acidic conditions (Fig. 22.1b) is considered one of the reasons for the accumulation of readily decomposable fractions in surface soil layers.

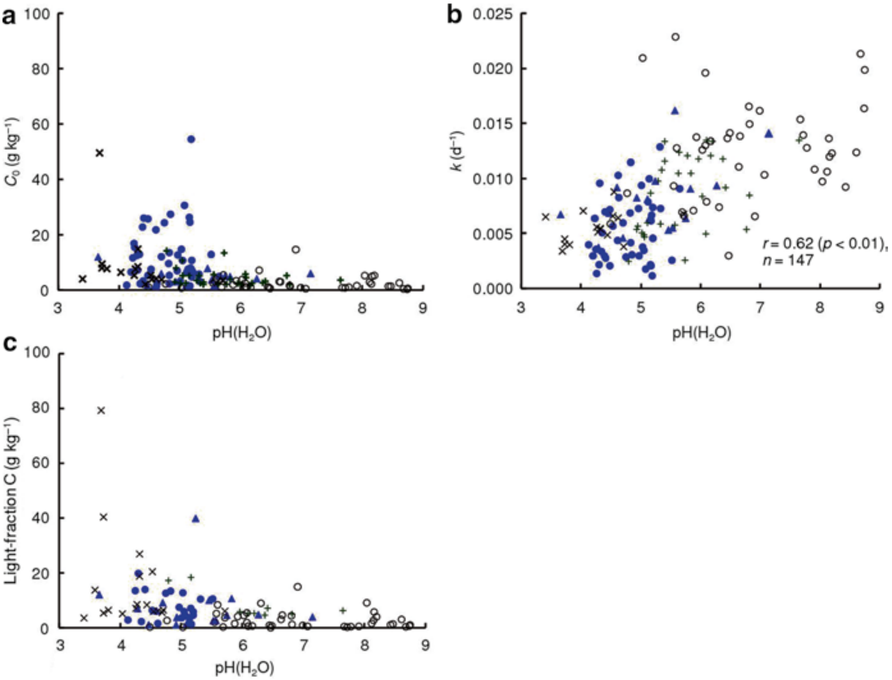

Fig. 22.1 Relationships between soil pH and the amount of potentially mineralizable C (C_0) (**a**) and decomposition rate constant, k (**b**) determined by the aerobic incubation, and light-fraction C (**c**) determined by density fractionation. ×, soils in Japan; +, soils in Thailand; ●, soils in Indonesia (Kalimantan); ▲, soils in Indonesia (Java and Sumatra); ○, soils from Eurasian steppes

The downward tendency of the k values under acidic conditions can also occur under actual soil ecosystems, and Funakawa et al. (2010) reported a correlation between the decomposition rate constant determined under laboratory incubation and that calculated on the basis of field measurements of soil respiration. The strong soil acidity can enhance the accumulation of readily mineralizable organic materials in the surface soils by decreasing the soil microbial activities for SOM decomposition.

In situ *C fluxes in Forest Ecosystems with Different Soil Acidity Levels*

The magnitude of DOC production in the O horizon varies among the soils. Comparing the DOC fluxes from the O horizon on the basis of C input, the DOC fluxes correspond to 4.1–13.8 % of C input (Fig. 22.2).

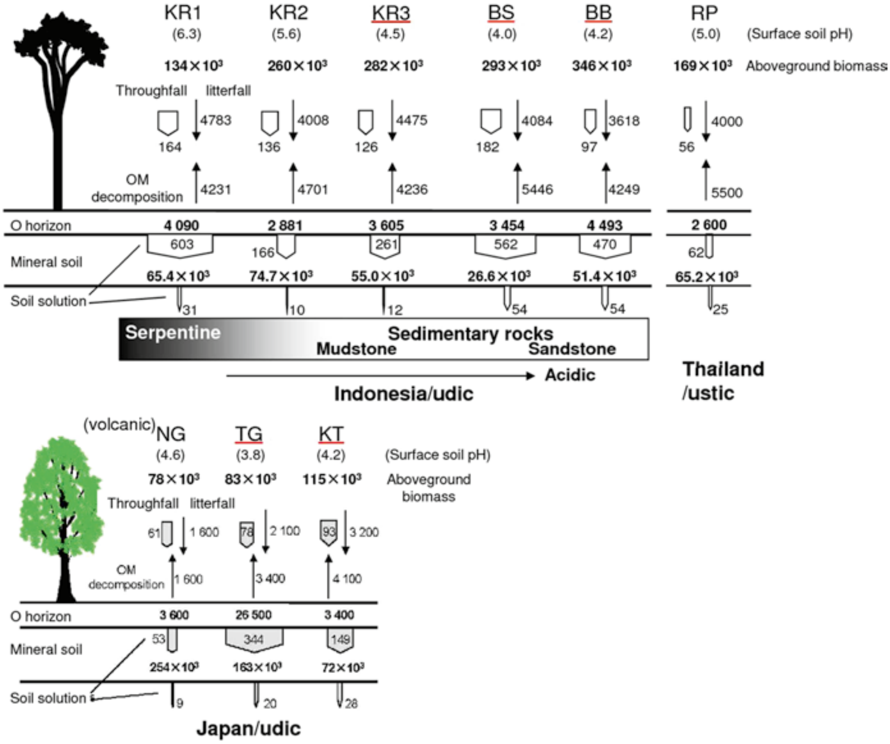

Fig. 22.2 The C stock (kg C ha^{-1}) and the annual C fluxes (kg C ha^{-1} year^{-1}) via litterfall, organic matter (OM) decomposition, throughfall and soil solution in forest ecosystems with different climatic and geological conditions. The C stock in soils at the depths of 0–30 cm was counted

According to data in the literature and from our study, the ratio of DOC flux to C input increases with decreasing soil pH (Fig. 22.3), with the exception of KR1. The substantial DOC translocation from the O horizon may be common to highly acidic soils (Spodosols and acidic Ultisols with soil pH<4.3) in a humid climate. This is consistent with the significant contribution made to podzolization and soil acidification by DOC, which is the source of organic acids (Ugolini and Dahlgren 1987; Do Nascimento et al. 2008). Lower soil pH may favor substantial DOC production due to enhanced litter solubilization by fungal activities (Kalbitz et al. 2000) and inhibited mineralization (Saggar et al. 1999; Kemmitt et al. 2006), and by recalcitrance of DOC produced from litter rich in polyphenol and lignin (Kalbitz et al. 2003, 2006).

In summary, the downward movement of DOC in acid soils increases the opportunity for subsoils to accumulate SOM as organo-mineral complexes, especially in soils under boreal or temperate forest.

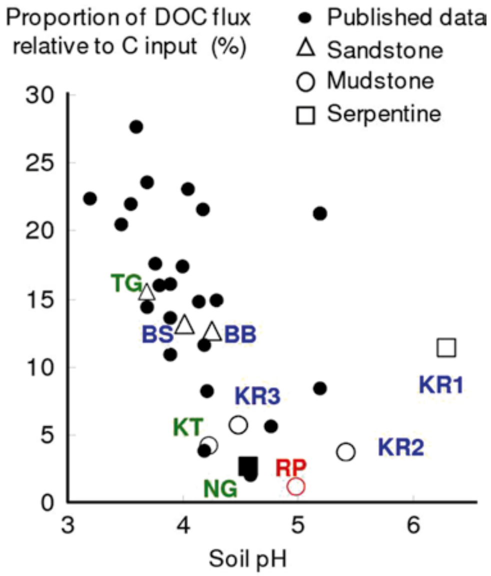

Fig. 22.3 Relationship between soil pH and proportion of DOC flux relative to C input in the O horizon (Data sources include Moore (1989), Moore and Jackson (1989), Yavitt and Fahey (1986), Qualls et al. (1991), Johnson et al. (2000), Tobón et al. (2004a, b), Schwendenmann and Veldcamp (2005), Kleber et al. (2007), Raich et al. (2007))

Conclusion

High soil acidity can enhance the storage level of soil organic materials in the form of (1) readily mineralizable organic materials in the surface soils and (2) organo-mineral complexes formed in subsoils as a result of accelerated leaching of DOC from the O horizon. Such processes should be involved in C dynamics modelling, especially when the aim is a precise simulation of organic materials in forested ecosystems.

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Part III
Soil Use and Carbon Management

Chapter 23
Is Percent 'Projected Natural Vegetation Soil Carbon' a Useful Indicator of Soil Condition?

Chris Waring, Uta Stockmann, Brendan P. Malone, Brett Whelan, and Alex B. McBratney

Abstract The concentration of Soil Organic Carbon (SOC) is often used as an indicator of soil condition and soil health. To be useful as an indicator, SOC must be considered in context, with soil type, climatic region, local rainfall, slope, and land use history influencing measured amounts of SOC. The concept of Percent Projected Natural Vegetation Soil Carbon (PNVSC) implicitly incorporates these context variables. Percent PNVSC is defined as a simple percentage comparing the contemporary measured soil carbon against a hypothetical amount of soil carbon that would be observed in the local landscape today, if the areas under managed agroecosystems remained under natural vegetation (which in this study is dry sclerophyll forest). The term 'natural' used in the PNVSC concept approximates with the natural system prior to agrarian settlement. Percent PNVSC was calculated for a 22,000 ha sub-catchment of the Hunter Valley, Australia and it showed a spatially weighted average of 73, indicating substantial soil carbon loss as a result of cumulative land use change over more than 100 years. The Percent PNVSC map highlights changes in soil carbon distribution across the landscape with mid-slope positions lower in the catchment showing the greatest loss of soil carbon. Viticulture has resulted in half of the original SOC being lost, compared to a 75 % PNVSC for unimproved

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pasture and an 83 % PNVSC for improved pasture. Average soil carbon loss due to mixed land-use change in this sub-catchment is 13,331 kg C/ha.

Keywords Percent Projected Natural Vegetation Soil Carbon • Percent PNVSC • Soil carbon • Soil health • Soil quality • Soil impact map • Land use impact

Introduction

There are many different indicators of the soil's condition each with specific meaning to soil scientists (McKenzie et al. 2002). However, that meaning or interpretation is often lost for the general public and policy makers. Messages from the soil science community regarding soil security need to be supported by evidence that resonates with diverse audiences and their interests.

Soil condition and soil quality terms may possess different meaning and different definitions for farmers and scientists. A qualitative soil condition score-card has been developed by Jenkins (2006) which assesses ten soil parameters with no overall value of the soil condition calculated. The United States Department of Agriculture proffers a soil conditioning index (SCI) based on Soil Organic Matter (SOM) which is one component of soil quality (USDA 2002, 2012). The SCI does not purport to be a soil quality index. SCI predicts if a particular management system will have a positive or negative trend in SOM. Quantitative soil condition indices that translate across regions or the globe remain elusive.

Here, we propose the concept of Percent Projected Natural Vegetation Soil Carbon (Percent PNVSC) which can be quantified as the percentage of contemporary measured soil carbon against some hypothetical projected soil carbon realisation from the local natural vegetation landscape. Percent PNVSC is defined here as total soil carbon rather than soil organic carbon (SOC) for ease of comprehension by the general public and policy makers. SOC data are more frequently available than total carbon and may form a reasonable proxy for total carbon as the most labile soil carbon fraction and largest soil carbon reservoir (Batjes 1996).

Percent PNVSC is a tool for spatial extrapolation and assessment of measured soil carbon values. Percent PNVSC is not a predictive simulation model for SOC based on input parameters, such as the SOCRATES model (Grace et al. 2006), RothC model (Coleman and Jenkinson 1999) and CENTURY model (Parton et al. 1987; Bandaranayake et al. 2003). These models require choice of local parameters, which may be uncertain or missing. Percent PNVSC complements simulation models by providing an assessment of local parameters from local data.

Natural vegetation soil carbon may be estimated by measuring soil carbon under comparable undisturbed natural vegetation nearby or estimated by modelling. Reference maps of natural vegetation soil carbon produced by existing models may be generated and refined over time through scientific discourse testing model assumptions. The task of comparing contemporary, modern-day, measured soil carbon to a reference value of projected natural vegetation soil carbon is simple, and open to all to produce Percent PNVSC maps at all scales and for a variety of purposes. This approach removes the skilled application of model parameters from the end users of Percent PNVSC maps, limiting the scope for model miss-application.

Farmers may find Percent PNVSC maps useful for managing their farms at the paddock scale. Percent PNVSC maps may highlight the cumulative impact of industrial agriculture to soil scientists and agronomists at the regional or national scale. Such maps would support policy decisions to help implement sustainable agriculture.

Materials and Methods

Soil Sampling

SOC (0–0.1 m) measurements from 1,560 locations within a 220 km^2 sub-catchment within the Hunter Valley, NSW, Australia (Fig. 23.1a) were used in this research. The data was collected over 10 years from 2001 to 2010.

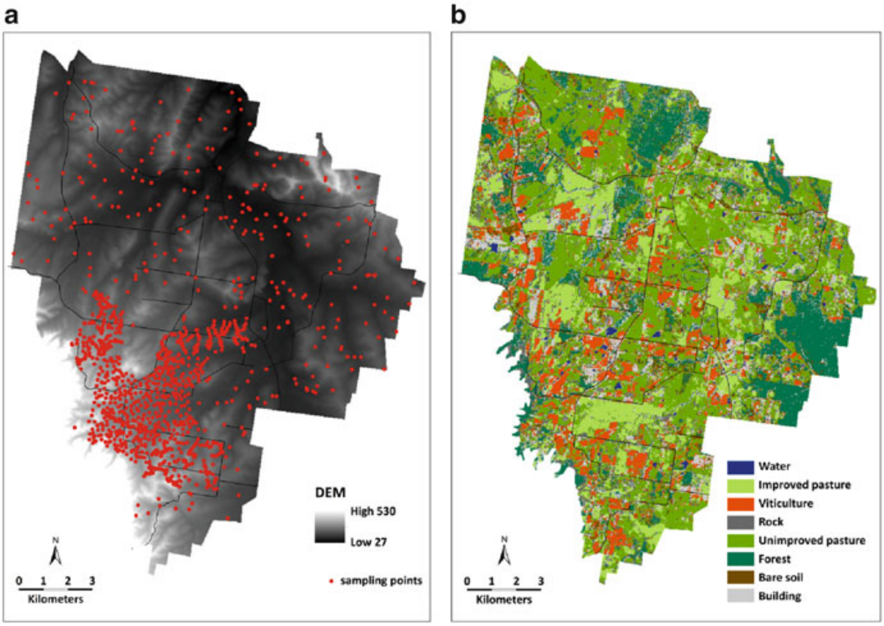

Fig. 23.1 (**a**) Soil sampling locations for SOC, and (**b**) land use and land classification map (*LULC*)

Spatially Distributed Covariates

A digital elevation model (DEM) on a 25 m raster was used to calculate a range of terrain attributes using the SAGA Geographic Information System. The terrain attributes generated were: slope, midslope position, analytical hillshading, aspect, plan curvature, profile curvature, and topographic wetness index. Data from a land use and land cover (LULC) map (Fig. 23.1b) derived from supervised classification of aerial imagery (Stabile 2011) was extracted using the nearest neighbour technique onto the 25 m raster. The LULC categories were: buildings, bare soil, forest, unimproved pasture, rock, viticulture, improved pasture and water. They were allocated a nominal classification identifier of 1–8.

Predicted Contemporary Carbon (CC)

The spatially distributed covariates were extracted using the nearest neighbour technique onto the locations of the 1,560 actual SOC samples to create a modelling data set. Multiple linear regression was used to model the multivariate relationship between the sample SOC and the covariates. The model was then applied to the full grid of spatially distributed covariates (25 m grid) to predict present-day, contemporary, C across the entire catchment. More explicitly, we predicted contemporary soil carbon for the natural vegetation in the sub-catchment—that is the soil carbon which we can observe today in areas of natural vegetation comprised of dry sclerophyll forest. We must note here that it is possible that this vegetation is in fact secondary. In addition, we predicted contemporary soil carbon for managed agro-ecosystems that is the soil carbon which we can observe today under managed agro-ecosystems in the sub-catchment which are predominantly pasture and vineyards.

Projected Natural Vegetation Soil Carbon (PNVSC)

In a simple approach, the Contemporary Carbon (CC) prediction model was applied to the grid of covariates (25 m grid) with the landcover parameter (LULC) uniformly set as forest across the entire catchment to predict natural vegetation soil C. The produced map of Projected Natural Vegetation Soil Carbon (PNVSC) therefore represents soil carbon which could be observed today if areas under managed agro-ecosystems remained under natural vegetation (dry sclerophyll forest). We then employed the generated maps of predicted CC and PNVSC to calculate Percent Projected Natural Vegetation Soil Carbon (Percent PNVSC), that is the temporal change in soil carbon.

This temporal change is expressed as a percentage, following Eq. 23.1:

$$\mathit{Percent\ PNVSC} = \frac{CC}{PNVSC} \times 100 \tag{23.1}$$

Percent PNVSC provides a metric to estimate the relative change in C between the present-day, contemporary C measured as SOC and that of the natural forested vegetation across the catchment.

Additionally, we tested the relationship between the sample SOC and the occurrence of soil types in this sub-catchment, using a map of predicted Australian Soil Classification (ASC) soil orders (Odgers et al. 2011). However, we found no indications that soil classes contributed to the variance in soil carbon across the study area. Soil classes were therefore not used in the predictions. The map of predicted Australian Soil Classification (ASC) soil orders was also used to explore whether the average Percent PNVSC was different for the range of ASC orders across the catchment. However, no soil carbon-soil class relationships were found.

Results

The model for predicting contemporary carbon from the spatially distributed covariates is shown in Eq. 23.2.

$$\begin{aligned} \mathrm{CC} = {} & 2.1264 + 0.0068\,\mathrm{DEM} + -0.0047\,\mathrm{wetness\ index} + 0.0004\,\mathrm{slope} \\ & + -0.0451\,\mathrm{midslope\ position} + \mathrm{match}(\mathrm{LULC}, \\ & \begin{array}{ll} \mathrm{Building}, & -0.3235, \\ \mathrm{Bare\ soil}, & 0.0384, \\ \mathrm{Forest}, & 0.8745, \\ \mathrm{Unimproved\ pasture}, & 0.0065, \\ \mathrm{Rock}, & 0.2261, \\ \mathrm{Viticulture}, & -0.8245, \\ \mathrm{Improved\ pasture}, & 0.2927, \\ \mathrm{Water}, & -0.2903) \end{array} \end{aligned} \tag{23.2}$$

The model suggests that CC is most influenced by the LULC category with less influence from elevation and terrain attributes. Applying Eq. 23.2 across all locations on the grid produced estimates of predicted CC that are mapped in Fig. 23.2a.

The model for predicting projected natural vegetation soil carbon from the spatially distributed covariates is shown in Eq. 23.3.

$$\begin{aligned} \mathrm{PNVSC} = {} & 2.1264 + 0.0068\,\mathrm{DEM} + -0.0047\,\mathrm{wetness\ index} + 0.0004\,\mathrm{slope} \\ & + -0.0451\,\mathrm{midslope\ position} + 0.8745 \end{aligned} \tag{23.3}$$

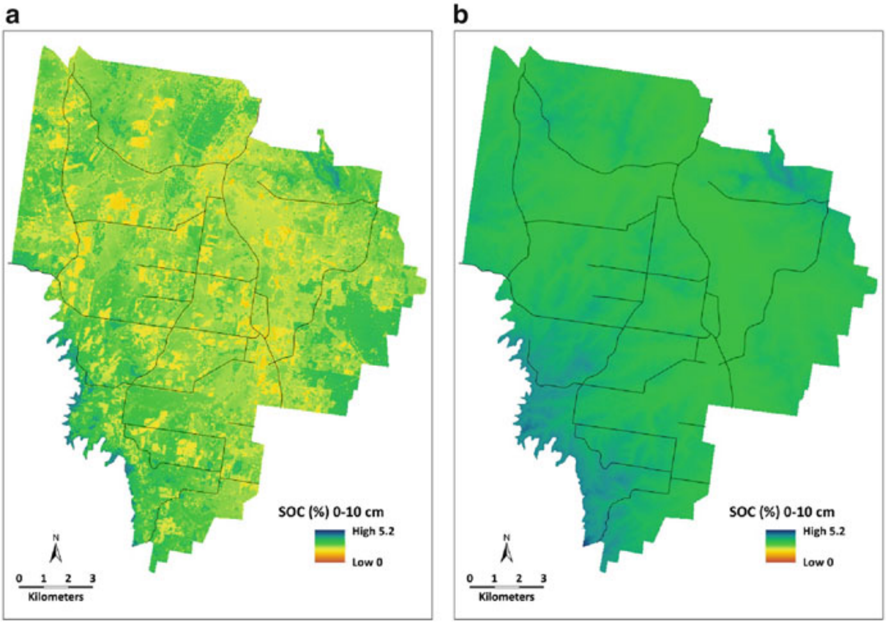

Fig. 23.2 (**a**) Predicted Contemporary Carbon (*CC*), and (**b**) Predicted Projected Natural Vegetation Soil Carbon (*PNVSC*)

Applying Eq. 23.3 across all locations on the grid produced estimates of PNVSC that are mapped in Fig. 23.2b.

Applying Eq. 23.1 to the spatially distributed estimates of CC and PNVSC produces an estimate of Percent PNVSC at each location on the 25 m grid. These results are displayed in Fig. 23.3a.

Discussion

A comparison of the PNVSC, Predicted CC and Percent PNVSC predictions averaged over the agriculturally important LULC categories is shown in Table 23.1. It shows that the biggest predicted difference in CC is to be found between viticulture (lowest) and forest (highest) categories. All the current LULC categories (except forest) have shown a lower predicted CC than that predicted to be present if the catchment remained forested as evidenced by the average Percent PNVSC values falling below one.

The catchment average Percent PNVSC, spatially weighted by LULC (excepting forest), is 73. The change in carbon mass per LULC was calculated using a uniform 1.4 Mg/m^3 soil bulk density. This is the observed bulk density from the top horizon of a local Dermosol (Australian Soil Classification Scheme (Isbell et al. 1997),

Fig. 23.3 Predicted Percent Projected Natural Vegetation Soil Carbon (Percent PNVSC)

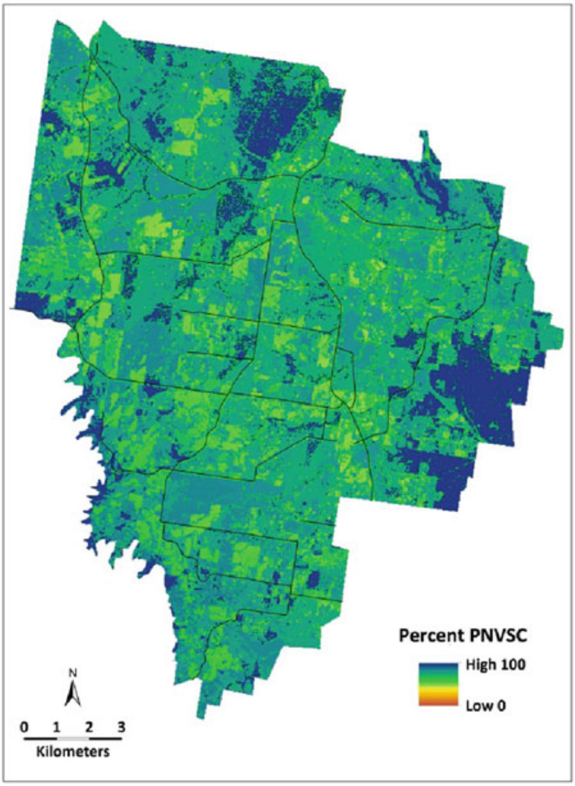

Table 23.1 Average PNVSC, Predicted CC, Percent PNVSC and the net loss or gain in soil C per hectare for the agriculturally important land use land cover (*LULC*) categories

Land use	Mean PNVSC %	Mean predicted CC %	Mean percent PNVSC %	Δ kg C/ha (0–0.1 m)
Forest	3.53	3.53	100	0
Improved pasture	3.52	2.94	83	8,120
Unimproved pasture	3.51	2.65	75	12,040
Viticulture	3.60	1.91	53	23,660

equivalent to a Cambisol in the World Reference Base soil classification scheme (IUSS Working Group WRB 2007)), which is the dominant soil order in the catchment. The change in carbon mass calculation showed that between 8,120 kg C/ha and 23,660 kg C/ha is predicted to have been lost from the best and worst performing LULC. The average loss of soil carbon (spatially weighted by LULC) across the three major land-uses in this 22,000 ha Hunter River sub-catchment is 13,331 kg C/ha.

This is a simple approach designed to illustrate the concept of Percent PNVSC and to stimulate discussion on techniques for conveying and quantifying soil carbon management issues. The data set was not gathered for this study and the sampling design was not optimised for the purpose. Accordingly, the modelling and the underlying assumptions are generalised. However, the predictions conform to the expectation that the vineyards are lower in SOC than the pastures and the forests in this sub-catchment.

Conclusions

The percentage of projected natural vegetation soil carbon (Percent PNVSC) identifies changes in soil carbon content for a location relative to an inferred uncultivated carbon content of the local landscape. Percent PNVSC displays the ability to discriminate carbon changes between different land-use classes across a large, diverse landscape. Percent PNVSC shows potential as a simple, efficient measure for conveying the magnitude of soil carbon loss due to management associated with different land-use.

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Chapter 24
Forest Fires and Soil Erosion Effects on Soil Organic Carbon in the Serrano River Basin (Chilean Patagonia)

Carlos A. Bonilla, Pablo A. Pastén, Gonzalo E. Pizarro, Virginia I. González, Athena B. Carkovic, and Rocío A. Céspedes

Abstract Forest fires have become a major threat to some soils in the Chilean Patagonia. More than 36,000 ha of predominantly native forest have been burned in the last four decades in the Serrano River basin, most of them in the Torres del Paine National Park, a world biosphere reserve. A study was conducted to evaluate the effects of forest fires and water erosion on the soil organic carbon (SOC) in the Serrano River basin. A total of 17 sites were sampled, three major soil types were found (Dystric Cambisols, Lithosols, and Luvic Phaeozems), and three main forest fires were identified. Soils were sampled at two depths and analyzed to determine their texture, SOC, cation exchange capacity, total N, P, and K, and aggregate stability. Soil erosion rates were estimated using the Water Erosion Prediction Project (WEPP) model with actual soil, vegetation, and weather data. The SOC content was the main significant difference between samples at depths of 0.2 and 0.4 m, at both burned and unburned sites. The 0.2-m-depth samples had an average SOC of 5.1 %, compared to 3.2 % for the 0.4-m-depth samples. The nutrient contents and CEC were also higher in the upper layer. The burned and unburned sites were not found to be different in their SOC contents or other soil properties, with the exception of P availability. As a result of the bareness of their soil, the burned sites had the highest water erosion rates (9.3 t ha^{-1} year^{-1}) and SOC losses (0.5 t ha^{-1} year^{-1}).

Keywords Forest fires • Native forest • Soil organic carbon • Water erosion • WEPP model

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Introduction

Forest fires can affect physical, chemical and biological soil properties, including the soil organic carbon SOC, availability of nutrients, water repellency, and aggregates stability (Arcenegui et al. 2008; González-Pérez et al. 2004; Murphy et al. 2006). These properties affect processes such as infiltration and soil erosion (DeBano 2000; Doerr et al. 2006). Typically, post-fire increases in runoff and erosion reduce the SOC in the soil profile (Larsen et al. 2009), affecting water bodies nearby as a result of soil transport and deposition.

Previous studies have shown that the effects of fires on soil properties are variable and site-dependent. For instance, the SOC content can either decrease or increase depending on the combination of many factors such as the type of fire (prescribed vs. wildfire), the fire severity and intensity, climate conditions, and site and soil characteristics (Doerr et al. 2006; González-Pérez et al. 2004).

Forest fires have become a major threat in the Chilean Patagonia, but no quantitative information on soil degradation and SOC changes is available. Furthermore, no measurements or estimates of the sediment yield and organic carbon contribution to the river system have been made. A study was conducted to evaluate the effects of forest fires and water erosion on SOC in the Torres del Paine National Park, an important landmark in Chile. The physical and chemical properties of sampled soils were measured and compared between burned and unburned sites. Because of the availability of actual soil and climate data, the Water Erosion Prediction Project (WEPP) model was used to estimate the pre- and post-fire sediment yields and organic carbon loss as a result of one of the largest recent fire events, which occurred in 2005.

Materials and Methods

This study combines field measurements and modeling. Fieldwork was carried out in the Serrano River basin in December 2012 to collect soil samples from burned and unburned sites in the Torres del Paine National Park. The soil samples were analyzed to determine selected properties, and the WEPP model was used to quantify the forest fire effects on soil and organic carbon losses resulting from water erosion.

Study Area and Forest Fire Events

The Serrano River basin is located in southern Chilean Patagonia (Fig. 24.1), and has an area of 6,673 km^2. The river basin encloses the Torres del Paine and Bernardo O'Higgins National Parks. The average annual precipitation ranges from 200 mm year^{-1} on the eastern side of the basin to more than 6,000 mm year^{-1} on the western side. The long-term average annual minimum and maximum temperatures

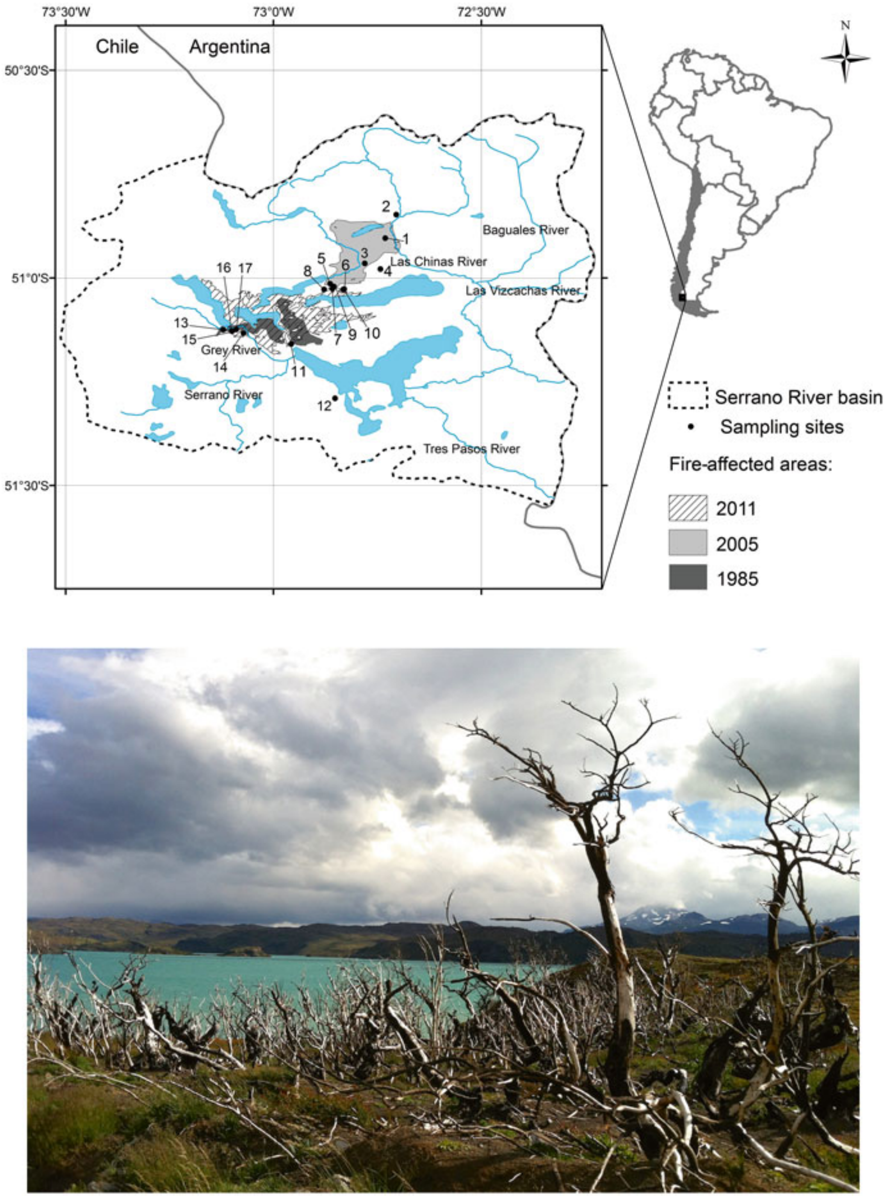

Fig. 24.1 Location of the Serrano River basin, sampling sites, and forest fires. The picture shows the fire effects in the study area, with trees killed and foliage and forest floor consumed and subject to water erosion

are 2.9 °C and 11.4 °C, respectively. The dominant soil types in the study area are Phaeozems, Cambisols, and Lithosols (IUSS Working Group WRB 2007). The average ground slope in the river basin is 20 %, and the dominant land cover is native forest (CONAF-CONAMA-BIRF 1999).

Most of the forest fires in the Serrano River basin occur in the Torres del Paine National Park, a highly sensitive ecosystem and world biosphere reserve encompassing lakes, rivers, waterfalls, glaciers, forests, and wildlife. Between 1985 and 2011, 29 human-caused fires were recorded, disturbing more than 36,000 ha of protected areas. The three largest fire events in the park in recent years occurred in 1985, 2005, and 2011, affecting 6,000 ha, 13,000 ha, and 17,000 ha, respectively. Figure 24.1 shows the spatial distribution of these forest fires in the study area.

Sampling Sites

A total of 17 sites were sampled and used for comparisons between burned and unburned sites (Fig. 24.1). Two locations, separated by approximately 10–15 m, were sampled at each site. The soils at the sites were sampled at two depths: 0.2 and 0.4 m, for all soil types. To evaluate the effects of fire, each burned site was matched to the closest unburned site on the basis of similarity of vegetation types. Burned sites included areas affected in 1985, 2005, and/or 2011 (Table 24.1).

Laboratory Analysis

The samples were sieved (≤2 mm) and air-dried. The soil analyses included determination of organic carbon content, total N, P and K, cation exchange capacity (CEC), texture, and aggregate stability. The organic carbon content was determined by oxidation with a mixture of dichromate and sulfuric acid (Nelson and Sommers 1996). Total N was measured using an elemental analyzer (TruSpec CN, Leco, St. Joseph, Michigan), by sample combustion coupled with thermal conductivity/IR detection. Total P was measured by the ICP method, and total K was measured by the microwave-assisted acid digestion method (EPA 2008). CEC was determined by saturation with sodium acetate or ammonium acetate, followed by extraction (Rhoades 1982). The sand, silt, and clay contents were measured by the hydrometer method. The aggregate stability was measured using a wet sieving apparatus (Eijkelkamp, Giesbeek, Netherlands), and calculated as the ratio of stable to total aggregates.

Water Erosion Modeling Scenarios

To quantify the soil and organic carbon losses as result of water erosion after the fire, the actual 2005 forest fire field conditions were simulated using the hillslope WEPP model v.2012.8 (Nearing et al. 1989). The other two largest fires in recent years (1985 and 2011) were not simulated because of the lack of sufficient soil and

Table 24.1 Soil properties analysis for sites burned and unburned at 0.2- and 0.4-m depths

				SOC	N	P	K	CEC	Aggregate stability
Type	Site	Year of fire	Vegetation type	%				cmol/kg	
Burned	1	2005	Forest	8.06/3.36	0.71/0.32	0.18/0.14	0.38/0.35	47.75/29.05	0.89/0.76
Unburned	2			4.12/1.60	0.27/0.11	0.08/0.04	0.35/0.27	23.00/11.90	0.93/0.78
Burned	3	2005	Shrubs	4.42/1.92	0.55/0.21	0.10/0.05	0.47/0.31	23.35/14.25	0.84/0.80
Unburned	4			4.14/2.33	0.52/0.29	0.09/0.07	0.51/0.35	24.25/19.45	0.81/0.89
Burned	5	2005	Shrubs	5.85/3.11	0.76/0.39	0.10/0.07	0.36/0.30	30.10/21.70	0.88/0.85
Unburned	6			4.61/3.19	0.52/0.36	0.09/0.08	0.36/0.32	26.30/22.25	0.89/0.72
Burned	7	2011	Shrubs	5.84/3.24	0.65/0.39	0.12/0.07	0.32/0.29	19.75/17.75	0.94/0.82
Unburned	8			4.45/2.91	0.56/0.34	0.07/0.07	0.28/0.25	17.10/13.60	0.93/0.98
Burned	9	2005/2011	Shrubs	5.11/2.45	0.66/0.26	0.09/0.07	0.35/0.36	24.60/15.50	0.94/0.85
Unburned	10			2.82/2.00	0.31/0.23	0.06/0.05	0.41/0.40	16.45/13.90	0.86/0.88
Burned	11	1985	Shrubs	6.64/4.25	0.71/0.50	0.12/0.10	0.37/0.31	29.05/22.75	0.91/0.90
Unburned	12			9.31/n.a.	0.36/n.a.	0.09/n.a.	0.17/n.a.	33.50/n.a.	0.88/n.a.
Burned	13	1985	Shrubs	2.86/3.09	0.28/0.33	0.06/0.05	0.09/0.08	11.35/14.15	0.68/0.80
Unburned	14			5.17/5.35	0.77/0.69	0.07/0.04	0.06/0.09	18.40/11.40	0.78/0.89
Burned	15	1985/2011	Forest	4.36/2.87	0.47/0.21	0.09/0.03	0.08/0.08	26.00/17.45	0.86/0.57
Unburned	16			3.07/2.49	0.31/0.18	0.06/0.03	0.08/0.06	16.75/15.30	0.57/0.72
Burned	17	2011	Shrubs	6.12/4.67	0.75/0.40	0.07/0.03	0.10/0.08	28.45/20.90	0.69/0.64
Unburned	14			5.17/5.35	0.77/0.69	0.07/0.04	0.06/0.09	18.40/11.40	0.78/0.89

Aggregate stability calculated as the ratio of stable to total aggregates. Soil property values separated by "/" correspond to 0.2- and 0.4-m depths
n.a. data not available

climate data. Three scenarios were simulated: (I) an unburned site, (II) a burned site (without vegetation), and (III) a hypothetical unburned site without vegetation. The effects of the 2005 fire on water erosion and SOC were calculated as the difference between scenarios I and II. The effect produced by the vegetation removal itself was calculated as the difference between scenarios I and III, and the effect produced by the change in soil properties was estimated as the difference between scenarios II and III.

Paired sites 1/2, 3/4, and 5/6 were used to evaluate burned and unburned conditions. Soil, management, slope, and climate files were prepared to represent the site conditions. Six soil files were built, one to represent the conditions at each site, based on field and laboratory measurements. Two WEPP management files were built to represent the dominant vegetation types in the area: shrubs at sites 3/4 and 5/6, and native Lenga Beech forest (*Nothofagus pumilio* (Poepp & Endl.) Krasser) at sites 1/2. These management files were built based on the WEPP database but modified to obtain a better representation of the sites' conditions. The WEPP climate file was built based on a 5-year-record of daily and hourly precipitation and temperature data collected at the Torres del Paine Station (from the day of the fire, 02/17/2005 to 02/17/2010). Hillslopes were simulated as being 200 m long and having the slope gradients measured at the sites, i.e., 22 % for sites 1/2, 9 % for sites 3/4 and 6 % for sites 5/6.

Statistical Analysis

The mean soil properties values at depths of 0.2 and 0.4 m at the burned and unburned sites were compared using Student's *t* test. All statistical analyses were performed with a level of significance of $P \leq 0.05$.

Results and Discussion

Soil Properties

The SOC content was the main significant difference between samples at depths of 0.2 and 0.4 m, at both burned and unburned sites (Table 24.1). The 0.2-m-depth samples had an average SOC of 5.12 %, compared to 3.19 % for the 0.4-m-depth samples. The nutrient contents and CEC were also higher in the upper layer.

In comparing the burned and unburned sites, the only significant difference in the soil properties at the 0.2-m depth was in the total P content. The 0.2-m-depth mean values of the SOC content were 5.5 and 4.8 % at the burned and unburned sites, respectively. However, for seven pairs of sites, the SOC content was higher at the burned site than the unburned site, and for two pairs of sites (11/12 and 13/14,

Table 24.2 Summary results for simulated water erosion scenarios at sites burned and unburned

	Scenario								
	I			II			III		
	Unburned			Burned			Unburned – no vegetation		
Site	2	4	6	1	3	5	2	4	6
Soil type	Hl	Hl	Hl-Bd	Hl	Hl	Hl-Bd	Hl	Hl	Hl-Bd
Original vegetation type	Forest	Shrubs	Shrubs	Forest	Shrubs	Shrubs	Forest	Shrubs	Shrubs
Slope (%)	22	9	6	22	9	6	22	9	6
Interrill erodibility (millions kg s m^{-4})	0.131	0.125	0.132	0.288	0.192	0.173	0.510	0.179	0.160
Rill erodibility (×1,000 s m^{-1})	0.215	0.138	0.148	0.234	0.229	0.249	0.349	0.205	0.221
Effective hydraulic conductivity (mm h^{-1})	2.01	3.63	4.78	2.80	2.30	2.90	0.46	1.35	2.12
Annual average rainfall–runoff events	31	3	1	10	9	9	32	14	10
Runoff (mm year^{-1})	36.38	2.62	0.79	19.33	7.60	12.50	50.01	13.33	11.46
Sediment yield (t ha^{-1} year^{-1})	0.02	0.00	0.00	9.25	0.39	0.33	52.63	0.64	0.20
Organic carbon loss (t ha^{-1} year^{-1})	0.001	0.000	0.000	0.537	0.017	0.019	2.325	0.027	0.009

Soil type: Hl: Luvic Phaeozems, Hl-Bd: transitional area between Luvic Phaeozem and Dystric Cambisol

Table 24.1), the SOC content was significantly lower at the burned site than at the unburned site. These last two pairs correspond to sites burned in 1985, with the largest number of years since the fire disturbance and time exposed to water erosion. The average aggregate stability was 0.85 in the 0.2-m-depth samples and was not significantly different between burned and unburned sites.

Compared to the 0.2-m-depth samples, the 0.4-m-depth samples showed higher soil variability (Table 24.1), but there were no significant differences in the mean values between burned and unburned sites.

Erosion by Water

For the simulated time period (2005–2010), the precipitation was fairly uniform from year to year, with a mean value of 846 mm year^{-1}, a minimum of 759 mm year^{-1} in 2007 and a maximum of 967 mm year^{-1} in 2008. An average of 141 rainfall events was recorded per year. Lower sediment yields were predicted for scenario I (Table 24.2) than for scenarios II (site5) and III (sites 2 and 4).

The analysis of the effects of the 2005 forest fire (i.e., the difference between scenarios I and II) revealed that soil losses were highly related to the slope, vegetation type, and change in soil properties (e.g., soil erodibility). Sites 1 and 2, which have forest cover and the steepest slopes of the six sites modeled, exhibited the largest increases in the interrill erodibility factor and sediment yield (9.2 t ha^{-1} year^{-1}). In contrast, the other four sites exhibited an increase in the sediment yield of approximately 0.4 t ha^{-1} year^{-1}. The changes in soil properties after the fire increased water erosion rates, so the mean annual SOC loss in scenario II reached its maximum value at site 1 (0.5 t ha^{-1} year^{-1}).

Similarly, the vegetation removal modeling (i.e., the difference between scenarios I and III) revealed significant increases in soil losses on steep slopes (site 2). The largest difference in sediment yield, 52.6 t ha^{-1} year^{-1}, was calculated for site 2. For the other sites, the difference was approximately 0.4 t ha^{-1} year^{-1}. As the rill and interrill erodibility values show (Table 24.2), in this study, the forest soils were more susceptible to erosion by water than the soils covered by shrubs. However, under natural conditions (scenario I), forest vegetation provides the best soil protection against water erosion, regardless of the slope (e.g., 22 % at site 2).

The soil properties change modeling (i.e., the difference between scenarios II and III) revealed increases and decreases in sediment yield depending on the soil type. After the fire, sites located in a transitional area between Luvic Phaeozem and Dystric Cambisol (5/6) exhibited an increase in runoff and thus in sediment yield (Table 24.2). The organic carbon loss as result of water erosion was 0.01 t ha^{-1} year^{-1} at site 6 (unburned) and 0.02 t ha^{-1} year^{-1} at site 5 (burned). In contrast, Luvic Phaeozem sites (1/2 and 3/4) exhibited reduced runoff and sediment yield after burning. The organic carbon loss was 0.03 t ha^{-1} year^{-1} at site 4 (unburned) versus 0.02 t ha^{-1} year^{-1} at site 3 (burned) and 2.33 t ha^{-1} year^{-1} at site 2 (unburned) versus 0.54 t ha^{-1} year^{-1} at site 1 (burned).

Conclusions

The soils in the study area had an average SOC content of 4.1 %, total N, P and K contents of 0.44 %, 0.08 % and 0.26 %, respectively, and CEC of 21 cmol/kg. Most of the values of these soil properties were higher in the upper soil layer, but with the exception of the P content at a depth of 0.2 m, they were not significantly different at burned versus unburned sites.

The modeling results showed that water erosion increased after the fire, mainly due to the effect of vegetation removal but also due to changes in soil properties and erodibility. The sediment yield increased from 0.02 to 9.25 t ha^{-1} year^{-1} and produced an estimated increase in SOC losses from 0 to 0.54 t ha^{-1} year^{-1}.

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Chapter 25
Soil Carbon Sequestration with Improved Soil Management in Three Tribal Villages in India

Ch. Srinivasarao, B. Venkateswarlu, Y. Sudha Rani, A.K. Singh, and S. Dixit

Abstract Under the National Initiative on Climate Resilient Agriculture (NICRA) project implemented by Indian Government, various climate resilient farm technologies (soil, water, nutrient, crop, livestock, forestry etc.) are being evaluated in 100 climatically vulnerable districts. As a part of NICRA, carbon balance was studied with EX-ACT model for three villages in Nalgonda and Khammam districts of Andhra Pradesh. The EX-ACT model computed carbon balance of 5,289 and 3,285 tonnes CO_2 equivalents (t CO_2e) in Nandyalagudem and Boringthanda villages and 12,861 t CO_2e in Nacharam village. Although farmers have awareness on C–positive practices, field implementation is meager due to lack of immediate income gains. Incentive based interventions might encourage field interventions which promote soil carbon sequestration and overall C balance in the system. Reduced tillage, crop residue recycling, water, nutrient and manure management and fodder and livestock interventions have been C positive practices followed in these villages which contributed positive C balance.

Keywords Agriculture • EX-ACT model • Carbon balance • Carbon sequestration • Tribal villages • Project interventions

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Introduction

Carbon emissions in agricultural production systems is dominantly majorly through improper crop management practices, deforestation, non-forest land use changes and over use of inorganic fertilizers which can result in loss of soil organic matter.

There is an opportunity to achieve climate-friendly agriculture by both sequestering carbon and reducing emissions through different interventions viz. enriching soil carbon by agronomic practices, livestock production technologies, balanced use of fertilizers and aforestation. Better agricultural practices improve C sequestration and help compensate raising CO_2 concentration (Allmaras et al. 2000; Srinivasarao et al. 2012) and loss of C by traditional agriculture may be recaptured. Rice cultivation is an important source of CH_4 and N_2O (Majumdar et al. 2000). Carbon emissions in the form of CH_4 from global rice area accounts for 70–80, 15 and 10 % from irrigated rice, rainfed rice and deep water rice, respectively. So, irrigated rice represents the most promising target for mitigation strategies (Wassmann et al. 2000).

In India, during 2011–2012, 93.9 million tonnes (mt) of wheat, 104.6 mt of rice, 21.6 mt of maize, 20.7 mt of millet, 357.7 mt of sugarcane, 8.1 mt of fibre crops (jute, mesta, cotton), 17.2 mt of pulses and 30.0 mt of oilseeds crops residues are produced (MoA 2012). Parts of these crop residues are used for animal feeding, but remaining crop residues are subjected to field burning. There was a drastic reduction in use of crop residues for cooking, as rapid expansion taking place in Liquid Petroleum Gas (LPG) connections for house-hold cooking purpose during last decade in rural India. Now, a large portion of the residues is burnt on-farm primarily to clear the field for sowing of the succeeding crop. On-farm burning of crop residues intensified in recent years due to shortage of labour and mechanization during harvest. More CO_2 emissions were produced from tilled soils than from zero-tillage or undisturbed soil. Tillage and soil disturbance strongly affect C as CO_2 emission by creating a soil environment favorable for oxidation and mineralization of organic C in the soil (Jabro et al. 2008). Livestock and crop husbandry are supplementary and balancing constituents of the Indian agricultural system. Enteric CH_4 emissions of livestock constitute nearly 50 % of the total CH_4 emission of the nation (MoEF 2004).

The project “National Initiative on Climate Resilient Agriculture” was initiated during 2010–2011 with an objective of demonstrating site specific technology packages on farmers’ fields for adapting to current climate risks. Under this, carbon balance studies were initiated in about 125 villages in 100 climate vulnerable districts of India in association with Zonal Project Directorates (ZPD) and Krishi Vigyana Kendra (KVK) (Village knowledge Centers) to evaluate the impact of climate resilient technologies implemented in these model villages in terms of carbon balance. In this paper we discuss such carbon balance studies in three rainfed tribal villages of two climate vulnerable districts (Nalgonda and Khammam) in Andhra Pradesh, India.

Materials and Methods

Methodology

The EX-ACT (Ex Ante Carbon Balance Tool) v 3.4 software is used in this study to estimate the green house balances in agricultures. EX-ACT (http://www.fao.org/tc/exact/en/) is a tool that provides ex-ante estimations of the impact of agricultural and forestry development projects on GHG emissions and sequestration, indicating its effects on a carbon balance. This tool has been developed by FAO's Policy Support Service (http://www.fao.org/tc/policy-support), Agricultural Development Economics Division (http://www.fao.org/economic/esa/esa-home/en) and Investment Centre (http://www.fao.org/tc/tci/en/).

EX-ACT is a land-based accounting system, measuring C stocks, stock changes per unit of land, as well as methane (CH_4) and nitrous oxide (N_2O) emissions expressed in tonnes of carbon dioxide equivalent per hectare (t CO_2 e ha^{-1}) and can compute the C-balance by comparing two scenarios: "without project" (i.e. the "Business As Usual" or "Baseline") and "with project". Main output of the tool consists of the C-balance resulting from the difference between these two scenarios (Fig. 25.1).

The model takes into account both the implementation phase of the project (i.e. the active phase of the project commonly corresponding to the investment phase), and "capitalization phase" (i.e. a period where project benefits are still occurring as a consequence of the activities performed during the implementation phase).

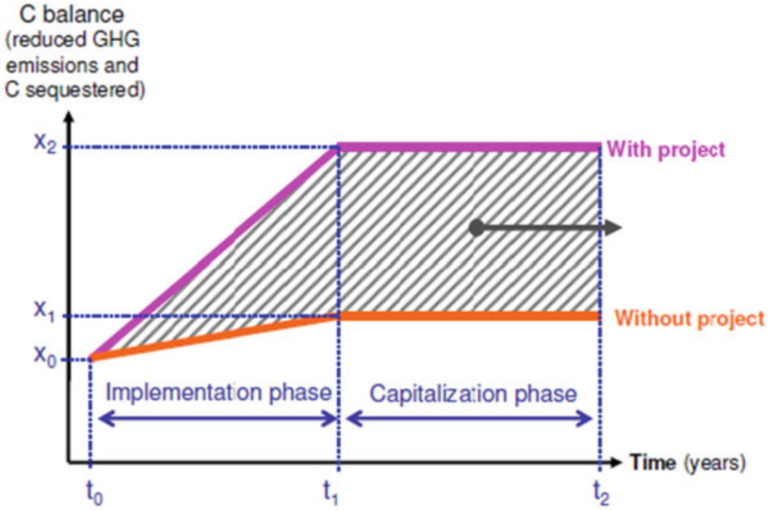


Fig. 25.1 Schematic representation of calculation of final C-balance with EX-ACT model

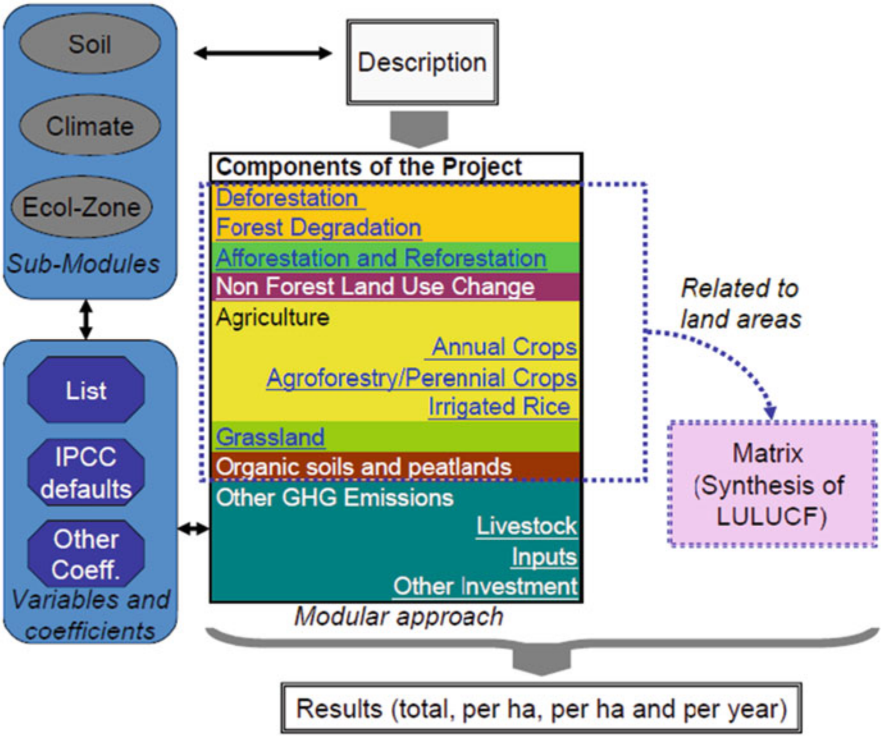


Fig. 25.2 Schematization of the modular EX-ACT structure (Source: Bernoux et al. 2010)

Usually, the sum of the implementation and capitalization phases is set at 20 years. EX-ACT was designed to work at a project level but it can easily be up-scaled at program/sector or national level (Bernoux et al. 2010).

The schematic diagram of modular structure of EX-ACT is presented in Fig. 25.2. EX-ACT accounts the default values of the five pools viz., above ground biomass, below ground biomass, soil, deadwood and litter as well as specific coefficients defined by users. The model computed results as negative (−ve) indicates sink of carbon and positive (+ve) indicates source of carbon.

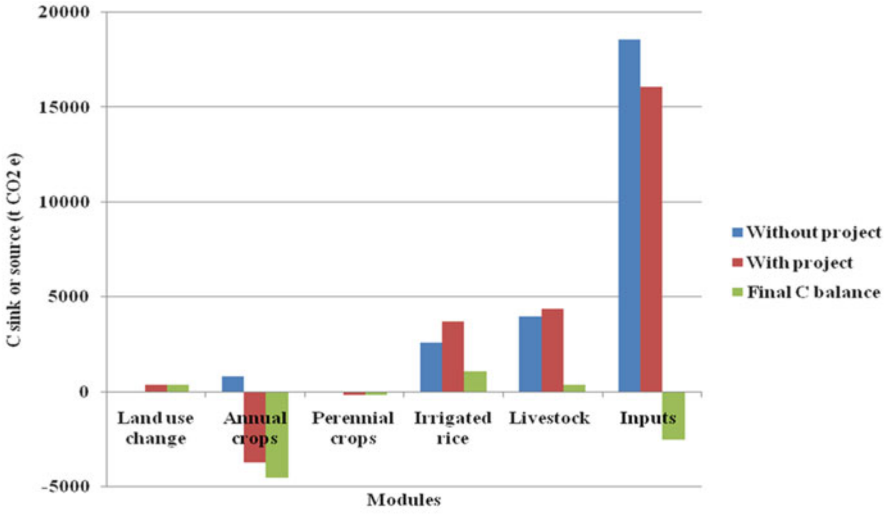
The districts were selected based on climatic vulnerability i.e. drought (Nalgonda district) and drought and heat stress (Khammam district). The two villages Nandyalagudem (194 ha) and Boringthanda (114 ha) in Nalgonda district and one village Nacharam (1,273 ha) in Khammam district were selected. Our analysis takes into account specific environmental features (soil and climate types) that effect C-balance estimation. Average climate is warm temperate with a mean annual temperature equal to 22 °C, dry the moisture regime and high active clay (HAC) soil in Nalgonda and Khammam districts. The interventions used in Nalgonda and Khammam districts to estimate the carbon balance are annual crops, perennial crops, chemical fertilizers and pesticides, irrigated rice, livestock and non forest land use change. The data required for present analysis collected by taking the whole village as a single unit and conducting the survey and interacting with the farmers in the village regarding agriculture and livestock.

Results and Discussion

The EX-ACT Model in Three Villages

The GHG mitigation potential of different agricultural interventions in three villages of Andhra Pradesh was computed using EX-ACT model (Bernoux et al. 2010) which was developed using the 2006 guidelines for National Greenhouse Gas Inventories (IPCC 2006). In Nandyalagudem, without project, the EX-ACT model created an emission of 26,004 t CO_2e where crop residue burning, improper use of fertilizers and manures are prominent. With project interventions e.g. reducing the crop residue burning, soil test based application of fertilizers and manure and water management and livestock the model indicated a decrease in GHG emissions (20,714 t CO_2e) and computed final C-balance as a sink of 5,289 t CO_2e (Fig. 25.3), mitigating 7,147 t CO_2e and emitting 1,857 t CO_2e with an average mitigation potential of −27.3 t CO_2e ha^{-1} $year^{-1}$.

The results of different agricultural interventions in Boringthanda village created a projected source of 16,797 t CO_2e ‘with’ interventions of the project



- Indicates carbon sink and + indicates carbon source

Fig. 25.3 Carbon balance (t CO_2e) computed by EX-ACT model in Nandyalagudem, Nalgonda district

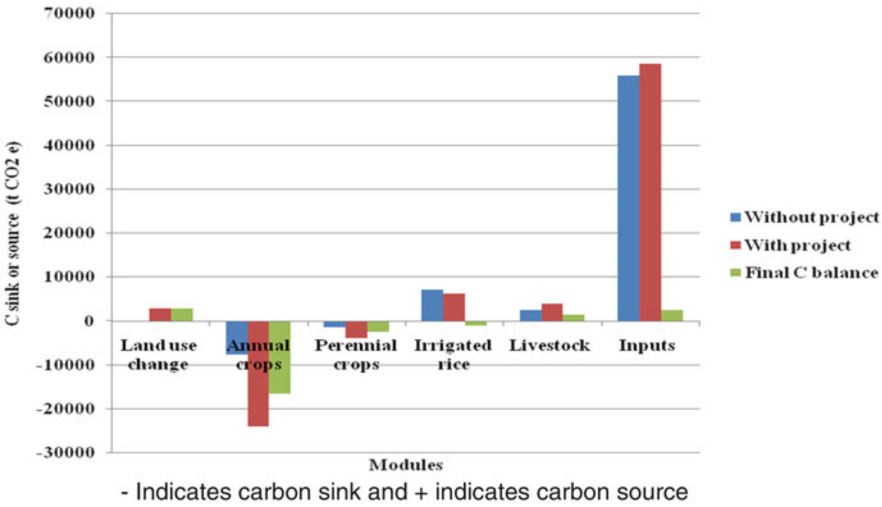


Fig. 25.4 Carbon balance (t CO_2e) computed by EX-ACT model in Nacharam, Khammam district

e.g. incorporation of crop residues, water and manure management and livestock management and 20,083 t CO_2e 'without' interventions of the project e.g., burning of crop residues, judicious application of fertilizers and EX-ACT model and resulted in a computed final C-balance as sink of 3,285 t CO_2e.

In Nacharam village of Khammam district, without interventions of the project, crop residue burning in cotton and redgram, reduced use of fertilizers and inappropriate water management in rice crop resulted in a source of 56,812 t CO_2e. By adopting the different improved practices e.g. crop residue incorporation, soil test based fertilizer application water management and planting of perennial crops 'with' project the model created a source of 43,951 t CO_2e and resulted in final balance computed by model as a sink of 12,861 t of CO_2e during 20 years (Fig. 25.4) according to model projections.

Practices Followed in Annual Crops

Total mitigation potential by adoption of improved crop management practices in three villages is equal to 0.96, 1.05 and 0.94 %, in Nandyalagudem, Borinthanada and Nacharam, respectively. In Nandyalagudem, Boringthanda and Nacharam villages, we estimated that with interventions in annual crops resulted in mitigation of carbon (−3,694, −2,477 and −23,953 t CO_2e, respectively) compared to before interventions of the project (834, 434 and −7,543 t CO_2e, respectively) and the EX-ACT model showed a final carbon balance as a sink of −4,528, −2,911 and −16,410 t CO_2e, respectively (−ve CO_2 means sink and +ve CO_2 means source).

Management practices to increase soil C stocks include reduced tillage, green manuring, increased production and recycling of crop residue, perennial crops (including agroforestry) and soil test based fertilizer application. The annual crops created more C emissions without project in three villages when compared with project interventions. In these villages, pigeon pea and cotton residue burning is a common practice. Burning of crop residues resulted in emissions of GHGs like CO_2, CH_4 and N_2O (Wang and Christopher 2003) and likely inhibits the growth of microbial population and promotes a negative C balance. With interventions of the project, incorporation of crop residue was started in place of burning in these tribal villages is estimated to have contributed to a positive C balance. Incorporation of crop residue enhances SOC concentration compared to plot with removal of crop residues (Dersch and Bohm 2001). Zero or reduced tillage is assumed to increase SOC and there by improved the soil fertility (Blanco-Canqui and Lal 2008). Similarly the model assumes that organic carbon from manure provides the energy source for the soil microbial environment stabilizes nutrients and make them available to crops. In other studies we have shown various organic resources along with reduced chemical fertilizer application resulted in high C-sequestration in predominant rainfed production systems in India (Srinivasarao et al. 2013).

Plantation Crops

The perennial module in EX-ACT model showed carbon balance created as a sink of 2,450 t CO_2e. it was observed that with plantations of perennial crops resulted in mitigation of carbon emission and created a sink of 3,885 t CO_2e ‘with’ project compared ‘without’ interventions of the project (−1,435 t CO_2e) in Nacharam village. Conversion of wastelands and annual cropped area in to perennial crop plantation resulted in increase in C stock by creating the changes in soil and biomass carbon. In this village, due to lack of commercial price for cotton, farmers converted the cotton area into perennial crops such as mango (Fig. 25.4) resulted in creating of C stock in soil (Branca et al. 2013). High residue production, perennial crops and reduced tillage will promote C sequestration according to model projections.

Irrigated Rice

The irrigated rice module in EX-ACT model computed carbon balance as source in Nandyalagudem and Boringthanda (1,090 and 174 t CO_2e, respectively), whereas as in Nacharam, model computed it as a sink (−908 t CO_2e). In Nandyalagudem (Fig. 25.3) and Boringthanda, without project, farmers applied farm yard manure to rice fields, whereas with project, straw incorporated into the field which results in more green house gas emission (2,629 and 355 t CO_2e, respectively) compared without project (3,719 and 529 t CO_2e, respectively). The C source emitted

1,090 and 180 t CO_2e in Nandyalagudem and Boringthanda, respectively and mitigated −908 t CO_2e in Nacharam using the irrigated module. Emissions are from CH_4 only and there is no release of N_2O emissions due to incorporation of straw into the field and intermittent flooding of rice. Amendment of crop residues mitigate C source due to increased soil organic carbon (SOC) (van Vliet et al. 2007) and reduced nitrous oxide emissions (Pathak et al. 2006). Organic matter application to reduce C sources could be a successful approach for mitigation of CH_4 and N_2O from rice fields (Guangxi Xing et al. 2009).

Livestock Interventions

Livestock interventions in these villages resulted in sources of green house gases. Buffaloes and dairy cattle number was also increased ‘with’ project which in turn resulted in enteric methane emissions during digestion. ‘With’ project, it was observed that by adopting improved feeding practices (Mineral mixtures, feeding green fodders e.g. CO-1, CO-5) and breeding practices (Artificial insemination, planned cross-breeding or selection within breeds) can mitigate the methane emissions by 19.3, 14.1 and 3.8 % in Nandyaladudem, Boringthanda and Nacahram, respectively. EX-ACT model computed carbon balance as source (383, 954 and 1,461 t CO_2e, respectively) in Nandylagudem, Boringthanda and Nacharam villages. Feeding management with fodder and mineral mixture and with improved breeding management practices shows potential reduce the GHGs.

Inputs

The input module in model computed carbon balance as source in Nandyalagudem and Boringthanda whereas, in Nacharam, model computed balance as sink. The C sources are more ‘without’ project (18,557 and 10,685 t CO_2e, respectively) compared ‘with’ project (16,068 and 9,144 t CO_2e) in Nandyalagudem and Boringthanda where the fertilizers applied based on soil testing which resulted in reduced use of nitrogenous fertilizers. Soil test based fertilization resulted in decrease in emissions of CO_2 (1,147 and 754 t CO_2e, respectively) and N_2O (1,342 and 787 t CO_2e, respectively). In Nacharam, rainfed and tribal village, without project due to lack of awareness, the usage of N fertilizer was sub-optimal and involved no K usage. With interventions of the project, farmer’s applied fertilizers based on soil testing due to which model created a source of GHG emissions. Nitrogen fertilizer can be responsible for the N_2O emissions from the soil subsequent to its application (Kindred et al. 2008). Optimizing N fertilizer rates could provide a possible GHG mitigation measure and may reduce the GHG intensities.

Conclusions

In three rainfed tribal villages indicated that crop residue recycling, use of high yielding cultivars, green manure crops, reduced tillage operations with good agronomic practices resulted in a positive carbon balance. Straw incorporation in paddy fields also increased the positive carbon balance by improving the use efficiency of nitrogen which in turn improve soil fertility and reduce nitrous oxide emissions.

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Chapter 26
Assessment of Near-Surface Soil Carbon Content Across Several U.S. Cropland Watersheds

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Abstract The Cropland Conservation Effects Assessment Project (CEAP) was initiated in the USA to provide a scientific basis for assessing effectiveness of conservation practices on water and soil quality. In 2006, sampling was initiated within a number of USDA-ARS experimental watersheds to measure and assess management impacts on near-surface (0–5 cm) soil quality indicators. Here, we focus on soil organic carbon (SOC) content because of its influence on key soil quality indicators. The sampling schemes for each of the 12 locations (<1,500 samples) in the states of Georgia, Iowa, Indiana, Maryland, Missouri, Mississippi, New Hampshire, Ohio, Oklahoma and Texas, were designed to address individual objectives. We used the Soil Management Assessment Framework (SMAF) to score the measured data so that climate and inherent soil properties would be taken into account. The SOC-SMAF scoring algorithms uses a more-is-better model reflecting SOC concentrations associated with high productivity and minimal environmental impact. Interactions include soil type, climate, and management practices such as tillage and crop rotation, which influence SOC content at each sampling site. Measured SOC contents ranged from 3.0 to 21.7 g kg^{-1} and SMAF-SOC scores ranged from 0.09 to 1.00, where 1.00 is an optimum level of SOC with regard to most soil functions. This assessment showed that SOC evaluations need to be soil- and site-specific because many factors, including environmental influences and inherent soil characteristics, influence SOC levels.

Keywords Soil quality • Near-surface • Soil organic carbon • SMAF

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Introduction

Soil organic carbon (SOC) contributes to soil functionality with regard to nutrient cycling, productivity, water partitioning, and environmental buffering, making it a leading predictor of soil quality; however, it is difficult to determine if the SOC content for a given soil is sufficient for these tasks. Soil quality and its assessment are soil and site specific, and depend on a variety of factors, including inherent soil characteristics, environmental influences such as climate, and human values such as intended land use, management goals, and environmental protection. The Soil Management Assessment Framework (SMAF; the most recent version is available from D.E. Stott) provides a method by which to score dynamic, management-sensitive soil quality indicators, including SOC. The SMAF uses soil taxonomy as a foundation for assessment, allowing for the modification of scoring indicator values to be based on soil suborder characteristics, and providing a contextual basis for indicator interpretation. The SMAF-SOC scoring curves were developed using the extensive USDA-NRCS National Resource Inventory database.

Besides SMAF, there are other soil quality assessment tools available (Stott et al. 2010), such as the AgroEcosystem Performance Assessment Tool (AEPAT) (Liebig et al. 2004), Cornell Soil Health Test (Idowu et al. 2008), and the Soil Conditioning Index (SCI) (USDA-NRCS 2002). The SCI estimates trends in the soil organic C (SOC) content, but when the SCI was compared with the SMAF-SOC indicator the SMAF-SOC was more successful in separating the tested cropping systems in the semiarid, hot, sandy soils of the Southern High Plains of western Texas, which included cotton and wheat rotations, high-residue forage sorghum, conservation grassland, and native rangeland (Zobeck et al. 2007).

The Conservation Effects Assessment Project (CEAP) was initiated in 2003 to provide a scientific basis for assessing effectiveness of conservation practices by the USDA Natural Resources Conservation Service (NRCS) (Richardson et al. 2008). The initial focus was to assess conservation practice effects on water quality in USDA Agricultural Research Service (ARS) CEAP cropland experimental watersheds. In 2006, an effort was undertaken to assess the impact of these same conservation practices on near-surface soil quality, which included the assessment of soil organic carbon (SOC) (Stott et al. 2011).

Each watershed had its own set of hypotheses controlling the sampling. However, in this paper, we give a brief overview of the cross-watershed results for SOC in the 0–5 cm depth.

Materials and Methods

Study Sites

The samples were collected from 12 USDA-ARS cropland experimental watersheds (Fig. 26.1; USDA-ARS 2013) in 2006–2008: South Fork of the Iowa River, IA (Stott et al. 2011); North Walnut Creek, IA; St. Joseph River/Cedar

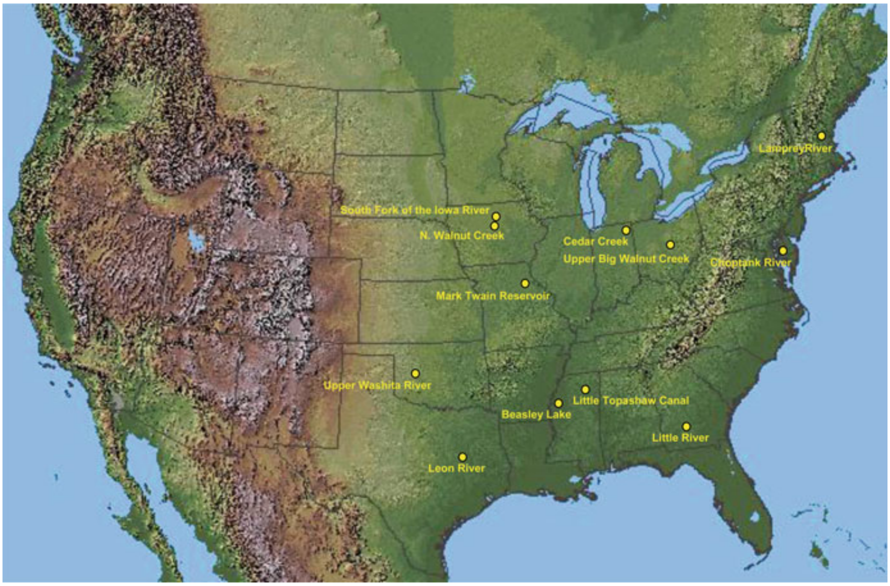

Fig. 26.1 Location of the 12 experimental watersheds assessed for near-surface soil organic carbon content. Basic topographic map from the USGS at http://nationalatlas.gov

Creek, IN; Lamprey River, NH; Mark Twain Reservoir/Goodwater Creek, MO; Choptank River, MD, Little River, GA; Beasley Lake, MS; Goodwin Creek, MS; Upper Big Walnut Creek, OH; Upper Washita River, OK; and Leon River, TX (Stott et al. 2013).

Soil Sampling and Analysis

Twenty soil cores were collected from the surface 0–5-cm within a 3-m radius of each sampling site using a 3.2-cm-diameter soil probe, and then composited. Surface residue was cleared from the sampling area, so all samples started at the soil surface. Composite samples were placed in plastic bags, sealed, and held in coolers until they could be transported to the laboratory for analysis. Upon arrival in the laboratory, the samples was air-dried, ground to pass a 2-mm sieve, bagged, and stored at 4 °C until used.

Total soil C was measured by dry combustion (EA1112 Flash NC Elemental analyzer, Thermo Finnegan Scientific, Inc., Waltham, MA) using air-dried, ground soil. For samples with a pH of 7.3 or greater, soil inorganic carbon was quantified according to the method of Sherrod et al. (2002). The SOC content was calculated as the difference between total and inorganic C.

SMAF Analysis

The SOC data were transformed into unitless values using previously published non-linear scoring curves (Andrews et al. 2004). Three inherent soil characteristics were used to modify the SOC indicator scores: (a) Soil Taxonomic suborder (a surrogate for inherent soil organic matter; e.g. a 2 % SOC content in an Ultisol would be considered high and receive a high score, while in a Mollisol, it would be considered low and would receive a low score); (b) soil texture; and (c) climate, i.e. annual precipitation and average annual temperature. The SMAF-SOC indicator scoring curves follow a more-is-better (upper asymptotic sigmoid curve):

$$y = a / 1 + b * \exp\left(-c * SOC\right) \tag{26.1}$$

where y = the SMAF-SOC indicator score, SOC is expressed as percent by mass, a = 1, b = 50.1, and c is the site-specific factor $c = (c_1 * c_2) + (c_1 * c_2 * c_3)$, c_1 is the organic matter class (suborder) parameter, c_2 is the texture class parameter and c_3 is the climate class parameter (for site-specific values refer to the SMAF model).

Results

Two of the 12 watersheds (Fig. 26.2), South Fork and Cedar Creek, had large ranges in SOC content (6.1–221.3 and 12.1–228.6 g kg^{-1}, respectively) skewing the mean contents higher (30.6 and 27.9 g kg^{-1}, respectively) than the median values (27.0 and 21.2 g kg^{-1}, respectively), while in the other watersheds, the values were similar (±2.3 g kg^{-1}). These two watersheds were characterized by pothole topography, and some of the sites with depressional areas included organic soils.

The Midwestern watersheds were typically corn-soybean or corn-soybean-small grain or legume rotations, with median SOC contents ranging from 18.5 to 27.2 g kg^{-1}. The Eastern Coast watersheds were dominated by pastures, and pine timberland as well as the ubiquitous corn-soybean rotation. The Lamprey River sites were predominately long-term pasture, resulting in a relatively high SOC median contents (35.6 g kg^{-1}) compared to the other regional watersheds (6.8–11.0 g kg^{-1}). The Southern Mississippi Valley Watersheds were dominated by corn, soybean, cotton, hardwood forests and pine timberland, with median 10.2–15.9 g kg^{-1} SOC contents. The Southern Great Plains sites included long-term pastures, cotton, peanut, grain sorghum, and winter wheat, with median SOC contents ranging from 8.9 to 26.5 g kg^{-1}.

The SMAF-SOC scores (Fig. 26.3) were wide-ranging (0.05–1.0, which is optimum) for all watersheds, reflecting the range of soil types, cropping and

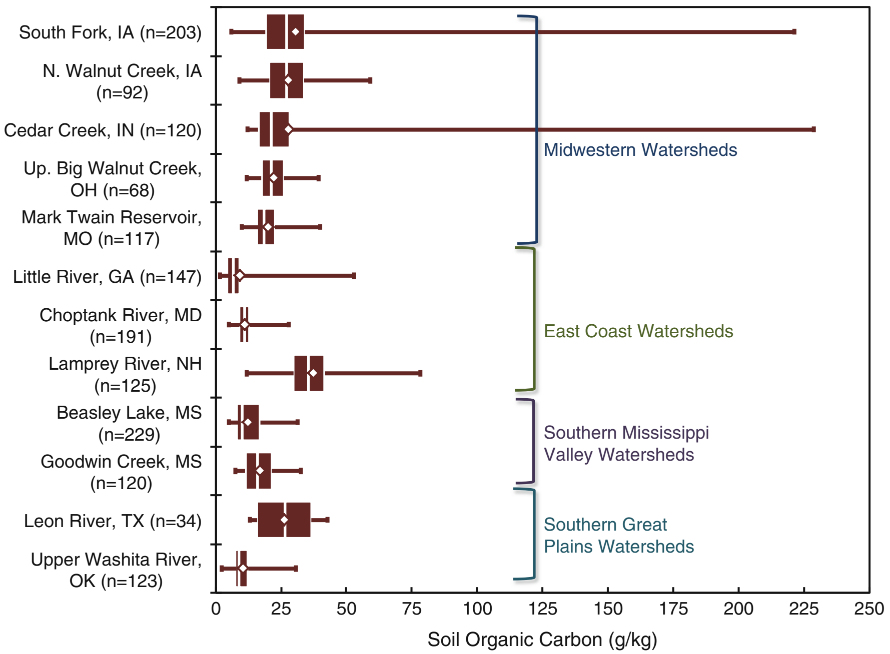

Fig. 26.2 Near-surface (0–5 cm) soil organic carbon (*SOC*) content in 1,569 soils from 12 USDA-ARS Cropland Experimental Watersheds. The *boxes* represent the 2nd and 3rd quartiles separated by a *line* representing the median SOC content, the *bars* represent the range of SOC contents and the *diamonds* (◊) represent the mean SOC content

management systems, and climatic conditions. The portion of the Lamprey River watershed that was sampled was primarily long-term (>20 year) pasture, hence the over-all high score (median = 1.00; mean = 0.90). The lowest median scores were from the Beasley Lake and Upper Washita River watersheds, 0.18 and 0.16, respectively, however the mean scores were substantially higher, 0.33 for both, which means that this groups of soils were performing at only 33 % of their potential with regard to soil functions impacted by the SOC.

When data were sorted based on five tillage classes (Figs. 26.4 and 26.5), the rotational tillage had the lowest median and mean SOC contents (1.10 and 1.06 g kg^{-1}, respectively), but had the highest median and mean SMAF-SOC scores (0.92 and 0.77, respectively) of the tillage management schemes. All the rotational tillage systems were recently implemented (<5 year), thus prior soil condition and management systems influenced the data and scoring. While conventional tillage SOC contents was similar to the remaining tillage management systems (Fig. 26.4), the median and mean SMAF-SOC scores (Fig. 26.5) were significantly lower (0.42 and 0.48, respectively) than the others (0.64–0.92 and 0.60–0.77, respectively).

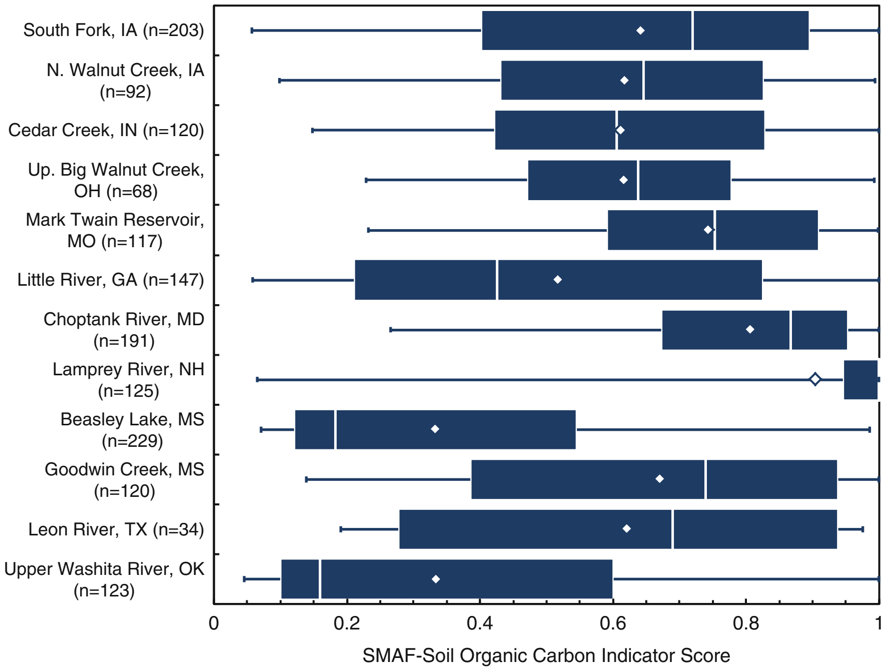

Fig. 26.3 The Soil Management Assessment Framework SOC indicator scores for near-surface (0–5 cm) soil organic carbon (*SOC*) in 1,569 soils from12 USDA-ARS Cropland Experimental Watersheds. Soils were compared to similar soils across the country. A score of 1.0 represents optimum SOC contents. The *boxes* represent the 2nd and 3rd quartiles separated by a *line* representing the median SOC content, the *bars* represent the range of SOC contents and the *diamonds* (◊) represent the mean SOC content

The number of sites that had manure applications (Figs. 26.4 and 26.5) was relatively low compared to the non-manured sites, and there was little difference between the two management systems. Regional differences in inherent soil differences overwhelmed possible differences due to manure management, thus this management factor would be best analyzed on an individual watershed basis where variations in soil and environmental properties can be minimized.

Discussion

This paper presented an indication of the current status of the near-surface SOC content across the non-irrigated cropland areas of the U.S. The majority of the fields sampled had between 50 and 90 % of optimum SOC content (a SMAF-SOC score

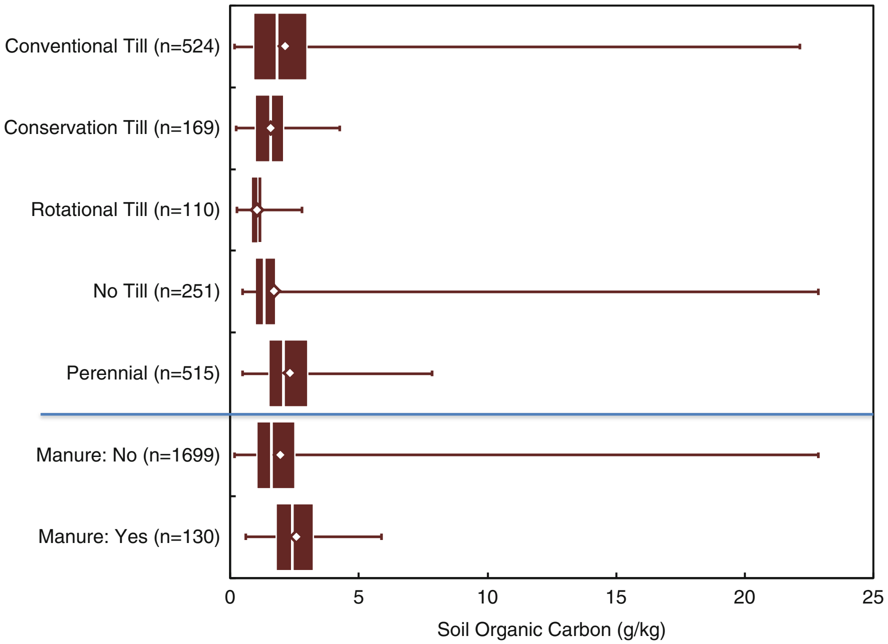

Fig. 26.4 Near-surface (0–5 cm) soil organic carbon (SOC) content in 1,569 soils from 12 USDA-ARS Cropland Experimental Watersheds sorted by tillage management (above the *blue line*) and manure treatment (below the *line*). The *boxes* represent the 2nd and 3rd quartiles separated by a *line* representing the median SOC content, the *bars* represent the range of SOC contents and the *diamonds* (◊) represent the mean SOC content (Color figure online)

of 0.5–0.9; Fig. 26.3). The Choptank River, MD and Lamprey River, NH watersheds had higher scores as the sites sampled were dominantly in long-term pastures or woodlands. A majority of fields located in the southern U.S. watersheds (Little River, GA; Beasley Lake, MS; Washita River, OK) had low scores and below 60 % of the optimum. These soils were under continuous cotton, and although no longer planted to cotton, the impact of the long term cultivation on SOC is still present. The other two southern watersheds (Goodwin Creek, MS, Leon River, TX), had reasonable scores and were primarily under long-term pastures.

The impact of tillage on SOC functionality was: conventional < conservation < no-till < pasture. However, rotational tillage fields, where soil is tilled before planting corn, but soybean is no-till planted, performed higher than the other management systems. This is probably due to the history and location of the fields, i.e. fields where soils typically remain wet in the spring unless soil residue is tilled-in to promote drying.

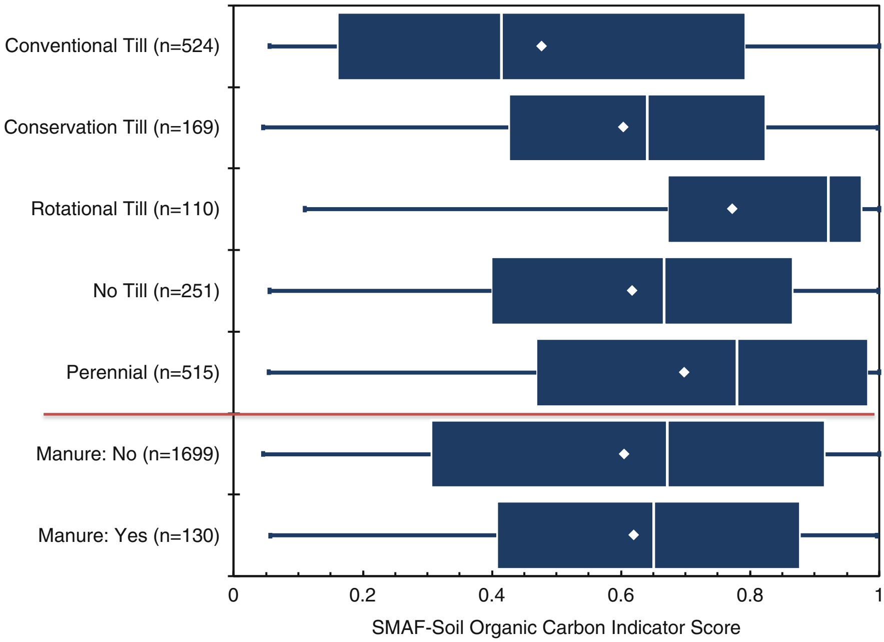

Fig. 26.5 The Soil Management Assessment Framework SOC indicator scores for near-surface (0–5 cm) soil organic carbon content of 1,569 soils from 12 USDA-ARS Cropland Experimental Watersheds sorted by tillage management (above the *blue line*) and manure treatment (below the *line*). The *boxes* represent the 2nd and 3rd quartiles separated by a *line* representing the median SOC content, the *bars* represent the range of SOC contents and the *diamond* (◊) represents the mean SOC content (Color figure online)

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Chapter 27
Mineralizable Soil Organic Carbon Dynamics in Corn-Soybean Rotations in Glaciated Derived Landscapes of Northern Indiana

Zamir Libohova, Diane E. Stott, Phillip R. Owens, Hans E. Winzeler, and Skye Wills

Abstract The concerns about climate change have increased interest in understanding differences in soil carbon pools and availability. The objective of this study was to assess total Soil Organic Carbon (SOC) and mineralizable SOC (C_{min}) dynamics and spatial distribution as controlled by slope position, in glaciated northern Indiana. We collected 210 soil samples from the 0 to 25 cm surface layer along 10-point transects along a soil catena. Total SOC was determined by dry combustion and C_{min} by incubation. The spatial distribution of total SOC followed patterns related to soil wetness. Overall, the depression areas stored between 50 and 141 Mg C ha^{-1} or between 50 and 68 % more total SOC when compared to the drier areas. After 28 days of incubation (C_{min}), depressions released 1.2 Mg C ha^{-1}, which was significantly more than the drier areas at 0.8 Mg ha^{-1}. These differences indicate the potential of wetter areas, to store C if converted to C accruing management practices. The mean daily rate of C-CO_2 evolved decreased exponentially during the first 28 days from 1.5 to 0.2 μg g^{-1} h^{-1}. The management of these targeted areas can potentially increase soil C stock in arable lands and assist managers in developing systems that will sequester soil carbon.

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Keywords Mineralizable soil organic carbon • Carbon pool • Soil-landscape

Introduction

Concerns about climate change, especially global warming associated with high levels of atmospheric CO_2, has brought new interest to the role of the SOC pool as a sink for CO_2. The large size of the SOC pool compared to other terrestrial pools highlights its significance as a sink for atmospheric CO_2 (Vanhala et al. 2007). The total SOC pool, to a depth of 2.0 m, is estimated to be about 2,400 Gt C, about three times as much as the amount of atmospheric CO_2 and about five times greater than storage in terrestrial biota C (IPCC 2001, 2007). SOC plays an important role in soil as a medium for plant growth and food production by providing plant nutrients, improving physical properties and facilitating nutrient availability (Hillel and Rosenzweig 2009). SOC is also a critical component for ecosystem functions because it improves soil structure and available water holding capacity and increases water infiltration and reduces erosion by wind and water (Matson et al. 1997; Stott et al. 1983, 1999).

The balance of the SOC stock has been and continues to be influenced by human activities such as clearing vegetation, cultivation and other land use changes (Hillel and Rosenzweig 2009). The estimated losses of SOC from anthropogenic activities are between 40 and 78 Gt or approximately 23–35 % decline from the human pre-intervention levels in the US corn belt (Lal 2002; Lal et al. 1998; IPCC 2001; Matson et al. 1997; Hillel and Rosenzweig 2009). Yet SOC sequestration is the mechanism that has the most potential of the current greenhouse gas mitigation strategies (Smith et al. 2007).

In addition to anthropogenic activities, climatic conditions influence the SOC stock and its distribution on global and regional scales (Parton et al. 1987; Kern 1994). Soils in relatively colder and/or wetter conditions, such as Gelisols, Mollisols, and Histosols, are estimated to contain between 120 and 312 Gt SOC, which is 3 times more than soils in warmer and drier conditions (Hillel and Rosenzweig 2009). Mollisols in the 48 contiguous states are the largest contributors to the SOC pool in the USA, with about 31–39 % of the total SOC (Gou et al. 2006).

At finer scales, the total SOC stock and distribution is influenced by its location relative to landscape position (Da Silva et al. 2001; Hishia et al. 2004; Li et al. 2006; Moorman et al. 2004; Ritchie and McCarty 2003; Pierson and Mulla 1990; Thompson and Kolka 2005). SOC is related to terrain attributes that reflect topography or landscape positions (Thomson and Kolka 2005). The SOC decreases in the following order: lower>middle>upper slope positions (Li et al. 2006). Slope gradient and length alone are not the controlling factor, however, they control water movement within a landscape, which provides differences in soil environments creating soil differentiation, hence soil carbon patterns and distributions. The spatial distribution of total SOC has been altered; however, differences in total SOC due to the soil water regime present before human intervention are still present and measurable, as documented by soil surveys conducted during the last 100 years (Jenny 1941; Jenny and Leonard 1934; USDA-SCS 1971; Tan et al. 2004; Guo et al. 2006).

The introduction of conservation practices such as cover crops, minimum till and no-till can slow down, but may not stop the loss of total SOC (Baker et al. 2007; Gesch et al. 2007; Venterea et al. 2006), especially in the Corn Belt. In the long term, their continuation may lead to the depletion of SOC pools, overall and perhaps with different depletion rates between lower and higher slope positions. In this context, the spatial distribution of total SOC and C_{min}, needs to be assessed to estimate how much C is stored and/or contributes to atmospheric CO_2.

While there have been many studies on the spatial distribution of total SOC across landscapes there are few that combine this with C_{min}. According to Zou et al. 2005, labile or potentially mineralizable SOC is the fraction with the most rapid turnover times, usually released within the first 4 weeks and is generally considered the most active fraction. It is also very sensitive to disturbance and management (Coleman et al. 1996; Harrison et al. 1993). Also, Zou et al. (2005) provides a biological definition of labile SOC as the microbially degradable C associated with microbial growth, which is both chemically degradable and physically accessible by soil microbes. Paul et al. (1999) define C_{min} as "active C" with a mean residence time of 30–60 days and based on curve analysis of CO_2 evolution plotted on per unit time during laboratory incubations. In this study, we assessed labile C pool as defined by Zou et al. (2005) represented by the CO_2 evolved during the first 28 days (readily mineralizable C, C_{min}).

The objective of this study was to assess total SOC and C_{min} dynamics and spatial distribution as controlled by slope position, in the recently glaciated derived landscape in northern part of Indiana that are in corn-soybean rotation The hypothesis was that the relative size of total SOC and C_{min} differs with slope position and soil type.

Materials and Methods

Study Site and Soils

Howard County, located in north-central Indiana, covers about 760 km^2 and represents the relatively new 15,000–20,000 years old Wisconsinan glaciated landscape (Fig. 27.1). Loess deposits cover the entire county and vary in thickness from 20 to 90 cm. In the Soil Survey Geographic database (Soil Survey Staff 2010b) there are 18 soil series in the county with 5 soil series formed in loess and covering 80 % of the area: Blount, Pewamo, Fincastle, Brookston, and Crosby. The remaining 20 % of the area is dominated by Fox and Ockley soils formed on outwash that was deposited during glacier melt and retreat, and Genesee and Shoals soils formed on recently deposited alluvium materials along the streams. Mollisols cover about 40 % of the county and are represented by poorly and/or very poorly drained Brookston, Kokomo, Patton and Pewamo soil series. These soils occupy slight depressions and lower slope positions.

Alfisols also cover about 40 % of the county and are represented by somewhat poorly drained and/or moderately well-drained Blount, Crosby, Fincastle, Miami and Morley soil series. These soils occupy flat summits and backslope positions.

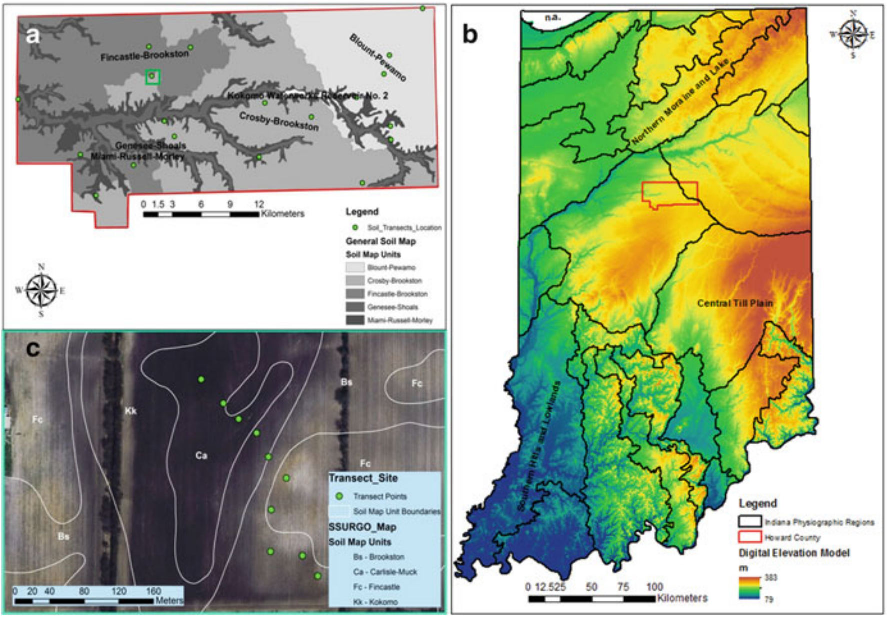

Fig. 27.1 (**a**) Howard County major soil landscapes, (**b**) Indiana physiographic regions, and digital elevation model, (**c**) soil transects and transect points in a selected soil transect crossing SSURGO soil map units in Howard County

This region is located in the eastern part of US Corn Belt and represents heavily managed agro-ecosystems dominated by corn-soybean (*Zea mays*. L – *Glycine max* L.) rotation. All our samplings sites were located in chisel-disk tillage and tile drained corn-soybean rotation fields with pH ranging from 6.5 to 7.1 and silt loam surface textures (Soil Survey Staff 2010).

Field Observations and Soil Sampling

The county was divided into seven zones based on geomorphologic regions (Franzmaier et al. 2004; Soil Survey Staff 2010a). At a minimum, 3 transects, consisting of 10 points, were conducted for each zone resulting in 210 geo-referenced points (Fig. 27.1), but 14 soil samples were unusable reducing the number of soil samples to 196. The transects were designed to capture the catena of the representative soil map units typical of the landscape, with the starting and finishing points at the highest and lowest landscape positions, respectively. The distance between points varied for each transect depending on the slope length from the highest to lowest position on the landscape.

Soil samples were collected for each point along transects. Each sample consisted of about 250 g collected from the surface to a depth of 25 cm, which was the A_p horizon. The soil sampling was done in early spring right after soil thawed and before planting when water tables were between 30 and 50 cm below surface. For the thick mollic epipedons (>40 cm) with stratification, separate samples were taken from the top layer (erosion deposition) and the lower layer (buried mollic).

Soil Analysis

Total SOC and N were determined by dry combustion at 1,000 °C (CHN 2000, Leco, St Joseph, MI, USA), and since there were no detectable carbonates, total carbon measurements were considered equal to total SOC. C_{min} was determined via incubation method (Zibilske 2004). About 40 g of soil was added to a 100 mL glass beaker, and deionized water was added to bring the sample to 60 % water-filled pore capacity determined to be the optimum soil water content for microbial activity (Linn and Doran 1984). The Gas Chromatograph (GC) used for CO_2 concentration determination was a Varian model 3800 (Varian, Inc., Walnut Creek, CA) equipped with a CombiPal autosampler (CTC Analytics AG, Zwingen, Switzerland) and a thermal conductivity (TCD) detector. The gas concentration of samples was calculated by comparison to the standards. The cumulative CO_2 evolved from the incubation was calculated by progressively adding the measured CO_2 to the previous reading (day 3 to that of day 7, continuing until day 28). The daily CO_2 evolved from the incubation was calculated from the measured CO_2 at the end of each period divided by that period length. The readily mineralizable (C_{min}) SOC pool was calculated from the total amount of CO_2 evolved during the first 28 days.

For the calculation of SOC pool size in Mg C ha^{-1} the soil bulk density for organic soils was determined to be 0.9 g cm^{-3} and for rich organic soils (the Haplosaprists) was determined to be 0.45 g cm^{-3} and 1.14 g cm^3 for the other soils indicated by measured values of soil pedon data from the USDA-NRCS Charles Kellogg National Soil Survey Laboratory.

Statistical Analysis

The Box-Cox Procedure (Box et al. 1978) was conducted to determine if the data needed transformation before analysis of variance. The analysis of variance general linear model (GLM) procedure in SAS (SAS Institute 2003) was used to assess the effects of slope position categorical variable on total SOC and evolved CO_2 continuous response variables. Analysis of variance was conducted to assess the effect of slope position on total SOC and C_{min}.

Results and Discussions

Spatial Distribution of Total SOC

The measured total SOC content showed significant trends with slope position (Table 27.1). The spatial distribution of total SOC followed patterns related to soil wetness. Depression areas represent soils with water accumulating for longer time periods. The mean total SOC for depression areas was 67 Mg ha^{-1}, which was double and significantly higher than that of the sideslope and summit positions with 35 and 30 Mg ha^{-1}, respectively.

The measured total SOC in this study represented only the top 25 cm of the soil, however research has shown that the majority of total SOC, between 50 and 65 %, is stored in the upper 30 cm of soil (Garten and Ashwood 2002; Harrison et al. 2003; Tan et al. 2004). Overall, these wet areas stored between 50 and 141 Mg C ha^{-1} or between 50 and 68 % more total SOC compared to the relatively better drained areas. Other researchers (Garten and Ashwood 2002; Jacinthe et al. 2001; Moorman et al. 2004; Manies et al. 2001; Pierson and Mulla 1990; Pennock et al. 1994; Ritchie and McCarty 2003; Li et al. 2006) have found similar patterns of total SOC spatial distribution. Significant differences in total SOC between summit and toeslope slope positions have also been found (Pierson and Mulla 1990; Li et al. 2006; Moorman et al. 2004 and Da Silva et al. 2001). The higher amounts of total SOC in lower slope positions and depressions can also be the result of management practices. Others have found that on cultivated landscapes, in addition to water movement, management practices, especially tillage affects the spatial distribution of SOC via erosion (Paul et al. 1999; Chatterjee and Lal 2009; Ussiri and Lal 2009; Ritchie and McCarty 2003; Li et al. 2006). Ritchie and McCarty (2003) found total SOC content values of 14 g kg^{-1} in deposition areas that were significantly higher than in the upland areas, with mean SOC content of 11 g kg^{-1}, and they attributed the differences mainly to erosion.

The majority of the study area has been tiled drained for close to 100 years (USDA-SCS 1971); however soils in the wetter areas still have twice the amount of total SOC compared to soils in drier areas. The measured differences in low relief areas could be attributed mainly to long term soil wetness conditions that prevailed

Table 27.1 Results of analysis of variance (Proc-GLM) of total soil organic carbon by slope position

	Total SOC (Mg ha^{-1})			
Slope position	n	Mean	St. Error[a]	Sig[b]
Depression	65	67	4.7	a
Sideslope	85	35	1.3	b
Summit	46	30	1.4	b

[a] *St. error* standard error

[b] *Sig* significance. Letters indicate significance within categories

Table 27.2 Readily mineralizable SOC (C_{min} – 0–28 day incubation), in μg g^{-1} soil and Mg ha^{-1} grouped by slope position

Slope position	n	μg g^{-1} soil	St. Error[a]	Sig[b]	Mg ha^{-1}	St. error[a]	Sig[b]	% of SOC[c]
Depression	65	406	19	a	1.07	0.05	A	1.6
Sideslope	85	291	9	b	0.87	0.03	B	2.5
Summit	46	282	12	b	0.85	0.04	B	2.8

[a] *St. error* standard error

[b] *Sig* significance. Letters indicate significance within categories

[c] Percentages are calculated based on Mg C ha^{-1}

for 10,000–15,000 years after the glacial retreat as well as anaerobic conditions still present and total SOC deposits from erosion. The difference between slope positions represents the potential to store C if carbon sequestering management systems were put into place. The continuation of current practices (tile drainage and cultivation) most likely will lead to continued losses of total SOC and further release of CO_2 to the atmosphere. In this context, the bioassay for C_{min} pool is also important in estimating how much CO_2 can potentially contribute to the atmosphere.

CO_2 Evolved from Spatially Distributed Soil Samples

The measured evolved CO_2 from soil incubations showed significant differences with soil slope position. The differences were similar to those observed in total SOC, following patterns related to soil wetness (Table 27.2). The evolved CO_2 was higher in the depression areas, which represent soils with water accumulating for longer time. Similar results are reported by Reichstein et al. (2000) when comparing the CO_2 evolved between ridges and gullies. These results are also similar to those of Bernal et al. (1998) and Paul et al. (1999), and indicate that after disturbance the total SOC is initially released in great amounts followed by a sharp decrease after the first month of incubation under ideal conditions.

The mean daily rate of evolved CO_2 was significantly higher for depression areas compared to sideslope and summit during the first 28 days of incubation and decreased with time (Fig. 27.2).

The highest daily rate of evolved CO_2 for soils in all landscape positions was at day 3 and decreased exponentially by an order of magnitude by the end of the first 28 days. Similar trends in daily CO_2 evolution with time have been found by Stott et al. (1986) and Paul et al. (1999). Paul et al. (1999) used a curve fitting analysis to relate these trends to active releasing SC pools. The daily rate of evolved CO_2 during the first 28 days resembled a bell shaped curve that decayed exponentially, which also conforms to the plant litter decomposition model by Olson (1963). One of the implications of the model would be that under ideal conditions, as provided during incubation, major losses of soil C would occur within a short period of time.

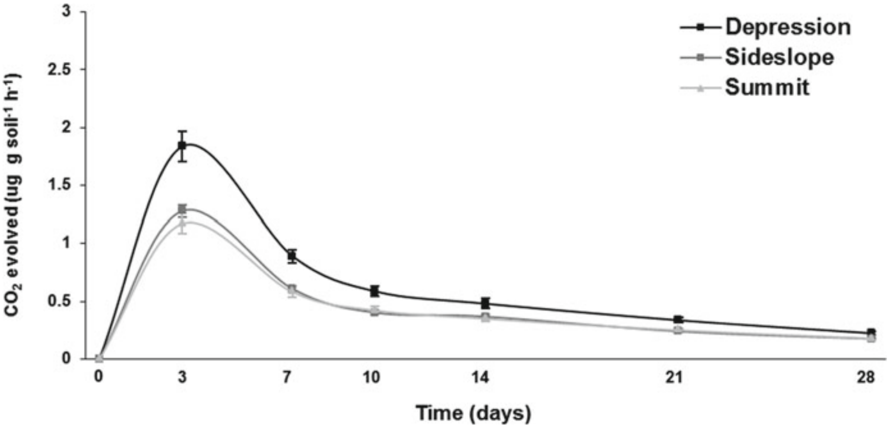

Fig. 27.2 Daily CO_2 evolved rate from different slope positions. *Bars* represent standard error

Size and Stability of Soil Carbon Pools

Both total SOC and C_{min} pools showed trends related to slope position following patterns related to soil wetness (Table 27.2). The C_{min} pool for the depression areas was 406 μg C g^{-1} soil and was significantly larger than that of the sideslope and summit positions.

The C pool size differences between wetter and drier areas, calculated in Mg C ha^{-1} (Table 27.2), were in general, similar. The mean C_{min} pool size for the depression areas was 1.07 Mg ha^{-1}, which was significantly greater than for sideslope and summit positions at 0.86 Mg C ha^{-1}. Depressions represent wetter areas compared to sideslopes and summits that represent better drained and drier soils.

C_{min} expressed as percent of total SOC showed reverse trends with soil wetness as compared to being expressed as mass per unit soil or unit area (Table 27.2). Depressions located on lower elevations areas, evolved on average only 1.6 % of the total SOC compared to drier soils which evolved 2.6 % of the total SOC during 28 days.

Conclusions

The spatial distribution of total SOC and CO_2 evolved during incubations followed patterns related to soil wetness. Overall, areas with water accumulating for longer time periods, stored 50–68 % more total SOC compared to drier areas. The depression areas also evolved more CO_2 compared to drier areas. For all landscape positions, the release of CO_2 was initially rapid and followed a negative exponential decrease. This indicates that under ideal conditions total SOC in wetter areas, when disturbed, would decrease at a faster rate within a short period of time than in drier areas. Though these conditions are only met occasionally over time they could result in substantial total SOC loses. The differences between wetter and drier areas indicate the potential of the former to store and/or release CO_2.

Overall, the results from this study highlight the importance and potential of soils in the Midwest United States to play a major role in either sequestering or releasing atmospheric CO_2. Cultivated fields with corn and soybean were the focus of this study. The incorporation of other land uses like forest and management practices such as cover crops, conservation tillage and no till would provide a better evaluation of their effects on the spatial distribution of total SOC and its stability.

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Chapter 28

Long-Term Soil Organic Carbon Changes as Affected by Crop Rotation and Bio-covers in No-Till Crop Systems

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Abstract Soil organic carbon (SOC) sequestration is a potential negative-feedback for climate-warming gases in agriculture. The rate of no-tillage SOC storage is not well known due to large temporal and spatial biogeochemical and management variations. Therefore our objective was to compare long-term SOC fluxes at a no-till field site in Milan, Tennessee on Oxyaquic Fragiudalfs, in a split-block design with four replications. The whole-block was cropping sequences of corn, soybeans, and cotton with split-block bio-cover treatments of: winter wheat, hairy vetch, poultry litter, and a fallow control. Soil carbon flux was calculated at soil surfaces (0–5 cm)

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for years-0, 2, 4, and 8. During the first 2 years, small annual losses occurred in carbon over all treatments (1.40 Mg ha^{-1}). During this time, cotton sequences lost significantly more surface SOC than other rotations. However, by year-4, SOC began to stabilize. By year-8, sequences with high frequencies of soybean and with greater temporal complexity generally gained greater SOC levels at 0–5 cm. Also, poultry litter bio-cover gained more surface SOC compared to wheat, vetch and fallow covers. Across all sequences and bio-covers, SOC had increased 1.47 Mg ha^{-1} after 8 years from pre-experimental levels of 9.20 Mg ha^{-1}; suggesting long-term beneficial effects on C storage under no-till and diverse cropping sequences.

Keywords No-tillage • Crop sequence • Soil organic carbon • Cover crop • Bio-cover • Carbon sequestration

Introduction

Concerns about global warming have led to heightened interest in sequestration of atmospheric CO_2 in agricultural soils. Agricultural soils under no-tillage production can sequester atmospheric carbon ((C) West and Post 2002). Renovative measures and restoration of degraded soils may reduce atmospheric CO_2 enrichment by 0.4 to –1.2 Pg C $year^{-1}$ (5–15 % of total greenhouse gas emissions in 2000) over the next 20–50 year (Lal 2004). However, rates of C storage in no-tillage systems is not well quantified as climate, soil texture, fertilization, crop rotation, and bio-cover type affect the rate and volume of C sequestration.

Under no-tillage management, atmospheric carbon fixed by crops in root biomass and residues can be protected from rapid oxidation; thereby increasing C sinks (Franzleubbers 2005). Soil organic carbon (SOC) pools are comprised of: (i) a recalcitrant or inherent fraction that is slowly mineralized and referred to as humus in subsoil layers, and (ii) the labile or dynamic pool that can change due to climate and management (Lal 2004). Among conservation tillage practices, no-till creates the least amount of soil disturbance, as planters use a disk or coulter to cut a narrow furrow during sowing rather than mixing upper horizons (Angers and Giroux 1996). This lack of disruption maximizes recalcitrant C formation, as complex polymers of C are decomposed into monomeric units and eventually converted into C pools that are stored for centuries (Chivenge et al. 2007).

Beyond reducing atmospheric CO_2 enrichment and subsequent climate change mitigation, there are auxiliary impacts of soil C storage, such as enhancing soil quality [e.g., cation exchange capacity (CEC)], crop productivity, reducing erosivity, as well as improving crops ability to tolerate drought. As, according to Emerson (1995), a 1 g increase of soil organic matter resulted in available soil moisture content increasing by 1–10 g. Similarly, declines in SOC stocks of 1 g kg^{-1} decreased the CEC by 4.3 mmol kg^{-1} in unproductive, low activity clays (Bationo and Mokwunye 1991; DeRidder and VanKeulen 1990). Therefore, no-till practices may improve soil fertility and quality by increasing soil nutrient retention, aggregation and available water, while reducing atmospheric CO_2 levels compared to conventional tillage (Franzluebbers 2005; Lal 2005; West and Post 2002).

Agricultural soils have the capacity to act as C sinks rather than sources under long-term, no-tillage implementation. A meta-analysis of 67 global, long-term studies by West and Post (2002), found that the conversion from conventional tillage to no-till management resulted in average C sequestration rates of 57 ± 14 g C m^{-2} $year^{-1}$ in the first 15-cm of depth. Lal et al. (1998) also estimated that the total amount of carbon in US cropping soils that can be sequestered is between 2,500 and 3,500 million megatons. A review by Franzluebbers (2005) estimated a rate of 0.42 ± 0.46 Mg ha^{-1} $year^{-1}$ in the southeastern US (10 ± 5 year).

Management practices that increase dynamic C pools include residue retention, manure, nitrogen (N) fertilization, cover crops, and conservation tillage (Lal 2005); however, SOC fluxes within a system are contingent upon interacting factors of climate, frequency and cropping sequence, and soil biota. Studies have found that increased residues and soil C additions are positively correlated (Duiker and Lal 1999); however, this relationship may be confounded by residue characteristics. Drinkwater et al. (1998) suggest low C:N residues increased C retention in soil. Rotation complexity (i.e., shifting from monoculture to continuous rotation cropping or increasing the number of crops in a rotation) may also enhance C sequestration under systems converted from conventional to no-till. However, in existing no-till systems, some studies have shown that enhancing complexity did not result in increased SOC (Franzluebbers 2005; West and Post 2002).

Adoption of bio-covers and no-tillage could enhance soil quality, CEC, water-holding capacity, soil aggregation, and reduce erosivity. However, data on sequestration rates per cropping sequence and bio-covers are sparse and such data are needed for C balances and modeling, as well as for promoting effective management strategies that maximize SOC sequestration. Our objective was to evaluate C dynamics in efforts to optimize C storage and crop productivity by quantifying soil C impacts from bio-covers, cropping sequences, and their interactions under no-till production.

Materials and Methods

The experiment used a split-block treatment design with four replications. The whole-block treatment consisted of cropping sequences (see Table 28.1 for whole plot sequences) and the split-block treatment consisted of four bio-covers. Different cropping sequences of corn (*Zea mays*), cotton (*Gossypium hirsutum*), and soybean (*Glycine max*) were repeated in 4-year cycles (i.e., Phases I and II). Bio-covers of wheat (*Triticum aestivum*), vetch (*Vicia villosa*), poultry litter, and fallow control were repeated annually under no-tillage production. This created 52 sequence x bio-cover combinations applied to separate 6.1 × 12.2 m subplots. Treatment combinations were applied to plots at the University of Tennessee's Research and Education

Table 28.1 Cropping sequence (1–13) main effects for total organic soil carbon measurements at the 0–5 cm at the research and education center at Milan, Tennessee from 2002 (Year-0) to 2009 (Year-8)

	2002[a]	2003	2004	2005
Crop sequence	2006[a]	2007	2008	2009
1	Cotton (Ct)	Cotton	Cotton	Cotton
2	Corn (Cr)	Corn	Corn	Corn
3	Soybean (S)	Soybean	Soybean	Soybean
4	Soybean	Soybean	Corn	Cotton
5	Corn	Soybean	Corn	Soybean
6	Soybean	Cotton	Soybean	Cotton
7	Soybean	Cotton	Corn	Soybean
8	Corn	Corn	Soybean	Cotton
9	Corn	Cotton	Soybean	Corn
10	Cotton	Soybean	Cotton	Corn
11	Cotton	Soybean	Corn	Cotton
12	Cotton	Corn	Cotton	Soybean
13	Cotton	Corn	Cotton	Corn

[a] 2002–2005 = Phase I; 2006–2009 = Phase II

Center at Milan (RECM; 35.9′ °N, 88.75′W), located in the Gulf Coastal Plain and on a Loring B2 series (Fine-silty, mixed, thermic Oxyaquic Fragiudalf).

In 2001 (year-0), the site was planted in corn, soybean in 2000, and cotton in 1999, with wheat and hairy vetch planted each winter, and the winter prior to the study was left fallow. This site was under no-tillage for 16-year prior to experimentation. Poultry litter bio-cover plots received the equivalent of 66.7 kg N ha^{-1} [A&L Analytical Laboratories, Inc. (Memphis, TN)]. Corn plots received 128.5 kg N ha^{-1} and the cotton received 33.4 kg N ha^{-1} as sidedress applications. Varieties planted were ‘PM 1218 BG/RR’ and ‘DP 117 RRBG’ cotton; ‘DKC 6410 RR’ and DKC63-81’ corn; and, ‘USG 7440nRR’ soybean for Phase I and II, respectively. Cotton was planted on 102-cm rows with corn and soybean on 76-cm rows. A second experimental location at Springhill, TN was carried out without cotton and will not be included in results presented herein.

Benchmark samples (year-0) were taken at soil surfaces (0–5 cm) and subsurfaces (6–15 cm) before cropping sequence and bio-cover treatments began in 2002 and again in 2004 (year-2), 2006 (year-4; end of Phase I) and 2009 (year-8; end of Phase II) and fluxes in SOC were calculated by subtracting year-0, to that of the final year, or Phase II (year-8). Cores were air dried, ground (<2 mm), and tested for carbonates. Soil C was measured by near infrared diffuse reflectance spectroscopy (NIR), using Labspec Pro® scanning spectrophotometer (Analytical Spectral Devices, Inc., Boulder, CO) at 400–2,500 nm from 2002 to 2006. In Phase II, samples were analyzed via combustion with a Flash EA 1112 Series NC Soil Analyzer (Thermo Electron Corporation, Waltham, MA); as NIR is a good predictor of SOC compared to the combustion method [$r^2 = 0.85$ (Wight 2007)].

Changes in soil carbon values over the 8-year period were analyzed using the Mixed procedure (SAS 2007). Mean separation was performed by the SAS macro "pdmix800" (Saxton 1998) with Fisher's Least Significant Difference and Type I error rate of 5 %. Analysis of variance tests were performed to identify differences caused by crop sequence, bio-cover and their interaction.

Results and Discussion

Overall, losses in topsoil carbon were observed during the first 4 years (end of Phase I) when compared across both cropping sequences and bio-covers at RECM (0.27 Mg ha^{-1} $year^{-1}$). Subsurface soil layers showed similar trends, with mean SOC losses of 0.36 Mg ha^{-1} $year^{-1}$ (data not shown). After 8 years (end of Phase II), SOC had recovered and surpassed initial levels, with mean surface gains of 1.33 ± 0.28 Mg ha^{-1} $year^{-1}$. Cropping sequences (1–13) were significant for surface SOC at the end of the 8 years observation period ($P = 0.02$), and SOC flux was impacted by bio-covers ($P < 0.0001$) when compared to initial levels. However, treatment sequence x bio-cover interactions did not impact SOC flux at the 0–5 cm depth ($P = 0.99$).

Sequences with high frequencies of corn and cotton generally lost more surface SOC than soybean sequences, which was similar to trends found in 2004. The continuous corn sequence lost more surface C than sequences with temporal sequences containing soybeans [particularly sequence numbers: 4, 7, 8, and 12; Table 28.1 ($P < 0.05$)]. Greatest C gains occurred in the soybean-soybean-corn-cotton (S-S-Cr-Ct) sequence, which was also the case at the end of 4-year (0.3 Mg ha^{-1}) (Fig. 28.1a, b). It seems that mono-cropping sequences proved to sequester less C than sequences with greater crop sequence diversity.

Bio-covers averaged 10.67 Mg C ha^{-1} by the end of year-8 [Phase II; Fig. 28.2a]. Poultry litter lost significantly less carbon than hairy vetch, wheat, and fallow bio-covers ($P < 0.05$) at 0–5 cm depth (Fig. 28.2b). Mean SOC gains were 3.91, 2.03, 1.41, and 1.36 Mg ha^{-1} for poultry litter, wheat, fallow, and vetch, respectively. Plots receiving poultry litter and planted with sequences high in soybean tended to gain more C than sequences frequently planted with cotton or corn. This could be due to greater N [and phosphorus (P)] contributions fulfilling required C:N ratios for mineralization of C substrate.

Bio-cover type did not influence SOC flux at the 6–15 cm depth ($P = 0.65$). Similarly, sequence variation was not significantly impactful on soil carbon sequestration at the 6–15 cm depths ($P = 0.60$), nor were any cover x sequence interactions [$P = 0.75$ (data not shown)]. This suggests that sub-soil C pools require more long-term (>8 year) cropping sequences and residue additions under not till management for greater C retention. Particularly, considering inherent C fractions in sub-soils are not as affected by short-term (<decade) residue type or crop sequence compared to that of surface C pools; likely due to a lack of residue mixing at lower soil horizons as well as labile C being readily consumed by microbes in the rhizosphere.

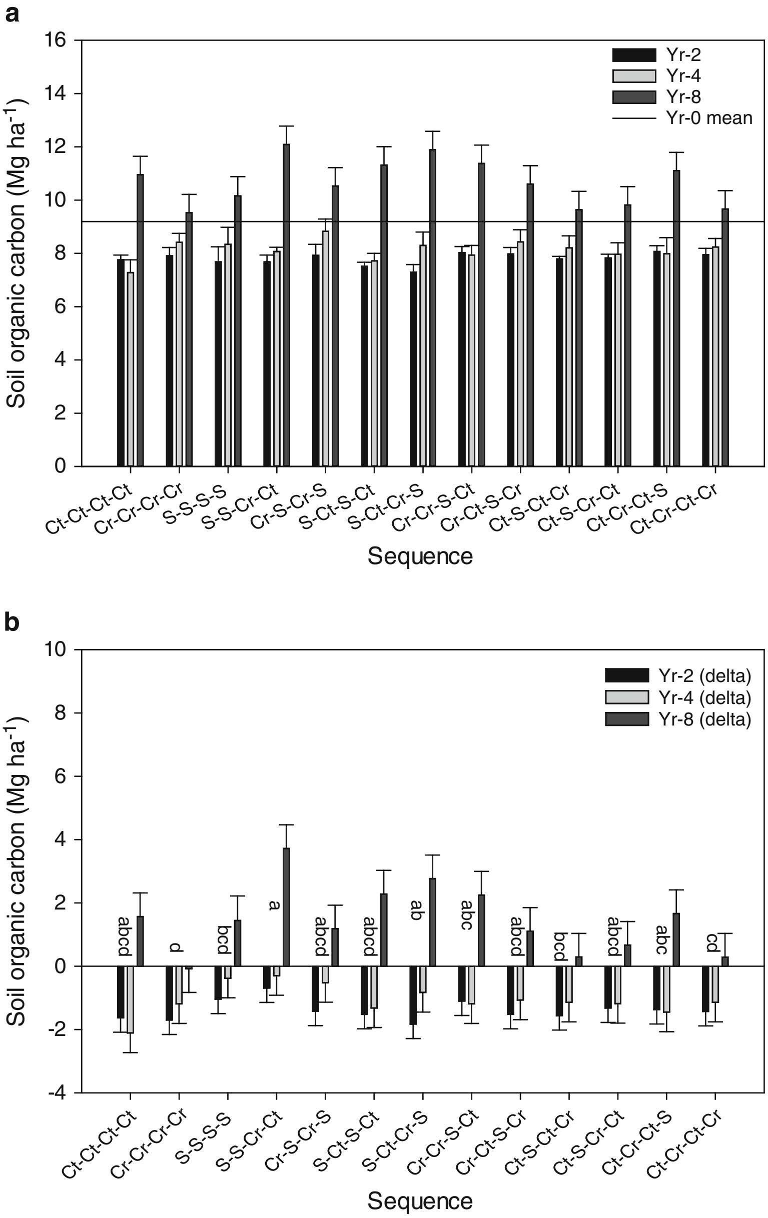

Fig. 28.1 (**a**) Total organic soil carbon at 0–5 cm depth by cropping sequence (pooled across biocover treatments) at the research and education center at Milan, TN from 2000 to 2009. Vertical bars are +/− one standard deviation. Year-0 mean lines were taken across all sequences and biocovers. (**b**) Delta SOC (Change) was derived by subtracting Year-0 from Year-2, Year-4, and Year-8. Different letters indicate end of Phase II mean differences compared to Year-0 among cropping sequences ($P < 0.05$)

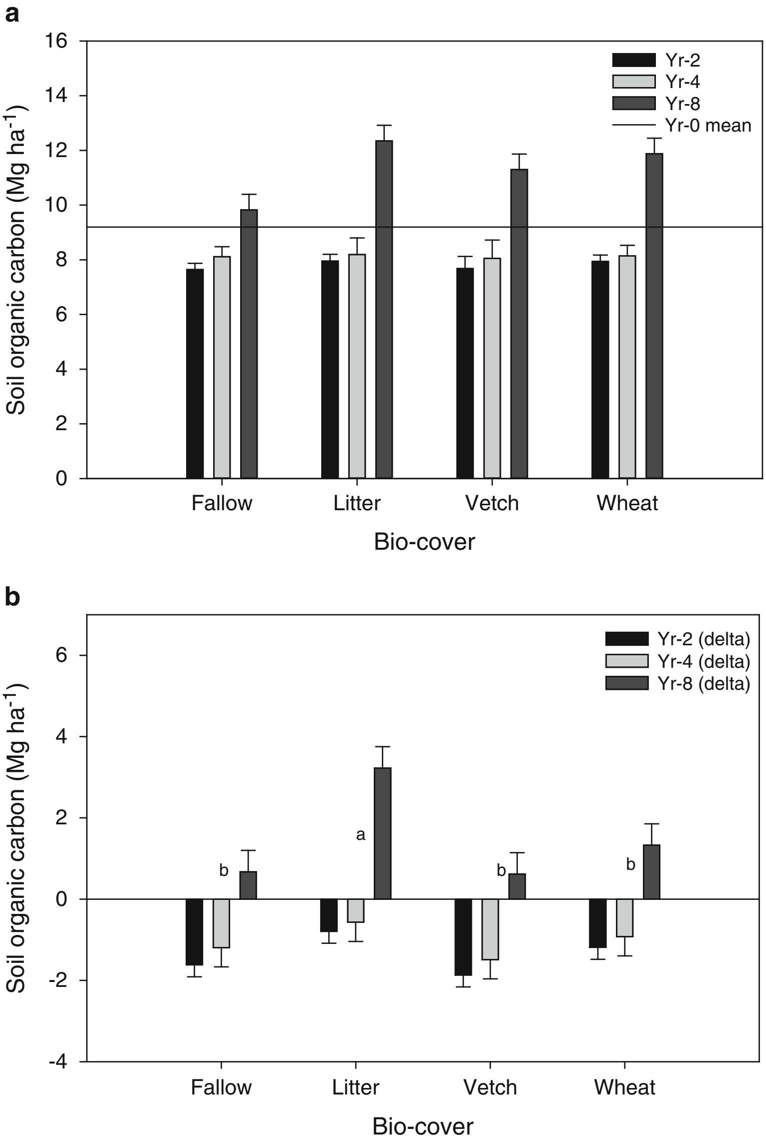

Fig. 28.2 (**a**) Total organic soil carbon at 0–5 cm depth by bio-cover (pooled across sequence) at the research and education center at Milan, TN from 2000 to 2009. Vertical bars are +/− one standard deviation. Year-0 mean lines were taken across all sequences and bio-covers. (**b**) Delta SOC (Change) was derived by subtracting Year-0 from Year-2, Year-4, and Year-8. Different letters indicate end of Phase II mean differences compared to Year-0 among bio-cover treatment ($P < 0.05$)

Discussion and Conclusions

Soil organic carbon sequestration in no-till agrosystems represents an opportunity to offset a portion of anthropogenic CO_2 emissions and improve soil quality for crop production in the southeast USA. Continuous (over an 8-year period) no-till combined with crop rotations and bio-covers effectively sequestered surface (0–5 cm) C. Observed increases in SOC (2 % C year^{-1}) are similar to those estimated by others in the southeastern USA [1.5 % C year^{-1} (Franzluebbers 2005)]; albeit increases were not observed until after the fourth year in this study. Temporal sequestration rates are affected by previous management, site history, weather patterns and existing nutrient profiles and the presented SOC results may not be directly comparable within or between regions. These data provide an estimate of sequestration rates within the top 5-cm under our tested management practices and soils.

Implementation of no-tillage is generally thought to augment SOC pools but surface losses occurred during the first four study years. This trend followed a precipitous increase for the Phase II sampling period, resulting in 15.98 % greater C than pre-experimental levels. Initial losses could be attributed to the 'priming effect' as depolymerization rates likely increased due to applications of nutrient-rich residue and fertilizer following an extended fallow period (with low quality C sources), thereby promoting microbe metabolism by adding new substrate for decomposition, particularly under the mild winter conditions at west TN (NOAA 2008). Previous studies have documented negative impact on total SOC resulting from production shifts (e.g. shallow to deep rooted species), due to organic soluble C (e.g. glucose) stimulating metabolism of non-labile C (Fontaine et al. 2003). Once priming effects has subsided, metabolism reverts to baseline levels (Stockmann et al. 2013), as was the case in our study. However, such effects are often more immediate that attenuated, long-term.

Enhancement of rotation complexity is projected to increase C sequestration (Franzluebbers 2005; West and Post 2002), which was observed in this study, considering more temporally complex systems resulted in greater SOC. Specifically, sequences with greater soybean frequencies tended to lose less C in the first phase and rebound more in the second phase than other sequences when combined with poultry bio-covers, suggesting the stimulation of C transformations under greater flushes of N and P, which are required for microbial biomass assimilation and is linearly related to soil biomass C (DeForest and Scott 2010).

Increasing trends in crop acreage under reduced-tillage has created an impetus for greater understanding of how this management strategy affects soil-C fluctuations. Changes in SOC storage in this study suggest no-tillage systems can result in appreciable C sequestration within 8-year of implementation. The level of improvement depends on cropping sequence complexity and bio-cover type. Systems in this study may be approaching a new 'steady carbon state'.

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Chapter 29
Perennial Grasslands Are Essential for Long Term SOC Storage in the Mollisols of the North Central USA

Gregg R. Sanford

Abstract Long-term agricultural research sites like the Wisconsin Integrated Cropping Systems Trial (WICST), with annual and perennial cropping systems growing alongside rotationally grazed pasture and native prairie plantings, provide invaluable insight into the carbon sequestration potential of agriculture in the North Central USA. Analysis of soil organic C (SOC) stocks during the first 20 years of the WICST study showed that annual row crop agriculture lost 5.5 Mg C ha^{-1}, while rotationally grazed pasture was a significant sink to 0–60 cm depth (5.1 Mg ha^{-1}). While SOC changes for the Prairie, Conservation Reserve Program planting (CRP), and forage systems were not significantly different from zero when considered independently of one another, differences between systems suggest a trend of SOC accumulation in Prairie and loss in the CRP and forage systems. Carbon stabilization and accretion on the fine textured Mollisols of the North Central U.S. may not be possible, even under agricultural best management practices, without the inclusion of perennial grasses.

Keywords Prairie • CRP • Biofuels • Carbon Sequestration • Grazing

Introduction

Agricultural lands have been promoted as promising and economically viable sinks for atmospheric C (Conant et al. 2007; Lal 2008). Lal (2004) suggested that the carbon sequestration potential of agricultural soils for the near future (25–50 years)

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would be modest (50–100 Pg C) but important as it is a functional reservoir for CO_2. Practices such as no-till farming (NT) (West and Post 2002; Huggins et al. 2007), nitrogen fertilization (Huggins et al. 1998; Nafziger and Dunker 2011), animal and green manures (Ogle et al. 2005), and increased use of perennials crops (Huggins et al. 1998; West and Post 2002) have been suggested as ways to manage agricultural lands for carbon storage. There is general agreement that such practices have beneficial effects on soil carbon status, but long-term soil organic carbon (SOC) stabilization is dependent on soil texture, mineralogy, and the environment (Kögel-Knabner et al. 2008; Fierer et al. 2009; Schmidt et al. 2011) making it unlikely that a standard set of farming practices will have the same beneficial effects when adopted under diverse edaphic conditions.

There is a growing body of scientific literature that offers contradictory results related to SOC sequestration under agronomic best management practices (Huggins et al. 2007; Luo et al. 2010; Sanford et al. 2012). Huggins et al. (2007), in a study of tillage and crop rotations effects on SOC in southern Minnesota, report losses of 3.7 and 1.6 Mg SOC ha^{-1} for low productivity or aggressively tilled systems and high productivity or minimally tilled systems respectively. They concluded that under the best case scenario of highly productive continuous corn and reduced tillage, stabilization of initial SOC would require reducing decay rates by over 50 % or doubling C inputs. These findings are supported by those of Sanford et al. (2012) who showed 20 year losses of SOC in six common Wisconsin agroecosystems despite the use of agricultural best management practices (NT, perennials, manure). Luo et al. (2010) in a meta-analysis of 69 paired experiments found that conversion from conventionally tilled to no-till farming practices affected the distribution, but not the concentration of SOC (>40 cm) under similar crop rotations.

The Mollisols of the North Central USA account for 85 % of national corn production, 25 % of the nation's SOC stocks (Guo et al. 2006; USDA 2013), and figure prominently in efforts to re-claim historically depleted SOC reserves. A potential management strategy for SOC accretion, that does not rely upon annual row crops or perennial forage rotations, is the re-establishment of grasslands and native prairie vegetation for agricultural production (forage and biomass). This strategy is gaining traction as the benefits of rotational grazing are increasingly recognized (Follett and Reed 2010; Oates et al. 2011) and perennial grasses such as switchgrass (*Panicum virgatum* L.), big bluestem (*Andropogon gerardii* Vitman) and giant miscanthus (*Miscanthus x giganteus* Greef & Deuter ex Hodkinson & Renvoize) are promoted for bioenergy production (Heaton et al. 2008; Hong et al. 2013).

Long-term agricultural research sites like the Wisconsin Integrated Cropping Systems Trial (WICST), with annual and perennial cropping systems growing alongside rotationally grazed pasture and native prairie plantings, provide insight into the carbon sequestration potential of diverse agroecosystems. Recent work at the WICST demonstrated the importance of pasture grasses in stabilizing SOC in the 0–30 cm soil depth and the general loss of SOC in well managed annual and perennial crop rotations (Sanford et al. 2012). To better understand the importance of perennial grass systems in the SOC dynamics of fine textured Mollisols, two native species plantings were compared to the three general land cover groups

(LCGs) of the WICST core trial (grain, forage, and pasture). These native plantings included a native prairie restoration (Prairie) typical of the vegetation historically found in southern Wisconsin, and a lower diversity native plant mixture promoted through the USDA's Conservation Reserve Program (CRP) for the stabilization of highly erodible land.

Methods

The Wisconsin Integrated Cropping System Trial (WICST) was initiated in 1989 at the University of Wisconsin Arlington Agricultural Research Station (43°18′N, 89°20′W), Arlington, WI, USA. Six cropping systems are present in the core trial: three cash grain, two crop based dairy forage rotations, and one pasture based dairy system (Posner et al. 1995). In 1989 a cool season grass mix (Kentucky Bluegrass [*Poa pratensis* L.], Quackgrass [*Elymus repens* L. Gould], Smooth Bromegrass [*Bromus inermis* Leyss.]) was planted at WICST in 1.2 ha not occupied by the core trial. In 1998, the cool season grasses were plowed under and the site was planted to soybeans. The following growing season two native perennial systems were established. The two systems were (1) a native prairie planting (Prairie: 25 species mix) and (2) a planting mix typical of those used in the Conservation Reserve Program (CRP: 6 species mix). Further establishment details can be found in Simonsen et al. 2002.

Soil sampling and SOC determination (g SOC [kg soil]$^{-1}$ and Mg SOC ha^{-1}) followed the same protocols as those outlined in Sanford et al. (2012), as follows: two time points [1989 & 2009]; 4 soil depths [0–15, 15–30, 30–60, and 60–90 cm]; and six cores/depth/plot including calculations of equivalent soils mass (Lee et al. 2009). For the two native plantings (Prairie & CRP) an additional set of soil samples were collected (0–15 and 15–30 cm only) and analyzed at the time of system establishment (1999).

Analyses were conducted to compare changes in SOC (g kg^{-1} and Mg ha^{-1}) between the three LCGs from the WICST core trial (grain, forage, pasture) and the two native species plantings (CRP, prairie). The five LCGs analyzed were therefore: Grain (CS1, CS2, and CS3), Forage (CS4, CS5), Pasture (CS6), CRP, and Prairie. All statistical analyses were conducted using linear mixed effects models in SAS v 9.3. (see Sanford et al. 2012 for greater detail on statistical methodology).

Results and Discussion

Analysis of changes in SOC (g kg^{-1}) revealed significant differences ($p<0.05$) between grain, forage, and pasture for each of the four soil profiles analyzed. This trend held in the analysis of ΔSOC Mg ha^{-1}. When looking at the grain, forage, and pasture side by side (Figs. 29.1 and 29.2), with a $\Delta=0$ reference line, the pasture

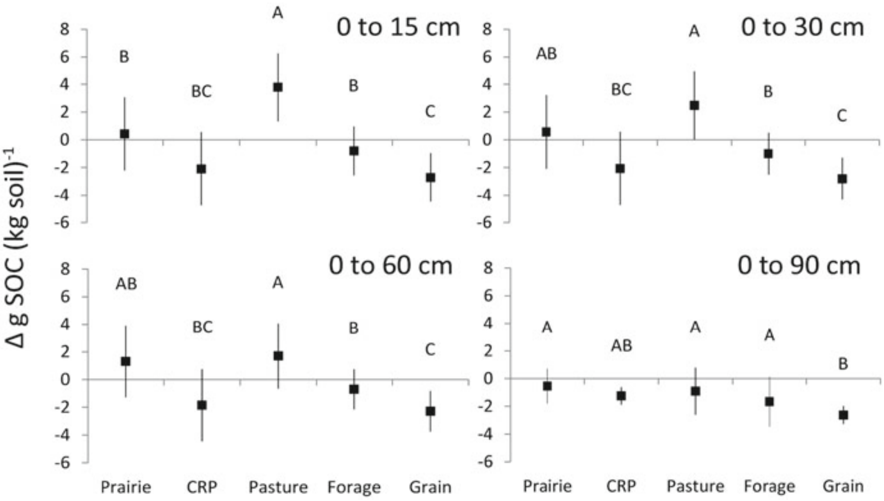


Fig. 29.1 ΔSOC concentration (1989–2009) comparison of Prairie and CRP plantings to the three land cover groups in the core WICST trial (Pasture, Forage, & Grain). ΔSOC values for each system represent the average change in SOC over the soil horizon analyzed. Error bars represent 90 % confidence limits to test difference of system mean from zero. Letters represent significant differences between systems within a given depth (Fishers LSD, α = 0.1)

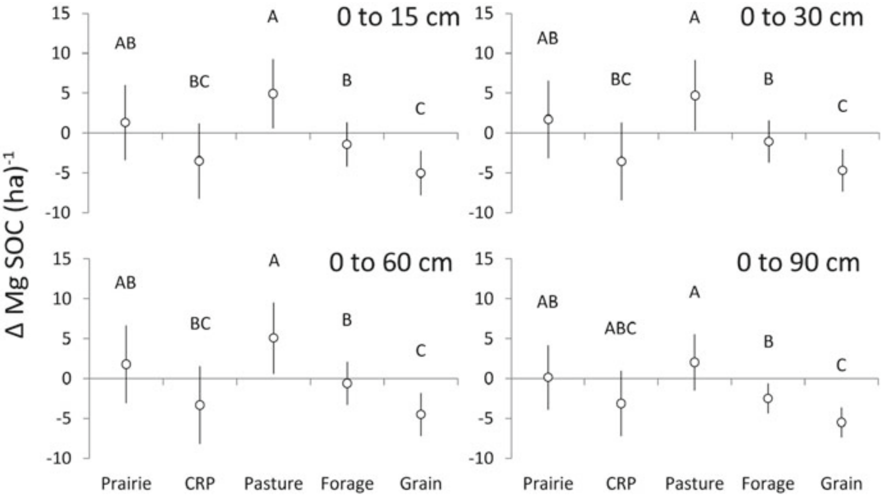


Fig. 29.2 ΔSOC mass comparison of Prairie and CRP plantings (1989–2009) to the three land cover groups in the core WICST trial (Pasture, Forage, & Grain). ΔSOC values for each system represent the average change in SOC over the soil horizon analyzed. Error bars represent 90 % confidence limits to test difference of system mean from zero. Letters represent significant differences between systems within a given depth increment (Fishers LSD, α = 0.1)

and grain differed. The pasture was not only a significant sink of atmospheric CO_2 in the surface 0–60 cm profile (Fig. 29.2), when the entire soil profile was considered it was statistically indistinguishable from zero (Figs. 29.1 and 29.2) indicating that the Pasture has effectively stabilized SOC over 20 years at WICST. These findings are similar to those reported by Sanford et al. (2012) who showed that pasture C accumulation was significant in the 0–15-cm horizon. Sequestration of SOC in the surface horizons of the pastures was likely the result of both the quantity and quality of belowground net primary production. In perennial grass systems like the rotationally grazed pasture, 80–90 % of the belowground biomass is concentrated in the surface 30 cm of the soil and is dominated by fine roots (0–2 mm) (Jackson et al. 1996; Rasse et al. 2005).

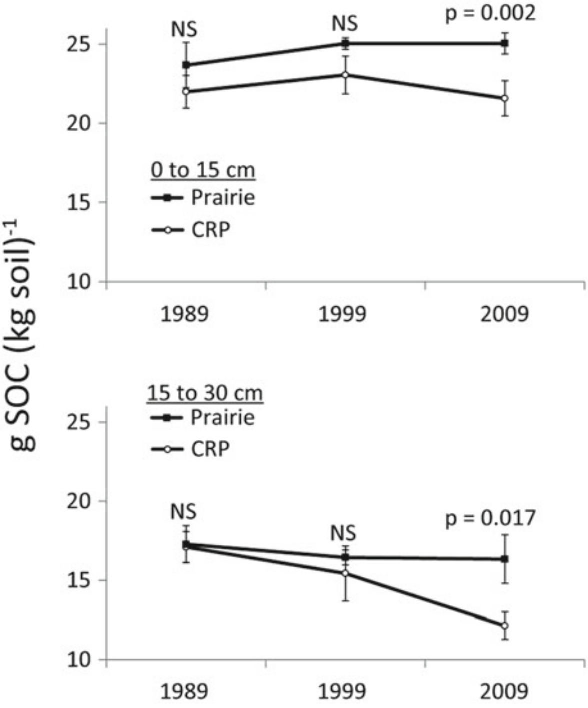
The opposite trend was observed for grain, where mean SOC losses were significant. This was likely the result of limited below ground carbon inputs (DeLuca and Zabinski 2011), historical SOC losses following the cessation of manure application to these fields at the start of WICST (Sanford et al. 2012), and mineralized SOC loss from tillage (Lal 2008). The pasture and grain were significantly different from one another in each of the eight profiles studied (Figs. 29.1 and 29.2).

Statistical differences between the prairie, CRP, forage, and pasture LCG's were less pronounced and highlight the importance of grassland systems in stabilizing SOC. The prairie system was similar to pasture followed by the forage LCG. The CRP was comparable to the grain LCG in all soil profiles considered. Although mean ΔSOC values in CRP suggest carbon losses similar to those observed in the grain LCG this was not statistically significant.

The beneficial effects of a perennial system on SOC accretion are in part related to the advantages of reduced tillage as well as the fact that perennial plants allocate greater C resources belowground than annual crops. The influence of belowground biomass on SOC dynamics cannot be understated, playing a greater role in the long term stabilization of soil C than inputs from aboveground biomass (Rasse et al. 2005; Katterer et al. 2011). While aboveground productivity in tallgrass prairies may not differ from that of annual cropping systems, belowground productivity is far greater than that of annual systems (Guzman and Al-Kaisi 2010; DeLuca and Zabinski 2011). DeLuca and Zabinski (2011) reported that under tallgrass prairie, belowground net primary production can range from 8 to 15 Mg ha^{-1} $year^{-1}$ with an estimated 3–5 Mg ha^{-1} $year^{-1}$ retained in the soil.

The differences observed between Prairie and CRP suggest that species diversity has played a role in SOC stabilization and accretion at WICST. In the case of both the prairie and CRP plantings, the plots were in cool season grasses between 1989 and 1997 at which point they were tilled and planted to soybeans for a year prior to initiation of the native plantings (Simonsen et al. 2002). The SOC values for these systems therefore represent an 8-year period of C3 grass followed by a period of soil disturbance, and then a 10-year period of native grasslands. Evaluation of g SOC (kg $soil)^{-1}$ data from the three time points (1989, 1999, 2009) shows a steady increase in SOC between 1989 and 1999 in the 0–15 cm horizon, and a steady decrease in SOC during the same time period in the 15–30 cm horizon (Fig. 29.3). Following tillage, and upon conversion to prairie and CRP, SOC in the prairie

Fig. 29.3 SOC concentration over time in the WICST Prairie and CRP plantings. Between 1989 and 1999 the systems were planted to C3 grasses, prairie and CRP were established in 1999. Error bars show ±1 s.e., *NS* = non-significant



system stabilized between 0 and 15 cm and increased between 15 and 30 cm depth. The trend for CRP was different, with SOC loss occurring between 0 and 15 cm, and the rate o loss increasing in the 15–30 cm layer. Between 1999 and 2009, the CRP system changed from being comparable to the prairie to having significantly lower SOC levels in both the 0–15 and 15–30 cm soil layers ($P = 0.002$ and 0.017, respectively).

There have been some reports on the enhanced SOC sequestration capabilities of diverse native systems compared to less diverse systems (e.g. Fornara and Tilman 2008; De Deyn et al. 2011). As species diversity increases, plants make greater use of the resources in an ecosystem and net productivity (above- and below-ground) increases (Hector et al. 1999; Spehn et al. 2005; Tilman et al. 2006).

Conclusions

Long-term agricultural research sites provide invaluable insight into the carbon sequestration potential of diverse agroecosystems. Analysis of SOC stocks during the first 20 years of WICST showed that annual row crop agriculture lost a significant amount of C (−5.5 Mg ha^{-1}) while rotationally grazed pasture was a significant sink (5.1 Mg ha^{-1}). Prairie, CRP, and forage systems were not significantly different from one another, but followed a trend suggesting that the prairie system was sequestering SOC, while the CRP and forage systems were losing SOC. Differences between SOC stock in prairie and CRP following establishment in 1999 ($p < 0.05$) suggest a link between SOC accumulation and plant functional diversity in native grasslands. Results from this and other similar investigations highlight the importance of perennial grass systems for maintaining and building SOC stocks. Carbon stabilization and accretion on the fine textured Mollisols of the North Central U.S. may not be possible, even under agricultural best management practices, without the inclusion of perennial grasses.

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Chapter 30
Soil Organic Carbon Redistribution by Erosion on Arable Fields

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Abstract Colloids are thought to move easily, consequently both mineral and organic colloids are overrepresented in runoff and soil loss, which causes selective erosion. Soil loss compound is a function of scale. The enrichment of soil organic carbon (SOC) and of the clay fraction in soil loss was studied at two sites in Hungary. A rainfall simulator was applied to describe selective erosion at micro (<1 m^2) and plot (2×6 m) scale. At field scale, soil loss samples were taken from 25 to 50 m intensively tilled runoff plots to assess SOC losses. At plot scale, selective erosion takes place as redistribution within the plot with crust formation. Thin sections demonstrate the horizontal structure of the particles on the surface covered by SOC and clay colloids. The rate of SOC enrichment is inversely proportional to the amount of soil loss. Enrichment is significant in the settled (coarse) part of soil loss, while – in

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contrast to the plot scale results – there is no SOC surplus in the suspended part. SOC components of high molecular weight seem to be increasingly vulnerable to erosion and they are overrepresented in soil loss. Because of their high stability carbon sequestration occurs in the buried horizons.

Keywords Soil organic carbon • Selective erosion • Soil loss • Enrichment factor • SOC compound

Introduction

Soil organic carbon (SOC) is related to soil physics, biology and chemistry. Increasing SOC content results in better aggregate stability and well-developed soil structure. In general, SOC content decreases with depth. SOC mobility in soil depends on its chemical characteristics and polymerization (Szalai et al. 2010). Fulvic acids, like other components of low molecular weight, are more soluble, therefore they are more mobile and vulnerable to mineralization. In most of the soils, the humus and clay colloids often build up strongly related organo-mineral complexes.

Sheet erosion causes SOC redistribution in the landscape (Lal 2005). SOC loss has a degrading effect upon the structure and fertility of the soil (Stavi and Lal 2011) and it can produce harmful processes like eutrophication. As the colloids have the smallest weight compared to their surface, they are especially prone to runoff. Enrichment Factor (EF) represents the intensity of increase in organic or mineral component in soil loss in comparison with the original topsoil (Farsang et al. 2012; Nagy et al. 2012).

Soil erosion is a scale dependent phenomenon (Centeri et al. 2009). Investigations into smaller plots, result higher soil loss. As the study site becomes larger in size, the net soil loss as well as EF change. The measured values are not equivalent among the different spatial scales and no general relation has been found yet (Chaplot and Poesen 2012).

The aim of this paper is to compare SOC enrichment values among various scales on intensively tilled arable land. It was also investigated if there are any differences in SOC compounds of soil loss or whether there are any specific humus components that tend to be increasingly prone to soil erosion.

Materials and Methods

Intensively tilled Cambisols and Luvisols were tested for their erosivity at different scales in Hungary. Micro and plot-scale measurements were carried out on 12 m^2 plots at Visz (N46.72412°, E17.79137°) (Fig. 30.1) using the Pannon R-02 rainfall simulator (Centeri et al. 2011). Cambisol in seedbed condition and pasture were treated by constant rainfall intensities within a range of 30–40–60–90–130 mm per hour. Thin sections were made from the uppermost few centimeters of the plot surface after rainfalls (Jakab et al. 2013).

At the field scale, four tilled runoff plots were investigated at Szentgyörgyvár (N46.74831°, E17.14674°) on a Luvisol (Fig. 30.1). Each plot was 50×25 m in

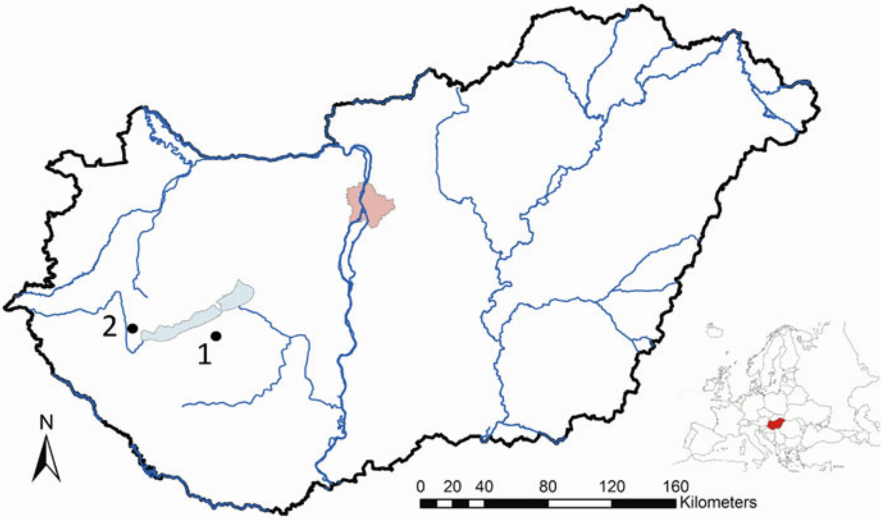

Fig. 30.1 Location of the study sites in Hungary *1* Visz, *2* Szentgyörgyvár

size. A detailed description of the design, soil and methodology was presented by Kertész et al. (2007). During the spring of 2013, three precipitation events generated runoff and soil loss, even though the plots were covered by oil seed rape.

SOC values were determined from the original topsoil as a control, and EF values were calculated from the soil losses. To determine SOC compounds, samples were taken from the Szentgyörgyvár runoffs. Since the separation of water and soil from runoff was done by settling, both the suspended and the settled sediments were sampled and measured. Differences were analyzed by using one-way ANOVA and post hoc Tukey test.

SOC and total nitrogen (TN) were measured by NDIR-chemiluminescent analyzer (Tekmar Dohrman Apollo 9000 N). Particle size distribution was determined by using laser diffraction analyzer (Fritsch Analysette Microtech A22).

SOC compounds were characterized by UV–VIS spectrophotometry (Shimadzu 3600) from 0.5 M NaOH solute sediment samples. E_4/E_6 indexes (Tan 2003) as well as ultraviolet absorbance ratio index (URI, UVA_{210}/UVA_{254}) (Her et al. 2008) were calculated and absorbance values at 280 nm (Chin et al. 1994) were recorded to typify SOC compounds.

Results

All the precipitation events investigated triggered soil redistribution, runoff and soil loss. At micro scale (within a few dm), it is evident that the originally uniform soil became disaggregated as a result of soil erosion (Fig. 30.2). The disperse pattern of

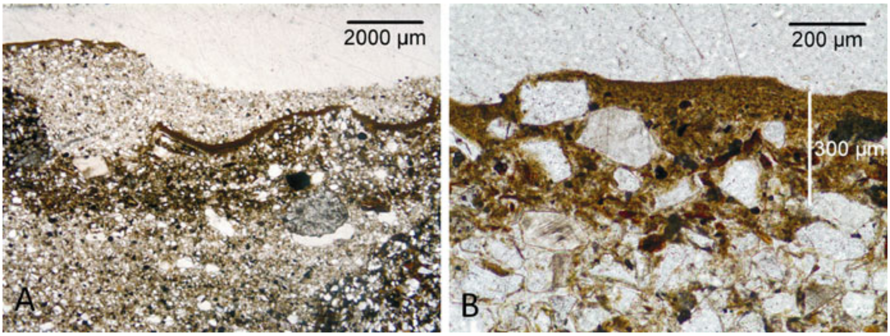

Fig. 30.2 Thin sections of the separated, overlaying sediment horizons after two precipitation events (Note SOC enrichment on the covering sediment layer, which was leached down than buried by the following precipitation event)

the colloids and the bigger particles on the soil surface was broken down resulted from splash erosion and runoff delivery. The redistributed uppermost part could be divided into a 0.2–0.3 mm thin colloid film at the top and a coarse fraction below. At the beginning of the following rainfall event, the thin SOC and clay coat is presumed to be leached downwards into the soil. As surface runoff forms, colloidless, coarse sediment covers the former crust. At the end of the precipitation event, organo-mineral complexes from the remained puddles settle on the surface again as it was proved previously by Jakab et al. (2013).

SOC content of soil loss triggered by the rainfalls of various intensities varied. EF >1 represents SOC surplus volume in soil loss. EF values are presented as the function of recent sediment load of runoff in case of rainfall simulator studies on pasture and seedbed condition (plot scale), and at the field scale under rape (Fig. 30.3). In most cases EF is higher than 1 except for pasture where no direct relationship between EF and sediment load was found. Consequently on the newly tilled, uncovered plot, EF values are >1 and there is an inverse ratio of SOC content to soil concentration in runoff. The closest correlation was found at the field scale but soil concentration values in runoff are much lower here because of the rape cover and the sediment redistribution effect within the field.

At the field scale, soil loss was divided into suspended part and settled part because of the differences in SOC. In the suspended part clay particles are overrepresented and 50–80 % of the grains are smaller than 4 µm. Although SOC contents of both suspended and settled parts vary there is a significant difference between the settled part and the topsoil (Fig. 30.4a). While in the settled part EF is always >1, sometimes there is no enrichment in the suspended part but it occurs when a heavy runoff delivers a large amount of soil loss. Total soil loss values represented by the weighted averages do not have different SOC contents in comparison with the original topsoil.

There is a wide variation in total nitrogen content in both types of sediments, and no significant differences were found (Fig. 30.4d). C/N ratio refers to SOC

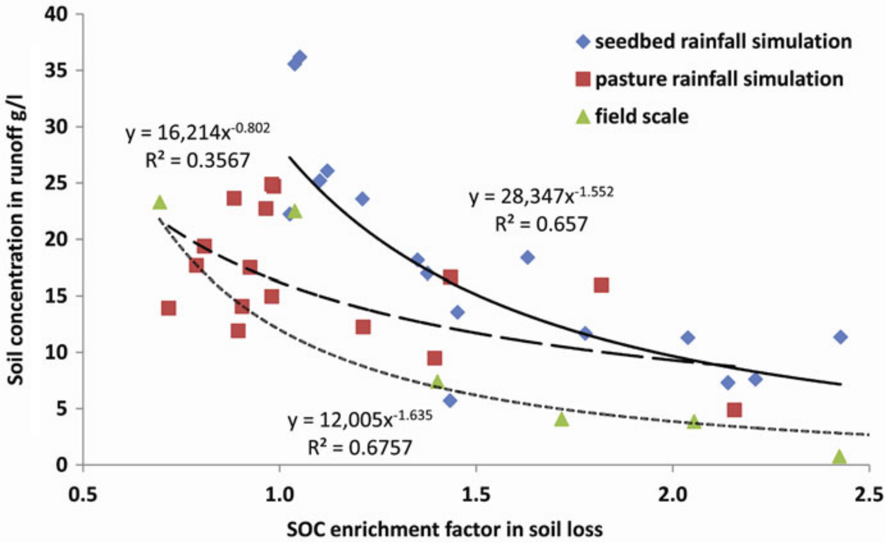

Fig. 30.3 Connections between soil concentration in runoff and SOC enrichment factor measured by various intensity rainfall simulations on 12 m^2 plots (seedbed condition soil and pasture) and on the field scale (25 × 50 m covered by oil seed rape) runoff plots (n = 15, n = 16, n = 6)

compound and lower values represent considerable molecular weights. Both sediment types have higher values than the original topsoil but the difference is only significant for the settled sediments which means that the erosion is selective for the more mobile SOC components of low molecular weight.

E_4/E_6 ratio means of soil loss are lower than that of the topsoil, only the SOC compound of suspended sediment differs significantly from the settled sediment and topsoil values (Fig. 30.4e). The suspended SOC has components with the highest molecular weight whereas the poorly developed humus molecules remain on the settled part or on the surface.

For the C/N ratio (Fig. 30.4b), and the absorbance at 280 nm (Fig. 30.4c), the original topsoil had a constant SOC compound value which became diverse in soil loss due to the redistributing effect of the rainfall. Presumably, the main process is a physical redistribution but some sort of chemical process such as oxidation or degradation is also possible. On the basis of URI values, SOC of the settled sediment is dominated by humic acids while the suspended part has more condensed components like humins (Fig. 30.4f). In accordance with the results of E_4/E_6 ratio, the original topsoil has the lowest degree of condensation, although the difference is significant only between the topsoil and settled sediment values.

The aromaticity character and the higher density of functionality groups were predicted by the absorbance at 280 nm as well, which resulted in an increase both in settled and suspended sediments in comparison with the original topsoil only the

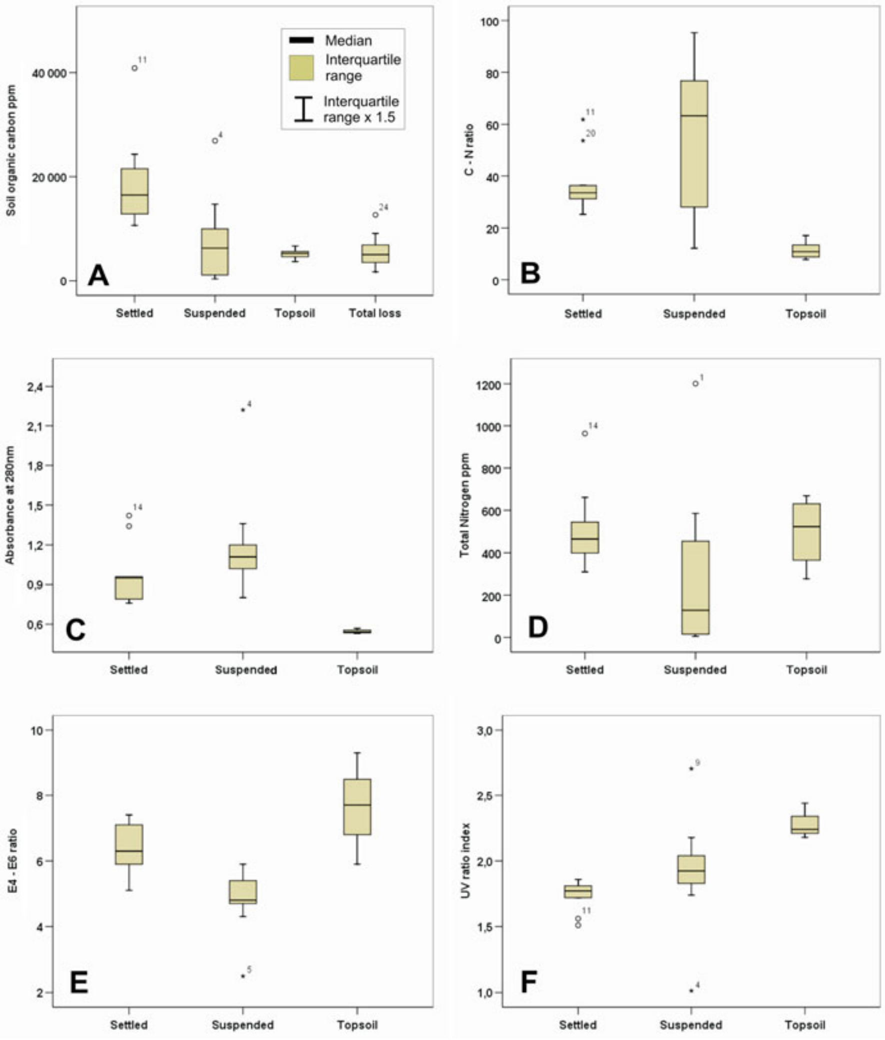

Fig. 30.4 SOC content (**a**) and compounds (**b**: C/N ratio; **c**: Absorbance at 280 nm; **d**: Total Nitrogen content; **e**: E4/E6 ratio; **f**: UV ratio Index) in settled and suspended soil loss compared to the original topsoil values at Szengyörgyvár field scale study sites. SOC compounds are derived from UV–VIS absorbance spectra of NaOH solute samples

difference between the suspended sediment and the topsoil is significant (Fig. 30.4c). There is an obvious contradiction between the results based on the C/N ratio method and on the three other, spectroscopic SOC compound prediction methods. A possible reason is that the C/N ratio is not directly affected by the molecular weight and aromaticity.

Conclusions

The value of EF depends on the total soil loss amounts but it is also affected by the vegetation cover. The lower is the amount of the deposited material the higher is EF value (up to 2.4). The components delivered first are the colloid particles with high SOC content. Precipitation events or snow melting with low soil loss values can be as erosive as heavy rainstorms.

At micro scale, SOC seems to be delivered together with other soil colloid particles but at the field scale there is no SOC enrichment in the suspended part of the soil loss. That fact questions the relevance of clay-SOC migration although enrichment is clear in the settled sediment. Possible reasons can be the burial of the particles rich in SOC covered by the coarse fraction during sedimentation or the lack of disaggregation in soil loss. Our results suggest that the main part of SOC is deposited and buried within the catchment.

The SOC compound of soil loss is not equal to that of the original topsoil. Significant differences were measured in relation to topsoil vs. suspended sediment and topsoil vs. settled sediment but the composition of the two types of sediments were similar. Absorbance at 280 nm method, E_4/E_6 and URI methods indicate the enrichment of SOC components of higher molecular weight with condensation of aromatic carbon in soil loss, while C/N ratio method shows the opposite trend. Since the well-humified components seem to be more stable, the buried soil loss is overrepresented in high molecular weight components, therefore carbon sequestration occurs in the deeper horizons.

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Chapter 31
Relating Soil Carbon and Soil Structure to Land Use Management

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Abstract Livestock products from grass contributed €24 billion to the Irish economy in 2011. Mismanagement due to pressure to intensify production results in soil quality deterioration and reduced productivity. This study assessed soil C content (0–10 cm) over a range of land use management from 20 arable crop farms and 20 grassland farms in Ireland. Visual Evaluation of Soil Structure (VESS) was used to score (Sq) each field. The average Sq score was 2.15 for arable land and 2.24 for grassland, with no significant difference between land uses. However, fields under minimum tillage had a significant lower Sq (better soil structure) than fields under conventional tillage. Under grassland management, an increase of Sq (decrease in soil structural quality) with intensification of management was found ($R^2=0.7$). The soil C ranged from 15 to 53 g C kg^{-1} soil under tillage management and from 37 to 104 g C kg^{-1} soil under grassland. It indicates a greater capacity of C storage under grassland. There was a negative correlation between Sq and soil C both under arable and grassland (lower C content with decreased quality). The results indicated that soil management was largely sustainable in term of soil structure (Sq score), but if management intensity increases, many farms could decrease their soil quality.

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Introduction

Soil quality is the capacity of a soil to function while sustaining productivity, maintaining or enriching water and air quality and supporting human health and habitation (SSSA, S-581). Protection of soil quality under intensive land use is important and is a major challenge for agriculture. A basic assessment of soil quality is necessary to evaluate soil health status and to understand the relationship with the land use management (Dexer 2004; Smith 2008). Soil structure is a contributor to, and indicator of soil quality (Mueller et al. 2013). There has been much work examining the interaction of soil structure and tillage (Vyn and Raimbult 1993; Arshad et al. 1999) and grassland (Hassink 1992). There are physical (Karami et al. 2012), chemical and biochemical (Abiven et al. 2009) impacts on soil structure and mechanical deformation is influenced by water content (Watts and Dexter 1998), and pore structures. Soil C is a key factor in maintaining and improving soil quality considering its significant contribution to soil aggregation and structure (Chivenge et al. 2011).

Land use influences soil structure through management and intensity of production. Studies have shown that conventional tillage can break down soil aggregates, reduce SOC and cause degradation (Elliott 1986). While reduced tillage management (no till, zero till) can stabilize soil aggregates (Lal 2002) and protect soil C from decomposition (Syswerda et al. 2011), it can lead to soil compaction (Reichert et al. 2009). Grassland has a greater C content and better pedal structure than soils under arable cropping (Toenshoff et al. 2013; Kodešová et al. 2011). Soils typically gain 3–5 % C when cropland is converted to grassland (Guo 2002). However, soils under grassland have a wide range of C content under different management (Baron et al. 2002). Intensive grazing can reduce soil quality by causing disruption of aggregates and compaction of the surface soil layer, and deforming aggregates can lead to the creation of a flat, comparatively impermeable surface layer composed of dense, unstable clods (Warren et al. 1986). These structural changes influence the soil microbial community and their function (Hiltbrunner et al. 2012). Manure application has been shown to be a positive management for soil structure by increasing aggregate formation and stability (Karami et al. 2012) and soil microbial activity.

Methods have been developed to visually assess soil structural quality. One such method is visual evaluation of soil structure (VESS) (Guimarães et al. 2011), which originated from the method of Peerlkamp (1959) with improvements by Ball et al. (2007). It is a semi-quantitative method that scores the upper 20 cm of soil by visible layers based on color, effort of block extraction, aggregate break up, roots, visible pores, aggregate size and aggregate shape. VESS has been shown to be a valid method for soil structure assessment in European countries, Canada, Australia and China (Ball and Douglas 2003; Mueller et al. 2009b). There is not much information about how well VESS scores (Sq) relate to key soil properties and soil management.

The objectives of this study were to assess soil structure status under arable and grassland management by the VESS method, and to identify key relationships with land use management and soil C content.

Material and Methods

Soil Sampling and Laboratory Analysis

Surface soil samples (0–10 cm) were taken from 20 arable and 20 grassland fields in the eastern half of Ireland between July and November, 2011 when soil water status was suitable from deploying the VESS method. The sites were chosen to be representative of Irish conditions by pre-interview with the farmers before sampling. The sites were located between latitude 52°8′12 °N and 54°20′12 °N and longitude 6°22′42 °W and 8°16′05 °W. Mean daily temperature in summer ranged from12.3 to 15.7 °C, in winter from 4.0 to 7.6 °C, and annual rainfall in the east of Ireland is between 750 and 1,000 mm (http://www.met.ie). In each field, five subplots were identified by walking a ‘W’ in a square 30 m × 30 m, randomly oriented in a homogenous area of the field avoiding gates, feeding and drinking areas and headlands. Each sample comprised of ten sub-samples taken randomly at each point of the ‘W’. Soil bulk density samples were taken using the core method (Blake and Hartge 1986). Soil water content was determined by oven drying (105 °C for 16 h). Texture was measured using the pipette method (Gee and Or 2002). Soil C was measured with a CHN analyzer (TruSpec CN, LECO Corporation).

For grassland fields, classification by management intensity was conceptualized using a classification cube where the time since last reseeding, nitrogen fertilizer input and stocking rate form the x-axis, y-axis and z-axis, respectively. Three levels of intensity were defined for each axis from low to high (Table 31.1). The length of the cubic body diagonal (approx. 5.2 units for a cube 3 × 3 × 3 unit) was treated as the maximum intensity. For each field, the reseeding, N input and stocking rate were classified (Table 31.1) and used to calculate the management intensity as the length of body diagonal relative to the maximum possible (5.2). The value was then rounded to the nearest whole number to create 5 integrated management intensity classes. For arable cropping fields, two sub-groups of fields were classified by tillage types as conventional tillage (CT) and minimum tillage (MT).

Table 31.1 Threshold values for management intensity used to classify grassland fields

Intensity	N usage[a] (kg ha^{-1})	Sward ages (years since last reseeding)	Stocking rate (LSU ha^{-1})
1	0–43	≥20	<1.5
2	43–129	10–20	1.5–2.5
3	≥129	0–10	≥2.5

[a] The national average N-overall usage in grassland was 86 kg ha^{-1} according to the National Fertilizer Application Survey (Lalor et al. 2010); here we used 0.5× and 1.5× the average (43, 129 kg ha^{-1}) as threshold values

The VESS Method

At each subplot VESS was deployed according to the procedure in Guimarães et al. (2011), and each identified layer of soil in the top 20 cm was classified into one of five categories where Sq1 and Sq2 are considered as good quality requiring no change in management, Sq3 is acceptable soil quality but change in management would protect from further decline, and Sq4 and Sq5 indicate poor soil that needs urgent change in management for sustainable productivity. For the method, a soil block (20 × 20 × 20 cm) was extracted by spade and transferred onto a tray, described and then cut into two pieces. One half was broken by hand, keeping soil in relative alignment and scores assigned to each layer identified according to the standard description card. The final score was calculated by weighting using the depth of each soil layer.

Statistic Analysis

The data are presented as the mean value of samples from each subplot and replicate. The mean comparison of soil parameters under tillage and grassland systems was conducted using parametric methods and for Sq using non-parametric methods. Spearman's rho correlation was used to analyze Sq and Pearson product moment correlation all other properties. All statistical analysis was completed using SPSS statistic 20 software.

Results

All sites including arable lands and grassland, soils are clay loam, loam or sandy loam by soil texture (data is not showed here). Of the twenty fields under arable cropping, three were outliers using the VESS method, with two having single grain structure, which is not described by VESS, and one had an unusually fine texture (silty clay) that made application of VESS impossible (Ball et al. 2007; Askari et al. 2013). Therefore, 17 sites were considered for VESS but soil carbon comparison was conducted on all 20 sites. In soils under grassland, six were under high management intensity (score 5), four were under moderately high intensity (score 4), two were under moderate intensity (score 3), four fields were under moderately low intensity (2) and five were under low intensity (score 1). All were analyzed using VESS.

Soil structural quality showed an acceptable status according to the interpretation proposed by the method developers with Sq score ranging from 1.0 to 3.5. There was no significant difference in the average Sq score between soils under tillage (2.15) and grassland (2.24). Soil C content ranged from 15.1 to 53.2 g C kg^{-1} under tillage and from 37.5 to 103.8 g C kg^{-1} under grassland, indicating grassland has significantly greater C content ($P < 0.01$) as expected. Soil water content was also significantly

Table 31.2 Means of selected soil parameters at the time of field sampling (by column, the letter indicates a significant difference at P<0.01)

Land use type	Sq score	Soil C (g kg^{-1} soil)	Water content (g 100 g^{-1} soil)	Bulk density (g cm^{-3})
Tillage	2.15 ± 0.65^{A}	31.4 ± 7.46^{A}	28.8 ± 8.6^{A}	1.11 ± 0.11^{B}
Grassland	2.24 ± 0.74^{A}	61.0 ± 15.13^{B}	52.8 ± 16.4^{B}	0.79 ± 0.11^{A}

Table 31.3 Correlation between selected soil properties under tillage and grassland management

	Sq	Soil C	Water content	Bulk density
Tillage system				
Sq	1	–0.044	0.366**	–0.047
Soil C		1	0.035	–0.469**
Grassland system				
Sq	1	–0.623**	–0.182	0.335
Soil C		1	0.499*	–0.544*

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

greater under grassland than tillage ($P<0.01$), and bulk density was significantly lower under grassland ($P<0.01$) (Table 31.2).

Under tillage management, fields under minimum tillage showed a significantly lower Sq of 1.95 than fields under conventional tillage with Sq of 2.29 (see data in Askari et al. (2013)). The increase of Sq score with management intensity under grassland ($R^2=0.7$), indicating a deterioration in soil structure quality with increased management intensity, but only one site had reached the critical limit of $Sq \geq 4.0$. Soil C significantly decreased with management intensity under grassland ($P<0.05$). There was a strong negative correlation between Sq and soil C in grassland fields (decreased quality related to lower C content), but not in tillage fields (Table 31.3).

Discussion

Conventional tillage and minimum tillage for cereal production are the most common arable systems in Ireland (Lafferty et al. 1999). The range of intensity of management found in Ireland as reported in National Farm Surveys was captured by the sampling strategy. The grassland sites were also representative, however the grassland management is less commonly found elsewhere in the world, being largely low-cost, grass-based, rotational grazing for milk or meat production.

In general, the Sq scores indicated that the sample sites had good soil structure, which was sustainable under current management for both arable and grassland systems. The significantly better soil structure under minimum tillage was in agreement with other studies (Mueller et al. 2009a, b; Soane et al. 2012), and it might be due to more effective porosity and better soil aggregation than under conservation tillage (Bhattacharyya et al. 2006), since conventional tillage can result in a smaller aggregates and soil structural degradation (Munkholm et al. 2005). Compared to arable land, grassland has a diversity of management, largely related to the factors used for classification (Table 31.1), which might be expected to result a varied soil structural quality. The deterioration of soil structural quality under more intensive grazing could be evidence that such grazing can damage soil structure and result in compaction (Hiltbrunner et al. 2012; Bell et al. 2011), particularly if grazing coincides with prolonged wet periods.

Arable land for food production is typically managed with inorganic fertilizer to maintain high yield (Stewart et al. 2005). In addition to limited plant residue return to the soil, the C content of the soil was lower than that in grassland, as found in this experiment. Given that soil C is a key factor in soil structure formation, and organic carbon enhances aggregate stability (O'Brien and Jastrow 2013), the difference in the relationships between soil C with Sq score under arable and grassland management perhaps indicates the important function of stable soil aggregates in maintaining soil structure. The weak relationship between Sq and soil C under arable management requires further investigation, but suggests C content cannot be used as a soil quality indicator under arable management. Long-term experimentation has shown improved soil structural quality under minimum compared to conventional tillage management (McGarry et al. 2000; Askari et al. 2013). This is believed to be due to limited disturbance of aggregates resulting in aggregate stability and protection of soil carbon. The results might suggest that tillage management in Ireland is not sufficiently intensive to reach a critical threshold for soil damage, but this requires further investigation. The strong relationship between Sq and C under grassland management indicated that for this range of management intensity, small changes are likely to have a detectable effect on both stored C and structural quality.

Conclusion

Nearly all of the sites visited had a $Sq < 3.5$, which indicated that under the range of arable and grassland management intensity typically found in Ireland, structure has not deteriorated to unacceptable levels ($Sq \geq 4.0$). Arable land had slightly better soil structural quality under minimum tillage than that under conventional tillage. For grassland, more intensive management seems to be leading to slight deterioration in soil structural quality and this situation should be observed carefully and managed for long-term sustainable productivity. For grassland management, soil C was a useful indicator of both management intensity and structural quality (as described by Sq). For tillage management soil C did not relate in the same way to structural quality and management, and requires further research.

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Chapter 32
Microbial Biomass Carbon and Nitrogen Under Different Maize Cropping Systems

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Abstract Soil microbial biomass carbon (C) and nitrogen (N) under different maize cropping systems were evaluated at Kampe Irrigation Project farmlands in Southern Guinea savanna region of Nigeria. In 40-ha irrigated plots that have been cultivated for minimum of 3 years with sole maize, maize/okra, and maize/cowpea intercrops, maize/okra relay cropping and a 5 year fallow were sampled and analysed for organic C, microbial biomass C and N. Microbial biomass C and organic C were significantly lower ($P<0.05$) in sole maize, maize/okra intercrop and maize/okra relay plots compared to maize/cowpea intercrop and fallow plots. Microbial biomass C in maize/cowpea plot was twice as high than that of sole maize and maize/okra relay cropping. The microbial biomass N in maize/okra intercrop (62 mg/kg) and maize/cowpea intercrop (60 mg/kg) was significantly ($P<0.05$) higher than other plots. The microbial biomass C:N ratio in soils under sole maize, maize/cowpea intercrop and maize/okra relay was significantly ($P<005$) higher than other treatments. It is concluded that soil microbial biomass and organic C can be enhanced in maize cropping system through intercropping with legumes and application of short fallow.

Keywords Microbial biomass • Cropping system • Fallow • Maize • Okra

Introduction

Soil microorganisms are important in the mineralization of nutrients that are needed for plant growth. Soil microbial processes can be measured through the determination of microbial biomass C in the soil (Jenkinson and Ladd 1981; Benintende et al. 2008).

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Microbial biomass is an important source and sink of nutrient and a significant indicator of soil quality (Qu and Wang 2008).

The Kampe Irrigation Project (KIP) is one of the Nigerian government initiatives to increase food production. The project is estimated to irrigate about 4,100 ha of land for the production of crops like maize, vegetables, sorghum and rice (Adeniran et al. 2010). In the irrigated farmlands, farmers cultivate different types of crops planted solely or intercropped with other crops. It is well established that farming management activities have various effect on soil microorganisms (Silva et al. 2010; Sun et al. 2009). Many maize farmers in the KIP farmlands tend to adopt a cropping system continuously for many years taking advantage of all year round irrigation. This intensity of cultivation has made it imperative to evaluate the quality of soil in the KIP farmlands.

Silva et al. (2010) stated that studies of microbial biomass may be valuable as adjunct to research on the effect of agricultural practices on soil quality and productivity. Since information was lacking on the biological properties of soils in many KIP farmlands, the research was conducted to determine the microbial biomass C (MBC), microbial biomass N (MBN) and organic C as affected by maize cropping systems in KIP farmlands.

Materials and Methods

Study Site

The experiment was carried out at KIP Site, Ejiba, Kogi State, Nigeria, located between longitude 6°37′ E and 6°42′ E and latitude 8°34′ N and 8°38′ N of the equator. The soil classification was typic rhodustalf. The project irrigates about 4,100 ha of land for the production of maize, vegetables, sorghum, and rice all the year round. Irrigation is usually the gravity method.

At one of the site in Ejiba (about 40 ha), farmers' fields (farmlands) adjacent to each other with four different maize cropping systems were selected for the study. All selected farmlands have had a minimum of 3 years of maize cropping systems, and each of the farmlands was about 1 ha in size and under cultivation when soil sampling was done. The maize cropping systems identified were: sole cropping (MA), maize/okro intercropping (M-OI) and maize/cowpea intercropping (M-CI), maize/okro relay cropping (M-OR) and fallow land (FA). All the four maize fields have had fertilizer applications (mostly urea (100 kg/ha) and NPK 20:10:10 (200 kg/ha) for MA, M-OI and M-OR and triple superphosphate (80 kg/ha) for M-CI) at every season of cultivation. The FA had been fallowed 4 years and the last crop before it was fallowed was sole maize. Ridging was common to all the maize fields in order to allow irrigation water in the furrow. The farmers usually apply the maize stovers and other crop residues on soil surfaces after harvesting.

Table 32.1 Soil physical and chemical properties of KIP farmlands used for the study

Soil property	FA[a]	MA[b]	M-CI[c]	M-OI[d]	M-OR[e]
pH (H_2O)	6.8	6.0	6.6	6.4	6.0
Total N (g/kg)	0.64	0.53	0.61	0.49	0.49
Available P (mg/kg)	21.86	17.29	16.65	13.86	20.42
Mg (cmol kg^{-1})	0.89	0.53	0.72	0.44	0.38
Ca (cmol kg^{-1})	1.24	0.39	1.63	0.52	0.46
K (cmol kg^{-1})	0.23	0.08	0.15	0.13	0.11
Na (cmol kg^{-1})	0.14	0.02	0.11	0.07	0.04
Sand (g/kg)	771	887	759.6	882	892
Silt (g/kg)	39	58.9	41.2	53	59.5
Clay (g/kg)	190	54.1	199.2	65	48.5

[a]Fallow; [b]Sole maize; [c]maize/cowpea intercrop; [d]maize/okra intercrop; [e]maize/okra relay cropping

Soil Sampling and Analyses

Soil samples were randomly collected from the selected farmlands at 12 different points which were bulked into three sample replicates. Each replicate sample was divided into two for microbial and chemical analyses. Field moist samples were passed through a 2 mm sieve to remove plant materials prior to microbial analysis and stored at 4 °C. For chemical analysis, samples were air dried and grounded to pass through 0.5 mm diameter sieve. Soil pH was obtained in a 1:1 soil:water ratio (IITA 1982); total N by the macro-Kjeldahl method (Bremner and Mulvaney 1982); organic C by chromic acid digestion (Heanes 1984); Phosphorus and exchangeable cations were done by Mehlich 3 extraction (Mehlich 1984). Available P was determined colorimetrically using the Technicon AAII Autoanalyser, the cations (Ca, Mg, K) using Atomic Absorption Spectrophotometer and Na by flame photometry (IITA 1982). Particle size analysis was done according to the Bouyoucos (1951) hydrometer method using sodium hexamataphosphate as the dispersant. A summary of the physico-chemical properties of the soils is given in Table 32.1. Soil microbial biomass C and N were determined using the fumigation-extraction procedures proposed by Vance et al. (1988) and Brookes et al. (1985), respectively.

Statistical Analyses

The experimental design for the study was Randomized Complete Block Design (RCBD) with three replicates. Treatments were statistically evaluated by analysis of variance using Fischer LSD to compare means at $P<0.05$. All statistical analyses were performed using the statistical package SAS version 9 (SAS 2009).

Results and Discussion

The soil used for the study revealed a near neutral to slightly acidic soil (Table 32.1). Total N of the soil was very low but available P was moderate in the five fields. The exchangeable Ca and Na were relatively high for FA and M-CI field compared to other fields. The organic C of the soils revealed significantly ($P < 0.05$) higher content in the M-CI and FA than other cropping systems which was more than 500 % (Fig. 32.1).

Soil analyses confirmed that the field used for MA was relatively lower in fertility compared to the fields for other maize cropping systems. MA had the lowest organic C and cation exchange capacity (CEC) which probably lowered microbial biomass in the soil because close positive correlation have been shown to exist between soil organic C, CEC and microbial biomass C (Huang et al. 2004; Loureiro et al. 2010).

The MBC in M-CI was significantly ($P < 0.05$) higher than other maize cropping systems. There was more than two-fold increase when it was compared with MBC of sole maize (Table 32.2). Also, the FA had MBC that was significantly higher ($P < 0.05$) than other maize cropping systems except that of M-CI. The MBN was also significantly higher in M-CI and M-OI than the other cropping systems. Higher organic C, MBC and MBN observed in the M-CI is an indication of higher soil quality in the system. Similar results have been observed with the intercropping of legumes with other crops (Song et al. 2007; Sun et al. 2009). Higher organic C and MBC in M-CI and FA fields were probably due to the amount of root residues in the soil and activity of the living root of cowpea in M-CI. Close spacing and density of plants in M-CI and FA allowed more root residues than other maize cropping systems. Okra used in M-OI had more than twice the spacing of cowpea when intercropped with maize.

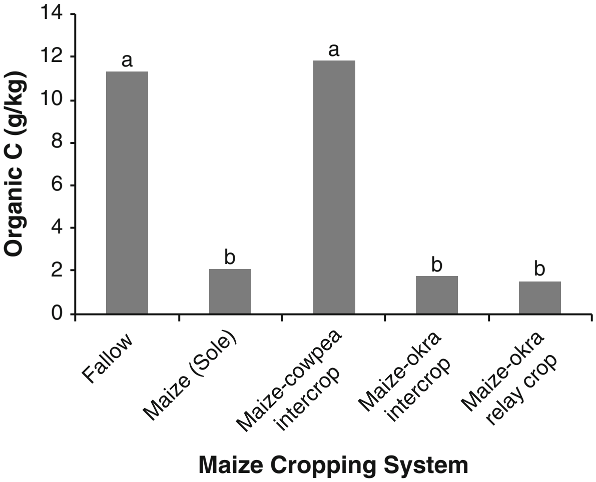

Fig. 32.1 Organic C of KIP farmlands as affected by maize cropping systems. *Bars* with the same letters are not significantly different according to Fischer LSD ($P > 0.05$)

Table 32.2 Soil microbial biomass C and N and their ratio as affected by maize cropping system in KIP farmlands

Maize cropping systems	MBC (mg/kg)	MBN (mg/kg)	Microbial C:N ratio
Fallow	220.67	44.58	5.0
Maize (Sole)	121.67	24.33	5.1
Maize-cowpea intercrop	246	60.3	4.1
Maize-okra intercrop	133	61.61	2.2
Maize-okra relay crop	127	25.31	5.1
LSD (0.05)	16.87	8.82	1.3

LSD (0.05) – significant at $P<0.05$

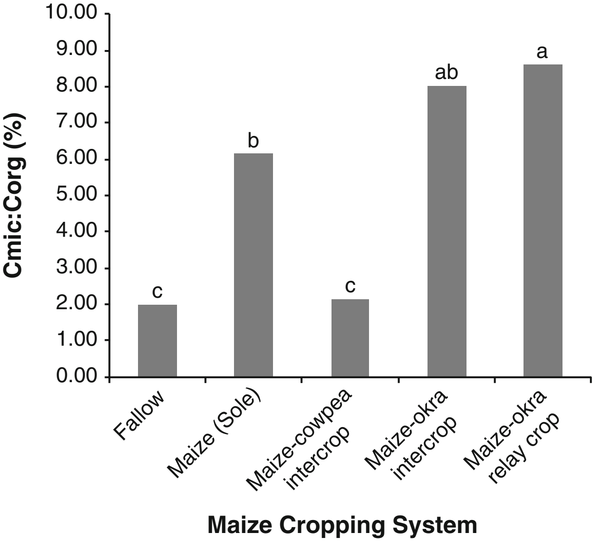

Fig. 32.2 The percentage microbial biomass C to Organic C (Cmic: Corg) of KIP farmlands as affected by maize cropping systems. *Bars* with the same letters are not significantly different according to Fisher LSD ($P>0.05$)

The microbial C:N ratios which ranged from 2.2 to 5.1 in all the fields were generally low but within the range observed in some previous studies (Smith and Paul 1990; Balota and Auler 2011). The low C:N ratio may probably be due to composition of microbes in the soil, as was also found by Smith and Paul (1990). Bacteria were probably more active than fungi in KIP farmlands because average fungi have a greater C:N than bacteria with C:N of fungal biomass expected at 5–15 and that of bacteria at approximately 3–6 (Strickland and Rousk 2010). The flood irrigation practiced in KIP allows water to remain in the furrows of the ridges creating intermittent anaerobic condition in soil which may not support the growth of many fungi. It has been stated that C:N ratio of fungal hyphae is higher than those of bacteria (Anderson and Domsch 1980).

In this study, the percentage of MCB to organic C (Cmic: Corg) ranged between 2.2 and 8.6 (Fig. 32.2) which was consistent with the range of 2.9–7.8 observed by Balota and Auler (2011) in a tropical environment. It is interesting to note that M-CI and FA that had highest MCB had the lowest Cmic: Corg and the Cmic: Corg in the three other cropping systems was in fact higher than 5 %. In spite of low organic C in the soil of M-OI, M-OR and MA, the enrichment of microbial biomass was proportionately higher than those of M-CI and FA.

Conclusions

The biological properties of maize farmers' fields in the KIP farmlands were different due to the cropping systems that were practiced. Legume intercropping with maize offers cropping system that may increase soil quality as indicated by the organic C, MBC and MBN in the M-CI field. Farmers in KIP farmlands need to incorporate into their cropping systems legume intercropping or rotation, but short fallow periods can also help the soil to sustain soil quality.

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Chapter 33
Mitigation Effect of Farmyard Manure Application on Greenhouse Gas Emissions from Managed Grasslands in Japan

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Abstract Applying manure can lead to decrease of chemical nitrogen (N) fertilizer use and increase of soil carbon (C) sequestration. The effect of manure application on net ecosystem C balance (NECB), methane (CH_4) and nitrous oxide (N_2O) emissions and global warming potential (GWP) was examined at four managed grasslands on Andosols in different climatic regions in Japan for 3 years. At adjoining manure and fertilizer plots in each site, net ecosystem exchange (NEE) and CH_4 and N_2O fluxes were measured by the eddy covariance method and dark chamber methods, respectively. Manure application decreased fertilizer N application rate in manure plot to 65–88 % in fertilizer plot. NECB (= NEE−C applied in manure + harvested C) was higher in fertilizer plot (1.9 ± 0.9 MgC ha^{-1} $year^{-1}$) than

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in manure plot (−1.8 ± 1.8 MgC ha^{-1} $year^{-1}$), indicating that the soils in fertilizer plots lost C. There was no significant difference in harvested C between fertilizer and manure plots (4.3 ± 0.8 and 4.1 ± 0.6 MgC ha^{-1} $year^{-1}$, respectively). NEE showed more CO_2 uptake in fertilizer plots (−2.4 ± 1.1 MgC ha^{-1} $year^{-1}$) than in manure plots (−1.6 ± 0.7 MgC ha^{-1} $year^{-1}$), but manure application could compensate for the shortage in NEE. CH_4 emission was close to zero, while the N_2O emission was greater in manure plots (6.2 ± 3.7 kgN ha^{-1} $year^{-1}$) than in fertilizer plots (3.6 ± 3.2 kgN ha^{-1} $year^{-1}$). The difference of GWP between manure and fertilizer plots showed a negative relationship with manure C application rate ($y = -4.45 \ln(x) + 2.84$; $R^2 = 0.85$; $p < 0.01$), indicating that manure application rate more than 2 MgC ha^{-1} $year^{-1}$ can mitigate global warming in the Japanese grasslands.

Keywords Carbon dioxide • Global warming potential • Methane • Net ecosystem carbon balance • Net ecosystem exchange • Nitrous oxide

Introduction

Grasslands account for approximately 40.5 % of the earth's terrestrial land area, and are important ecological and socio-economic resources through their contribution to biodiversity and their use for food, forage, and livestock production (Adams et al. 1990; White et al. 2000; Soussana et al. 2007). Chemical fertilizer and farmyard manure are applied to grasslands to increase productivity, especially in developed countries (Bouwman et al. 2002b). At the same time, grasslands contribute to the biosphere-atmosphere exchange of greenhouse gases, with their fluxes intimately linked to management. Carbon dioxide (CO_2) is exchanged between the soil, vegetation and atmosphere. Grassland soils are large stores of carbon (C), and thus can act as a net sink for atmospheric CO_2 (Soussana et al. 2004). Improving the primary productivity of grasslands by nitrogen (N) fertilizer supply may favor below-ground C storage and increase soil organic C (Conant et al. 2001). In addition, manure application increases C input to soil and consequently enhances SOC concentration (Lal 2004).

Natural grassland can be a methane (CH_4) sink, where CH_4 is oxidized to CO_2 or assimilated into microbial biomass in aerobic condition (Mosier et al. 1991). Application of chemical N fertilizer might decrease CH_4 uptake (Mosier et al. 1991), and the form of applied N has a significant effect on CH_4 metabolism.

In grassland soils, nitrous oxide (N_2O) is produced as a by-product and intermediate of microbial nitrification and denitrification processes, respectively (Bouwman 1990). These processes require mineral N (ammonium and nitrate) as a substrate, and are controlled by soil moisture content, temperature, pH and organic C (Bouwman 1990; Maag and Vinther 1996; Mosier 1998; Yamulki et al. 1997). The application of chemical N fertilizer and livestock manure could augment N_2O emissions, and N_2O emissions can be affected by fertilizer type (Bouwman et al. 2002a;

Akiyama and Tsuruta 2003; Akiyama et al. 2006; Mori and Hojito 2011). Manure with a large and easily mineralizable organic C content stimulates microbial activities and thus N_2O emissions (Drury et al. 1991; Chadwick et al. 2000).

This paper reports on the evaluation of the effect of farmyard manure application in four Japanese managed grasslands on Andosols under different climatic regions ranging from warm to cool temperate, with a full accounting of greenhouse gas emissions.

Materials and Methods

Site Description

The study was conducted for 3 years, from October 2004 to December 2007. The grasslands were located at Nakashibetsu (NKS; 43°32′N, 144°58′E), Shizunai (SZN; 42°26′N, 142°29′E), Nasushiobara (NSS; 36°55′N, 139°56′E) and Kobayashi (KBY; 31°58′N, 130°56′E). Annual mean air temperatures were 5.2, 7.9, 12.2 and 15.8 °C in NKS, SZN, NSS and KBY, and annual precipitation was 1,160, 1,365, 1,561 and 2,595 mm year^{-1}, respectively.

The soils at all sites were classified as Andosols (IUSS Working Group WRB 2006), and were categorized as well-drained soils, except for the SZN site where a mottled layer was observed 36 cm below the soil surface. The pH of the topsoil ranged from 5.3 to 6.1 before the treatments were initiated. The ranges of soil total C and total N contents of topsoil were 36.8–65.2 g kg^{-1} and 3.31–5.10 g kg^{-1}, respectively (Shimizu et al. 2013). The dominant grass species were Timothy (*Phleum pretense* L.) at the NKS site, reed canarygrass (*Phalaris arundinacea* L.) and meadow foxtail (*Alopecurus pratensis* L.) at the SZN site, Orchardgrass (*Dactylis glomerata* L.) and Italian ryegrass (*Lolium multiflorum* Lam.) at the NSS site, and Italian ryegrass and Southern crabgrass (*Digitaria ciliaris* (Retz.) Koeler) at the KBY site. All the sites were managed as hay meadow, where no animals were grazed during the study period. Grass was harvested twice per year at the NKS and SZN sites, and three or four times per year at the NSS and KBY sites. During the study period, over-seeding was conducted at the NSS site in September 2007, and at the KBY site in October 2007 to maintain grass productivity.

Management Practices

Two treatments were set up: one for treatment with chemical fertilizer (fertilizer plot); the other with cattle manure and chemical fertilizer (manure plot) at all the sites. Fertilizer was applied at the beginning of grass growing and after each harvest. The mean application rates of fertilizer N in fertilizer plots were 99 ± 1, 140 ± 58, 198 ± 12, 205 ± 36 kgN ha^{-1} $year^{-1}$ in the NKS, SZN, NSS and KBY sites, respectively. Ammonium-based fertilizer or combination fertilizer of ammonium and urea were applied. Beef cattle or dairy cattle manure was applied at the manure plots once a year after last harvest in the NKS, NSS and KBY sites, and in spring in the SZN site. The mean application rates of manure were 42.0 ± 3.5 Mg (4.9 ± 0.4 MgC, 240 ± 32 kgN) ha^{-1} $year^{-1}$ in NKS site, 43.7 ± 0.4 Mg (6.5 ± 1.0 MgC, 292 ± 50 kgN) ha^{-1} $year^{-1}$ in SZN site, 25.8 ± 9.3 Mg (3.1 ± 1.0 MgC, 131 ± 60 kgN) ha^{-1} $year^{-1}$ in NSS site, 16.7 ± 5.8 Mg (2.9 ± 0.9 MgC, 215 ± 86 kgN) ha^{-1} $year^{-1}$ in KBY site, respectively. The difference in rate among sites was based on the adequate amount of potassium application to the fields, and the mean application rates of fertilizer N in manure plots were 64 ± 23, 95 ± 64, 174 ± 31, 160 ± 18 kgN ha^{-1} $year^{-1}$ in the NKS, SZN, NSS and KBY sites, respectively. The manure application decreased chemical fertilizer N application rate to a range of 65–88 %. At the manure plots, nutrient supply rate from manure was estimated by multiplying application rate by mineralization rate, and the difference between nutrient supply rate from manure and application rate in fertilizer plots was supplied with chemical fertilizer. The N mineralization rates were estimated based on Uchida's model (Shiga et al. 1985) which was developed in Japan, and were 13.2, 7.02 and 5.53 % of total manure N in the first to third years after manure application, respectively. The mineralization rate of phosphorus and potassium from the manure was estimated based on a handbook on animal waste management and utilization in Hokkaido published in 2004 (Anonymous 2004), namely 20 % of phosphorus and 70 % of potassium are available in the applied year, 10 % of phosphorus and 10 % of potassium are available the second year, respectively.

Environmental Variables

Daily air temperature and precipitation data were either obtained from a meteorological station located at the facility housing site in NSS or from the nearest Automated Meteorological Data Acquisition System (AMeDAS) station of the Japan Meteorological Agency in NKS, SZN and KBY.

Net Ecosystem Carbon Balance Measurements

Each treatment plot at four sites was equipped with an eddy covariance system in autumn 2004 for the measurement of net ecosystem exchange (NEE) of CO_2. Hirata et al. (2013) reported annual NEE from 2005 to 2007 at all sites and plots, and the data sets were used in this study.

Net ecosystem carbon balance (NECB) in managed grasslands includes C input through manure application and C output through crop harvest and grazing as well as NEE (Shimizu et al. 2009). In this study, the sites and plots were not grazed, and NECB was estimated using the following equation:

$$\text{NECB} = \text{NEE} - \text{C applied in manure} + \text{harvested C}$$

Positive NECB represents C loss from the ecosystem. The harvest for all the sites and plots were also reported by Hirata et al. (2013). The amount of harvested C was estimated at every harvest from dry weight of harvested biomass per unit ground area multiplied by C content of dry biomass.

CH_4 and N_2O Emission Measurements

CH_4 and N_2O fluxes from soil to atmosphere were measured by the dark chamber method with four or six replications per each treatment plot. Shimizu et al. (2013) reported the annual CH_4 and N_2O emissions from 2005 to 2007 at all sites and plots, and the data sets were used in this study. The flux measurements were basically conducted every few weeks during the crop growing season, but the frequency was increased to twice per week just after fertilization, and was decreased to once a month during the snow cover season.

Global Warming Potential

Global warming potential (GWP, Mg CO_2eq-C ha^{-1} year^{-1}) for a time horizon of 100 years was calculated by following equation:

$$\text{GWP} = \text{a NECB} + \text{b } CH_4 \text{ emission} + \text{c } N_2O \text{ emission}$$

where the units of NECB, CH_4 emission and N_2O emission are MgC ha^{-1} year^{-1}, kgC ha^{-1} year^{-1} and kgN ha^{-1} year^{-1}, respectively; a, b and c are the conversion factors which are 1 for CO_2, $10^{-3} \times (16/12) \times 25 \times (12/44)$ for CH_4 and $10^{-3} \times (44/28) \times 298 \times (12/44)$ for N_2O, respectively (IPCC 2007). In the calculation, the NECB was assumed as a CO_2 balance, that is, harvested C relates to CO_2 emission from the field, and C applied in manure relates to CO_2 uptake by the field.

Results and Discussion

Net Ecosystem Carbon Balance

The harvested C ranged from 2.9 to 5.5 MgC ha^{-1} year^{-1}, and there was no significant difference in harvested C among the sites and between the fertilizer and manure plots (Fig. 33.1a). Gilmanov et al. (2007) reported a strong positive effect of

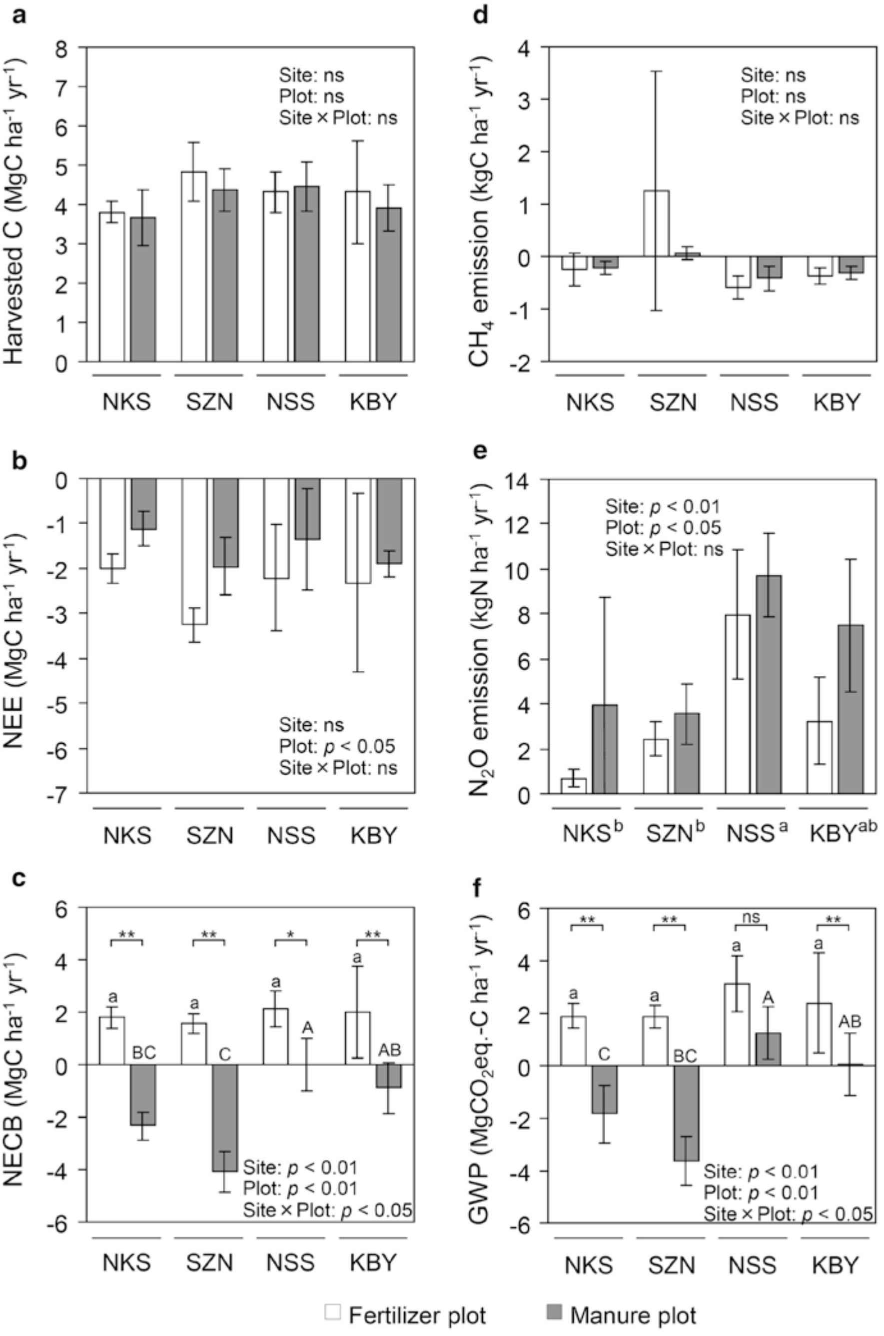


Fig. 33.1 Comparison of harvested carbon (C) (**a**), net ecosystem exchange (NEE) of CO_2 (**b**), net ecosystem carbon balance (*NECB*) (**c**), CH_4 emission (**d**), N_2O emission (**e**) and global warming potential (*GWP*) (**f**) between the manure and fertilizer plots and among the four sites. NKS, SZN, NSS and KBY represent Nakashibetsu, Shizunai, Nasushiobara and Kobayashi, respectively. *Error bar* represents standard deviation (n=3). *ns*, non significant, *; $p<0.05$, **; $p<0.01$, and different letters indicate significant differences at the 0.05 level (two-way ANOVA and Turkey HSD *post hoc*)

precipitation on the gross primary production for European grassland in the range of 300–800 mm year^{-1} in annual precipitation, and no clear correlation in the range higher than 800 mm year^{-1}. In this study, annual precipitation ranged from 981 to 3,085 mm year^{-1}, therefore the production was unlikely to be limited by precipitation. The harvested C in the fertilizer and manure plots were 4.3 ± 0.8 and 4.1 ± 0.6 MgC ha^{-1} year^{-1}, respectively. The difference of harvested C between the treatments did not relate to application rate of manure C (Fig. 33.2a). These data indicate that the manure application combined with chemical fertilizer application did not reduce harvested C compared with chemical fertilizer only application.

There was no significant difference in NEE among sites, but significant differences were found between the treatment plots ($p < 0.05$) (Fig. 33.1b). The NEE in the fertilizer and manure plots were −2.4 ± 1.1 and −1.6 ± 0.7 MgC ha^{-1} year^{-1}, respectively. This indicates more net CO_2 uptake in the fertilizer plots. However, there was no significant difference in grass production between plots because harvested C in both plots were in the same range. Therefore, the differences in NEE between the plots is likely caused by organic matter decomposition. The difference of NEE between treatments was 0.9 ± 0.9 MgC ha^{-1} year^{-1} on average, and the rate of C loss as CO_2 from total amount of C applied in manure in 3 years was estimated as 25 ± 37 %. However, the difference of NEE showed no clear correlation with application rate of manure C (Fig. 33.2b). This is probably because the decomposition rate of manure may be intricately affected by temperature (Kirschbaum 1995), soil moisture (Murwira et al. 1990) and C:N ratio of the manure (Delve et al. 2001).

There were significant differences in NECB among sites ($p < 0.01$), and between treatment plots ($p < 0.01$) (Fig. 33.1c). In addition, there was significant interaction of sites and treatments ($p < 0.05$). For all sites, NECB was higher in fertilizer plots (1.9 ± 0.9 MgC ha^{-1} year^{-1}) than in manure plots (−1.8 ± 1.8 MgC ha^{-1} year^{-1}) (Fig. 33.1c). These results indicate that grassland soils of all sites will lose C without manure application. The difference of NECB between manure and fertilizer plots had a negative relationship with application rate of manure C ($y = -3.98 \ln(x) + 1.86$; $R^2 = 0.89$; $p < 0.01$) (Fig. 33.2c). This indicates that an application rate of manure C more than 1.6 MgC ha^{-1} year^{-1} can make NECB in manure plots smaller than in fertilizer plots.

CH_4 Emission

The CH_4 emissions ranged from −0.8 to 0.1 kgC ha^{-1} year^{-1} except for SZN site of 2007 (3.89 and 0.21 kgC ha^{-1} year^{-1} for fertilizer and manure plots, respectively). There was no significant difference in CH_4 emission among sites (Fig. 33.1d). CH_4 production and consumption are reported to be strongly controlled by soil moisture (van den Pol-van Dasselaar et al. 1998; Kammann et al. 2001). Soil moisture content was greater in the poorly drained soil at the SZN site than in the well drained soils at the other sites (Shimizu et al. 2013). The large CH_4 emissions at the SZN site could be caused by a large soil moisture content.

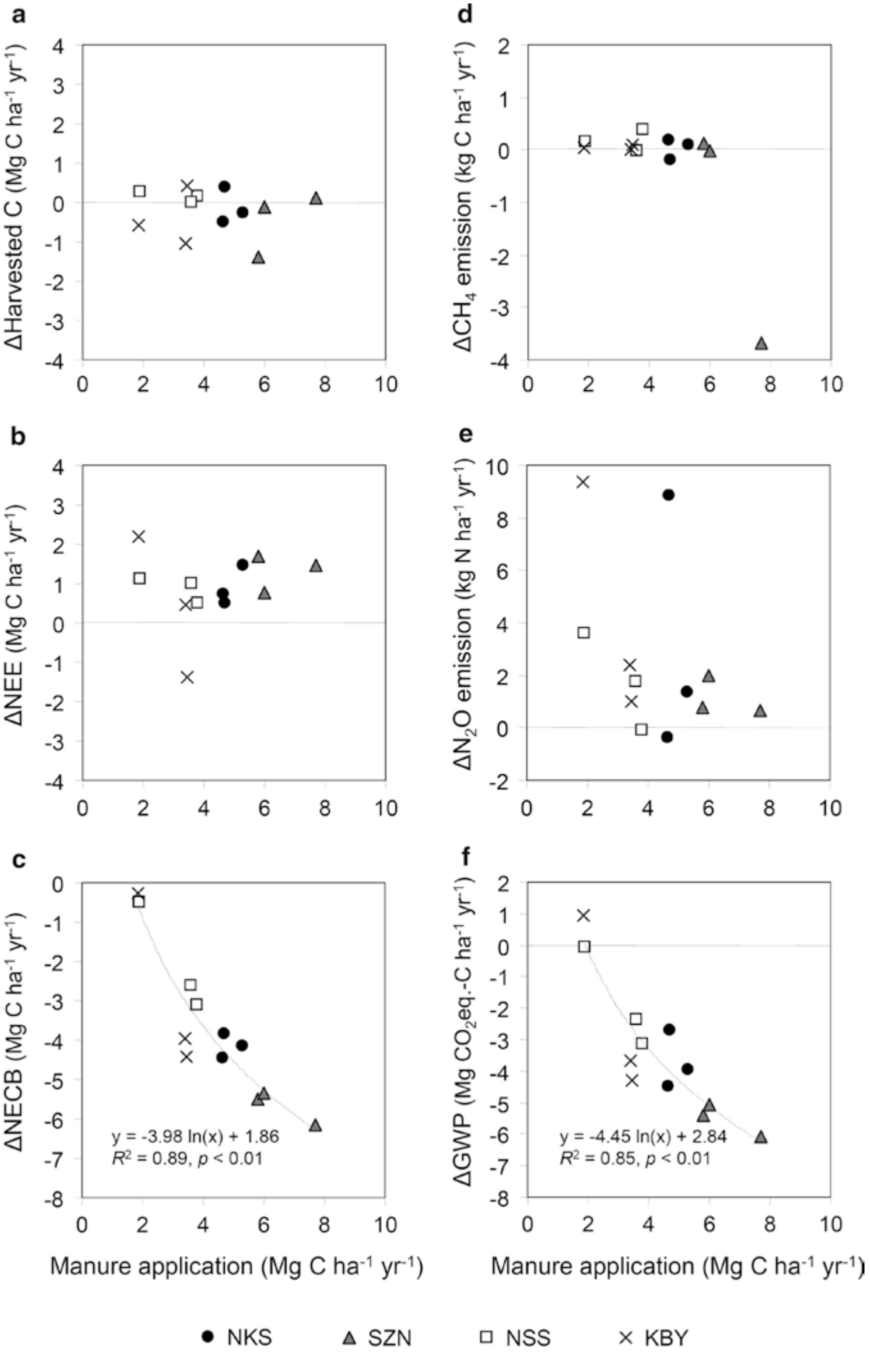


Fig. 33.2 The difference in harvested carbon (C) (**a**), net ecosystem exchange (*NEE*) of CO$_2$ (**b**), net ecosystem carbon balance (*NECB*) (**c**), CH$_4$ emission (**d**), N$_2$O emission (**e**) and global warming potential (*GWP*) (**f**) between the manure and fertilizer plots (Manure plots – Fertilizer plots) compared with the application rate of manure C. NKS, SZN, NSS and KBY represent Nakashibetsu, Shizunai, Nasushiobara and Kobayashi, respectively

The CH_4 emission in the fertilizer and manure plots were 0.01 ± 1.25 and −0.22 ± 0.23 kgC ha^{-1} $year^{-1}$, respectively, and there was no significant difference between plots (Fig. 33.1d), and the difference of CH_4 emission between treatments did not relate to application rate of manure C (Fig. 33.2d). The application of fertilizer N can reduce CH_4 uptake (Mosier et al. 1991). However, in our study sites, there was no apparent correlation between CH_4 emission and the application rate of chemical fertilizer N, including control plots, which received neither fertilizer nor manure (Shimizu et al. 2013). Kammann et al. (2001) also reported that no inhibition of CH_4 oxidation occurred regardless of the amount of N fertilizer applied, while average CH_4 uptake rates were decreased with increasing mean soil moisture.

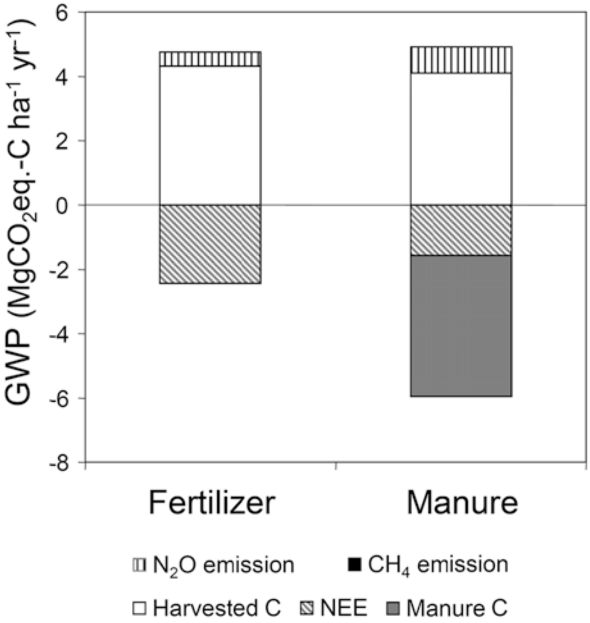
N_2O Emission

There were significant differences in N_2O emission among sites ($p < 0.01$) (Fig. 33.1e). The N_2O emission was highest in NSS site (4.7–11.8 kgN ha^{-1} $year^{-1}$), and followed by KBY (1.5–10.8 kgN ha^{-1} $year^{-1}$), SZN (1.5–4.9 kgN ha^{-1} $year^{-1}$) and NKS (0.3–9.5 kgN ha^{-1} $year^{-1}$) sites. Shimizu et al. (2013) reported that background N_2O emission and fertilizer induced N_2O emission factor were positively correlated to precipitation. Most likely the higher N_2O emissions in the NSS and KBY sites were caused by higher precipitation, resulting in enhanced denitrification. Shimizu et al. (2010) reported that N_2O at the SZN site was produced mainly by denitrification based on the results of N_2O/NO ratio. Mori and Hojito (2011) reported that cumulative precipitation during the 18-day period before and the 12-day period after N application were important control factors for N_2O emissions. This indicates that not only the amount of precipitation but also the timing of N application with respect to precipitation was an important factor controlling N_2O emission, and lead to the inter-sites and inter-annual variation of N_2O emissions.

The N_2O emission in manure plots was 6.2 ± 3.7 kgN ha^{-1} $year^{-1}$, and greater than that in the fertilizer plots of 3.6 ± 3.2 kgN ha^{-1} $year^{-1}$ ($p < 0.05$) (Fig. 33.1e). Compared to N_2O emission induced by chemical fertilizer, relatively low N_2O emissions (<1 % of the N applied) have been found for animal manures applied to grassland (Velthof et al. 1997; Chadwick et al. 2000; Akiyama and Tsuruta 2003; Mori and Hojito 2011). However, in this study, we used chemical N fertilizer in the manure plots. High available C from applied manure and mineral N from chemical fertilizer may have enhanced denitrification and N_2O production in the manure plots. There was a tendency for the difference of N_2O emission between the treatments to decrease with the increase of the application rate of manure C (Fig. 33.2e). Large rates of manure application can reduce chemical N fertilizer application rate and may reduce N_2O emission in manure plots (Mori and Hojito 2012).

Manure will be mineralized slowly and have a long-term effect after application (Ginting et al. 2003). It will also promote N_2O emissions by providing substrates for nitrification and denitrification. Jager et al. (2011) have reported that CO_2 and N_2O emissions from arable soils increased with increasing soil C and N stocks as a result

Fig. 33.3 Comparison of the contribution of the components of global warming potential (*GWP*) between the manure and fertilizer plots



of the regular application of farmyard manure for many years. However, large N availability will also increase plant growth (Baer and Blair 2008). Therefore, continuous application of manure can reduce supplementary application rates of chemical fertilizer over the years in the manure plots. This may mitigate N_2O emission. At the NSS site, Mori and Hojito (2012) reported that reduction in supplementary application rates of chemical N fertilizer in manure plots could have reduced the N_2O emissions compared with the emissions in fertilizer plots from the fourth year.

Global Warming Potential (GWP)

There were significant differences in GWP among sites ($p<0.01$), and between treatment plots ($p<0.01$) (Fig. 33.1f). In addition, there was significant interaction of sites and treatments ($p<0.05$). The GWP was greater in fertilizer plots than in manure plots except at the NSS site. The difference of GWP between the manure and fertilizer plots had a negative relationship with application rate of manure C ($y = -4.45 \ln(x) + 2.84$; $R^2 = 0.85$; $p<0.01$) and was negative at an application rate of manure C more than 1.9 MgC ha^{-1} $year^{-1}$ (Fig. 33.2f). This indicates that increasing application rate of manure C can mitigate global warming at least at the site scale.

Figure 33.3 shows that major contributors of GWP were components of NECB. In the fertilizer plot, harvested C was larger than NEE, which made GWP positive (2.3 ± 1.1 $MgCO_2$eq.–C ha^{-1} $year^{-1}$). However in manure plots, the sum of C applied in manure and NEE was larger than harvested C, which made GWP negative (−1.0 ± 2.1 $MgCO_2eq.–C\ ha^{-1}\ year^{-1}$). N_2O emission contributed significantly to GWP, while the contribution of CH_4 emission was negligible.

Conclusion

Farmyard manure application in Japanese managed grassland significantly decreased Global warming potential (GWP) significantly without reduction of harvest of grass compared with chemical fertilizer only application. Chemical fertilizer only application decreased soil carbon stock in Japanese grasslands. The major component of GWP was net ecosystem carbon balance. However, contribution of N_2O emission was not negligible. Contribution of CH_4 emission was of minor importance.

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Chapter 34
Clay Addition and Redistribution to Enhance Carbon Sequestration in Soils

G. Jock Churchman, Andrew Noble, Glenn Bailey, David Chittleborough, and Richard Harper

Abstract The association of organic carbon (SOC) with clay in soils means that additions of clay to soils can increase the capacity of the soils for storage, and, eventually, sequestration of C. Addition of a fine-textured waste from bauxite processing to sandy soils for up to 29 years has led to increases of about 12 Mg C ha^{-1}, with a strong ($r^2 = 0.93$, $P < 0.001$) correlation between clay content and SOC. An increase of 2.2 Mg C ha^{-1} has also occurred after 8 years in a sandy topsoil amended with subsoil clay-rich material. Bentonite addition increased plant yield in degraded and light-textured soils in tropical Australia. In Thailand, addition of clay-rich materials, particularly bentonite, but also clayey termite mound material, greatly increased the productivity of a degraded light-textured soil.

Examination of soil modified by redistribution of subsoil clay into sandy topsoil by mechanical inversion showed the growth of roots in incorporated lumps of clay. Electron micrographs of clay-rich soils showed that fine mineral material (clay) can become closely associated with roots and other organic matter, which can protect them from decomposition. Roots within added or redistributed clay, along with microbes and their products, may become coated, enabling carbon sequestration in the long-term.

Keywords Clay wastes • Subsoil clay • Plant productivity • Roots • Sandy soils • SOC

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Introduction

The build-up of carbon-based gases in the atmosphere (principally $CO_2$and CH_4) is thought to be a major cause of climate change (e.g., Rockström et al. 2009). Strategies for reversing their increased concentration aim to shift substantial C from the atmospheric pool into one of the other major natural pools of C, i.e. the oceanic, geologic, soil and biotic pools (Lal 2004). Of these, the soil pool, and, in particular, that of soil organic carbon (SOC), offers a strong prospect of success because it is relatively stable.

Land use changes and soil management have led to a considerable loss of C from the SOC pool (Lal 2004). Improved management practices involving minimal soil disturbance in the preparation, sowing and harvesting of crops as well as in pastoral farming could restore lost C (Lal 2004). However, cultivation over a long period of time may affect organic matter content and microaggregation (e.g., Balesdent et al. 1988; Jastrow et al. 1996) and, as a result of erosion, both the mass and content of fine particles (Balesdent et al. 1988; Churchman et al. 2010). Since each soil has a capacity for organic C that is largely dependent upon their silt+clay contents (Hassink 1997; Stewart et al. 2008), loss of fine particles, and loss of soil mass means that cultivation over a long term can decrease the capacity of soils to sequester C from the atmosphere. Decreases in the concentration and stability of microaggregates that protect organic C (Hassink and Whitmore 1997; Churchman et al. 2010) diminishes the capacity of soils for C sequestration. Experiments to test the possibility of increasing the uptake of organic C by soils through adoption of conservation management practices have given equivocal results, e.g., Powlson et al. (2012). Increases in SOC contents after no-till treatments can be explained by a redistribution of SOC into uppermost horizons at the expense of lower horizons of the same soils, rather than by an increase in total SOC in the profile (Baker et al. 2007). Zero tillage can increase emissions of the greenhouse gas N_2O and any positive effects of zero tillage on SOC are reversible (Powlson et al. 2012).

It has long been known (e.g., Greenland 1965) that clays and organic matter can be strongly associated in soils. The concentrations of organic C and clay were strongly correlated in a set of 65 soils (mainly Mollisols) in the US Southern Great Plains (Nichols 1984). Carbon is sequestered when it persists in the soil for a long time, at least 100, and maybe thousands, of years. It was once thought that it persists because it is transformed from its plant and microbial forms into forms that are recalcitrant because of their molecular structures (Marschner et al. 2008). Comparatively recalcitrant charcoal-like forms of C are widespread in soils but are usually a minor component of the total organic matter and are marginally important for organic matter cycling (Schmidt et al. 2011). Instead, recent evidence (e.g., Lehmann et al. 2007; Schmidt et al. 2011) indicates that microaggregation largely explains the extent to which a soil may sequester carbon. Microaggregates effectively comprise fine mineral material, including oxides of Fe, Al and Mn as well as secondary aluminosilicates with appropriate exchangeable cations that constitute protective shells (Wan et al. 2007) or the linings of small pores (McCarthy et al. 2008). They incorporate organic matter with a wide range of origins and composition (Schmidt et al. 2011).

Here, we investigated the modification of sandy soils by addition of clays that is a common practice in parts of Australia. We examined possible mechanisms for the enhancement of SOC resulting from additions of clays (including other fine materials) to soils.

Clay Additions and Hydrophobicity

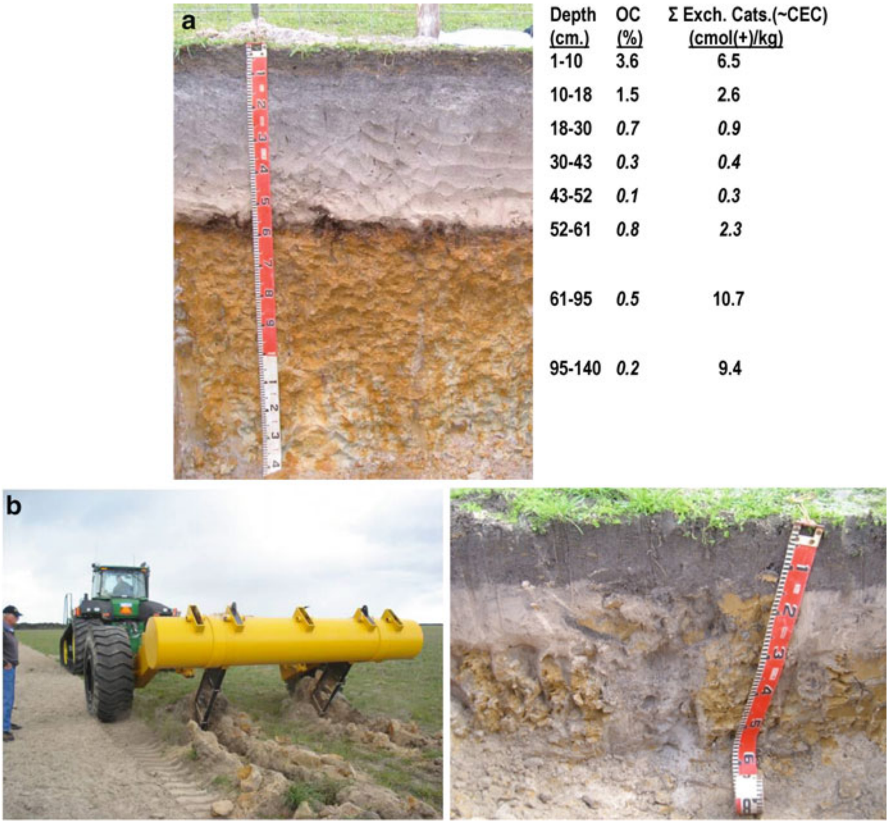
Over extensive areas of southern Australia non-wetting (hydrophobic) sandy soils are common which produce patchy and poor yields of crops and pasture (McKissock et al. 1998; Cann 2000). Additions of fine particles of different kinds can overcome the hydrophobicity of these soils (Ward and Oades 1993). The addition of clay where it occurs in high concentrations locally (as in the B horizons of the common sand-over-clay texture contrast, or 'duplex' soils, Fig. 34.1a) provides a cheaper and longer-lasting solution than the use of non-wetting agents (Cann 2000). Up to 160,000 ha of land in South and Western Australia has been enhanced by clay additions over more than 40 years (Cann 2000; D. Davenport and D. Hall, pers.comm.).

Methods Used for Adding and Redistributing Clays in Soils

Two main methods are used in southern Australia for modifying sandy soils (Fig. 34.1a). Clay spreading involves application of clay-rich materials from an external source commonly at rates of 100–250 Mg clay ha^{-1} (Cann 2000). Most benefit arises when the clay is incorporated evenly in the top 10–15 cm of the soil. The other main method, delving (Fig. 34.1b), is designed to redistribute clay from fine-textured, clayey B horizons into coarse-textured, sandy A and E horizons (Desbiolles et al. 1997). It involves a mechanical inversion of the lower horizon material so that it is brought to, or near, the surface.

Results

Clayey wastes from industry have been added to soils by surface spreading to increase SOC uptake and plant productivity. Residues from bauxite processing (85 % silt, 11 % clay and 4 % sand) had been added to sandy soils in Western Australia over a 19–29 years period. There were increases in SOC in the top 30 cm which ranged from 0.1 to 0.65 % resulting in a significant ($P<0.01$) increase of 11.6 Mg C ha^{-1} across these sites with a strong ($r^2=0.93$, $P<0.001$)



Depth (cm.)	OC (%)	Σ Exch. Cats.(~CEC) (cmol(+)/kg)
1-10	3.6	6.5
10-18	1.5	2.6
18-30	*0.7*	*0.9*
30-43	*0.3*	*0.4*
43-52	*0.1*	*0.3*
52-61	*0.8*	*2.3*
61-95	*0.5*	10.7
95-140	*0.2*	9.4

Fig. 34.1 (**a**) Profile of a duplex (sand over clay) soil, common in southern and western Australia. Italicised OC and Exchangeable cations values are low, indicating low organic C and low clay (Reproduced with permission from Rural Solutions SA). (**b**) Clay from B horizons is moved into sandy A2 horizon by delving (process shown at *left*, result at *right*). *Left side image* from http://www.precisionag.com.au/page16.php; *Right side image* reproduced with permission from Rural Solutions SA

correlation between clay content and SOC for the 0–5 cm layer (Fig. 34.2). Assuming a linear rate of accumulation of C, this amounts to an annual accumulation of 1.9 $MgCO_2$-eq ha^{-1} $year^{-1}$ (R.J. Harper et al. 2012).

Hall et al. (2010) reported increases in C (of 2.2 Mg C ha^{-1}) 8 years after 300 Mg ha^{-1} of a kaolinitic subsoil (32 % clay) had been added to the top 10 cm of a soil in Western Australia by delving. The soil contained only 1 % clay and delving raised the topsoil clay content to 6 %. Delving may add to topsoil SOC by simple addition. Bailey and Hughes (2012) found that when clay lumps were mixed into sandy A2 horizons (Fig. 34.1a) in 11 delved sites in South Australia, the mean SOC content was increased from 0.3 % for the undelved sandy material to 0.7 %.

Augmenting the clay content of light-textured soils has been shown to enhance plant production. Churchman and co-workers (unpub. results, 2002) found that addition of 12.5 % by weight of foundry waste containing 35 % bentonite clay overcame

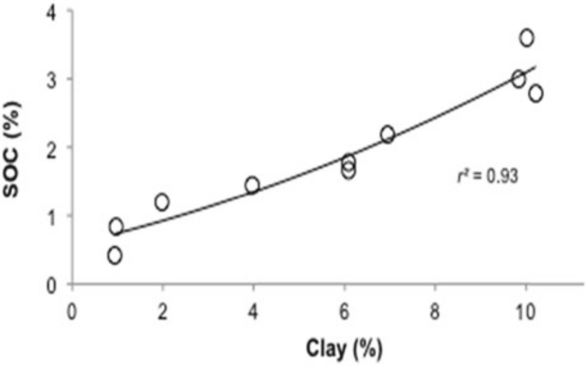


Fig. 34.2 Organic carbon (SOC) (%) in relation to clay (<2 µm) (%) in surface 0.05 m of a sandy soil 29 year after addition of fine-textured bauxite waste (From Harper et al. 2012)

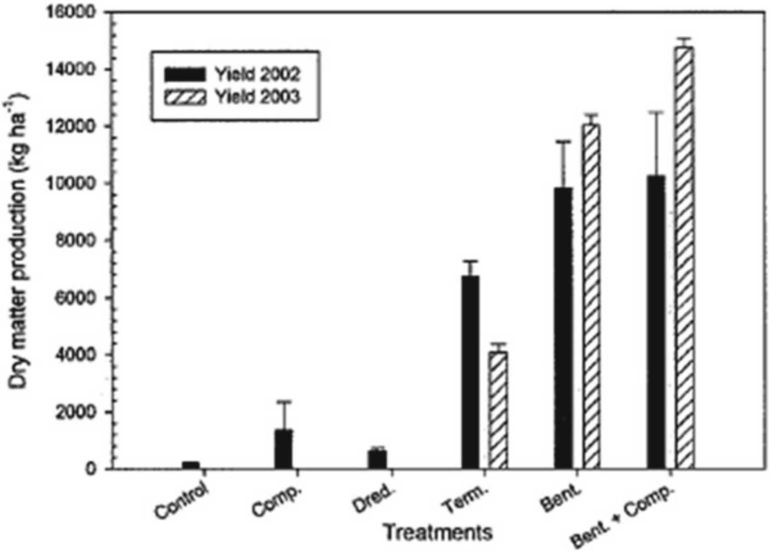


Fig. 34.3 Yield of forage sorghum on a sandy soil over 2 years following additions of: leaf compost 10 Mg ha^{-1} (Comp.); dredged pond material 240 Mg ha^{-1} (Dred.); termite mounds 120 Mg ha^{-1} (Term.); and bentonite 50 Mg ha^{-1}(Bent.); Bent. + Comp. (From Noble and Suzuki 2005. Reproduced with permission from IWMI)

its hydrophobicity and trebled dry matter production. Approximately one million tonnes of bleaching earths, i.e., acid-activated bentonites, are released as wastes from cooking oil manufacture world-wide every year (Crossley 2001). Addition of this material to degraded sandy soils in Thailand following co-composting with common farm wastes was shown to enhance soil chemical and physical properties, resulting in increases of up to three times in the dry matter yield of maize (Soda et al. 2006).

When 40 t ha^{-1}bentonite had been added in pot trials to a degraded Oxisol and to a light-textured Ultisol, both from tropical northern Australia, forage sorghum biomass production showed 3.1-fold and 7.7-fold increases in the Oxisol and Ultisol, respectively (Noble et al. 2001). Field trials over 2 years on sandy soils in Northern

Thailand (Fig. 34.3) showed almost no growth of forage sorghum on unmodified soil but increases of up to about 100-fold after addition of different locally-sourced materials to the soil (Noble and Suzuki 2005). Yield increases were only slight when compost and dredged material from ponds were added, but substantial for additions of clay-enhanced termite mound material and especially high when a low quality bentonite (CEC = 27.2 $\text{cmol}_c\ \text{kg}^{-1}$) was added, even without compost. No measurements were made of SOC contents in this study. However, increases in inorganic C contents are likely to occur with increased plant productivity, especially through the decomposition of roots left in the ground after harvesting (Schmidt et al. 2011).

Possible Mechanism

Bailey (2006) observed that clay-rich lumps (Fig. 34.4) redistributed within soils by delving contained a high concentration of roots, attracted by water and nutrients associated with the added clay (Bailey and Hughes 2012). These may help encourage an increased uptake of SOC.

The soil in the transmission electron micrographs of Fig. 34.4c is an Alfisol described by Churchman et al. (2010) and Churchman (2013). These three images illustrate the probable outcome of microbiological and physicochemical changes brought about after roots have inhabited the clay lumps for a period, probably following their death and partial decomposition under cycles of wetting and drying. The uppermost micrograph shows fine roots and root hairs are closely associated with mineral matter, particularly clays and secondary oxides of Fe, Al and Mn (together, ‘clay’), which are dark in color, along with shards of quartz broken by the knife blade. The clay coats much of the organic material as seen in the micrographs at lower left and right. The micrograph at lower left shows extracellular polysaccharides surrounded by clay while that at lower right shows bacterial cells similarly coated. The organic material in these two cases is particularly labile. Roots within the lumps of clay (Fig. 34.4b), products of their microbial breakdown, as well as microbes, may all become protected by clay coatings.

Discussion

Organic C is often associated with clays in soils, hence we postulate that additions of clay to soils can enhance storage of C. In southern Australia, addition of clay has to sandy soils is a widely accepted technology for overcoming hydrophobicity.

The addition of fine-textured wastes from bauxite mining to sandy soils for 29 years has shown significant increases in SOC that are strongly correlated with the clay contents of the soils.

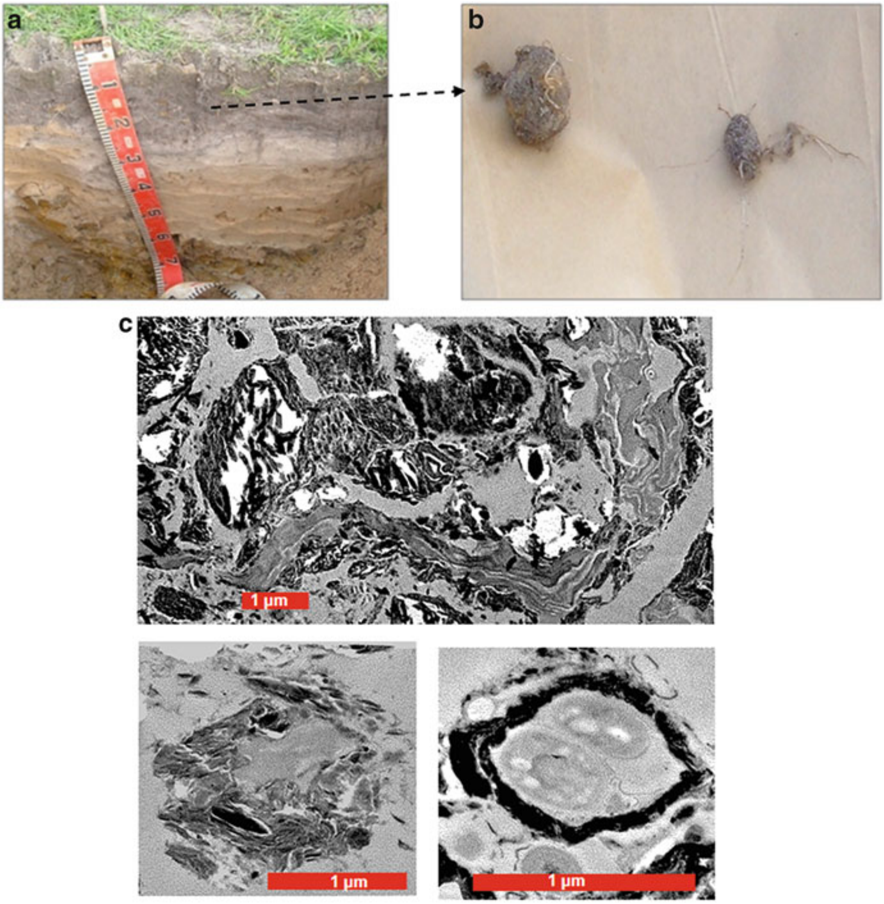


Fig. 34.4 (**a**) A delved soil profile; (**b**) lumps of clay moved from B to A2 horizon by delving, with incorporated roots (From Bailey 2006, with permission from Rural Solutions SA); (**c**) Transmission electron micrographs (TEM) of ultrathin sections of the upper 5 cm of an Alfisol, showing *dark*, mineral matter surrounding (*top*) plant cells, probably fine roots (*lighter coloured*), and also quartz shards, (*lower left*) extracellular polysaccharide (identified by staining), and (*lower right*) bacteria (From Churchman 2013, with Permission from Tubitak)

Addition of subsoil clay to a sandy soil has also increased its SOC content after 8 years. Additions of clay-rich materials, especially bentonites, greatly increased the productivity of soils. Plant roots have selectively colonized clay that is redistributed from subsoil into sandy topsoil suggesting that SOC may be protected from decomposition by surrounding clay, as was shown by electron microscopy in some clay-rich soils.

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Part IV
Soil C and the Environment

Chapter 35
Soil Carbon Management and Climate Change

Rattan Lal

Abstract Among global issues of the twenty-first century are: population growth, increase in energy demand, enrichment of atmospheric concentration of greenhouse gases (GHGs) and the attendant climate change, increase in food production needed to meet the demands of growing and increasingly affluent population, and aggravated risks of soil and environmental degradation. Thus, enhancing the magnitude and mean residence time (MRT) of soil carbon (C) pool is integral to any strategy of addressing these and other related global issues. The promise of soil C sequestration is based on the magnitude of net biome productivity (NBP) of ~3 Pg C/year, and the hypothesis that some of the NBP can be retained in the soil to offset emissions and also enhance the resilience of soil and agroecosystems to climate change. Complementary to soil organic C (SOC) is soil inorganic C (SIC) pool, together estimated at ~4,000 Pg to 3-m depth, and play a major role in the global C cycle (GCC). The soil C sink capacity has been enhanced by depletion of the antecedent SOC pool in degraded soils. Despite the large potential of 0.5–1 Mg C/ha/year, there are numerous uncertainties: (1) increased emissions of GHGs with increase in the atmospheric concentration of CO_2 because of accelerated decomposition and erosional processes, (2) change in the rate of C uptake in soils of the tropics by climate change, (3) impact of chemical weathering of silicate rocks in altering terrestrial sinks, (4) unknown fate of C transported by erosional processes, (5) a possible positive feedback from the melting of permafrost, (6) decrease in capacity of terrestrial sinks because of soil degradation, and (7) the effects of wild/managed fires on soot, charcoal and NBP.

These uncertainties interact with mechanisms of SOC stabilization and those which enhance its MRT. These mechanisms include: physical protection through deep placement and formation of stable aggregates, interaction between SOC and

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clay minerals, landscape position, and humification leading to formation of recalcitrant fractions. There is a vast potential of SOC sequestration through adoption of recommended management practices on croplands (e.g., conservation agriculture, cover cropping, integrated nutrient management) grazing lands (e.g., controlled grazing, better forage/tree species, soil and water conservation), forestlands (e.g., afforestation, stand management, species selection), wetland/peatland restoration, and reclamation of degraded soils. Comparatively low rate of SIC sequestration as pedogenic carbonates exist in vast arid and semi-arid lands, and in agroecosystems irrigated with good quality water. However, there are also challenges of credible measurements of small changes in soil C in a relatively large pool, and of scaling up the data from profile to watershed and regional scale. There are numerous co-effects of soil C sequestration including improvements in soil quality, increase in agronomic productivity, enhancement of biodiversity, reduction in non-point source pollution etc. Payments to land managers for ecosystem services and trading of C credits may enhance adoption of recommended technologies especially by resource-poor farmers, and small landholders in the tropics. Researchable priorities include understanding of trends and variability in principal determinants of SOC pools and its MRT, assessing the impact of C-climate feedbacks and understanding coupled cycling of C with other elements (N, P, S) and H_2O. Soil C sequestration has a finite sink capacity. However, it has numerous co-benefits (e.g., food security), and is a cost-effective, win-win option, and a bridge to the future until low-C or no-C fuel sources take effect.

Keywords Soil quality • Soil C pool • Conservation agriculture • Co-benefits of soil C sequestration • Agronomic productivity • Energy use • Biofuels • Smallholder farmers

Introduction

The primary global energy consumption in 2008 was 500 EJ (EJ = exajoule = 10^{18} J), and it is growing on an average rate of 2 %/year. Of the total consumption, 80 % originates from fossil fuels (GEA 2012) contributing to continuous increase in atmospheric concentration of CO_2 and other greenhouse gases (GHGs). Atmospheric concentration of CO_2 passed the historic 400 ppmv mark in May 2013, with the ever increasing risks of attendant global temperature increase accelerating the greenhouse effect. The early Earth was kept warm by the natural greenhouse effect (Kasting 2013). However, the accelerated greenhouse effect by human activities is now considered to be the cause of global warming and the abrupt climate change. Therefore, the climate change mitigation goal is to limit a global mean temperature increase to <2 °C above the pre-industrial level (Meinshausen et al. 2009, 2011; UNFCCC 2010). Achieving this goal implies reducing net global GHG emissions from energy and industry sectors to 30–70 % of 2000 levels by 2050, and to zero or net negative emissions in the second half of the twenty-first century (GEA 2012). However,

Table 35.1 Actual and the projected world population between 1950 and 2100 (U.N. 2013)

	World	India	USA	Nigeria	Congo	Uganda	Tanzania	China
Year	10^9	10^6						
1950	2.53	376.3	157.8	37.9	0.8	5.2	7.7	543.8
2000	6.06	1,013.7	278.4	111.5	2.9	21.8	33.5	1,277.6
2013	7.16	1,252.1	320.1	173.6	4.5	37.6	49.3	1,385.6
2025	8.08	1,418.7	350.6	239.9	6.0	54.8	69.3	1,449.0
2050	9.55	1,620.1	400.9	440.4	10.6	104.1	129.4	1,385.0
2100	10.85	1,546.8	462.1	913.8	21.3	204.6	275.6	1,085.6

achieving these goals is likely to be even more of a challenge than ever before because of the rapid growth in the world's population (Table 35.1) and the increasingly affluent lifestyle. The 2013 revision of the World Population Prospects by the U.N. predicted population~~s~~ in 2100 at ~11 billion, 1 billion more than estimates made in 2011. The population of the African continent, presently at 1.1 billion, will increase to 4.1 billion by 2100, or more than a third of the world's total population. By 2100, six countries which will account for >50 % of the world population increase will be India, Nigeria, USA, Congo, Tanzania, and Uganda (Table 35.1). With the exception of USA, natural resources of all other five countries are already under great stress. Food production in some African countries will have to be tripled or quadrupled to meet the growing demands. Thus, soil resources of countries in South Asia (SA), Sub-Saharan Africa (SSA), and elsewhere must be restored and sustainably used. It is precisely in this context that the importance of restoring soil quality and sustainable intensification (SI) of agriculture in SA, SSA, and elsewhere (e.g., China, the Andean region, Central America, and the Caribbean) can never be over emphasized. Therefore, the objective of this article is to describe the importance and rational of managing world's soils as a sink of atmospheric CO_2, adapting and mitigating climate change, enhancing agronomic productivity, and achieving food security for the increasing world population.

Population, Energy and Soil Carbon Nexus

There is a strong relationship between population and the anthropogenic emissions (Fig. 35.1). On average increase in human population by 1 billion increases total (fossil fuels and land use conversion) CO_2-C emissions by 1.4 Pg C/year. The impact of human population on natural resources depends on the total population (P), affluence (A), and the technology (I = PAT; Ehrlich and Holdren 1971). With increase in population (Table 35.1) and the increasing affluence of the population in emerging economies, the impact on Earth's ecosystems is likely to be even greater than has been in the past. Therefore, identifying alternate sources of energy such as biofuel (Azar et al. 2010, 2013) etc. are also being carefully considered to reduce the net emissions economically and technologically (Rogelj et al. 2012, 2013; den Elzen

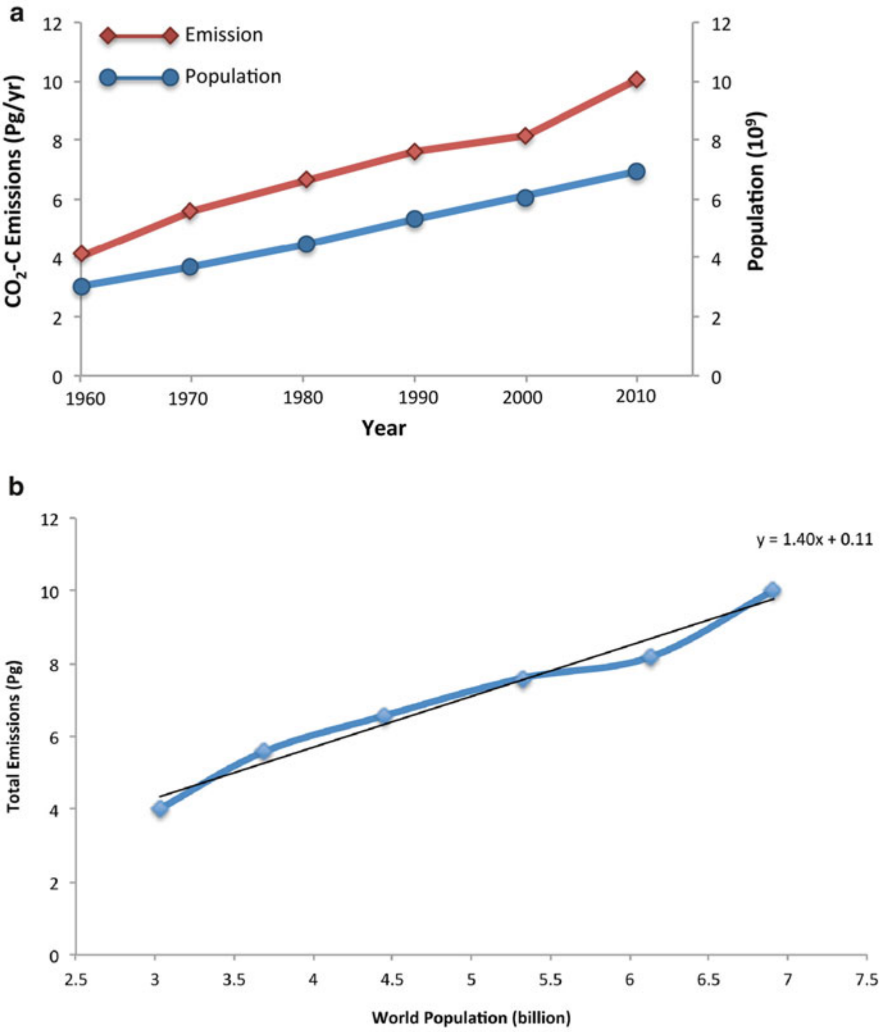

Fig. 35.1 Population-emission nexus between 1960 and 2010: (**a**) Temporal changes in human population and CO$_2$ emissions, (**b**) Relationship between the world population and total anthropogenic emissions (fossil fuels and land use change) (Redrawn from U.N. 2013)

and Van Vuuren et al. 2007; Van Vuuren et al. 2007). The goal is to establish relationship between short-term emissions and long-term concentration targets (van Vuuren and Riahi 2011).

With the business as usual, meeting the target of limiting global warming to <2 °C will be a daunting task (Lowe et al. 2009; Ranger et al. 2012), and there is a potential risk of irreversibility (Solomon et al. 2009). Thus, several options are being considered including the carbon capture and storage (Azar et al. 2006; Keith 2009), pros and cons of biofuels (Azar 2011; Popp et al. 2011), recarbonization of

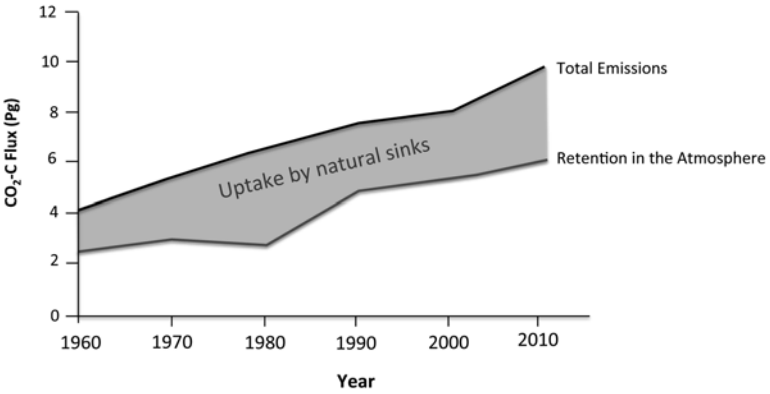

Fig. 35.2 Temporal changes in anthropogenic emission, and the increase in the atmospheric CO_2-C pool between 1960 and 2010 (Redrawn from Tyndall Centre 2011)

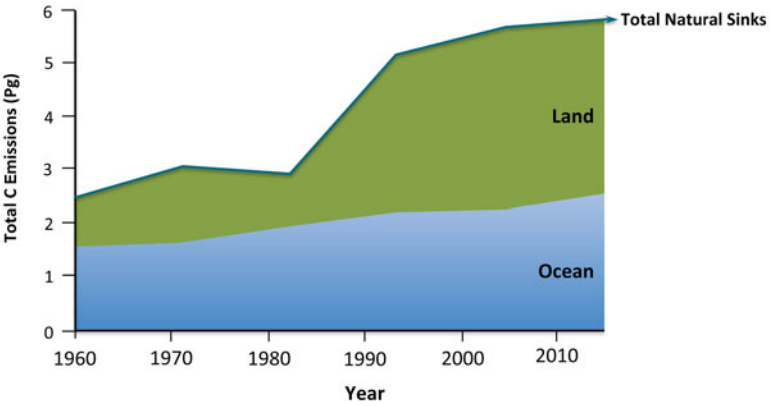

Fig. 35.3 Temporal changes in the natural sinks of anthropogenic CO_2-C emissions (Redrawn from Tyndall Centre 2011)

the biosphere (Lal and Stewart 2012) etc. The challenge of limiting increase in global temperature to <2 °C is accentuated by several factors including the need for long-term socio-economic development (Riahi et al. 2007). Further, the peak warming caused by a given cumulative CO_2 emissions is insensitive to the emission pathway (Allen et al. 2009; Parry et al. 2009).

Natural sinks of anthropogenic CO_2 emissions have played an important role in moderating the build up of CO_2 in the atmosphere since the Industrial Revolution. The capacity of natural sinks to absorb some of the anthropogenic emissions has increased with increases in emissions between 1960 and 2010 (Fig. 35.2). Indeed, the growth of atmospheric CO_2 pool has been slower because of the uptake by ocean and land. Furthermore, the capacity of both sinks has increased along with increase in anthropogenic emissions over the last 50 years (Fig. 35.3). Yet, there are indications that the capacity of natural sinks is decreasing (Canadell et al. 2007). Therefore, numerous scenarios of emission pathways (Rogelj et al. 2011), relative merits of reducing concentrations of CO_2 versus CH_4 and N_2O (Johansson et al. 2006), and other options of fixing the planet (Trenberth 2010) are among the menu of options being considered. World soils, an important and dynamic component of land, have a critical role in the global carbon cycle (GCC) and in moderating the climate.

Role of Terrestrial and Soil Carbon Sinks

Land-based sinks have moderated the increase in atmospheric uptake of CO_2, with a progressive increase in annual uptake/absorption from 1 Pg C/year in 1960 to 3.1 Pg C/year in 2010 (Fig. 35.3). World soils have a large total C pool, but finite C sink capacity. The soil C pool has two distinct components: soil organic carbon (SOC) and soil inorganic C (SIC). The SOC pool is highly dynamic, reactive, and sensitive to land use, climate change, and management. Measured to 3-m depth [and including the recent estimates of the large C pool in permafrost soils (Cryosols)], total soil C pool is estimated at 4,000 Pg. The SOC pool in the surface 0–1 m depth (1,550 Pg) has numerous functions, and generates a range of ecosystem services (Lal et al. 2013). Important among these services are improvement of the net primary productivity (NPP), and sequestration of atmospheric CO_2 (Table 35.3).

Concentration of SOC must be maintained above the critical or threshold level of 1.2–1.5 % in the root zone (15–30 cm depth). In comparison, SOC concentration of some soils in SA is <0.1 % in the root zone. Most soils of agroecosystems in developing countries have been perpetually managed by extractive farming practices, which exacerbate SOC depletion and also emission of GHGs (Table 35.4). These practices include removal of crop residues for other competing uses (e.g., animal feed, fencing, roofing, household fuel), open and uncontrolled grazing, use of animal dung as household fuel, and none or little off-farm input (e.g., fertilizers, manure, mulch). In addition, the depletion of SOC concentration in agroecosystem is exacerbated by rapid decomposition at continuously high temperatures, and preferential removal through accelerated soil erosion by water and wind (Fig. 35.4). There also exists a strong relationship between agronomic productivity and SOC concentration at variable levels of off-farm inputs (Fig. 35.5). The threshold level, below which the response to external inputs is low, may also differ among land uses, and is generally higher for seasonal crops than perennial tree plantations or pastures. These relationships can be strongly confounded by the prevalent and the projected climate, especially the frequency and intensity of extreme events (e.g., drought). The latter are triggered by climate change caused by increasing atmospheric concentrations of radiatively active GHGs. Thus, there is a growing interest in identifying technological options of SOC management that may reduce the net anthropogenic emissions and achieve zero or negative emissions during the second half of the twenty-first century. World soils can be a sink of atmospheric CO_2, especially those of the agroecosystems and degraded/desertified lands with severely depleted

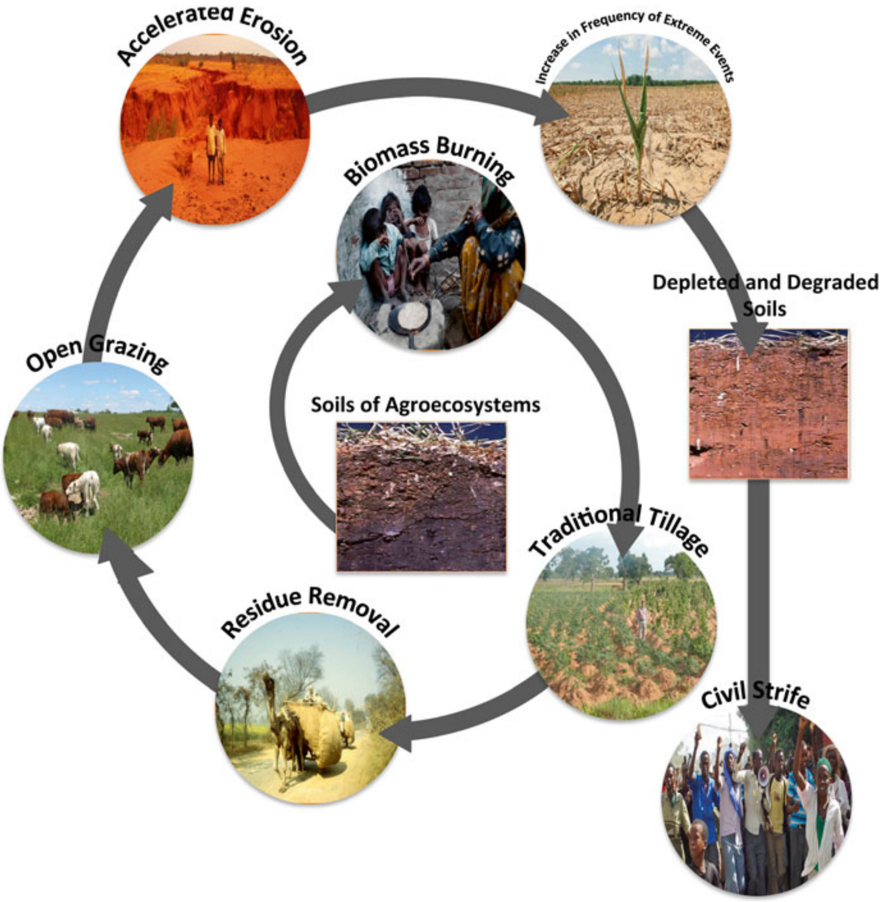

Fig. 35.4 The depletion of soil organic carbon pool by long-term use of extractive farming practices, accelerated soil erosion, and increase in frequency of extreme events (e.g., drought) by changing climate and disrupts political notability by degrading soils and the environments

SOC pool. The strategy is to utilize their C sink capacity through soil restoration by conversion to an appropriate land use and adoption of sustainable soil/crop/water/livestock management practices.

Utilizing CO_2 Sink Capacity of World Soils for Mitigating Climate Change

Anthropogenic emissions are presently estimated at ~10 Pg C/year from fossil fuel combustion and land use conversion including soil cultivation and drainage of peatlands (refer Table 35.2). The atmospheric C pool, estimated at about 800 Pg, is

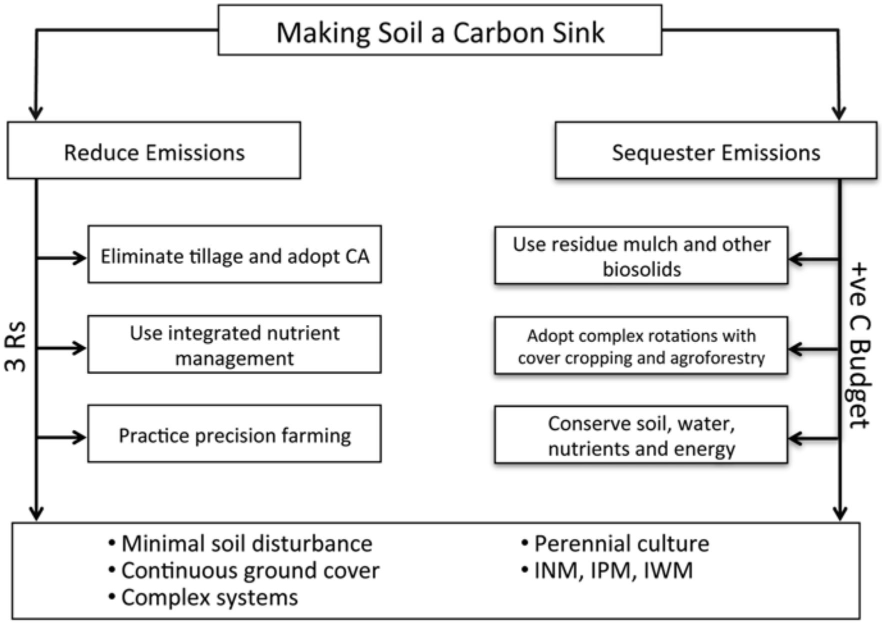

Fig. 35.5 Strategies of making world soils into a major sink of atmospheric CO_2 (3Rs = Reduce, Reuse and Recycle)

Table 35.2 Anthropogenic emissions (Pg C/year) CO_2-C from fossil fuel combustion and land use conversion

Year	Fossil fuel emissions*	Land use conversion	Total
1960	2.57	1.45	4.02
1970	4.05	1.53	5.58
1980	5.32	1.25	6.57
1990	6.15	1.45	7.60
2000	6.75	1.43	8.18
2010	9.14	0.87	10.01

Adapted from Boden et al. (2010)

*Fossil fuel emissions were 9.47 pg for 2011, 9.7 pg for 2012 and 9.9 pg for 2013

increasing at a rate of about 4.2 Pg C/year. However, a large part of anthropogenic emissions being absorbed by natural sinks (e.g., ocean, trees, soil, etc.), may be due to the uptake by the SOC and SIC pools. Further, the possible decrease in the C sink capacity of natural ecosystems (Canadell et al. 2007) may be attributed to the acidification of oceans and degradation of soils. Degraded and depleted soils of agroecosystems, especially those prone to accelerated erosion by water and wind and managed by extractive farming practices for a long time, contain lower SOC pool than their un-degraded counterparts and those under natural ecosystems. Some severely depleted soils and agroecosystems have lost 30–50 % of their antecedent SOC pool in temperate climates and up to 75 % or more in tropical biomes (Lal 2004). Therefore, the process of conversion of natural to agroecosystems

Table 35.3 Ecological benefits of managing soil organic carbon content and its maintenance at above the threshold level in the root zone for soils of the smallholder farmers of the tropics

Soil	Water	Climate change
1. Improve soil structure	1. Reduce runoff and increase infiltration	1. Sequester atmospheric CO_2
2. Increase nutrient retention and availability	2. Create favorable hydrological balance	2. Oxidize CH_4
3. Enhance available water capacity	3. Decrease risks of non-point source pollution, and hypoxia of coastal ecosystems	3. Decrease emission of N_2O
4. Reduce soil's susceptibility to erosion	4. Enhance ground water recharge	4. Adapt agroecosystems to climate change
5. Decrease risks of soil compaction	5. Improve quality of natural water	5. Increase buffering against extreme climatic events (drought)
6. Enhance disease suppressive attributes	6. Denature and absorb pollutants	6. Create favorable growing season duration
7. Increase soil biodiversity	7. Increase renewal and supply of fresh water	7. Improve microclimate close to the ground surface
8. Moderate soil heat capacity	8. Moderate stream flow	8. Off-set anthropogenic emissions

(by biomass burning, land drainage, deforestation, plowing) and of subsequent management render these biomes a major source of principal GHGs (e.g., CO_2, CH_4, N_2O). Indeed, world soils have been a major source of GHGs ever since the dawn of settled agriculture (Ruddiman 2003, 2005).

The C sink capacity, difference between the SOC pool of degraded vs. un-degraded and those under natural ecosystems, may be 20–30 Mg C/ha. Furthermore, soils of agroecosystems are of an inferior quality when their SOC pool declines to a level below the critical threshold. Indeed, critical soil functions and provisioning of essential ecosystem services are strongly jeopardized if the SOC concentration declines below the critical threshold value of 1.2–1.5 % in the root zone (~30 cm depth; see Fig. 35.4). Furthermore, the magnitude of depletion of SOC pool in soils of world's croplands is estimated at 66 ± 12 Pg C (Pg = petagram = 10^{15} g = 1 gigaton; Lal 1999). There are two strategies of making soils of managed ecosystems a net sink of atmospheric CO_2: by reducing emissions and sequestering emissions (Fig. 35.5) Conversion to a restorative land use and adoption of best management practices (BMPs) can create a positive ecosystems C budget and sequester atmospheric CO_2 by conversion of biomass-C into relatively stable humus with a longer mean residence time (MRT). Despite numerous uncertainties involved in the land use scenarios (van Vuuren et al. 2007) and social/human dimensions (Riahi et al. 2007), it is argued that use of bioenergy and sequestration of atmospheric CO_2 (by biotic and abiotic processes) can limit the atmospheric concentration of CO_2 (Azar et al. 2006, 2010). While the C sink capacity of world soils is finite (66 ± 12 Pg), soil C sequestration can enhance resilience of agroecosystems to extreme climate events (e.g., drought), and also absorb atmospheric CO_2 and other GHGs (Table 35.3).

Factors Governing SOC Sink Capacity

The SOC sink capacity depends on both natural and the anthropogenic factors. Important among natural factors are soil properties, landscape position, drainage, and climate. The SOC capacity and its MRT are more in soils of cool and humid than those of warm and dry climate. The SOC capacity is more in poorly drained than in well and excessively drained soils. Among soil properties, principal determinants are profile depth, clay and silt contents, and predominance of 2:1 and expanding lattice (e.g., montmorillonite, vermiculite) clay minerals or high-activity clays (HAC). Soil characteristics that favor formation of stable micro- and maco-aggregates or the so-called "strongly structured" or "structurally-active" soils have higher SOC sink capacity compared with those of the "weakly structured" or "structurally-inert" soils. In addition, landscape position and the slope aspect are also important determinants of soil C sink capacity and its MRT. For example, soils located on the south facing (in the northern hemisphere) and on foot/toe slope positions have high SOC sink capacity and long MRT.

Managing Soils for Reducing and Sequestering Emissions

Soils can be source of GHGs because of land misuse and mismanagement. As discussed in section "Role of terrestrial and soil carbon sinks", several traditional agricultural practices, such as those practiced by resources-poor and small landholders, exacerbate emission of GHGs (Table 35.4, Fig. 35.4). Cultivation of rice (*Oryza sativa*) paddies by puddling and traditional inundation also exacerbate methanogenesis and denitrification.

In contrast, soils of agroecosystems can be a sink of atmospheric CO_2 and CH_4 through conversion to a restorative landuse and adoption of those BMPs that improve soil structure and the overall quality (Fig. 35.5). The strategy is to create a positive C (along with N, P, and S) budget, and improve aggregation. Not only should the biomass-C be added into the agroecosystems, but also availability of N, P, and S etc. be enhanced to convert labile C in crop/animal residues into relatively stable humus. Strategies of creating positive ecosystem C budget include: (i) controlling soil erosion, (ii) conserving soil water, (iii) moderating soil temperature, (iv) enhancing soil structure and formation of stable aggregates, (v) improving soil fertility (especially availability of N, P, S, Ca, Mg etc.), (vi) increasing depth distribution of root biomass, (vii) enhancing soil biodiversity or bioturbation, and (viii) improving NPP.

A strong relationship exists between NPP, the SOC concentration in the root zone and the nature and amount of off-farm input (Fig. 35.6). The response of NPP to input depends on land use (seasonal vs. perennial) and on antecedent SOC concentration. The threshold/critical SOC concentration, above which response to input is high within the sigmoidal curve, may also differ among land use, soil characteristics, and climate. Dyson (2008) put it more succinctly, "If we control what plants do with carbon, the fate of CO_2 in the atmosphere is in our hands."

Table 35.4 Greenhouse gases emitted through the traditional agricultural practices followed by the small landholder farmers of the tropics

Practice	Greenhouse gases
1. Biomass burning	CO_2, CH_4, N_2O, blackC
2. Plowing, ridging, mound construction	CO_2,
3. Manuring (heap)	N_2O, CH_4, CO_2
4. Rice paddies	CH_4, N_2O
5. Residue removal and burning	CO_2, N_2O, blackC
6. Using manure as cooking fuel	BlackC, CO_2, CH_4, N_2O
7. Excessive drainage	CO_2, N_2O

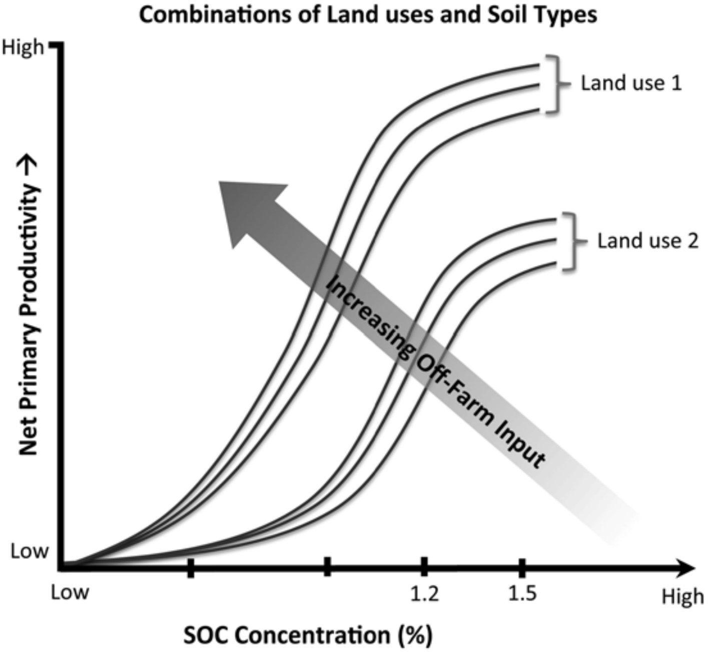

Fig. 35.6 Impact of SOC concentration on agronomic productivity for different land uses under variable levels of inputs

Sustainable Intensification of Agroecosystems

Decreasing availability of prime agricultural land, because of conversion to non-agricultural uses and degradation by a range of processes (physical, chemical, and biological), necessitate the strategy of "Cultivate the best and save the rest" (for nature conservancy). Thus, the term "sustainable intensification" (SI) of agroecosystems implies producing more NPP from less land, water, energy, nutrients, and time. A successful strategy of SI must minimize losses of soil, water, nutrients, energy-based

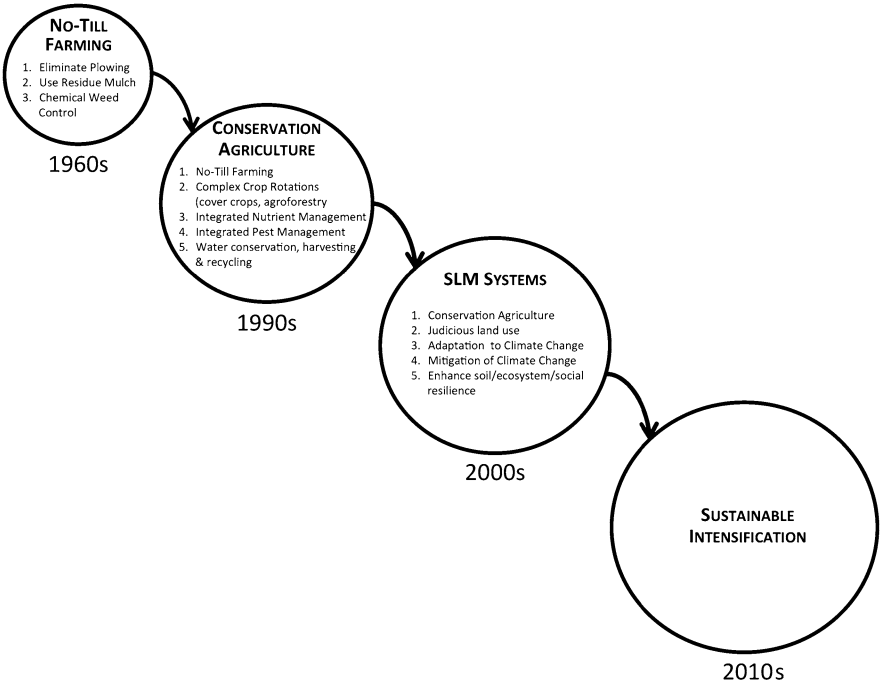

Fig. 35.7 Evolution of conservation agriculture and sustainable intensification since 1960s

input, and maximize the use efficiency. Indeed, the concept of SI emerged after the "dust bowl" syndrome, and materialized in the form of no-till (NT) farming in the 1960s, as a system to reduce risks of soil erosion. The practice of NT farming was expanded to include other components (e.g., complex rotations, integrated nutrient management) to conservation agriculture (CA) in the 1970s and to sustainable land management (SLM) in the 2000s (Fig. 35.7). The natural transformation of SLM into SI in the 2010s is necessitated because our growing population is becoming more affluent and the natural resource base is diminishing. Conversion of traditional practices to CA has numerous advantages including the benefits of enhancing and managing SOC and raising its concentration to above the critical/threshold level because it is an essential component of SI (Table 35.5).

Potential and Challenges of Conservation Agriculture

Research information available about CA since the 1960s from diverse agroecoregions have convincingly demonstrated a wide range of benefits, both biophysical and socioeconomical (Table 35.6). These benefits accrue from the strategies outlined under section "Managing soils for reducing and sequestering emissions" of creating a positive soil/ecosystem C budget. The SOC concentration is also

Table 35.5 Agronomic benefits of enhancing and managing organic carbon in soils of agroecosystems to above the threshold level

Productivity	Income and wellbeing
1. High crop yields	1. High net profit
2. Stable productivity	2. Savings in inputs and labor
3. High use efficiency of inputs (i.e., fertilizers, nutrients)	3. Increase in land value
4. Disease suppressive soils (low nematode infestation)	4. Assured minimum return in the worst case scenario
5. Low dependence on external inputs	5. Decreased risks by abiotic and biotic factors
6. Ease of soil/seedbed preparation	6. Flexibility in timing of farming operations
7. Increase land use capability	7. Another income stream by trading carbon credits
8. New opportunities in crop diversification	8. Improved human nutrition and health

Table 35.6 Benefits of Conservation Agriculture (CA)

Biophysical	Socio-economic
1. Controlling erosion	1. Decreasing fuel use
2. Conserving water and enhancing drought resilience	2. Increasing profit margin
3. Reducing the maximum soil temperature	3. Saving labor
4. Improving soil structure and aggregation	4. Alleviating drudgery
5. Improving SOC content and C sequestration	5. Enhancing environment quality and human wellbeing
6. Improving crop yields	6. Facilitating timely sowing and performing other farm operations
7. Promoting a uniform crop stand	7. Decreasing weed infestation
8. Increasing cropping intensity	8. Creating opportunities for multiple cropping
9. Adapting to climate change	9. Increasing acceptance by woman farmers
10. Mitigating climate change	10. Improving land value

important in relation to soil fertility, sustainable agricultural systems, and the soil/environment quality. Johnston et al. (2009) cited a quotation from Sanskrit literature written about 3,500–4,000 years ago regarding the importance of a fertile soil:

> Upon this handful of soil our survival depends. Husband it and it will grow our food, our fuel and our shelter, and surround us with beauty. Abuse it, and the soil will collapse and die taking man with it

The ancient Sanskrit literature being immensely voluminous, it may be difficult to find the exact source of the citation. However, the ecological and pedological rational of the citation are and will remain valid in perpetuity. Good soil husbandry involves a judicious management of SOC concentration and pool. In addition to numerous biophysical benefits, there are also key socio-economic benefits of CA

Table 35.7 Constraints to adoption of conservation agriculture by small landholders

Biophysical	The human dimension
1. Farm size (<2 ha)	1. Land tenure issue
2. Non-availability of essential inputs and tools	2. Social, gender, ethnic issues 3. High labor demands
Seed drill that can also be used on sloping lands	4. Poor access to market, and unfavorable timing of market
Herbicides	5. Lack of credit facilities
Sprayers	
Tractors	
3. Perennial weeds and pests	6. Poor institutional support
4. Competing uses of crop residues	7. Lack of incentives
5. Unfavorable soil properties	8. Lack of access to safety devices for use of chemicals
Low soil organic matter content	
Structurally inert soils	9. Health issues related to malnutrition and use of chemicals
Low activity clays	
Prone to crusting/compaction	10. Poor awareness among policy makers about stewardship of soil and natural resources
Low inherent fertility (N, P, K micronutrients)	11. Open grazing
Low water holding capacity	12. Biomass burning, wild fires
	13. Mindset
6. Use of cover crops as fodder	14. Lack of knowledge about CA and low skills to use it
7. Use of dung as household fuel	15. Walking barefoot through stubbles and crop residues
8. Soil and nutrient erosion	16. Poor soil governance
9. Steep terrain (Andean region and Nepal)	
10. Severe drought stress soon after sowing	
11. Uncertain and high intensity of monsoon rains	
12. Lack of irrigation facilities	

relevant to some critical issues of human dimensions pertinent to small landholders in developing countries (Table 35.6). With retention of crop residue mulch and elimination of mechanical soil disturbance, soil C sequestration and increase in SOC pool in the surface layer are among principal advantages of CA adoption.

Despite the available research information about application of CA in diverse agroecosystems, adoption of CA has been slow. Globally, CA is adopted on about 150 Mha or ~10 % of the world's croplands (Friedrich et al. 2012a, b). Further, CA is not being adopted in developing countries of the tropics and sub-tropics where it is needed the most. Indeed, there are several constraints to adoption of CA, both biophysical and the human dimension (Table 35.7). Small farm size, and non-availability of essential inputs, and compacted and depleted soils are among major issues.

Table 35.8 Competing uses of crop residues

System	Uses of residues
1. Mixed farming, livestock	Fodder, bedding
2. Rural households	Cooking fuel
3. Infrastructure	Fencing, construction material
4. Industrial uses	Cellulosic ethanol, co-combustion
5. Products	Baskets, hats

Table 35.9 Merits of including cover crops in the rotation cycle involving conservation agriculture

Merits	Concerns
1. Continuous ground cover	1. Competition with food crops
2. Mulch material	2. Hibernation of pests and pathogens
3. Nutrient cycling	3. Nutrient immobilization by cereals
4. Biological nitrogen fixation	4. Voluntary regrowth as weeds
5. Soil carbon sequestration	5. Need for extra herbicides
6. Soil and water conservation	
7. Soil temperature moderation	
8. Soil biodiversity increase	
9. Weed suppression	
10. Nematode control	
11. Reduced soil compaction	
12. Disease suppressive soils	
13. Increase in crop yield	

Retention of crop residue mulch at the rate of 4–6 Mg/ha is essential to soil and water conservation, nutrient cycling, soil structure improvement and biodiversity (e.g., earthworms, microbes) enhancement. Yet, resource-poor farmers cannot afford to retain crop residues on the land because of its numerous competing uses (Table 35.8). Thus, retention of crop residues as mulch can be facilitated or incentivized by payments to farmers for the cost of ecosystem services of global significance generated by the retention of crop residues mulch and the attendant increase in SOC pool (Lal et al. 2013). Therefore, a fair assessment of opportunity cost of crop/animal residues and payments made through a transparent and just system are important to a widespread adoption of CA, and utilization of soil C sink capacity.

Incorporation of an appropriate cover crop in the rotation cycle is another important component of a successful CA system. There are numerous benefits of growing a cover crop (Table 35.9). Similar to the issues with retaining of crop residues mulch, there are also constraints to incorporation of a cover crop in the rotation cycle. Identifying an appropriate cover crop is only one of numerous concerns (Table 35.9). Other concerns include competition for land needed for growing food crops, hibernation of pests and pathogens, nutrient immobilization creating deficiencies of essential nutrients (N) for the food/cash crop, and need for extra herbicides to control/suppress regrowth especially of climbers (e.g., *Mucuna,* *Centrosema, Pueraria*). An appropriate cover crop must also have food/fodder value of interest to small landholders vulnerable to food insecurity.

Strategies to Promote Adoption of Conservation Agriculture

Adoption of CA has numerous ecological, social, economic and political benefits (Fig. 35.8). Its adoption sets in motion an upward spiral. In the context of numerous societal benefits (e.g., sequestering C, reducing non-point source pollution, enhancing biodiversity, improving supply and quality of renewable fresh water resources), it is in the interest of the world community to promote the widespread adoption of

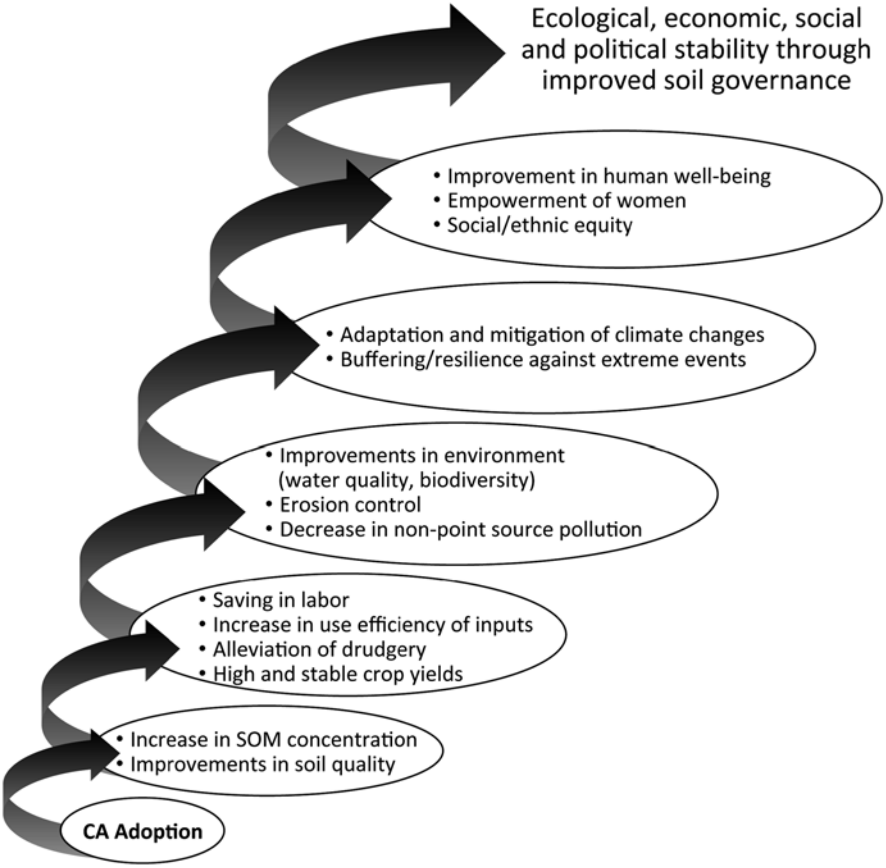

Fig. 35.8 Adoption of CA has numerous benefits to the natural ecosystems, human well-being, and political stability

Table 35.10 Strategies of enhancing the adoption of CA, especially by small landholders in developing countries

Concept	Strategy
1. Improving education, curricula	1. School, undergraduate and graduate training
2. Enhancing institutional capacity	2. Training research and extension staff
3. Creating farmer groups	3. Develop and strengthen farmer organizations
4. Empowering women	4. Create organizations to support women farmers
5. Identifying policy interventions	5. Enhance awareness of policy makers
6. Involving private sector	6. Strengthen linkages with industry
7. Providing appropriate equipment	7. Develop equipment (seed drill, sprayer), rental and repair organizations
8. Improving credit availability	8. Provide credit opportunities
9. Starting pilot project	9. Establish pilot projects in key biomes/ecoregions
10. Initiating demonstration plots	10. Initiate demonstration plots and farmer field days

CA. Apparently, creating another income stream for farmers through payments for ecosystems services is one of several strategies (Lal et al. 2013). Linking farmers to market and providing credit for essential inputs are also crucial to increasing CA adoption. Improving education, beginning with the primary school through a graduate degree program, by revising the curricula is important. The latter must include essential components of SI, which are also important to the stewardship of natural resources (Table 35.10).

Then, there is a question of mindset. It is difficult to alter the perceptions based on cultural traditions practiced for millennia. This is where the education, and an appropriate mix of science and ethics (religion) may be crucial to tackling the mindset and addressing cultural traditions (Baudron et al. 2011).

Biofuels and Biochar

Biomass is considered to be the important source of renewable energy in the near future (Junginger et al. 2008). Both modern and traditional biomass represents a large fraction (>10 %) of the world's energy consumption (Seo et al. 2010). Using biomass for bioenergy has its own pros and cons. Some consider the strategy of using biomass for biofuel as a nightmare rather than a dream come true (Azar 2011). During the 1970s, Hans Jenny (1980) also emphasized the critical importance of maintaining SOC pool. Both traditional and modern biofuels impact the ecosystem and SOC pool and dynamics (Fig. 35.9). Traditional biofuels (e.g., fire wood, crop residues, and animal dung) accelerate soil erosion, exacerbate nutrient depletion, accentuate gaseous emissions, and increase risks of water pollution and eutrophication. An important consequence of long-term use of animal dung and crop residues as biofuels is depletion of SOC pool and attendant degradation of soil and water resources, and emission of GHGs into the atmosphere. Reversing the downward

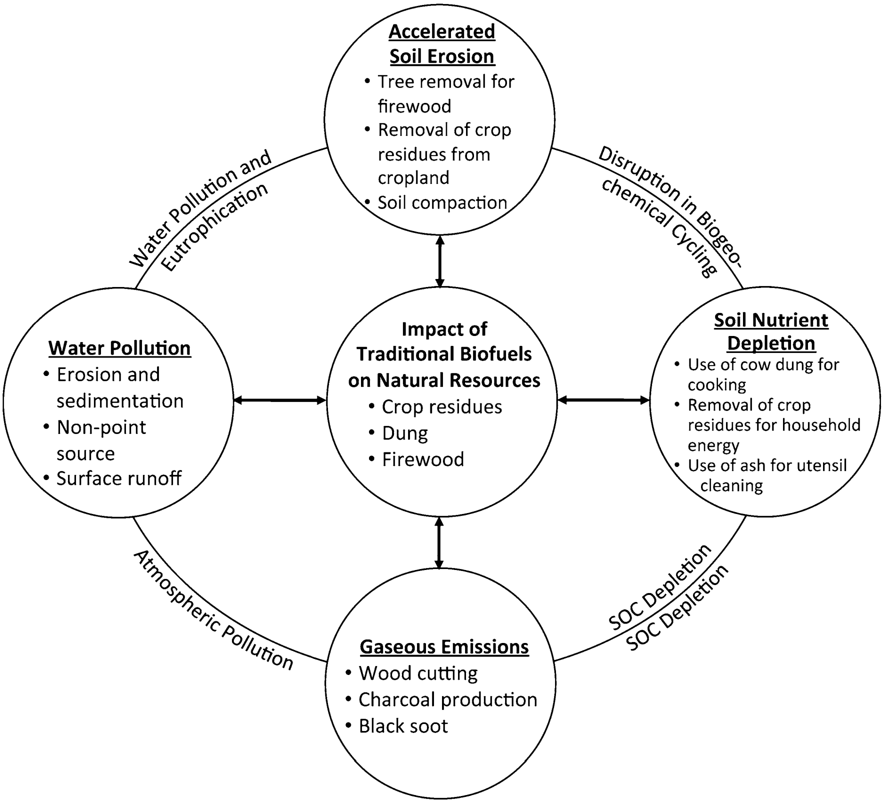

Fig. 35.9 Impacts of traditional biofuels on soils and the environment

spiral of degradation would require provisioning of clean cooking fuels for rural communities in developing countries (SA, SSA, etc.). A similar dilemma exists with use of biochar as a soil amendment. Pyrolysis and gasification of biomass under low or no oxygen conditions and controlled temperature lead to production of biochar (Fermoso et al. 2009; Bhat et al. 2006; Ollero et al. 2003). Whereas the use of biochar as a soil amendment can improve soil quality, its benefits for removal of atmospheric CO_2 and sequestration in soil are debatable. Process-oriented research information, based on complete life cycle analysis (LCA) of biomass and the pyrolysis process, is needed to assess the net C sequestration and energy saving potential of a biochar amendment (Fig. 35.10).

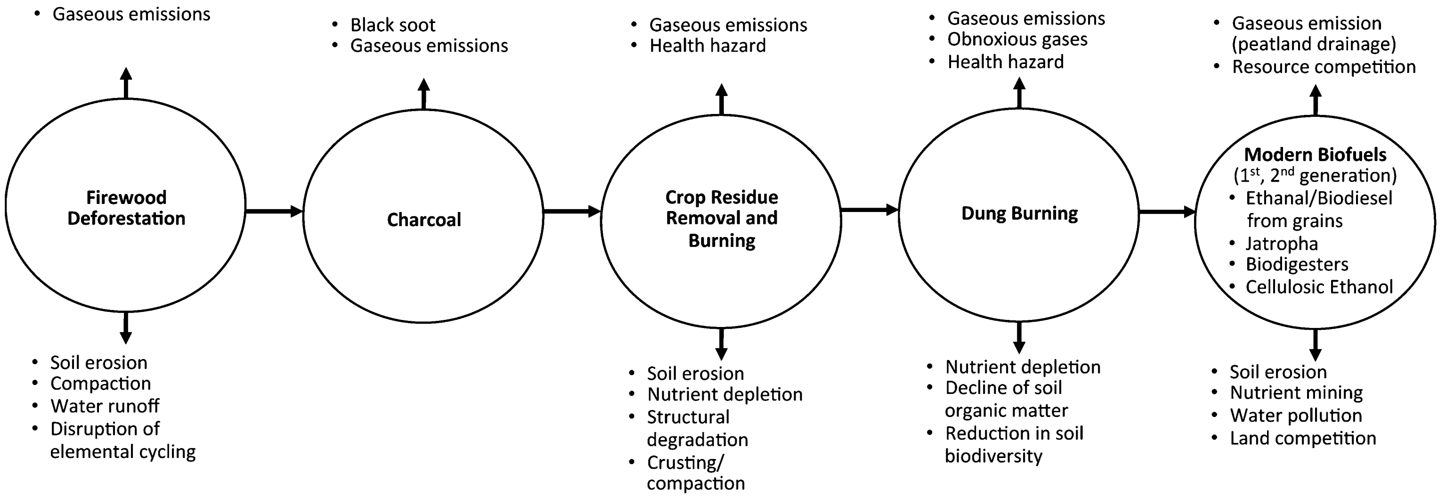

Fig. 35.10 The continuum linking traditional and modern biofuels, with both having risks of adverse impacts on soils, water and other natural resources

Research Priorities

There are several known and other unknowns of SOC dynamics (Stockman et al. 2013). These critical unknowns must be addressed to make SOC an effective and operational C sink. Some important unknowns that emerge as researchable priorities are briefly described below:

1. Predict how Earth's ecosystems will respond to the global climate change (US- DOE 2008), especially with regards to the impact on the soil C cycle and its interaction with cycling of H_2O, N, P, S and other key elements. Whether world soil will be a source (e.g., Cryosols, Histosols) or sink depends on how the future climate change and thus the atmosphere may impact SOC pool in the pedosphere and its interaction with the hydrosphere, the biosphere, and of course the anthroposphere. Further, it is also important to know how difficult would it be for sensitive ecosystems to recover from dangerous levels of global warming (Lowe et al. 2009)?
2. Study the pathways of natural sinks (e.g., pedosphere, biosphere, hydrosphere) in a changing climate? There are concerns that C sink capacity of land and oceans may peak by mid-century (US- DOE 2008). Thus, it is important to understand future perspectives of the response of SOC pool to climate and land use changes (Eglin et al. 2010).
3. Determine the scale that provides the optimal relationship between climate and SOC pool and how the relationship may vary at multiple scales (Wang et al. 2010)?
4. Assess the site-specific impacts of biomass burning, CA/SI systems and of cropping/farming systems on soil C and N stocks and gaseous emissions, with regards to dry/wet year comparison?
5. Evaluate the impact of dissolved organic carbon (DOC) on the pedospheric processes and on the global carbon cycle?
6. Identify the connection between agriculture/sylvan systems and the lacustrine ecosystems with regards to transport and fate of SOC to aquatic ecosystems?
7. Determine/model the impact of climate change on SOC pool in Cryosols (permafrost) and peatlands?
8. Test the clay-to-carbon saturation concept for a wide range of clay minerals and textural classes (Schjonning et al. 2011).
9. Evaluate fate of SOC transported by erosional processes over watershed scale, and determine whether erosion is a source or sink of atmospheric CO_2.
10. Establish relationship between SOC pool and NPP or agronomic yields for different management scenarios.

Conclusions

Population driven accelerating demands for food and energy are adversely impacting natural resources, and elevating atmospheric concentration of GHGs. High risks of abrupt climate change have necessitated identification of strategies which limit global warming to 2 °C beyond the pre-industrial level. It is in this context that management of SOC pool has a finite but cost-effective option of sequestering atmospheric CO_2 as soil humus. The C sink capacity of soils of agroecosystems and other degraded/desertified lands depend on C loss through historic land use and management, and is estimated at 20–30 Mg C/ha or 66 ± 12 Pg. Conversion to a restorative landuse and adoption of best management practices that create a positive C budget (along with those of N, P, S) can sequester atmospheric CO_2 as soil humus, and also as secondary carbonates. Examples of these practices include no-till farming, conservation agriculture, sustainable intensification, integrated nutrient management and complex farming systems such as agroforestry. There also exists a close relationship between SOC concentration and agronomic productivity. The critical threshold for most soils is between 1.2 and 1.5 % but can be as high as 2.0 %. Despite its numerous benefits (economic, ecologic, and sociologic), CA/SI systems are not adopted by small landholders and resource-poor farmers because of the competing uses of crop residues and other constraints. Thus, payments to farmers for provisioning of ecosystem services can incentivize them and promote the adoption of recommended or best management practices. In the meanwhile, there is a strong need to assess the importance of biofuels, biochar and other options critically and objectively based on thoroughly conducted life cycle analyses.

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Chapter 36
GlobalSoilMap and Global Carbon Predictions

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Abstract The *GlobalSoilMap* project is representative of a global consortium of scientific institutions involved in soil survey and soil science. The *GlobalSoilMap* group was formed as an outgrowth of the International Union of Soil Sciences Working Group for Digital Soil Mapping with the purpose of providing consistently produced soil property information at 100 m resolution across the world. This information will aid in solving some of the key environment and societal issues of the day, including food security, global climate change land degradation and carbon sequestration. Data would be produced using mostly the storehouse of existing legacy soils data along with geographic information and a range of covariates. A range of modeling techniques is used dependant on the complexity of the background soil survey information. The key soil properties that would be most useful to the modeling community and other users are: organic carbon (g/kg), texture (sand %, silt %, clay % and coarse fragments %), pH, depth to bedrock or restrictive layer. Predictions are made at specified depths with uncertainty values assigned to each prediction.

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An innovative splining technique will be employed to provide a continuous prediction of soil property values throughout the depth of each profile. Maps have been produced at the country level in the Australia, Canada, Denmark, Nigeria, South Korea and the US and work is on-going in many other parts of the world.

Keywords Digital soil mapping • Organic carbon • Splinning

Introduction

The need to address growing environment and societal needs such as land degradation, global food security, climate change mitigation, biodiversity issues, water quality and quantity and energy issues have elevated the need for higher quality, consistent and relevant soil information across the world. It is now commonly accepted that on our current population growth, our food production will need to double in just a few decades to support the growing world population. Our understanding of soil functional capability, soil's resilience to respond to changing environments and resistance to degradation are key factors in the overall information needed to solve these significant issues and problems.

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Fig. 36.1 *GlobalSoilMap* nodal boundaries

The *GlobalSoilMap* Project is designed to provide updated soil property functional information that is key to solving some of the world's most critical problems as well as to understand how the soil can be best used and managed. The information is designed to be consistently produced and in a format that is compatible with other resource information (satellite data, digital elevation models, climatic information, geological information, etc).

The *GlobalSoilMap* project originated as an outgrowth of the International Union of Soil Sciences Working Group on Digital Soil Mapping. The Working Group understood that there is a demand for up to date, relevant and pragmatic information for the soil resource. The group also recognized there are major gaps and inconsistencies in the existing information and that digital soil mapping offers a means to generate information at resolutions that provide data at the landscape and field scale that make use of advanced technology and data systems and can be produced efficiently.

The *GlobalSoilMap* consortium is made up of institutions that are leaders in producing, analyzing and interpreting soil survey information from around the world. This unique consortium is responsible for developing and coordinating overall policies and technical procedures that can be applied throughout the project, along with exploring fund raising potentials, building partnerships and developing data.

The consortium partnership is developed on the basis of regional nodes. Each node has a designated lead institution that is responsible for building partnerships and leading the development of the data within the individual node. Figure 36.1 displays the nodal boundaries for the *GlobalSoilMap* project. Individual countries within the nodes are encouraged to coordinate with the lead institution on the development of data and building of expertise and capacity within each of their individual countries.

Soil organic C (SOC) is one of the key soil properties that has been chosen by the GlobalSoilMap consortium. Here, we present some background and first SOC maps for different parts of the world.

Background

The *GlobalSoilMap* project was designed to take advantage of the large storehouse of legacy soil information that is available in many countries around the world. Legacy data that can be used to produce soil property information are polygon soil maps, point pedon data and soil property databases. This information combined with other co-variate environmental information, such as climatic data, remote sensing information (satellite and digital elevation models) and geological data make up the tools to produce digital soil mapping models. This information can be produced even with limited background information (Hartemink et al. 2008).

A range of modeling techniques will be used dependant on the complexity of the background soil survey information. Figure 36.2 is the Digital Soil Mapping Workflow diagram that documents available soil data and the possible modeling options for producing raster based soil property information. The consortium has also produced *GlobalSoilMap* Standards and Specifications (Arrouays et al. 2013)

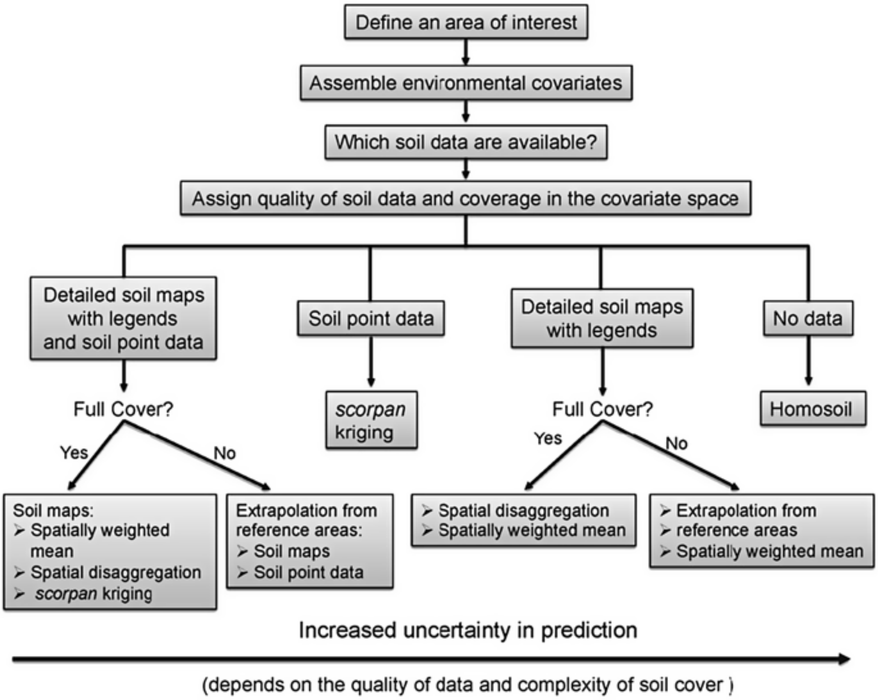

Fig. 36.2 Digital Soil Mapping Workflow to be used in creating *GlobalSoilMap* soil property information

that will guide the development of data. There are five basic tenants to the Standards and Specifications:

1. The spatial entity,
2. The soil properties to be predicted (and the date associated with their prediction)
3. The uncertainties for each soil property
4. The age of the data or information used to estimate the predicted properties
5. The validation measure to be used and reported.

The primary spatial entity that will be delivered is a single point value located at the centre point of the same global grid of 3 arc-seconds by 3 arc-seconds (100 m by 100 m). In the vertical dimension, predictions of soil property values and their associated uncertainties will be made to 2 m (if possible) with data reported for six depth intervals of 0–5 cm, 5–15 cm, 15–30 cm, 30–60 cm, 60–100 cm and 100–200 cm. Twelve soil properties will be predicted at each location. These are: (1) total profile depth (cm), (2) plant exploitable (effective) soil depth (cm), (3) organic carbon (g/kg), (4) pH (×10), (5) sand (g/kg), (6) silt (g/kg), (7) clay (g/kg), (8) gravel (m3 m-3), (9) ECEC (cmolc/kg), (10) bulk density of the fine earth (< 2 mm) fraction (excludes gravel) (Mg/m3), (11) bulk density of the whole soil in situ (includes gravel) (Mg/m3) and (12) available water capacity (mm). Additional soil properties including, for example, EC (dS/m) may be predicted at the discretion of the nodes but these are not mandatory.

Each soil property will have an estimate of the uncertainty associated with the prediction for each depth (for properties reported by depth) for each grid location. Uncertainty here is defined as the 90 % prediction interval (PI), which is the range in values within which the true value at any point prediction location is expected to be found 9 times out of 10 (90 %).

Soil Organic C Maps

From the inception of the project, the Consortium realized that focusing on providing functional soil properties was going to be a key element of the project. Baseline data for terrestrial carbon was at the top of the list for information to be mapped. The following figures depict three countries efforts to provide soil carbon data following the *GlobalSoilMap* standards and specifications.

Figure 36.3 is the standard *GlobalSoilMap* depths for the United States derived from STATSGO2, US General Soil Map. These data have been produced using spatially weighted mean calculation (Hempel et al. 2012).

Figure 36.4 is the standard *GlobalSoilMap* depths for South Korea derived from interpolated point data to 100 cm. (personal communication with S.Y. Hong).

Figure 36.5 is the standard *GlobalSoilMap* depths for the major cropland areas of Canada derived from Soil Landscapes of Canada Soil Map. These data have been produced using spatially weighted mean calculation (Hempel et al. 2012).

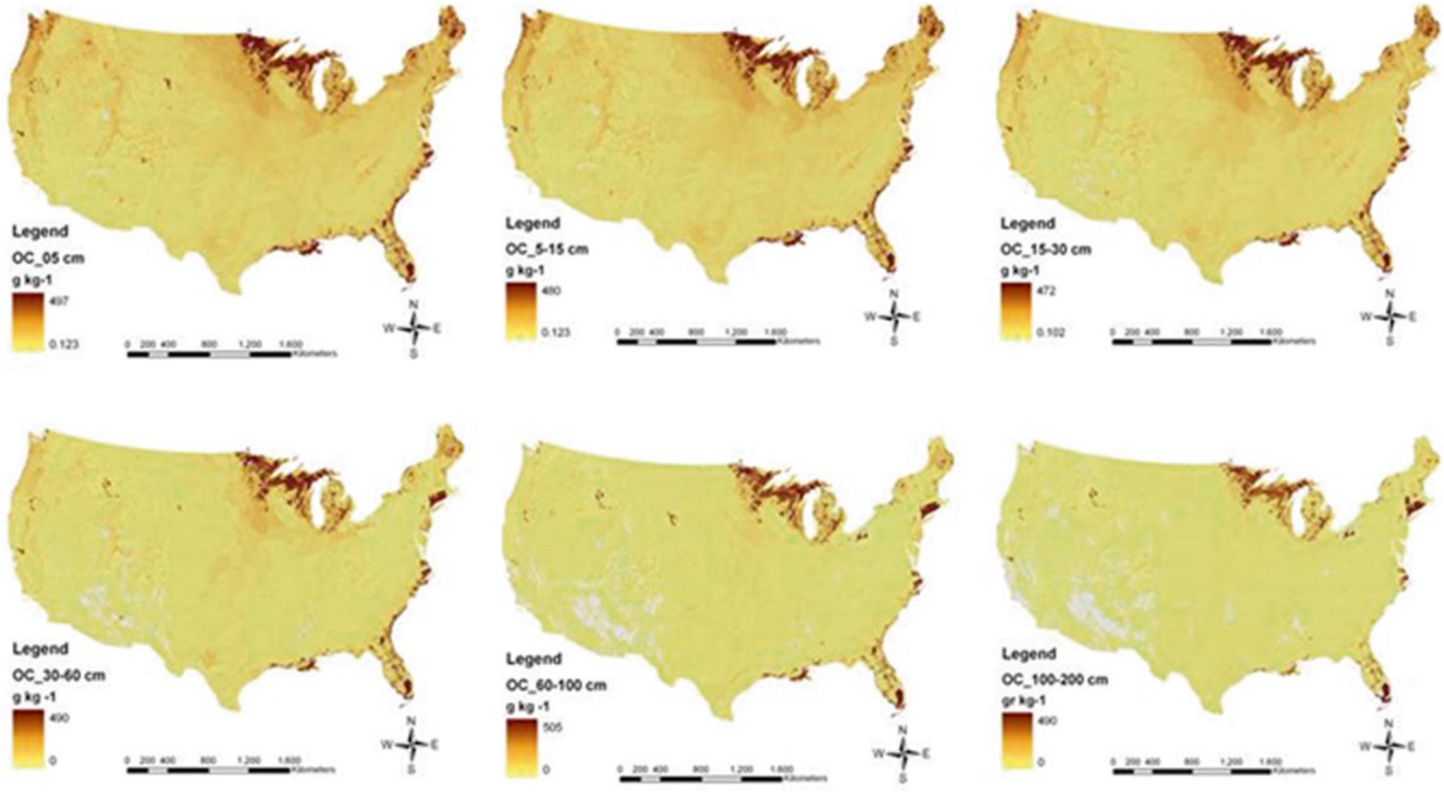

Fig. 36.3 Soil Organic Carbon, United States, standard *GlobalSoilMap* depths based on STATSGO2 derived using spatially weighted means calculation

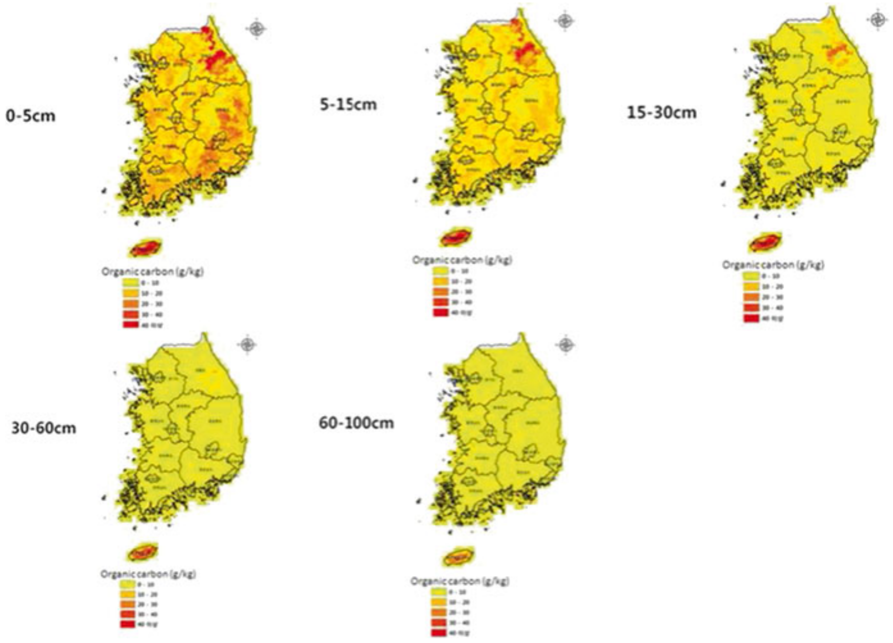

Fig. 36.4 Soil Organic Carbon, South Korea, standard *GlobalSoilMap* depths to 100 cm based on point data, derived using spatial interpolation techniques

Figure 36.6 is the standard *GlobalSoilMap* depths for Denmark derived from interpolated point data to 100 cm (0–30 cm is combined due agricultural mixing to this depth) (personal communication with M. Greve).

Additionally, there are many other countries that have used and are testing the *GlobalSoilMap* standards and specifications to produce and terrestrial carbon stock information including Australia, parts of Indonesia, Denmark, France, The Netherlands, Algeria, Tunisia, other parts of Africa, Mexico, Columbia and parts of Antarctica.

Conclusion

The *GlobalSoilMap* project brings together a host of institutions that have long histories of working in the production, interpretation and advancement of soil science and soil survey information. This international consortium has developed the first ever set of standards and specifications for producing soil survey information using digital soil mapping techniques and methodologies. Included in the standards are innovative concepts such as reporting uncertainty information with predictions for soil carbon as well as other soil properties. Such information has long been lacking from soil survey data in general. Uncertainty information is not only important in

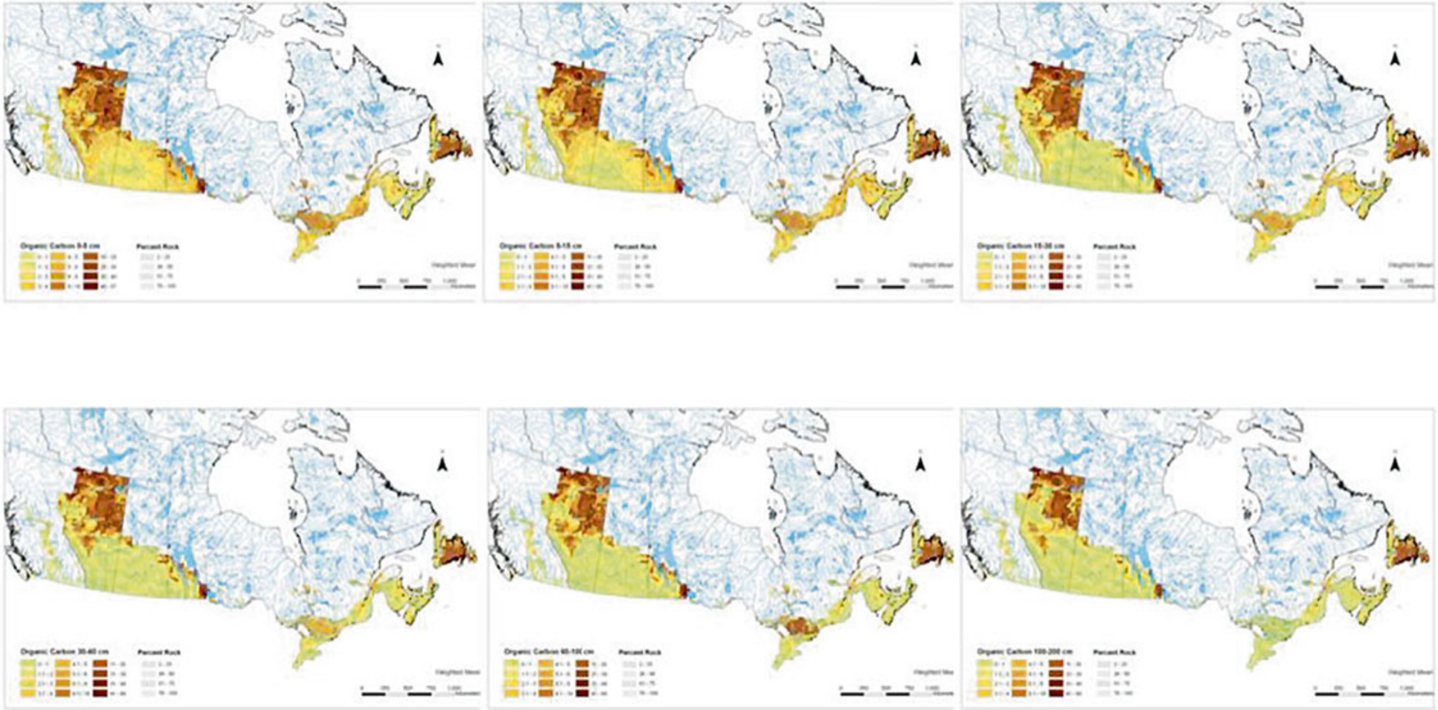

Fig. 36.5 Soil Organic Carbon, Canada, standard *GlobalSoilMap* depths based on Soil Landscapes of Canada derived using spatially weighted means calculation

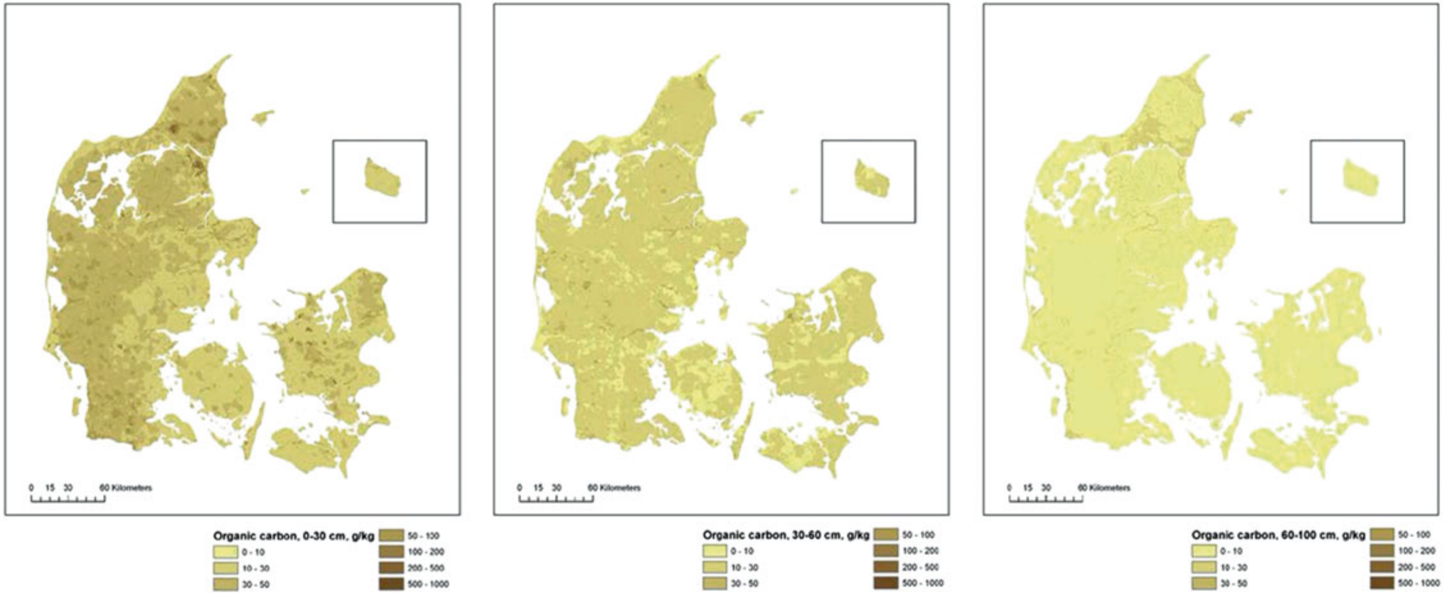

Fig. 36.6 Soil organic carbon, Denmark, standard GlobalSoilMap depths derived from interpolated point data to 100 cm (0–30 cm is combined due agricultural mixing to this depth)

deciding how best to use the data, but is also a key component for planning where additional sampling is needed (areas of low uncertainty values) to bring the data to an acceptable level of confidence needed to make decisions.

Additionally, the soil depth functions (splines) are an excellent added value component to the information. These depth models provide values for a soil property such as carbon at each location (pixel) for any depth along the soil column or aggregated values for any range of depths along the soil column (i.e. carbon stock from 0 to 90 cm or 50 to 150 cm).

As soil resource information becomes more and more important to the world community as a component of resource planning, the *GlobalSoilMap* project has proven to be an effective means of providing consistent and relevant information at a resolution that can be effectively used at the landscape and field level. It is possible to produce this data irrespective of the type of background information that is at hand with a variety of methodologies.

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Chapter 37
Distribution of Organic Carbon in the Soils of Antarctica

James G. Bockheim and Nick W. Haus

Abstract Antarctica can be divided into nine ice-free regions. Only 0.35 % of the continent is ice-free, amounting to 49,500 km^2. Profile quantities of soil organic carbon (SOC) determined on a mass per area basis are greatest along the Antarctic Peninsula, intermediate in East Antarctica, and lowest in the Transantarctic Mountains (TAMs). Sea-birds input very large quantities of manure in terrestrial environments and are the dominant factor influencing SOC levels in Antarctic soils. In the McMurdo Dry Valleys, profile quantities of SOC are related to proximity to water sources. From chronosequence studies, the amounts of SOC in the TAMs peak in about 2 kyr and decline thereafter but SOC storage in soils of the Antarctic Peninsula continue to rise after 8 kyr. Because of a dramatically warming climate, the ice-free area of Antarctica is increasing and there is evidence that the soils may be acting as a sink rather than a source for atmospheric carbon dioxide.

Keywords Carbon storage • Seabirds • Climate change

Introduction

Only 0.35 % or 49,500 km^2 of Antarctica is ice-free. Soil organic C (SOC) concentrations have been measured at numerous sites in the Transantarctic Mountains (TAMs) and along the Antarctic Peninsula, but few data are available for other regions. To date only the study by Claridge et al. (2000) has estimated SOC storage in Antarctic soils. Claridge et al. (2000) estimated that the soils of Antarctica may contain a total C stock of 725 Mt, with 600 Mt from soils of the Antarctic Peninsula.

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With climate warming along the western Antarctic Peninsula (Bockheim et al. 2013), there is considerable interest in the storage and dynamics of SOC in the soils of Antarctica. The objective of this study is to construct SOC storage for soils in selected regions of Antarctica.

Study Area

Antarctica can be divided into nine ice-free regions (Fig. 37.1). The largest ice-free area is the Transantarctic Mountains – TAMs (24,200 km^2), followed by the Antarctic Peninsula and its offshore islands (10,000 km^2), with smaller areas (from largest to smallest) scattered around the periphery of the continent in MacRobertson Land, Queen Maud Land, the Ellsworth Mountains, the Pensacola Mountains, Enderby Land, Wilkes Land, and Marie Byrd Land.

There are three predominant climates in Antarctica: a mild-wet-maritime climate along the western Antarctic Peninsula (region 8 west), a cold-moist-maritime climate along the eastern Antarctic Peninsula (region 8 east) and East Antarctica (regions 2 through 4), and a very cold-hyperarid-inland climate elsewhere in the

Fig. 37.1 Eight major ice-free regions of Antarctica. The total ice-free area is 49,500 km2 or 0.36% of the continent

interior mountain ranges (regions 1 and 5 through 7). On the Antarctic Peninsula, the mean annual air temperature (MAAT) and mean annual (water-equivalent) precipitation (MAP) range from −1 to −2 °C and 500 to 1,500 mm, respectively. In East Antarctica, the MAAT and MAP range from −9 to −11 °C and 200 to 700 mm; and in the mountains from −15 to −25 °C and 10 to 200 mm.

Whereas region 8 west has abundant plant cover in places, including mosses and also two higher plants (*Colobanthus quitensis* and *Deschampsia antarctica*), the plant cover is sparse elsewhere on the continent. Seabirds are abundant in coastal regions throughout the continent, particularly along the western Antarctic Peninsula. Landforms in Antarctica range from late Holocene along the western Antarctic Peninsula and in coastal areas throughout Antarctica to Miocene-aged (11–14 Ma year) in the TAMs. Till derived from a variety of rocks is the dominant parent material. The topography is steep throughout much of the ice-free areas of Antarctica except along the valley floors in the TAMs.

Methods

We reviewed 113 published studies from the Web of Science (Web of Knowledge) using search words "soil organic carbon" and "Antarctica," obtained data from the US Department of Agriculture Natural Resource Conservation Service database (Soil Survey Division Staff 2013), and used our own data for the analysis. Most of the published data pertain to topsoils only but data were provided for complete profiles of SOC by Beyer (2000), Beyer et al. (2000), Hofstee et al. (2006), and Beilke and Bockheim (2013). Very few studies provide data on bulk density and we estimated bulk density based on published data for various pedogenic horizons. Profile storage of SOC was determined as the product of horizon thickness, bulk density, and %SOC, corrected for material >2 mm, and summed to a depth of 80 cm. Since there is very little SOC below 80 cm depth in most Antarctic soils, because of bedrock or permafrost, these values can be used for comparisons of soils in other ecoregions.

Results

Profile Storage of SOC

Profile quantities of soil organic carbon (SOC) are highest in organic soils, followed by ornithogenic soils, and then mineral soils. Organic soils may be limited to regions 2 through 4 and 8; SOC storage in these regions ranges from 30 to as high as 63 kg/m^2 for deep organic materials (Table 37.1). Ornithogenic soils occur in areas affected by high levels of seabird manuring, where formation of a complex suite of phosphate minerals dominants the soil chemistry and mineralogy. The heterogeneous distribution and constitution of seabird rookeries, as well as the redistribution of

Table 37.1 Soil organic carbon storage in Antarctic soils

Region	Pedon	Depth (cm)	SOC (kg/m^2)	Classification	References
			Mineral soils		
4	D2	36	7.8	Lithic Haplorthels	Beyer et al. (2000)
4	L2	15	0.1	Lithic Haplorthels	Beyer et al. (2000)
4	B14B	13	2.0	Lithic Haplorthels	Beyer et al. (2000)
4	WP5	80	8.3	Typic Spodorthels	Beyer et al. (2000)
4	A11	80	1.4	Lithic Aquiturbels	Beyer et al. (2000)
5b	84–47	80	0.11	Petrosalic Haplorthels	Beilke and Bockheim (2013)
5b	12	80	1.2	Typic Haploturbels	Hofstee et al. (2006)
5b	SB	80	0.4	Typic Haplorthels	Soil Survey Division Staff (2013)
5b	GH	80	0.4	Typic Haplorthels	Soil Survey Division Staff (2013)
5b	BP	80	0.2	Nitric Anhyorthels	Soil Survey Division Staff (2013)
5b	DJP	80	0.1	Typic Haplorthels	Soil Survey Division Staff (2013)
8	CP03	80	1.1	Typic Gelorthents	This study
8	CP06	80	9.9	Typic Humigelepts	This study
8	CP11	80	9.1	Aquic Humigelepts	This study
8	CP12	80	3.6	Typic Gelorthents	This study
8	CP14	80	7.6	Typic Gelorthents	This study
8	CP17	80	6.1	Aquic Humigelepts	This study
8	CP18	80	4.8	Typic Gelorthents	This study
8	CP19	80	4.4	Typic Gelorthents	This study
8	CP23	80	17.1	Typic Humigelepts	This study
8	CP27	80	10.4	Typic Humigelepts	This study
8	L12	80	4.0	Typic Gelorthents	This study
8	L17	80	4.4	Typic Humigelepts	This study
8	L18	80	9.2	Typic Humigelepts	This study
8	L19	80	3.2	Typic Humigelepts	This study
			Organic soils		
4	M2	22	9.1	Lithic Hemistels	Beyer et al. (2000)
4	M1	13	9.8	Lithic Fibristels	Beyer (2000)
4	WP4	40	29.1	Typic Hemistels	Beyer (2000)
8	CP05	80	62.8	Lithic Cryofolists	This study
8	CP21	33	11.0	Typic Cryofolists	This study
8	CP09	80	30.8	Typic Cryosaprists	This study
			Ornithogenic soils		
3	As	20	7.0	[ornithogenic soil]	Zhu et al. (2009)
3	Ss2	20	2.7	[seal colony]	Zhu et al. (2009)
4	A13	80	1.6	Typic Spodorthels	Beyer et al. (2000)
4	WP1	14	0.4	[ornithogenic soil]	Beyer et al. (2000)
5b	1	80	35.3	Typic Haplorthels	Hofstee et al. (2006)
5b	3	80	28.8	Typic Aquorthels (abandoned)	Hofstee et al. (2006)
8	CP10	50	3.5	Lithic Humigelepts	This study

dissolved carbon results in a highly variable SOC storage in areas with ornithogenic soils. Soil OC variability is also directly dependent on the period of rookery occupancy and indirectly dependent on increased vegetation growth associated with seabird manuring; SOC storage in ornithogenic soils ranges from 1.6 kg/m^2 in an abandoned rookery at Casey Station to as high as 35 kg/m^2 in an active rookery in North Victoria Land. In mineral soils, SOC storage is greatest along the Antarctic Peninsula and the South Shetland Islands (6.8 ± 1.1 kg/m^2), intermediate in East Antarctica (3.9 ± 1.7 kg/m^2), and least in the TAMs (0.40 ± 0.17 kg/m^2).

Discussion

Factors Influencing SOC Storage

Seabirds and nesting birds constitute the dominant factor influencing SOC levels in Antarctic soils (Beyer 2000; Beyer et al. 2000; Park et al. 2007). The mechanism whereby seabirds influence soil development and accumulation of SOC is depicted in Fig. 37.2. Ice-free areas with large deposits of seabird manure undergo phosphatization, the process whereby a suite of phosphate minerals are

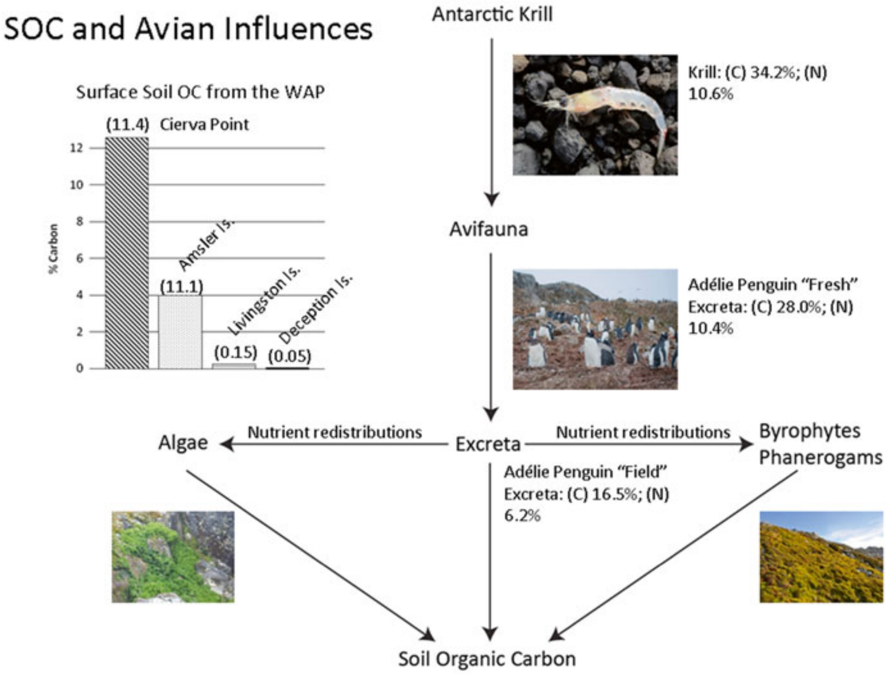

Fig. 37.2 Avian influences on soil organic carbon in maritime Antarctica

precipitated resulting in the formation of ornithogenic soils. Ornithogenic soils are best expressed directly under active Adélie (*Pygoscelis adeliae*), chinstrap (*P. antarctica*), or gentoo *(P. papua)* penguin rookeries but are also commonly found at abandoned rookeries, where ornithogenic soils remain hundreds to thousands of years later (Myrcha and Tatur 1991). An estimated 200,000 Mg of C and 20,000 Mg of P is deposited annually in rookeries of maritime Antarctica from Adélie and Chinstrap penguin excrement (Pietr et al. 1983; Myrcha and Tatur 1991). The high levels of seabird manure are a function of nutrient upwelling at the Antarctic Convergence and along the continental shelf of the Antarctic Peninsula; nutrients feed large blooms of phytoplankton to sustain Antarctic krill, which are subsequently consumed and excreted by seabirds to develop the soils of maritime Antarctica.

The effects of the high levels of soil C (>4 %), N (>2 %), and P (>1 %) are not isolated to areas with direct manure inputs. The two main transport mechanisms whereby nutrients are removed from rookeries are wind erosion and water solution. Bird trampling and unfavorable chemical conditions result in rookeries that are almost entirely devoid of vegetation, leaving nutrient rich surface soils susceptible to wind and water erosion. Nutrient rich solutions have been observed moving downslope at several abandoned rookeries in the South Shetland Islands where geologic uplift has stranded marine terraces at higher elevations (Myrcha and Tatur 1991). The effects of these allochthonous nutrients on SOC can be either direct (deposition of organic acids and detritus), or indirect as the nutrients stimulate vegetative growth (algae, mosses and vascular plants).

In the McMurdo Dry Valleys, concentrations of SOC in the topsoil are related to proximity to water sources (Burkins et al. 2000; Ayres et al. 2007). Referred to as the hyporheic zone, this critical transition zone between aquatic and terrestrial ecosystems features not only a comparatively high biodiversity but also greater populations of organisms such as nematodes and rotifers than in other areas.

From chronosequence studies, the amounts of SOC in the TAMs peak in about 2 kyr and decline thereafter. Soil OC increases with time to at least 8 ka in the South Shetland Islands and along the Antarctic Peninsula (Strauss et al. 2009; This study).

SOC Storage in a Warming Climate

The land area is increasing in many areas of the Antarctic Peninsula. For example, at Palmer Station the Marr Piedmont Glacier has been retreating ~10 m/year since the early 1960s, exposing new materials for plant establishment and soil development. Strauss et al. (2009) reported a 2.5- to 5-cm thick organic horizon forming in about 2 kyr on Stepping Stone Island near Palmer Station. A warming experiment showed that total OC pools in the aboveground biomass, litter, and organic soil horizon at Palmer Station were significantly greater when diurnal and daily canopy air temperatures were raised by 2.3 and 1.3 °C, respectively (Day et al. 2008).

There are significant and positive correlations between SOC and cultivable fungal abundance (Arenz and Blanchette 2011) and nematodes, rotifers and tardigrades (Ayres et al. 2007).

Conclusions

From our work the following can be concluded:

There are insufficient data available for quantifying SOC storage in Antarctic soils.

- Based on limited data, SOC storage is greatest in organic soils, followed by ornithogenic soils, and then mineral soils.
- Soil region 8 (Antarctic Peninsula) has the greatest storage of SOC, followed by East Antarctica (region 4), with the least storage in soils of region 5b (Transantarctic Mountains).
- Key factors influencing SOC storage in Antarctic soils include the presence of seabirds (all coastal areas), the proximity to water sources (McMurdo Dry Valleys), and soil age (regions 4 and 8).
- Based on limited information, continued warming along the Antarctic Peninsula is likely to expose more area for soil development and plant colonization, possibly leading to a reduction in atmospheric CO_2.

Acknowledgments This project was supported by the U.S.A. National Science Foundation, Office of Polar Programs, Antarctic Sciences, grant OPP-0943799.

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Chapter 38
Carbon Balance in Soils of Northern Eurasia

Vladimir Stolbovoy and Andrei Ivanov

Abstract Current rise in temperature and precipitation in Northern Eurasia leads to a positive carbon balance (CB) and C sequestration (72 ± 32 million tons of carbon (Mt C) annually) in the soils of tundra, forest-steppe, steppe, and semidesert natural zones. The CB of deep peat bogs (about −141 Mt C) and surface O horizons (about 221 Mt C) under grasses and shrubs are the main drives of the regional CB.

Spatially explicit analysis demonstrates a complex mosaic of CB by different Land Use and Cover (LUC) classes (from −0.1 Mt C under cropland to 221 Mt C under grasses and shrubs) and natural zones (from −71 Mt C in the forest-tundra and northern taiga to 193 Mt C in the steppe zone). These differences make it difficult to establish representative CB for the entire region. The extrapolation of the negative CB in deep peat bogs occupying about 16 Mha over the entire tundra zone (nearly 260 Mha) results in a misleading conclusion about enhanced degradation of soil organic matter (SOM) in this zone upon climate warming, which might further increase the concentration of greenhouse gases in the atmosphere.

The regional analysis of the spatially explicit CB contributes to our understanding of the pedogenic processes and mechanisms driving regional C dynamics in soils.

Keywords Carbon cycle • Soil carbon balance • Greenhouse gases

Introduction

Northern Eurasia with Russia as its largest part is a vast area covering nearly 11 % of the global terrain. It is characterized by considerable geographic diversity encompassing eight natural zones and about 70 % of the World Reference Soil Groups

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(WRB 2006). Nearly 75 % of the territory of Russia lies in the permafrost zone with soils enriched in the SOM in the form of surface litter and peat. These substances are susceptible to decomposition upon climate warming contributing to the enhanced emission of greenhouse gases (GHG). However, in spite of numerous publications following this notion, surprisingly little data is available to prove it.

In recent decades, tremendous efforts have been made to revise individual compartments of the terrestrial C cycle, including C stocks in vegetation (Nilsson et al. 2000), soils (Stolbovoi 2000, 2002, 2006) and peats (Tarnocai and Stolbovoy 2006), net primary production of vegetation (Nilsson et al. 2000), respiration by heterotrophs (Stolbovoi 2002), C discharge into the ocean with river flows (Romankevich and Vetrov 2001), major biogeochemical C fluxes (Stolbovoi et al. 2004), etc. By and large, all these studies address the problem of the impact of climate change on the global C cycle and the role of terrestrial ecosystems and, particularly, soils in the related processes. In addition to the academic interest, this knowledge has many practical implications related to our understanding of the mechanisms driving climate change; to food and fiber production and efficiency of agriculture and forestry; to soil, water, and air quality; and to functioning and evolution of ecosystems and the Earth system as a whole.

Several studies report that C fluxes are temporary and spatially dynamic in nature. For example, heterotrophic respiration (HR) varies by 30 % from year to year for a given soil and changes by 400 % from soil to soil at relatively short distances in Russia (Stolbovoi 2003) and globally (Raich and Schlesinger 1992). Similar interannual and annual variability have been found for C concentrations in river water (Romankevich and Vetrov 2001). The high variability of C fluxes and random sampling of the latter make it difficult to estimate regional C balances.

This paper is aimed at estimating the CB in soils of Northern Eurasia on the basis of spatially explicit inventories of C fluxes. The intention is to describe the fluxes of C in soil horizons and total soil profiles in order to understand pedogenic mechanisms driving dynamics of soil C pools and examine credible representativeness of CB for the large and naturally diverse geographical areas.

Terms and Concepts

It is known that a considerable part of the plant litter undergoes complete oxidation resulting in the escape of CO_2 back to the atmosphere. Minor portions of litter are subjected to microbial metabolism with release of nutrients cycling between SOM and microbial biomass. This cycling results in microbial mediated polymerization of organic compounds (phenol production) and humus formation (Stevenson 1994). As a catalytic oxidation-reduction reaction, the decomposition produces a number of organic acids having carboxyl (COOH) groups. The latter easily dissociate their protons (H^+) and induce rock weathering. The remaining carboxylate anion (COO^-) forms soluble complexes with metal cations released by weathering.

This process leads to formation of dissolved organic substances (DOSs) giving rise to migration and water transport of organic constituents to the hydrosphere and lithosphere. It is reported that river discharge contributes nearly 15 % to ocean C turnover, and that terrain is the only source of essential nutrients for the oceans (Romankevich and Vetrov 2001). Some amounts of DOSs penetrate down through the soil profile and are sorbed by soils and minerals in the vadose zone (Kramer 1994). A fraction of DOS entering the lithosphere contributes to formation of fossil fuels (Thurman 1985).

The mentioned above processes result in the development of soil profiles. With respect to behavior of C, it is reasonable to distinguish between surface organic (O) horizons, the topsoil humus-accumulative (A1) horizons, and the underlying humus-illuvial (Bh) horizons. Each WRB soil group has its own combination of these major horizons. Thus, Histosols consist of the O horizon, Podzols have the O and Bh horizons, native Chernozems have the O and A1 horizons, Podzoluvisols have the O, A1, and Bh horizons, etc.

The net CB of a soil (dS) can be calculated as follows:

$$\mathrm{dS} = \mathrm{dO} + \mathrm{dA1} + \mathrm{dBh}, \tag{38.1}$$

where O, A1, and Bh are the horizons explained above, and d denotes the difference between C input into these horizons and C output from them.

To calculate the CB in particular horizons, the following equations can be used:

$$\mathrm{dO} = \mathrm{DetA} - \left(\mathrm{DecA} + \mathrm{Trans} + \mathrm{Mig}\right), \tag{38.2}$$

where dO is the annual CB of the O horizon, DetA is the C input into the O horizon with the litter of the aboveground vegetation (plant detritus), DecA is the decay of DetA, Trans is the transport (removal) of particulate and dissolved organic substances with surface water, and Mig is the downward migration of soluble C.

$$\mathrm{dA1} = \mathrm{DetU} + \mathrm{Hum} - \left(\mathrm{DecU} + \mathrm{Min}\right), \tag{38.3}$$

where dA1 is the annual CB in the humus horizon, Hum is the rate of humification of the underground plant litter (underground detritus DetU), DecU is the decay of DetU, and Min is the rate of humus mineralization.

$$\mathrm{dBh} = \mathrm{Mig} - \left(\mathrm{Deep\,Leak} + \mathrm{URO}\right), \tag{38.4}$$

where dBh is the annual CB in the humus-illuvial horizon; Mig is the amount of soluble C migrated from topsoil horizons; Deep leak is the transport of soluble C into the deep lithosphere; URO is the lateral underground runoff.

We used a set of independent georeferenced databases (Stolbovoi and McCallum 2002) and newly established spatially explicit databases on C transport by surface water, downward migration of dissolved organic matter, underground runoff, and deep leak. The calculation exploited raster datasets (1 × 1 km grid) assembled in the ArcInfo Grid allowing for CB computations and visualizations, including map production.

Consistency Control

The GIS analysis of independently established spatially explicit databases is meaningful, if the vital consistency among them is demonstrated. For this reason, the spatially explicit dependence of heterotrophic respiration (HR) on NPP was investigated (Fig. 38.1). Data on these characteristics were derived from independent georeferenced databases (HR was derived from the soil database, and NPP was derived from the vegetation database). As seen from Fig. 38.1, these parameters display good correlation (R2 = 0.83) for cropland (Fig. 38.1a) and forests (Fig. 38.1b). Acceptable coefficients of determination are found for wetlands (R2 = 0.68, Fig. 38.1c) and for grasses and shrubs (R2 = 0.56, Fig. 38.1d). Note that the last two categories represent complex LUC classes; thus, wetlands may include swampy forests, and grasses and shrubs may include dwarf swampy forests; etc. However, in spite of this mixture, the consistency analysis illustrates reasonably good correspondence between NPP and HR. This finding is in line with widely reported good correspondence between these two parameters for Russia and globally (Raich and Schlesinger 1992; Stolbovoi 2003).

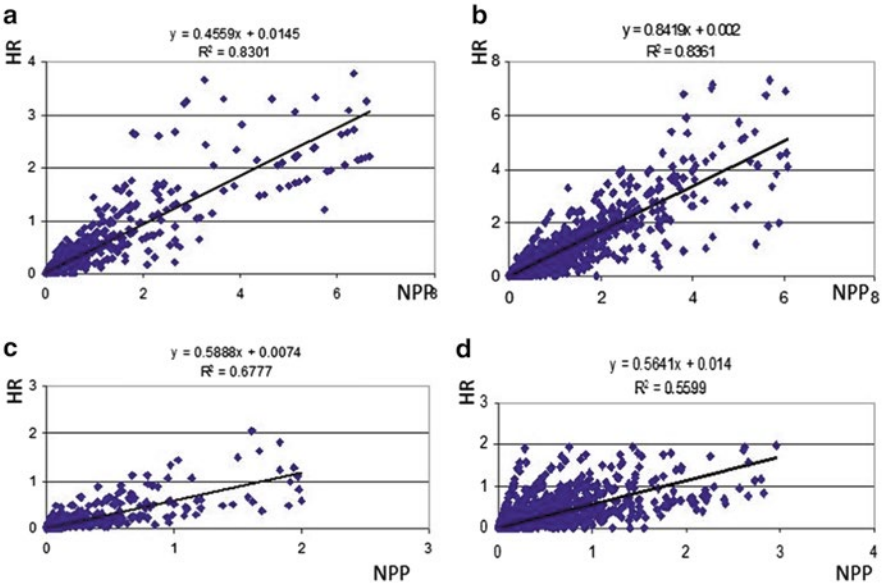

Fig. 38.1 Spatially explicit correlation between independent datasets on soil heterotrophic respiration (*HR*) and net primary production (*NPP*) of vegetation. (**a**) Cropland (n = 3,277), (**b**) Forests (n = 8,212), (**c**) Wetlands (n = 2,097), (**d**) Grasses and Shrubs (n = 8,086)

Results and Discussion

Figure 38.2 illustrates spatial distribution of the CB in individual soil horizons and entire soil profiles. Spatial domination of boreal forests is clearly seen on all the maps. The forest soils have a negative CB in the O horizon (brownish color, Fig. 38.2a) and slightly positive CB in the A1 and Bh horizons (light green, Fig. 38.2b, c, respectively). The resulting CB for the total soil (orange, Fig. 38.2d) remains negative. In the tundra soils, the CB is different. It is positive (green, Fig. 38.2a) in the O horizon, close to zero in the A1 horizon (yellow, Fig. 38.2b) and negative (pink, Fig. 38.2c) for the Bh horizon. The resulting CB for the total soil in the tundra is positive. The CB for the total soil under cropland (steppe areas) is close to zero or slightly positive (green, Fig. 38.2d). It is important that the maps illustrate the diversity of CB patterns for separate soil horizons and entire soil profiles. None of the maps closely follows the patterns on the other maps.

Table 38.1 contains quantitative parameters of CB for individual soil horizons and entire soil profiles. The CB for the O horizon varies by LUC classes and by natural zones. Soils under cropland do not have the O horizon and are ignored. Soils of pastures show degradation of the O horizon (−30.4 Mt C in total) in all natural zones, except for steppes (9.5 Mt C). Soils under forests display the overall degradation of the O horizon (−39 Mt C), which is particularly pronounced in the boreal forest (taiga) zones. The CB is positive in the forest-steppe, steppe, and semidesert soils. Swamps (30–50 cm peat) are characterized by the growth of the O horizon virtually in all natural zones (39.9 Mt C). At the same time, bogs (> 50 cm peat) show considerable decay of the O horizon (−141.8 Mt C) in virtually all natural zones. Grasses and shrubs indicate the growth of the O horizon (221.6 Mt C) in all natural zones.

The CB of the A1 horizon is positive for all soils (Table 38.1). In general, the increase in humus is quite small in cropland and pastures, as well as in swamps and bogs. A more significant humus accumulation is found for forest soils and for soils under grasses and shrubs. The intensity of humus enrichment in soils slightly varies by natural zones. Note a significant increase in humus content in the cold zone, such as taiga and tundra.

The CB for the Bh horizon is positive in total (Table 38.1), which is mainly caused by intensification of humus illuviation in the middle taiga soils. Shallow peat swamps demonstrate an intensification of humus illuviation in all natural zones. The intensity of humus illuviation declines in the soils of cropland and pastures and grasses and shrubs.

As shown in Table 38.1, the subtotal CB is positive for all the soil horizons and total soil (72.0 Mt C). The most significant increase of C is observed for the O horizon (50.4 Mt C). This is twice as much as the subtotals for the A1 (12.7 Mt C) and Bh (12.9 Mt C) horizons.

Mostly, the positive CB is driven by accumulation of C in soils under grasses and shrubs (221.4 Mt C). As indicated above, this LUC class encompasses mainly deciduous shrubs providing abundant litter. Considerable increase of C is observed in the forest-steppe zone with broadleaf deciduous trees (45.6 Mt C) and in tundra swamps (20.7 Mt C).

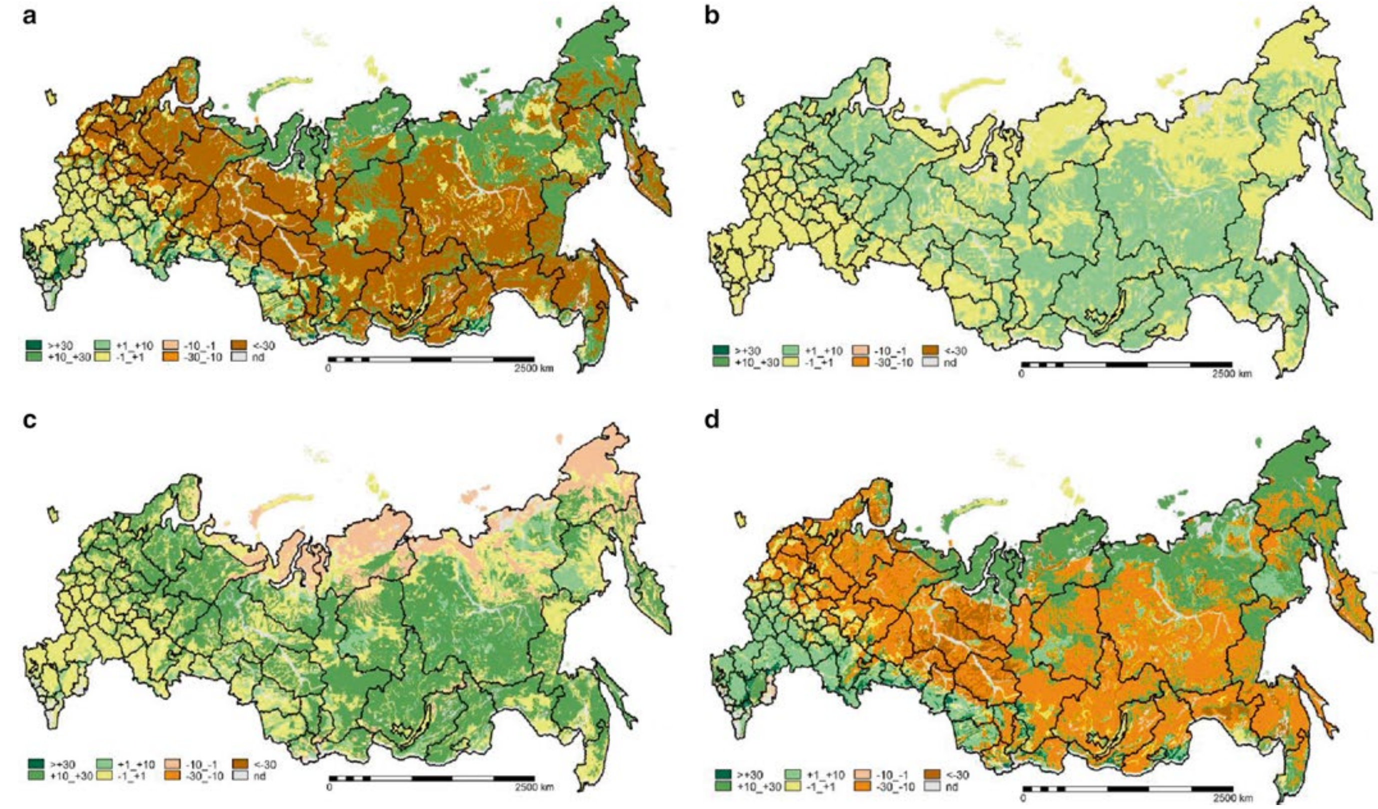

Fig. 38.2 Carbon balance for soil horizons and entire soil profiles. Boundaries of administrative regions of Russia are indicated. (**a**) Organic (O), (**b**) Humus (A1), (**c**) Humus-illuvial (Bh), (**d**) Total soil

Table 38.1 Balance of C fluxes (Mt C) by soil horizons and total soil

Zone\LUC	Cropland	Pasture	Forest	Swamps, 30–50 cm peat	Bogs, >50 cm peat	Grasses & shrubs	Total zone
Organic horizon (O)							
Tundra	0	–3,6	–0,9	19,9	–17,0	17,7	16,1
Forest-tundra & northern taiga	0	–2,2	–43,5	15,8	–52,4	12,0	–70,3
Middle taiga	0	–16,1	–32,1	–0,4	–43,6	22,7	–69,5
South taiga	0	–12,4	–24,9	–0,5	–31,1	10,6	–58,3
Forest-steppe	0	–4,6	17,5	0,6	–0,2	8,4	21,7
Steppe	0	9,5	43,8	3,9	2,4	127,8	187,4
Semidesert	0	–0,9	1,1	0,6	0,1	22,4	23,3
Total LUC	0	–30,3	–39	39,9	–141,8	221,6	50,4
Humus horizon (A1)							
Tundra	0	0	0	0,1	0,2	0,5	0,8
Forest-tundra & northern taiga	0	0	0,7	0,1	0,2	0,1	1,1
Middle taiga	0	0	4,0	0,2	0,4	0,8	5,4
Southern taiga	0,1	0	1,6	0,3	0	0,2	2,2
Forest-steppe	0,1	0	0,5	0	0	0,1	0,7
Steppe	0,7	0,3	0,5	0	0	0,8	2,3
Semidesert	0	0	0	0	0	0,2	0,2
Total LUC	0,9	0,3	7,3	0,7	0,8	2,7	12,7
Humus-illuvial horizon (Bh)							
Tundra	0	–0,1	–0,2	0,7	–0,2	–4,9	–4,7
Forest-tundra & northern taiga	0	0	–2,0	0,7	–0,6	–0,2	–2,1
Middle taiga	–0,2	–0,2	11,9	1,7	0,3	0,6	14,1
Southern taiga	–0,6	–0,2	3,5	0,2	0,4	0,3	3,6
Forest-steppe	–0,5	–0,1	–0,4	0	0	–0,1	–1,1
Steppe	0,4	0,1	1,3	0,1	0,1	1,8	3,8
Semidesert	–0,1	–0,2	0	0	0	–0,4	–0,7
Total LUC	–1,0	–0,7	14,1	3,4	0	–2,9	12,9
Total soil							
Tundra	0	–3,7	–1,1	20,7	–17,0	13,3	12,2
Forest-tundra & northern taiga	0	–2,2	–44,8	16,6	–52,8	11,9	–71,3
Middle taiga	–0,2	–16,3	–16,2	1,5	–42,9	24,1	–50,0
Southern taiga	–0,5	–12,6	–19,8	0	–30,7	11,1	–52,5
Forest-steppe	–0,4	–4,7	17,6	0,6	–0,2	8,4	21,3
Steppe	1,1	9,9	45,6	4,0	2,5	130,4	193,5
Semi-desert	–0,1	–1,1	1,1	0,6	0,1	2,0	22,8
Total LUC	–0,1	–30,7	–17,6	40,0	–141,0	221,4	72,0

The analysis does not include any changes in the LUC. Thus, the indicated changes of the CB in the soils most likely driven by climate change. The Fifth National Communication of the Russian Federation (2010) reports that the average climate warming for Russia in 1976–2006 reached 1.33 °C, which was nearly two times higher than the global average of 0.74 °C. The average annual precipitation for the same period increased by 7.2 mm per decade.

According to some authors (e.g., Lal 2012), the increase in the mean annual temperature (MAT) initiates SOM degradation, which coincides with negative CB. Alternatively, the rise of mean annual precipitation (MAP) stimulates SOM enhancement. As discussed above, these rules are not fully applicable for the LUC classes in Russia. For example, the MAT increase in the tundra shifts CB towards C accumulation in soils (Table 38.1). This evidence is found for shallow peat swamps. The MAT rise increases the depth of the active layer, which favors peat growth. Grasses and shrubs provide another example of C increase in soils with the rise in MAT in all natural zones.

The CB in bogs is negative, which is particularly common for the O horizon. The main reason for this is a relatively high rate of HR in bogs as compared with swamps. As shown earlier (Stolbovoi 2002), the HR in bogs is two times higher than in swamps (290 and 147 Mt C, respectively). One of the explanations might be the widely accepted theory on acceleration of litter decomposition due to the MAT rise, the so called Q10 factor.

The CB for boreal forests is negative, which is in line with the general idea of SOM degradation due to MAT increase (Table 38.1). This degradation is most commonly observed in the O horizon. Note that the faster decay of the litter coincides with the accelerated growth of the forest vegetation (Nilsson et al. 2000). As discussed earlier (Stolbovoi 2006), the litter horizon is the main reservoir of essential nutrients in the boreal forest. This depository allows preserving the production potential at a high level in spite of the low actual productivity of the stand. The intensification of the litter decay liberates nutrients supporting tree growth. In addition, accelerated decomposition of the O horizon stimulates humus formation in the A1 horizon and C accumulation in the Bh horizon (Table 38.1). Thus, growth of trees, together with a higher rate of C accumulation in the A1 and Bh horizons, are the main mechanisms to reduce nutrients from leaching.

The CB in the soils of forest-steppe, steppe, and semi-deserts is positive, which is in line with the MAP increase.

The CB in soils of grasslands and shrublands is positive for all the horizons and for the total soil (Table 38.1). The intensive accumulation of C is observed in steppe soils. This observation coincides with increase of MAP that stimulates the growth of shrubs and extra production of litter. Consequently, steppe soils show an increase in humus content and humus absorption in underlying horizons. However, due to the semi-arid (ustic) soil water regime, intensity of C migration is limited, which is in accord with negative CB in underlying soil horizons.

Cropland demonstrates slightly negative CB in the total soil (Table 38.1). This is in line with results of the country-wide field survey (Krylatov 1996). As shown earlier

(Stolbovoi 2002), historical loss of C from cultivated soils is about 3.6 Pg for Russia. However, a recent MAP increase turns the CB in the A1 horizon (plow layer) to slightly positive values. The latter fact illustrates that cropland soils subjected to deep dehumification in the past become extremely sensitive to the environmental changes.

Pasture soils show a negative CB in the total soil, which is mainly caused by degradation of the O horizon in all natural zones, except for steppes (Table 38.1). The historical loss of C from pasture soils is nearly 1.1 Pg, which is caused by improper management, selective consumption of productive species (Stolbovoi 2002).

Uncertainty

The evaluation of uncertainty is crucial for any estimates. It is assumed that variability (Cv) of C fluxes is 30 %. The standard error of the estimate of the total CB is a sum of the errors $s(\Sigma)$ described by the following equation:

$$s(\Sigma) = \sqrt{s_O^2 + s_{A1}^2 + s_{Bh}^2}, \quad \text{where}$$

s_O, s_{A1}, s_{Bh} are standard errors of the CB in the O, A1, and Bh horizons, respectively.

Calculations indicate that the total error of the CB estimate in the total soil is 16.0 (Mt C) with a confidence level P = 0.67. The total error for an estimate with a higher confidence (P = 0.95) would be twice as much (±32.0 Mt C).

Conclusions

Current rise in temperature and precipitation in Northern Eurasia results in a positive CB and C enrichment in soils (72 ± 32 Mt C annually). However, the response of different soils to these climate changes is highly variable. An increase in the C content is observed in the soils of tundra, forest-steppe, steppe, and semidesert natural zones. A decrease in C content takes place in soils of boreal forests, where extra litter decay and liberation of essential nutrients support forest growth. Deep peat bogs illustrate a negative CB with the loss of C. Shallow peat swamps and soils of grasslands and shrublands show a positive CB and gain C. For all natural zones and for different LUC classes, surface O horizons are most sensitive to climate change. The A1 and Bh horizons are relatively conservative; the overall accumulation of C in them is twice as low as in the O horizon.

Spatially explicit analysis demonstrates a complex mosaic of CB by different LUC classes and natural zones. In this situation, it is difficult to find geographically representative data for the region; the reliability of data extrapolation from other regions is limited. Global conclusions based on random and fragmented observations might be misleading. For instance, the CB for deep peat bogs is negative in tundra.

However, this soil occupies only a small fraction of the tundra territory (about 16 Mha from the total of 260 Mha). The extrapolation of the negative CB in tundra bogs over the entire tundra zone is confusing. It results in a misleading conclusion about degradation of the SOM in tundra soils upon climate warming, which should further contribute to increasing concentration of greenhouse gases in the atmosphere. The CB of agricultural soils is negative for all natural zones. The loss of C is especially high in the soils of pastures. This is caused by their improper management.

The regional analysis of the spatially explicit CB contributes to more precise estimates of the rate and magnitude of C dynamics in soils. In addition, this approach allows for in-depth understanding of the pedogenic processes and mechanisms driving regional C cycle.

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Chapter 39
Topsoil Organic Carbon Map of Europe

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Abstract In 2009, within the framework of the European Land Use/Cover Area frame statistical Survey (LUCAS), a soil sampling campaign was implemented in 25 countries. About 22,000 composite topsoil samples were collected following a standardized sampling methodology and analysed in one laboratory. In this study, we present the first map of topsoil organic carbon (OC) content estimates for part of the European Union based on that comprehensive sampling programme. A digital soil mapping (DSM) by regression kriging (RK) approach was followed, and the covariates selected by the model were: land cover, elevation and slope, accumulated annual average temperature and the precipitation over potential evapotranspiration ratio, lithology, net primary productivity, and sand content. The results show high OC contents in northern latitudes and low contents in southern European countries which corroborates current expert knowledge. The overall model-fitting performance (R^2) is 0.52 and the root mean squared error of the RK predictions equals 77 g C kg^{-1}. Kriging of the regression residuals create hot-spots of OC content predictions

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on the map which are not believed to be realistic. It was concluded that different DSM techniques should be tested on the OC measurements data from the LUCAS database to try and improve the predictions and that validation against national datasets should be performed.

Keywords Digital soil mapping • Harmonized soil database • Soil organic carbon • Regression kriging • Europe

Introduction

Soil organic carbon pools have received increasing attention from policy-makers at national and sub-national levels because of their relevance to agriculture and food security, climate change, air and water pollution and biodiversity. In its Thematic Strategy for Soil Protection, the European Commission (2006) has recognised the decline in soil organic matter as one of the main threat to European soils. The proposed Soil Framework Directive (European Commission 2006) called for the delineation of the areas in Europe threatened by soil organic matter decline and for the establishment of appropriate measures to reverse this negative trend. A first step to achieve these goals is to establish a baseline SOC level on which management decisions can be taken.

The only currently existing map of estimated topsoil organic carbon content across Europe, so-called OCTOP map, (Jones et al. 2005) was created by applying a set of pedo-transfer rules on a combination of spatial data layers representing soil properties, land use and temperature. The relationship between organic carbon (OC) content classes and the covariates was inferred by expert-knowledge and the produced estimates verified against measured OC content from national surveys of the United Kingdom and Italy. Although OC measurements were part of most national soil surveys, Jones and co-authors (2005) found that they were not always publicly available and were often lacking accurate geo-references. In addition, they considered that the amount of data was insufficient to generate a spatial distribution at an acceptable scale and therefore excluded to apply a point-based extrapolation procedure. Although the map was recognized to provide realistic OC content estimates, it does not provide the baseline requested by the Soil Framework Directive since covariates from various periods were used.

Digital soil mapping (DSM) is defined by Lagacherie et al. (2007) as “the creation and population of spatial soil information systems by numerical models inferring the spatial and temporal variation of soil types and soil properties from soil observation and knowledge and from related environmental variables”. Numerous studies used DSM techniques to predict OC spatial distribution at the field scale (Chen et al. 2008; Vågen et al. 2013), subnational (Vasques et al. 2010; Rawlins et al. 2009; Grimm et al. 2008), national scale (Martin et al. 2011; Bui et al. 2009; Meersmans et al. 2011; Li et al. 2013) and the global scale (Sanchez et al. 2009). Minasny et al. (2013)

demonstrated the challenges of mapping the spatial variability of soil carbon contents because of scarcity of data and the disparity of measurement techniques for soil total and organic carbon, sampling times, depths and methodologies.

In 2009, the European Commission consequently designed the first harmonized soil sampling campaign at European Union (EU) level, the so-called LUCAS (Land Use/Cover Area frame statistical Survey) topsoil survey. In spring and summer that year, approximately 22,000 soil samples were taken in 25 EU Member States using a standardized protocol with samples sent to a single laboratory for physico-chemical analyses. The objective of this study is to analyse the OC data by regression kriging and produce the first map of OC content in Europe based on an annual comprehensive database of topsoil samples.

Materials and Methods

Soil Data

The samples from the LUCAS survey were collected to a depth of 20 cm by field surveyors taking five soil cores within the sampling area and bulking them to a composite sample for each site. Sampling locations were selected using a Latin hypercube-based stratified random sampling design, in order to be representative of land use and topographic features (Montanarella et al. 2011). The LUCAS-topsoil survey sampling locations and measured OC values are shown in Fig. 39.1. The laboratory received the air-dried and sieved (<2 mm) soil samples and analyzed them for 13 physico-chemical properties, among which particle-size distribution, total nitrogen, phosphorus and potassium content, pH, carbonate content and total carbon content. Visible and near infrared diffuse reflectance was measured using a FOSS Rapid Content Analyzer (NIRSystems, INC.), operating in the 400–2,500 nm wavelength range, with 0.5 nm spectral resolution. Total carbon content was determined after dry-combustion in an Elementar VarioMax CN analyser. The carbonates present in the sample were determined volumetrically by addition of hydrochloric acid and measure of the volume of CO_2 produced. Soil organic carbon content was determined by subtracting the carbonate content from the total carbon content.

Environmental Covariates

In order to predict the OC content, a database of environmental covariates with full spatial coverage was compiled, including:

(a) *land cover*, obtained from the European inventory CORINE 2006 (EEA 2012); (b) SRTM-derived *elevation and slope*; (c) *accumulated annual net primary productivity* (NPP), obtained from MODIS MOD17 project (Running et al. 1999);

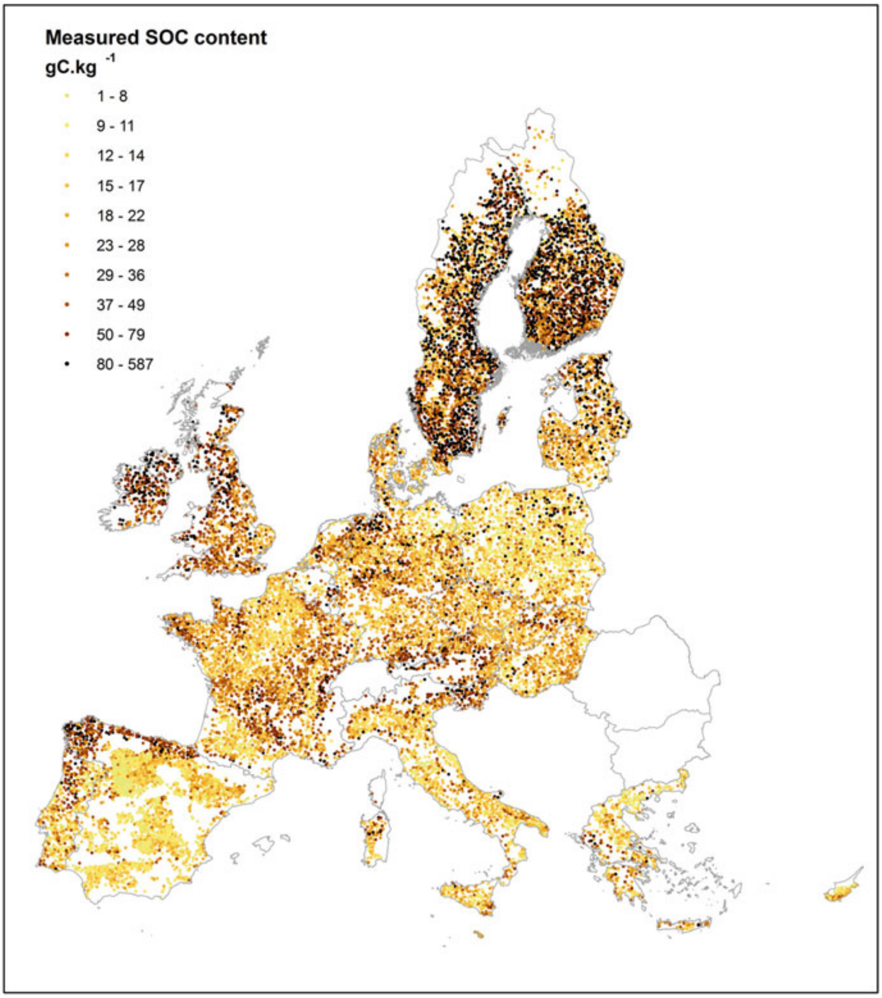

Fig. 39.1 LUCAS topsoil-survey, measured SOC content at sampling locations

(d) main lithological units of the pre-Quaternary *geology* (Asch 2003); (e) *accumulated annual temperature*, generated using climatic data from the European PESERA erosion project (Kirkby et al. 2008); (f) *accumulated annual precipitation over potential evapotranspiration ratio* (P/P0), generated by combining PESERA and WorldClim (http://www.worldclim.org) datasets; (g) *sand and clay content*, derived by geo-statistical techniques from the LUCAS topsoil samples particle size distribution (Ballabio, personal communication); (h) latitude.

NPP and climatic annual accumulated data were averaged for the 2000–2009 period. A spatial resolution of 500 m was chosen.

Pearson correlation coefficients were calculated to check for collinearity between covariates and a threshold of 0.7 was decided for covariate exclusion.

Spatial Prediction

Regression kriging (RK) technique (Matheron 1969) was used to map the spatial distribution of OC content. A multiple linear regression was fitted between the log-transformed OC measurements and the independent variables by the ordinary least squares method. A forward/backward-stepwise regression was carried out to derive the best subset of predictors, using the Akaike information criterion (Akaike 1974) and the importance of the selected covariates was evaluated by calculating the t-statistics from tests with the null hypotheses that each regression coefficient equals zero. The performance of the prediction model was assessed by leave-one-out cross-validation (Hastie et al. 2009).

Results and Discussion

Environmental Covariates Selection and Linear Regression

High collinearity was found between sand and clay (−0.70), latitude and temperature (−0.89), latitude and clay (−0.70) (results not shown). Clay and latitude were therefore excluded from the regression analysis. Their influence on OC content will however be discussed (with sand and temperature respectively) since the dismissal of one between two correlated covariates is random. The stepwise regression kept the remaining independent variables.

The screening of variable importance by t-test gave in descending order of relevance: temperature, elevation, inland wetlands and sand content as the most significant independent variables (Table 39.1). Although the regression is empirical and the data were collected all over Europe, most of the observed trends can be explained by biophysical processes. Temperature ($|\text{t-value}| = 30.2$) is one of the main drivers of biochemical reactions and therefore has a major importance in the dynamics of soil carbon decomposition and respiration (Davidson and Janssens 2006). Latitude illustrates the climatic variations across Europe and highlights the influence that both temperature and water regimes have on OC dynamics (Post et al. 1982; Raich and Schlesinger 1992). OC content is generally expected to vary with elevation ($|\text{t-value}| = 17.4$), as a response to changes in the abiotic (temperature) and biotic (quality and quantity of organic matter inputs) environment (Garten and Hanson 2006). The land cover classification ($|\text{t-value}|_{\text{inland wetlands}} = 16.4$) includes peat bogs (organic

Table 39.1 Relative importance of the independent variables in the multiple linear regression model, expressed by the absolute value of the t-statistic

Independent variables	|t-value|
Intercept	58.4
TEMPERATURE	30.2
ELEVATION	17.4
Inland wetlands	16.4
SAND CONTENT	14.3
Acid magmatic and metamorphic rocks	13.8
P/P_0	13.0
NPP	12.9
Mixed forest	11.9
Coniferous forest	11.7
Other rocks	9.4
Transitional woodland – shrub	8.4
Moors and heathland	7.4
Natural grassland	6.7
Arable land	5.7
Pastures	5.4
Basic magmatic and metamorphic rocks	4.5
Broad-leaved forest	4.2
Sclerophyllous vegetation	4.1
Water bodies	2.7
Limestones	2.5
SLOPE	2.5
Basic to ultra-basic rocks	2.1
Open spaces with little or no vegetation	1.1
Permanent crops	0.6
Acid to intermediate rocks	0.6
Intermediate to basic igneous and metamorphic rocks	0.5
Intermediate magmatic and metamorphic rocks	0.4
Maritime wetlands	0.3
Ultra-basic magmatic and metamorphic rocks	0.3
Heterogeneous agricultural area	0.2

soils) whose high water content decreases organic matter decay. As for the sand content effect on OC levels (|t-value| = 14.3), it can be explained by the higher mineralization rate in well-aerated sandy soils. In addition, OC is associated with soil mineral components, and particularly with clay and silt size particles (Cheshire et al. 2000), which are indirectly expressed by sand content. The sorption of organic molecules to clay minerals is assumed to stabilize SOM (Lützow et al. 2006; Oades 1988) and therefore plays a crucial role in OC dynamics. The coefficient of determination (R^2) of the linear regression performed, adjusted for the amount of independent variables, equals 0.38.

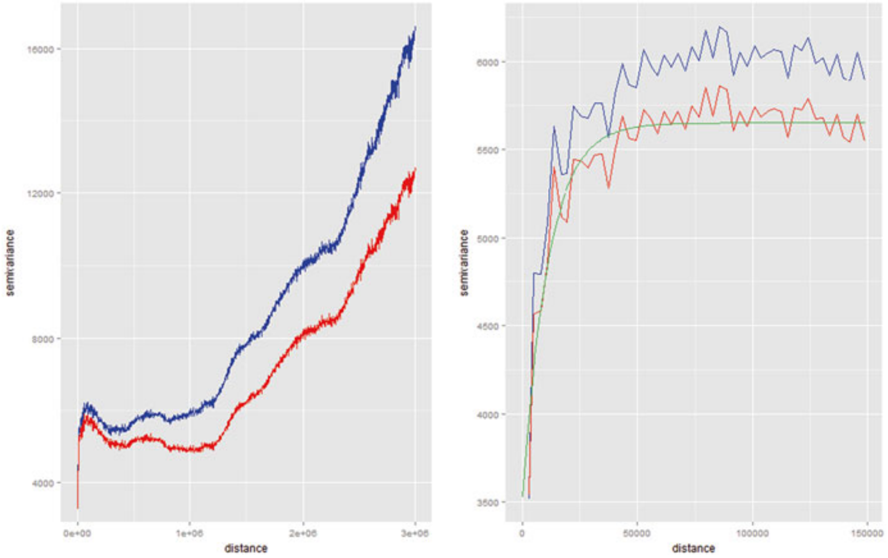

Fig. 39.2 Empirical variograms of OC measurements (*blue*) and regression residuals (*red*) with 3,000 km (*left*) and 150 km (*right*) cut-off. The *green line* represents the variogram model fitted for the kriging of the regression residuals (Color figure online)

Kriging and Variogram Modeling

We compared the empirical variograms of the original OC measurements and of the regression residuals. In order to observe the effect of the regression at different range, 150 km and 3,000 km cut-off were chosen (Fig. 39.2). At 150 km the nugget had slightly decreased after regression. As the nugget encompasses the variability of OC content occurring at distances smaller than the minimum sampling distance, its decrease is explained in this case by the use of environmental covariates that have a spatial variation occurring at less than 2 km distance (e.g. slope, NPP, land cover). At 3,000 km we observed a decrease in variance of approximately 25 %. This reflects the part of OC variability explained by the climatic covariates in the regression model. Considering a cut off of 150 km, the variogram is monotonically increasing and reaches a sill at 70 km range. The empirical variogram was fitted (Fig. 39.2) using an exponential function, with a nugget to sill ratio of 0.7. The map of the kriged residuals shows hotspots (in Slovenia and most northern European countries) resulting from the presence of statistical outliers in the OC data, namely organic soils (Fig. 39.3). The centre of each spot corresponds to the location of a LUCAS sample where high OC content was measured and which value accounts for a great part of the kriging estimates of the surrounding pixels.

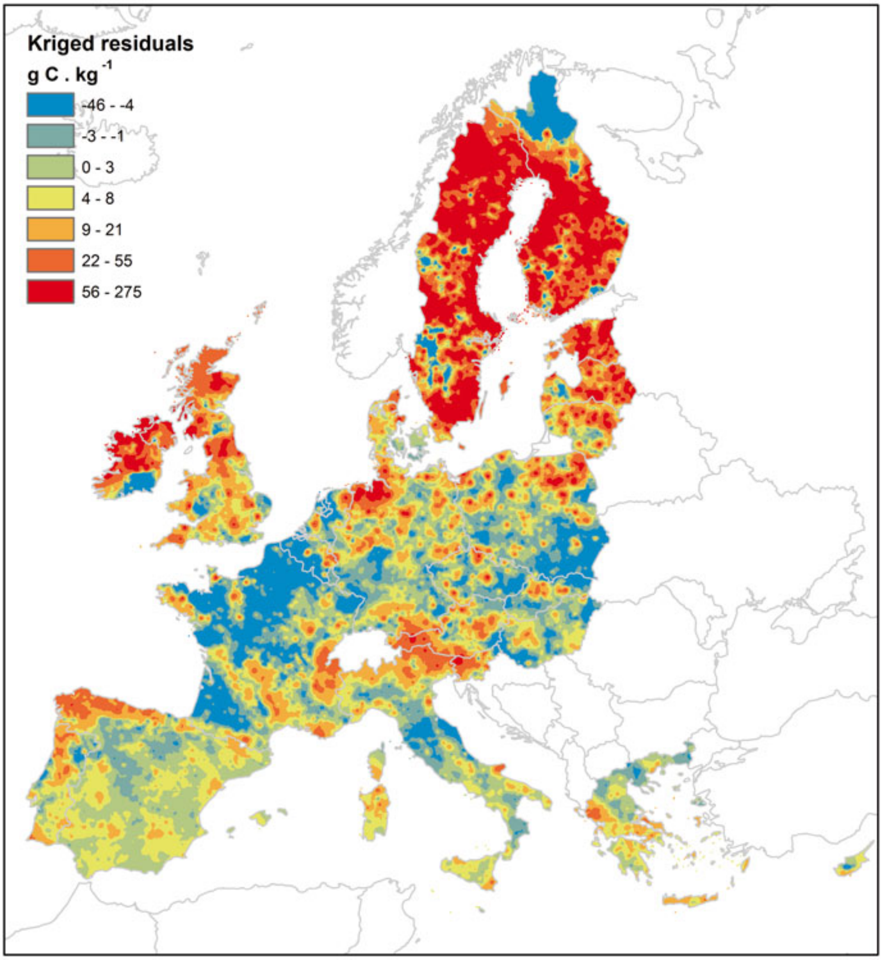

Fig. 39.3 Kriged regression residuals

OC Content Prediction and Model Accuracy

The predictions of OC content produced by regression kriging (RK) (Fig. 39.4) show values ranging from 10 to 450 g C kg^{-1}, with a mean of 49 g C kg^{-1} and a median of 28 g C kg^{-1}. The topsoils (percentile 0.20) that have OC content lower than 15 g C kg^{-1} are found in Mediterranean countries but also in Belgium, the Netherlands, France, Germany, Poland, Czech Republic, Slovakia, Hungary and Denmark. When overlaying the land cover data, we observed that the areas with low OC content correspond mostly to arable land. The topsoils (percentile 0.80 and beyond) with OC content greater than 77 g C kg^{-1} are predominantly found in Northern Europe but also in Belgium, Austria and Slovenia. They mostly correspond to moors,

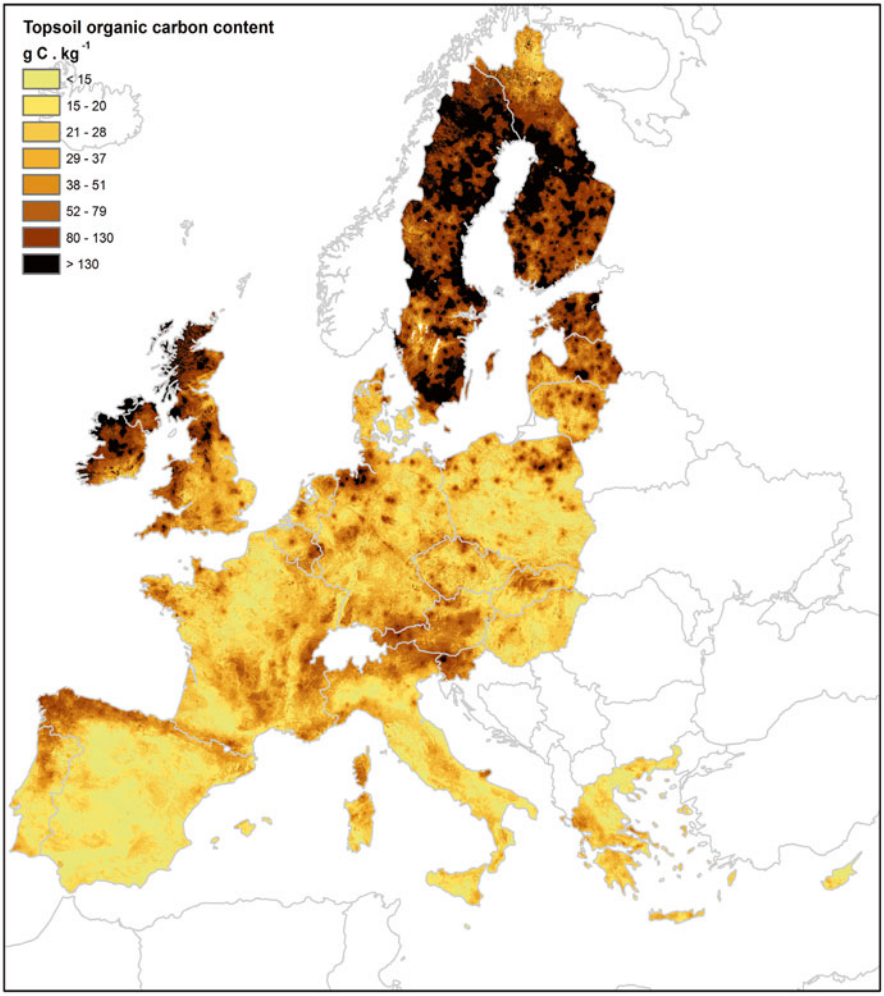

Fig. 39.4 Topsoil organic carbon content estimates, obtained by regression kriging

heathlands and coniferous forests. The presence of spots on the map indicating high level of OC is not believed to give a realistic picture of the OC status in topsoils.

The model prediction accuracy was assessed, at the sampling locations, by comparing the measured OC content with the value predicted by the RK interpolation. The root mean squared error (RMSE) of the RK predictions equals 77 g C kg^{-1}. The histogram of regression kriging residuals (Fig. 39.5) shows that most residuals are negative, demonstrating a general over estimation of OC content at sampling locations. The spatial distribution of prediction residuals (Fig. 39.6) shows that large residuals (in absolute value) mostly occur in northern Europe. The highly positive values occur in areas where there are organic soils for which OC content was underestimated by the model whereas the negative values probably correspond to areas close to peat bogs for which the kriging pull the estimation up.

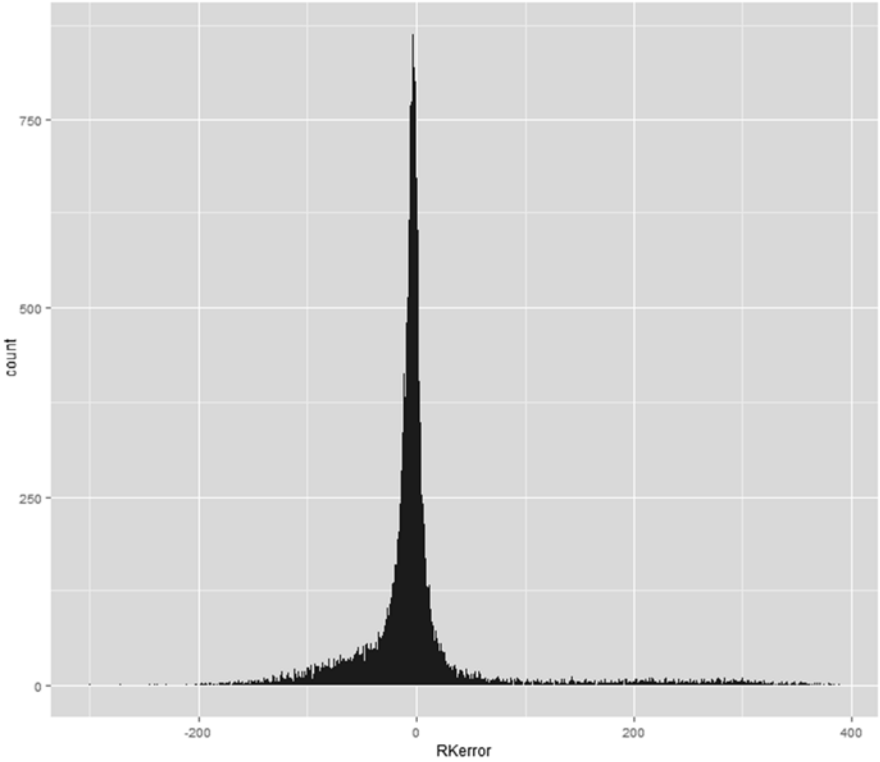

Fig. 39.5 Histogram of the regression kriging residuals

The concentration of large residuals in northern latitudes can be explained by the difficulty to model the presence of microtopography and consequent highly variable water regimes that influence mineralization rate and therefore OC dynamics. Low residuals (in absolute value) mostly occur in areas with the most common (i.e. less variable) features of European landscapes (arable land, low elevation and slope) that were better modelled by the regression. The R^2 of the regression kriging model equals to 0.52 which means that kriging increased the fitting by 0.14. The leave-one-out cross-validation gave an R^2 of 0.12.

Comparison with the Topsoil Organic Carbon Content Map of Jones et al. (2005)

The two maps show a similar gradient of OC content decreasing from North to South, with OCTOP predicting higher contents in Scandinavia and Scotland. High contents in mountainous areas are presented by both maps, yet with lower estimates in the Alps and Dolomites on the map presented in this chapter. In addition, there is a clear

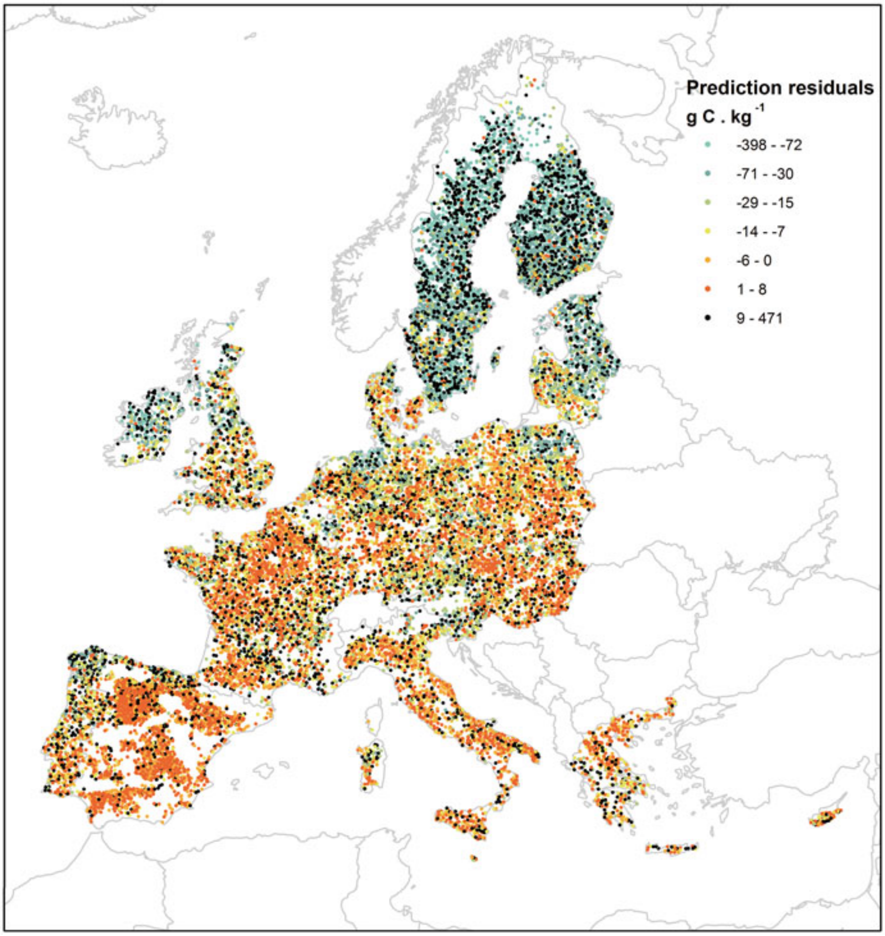

Fig. 39.6 Regression kriging residuals at sampling locations

difference in prediction in eastern Europe where our map predicts lower values. Even though the prediction methods were extremely different (expert-knowledge based pedo-transfer rule vs. regression kriging), the use of land cover and temperature as common covariates to both maps explains the overall similarity in the patterns presented. An in-depth comparison of the two maps was not in the scope of this work.

Conclusions

The study has constructed the first map of topsoil organic carbon content for parts of Europe based on a comprehensive sampling programme, the LUCAS-soil survey. For 25 countries of the European Union, our map provides the baseline topsoil OC estimates for the year 2009 and is seen as the first attempt to answer the questions of the proposed Soil Framework Directive regarding the decline in soil organic matter in Europe.

The predictions obtained by regression kriging mostly corroborate the current expert knowledge of the range of OC contents and their variability across Europe, yet with some differences observed in northern and eastern Europe. The high OC values are outliers in the database that are responsible for a large proportion of the prediction error. Modelling the mineral soil data separately from the organic soil data should be examined in the future as a means to improve the accuracy of the predictions. Also, interpolation techniques that do not treat regression residuals separately, as in RK, could be tested and their performance compared. A full validation would require a resampling campaign to provide a random validation sample. The resampling should target areas where we obtained high prediction error and cover the full range of values taken by the covariates. In the meantime there is scope for comparing our OC predictions with OC data available from other European and national sources (Arrouays et al. 2001; Baritz et al. 2011; Batjes 1996; Howard et al. 1995; Lettens et al. 2004).

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Chapter 40
Soil Organic Carbon Content in the Topsoils of Agricultural Regions in Croatia

Stjepan Husnjak, Aleksandra Bensa, Hana Mesic, and Danijela Jungic

Abstract Here we present soil organic carbon (SOC) content in the soils of agricultural regions and subregions of Croatia, and how these are affected by climate, geomorphology, soil conditions, and land use. For research, Northwestern (NP) and the Eastern Pannonian (EP), Mountain (M), then North (NA) with South Adriatic (SA) subregions was selected. Data for the SOC content was collected during the mapping of Croatia at a scale 1:50.000. Decreasing trend in rainfall M>NP>NA>SA>EP, and air temperatures SA>NA>EP>NP>M is defined. The NP and EP subregion have a lowland relief and flat to almost flat terrain, whereas NA is lowland and hilly-mountainous relief, M is mountainous and SA hilly and mountainous relief. In the NP and EP subregions, dominating parent material is loess and alluvial deposits, at NA limestones, dolomites and marl, and at M and SA limestones and dolomites. Average SOC content in the studied agricultural subregions varies from 1 to 2 % in arable soils and 2 to 4 % in soils under grassland or forest. SOC was the highest in forest soils in Mountainouus region because wet and cold climate and the lowest in arable soils of Northern subregion of Adriatic region because higher mineralization.

Keywords SOC • Topsoil • Agricultural subregions • Croatia

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Introduction

Soil organic C (SOC) is an important part of the soil and reduction of SOC directly affects biodiversity (European Commission 2002). Maintaining the amount of SOC in the soil, is an important in Croatia (Bisko et al. 2009; Husnjak et al. 2011) and some studies indicate a significant reduction of humus in agricultural soils compared to forest ecosystems (Martinovic 2000; Bogunovic et al. 2010).

Organic carbon content is a universal indicator of soil quality, which significantly influences the physic-chemical properties of soil. Soil carbon it is at the center of attention due to the international Convention on Climate Change (UNFCCC), United Nations Convention on Biological Diversity (UNCBD) and United Nations Convention to Combat Desertification (UNCCD), Mesic et al. (2012). Estimates on the SOC content should be a first step in developing a strategy to protect soil.

The main objective of this paper is to present the state of SOC content in agricultural and forest soils for different agricultural regions in Croatia. We have aimed to determine whether there were differences caused by climatic and geomorphological conditions, and land use. The SOC content is based on data collected in the period 1978 to 1985, in the framework of the Croatian Basic Soil Map at a scale or 1:50,000 (OPK 1978–1985). Due to the lack of recent data we find necessary to compare this legacy SOC data with more recent data. This paper also proposes guidelines for the methodology development of soil monitoring.

Materials and Methods

Based on the maps of agricultural Croatian regions (Basic et al. 2001), the following regions were chose: Northwestern and Eastern Pannonian subregion, Mountains, and Northern and Southern Adriatic region (Fig. 40.1). The data on SOC content in the surface layer of soil profiles was collected during the production of Basic Soil Map of Croatian (scale 1:50,000), particularly map sheets Cakovec 1 and 2, Osijek 3 and 4, Gospic 3 and 4, Rovinj 2 and 4, and Makarska 1 and 2. Climatic features of agricultural subregions are shown on the basis of climatic data for the 30-year period period (DHMZ 2012). Inventorying locations of soil profiles under forest, grassland and arable land was based on the land-use maps (DZZP 2004). Features of the relief are shown on the map terrain altitude (Husnjak 2000) and soil characteristics on the basis of a Soil map of Republic of Croatia scale 1:300.000 (Bogunovic et al. 1996).

Agricultural Subregions

Climatic Characteristics

Basic climatic characteristics of selected agricultural subregions were determined based on the average monthly and annual values of precipitation and air temperature for the 30-year period (DHMZ 2012). As part of the Pannonian regions,

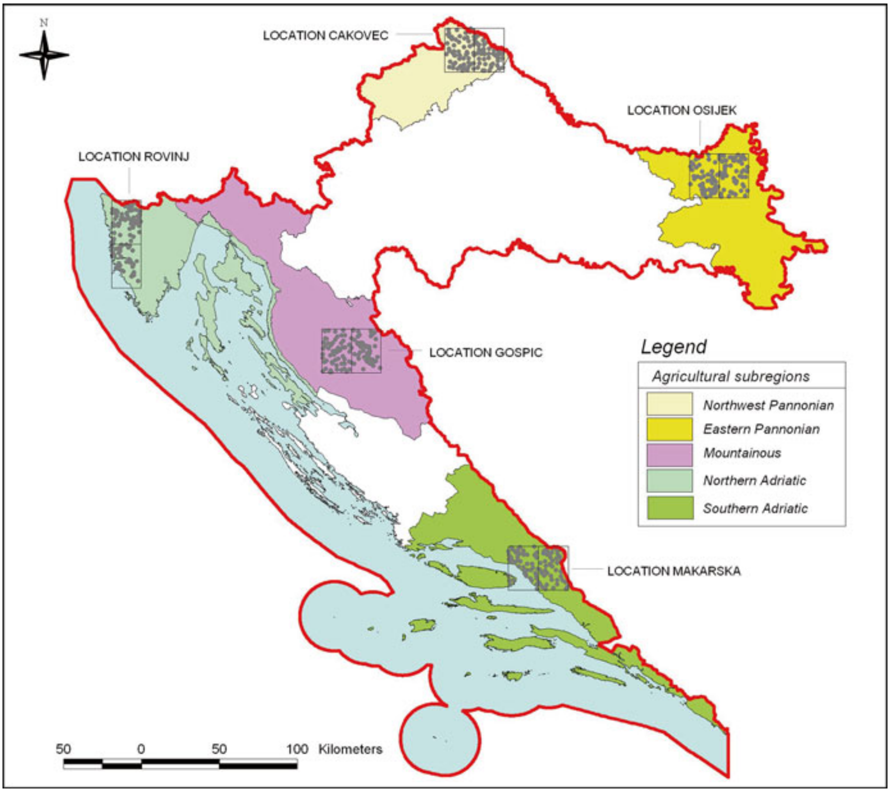


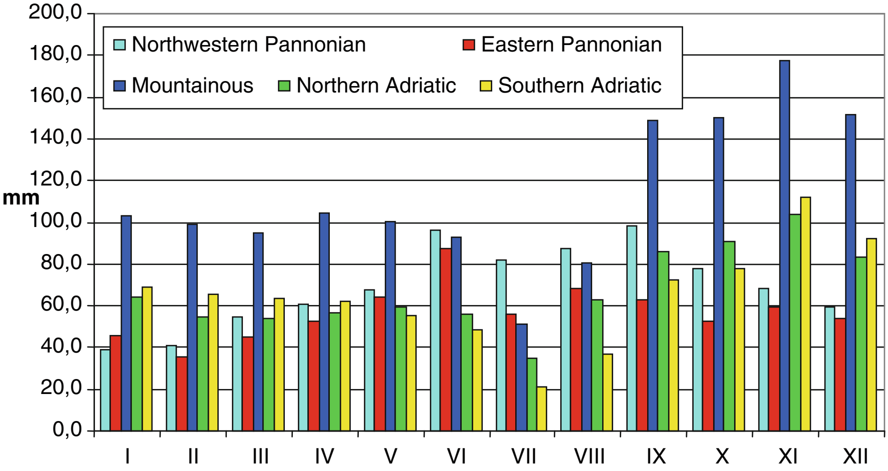
Fig. 40.1 Agricultural subregions with positions of pedological map sheets and locations of soil profiles

Northwestern and Eastern subregions differ with regard to monthly and total rainfall amounts. In almost every month (except January) monthly precipitation was higher in the Northwestern subregion compared to the Eastern. The Mountainous subregion has the highest rainfall (672.4 mm) and twice as high compared to the Eastern Pannonian subregion (Graphs 40.1 and 40.2).

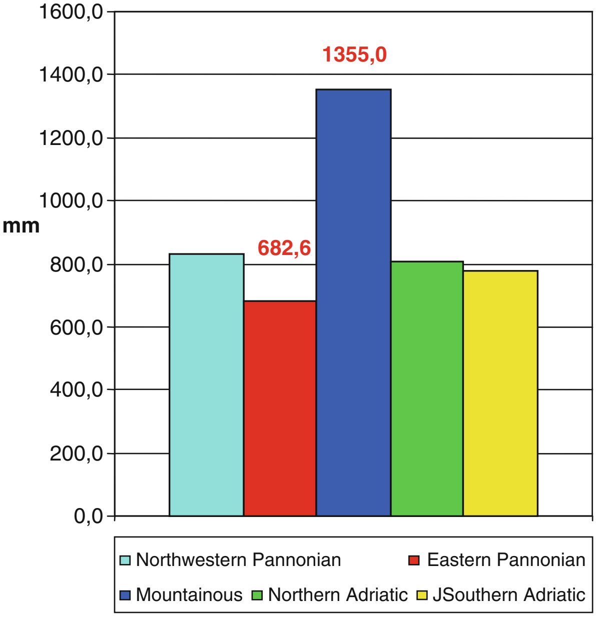
The Mountainous subregion was the coldest with average annual values of air temperature 9.1 °C, and Southern Adriatic the hottest with 16.4 °C. Eastern Pannonian subregion was only 0.2 °C warmer than the Northwestern, while Southern Adriatic subregion was 2.0 °C warmer than the Northern Adriatic (Graphs 40.3 and 40.4).

Relief Characteristics

Northern and eastern Pannonian subregions, characterise dominates lowland relief, with flat to almost flat terrain. Dominates mountainous relief with varying terrain from flat to moderate slopes characterise Mountainous subregion. Northern Adriatic



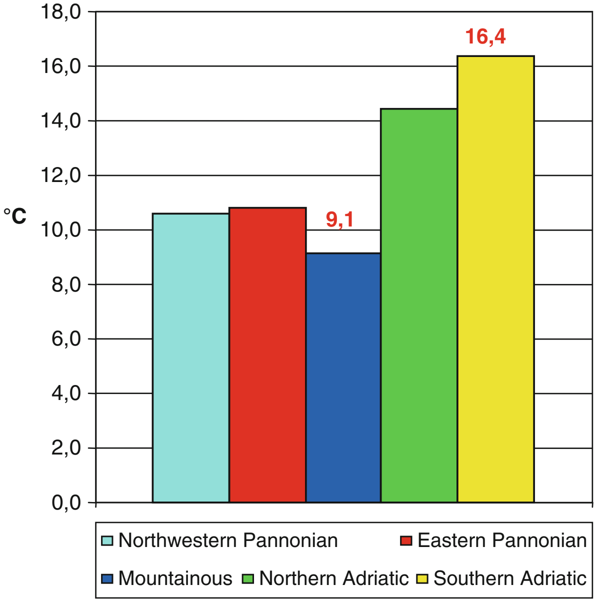
Graph 40.1 Average monthly rainfall (1981–2010) in agricultural subregions

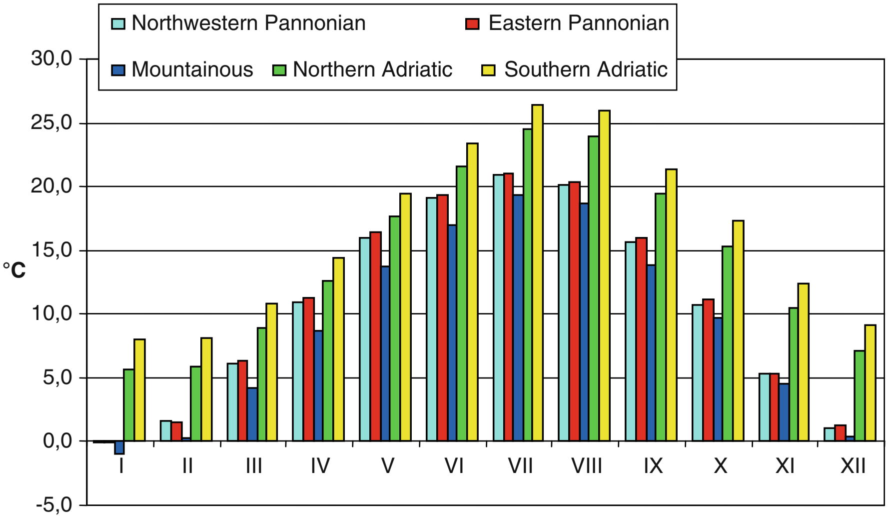


Graph 40.2 Average annual rainfall (1981–2010) in agricultural subregions

subregion characterise considerable presence of lowland and hilly relief with flat to gentle slopes terrain. Southern Adriatic subregion characterise huge heterogenity of relief that ranges from sea level to over 1,000 m a.s.l. with terrain ranging from mild to steep slopes (Fig. 40.2).

Graph 40.3 Average annual values of air temperature (1981–2010) in agricultural subregions





Graph 40.4 Average monthly values of air temperature (1981–2010) in agricultural subregions

Soil Properties

The dominant soil types that occur in the study area of particular subregions, and their main characteristics are shown in Table 40.1. In the study area in northern and eastern Pannonian subregions, dominate non-calcareous soils developed on loess

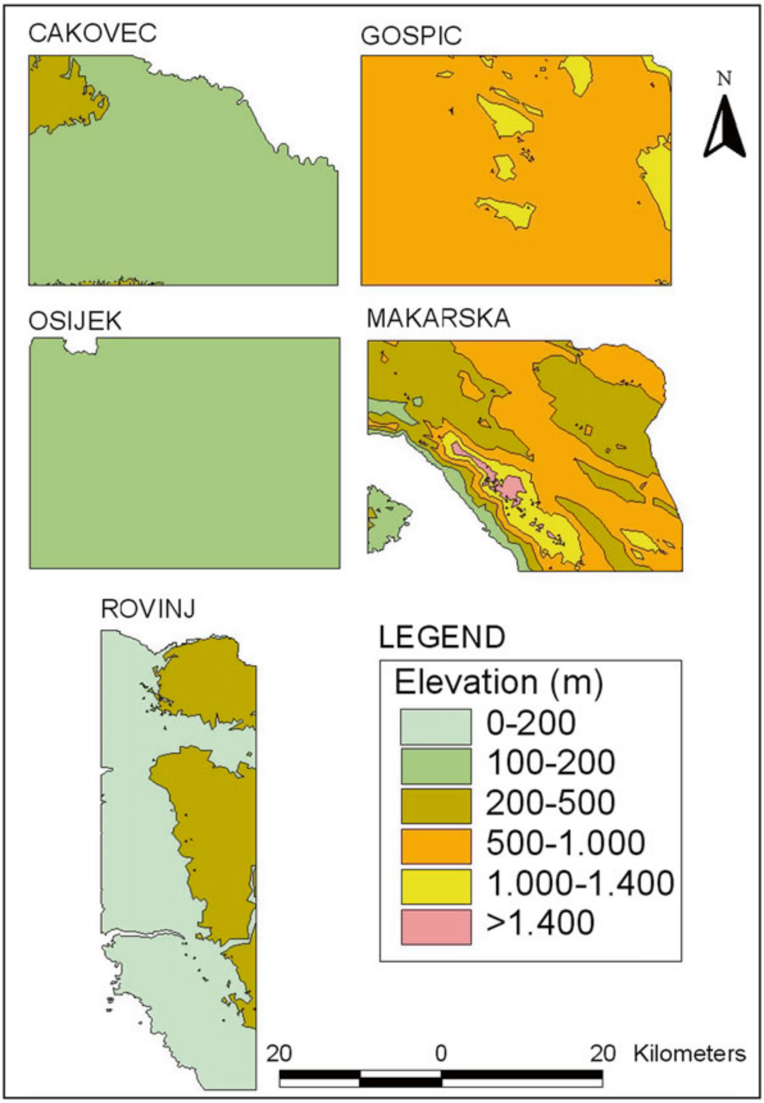


Fig. 40.2 Terrain slope of locations (map sheets) included in this research

and non-calcareous and calcareous soils on alluvial deposits. In Mountain subregion dominate non-calcareous soils developed on limestone and dolomite, and on loess. In the northern Adriatic subregion is slightly higher representation of non-calcareous soils developed on limestone and dolomite compared to calcareous soils developed on marl. In southern Adriatic subregion, dominate non-calcareous soils developed on limestones and dolomites.

Table 40.1 Main soil types and their basic properties

Agricultural subregion	Main soil types (in FAO terms)	Parent materials	Dominant way of wetting	Dominant soil texture	Dominant soil reaction (pH)
Northwestern Pannonian	Calcic Luvisols	Loess	Automorphic	Silty loam/silty clay loam	Acid
	Eutric Cambisols	Loess	Automorphic	Silty loam	Slightly acid
	Eutric Gleysols	Alluvial deposits	Hypogleyic	Clay loam	Slightly acid
	Mollic Fluvisols	Alluvial deposits	Semigleyic	Silty loam	Slightly alkaline
	Calcaric Fluvisols	Alluvial deposits	Alluvial	Sandy loam	Alkaline
Eastern Pannonian	Eutric Gleysols	Alluvial deposits	Hypogleyic	Clay loam	Slightly acid
	Calcic Luvisols	Loess	Automorphic	Silty loam/silty clay loam	Acid
	Calcaric Fluvisols	Alluvial deposits	Alluvial	Sandy loam	Alkaline
	Eutric Cambisols	Loess	Automorphic	Silty loam	Slightly acid
	Calcic Chernozemems	Loess	Automotrphic	Silty loam	Neutral/slightly acid
	Mollic Gleysols	Alluvial deposits	Hypogleyic	Silty clay	Slightly alkaline
Mountainous	Cromic Cambisols	Limestones and dolomites	Automotrphic	Silty clay loam	Slightly acid
	Mollic Leptosols	Limestones and dolomites	Automotrphic	Silty loam	Slightly acid
	Dystric Cambisols	Loess	Automotrphic	Silty loam	Acid/very acid
	Rendzic Leptosols	Limestones and dolomites	Automotrphic	Silty clay loam	Alkaline
	Chromic Luvisols	Limestones and dolomites	Automotrphic	Silty clay loam	Acid/very acid
Northern Adriatic	Cromic Cambisols	Limestones and dolomites	Automotrphic	Silty clay loam	Slightly acid
	Aric Anthrosols	Limestones and dolomites	Automotrphic	Silty clay loam	Alkaline/neutral
	Calcic Vertisols	Marl	Automotrphic	Silty clay/clay	Alkaline
	Rendzic Leptosols	Marl	Automotrphic	Silty clay	Alkaline

(continued)

Table 40.1 (continued)

Agricultural subregion	Main soil types (in FAO terms)	Parent materials	Dominant way of wetting	Dominant soil texture	Dominant soil reaction (pH)
Southern Adriatic	Mollic Leptosols	Limestones and dolomites	Automotrphic	Silty loam	Slightly acid
	Cromic Cambisols	Limestones and dolomites	Automotrphic	Silty clay loam	Slightly acid
	Aric Anthrosols	Limestones and dolomites	Automotrphic	Silty clay loam	Alkaline/neutral
	Calcaric Regosols	Colluvial deposits	Automotrphic	Silty loam/silty clay loam	Alkaline

Results and Discussion

The average content of SOC in the surface horizons of arable soils for all agricultural regions of Croatia was 1.9 % C. The highest values were found in the Mountainous region (2.7 % C), and the lowest in the Northern subregion of the Adriatic region (1.4 % C), Table 40.2.

The average SOC content in surface horizons of soils under grassland of all subregions of Republic of Croatia is 3.6 % C. The average values of SOC were the highest in the Southern subregion of Adriatic region (5.6 % C), while the maximum was found in soils of the Mountainous region (11.3 % C), Table 40.3.

In soils under forest the average SOC content is the highest (3.6 % C). The comparison of the average values of SOC for all regions, reveals a maximum in the Mountainous region (5.0 % C), and the minimum in the Eastern subregion of Pannonian region (2,2 % C), Table 40.4.

The high SOC content in the Mountainous region of Croatia under wet and cold conditions are consistent with findings of others who found proportional relationship

Table 40.2 The content of organic carbon (%C) in agricultural soils – arable land

Region	Subregion	n[a]	Mean	Min[a]	Max[a]
Pannonian	Northwestern	98	1.9	0.3	4.9
	Eastern	94	1.5	0.2	7.2
Mountainous	Mountainous	57	2.7	0.7	5.7
Adriatic	Northern	49	1.4	0.5	3.6
	Southern	21	1.8	0.6	4.2
Total		319	1.9	0.2	5.7

[a] *n* number of samples, *Min* minimal content, *Max* maximum content

Table 40.3 The content of organic carbon in agricultural soils – grasslands

Region	Subregion	n	Mean	Min	Max
Pannonian	Northwestern	–	–	–	–
	Eastern	9	2.8	1.2	8.3
Mountainous	Mountainous	48	3.8	1.3	11.3
Adriatic	Northern	27	1.8	0.4	5.2
	Southern	23	5.6	0.5	10.8
Total		107	3.6	0.4	11.3

Table 40.4 The content of organic carbon in forest soils

Region	Subregion	n	Mean	Min	Max
Pannonian	Northwestern	14	2,7	0,6	11,4
	Eastern	13	2.2	0.8	3.4
Mountainous	Mountainous	24	5.0	0.8	13.9
Adriatic	Northern	46	2.3	0.8	8.8
	Southern	52	4.8	0.2	13.0
Total		149	3.6	0.2	13.9

of SOC and mean annual precipitation, as well as inverse association with mean annual temperature (Kirschbaum 2000; Alvarez and Lavado 1998; Garten et al. 1999; Jobbagy and Jackson 2000; Lemenih and Itanna 2004).

The SOC content in the soils of the forest is highest followed by soils under grasslands, while in soils under arable farming low SOC values were found. The low SOC content is the result of organic matter removal by the harvest and higher mineralization because of tillage. This was also found by Sokolovska et al. (2002) based on comparing natural and anthropogenized Luvisols in Turkey, Greece, Bulgaria and Spain by Birkas et al. (2007) on different soil types in Hungary, and by Bogunovic et al. (2010) by comparing the SOC in natural and anthropogenized Stagnosols in continental Croatia. In the Eastern subregion of Pannonian region and Southern subregion of Adriatic region in soils under grassland higher SOC values were found compared to soils under forest ecosystems. This is consistent with research Nikolaishvili and Matchavariani (2010) who found that the forests at lower altitudes have less organic matter than those in higher relief positions.

Further Research

The results showed SOC content in the period 1978–1985 for five agricultural subregions in Croatia and it provides valuable basic historical information. It is possible to compare these soil legacy data to the present situation, taking into account the diversity of agro-ecological factors of each agricultural sub-region. We suggest comparing data from the period 1978–1985 with new data in order to determine their reliability and possibilities of their use in the development of national and regional strategies for soil protection. As a second step, overall monitoring has to take place as described by the Rulebook on monitoring of agricultural land (OG 60/10) and Rulebook on forest ecosystem monitoring (OG 67/10), following the recommendation seated in Soil Monitoring Programme (Croatian Environment Agency 2008).

Conclusions

Average SOC content in the studied agricultural subregions of Croatia ranges from 1.4 % in arable soils to 5.6 % in soils under grassland or forest. The comparison between the average SOC values of all subregions showed that they were the highest in the Mountainous region, and the lowest in the Eastern subregion of Pannonian region. SOC in arable soils indicates a rapid reduction under intensive agricultural production, and the need to take measures for the protection of such soils.

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Chapter 41
Soil Carbon Variability in Some Hungarian and Croatian Soils

Milan Mesic, Márta Birkás, Zeljka Zgorelec, Ivica Kisic, Ivana Sestak, Aleksandra Jurisic, and Stjepan Husnjak

Abstract Loss of soil carbon and carbon storage were studied in different soil types in the agroecological conditions of the Pannonian plain and in the Mediterranean region. Total carbon concentration, pH and C:N ratio under pastures, meadows, forests, vineyards, gardens and crop fields were determined. Soil samples were taken in 2010 at depths from 0–3, 3–10, 0–30, 30–60 and 60–90 cm depending on the location, region, soil type and type of ecosystem. Soil pH varied between strongly acid 4.3 measured in crop field on distric Stagnosols (0–30 cm) to weakly alkaline 7.6 in a crop field on Chernozems; C:N ratio varied from 8 measured on distric Stagnosols to 39 on Cambisol calcaric; Soil carbon concentration observed in this study varied from 3.3 g C/kg at Szentgal on an agricultural crop field on Eutric Cambisol, in the deep layer (60–90 cm; L4) to 107.2 g C/kg on Regosol on karst measured in the surface layer of a Mediterranean grassland (0–3 cm; L10).

Keywords Carbon storage • Soil vulnerability • Pannonian plain • Mediterranean

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Introduction

Total carbon (C) in soils is the sum of organic and inorganic forms. Organic C is present in the soil organic matter (SOM) fraction, whereas inorganic C is largely found in carbonate minerals. In agroecosystems many different factors affect the balance between gains and losses of SOM (Brady and Weil 2010). The concentration of soil organic carbon (SOC) is a universal soil quality indicator with significant influence on several soil properties and functions.

In Croatia, a comparison involving the same soil type under agricultural and forest use was reported by Martinovic (2000). After several centuries of agricultural use in the Croatian Pannonian plain SOC in surface soil horizons of Luvisols was reduced by nearly 58 %, in Stagnosols by about 51 %, and in Eutric Cambisols by almost 60 %, compared to SOC concentration in the same soil type under forests. SOC concentration in Red Mediterranean Soils (*Terra rossa*) used for annual crops had decreased by 32 %, and under vineyards by 37 %, compared to SOC concentration in soils under forest.

Croatian agriculture in the Mediterranean part of the country began during the Roman Empire from where it spread to the continental part of the country (Mihalic 1973). The crop sequence was a two field crop rotation, fallow land and wheat or barley. Agriculture spread to the continental region where land was either developed from grasslands or forests. Crop rotation was intensified after the discovery of America in the sixteenth century and new crops such as maize (*Zea mays* L.) and potato (*Solanum tuberosum* L.) were introduced. Changes in SOC concentration under forests and under agricultural usage can be more easily understood. According to Meersmans et al. (2009), intensified land management practices affect the status of SOC. The increase in plough depth and a change in crop rotation result in a significant decrease of C near the surface for dry silt loam cropland soils. According to Álvaro-Fuentes et al. (2011) there is little information about SOC stocks and changes in Mediterranean areas on a regional scale. Rodeghiero et al. (2011) stated that natural or semi-natural environments in Mediterranean areas contain relatively high levels of SOC, while cultivated areas in the same region contain low or very low SOC.

The objective of our research was to compare soil carbon concentration due to different land use in different agro-ecological conditions of the Pannonian plain and the Mediterranean karst.

Materials and Methods

Soil samples were taken during the spring and summer of 2010 from different soil types with different soil profile depths (Table 41.1; Photos A–O). Sampling depths were 0–3, 3–10, 0–30, 30–60 and 60–90 cm depending on the location, region, soil type and the ecosystem (L1-L16). Soil samples were collected as composite samples (from 7 to 10 subsamples) in a random sampling scheme. Air dried soil

Table 41.1 Investigated locations

Location	Sampling depths/CM	Region	Ecosystem	Soil type	Latitude Longitude
L1	0–30 30–60 60–90	Hungary & Croatia Pannonian plain	Arable land	Chernozem	N 46°20′42,78″ E 20°49′51,24″
L2	0–30 30–60 60–90		Arable land	Chernozem	N 46°20′14,28″ E 20°51′34,32″
L3	0–30 30–60 60–90		Meadow	Chernozem	N 47°16′55,80″ E 20°53′41,82″
L4	0–30 30–60 60–90		Arable land	Eutric Cambisol	N 47°08′32,22″ E 17°40′49,02″
L5	0–30 30–60 60–90		Meadow	Eutric Cambisol	N 47°07′51,96″ E 17°42′46,98″
L6	0–30 30–55 55–80		Arable land	Distric Stagnosols	N 45°33′15,28″ E 16°31′51,00″
L7	0–3 3–10	Croatia – Island – Mediterranean	Meadow	Terra rossa	N 45°05′32,13″ E 14°18′28,07″
L8	0–30		Olive orchard with typical vegetation for Northern Mediterranean	Regosol on karst from Cambisol on limestone	N 45°06′34,19″ E 14°21′11,61″
L9	0–3 3–10		Pasture	Cambisol on limestone	N 45°04′10,84″ E 14°21′43,50″
L10	0–3 3–10		Pasture	Lithosol on limestone and dolomite	N 45°03′26,11″ E 14°21′50,26″
L11	0–30		Abandoned vegetable garden	Regosol on karst	N 45°02′ 23,68″ E 14°21′ 21,66″
L12	0–30		Vegetable garden	Regosol on karst	N 44°53′21,18″ E 14°19′58,02″
L13	0–30		Vineyard	Regosol on karst	N 44°53′31,50″ E 14°20′12,96″
L14	0–3		Pasture	Rendzina on dolomite and limestone	N 44°53′24,90″ E 14°20′04,26″
L15	0–3		Afforested area – *Pinus halepensis* forest	Cambisol on limestone	N 44°31′28,50″ E 14°27′23,34″
L16	0–3		Afforested area – *Pinus halepensis* forest	Cambisol on limestone	N 44°31′35,04″ E 14°27′07,68″

Photos A–O of all investigated locations and different land management patterns


A – L1 – Crop field, Mezohegyes, Hungary


B – L2 – Crop field, Mezohegyes, Hungary


C – L3 – Chernozem profile, Karczag, Hungary


D – L4 – Crop field, Szentgal, Hungary


E – L5 – Meadow, Szentgal, Hungary


F – L6 – Crop field, Potok, Croatia


G – L7 – Meadow, Cres, Croatia


H – L8 – Olive orchard, Cres, Croatia


I – L9 – Meadow, Cres, Croatia


J – L10 – Karst pasture, Cres, Croatia


K – L11 – Abandoned vegetable garden, Cres, Croatia


L – L12 – Vegetable garden, Lubenice, Cres, Croatia


M – L13 – Abandoned vineyard, Lubenice, Cres, Croatia


N – L14 – Karst pasture, Cres, Croatia


O – L15, L16 – Artificial forest, Mali Losinj, Croatia

samples were ground, sieved (<2 mm) and homogenized, then prepared according to the protocol for pre-treatment of samples for physical and chemical analysis (ISO 11464).

The soil samples were analysed for: pH, plant available P_2O_5 and K_2O, organic matter, total nitrogen, total carbon, total sulphur and carbonate concentration. In this paper results of total soil carbon are presented. Total carbon (TC) concentration and total nitrogen (TN) concentration were determined by dry combustion method (ISO 10694) and (ISO 13878) on CHNS analyzer (Vario Macro, Elementar 2006). Soil pH was determined in 1:2.5 (w/v) in (1 M KCl) soil suspension (modified ISO 10390).

Results and Discussion

Results of carbon concentration in typical Pannonian and Mediterranean soils are presented in Figs. 41.1 and 41.2. Total carbon concentration observed in this study varied from 3.3 g C/kg in Eutric Cambisols (60–90 cm depth) under cropland in Szentgal to 107.2 g C/kg measured in Regosol on karst under Mediterranean pasture vegetation (0–3 cm depth). Soil pH (in 1 M KCl, 1:2.5 (w/v)) varied between strongly acid 4.30 on a crop field from a distric Stagnosol (0–30 cm) in Potok (L6) and weakly alkaline (7.6) from a Pannonian crop field on a Chernozem (60–90 cm; L1) and C:N ratio varied from 8 to 39 from a Mediterranean vineyard on a Cambisol calcaric (0–30 cm; L13).

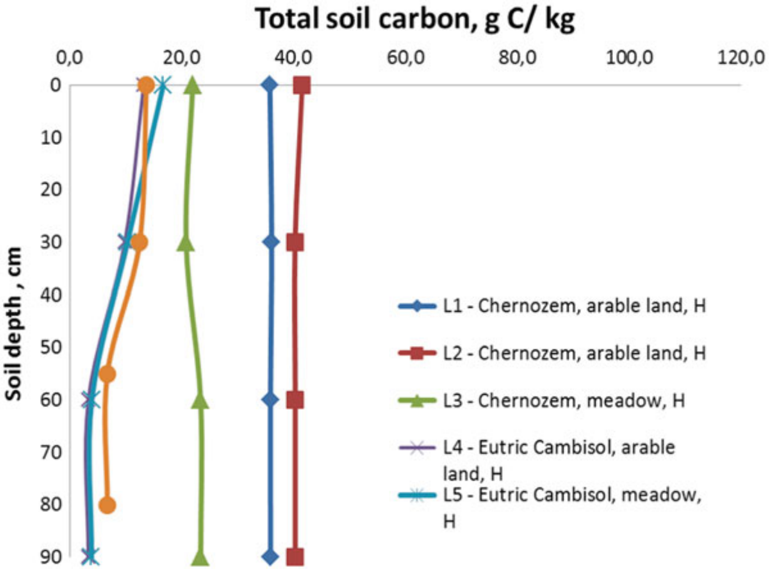

Fig. 41.1 Total soil carbon storage in typical Panonnian soils

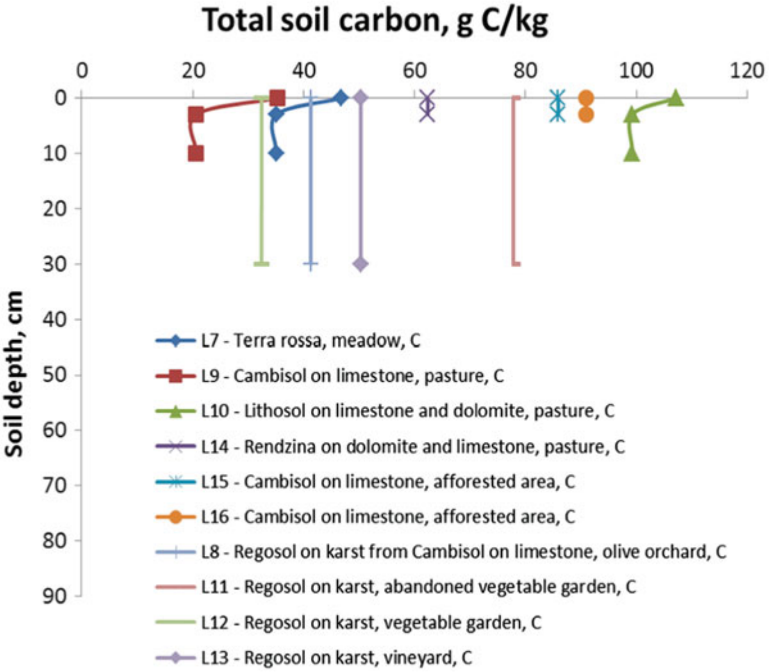

Fig. 41.2 Total soil carbon storage in typical Mediterranean soils

According to Hobley and Willgoose (2010) issues and considerations regarding measurement of carbon stocks, and particularly SOC stocks can be divided into several groups; sampling issues, temporal issues, measurement issues, and, finally issues of vertical distribution of SOC and sample depths. Carbon concentration in the soil is a result of pedogenetic processes and land management. The main difference in carbon storage between Pannonian and Mediterranean soils is related to the soil depth and parent material (aeolian sediments, alluvial sediments, dolomite and limestone). Although mean carbon concentration in topsoils from the Mediterranean environment is high, overall carbon storage is much higher in deep soils from the Pannonian region compared to shallow Mediterranean soils. The optimal C:N ratio is around 10 while a ratio over 30 is considered high and can result in nitrogen deficiency. According to our results from 31 samples C:N ratio varied between 8 and 39. The C:N ratio in cultivated surface Ap horizons commonly ranges from 8 to 15 (median ~12) and is generally lower in deeper layers of soil profile (Brady and Weil 2010). Soil microbes require a balance of nutrients from which they build their cells and extract energy. For maintenance and growth microbes need about 1 g of N for every 24 g of C in their substrate. If the C:N ratio is too high microbes seek available N from other sources and this can lead to depletion of soluble soil N. As a result, N deficiency can occur and decay of OM can be delayed. Most soils contain 1–10 % (10–100 g/kg) of C in surface horizon, with the majority having C concentration from 1 to 3 %. The most notable exceptions are organic soils (Histosols) that restrict the flow of oxygen to soil organisms thus reducing the rates of SOM decay. According to Paustian (2002) they may contain 10–30 % of C.

Cycling of carbon and nitrogen in soils is strongly influenced by land management practices. One question is how nitrogen fertilization influences SOC? There are numerous findings regarding the influence of mineral nitrogen fertilizer on soil organic carbon concentration but results have not been consistent. Positive correlations were reported by Halvorson and Reule (1999) in semi-arid areas in Colorado, and by Blevins et al. (1983) in Kentucky and by Raun et al. (1998) in Oklahoma. On the other hand, Khan et al. (2007) observed negative correlations after analyses of numerous long term cropping experiments in the USA and Denmark and England. Some researchers concluded there was no influence of N fertilization on SOC (Hofmann et al. 2009).

In addition to nitrogen fertilization, soil tillage and crop rotation (Birkás 2010) also significantly influence the soil organic C balance. Birkás et al. (2007) studied organic material concentration including its response to land use. On soils originally high in SOC they found five influencing factors: (1) number and extent of soil disturbances (affecting CO_2 emission); (2) crop residue mass and handling (incorporate, mulch, or mix as recycle); (3) soil moisture storage or loss (affected by soil disturbance); (4) timing of tillage; (5) depth and method of soil disturbance in summer (affecting CO_2 emission). They concluded that soil disturbance should be minimized to conserve SOC, and that frequent disturbance promotes SOC loss. Considering these factors land use techniques can be categorised as carbon wasting, acceptable and carbon preserving (Birkás 2010). Carbon management of soil may have more importance in mitigation of the extreme climate phenomena which will predictably affect the Pannonian region.

Conclusions

Variability in carbon concentration in the soils studied was high. The highest values were measured in shallow Mediterranean soils whereas total carbon stocks were highest in Pannonian soils as a result of increased soil depth. Monitoring of SOC changes in different Pannonian and Mediterranean soils will require broader collaboration between scientists from different countries, with common methodology for soil sampling and soil analyses.

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ISO 10694 – soil quality – determination of organic and total carbon with dry combustion method (“elemental analysis”)

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ISO 13878 – soil quality – determination of total nitrogen with dry combustion method (“elemental analysis”)

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Chapter 42
Stratification Ratios of Soil Organic Matter in Agro-ecosystems in Northeastern Brazil

S. Churka Blum, S.P. de Oliveira, N.B. de Lacerda, G.V. de Alencar, M.E. Ortiz Escobar, E.S. Mendonça, and T.S. de Oliveira

Abstract Soil organic matter (SOM) plays an essential role in increasing the sustainability of agricultural systems, combatting soil degradation, and increasing crop productivity with minimal environmental impacts. Studies of agricultural practices that promote the storage of SOM in soils are a priority, and this is especially the case in the fragile eco-systems of Ceará state, northeastern Brazil where low rainfalls hinder biomass production. In this study, stratification ratios of soil properties were used to assess soil quality under different agricultural systems. We measured the stratification ratio (SR) of soil organic matter pools (organic C, water soluble C, microbial biomass C, microbial activity, and total N) in four different agro-ecosystems (conventional and organic farms in Guaraciaba do Norte; irrigated pastureland in Fortaleza; and perennial and annual crops in Pentecoste and Limoeiro do Norte, and in paired natural forest controls). Most systems (organic farms in Guaraciaba do Norte, pastureland in Fortaleza, and perennial crops in Limoeiro do Norte) were found to improve soil quality in comparison to undisturbed forest, presenting SR above 2. Perennial crops and grasses were the most effective at protecting soils against degradation in irrigated systems, mostly due to the addition of more labile/less decomposed forms of SOM, while annual crops promoted less accumulation of organic matter due to intensive cultivation and low plant residue production. These results suggest that SR may be an effective soil quality indicator for agro-ecosystems in northeastern Brazil.

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Keywords Soil quality • Irrigated agriculture • Organic farming • Orchards • Plant residues • Organic matter

Introduction

Brazil's northeastern region has the country's highest rates of natural and socioeconomic inequality, recurrent droughts, and rural poverty (Sietz et al. 2006). Family farms occupy 83 % of rural properties in the northeast (BNB 2013). Smallholders in northeastern Brazil produce about 70 % of the food crops supplying the domestic market, which include maize, beans, cassava, and rice (Sietz et al. 2006). In recent years, efforts have been made to help family farms produce food in a more sustainable manner, employing techniques of soil conservation to reduce deforestation and discourage intensive soil management.

The clearing of native forest and the subsequent farming of newly deforested areas over the years have caused marked changes in chemical, physical, and biological soil attributes (Solomon et al. 2000; Lemenih et al. 2005; Assis et al. 2010; Miralles et al. 2012). These changes include a decrease in soil organic matter (SOM), which reduces microbial activity and the availability of most plant nutrients, mainly in the surface horizons (Solomon et al. 2007). The state of Ceará is considered one of the most degraded states in northeastern Brazil, with almost 30 % of its land classified as very severely degraded (Ortiz Escobar and de Oliveira 2008).

Soil organic matter is a critical component of the soil system, serving as a source and sink of nutrients and improving physical, chemical, and biological soil attributes. Because SOM plays an essential role in sustainable agricultural systems, combatting soil degradation, and increasing crop productivity (Bationo et al. 2007; Kimetu et al. 2008; Lal 2010), agricultural practices that replenish SOM are the cornerstone to recovering soil health (Doran et al. 1996) and should be highly recommended.

When organic residues are deposited on the soil surface, conservation agricultural systems lead to highly stratified soil organic carbon levels (Franzluebbers 2013). Franzluebbers (2002) proposed the stratification ratio (SR) of various SOM pools as an accessible soil quality index and noted that more research was needed to test its applicability in different agroecological zones. Given that information regarding agriculture in northeastern Brazil is scarce in the literature, we summarize here SRs of SOM pools in soils affected by various land use and management practices in different regions of the state of Ceará, in northeastern Brazil.

Materials and Methods

Data from various comparisons among land uses in the state of Ceará, Brazil were compiled. In Guaraciaba do Norte (4° 9′ S 40° 49′ W, 930 m a.s.l.) on a nutrient-poor Typic Quartzipsamment, soil samples were collected at depths of 0–0.10, 0.10–0.20, and 0.20–0.30 m in order to compare natural forest, sites under conventional and organic cropping systems, and organic orchards (de Alencar 2005). Total organic carbon (TOC) was determined in finely ground samples (passed through a 100 mesh-sieve) by wet oxidation method with external source of heating, according to Yeomans and Bremner (1988). Soil samples were subjected to the organic matter fractionation method as recommended by the International Society of Humic Substances (Swift 1996). Stratification ratios were calculated by dividing the 0–0.10 m values by the 0.20–0.30 m values.

In Fortaleza (3° 44′ S 38° 34′ W) samples were collected on a Typic Hapludult at depths of 0–0.025, 0.025–0.05, 0.05–0.10, and 0.10–0.20 m in order to compare irrigated pastureland to soils under natural forest. Water-soluble carbon (WSC), TOC (Yeomans and Bremner 1988) and total N (TN) were measured. Water-soluble C was extracted following de Mendonça and da Matos (2005). The mixture was placed on a horizontal shaker for 15 min, centrifuged at 900 g for 5 min and filtered through quantitative-grade filter paper. The method proposed by Yeomans and Bremner (1988) for C measurement was modified to quantify WSC: a 10 mL aliquot of the filtered solution was placed in digestion tubes and oven-dried at 65 °C until constant weight. Carbon was then quantified by wet digestion under external heating. Total soil nitrogen (TN) was quantified by sulfuric acid digestion followed by Kjeldahl distillation.

Soils in irrigated cropping systems (perennial and annual plants) were compared with those under native vegetation in Pentecoste (3° 40′ S 39° 18′ W) and Limoeiro do Norte (5° 7 S 37° 58′ W), where samples were collected at 0–0.05, 0.05–0.10, and 0.10–0.20 m in a Typic Udifluvent and at 0–0.05, 0.05–0.10, 0.10–0.15, and 0.15–0.30 m in a Typic Haplocambid, respectively. Biomass microbial C (MBC), TOC, TN, and microbial respiration (CO_2–C) were quantified in Limoeiro do Norte, while TOC and TN were assessed in Pentecoste. Total organic C and TN were measured as described previously for another locations. Microbial biomass C was determined by the irradiation-extraction method (Islam and Weil 1998), using 0.5 M K_2SO_4 as the extractant. MB-C content was measured by wet combustion (Yeomans and Bremner 1988). Microbial activity was measured by the quantification of the CO_2 emitted by microorganisms, using a short-term incubation experiment where CO_2 was collected using NaOH traps, collected at 2, 5, 10, 15, 20, 25 e 30 days after the incubation.

Results and Discussion

Organic management systems are an alternative for minimizing or mitigating the degradation of soil attributes by conventional farming practices, and as such have been proposed as a more sustainable practice (Green et al. 2005). Organic agricultural practices is more common in northeastern Brazil (Lima and Pinheiro 2004). Only 1.3 % of rural properties in the state of Ceará, however, have adopted organic cropping systems (IBGE 2006). High inputs of organic materials such as manure and green manure have increased the stratification ratios of total organic carbon (TOC)

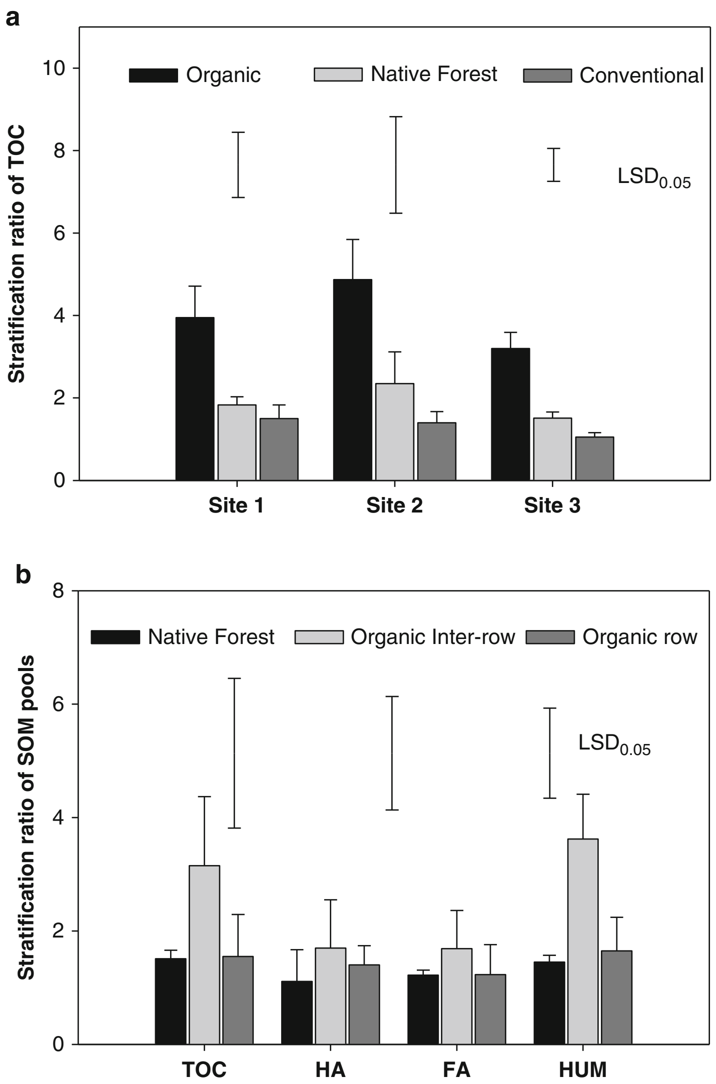

Fig. 42.1 Stratification ratios (0–0.10/0.20–0.30 m) of soil organic matter pools under different cropping systems and native forest in Guaraciaba do Norte, Ceará, Brazil. *Vertical bars* represent the LSD ($p < 0.05$). Organic and conventional cropping systems (**a**); Organic orchards and native forest (**b**). Total Organic Carbon (*TOC*); humic acid (*HA*); fulvic acid (*FA*); humin (*HUM*)

in three organically managed sites (Fig. 42.1a) for four (sites 2 and 3) and 6 years (site 1). Conventionally managed systems had the lowest stratification ratio of TOC, while organically managed areas had ratios that were two or three times higher (Fig. 42.1a). Similar trends were observed for organically managed orchards, in samples collected from rows and inter-rows (Fig. 42.1b). TOC and the fractions extracted according to solubility in acid and alkali solutions [humic acid (HA)

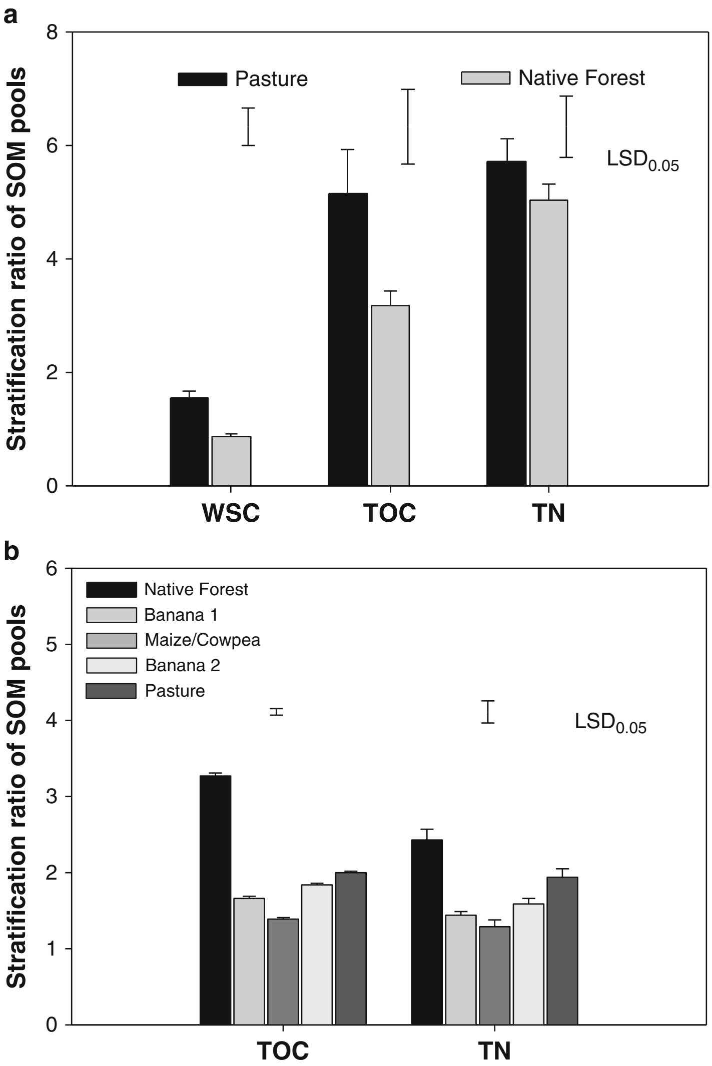

Fig. 42.2 Stratification ratios of SOM pools in irrigated areas of northeastern Brazil. (**a**) Irrigated pasture in Fortaleza (0–0.025/0.10–0.20 m) and (**b**) perennial and annual crops (0–0.05/0.10–0.20 m) in Pentecoste, Ceará, Brazil. *Vertical bars* represent the LSD ($p < 0.05$)

fulvic acid (FA) and humin (HUM)] mostly varied with management practice at the most superficial depths of sampling. Soils in organically managed systems have been shown to have higher OM levels than those in conventionally managed systems (Drinkwater et al. 1995; Melero et al. 2006), directly and indirectly benefiting soil fertility, besides chemical and physical soil properties.

The most striking differences between 10-year irrigated pastureland and native forest were in WSC and TOC (Fig. 42.2a), while TN did not differ significantly. The

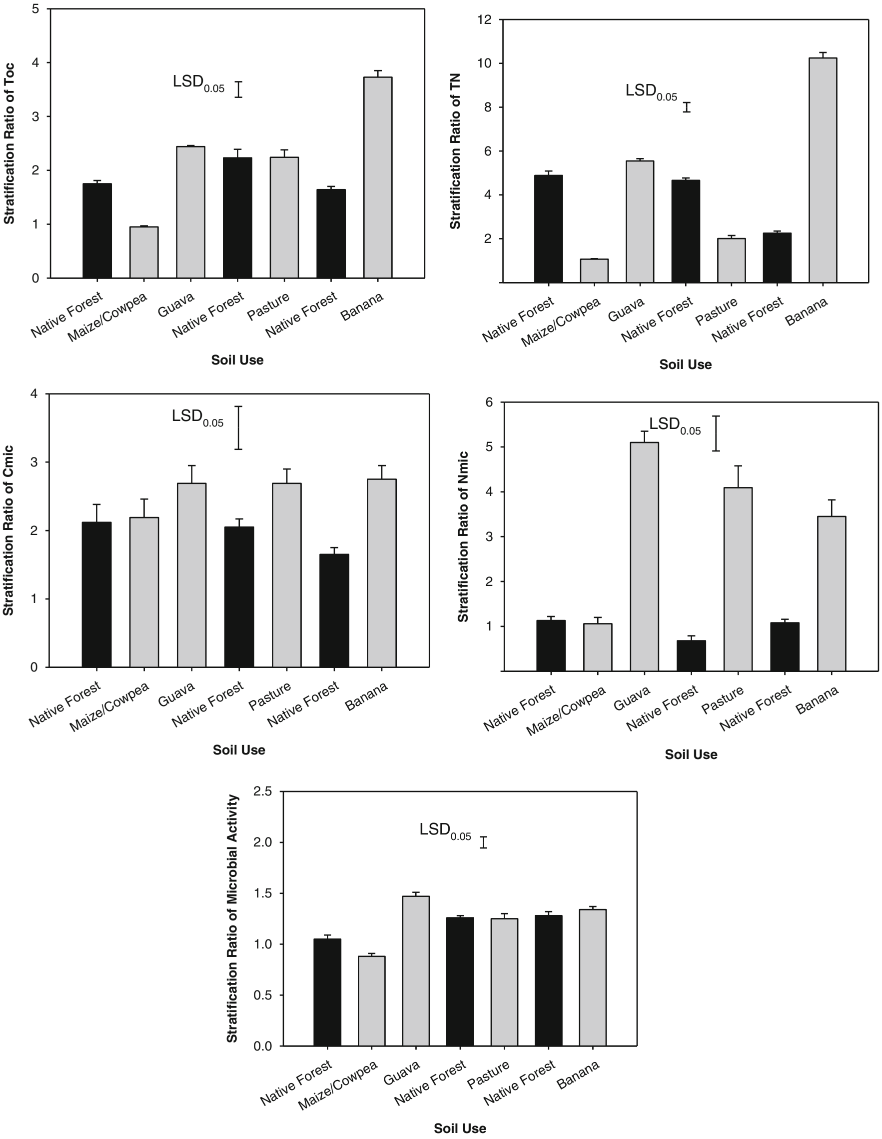

Fig. 42.3 Stratification ratios (0–0.05/0.10–0.15 m) of soil organic matter pools in irrigated cropping systems (perennial and annual crops) in Limoeiro do Norte, Ceará, Brazil. *Vertical bars* represent the LSD ($p < 0.05$)

greater TOC and WSC content at the pastureland area may be attributed to the greater amounts of roots or grass root exudates (Arshad et al. 2004). Variations in WSC contents were more pronounced than variations in TOC, suggesting that WSC can be used as a sensitive indicator that reflects recent changes in SOM caused by land use. In general, the conversion of forest to irrigated pastureland in Fortaleza did not result in OM depletion or a decline in soil quality.

Plant survival and growth in semiarid regions are linked to levels of available moisture, and irrigation boosts agricultural production substantially (Denef et al. 2009). Several irrigated areas on alluvial soils (Entisols) have been implemented in northeastern Brazil over the last few decades, and have helped improve the quality of life of small-scale farmers (Lacerda and Oliveira 2007). In Pentecoste the conversion of native forest to irrigated croplands has depleted SOM pools, especially in the surface soil layers (Fig. 42.2b), indicating that practices for restoring soil quality should be adopted. In Limoeiro do Norte most ratios exceeded 2 for the attributes evaluated in all land uses, except for the most intensive one (i.e., cultivation of maize and cowpea in succession; Fig. 42.3). Perennial cropping systems promoted the accumulation of OM in the soil surface, due to the absence of tillage and the constant input of plant residues.

Initially developed to compare experiments under conventional and no-tillage systems (Franzluebbers 2002), stratification ratios of SOM pools have received increasing attention in soil science because they have broad applications, particularly in providing an initial assessment of land use effects on soil functioning (Franzluebbers 2013). Several papers have explored stratification ratios of SOM pools in regions of the world including the Mediterranean (Melero et al. 2012; Corral-Fernandez et al. 2013; Lozano-Garcia and Parras-Alcantara 2013), the Middle East (Raiesi 2012; Jemai et al. 2012), South Africa (Dube et al. 2012), and China (Lou et al. 2012; Li et al. 2013). In Brazil, most work has focused on exploring no-till cropped areas (Sá and Lal 2009; Briedis et al. 2012), since the country harvests more than 60 % of its grain under this system (Derpsch and Friedrich 2009).

Conclusions

Our results seem to suggest that is possible to maintain or improve soil C and SOM fractions in northeastern Brazil by using irrigation, organic residues and strategies to preserve crop residues on the soil surface. More research is needed to encourage intercropping with perennial species and the use of fire-derived biomass as a Stable C source in this tropic semi-arid region.

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Chapter 43
Carbon Balance at the Regional Scale in Southern Brazil Estimated with the Century Model

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Abstract Modeling of soil organic C (SOC) dynamics associated with GIS can be useful to estimates C emissions and sequestration as a function of the changes in the land use and soil management. A balance of C emissions and sequestration was made at the regional scale using the Century model and GIS. Santana district in Ijuí, RS (28° 20′S and 53° 53′W) was selected where occur Hapludox, Orthents, Argiudolls, and Fluvents are common. We identified four homogeneous areas based on cropping systems, soil tillage systems, and native vegetation. These areas were converted into agriculture at different times. Soil samples were taken at 0–20 cm depth. The Century model was calibrated and validated based on the sampled areas and their estimates were generalized. We defined different simulation units that are similar zones in soil class, landscape elements (hilltops, slope, and depositional areas) and time of agricultural use (1901, 1957, 1965, 1976, and 1988). The agriculture use caused a 50 % reduction in SOC stocks from 1900 to 1986 (from 550.9 to 276.8 $\text{Mg} \times 10^3$), by the end of most intensive soil management period, which corresponded to emissions of $2{,}277.5 \times 10^3$ Mg of CO_2 into the atmosphere. Moreover the adoption of conservation agriculture management in 1987 enabled the recovery of C content of the soil. It is considered for 2007, compared with the original, recovery of the SOC stock in up to 60 % (337.7×10^3 Mg) when the soil

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C balance was positive in 276.5×10^3 Mg of CO_2. These results shows the CO_2 potential emission to the atmosphere by the forests removal and burning, as well as the potential of soil C sequestration by the adoption of soil conservation tillage systems. Century model adequately estimated the evolution of SOC stocks and CO_2 balance due to the use, land use changes, and soil management.

Keywords Greenhouse gases • Soil organic matter modeling • Carbon dynamic

Introduction

Climate change and uncertainty are of global concern in relation to the increase of greenhouse gases emissions and specially carbon dioxide (CO_2). The carbon (C) biogeochemical cycle where deforestation of native forest into croplands is considered to be an important factor responsible to CO_2 emissions to the atmosphere. Also, the reduction of soil organic carbon (SOC) is of concern as it is affected by soil management and cropping systems (Lal 1997, 2004; Mielniczuk et al. 2003).

Soil organic C stocks in the soil is a result of additions and losses of soil C over the time (Dalal and Mayer 1986; Bayer and Mielniczuk 2008). The amounts of crops C added to the systems via photosynthesis (CO_2) and the C losses during soil organic matter (SOM) mineralization as well as soil C removed from cropland by erosion (Mielniczuk et al. 2003) is affected by soil use and management.

Carbon cycling simulation models such as the Environmental Policy Impact Climate (EPIC) model (Williams et al. 1989), RothC model (Coleman and Jenkinson 1996; Rothamsted Research 2013), DAYCENT model (Del Grosso et al. 2001) and the Century model (Parton and Rasmussen 1994; NREL 2013) can analyze the impacts of alternative land covers and cropping and management systems on SOC sequestration across a wide spectrum of soil and climatic conditions. The Century model has been extensively used to evaluate SOC cycling and sequestration for grassland, forest, and agricultural ecosystems in different regions of the world. Examples of successful applications of the model include simulation of C cycling for 11 grassland sites in Africa, Asia, and North America (Parton et al. 1993) long-term cropping, woodland, and grassland sites in Europe (Kelly et al. 1997), forest to pasture chronosequences in the Brazilian Amazon region (Cerri et al. 2007), and changes in soil organic carbon stocks since the beginning of agriculture in representative areas within the main agricultural region of Rio Grande do Sul state, in southern Brazil (Tornquist et al. 2009; Bortolon et al. 2011). These and other studies underscore the versatility and utility of the Century model for evaluating SOC sequestration for alternative combinations of cropping and tillage systems.

In this study, we used the Century model and GIS to estimate the regional SOC stocks changes in the Santana district in Ijuí, RS, Brazil. The historical evolution of land uses and cropping systems were established, and management scenarios were studied from 1900 to 2007 to evaluate possible effects of forest to agriculture conversion and historical agricultural land use on the CO_2 emissions in this region.

Material and Methods

This research was conducted in Santana district, Ijuí municipality in Rio Grande do Sul State, Brazil (28° 20′S and 53° 53′W; elevation of 220–400 m), covering an area of 10,699 ha. Most of the area is owned by approximately 400 small farms of 25 ha (Fig. 43.1a). Soil types in the region are Hapludox (6,359 ha, 60 %), Orthent (1,833 ha, 17 %), Argiudoll (1,468 ha, 14 %), and Fluvent (1,009 ha, 9 %) (Fig. 43.1b). In the Brazilian Classification System (EMBRAPA 2006), these soils classified as the LATOSSOLO Vermelho distroférrico, NEOSSOLO Regolítico eutrófico, CHERNOSSOLO Argilúvico órtico, and NEOSSOLO Flúvico, respectively.

We have selected this region based on soil map availability, historical agricultural use and management, original native forest, and differences in the period of cultivation. The soil sampling purposes and historical land use and management were identified for four areas which were homogeneous in terms of cropping systems, soil management and native forest, but the areas were converted to croplands in different years. The areas were identified as Area 1 (51.1 ha), Area 2 (142.0 ha), Area 3 (77.1 ha), and Area 4 (102.2 ha).

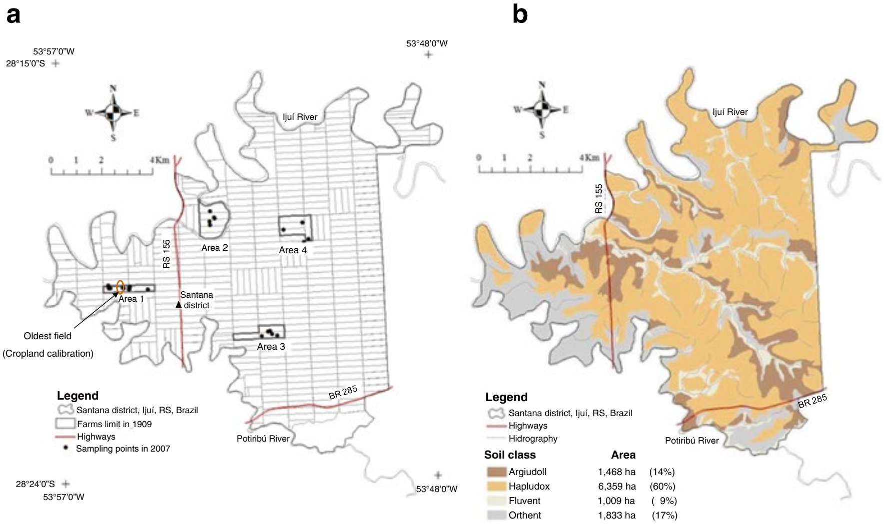

Fig. 43.1 Location of the four areas in the Santana district, Ijuí, RS, Brazil with spatial distribution of sites sampled in 2007 (**a**); and the soil survey map at a scale of 1:50,000 scale (**b**)

Table 43.1 Agricultural scenarios used in Century simulations for the Santana district, Ijuí, RS, Brazil (1901–2007)

Scenario (period)		Description
I	Colonial 1 (1901–1955)	Rotation: 2-years maize (summer)/fallow (fall-winter) and 1-year maize (summer)/wheat (winter); management: animal-draught moldboard plow, low-yield potential crop varieties, production based on natural soil fertility; Erosion: hilltops = 1.6 Mg ha^{-1} year^{-1}; slope = 2.0 Mg ha^{-1} year^{-1}; depositional areas = −1.08 Mg ha^{-1} year^{-1}.
II	Colonial 2 (1956–1970)	Rotation: 2-years maize (summer)/fallow (fall-winter) and 1-year soybean (summer)/wheat (winter); management: animal-draught moldboard plow, low-yield potential crop varieties, production based on natural soil fertility; Erosion: hilltops = 3.0 Mg ha^{-1} year^{-1}; slope = 4.0 Mg ha^{-1} year^{-1}; depositional areas = −2.2 Mg ha^{-1} year^{-1}.
III	Conventional tillage (1971–1986)	Rotation: 1-year soybean (summer)/wheat (winter); management: tractor drawn disk plowing and harrowing, wheat straw burning, medium yield potential crop varieties, N synthetic fertilizer (30 Kg ha^{-1} year^{-1}); Erosion: hilltops = 6.0 Mg ha^{-1} year^{-1}; slope = 8.0 Mg ha^{-1} year^{-1}; depositional areas = −4.2 Mg ha^{-1} year^{-1}.
IV	Reduced tillage (1987–1994)	Rotation: 1-year soybean (summer)/wheat (winter) and 1-year soybean (summer)/oat cover crop (winter); management: chisel plowing and disk harrowing, no wheat straw burning, medium yield potential crop varieties, N synthetic fertilizer (wheat 65 Kg ha^{-1} year^{-1}, oat 40 Kg ha^{-1} year^{-1}); Erosion: hilltops = 2.0 Mg ha^{-1} year^{-1}; slope = 3.0 Mg ha^{-1} year^{-1}; depositional areas = −1.5 Mg ha^{-1} year^{-1}.
V	No till (1995–2007)	Rotation: 1-year soybean (summer)/wheat (winter) and 1-year soybean (summer)/oat cover crop (winter); management: oat cover crop killed with herbicide in spring, no till, no wheat straw burning, high yield potential crop varieties, N synthetic fertilizer (wheat 65 Kg ha^{-1} year^{-1}; oat 40 Kg ha^{-1} year^{-1}); Erosion: hilltops = 0.6 Mg ha^{-1} year^{-1}; slope = 1.0 Mg ha^{-1} year^{-1}; depositional areas = −0.48 Mg ha^{-1} year^{-1}.

Soil samples were taken only on Hapludox with slopes less than 8 % and that were intensively used for agriculture. Soil samples were taken at 0–20 cm depth and analyzed for soil texture, soil bulk density and soil C content. Soil bulk density (SBD) was determined by the volumetric ring method (Blake and Hartge 1986), with stainless steel rings of 8.5 cm Ø × 5 cm depth placed in the center of each layer (0–10 and 10–20 cm). Total soil C concentration was determined by dry combustion (Nelson and Sommers 1996) in a CH Shimadzu analyzer. Soil texture determination was conducted with a modified pipette method used in Brazil (EMBRAPA 1997).

The agricultural management scenarios were established based on the land use and soil management history of the Santana district (Table 43.1).

The Century model was calibrated and validated based on the sampled areas (Bortolon et al. 2011) and their estimates were generalized to the entire area of Santana district (Bortolon et al. 2012). We defined different simulation units (SU) that are similar zones in soil class (Fig. 43.1b), landscape elements (hilltops, slope, and depositional areas) and time of cultivation (1901, 1957, 1965, 1976, and 1988). For delimiting the SU, we used ArcGIS 9.x (ESRI 2003). The Century model was used to estimate the CO_2 emissions to the atmosphere due the burning of the native forest remaining material, and also the balance of both C and CO_2 as a function of soil management since the beginning of cultivation.

The C balance ($C_{balance}$) due to soil management was obtained from Century model estimates as the difference between the amount of C added (CINPUT) and amount of C lost by microbial respiration (RESP(1)) and soil erosion (SCLOSA) in each management scenario. Furthermore, we assumed that 20 % of the C removed by soil erosion were mineralized by the soil biota and lost to the atmosphere as CO_2 while 20 % of the C accumulated in depositional areas were assimilated by the soil biota and removed from the atmosphere.

$$C_{balance} = CINPUT - \left[RESP\left(1\right) + \left(SCLOSA \times 0.2\right)\right] \tag{43.1}$$

Carbon balance results were expressed as:

$$CO_{2\ balance} = C_{balance} \times 3.67 \tag{43.2}$$

We also considered the amount of CO_2 emitted to the atmosphere due the burning of the remaining material from native forest after cutting 90 % of the trees and removal of timber, when the conversion of the forest into cropland. In this case, we considered the as CO_2 emissions from forest burning ($CO_{2\ \mathrm{deforestation}}$) the sum of the quantities of C contained in dead twigs (WOOD1C), the thick dead wood (WOOD2C) and the dead roots (WOOD3C), estimated by Century model in the month before burning, and multiplied by 3.67.

$$CO_{2\ deforestation} = \left(WOOD1C + WOOD2C + WOOD3C\right) \times 3.67 \tag{43.3}$$

The sum of the of Eqs. 43.2 and 43.3 results represented the environmental CO_2 balance in the different SU because we considered the CO_2 emissions from the land use conversion (forest-cropland), with the use of fire, and the CO_2 balance relative to soil management, where the potential CO_2 emission or sequestration is affected by adoption of different soil management systems.

The regional totals of SOC stocks and CO_2 balance were obtained by multiplying the results estimated in Mg ha^{-1} by the area occupied by the different SU. After that, these regional totals were grouped according to the different soil classes from Santana district.

Results and Discussion

Variation in the SOC stocks was affected by soil use and management (Table 43.2).

In 1900, soils from Santana district stocked 550.9×10^3 Mg of SOC, and most C was stored in Hapludox (57 % or 314.1×10^3 Mg) (Fig. 43.1b). The Orthents which

Table 43.2 Total SOC stocks changes from 1900 to 2007 in Santana district, Ijuí-RS, by soil class in the last year of adoption of different agricultural management scenarios[a]

	Total SOC stocks					
	1900	1955	1970	1986	1994	2007
Soil class	10^3 Mg					
Hapludox	314.1	239.0	212.7	164.0	184.0	201.5
Argiudoll	72.6	54.0	48.4	39.1	43.9	47.9
Orthent	115.9	67.8	59.4	46.3	50.8	54.7
Fluvent	48.3	35.0	31.9	27.4	30.9	33.7
Total	550.9	395.8	351.7	276.8	309.6	337.7
Difference in relation to 1900		−28.1 %	−36.2 %	−49.7 %	−43.8 %	−38.7 %
Difference in relation to previous		−28.1 %	−11.1 %	−21.3 %	+11.8 %	+9.1 %

[a] The agricultural management scenarios are: I – Colonial 1 (1901–1955); II – Colonial 2 (1956–1970); III – Conventional tillage (1971–1986); IV – Reduced tillage (1987–1994); V – No till (1995–2007)

corresponds to 17 % of the area represented 21 % (115.9 × 10^3 Mg) of the total SOC stocked in 1900, whereas the original SOC stocks of Argiudolls were 13 % (72.6 × 10^3 Mg) and Fluvents were 9 % (48.8 × 10^3 Mg). The proportional contribution of each soil type in relation to the total C stocks was little affected by agricultural use over time. However, the absolute values of the SOC stocks in each soil type were significantly affected by changing soil use and management. Even with adoption of conservationist agriculture practices after 1986 it was estimated that total SOC stock in the Santana district increased by 22 % from 1986 to 2007, but was 38 % below the initial level in 1900.

Those effects are reflected in the regional CO_2 balance (Table 43.3), where the CO_2 balance was negative from 1901 to 2007 independent of soil type and soil management scenario. The balance was more negative in 1986 when the total CO_2 emission to the atmosphere was 1,395.9 × 10^3 Mg if we consider the soil management impact and increasing to 2,227.5 × 10^3 Mg if we include the forest burned. Conservationist practices adopted by farmers after 1986 showed positive balance of CO_2 in 1994 (+104.9 × 10^3 Mg). Considerable CO_2 emission as well as sequestration was observed on Hapludox being the dominant soil in the Santana district (Fig. 43.1a). We observed that in 1986 50 % of the CO_2 emission was from Hapludox (1,395.9 × 10^3 Mg), which was reduced to 46 % in 2007 after 20 years of the adoption of conservation agricultural. In the same period the emissions occurred from Orthents increased from 28 % (1986) to 31 % (2007). This suggests that although Hapludox has been contributed largely to CO_2 emissions these soils had a greater potential to C sequestration compared to the other soil types. On the other hand, Orthent showed a lower potential to CO_2 sequestration which is explained by the differences in the soil texture with more chemical (interaction with mineral soil fraction) and physical (C protected in the soil aggregates interior) SOM protection with higher clay content in the Hapludox compared to the Orthents.

Table 43.3 CO_2 emissions (−) or sequestration (+) balance from 1900 to 2007 in Santana district, Ijuí-RS, by soil class in the last year of adoption of different agricultural management scenarios[a], related to 1900 (original condition) and 1986 (end of the conventional till), considering microbial respiration, erosion and deforestation

	CO_2 balance				
	1955	1970	1986	1994	2007
Soil class	10^3 Mg				
I. Relative to 1900					
Hapludox	−452.7	−551.7	−695.1	−607.3	−523.0
Argiudoll	−124.2	−146.2	−175.7	−155.4	−136.0
Orthent	−306.1	−343.2	−391.0	−372.2	−352.5
Fluvent	−99.7	−115.0	−134.1	−120.2	−107.8
Total (affected by management)	−982.7	−1.156.1	−1.395.9	−1.255.1	−1.119.3
Total (management + deforestation)	−1.1745.1	−2.007.7	−2.277.5	−2.147.5	−2.069.3
II. Relative to 1986					
Hapludox				+87.9	+172.2
Argiudoll				+20.5	+39.7
Orthent				+18.7	+38.4
Fluvent				+13.8	+26.2
Total (affected by management)				+140.9	+276.5
Total (management + deforestation)				+130.1	+265.7

[a] The agricultural management scenarios are: I – Colonial 1 (1901–1955); II – Colonial 2 (1956–1970); III – Conventional tillage (1971–1986); IV – Reduced tillage (1987–1994); V – No till (1995–2007)

Smith et al. (1997) used the Century model to evaluate the changes on SOC contents in wide range of soils from Canada. After 80 years of cultivation, sandy soils showed reduction of 31 % in the original SOC whereas loam soils had reduction of 22 % and in clayey soils the reduction was 16 %. Those variations were due to increase of SOM chemical and physical protection to microbial decomposition. In our study, after 85 years of agricultural soil use (from 1901 to 1986) with intensive management, the Hapludox (13 % of sand and 67 % of clay) had the SOC stock reduced in 47 % while the Orthent (51 % of sand and 33 % of clay) had the SOC stock reduced in 60 % (Table 43.2). If we consider the conservationist agriculture use (only 20 years) it is remarkable that Hapludox are more effective than Orthents in accumulate soil C. Since 1987–2007 the Orthent recovered only 12 % of original SOC stock losses against 25 % in the Hapludox.

Conclusions

These results show the potential for CO_2 potential to the atmosphere by forests removal and burning, as well as the potential of soil C sequestration by the adoption of soil conservation tillage systems. The Century model adequately estimated the evolution of SOC stocks and CO_2 balance due to the use, land use changes, and soil management. The model can be an important tool to study the impact of agriculture on both SOC stocks and global climate changes at regional scale.

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Chapter 44
Soil CO_2 Fluxes from Different Ages of Oil Palm in Tropical Peatland of Sarawak, Malaysia

Lulie Melling, Kah Joo Goh, Auldry Chaddy, and Ryusuke Hatano

Abstract Conversion of tropical peatland into oil palm plantation in Southeast Asia has been alleged to have increased the decomposition process via peat oxidation due to drainage and water management, raising the emission of soil CO_2. This is postulated to increase with age of oil palm cultivation. However, management also plays a role in soil CO_2 emissions from oil palm plantations. The objective of this study was to determine the controlling factors influencing soil CO_2 fluxes in different ages of oil palm on tropical peatland. The soil CO_2 fluxes were measured for 24 months from three palm ages (1, 5 and 7 years palm; S1, S2, S3) in tropical peatland of Sarawak, Malaysia using a closed-chamber method. The highest mean soil CO_2 flux was recorded in S3 (221 mg C m^{-2} h^{-1}) followed by S2 (195 mg C m^{-2} h^{-1}) and S1 (178 mg C m^{-2} h^{-1}) palms. The cumulative soil CO_2 fluxes for S1, S2 and S3 were 14.7, 16.4 and 18.5 t C ha^{-1} $year^{-1}$, respectively. Water table was found to have no correlation with soil CO_2 fluxes but water-filled pores space (WFPS) correlated negatively with soil CO_2 fluxes in all three different ages of oil palm. The increase in soil CO_2 flux with palm age was consistent with higher root biomass, suggesting that root respiration and microbial activity were associated with root exudates as major component of soil respiration in tropical peatland under oil palm.

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Keywords Water-filled pore space (WFPS) • Root biomass • Oil palm • Tropical peat

Introduction

The oil palm (*Elaeis guineensis* Jacq.) is currently the most productive oil crop in the world. Given that less suitable mineral soils are now available for development due to difficult terrain, and poor accessibility from the land to the ports due to a lack of infrastructure, the expansion of oil palm cultivation into vast unutilized peat soil areas is deemed necessary to drive development in Sarawak, provide job opportunity and eradicate rural poverty. Under natural condition of tropical peatland, the water saturated peat may impede root penetration and respiration which present a challenge for any agriculture development. This could be resolved through drainage, mechanical compaction and water management by maintaining the water table at 50–70 cm, which corresponds to the oil palm deep rooting system where the majority of roots are found in the upper 50 cm of the soil profile (Henson and Chai 1997). Drainage created an aerobic zone for better plant root respiration while compaction increases soil bulk density and reduces leaning problem due to poor root anchorage while at the same time increases moisture holding capacity via better capillary rise. However, lowering the water table in tropical peatland has been claimed to increase oxygen diffusion, promote higher microbial activity and accelerate peat oxidation causing higher soil carbon dioxide (CO_2) flux to the atmosphere (Nykanen et al. 1998; Jaenicke et al. 2010; Page et al. 2011).

Soil respiration comprises two components: microbial and root respiration (Moore and Dalva 1993; Tang et al. 2005). Plants may play an important role in soil respiration through their influence on root biomass. Soil CO_2 flux increased with root biomass (Wang et al. 2005; Luo and Zhou 2006) which agrees with the findings of Melling et al. (2013) for oil palms in peat soils. Similar results were also obtained for other plants where the contributions of root respiration to total soil respiration ranged from 40 to 70 % (Ohashi et al. 2000; Wang et al. 2006). In addition to root biomass, temperature, soil moisture and nutrient status are also key factors responsible for the variation in soil respiration through their influences on microbial and root activities (Davidson et al. 1998; Adachi et al. 2006). Microbial activity and root respiration have been found to increase with temperature (Wang et al. 2006) but decrease with soil moisture more than 60 % (Linn and Doran 1984).

Despite many studies on soil respiration rates, little work has been done on cultivated tropical peatland. Understanding on the factors responsible for soil CO_2 flux is crucial to explain the variations caused by land use change in tropical peatland. Hence, the objective of this study was to determine the controlling factors on soil CO_2 fluxes in different ages of oil palm on tropical peatland.

Table 44.1 Environmental characteristics and soil properties for oil palm plantation

	S1	S2	S3
Age of palm	(1 year palm)	(5 years palm)	(7 years palm)
Peat thickness (cm)	520	475	375
Relative humidity (%)	67.6 ± 1.8	74.9 ± 1.9	78.0 ± 2.0
Air temperature (°C)	33.8 ± 0.5	31.7 ± 0.5	30.6 ± 0.4
Soil temperature at 5 cm (°C)	27.9 ± 0.2	26.8 ± 0.2	26.6 ± 0.2
Soil temperature at 10 cm (°C)	27.5 ± 0.2	26.7 ± 0.2	26.5 ± 0.2
Annual rainfall (mm)	3,493	4,058	3,447
Water table (cm)	−56.4 ± 2.5	−66.6 ± 3.7	−55.6 ± 3.4
Water-filled pore space (%)	74.2 ± 1.3	81.2 ± 1.3	78.5 ± 1.5
Bulk density (g cm^{-3})	0.23 ± 0.004	0.21 ± 0.002	0.22 ± 0.003
Soil pH	3.6 ± 0.02	3.8 ± 0.04	3.9 ± 0.03
Loss of ignition (%)	94.4 ± 1.0	93.9 ± 1.1	94.2 ± 0.9
Total C (%)	55.6 ± 0.6	55.0 ± 0.8	56.1 ± 0.5
Total N (%)	2.1 ± 0.1	1.9 ± 0.1	1.9 ± 0.1
Base saturation (%)	40.7 ± 1.5	60.4 ± 2.4	61.8 ± 3.0

Values are mean monthly ± SE

Materials and Methods

The study was conducted at an oil palm plantation in Mukah, Sarawak, Malaysia (2° 51′ N, 112° 13′ E) on three sites, namely S1, S2 and S3, with oil palms of 1, 5 and 7 years, respectively. Further environmental and soil characteristics of each site are shown in Table 44.1.

Monthly measurements of soil CO_2 flux were carried out using a closed-chamber method for 24 months (July 2006–June 2008) (Crill 1991). Simultaneously all the environmental variables and soil samples were collected both during and after sampling as described in Melling et al. (2005).

Root dry weight estimation was done based on the Henson and Chai (1997) method. The standing root biomass was estimated from a linear regression of root on shoot biomass derived from intensive measurements of the palms.

Pearson correlation was used to determine if there is a correlation among variables and soil CO_2 fluxes. Simple linear regression analysis was used to determine the relationship between root dry weight and soil CO_2 fluxes. All statistical analysis was performed using the SAS version 9.2.

Results and Discussion

As shown in Fig. 44.1a, the monthly air temperature pattern was inversely related to the relative humidity (RH). Soil temperatures at 5 and 10 cm were relatively constant for all sites (Fig. 44.1b). In this study, the RH did not correlate with the soil CO_2

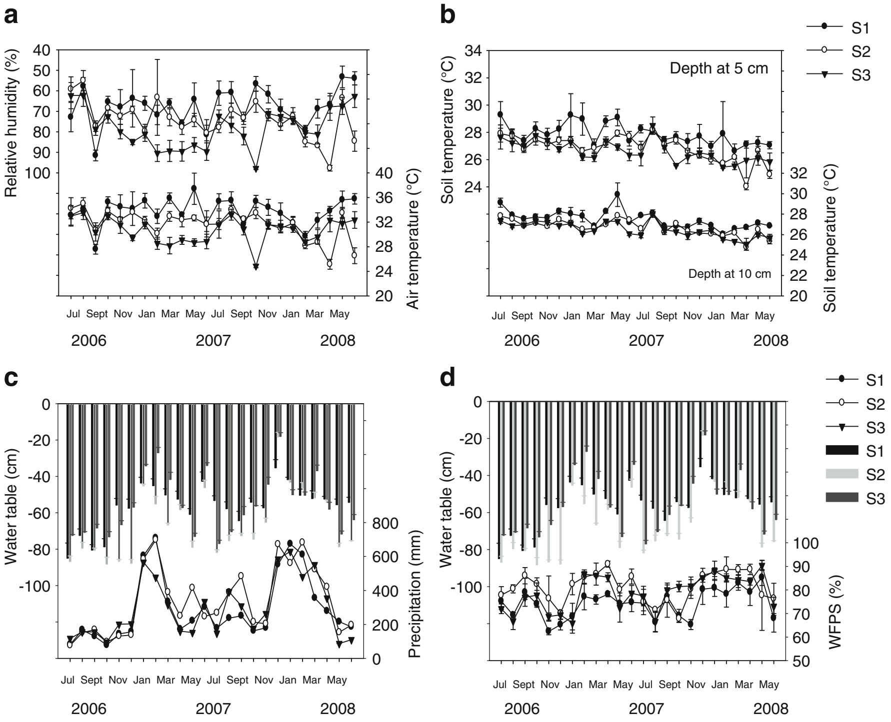

Fig. 44.1 Monthly mean for (**a**) relative humidity and air temperature, (**b**) soil temperature at 5 and 10 cm depth, (**c**) precipitation and water table and (**d**) precipitation and WFPS for different age of oil palm. Data represents means ± SE (n = 3)

fluxes but negatively correlated with the air and soil temperatures at 5 cm depth. As shown in Table 44.1, the RH increase with increasing palm age which might be attributed to the increase in palm canopy density. As the palm grows the size of its canopy increases and eventually closes (usually 4 years after planting). Open canopy in younger palms might cause the soil temperature to increase which will reduce microbial activity (Jauhiainen et al. 2008) thus lower soil CO_2 flux in the youngest palm.

With a total rainfall of more than 3,000 mm per year, the seasonal rainfall has a direct effect on the seasonal change in the water table (Fig. 44.1c) but did not influence the monthly variations in water-filled pore space (WFPS) (Fig. 44.1d). For all sites, the monthly mean WFPS was between 62 and 91 %.

As shown in Table 44.2, there were positive correlations between air and both soil temperatures and soil CO_2 fluxes ($p<0.05$) in S2. This relationship was enhanced when the water table was less than 75 cm (Fig. 44.3a). However, the above correlation was not obtained in S1 and S3. This shows that an increase in soil temperature with sufficient soil moisture would enhance soil organic matter decomposition, root-rhizosphere and microrhizal respiration (Fenn et al. 2010). Kuzyakov and Cheng (2001) and Tang et al. (2005) also found that soil temperature increases photosynthesis and root respiration leading to higher root exudation which serves as a C source for microbes and thus, enhances soil microbial activity, decomposition

Table 44.2 Correlation of soil CO_2 flux in different ages of oil palm with environmental variables

	Age of palm		
	S1	S2	S3
Variables	(n=72)	(n=72)	(n=72)
Air temperature (°C)	−0.09	0.27**	−0.11
Soil temperature at 5 cm (°C)	0.10	0.35**	−0.02
Soil temperature at 10 cm (°C)	−0.02	0.38**	−0.02
Water table (cm)	0.08	0.17	−0.09
Water-filled pore space (%)	−0.25**	−0.50**	−0.24*

Note: The top value in each parameter represents Pearson's correlation coefficient (r) with * and ** indicate with significance at $p<0.05$ and $p<0.01$, respectively

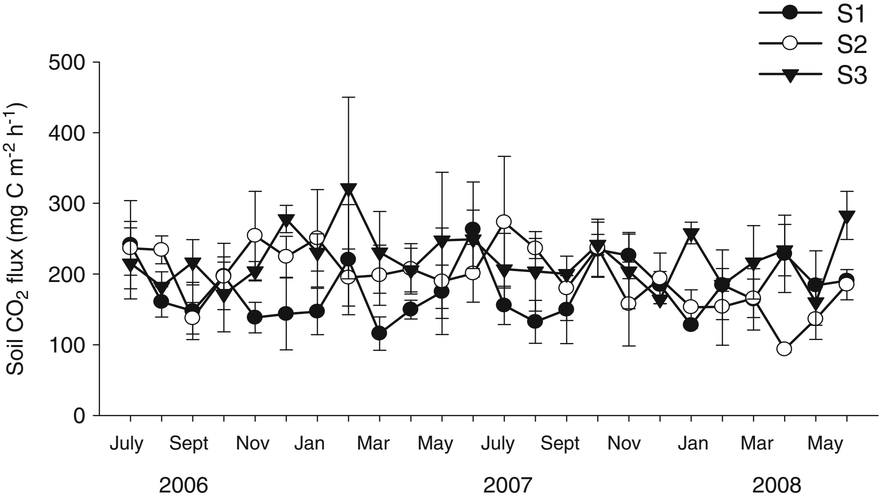

Fig. 44.2 Monthly means soil CO_2 flux for different age of oil palm. Data represents means ± SE (n=3)

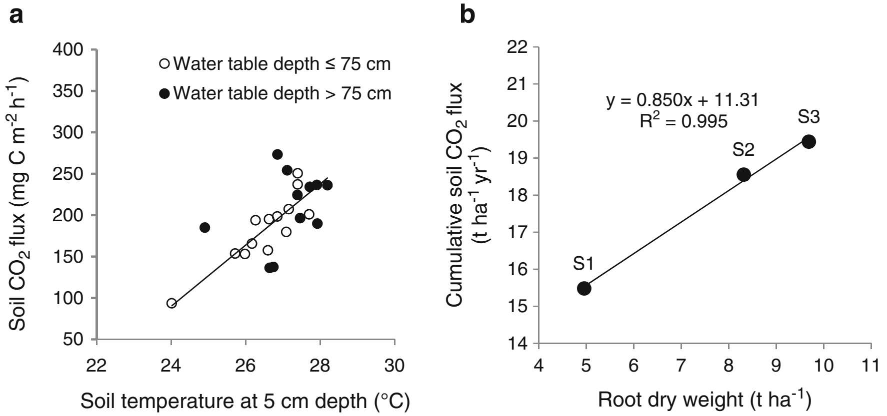

Fig. 44.3 (**a**) soil temp. at 5 cm depth and soil CO_2 fluxes S2 as influenced by depth of water table, (**b**) cumulative soil CO_2 flux and root dry weight in oil palm plantation ($p<0.05$)

Table 44.3 Mean soil CO_2 flux and annual cumulative for oil palm plantation

Age of palm	Soil CO_2 flux (mg C m^{-2} h^{-1})	Annual cumulative soil CO_2 flux (t C ha^{-1} $year^{-1}$)
S1	178 ± 8	14.7
S2	195 ± 9	16.4
S3	221 ± 8	18.5

Values are mean monthly ± SE (n = 24)

process and soil CO_2 production (Yuste et al. 2007). As shown in Fig. 44.3a, S2 also has no significant correlation between soil temperature at 5 cm depth and soil CO_2 when its water table was more than 75 cm. But this relationship was not obtained in S1 and S3 indicating that the effect of soil temperature and water table on soil CO_2 fluxes was site specific.

As shown in Table 44.2, there was no correlation between soil CO_2 fluxes and water table. Thus, the lowering of water table in tropical peatland for agriculture purposes, which have always been claimed to be the main factor causing an increase in soil CO_2 flux (Hirano et al. 2007; Hooijer et al. 2010; Page et al. 2011) could be site-specific. This contention is further supported by some studies where no distinct variation in soil CO_2 flux with season or water table was found in tropical region (Melling et al. 2005, 2012; Inubushi et al. 2003; Watanabe et al. 2009). In a tropical peat swamp forest in Kalimantan, Jauhiainen et al. (2005) had also observed that water table has lower correlation with soil CO_2 flux. A similar relationship was also found by Parmentier et al. (2009) in the Netherlands. Berglund and Berglund (2011) had found higher soil CO_2 flux in higher water table of 40 cm compared with 80 cm depth because of sufficient amount of air and moisture for optimal microbial activity. At the lower water table, moisture became the rate limiting factor for microbial activity causing a reduction in soil CO_2 emission.

In all the study sites, WFPS was negatively correlated with soil CO_2 flux (Table 44.2). In the development of an oil palm plantation on tropical peatland, other than drainage and water management, mechanical compaction is a pre-requisite. Compaction increases the soil bulk density, while reducing soil porosity and enhancing root activity (Melling et al. 2013) and also reduces the incidence of leaning. Lower porosity increases the capillary rise and water retention capacity resulting in higher WFPS which plays an important role in controlling soil CO_2 flux (Linn and Doran 1984; Melling et al. 2005, 2012). Microbial population and respiration generally increases with WFPS but when it reaches more than 60 % (Linn and Doran 1984), respiration activity starts to decrease. Higher WFPS reduces the diffusion rates of O_2 into the soil, thus inhibiting the underground biotic activity such as the respiratory activity of plant roots (Adachi et al. 2006; Castellano et al. 2011) all leading to lower soil CO_2 flux.

Mean soil CO_2 flux and annual cumulative flux as shown in Table 44.3 increased with palm age. Soil CO_2 flux in S3 was significantly higher ($p < 0.05$) than S1 and S2. The annual cumulative fluxes for the study sites were similar to the findings by Melling et al. (2005) and Adachi et al. (2006). There was also no distinct seasonal pattern for monthly soil CO_2 fluxes in all sites (Fig. 44.2). However, as shown in Fig. 44.3b, cumulative soil CO_2 flux increased linearly with root biomass ($R^2 = 0.995$), the latter due to increasing palm age are consistent with other studies (Ohashi et al. 2000; Adachi et al. 2006; Han et al. 2007). Oil palm root biomass is about 20–40 % of above ground biomass and it was found that total root respiration of 9 years old palm contributed 69 % of total soil respiration (Henson and Chai 1997). Melling et al. (2013) had also found that the contribution of root respiration to soil respiration is 62 %. Adachi et al. (2006) reported that soil respiration of oil palm plantation is mainly influenced by fine root biomass as 70 % of oil palm roots grow towards the soil surface (Reddy et al. 2002). This maybe the main reason for the older palm having higher soil CO_2 flux. Its larger root biomass would contribute more root residues and exudates as the C source for microbes and increase the microbial activity which in turn stimulates soil organic matter breakdown (Kuzyakov 2002). Figure 44.3b also shows that the heterotrophic respiration was similar for all three sites since they share a common intercept. This might be expected because microbial activity and decomposition are likely to be most active in the soil surface, which probably has similar properties in the three sites. Larger biomass is expected to have higher root respiration, root turnover and litter production (Pregitzer et al. 2008; Liu et al. 2009).

Conclusion

Soil CO_2 fluxes in oil palm plantation are not predominantly influenced by water table which had been alluded to by most studies but strongly influenced by soil WFPS and root biomass. Heterotrophic respiration was similar in the three sites with different palm ages and types of peat. Further studies should be conducted on the effect of root biomass on soil CO_2 fluxes in oil palm plantation on tropical peat soil.

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Chapter 45
Soil Organic Carbon Stocks, Changes and CO_2 Mitigation Potential by Alteration of Residue Amendment Pattern in China

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Abstract Proper estimation of China's national soil organic carbon (SOC) stocks, changes and mitigation potential are critical to adopt proper measures to protect SOC pools and to make strategies for the greenhouse gases (GHGs) mitigation. The data of SOC, bulk density from the Second State Soil Survey of China conducted in the early 1980s, and farmland CH_4 and N_2O emission induced by residue amendment were used to estimate the SOC pools, their changes during 1980s–2000s and farmland GHGs mitigation potential in China.

Soils were divided into paddy, upland, forest, grassland and waste land soils. The SOC stock is 89.61 Pg in China's 870.94 Mha terrestrial areas which encompasses 2473 soil series. The annual soil organic carbon accumulation rate in farmland of China is 23.61 Tg from 1980s to 2000s.

More carbon from amended organic matter (OM) was retained in paddy soil than in upland soil, but OM amendment in paddy soil led to large CH_4–C emissions, 9.95 % and 19.17 % of organic carbon inputs under intermittent and continuous flood conditions, respectively. OM amendment elimination in rice season could cut

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CH_4–C emissions by 3.4 Tg year^{-1}, accounting for 56 % of current CH_4–C emissions (6.1 Tg) and reducing global warming potential by 24.84 Tg year^{-1} CO_2–C equivalent, accounting for 50.3 % in China.

Keywords Soil organic carbon • Greenhouse gases • Rice field • Climate change • China

Introduction

Great efforts have been put on the estimation of soil organic carbon (SOC) stocks, dynamics and greenhouse gases (GHGs) mitigation potential by farming measures. SOC stock is a balance of organic carbon input and output, and enhanced SOC sequestration requires either an increase in new carbon input without an equivalent increase in mineralization of new input carbon and older soil organic matter (van Kessel et al. 2000). Amendments of manure, sewage sludge or straw has been demonstrated to be effective in soil carbon accumulation (Smith et al. 1997).

Arable land is an important source of CH_4 and N_2O, especially CH_4 emissions from rice cultivation. Enhanced CH_4 emissions due to residue or manure amendment to paddies have been well documented because the amended residue or manure increased the methanogen-dependent substrate availability and made the environment more favorable for CH_4 production by reducing the soil redox potential (Eh) (Majumdar 2003).

Residue and manure (organic matter) amendment to arable land is a common practice in the world. It can improve soil productivity, increase soil organic carbon, but also can lead to enhanced CH_4 and N_2O emissions. China experienced fast economical development and social change from 1980s to 2000s. Consequently, the assessment of the change of SOC pools, CH_4 and N_2O emissions, and their integrated effect on GHGs mitigation in China is needed for evaluation of policies and decision-making.

In this study, we used the data from 2,473 soil profiles from the Second State Soil Survey to estimate the SOC pools in 1980s, and data on SOC dynamics, CH_4 and N_2O emission collected from peer-reviewed papers (Huang et al. 2006; Xie et al. 2007, 2010) to estimate the SOC changes and GHGs mitigation potentials.

Materials and Methods

Estimation of SOC Pools

Data for SOC density calculation and SOC storage estimation of China's soils were obtained from the Second State Soil Survey completed in the early 1980s. The data were published in a series of monographs in the China Soil Series Vols. 1–6 (SSSSC

(State Soil Survey Service of China) 1993, 1994a, b, 1995a, b, 1996). 2473 soil series were identified in the Second State Soil Survey. Information on the soil series includes parameters on geological location, soil depth, organic matter content, bulk density, area, annual average temperature and precipitation, parent material and physical-chemical properties, but for some soil series, only a part of the parameters were provided.

In this study, we divided China's soil organic carbon pools into five sub-pools, paddy, upland, forest, grassland and waste-land according to their use in the early 1980s. In each sub-pool, surface and subsurface horizons were selected for analysis. For paddy and upland soil, tillage layers were designated as surface horizons, and for forest, grassland and waste-land soil, the surface horizons were the first genetic layers. Subsurface horizons were delineated by pedogenic characteristics as the zone between surface horizons and parent material or debris layers with little or no pedogenesis. Because orchards were always included in the upland in the second soil survey, and disturbed more intensively than forest, the carbon in orchards were included in upland in this study. Shrub and bamboo land was allocated as forest.

In the 2473 soil profiles, statistical data and typical data for organic matter contents, depth and bulk densities are provided, some with statistical data, some with typical data and some with both. The numbers of soil profiles with statistical organic matter contents, depth and bulk densities are 1,832, 1,832 and 581, respectively; and those with typical organic matter contents, depth and bulk densities are 2,469, 2,469 and 475, respectively. Typical organic matter contents, depth and bulk densities were used when a soil profile has no statistical data. When a statistical data in a soil profile is from two or more soil uses, the use of the soil in typical profile was used.

In the published China Soil Series Vols. 1–6 (SSSSC 1993, 1994a, b, 1995a, b, 1996), the data related with SOC are listed as soil organic matter (SOM). The SOM is converted to SOC by multiplying a constant of 0.580.

Because bulk densities did not fully follow the measurement of SOM in the Second State Soil Survey, the missing bulk densities were estimated from regression analysis between the available bulk densities and SOC contents for a given horizon and for a given kind of land use. For waste land, available bulk densities are too limited to do regression analysis with SOC for surface and subsurface horizons, respectively, so the bulk densities in the surface and subsurface horizons were combined for regression estimation of missing bulk densities. Xie et al. (2007) found that there were two regression patterns between SOC contents and bulk densities, one is logarithm, and the other linear. In the surface layer, the relationships between SOC and bulk densities in the paddy, forest and grassland are logarithmic, and in the upland it is linear. In subsurface horizons, relationships between SOC and bulk densities are linear. The regression equations reported by Xie et al. (2007) were used to estimate missing bulk densities in surface and subsurface horizons in paddy, upland, forest, grassland and waste land, respectively. Detailed calculations can be found in Xie et al. (2007).

Estimation of the Changes of SOC Pool and GHGs Mitigation Potential

Data were obtained from the literature in published peer-reviewed journal sources from the Web of Science, www.cqvip.com and www.cnki.net. Papers were selected by the following criteria: (1). Sampling sites and SOC determination method should be comparable with those in the Second State Soil Survey; (2). The area that samples covered in each paper should not be less than the county level. (3). total CH_4 and N_2O fluxes were available or could be converted from reported data.

We calculated per unit organic-matter-amendment-induced soil organic carbon accruement in paddies and uplands separately, and also per unit organic-matter-induced CH_4 emissions amended during paddy rice season and off-rice dryland crop season were calculated separately. Off-rice dryland crop season refers to the season during which water is drained and wheat, rape, broad bean, green manure or other dryland crops are planted or the land is kept at fallow. Calculations in detail can be found in Xie et al. (2007, 2010).

Results and Discussion

SOC Pools

Large variations in estimation of soil organic carbon storage in mainland of China are found, ranging from 50 to 183.1 Pg, with an average of 94.2 Pg and a median of 89.61 Pg (Table 45.1).

Soil organic carbon pools in the surface horizon in paddy, upland, forest, grassland and waste land are 0.82, 3.07, 15.67, 15.37 and 1.71 Pg, respectively; and in the subsurface horizons 2.09, 7.00, 20.56, 22.34 and 2.97 Pg, respectively (Xie et al. 2007). If we take 1,500 Pg as the global SOC pool (Batjes and Sombroek 1997), China's SOC pool is about 6.58 % of the global SOC storage in 6.4 % of the global terrestrial area.

The estimated average carbon density in China was 102.9 t ha^{-1}, which was a little bit less than that in a previous global study estimation of 106 t ha^{-1} (Batjes 1996). The carbon density in the surface horizons with an area-weighted depth of 19 cm, and in the subsurface horizons of 82 cm was 39.8 and 63.10 t ha^{-1}. Considering that the 0–30 cm topsoil contributes 54 % of the China's 1 m SOC storage (Wang et al. 2004), the carbon density in the top 30 cm in China should be 55.6 t ha^{-1}, larger than the world's average SOC density of 50 t ha^{-1}, and smaller than in 15 European countries with a mean density of 69.6 t ha^{-1} (Smith et al. 1997).

Table 45.1 Various estimates of soil organic carbon storage in the mainland of China (Pg)

C pool	Cover area (Mha)	Methods	References
183.1	945	Average SOC content and 1:10,000,000 soil map	Lin et al. (1997)
100	968	Osnabrück biosphere model	Peng and Apps (1997)
50	915	Average bulk density	Pan (1999)
100.2	925.45	First soil survey data and GIS	Wang and Zhou (1999)
92.4	877.63	Second soil survey data and 1:4,000,000 soil map	Wang et al. (2000)
119.76	959.63	Median C density	Ni (2001)
70.31	881.81	Mixed soil use	Wu et al. (2003)
82.65	901.14	CEVSA model	Li et al. (2003)
69.38	686.85	Vegetation category	Xie et al. (2004a)
84.38	923.97	Mixed soil use	Xie et al. (2004b)
89.1	92.81	1:1,000,000 soil database	Yu et al. (2007)
89.61	871	Divided soil use and Area weighted average SOC	This study

Table 45.2 Various estimations of annual increases of soil organic carbon storage in farmland of China (Tg)

Changes of C pool	Period	Method	References
15.6–20.0	1980–2000	Monitor data	Huang et al. (2006)
25.5	1985–2006	Monitor data	Pan et al. (2010)
16.6–27.8	1980–2000	Monitor data	Sun et al. (2010)
23.6	1980–2000	Monitor data	This study

Changes of Soil Organic Carbon in Farmland of China Between 1980s to 2000s

Several studies have shown that increase of soil organic carbon in farmland of China (Table 45.2), is mainly contributed by straw amendment. From 1982 to 2004, Agricultural productivity and the national economy were greatly enhanced. For example, the yield of three staple crops; rice, wheat and maize per ha increased ~30 %, ~50 %, and ~60 %, respectively (CAYEC 1983, 2005). Along with the increase of agricultural productivity and a reduction in removal of biogenic material for human's living energy, more organic material was incorporated into soils, which resulted in 0.472 Pg C (0.101 and 0.371 from paddy and upland, respectively) increase of farmland (156 Mha) soil organic carbon in the surface horizons in the last 20 years, equivalent to +0.606 % year^{-1}. Xie et al. (2010) found that along with the increase of straw amendment, soil organic carbon content increased, but the apparent conversion rate of amended straw carbon to soil organic carbon decreased with the increase of amendment years. The apparent conversion rate of straw carbon to soil organic carbon was kept at a constant level of 213.3 g kg^{-1} in paddy field, and 190.1 g kg^{-1} in upland soils at a 30 year average (Fig. 45.1). According to

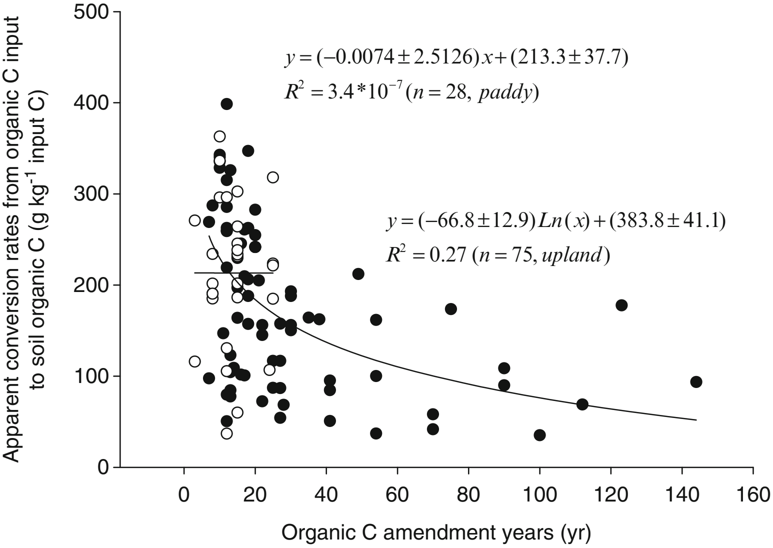

Fig. 45.1 Impacts of organic C amendment time (year) on its apparent conversion rate to paddy (*open circle*) and upland soil organic C (*filled circle*). Y is conversion rate (g kg^{-1}), x is organic C amendment time (year)

China's straw amendment rate of around 30 % of the total straw carbon production (Gao et al. 2002), Xie et al. (2010) estimated that annual straw amendments in rice season and non-rice season are 28.5 Mt and 79.5 Mt, respectively. Estimates of soil organic carbon increment from straw amendment were 21.19 Tg (6.08 Tg and 15.1 Tg in paddy and upland soil, respectively); which are comparable with the annual increase rate from soil monitor data (Table 45.2).

GHGs Mitigation Potential

The apparent conversion rates of organic carbon to CH_4–C under intermittent and continuous flooding management were 9.95 % and 19.17 % of the amended organic carbon, respectively (Fig. 45.2). No consistent trend could be established between N_2O emission and organic matter amendment (data not shown).

Although organic matter amendments during rice season can substantially increase soil organic carbon stocks, the increased carbon sequestration could not offset the enhanced CH_4-induced atmospheric radiative forcing due to the large percentage of organic matter carbon conversion to CH_4 during rice season (Table 45.3). This result strongly suggests that to mitigate the integrative warming effect, we should avoid adding organic matter carbon during flooded rice growing season as much as possible. From Table 45.3 we can also deduce that the integrative warming effect from organic matter amendments was much lower during the

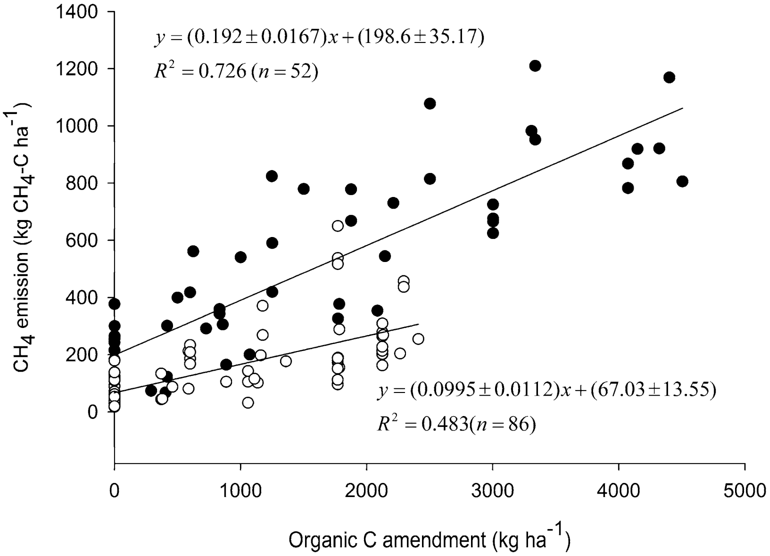

Fig. 45.2 Impacts of rice season organic C amendment on CH_4 emission at continuous flood (*filled circle*) and intermittent flood managements (*open circle*). Y is seasonal CH_4 emission (kg CH_4–C ha^{-1}), x is seasonal organic C amendment (kg C ha^{-1})

Table 45.3 Effects of organic matter amendment on carbon sequestration rate (g C kg^{-1} C input), CH_4 (g CH_4–C kg^{-1} C input) and N_2O (mg N_2O–N kg^{-1} C input) emission rate, and CO_2–C equivalent emission mitigation rate (g C kg^{-1} C input) at upland and rice season over the 30 years horizon[a]

Organic matter amendment		Carbon sequestration rate [a][b]	CH_4 emission rate [b]	N_2O emission rate [c][e]	CO_2–C equivalent emission rate[f]
Upland		190.1 ± 32.1	0	−99.4 ± 76.2	−202.8 ± 19.4
Off-rice season		190.1 ± 32.1	23.7 ± 2.8[c]	−38.0 ± 33.8	20.5 ± 15.6
Rice season	IF	213.3 ± 37.7	99.5 ± 11.2[d]	−128.2 ± 75.1	674.9 ± 41.2
	CF	213.3 ± 37.7	191.7 ± 16.7[d]	62.3 ± 60.6	1,537.4 ± 59.2

[a] Means ± 1SE.CF and IF represent continuous flooding and intermittent flooding during rice season, respectively

[b] Figure 45.1

[c] Xu et al. (2000)

[d] Figure 45.2

[e] Xie et al. (2010)

[f] CO_2–C equivalent emission = (−a*44/12 + b*16/12*25 + c*44/28/1,000*298)*12/44

off-rice season period than during the rice season. Additionally, during intermittent flooding conditions the combined radiative forcing was much less than under continuously flooded paddies, although a careful fertilizer N management is required as otherwise intermittent flooding conditions are prone to large N_2O emissions which could outbalance the reduction in CH_4 emissions.

Table 45.4 Changes of annual soil carbon sequestration, CH_4 emission and CO_2–C equivalent global warming potential (GWP) induced by the elimination of organic matter amendment in rice season of China (Tg year^{-1})[a]

Amendment pattern	Amendment	Unamendment
Soil carbon sequestration [a]	6.03[b]	–0.04
CH_4–C emission from rice season [b]	6.10[c]	2.70
CO_2–C equivalent GWP[d]	49.42	24.59

[a] In China in 2006, rice/wheat and rice/rape rotation area is around 13 Mha (wheat area is around 7 Mha, rape area is around 6 Mha before rice season), rice/fallow, rice-rice/fallow, rice-rice/green manure, rice-rice/vegetable or rice-rice-rice area, etc. is around 16 Mha (CAYEC 2007). Wheat, rape and early season rice straw carbon productions are around 45 Mt (C content 47.2 % (Shen 1998), 40 Mt (C content 44.7 % (Zhang et al. 2009), 30 Mt (C content 41.7 % (Shen 1998) (converted from the yield) (CAYEC 2007), respectively. China's straw amendment rate is around 30 % of the total straw carbon production (Gao et al. 2002), then the amended straw carbon on rice season contributed by wheat, early rice and rape straw is about 34.5 Mt. Apart from root biomass C of early rice (2.6 Mt) and wheat (3.3 Mt), Current straw carbon amendment during rice season could be about 28.5 Mt

[b] Average of Pan et al. (2010), Xu et al. (2012) and This study

[c] Average of Bachelet (1995), Cai (1997), Huang et al. (1998), Yan et al. (2003), Li et al. (2004), Huang et al. (2006), Yan et al. (2009)

[d] CO_2–C equivalent emission = (−a*44/12 + b*16/12*25)*12/44. We did not consider N_2O-induced GWP because we found that straw amendment had no effects on N_2O emission

Eighty percent and twenty percent of rice fields, respectively are subjected to intermittent and continuous flooding management in China (Li et al. 2002). Straw amendment contributed 3.36 Tg year^{-1} CH_4–C, and soil organic matter and rice root 2.70 Tg year^{-1}, which is comparable with the estimation of annual CH_4–C 6.1 Tg year^{-1} based on the field measurement data (Table 45.4). If straw amendment during the rice season is eliminated, methane emission could be cut by 56 % (Table 45.4).

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Chapter 46
Soil Organic Carbon Stocks Under Plantation Crops and Forest in the Rainforest Zone of Nigeria

Joseph S. Ogeh

Abstract The experiment was carried out with the aim of evaluating the topsoil carbon level of different plantation crop stand and forest stand and to assess the relationship between soil organic carbon and particle size. Soil samples were taken from the 0–30 cm depth of oil palm, teak, and dikka nut plantations and a virgin forest of about 18–20 years old Teak plantation had significantly higher soil organic carbon concentration than the oil palm, dikka nut plantations and virgin forest. Soil organic carbon were similar for the Dikka nut plantation and virgin forest but were both higher than the organic carbon value in the Oil palm plantation. There was a strong relationship between soil organic carbon and clay content ($r = 0.91$, $P < 0.05$) and a negative relationship between soil organic carbon and sand ($r = -0.84$, $P < 0.05$) and a relationship between soil organic carbon and silt ($r = 0.68$, $P < 0.05$).

The findings from this experiment suggest that Teak plantations may be advantageous for increasing soil fertility as regards to soil organic carbon.

Keywords Soil carbon stock • Top soil • Rainforest • Plantation crops • Forest land

Introduction

Soil organic carbon (SOC) is a main factor affecting soil quality and agriculture sustainability. Being a source and sink of plant nutrients, SOC plays an important role in terrestrial C cycle (Freixo et al. 2002). Land use has a strong effect on SOC storage, since it affects the amount and quality of litter input, litter decomposition rate, and stabilization of SOC.

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Forest and plantation can be carbon stores, and can also be carbon dioxide sinks when they are increasing in density or area. Land use changes especially when it involves afforestation and deforestation can have major impacts on carbon storage. Enhanced growth stores more carbon, but the cut vegetation releases CO_2; the net effect depends on many factors, such as prior and subsequent growth rates and the quantity and disposal of vegetation. Rising atmospheric CO_2 may stimulate tree growth, but limited availability of other nutrients may constrain that growth (Gorte 2009). Mature tropical forests, by definition, sequester little carbon because growth is equal to decay and tropical soils (above 25 °C) do not accumulate humus as do temperate forests (Jonathan 2006).

Life expectancy of forests varies throughout the world, influenced by tree species, site conditions and natural disturbance patterns. In some forests, carbon may be stored for centuries, while in other forests carbon is released with frequent stand replacing fires. Forests that are harvested prior to stand replacing events allow for the retention of carbon in manufactured forest products such as lumber. Vegetation is one of the primary factors contributing to soil formation (Champan and Reiss 1992) and many studies have shown the effects of individual tree species on soil chemical and physical properties (Chastain et al. 2006). Old-growth forests store little or no additional carbon, and new forest growth and efficient wood use can increase net carbon storage. The impacts vary widely, and depend on many factors, including soil impacts, treatment of residual forest biomass, proportion of carbon removed from the site, and duration and disposal of the products. To date, the quantitative relationships between these factors and net carbon storage have not been established (Gorte 2009).

Hassink et al. (1997) have suggested that organic carbon sequestration in soils is texture dependent and highly correlated to the proportion of fine particles. The release and sequestration of carbon (C) has received much attention due to its potential impact on global warming. In terrestrial ecosystem, soil plays an essential role in global carbon balance because the C stored in soil is essential to be four times greater than the total available in living vegetation and its ability to offset greenhouse gas emission through C sequestration (Lal 2004).

Ogeh (2012 unpublished) showed very low level of organic carbon in some plantation crops like coffee, cocoa, cashew and kola while that of the forest environment was significantly higher in a forest/savanna transition zone. The rationale for this experiment was to find out if similar results will be obtained in the rainforest zone. This study was carried out with the aim of evaluating the topsoil carbon level of different plantation crop stand and forest stand and also to find the relationship between soil organic carbon and particle size in the rainforest zone of Nigeria.

Materials and Methods

Study Area

The study was conducted around Benin City (Lat. 5° 58′ and 6° 20′N; long. 6° 16′ and 6° 45′E) using plantations which covers an area of about 12 ha. The specific plot were planted with oil palm *(Elaeis guinennsis),* Teak *(Tectonia grandis)* and

Dikka nut (*Irvingia gabonensis*) whose ages ranged between 18 and 20 years. A virgin forest was sampled to serve as control. The plantations are located within the Rainforest zone of Midwestern Nigeria. The sites used in this study was selected based on proximity of each plantation type to each other and similarity of soil texture, morphology and parent material. The soils are classified as Ultisols (USDA). The soils are formed from Coastal Plain sands which constitute the largest formation in this region. They are reddish and have a clayey sand top and clayey loam sub-horizons. The soils has been classified as Rhodic Paleudult (US) or Dystric Nitosol (FAO) (Ogunkunle 1986).

Soil Sampling

The plantations (Teak – *Tectonia grandis,* Dikka nut – *Irvingia gabonensis*, Oil Palm – *Elaeis guinennsis*) and virgin forest of about 3 ha each were divided into 300 plots of 10 × 10 m per plot. One hundred (100) of these plots were randomly selected for soil sampling. From each of the 10 × 10 m quadrant, five soil samples were randomly collected from the sampling depths of 0–30 cm, which is referred to as topsoil. The sampling was restricted to this depth because it provides the bulk of plant nutrients (Russell 1967).

Soil samples were air-dried, sieved, and analysed in the laboratory: Particle size composition was obtained by hydrometer method (Bouyoucos 1951); soil pH was determined potentiometrically in 0.01 M calcium chloride using a soil to calcium chloride solution ratio of 1:2 (Peech 1965); organic carbon was determined by the Detjareff method (Walkley and Black 1934). Total nitrogen was determined by the Kjedahl method.

Results and Discussion

The mean values of the soil parameter taken from the plantation and virgin forest are presented in Table 46.1. The trend for soil carbon was Teak > virgin forest > dikka nut > oil palm. Nitrogen level in the various plantations also followed the same trend. The high level of soil organic carbon may have been attributed to the heavy litter produced by teak. The textural classes in the plantations and virgin forest was sand and loamy sand as indicated in the table.

Table 46.1 Mean values of soil properties in the various plantation and virgin forest

		C	N	pH	Sand	Silt	Clay	Textural
Plantation/forest	Soil depth	g/kg			g/kg			Class
Dikka nut	0–30 cm	11.5	0.7	5.3	862	68	70	Sand
Teak	0–30 cm	14.1	1.1	5.3	808	92	100	Loamy sand
Oil palm	0–30 cm	7.4	0.6	5.2	872	69	59	Sand
Virgin forest	0–30 cm	12.2	1	5.0	815	95	90	Loamy sand

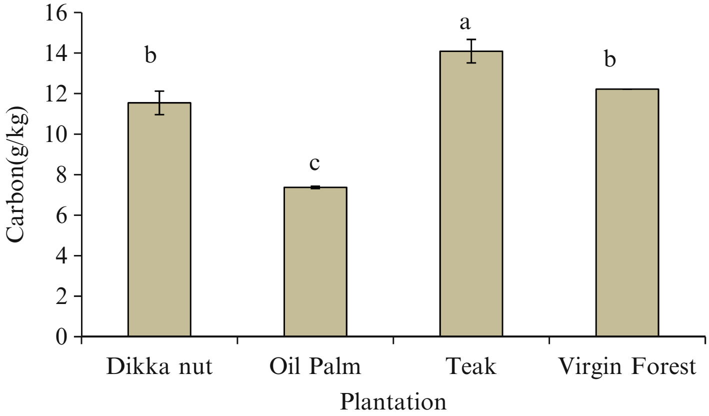

Fig. 46.1 Soil organic carbon under the different plantations. *Bars* with the same letter are not statistically different at P < *0.05*

Teak plantation proved to be higher ($P \leq 0.05$) in soil organic carbon level than the other plantation and the virgin forest (Fig. 46.1). Arrouays et al. 2006 found a strong relationships between particle size and organic carbon stock. They concluded that the upper decile values by textural classes can be used as a proxy of the maximal carbon storage potential. It might be more efficient to encourage practices favouring carbon accumulation in soils already having high OC stocks than to try to increase OC stocks in soils where present stocks are low. This conclusion is only from an additional carbon sequestration point of view. Indeed in the study most of the low C values were related to low clay content and therefore to low potential of C stabilization. They also said on the contrary numerous higher C contents, linked to high clay content, seem not to have reached their maximal potential of additional C sequestration, which is much higher.

Figures 46.2, 46.3, and 46.4 show the relationship between soil organic carbon and clay, sand and silt. There was a high positive relationship between soil organic carbon and clay. Though their work was on rangelands Gili et al. (2010) also had similar results that carbon stocks are positively related to the clay or fine particles contents, so changes in clay or fine particles contents could markedly affect soil organic carbon stocks. Fine particles affect soil organic carbon stocks through influencing the formation of clay-humus complexes that stabilize and retain more organic matter (Hassink 1997; Six et al. 2002).

Amponsah and Meyer (2000) working in Costa Rica found decreased SOC in teak plantations (16–27 years old) compared to undisturbed forests. They observed that the rotation age of teak in Costa Rica is seldom more than 60 years and it is unlikely that soils under teak plantation will ever recover pre-plantation SOC concentrations. The loss of leaf cover and lack of undergrowth in teak plantations are often cited as the sources for erosion and loss of SOC (Amponsah and Meyer 2000). But in my findings the Teak plantation were undisturbed which may have contributed to higher soil organic carbon compared to other plantation crops.

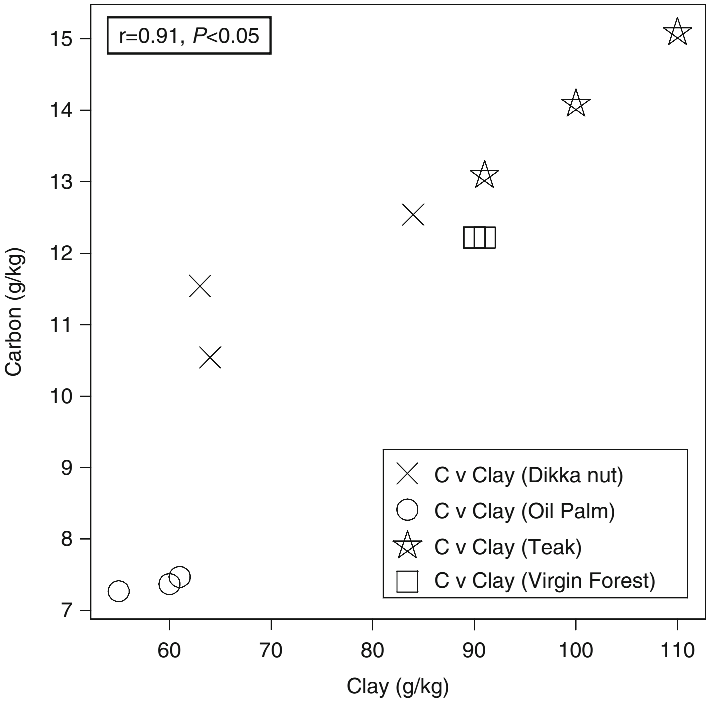

Fig. 46.2 Relationship between soil organic carbon and clay in the different plantation and virgin forest

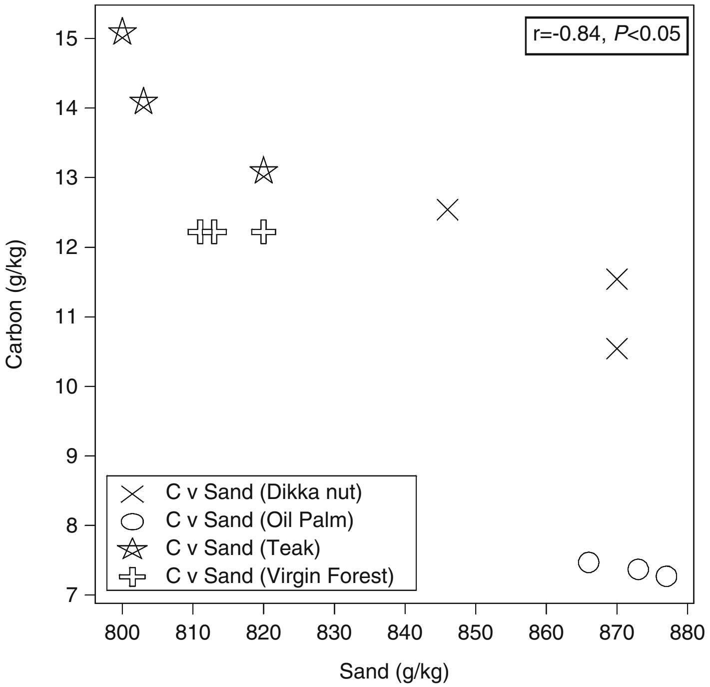

Fig. 46.3 Relationship between soil organic carbon and sand in the different plantation and virgin forest

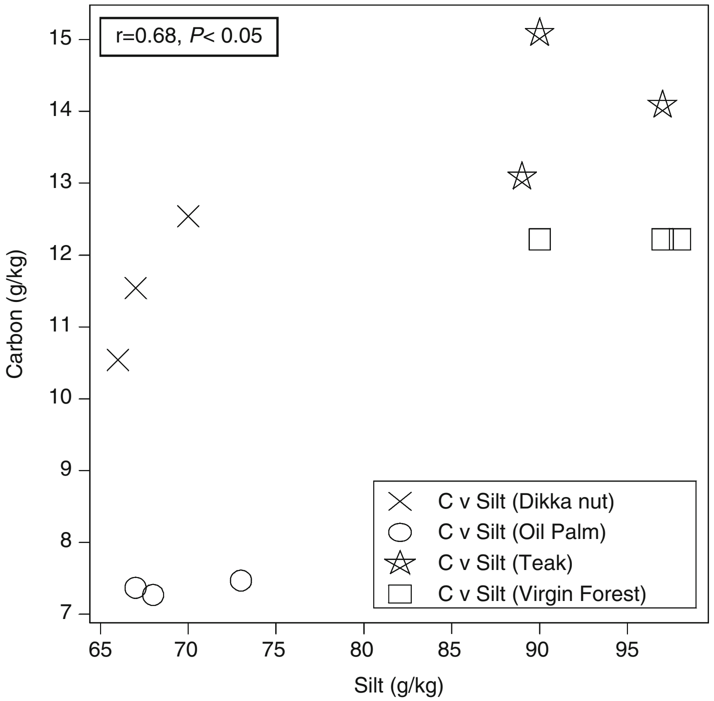

Fig. 46.4 Relationship between soil organic carbon and silt in the different plantation and virgin forest

Conclusions

Teak (*Tectonia grandis*) plantation are higher in soil organic carbon compared to soils under dikka nut, oil palm and virgin forest. Differences in SOC pool under different plantation were statistically significant ($P \leq 0.05$). The teak plantation had higher potential to store SOC among the plantation species. The Teak plantation was undisturbed which may have contributed to soil organic carbon better than other plantations. More land should be put under teak plantation as this may help in the utilization of atmospheric CO_2, serve as cover to, thereby preventing erosion, increasing yield potential of the soil and housing wildlife, microflora and microfauna.

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Chapter 47
Evolution of Soil Carbon Storage and Morphometric Properties of Afforested Soils in the U.S. Great Plains

Yury G. Chendev, Larisa L. Novykh, Thomas J. Sauer, Aleksandr N. Petin, Evgeny A. Zazdravnykh, and C. Lee Burras

Abstract The objective of this project was to use detailed soil profile descriptions and soil carbon analyses to determine the soil C sequestration potential of tree planting across climatic gradients in the U.S. Great Plains. Tree windbreak age ranged from 19 to 70 years and age of cultivation from 22 to ~110 years. At each site, soil pits were prepared within the tree planting, the adjacent crop fields, and nearby undisturbed grassland. Windbreak soils had consistently thicker soil organic carbon (SOC)-enriched A or A+AB horizons when compared to the crop fields. The thickness of A or A+AB horizons in the windbreak soils were comparable to the undisturbed grassland soils. A linear relationship was detected between the difference in A+AB thickness of soils beneath windbreaks and undisturbed grasslands and a climate index (hydrothermal coefficient, HTC). These results indicate that tree windbreaks with more cool and moist climate conditions are more favorable for SOC accumulation in the surface soil. The relationship between SOC accumulation and climate factors enables the estimation of soil carbon stocks in existing windbreaks and the prediction of potential carbon sequestration of future plantings.

Keywords Soil organic carbon • Afforestation • Soil transformation

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Introduction

The Energy Independence and Security Act of 2007 mandating that 60.5 billion liters of liquid biofuels be produced annually in the U.S. from cellulosic feed stocks by 2022. To meet this production goal it is estimated that 6.5–7.7 million hectares of land will need to be dedicated to feedstock production (Biomass Research and Development Board 2008). In the U.S. Great Plains there is potential for the production of biofuels from grains, crop residues, and dedicated perennial crops, including woody biomass (Rosenberg and Smith 2009). The region has a history of forest plantations as single to multiple rows of trees and/or shrubs as windbreaks or shelterbelts (Brandle et al. 2004). Windbreak plantings have been often employed in sub-humid to semi-arid regions with extensive plantings in both the steppes of Russia (Mirov 1935; Schroeder and Kort 1989) and the U.S. Great Plains (Droze 1977).

Tree windbreaks represent a multiple-benefit land use through their capacity to improve crop growth by modifying the local microclimate, sequester carbon in the soil and roots, and provide a renewable source of feedstock (above-ground biomass) for bioenergy production. Sauer et al. (2007) reported significantly greater soil organic carbon (SOC) in the surface 15 cm of soil beneath a 35 year-old shelterbelt in Nebraska as compared to the adjacent cropped fields. Hernandez-Ramirez et al. (2011), using stable carbon isotope techniques, found that 54 % of the SOC in the 0–7.5 cm soil layer within the Nebraska shelterbelt was tree-derived. Minimizing site disturbance, improved microclimate, and the increased diversity of plant species in tree windbreaks have been credited with reducing C losses and increasing the stability of SOC stocks.

The objective of this research was to determine the soil carbon sequestration potential of tree plantings on marginal agricultural soils across a climatic gradient in the U.S. Great Plains. Here we report on the U.S. phase of a project regarding soil transformations at three U.S. sites. Details of the Russian phase of this project have been reported elsewhere (Chendev et al. 2013).

Study Sites

Three sites representing a gradient in mean annual precipitation (MAP) from 528 to 696 mm and mean annual temperature (MAT) of 4.35–9.56 °C were selected for study (Table 47.1). The hydrothermal coefficient (HTC) of Selyaninov (1928) was used as a climate index, calculated as $HTC = \Sigma Q/0.1\Sigma T$ where Q is and T are precipitation (mm) and temperature (°C) during the growing season (defined as $T > 10$ °C).

The Reynolds, North Dakota site is situated on a broad flat landscape having less than 50 cm total relief. The site grades from the poorly drained upland of the glacial Lake Agassiz plain to the well drained stream terrace along Cole Creek. Parent materials are silty and clayey lacustrine sediments over calcareous loamy glacial tills and similarly textured alluvium. Groundwater is at ~2.5 m. The crop field has been cultivated approximately 110 years predominantly to small grains and more recently with some row crops including corn (*Zea mays*, L.), soybean (*Glycine max* (L.) Merr.),

Table 47.1 Sampling sites, elevation, mean annual temperature (MAT), mean annual precipitation (MAP), hydrothermal coefficient (HTC), and tree windbreak details

Site	Lat and long	Elev (m ASL)	MAT (°C)	MAP (mm)	HTC	Age of tree planting (years)	Tree species
Reynolds, ND	47° 42′ 13″ N 97° 10′ 59″ W	282	4.35	528	1.41	54	Green ash, red cedar and caragana
Huron, SD	44° 15′ 43″ N 98° 15′ 12″ W	397	7.71	582	1.31	19	Green ash
Norfolk, NE	42° 03′ 03″ N 97° 22′ 08″ W	492	9.56	696	1.47	70	Siberian elm, red mulberry, and cottonwood

Table 47.2 Soil series and taxonomic classification for sampling sites

Site	Soil series[a]	Soil taxonomy
Reynolds, ND	Antler-Mustinka silt loam	Fine-loamy, mixed superactive, frigid Aeric Calciaquolls
	LaDelle silt loam	Fine, smectitic, frigid Typic Argiaquolls
		Fine-silty, mixed superactive, frigid Cumulic Hapludolls
Huron, SD	Carthage fine sandy loam	Coarse-loamy, mixed, superactive, mesic Pachic Haplustolls
	Hand-Bonilla loams	Fine-loamy, mixed, superactive, mesic Typic Haplustolls &
		Fine-loamy, mixed, superactive, mesic Pachic Haplustolls
Norfolk, NE	Thurman loamy fine sand	Sandy, mixed, mesic Udorthentic Haplustolls
	Hadar loamy find sand	Sandy over loamy, mixed, superactive, mesic Udic Haplustolls

[a]Series identified from Soil Survey Geographic (SSURGO) database (http://soils.usda.gov/survey/geography/ssurgo/description.html)

or sunflower (*Helianthus annuus*). A six-row windbreak was planted in 1958 and now consists primarily of green ash (*Fraxinus pennsylvanica*), box elder (*Acer negundo*), red cedar (*Juniperus virginiana*), and caragana (*Caragana arborescens*). The adjacent grassland was formerly a pasture of primarily smooth brome grass (*Bromus inermis*). Soils at this site are mapped as Antler-Mustinka silt loams in the field and windbreak and LaDelle silt loam in the grassland adjacent to the stream (Table 47.2).

Soils at the Huron site were formed in loamy glacial till and meltwater sandy and loamy sand sediments and are moderately well or well drained. The soils are mapped as Hand-Bonilla loams and Carthage fine sandy loam (Table 47.2). The site had less than 3 % slope with groundwater at ~1.25 m. The entire site was in pasture until 1981 when it was plowed and cropped. In 1983 a 20+ row tree planting was established to evaluate different tree species and the grass area was returned to pasture. The field continued to be cropped to corn, soybean, or grain sorghum (*Sorghum bicolor* (L.) Moench).

The third site was located in Madison County, Nebraska northeast of the city of Norfolk. Soils at this site are very deep and somewhat excessively drained with sandy eolian parent material redeposited from glaciofluvial sands and loamy sands from the Elkhorn River valley. The soils are mapped as Thurman loamy fine sand and Hadar loamy fine sand (Table 47.2). Soils at this site have been cultivated or grazed since European settlement in the 1880s. Irrigation is necessary for optimum crop yield although dryland row crop (corn and soybean), wheat (*Triticum aestivum*, L.), and alfalfa (*Medicago sativa*, L.) are also cultivated. A 5-row tree windbreak was planted in 1942. Dominant species currently include Siberian elm (*Ulmus pumila*, L.), red mulberry (*Morus rubra*, L.), and cottonwood (*Populus deltoides* Marsh).

Methods

Soil profile descriptions were prepared for one crop field, tree, and grass site at each of the three sites in May of 2012. Two additional pits were prepared at the Norfolk site. As both sides of the windbreak at this site were cropped, pits were prepared in both fields. A second pit was also prepared in the windbreak as a 45–60 cm-tall ridge was observed in the middle of the windbreak. All soil pits were prepared by hand to a depth of 1.2–1.5 m. Horizon boundaries and profile descriptions were prepared from observations of three exposed soil faces. Horizon boundaries were measured at five sites on each exposed face. Presence of carbonates was determined by measuring the depth to effervescence following application of dilute acid to the pit sidewalls. Soil samples were taken from 0–15, 15–30, 30–45, 45–60, 60–80, and 80–100 cm depth increments. Visible roots were removed and a subsample passed through a 2 mm sieve, air dried, and roller-milled before total carbon and nitrogen analysis on a Fison NA 15,000 Elemental Analyzer (ThermoQuest Corp., Austin, TX). Soil inorganic carbon (SIC) was determined by modified pressure calcimetry (Sherrod et al. 2002) and SOC calculated by difference. Triplicate horizontal cores (7.8 cm id × 5.15 cm long) were taken from one exposed soil face to determine soil bulk density. Two cores were collected with a Dutch auger approximately 5 m on each side of the pits. These samples were taken at the same depth increments and analyzed with the same methods as for the pit samples. Results are presented for the means of pit and cores samples.

Results

Topsoil thickness (A+AB horizons) of the uncultivated grass soils decreased from north-to-south; 52, 44, 41 cm thickness for the Reynolds, Huron, and Norfolk sites, respectively (Fig. 47.1). These soils were considered representative of the original, pre-cultivation soil properties. At each site, there were also significantly greater thicknesses of the A+AB horizons in soils beneath tree plantings compared to the adjacent cultivated cropland soils. The difference in A+AB thickness between tree

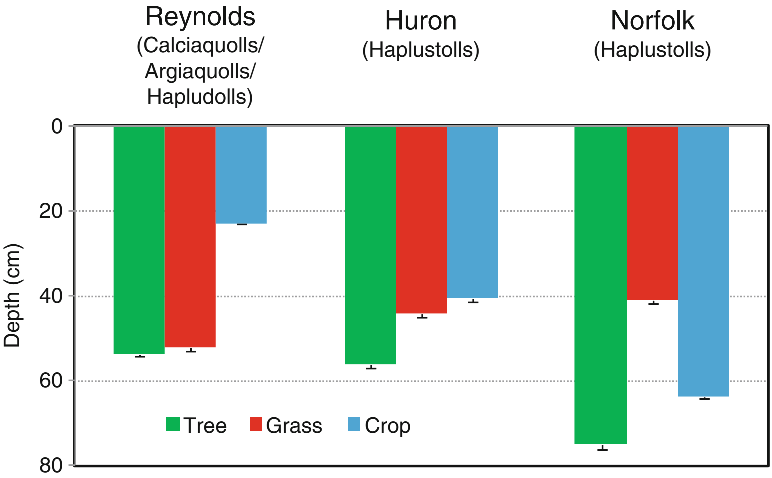

Fig. 47.1 Depth of A or A+AB horizons for U.S. sampling sites. *Error bars* are one standard error (n = 15)

and crop soils was 30.8, 15.5, and 11.2 cm for the Reynolds, Huron, and Norfolk sites, respectively, also following a north–south gradient. It is likely that these differences in thickness of the SOC-enriched surface horizons are due to both continued SOC loss from cropping practices, especially erosion and tillage, and SOC accumulation beneath the trees where there is both greater biomass input and limited soil disturbance.

Depth distributions of SOC and SIC content are consistent with the morphometric properties (topsoil thickness) and illustrate the contrasting effects of land use (Fig. 47.2). The Reynolds site had the greatest SOC and deepest humus-rich surface layers with the soil profile in the grassland having the highest SOC content and stocks at all depths (Fig. 47.2a). Also notable is the depletion of SOC in the cropland soil, especially from 15 to 60 cm. By contrast, the cropland soil had SIC present at all depths and SIC content from 30 to 60 cm represented almost 80 % of the total carbon in the profile at these depths (Fig. 47.2b). Neither grassland nor tree soil had SIC present above 45 cm but all three land uses had similar SIC below 60 cm.

Land use effects on soil thermal and moisture regimes may be the driving forces behind soil carbon transformations when grassland soils are cultivated or planted to trees. When compared with grasslands, cultivated soils have bare soil surfaces for extended periods and increased evaporation from the soil surface may bring pedogenic carbonates upward from underlying parent materials. Lower SIC in the 80–100 cm layer of the Reynolds cropland soil may indicate loss of carbonate due to this upward movement. Under tree cover, soil conditions are cooler with less evaporation from the soil surface than in grasslands and croplands, and carbonates would be more likely to leach (Khokhlova et al. 2013).

The soil beneath trees at the Huron site had greater SOC at all depths than the cropland and grassland soils and, like for the Reynolds site, the cropland soil again

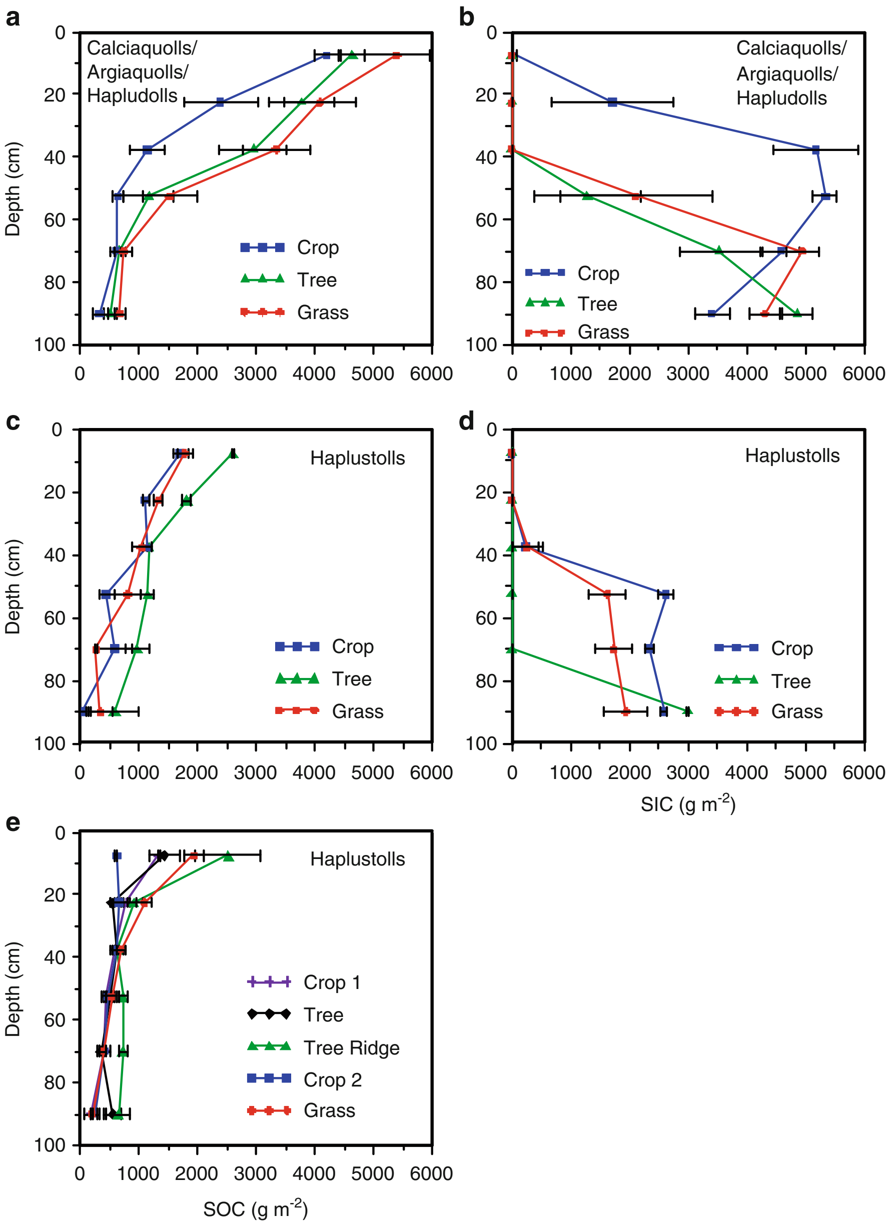

Fig. 47.2 Profiles of SOC and SIC for U.S. sampling sites. Note – no SIC was detected at the Norfolk site. *Error bars* are one standard error (n=3). (**a**) Reynolds SOC. (**b**) Reynolds SIC. (**c**) Huron SOC. (**d**) Huron SIC. (**e**) Norfolk SOC

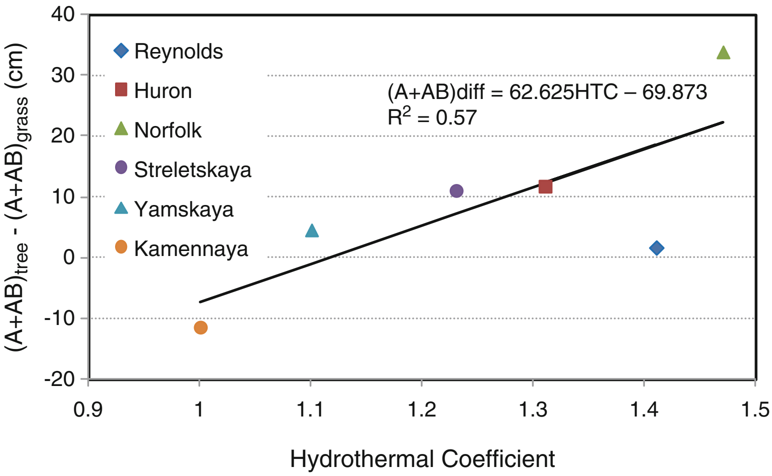

Fig. 47.3 Plot of difference of A+AB horizon thickness of tree and grass soils versus HTC for all U.S. and Russian sites (Chendev et al. 2013)

exhibited carbonate accumulation (Fig. 47.2c, d). The soils of the Huron site exhibited the most distinct changes in SOC and SIC following tree planting yet this location had the youngest trees (19 year-old). The SOC profiles were very similar for the grassland and crop field suggesting that cultivation had not led to significant SOC loss via erosion or decomposition of organic matter accelerated by tillage.

The Norfolk site had the oldest trees (70 year-old) yet exhibited the smallest changes in SOC with land use (Fig. 47.2e). The Tree Ridge profile was collected from a narrow ridge of soil running parallel within the windbreak. This soil exhibited SOC accumulation throughout the profile and is thought to be the result of deposition of topsoil from adjacent fields via wind erosion. The general low SOC and lack of carbonates at this site are likely due to the coarse-textured soils with low water-holding capacity limiting plant growth and warmer temperatures accelerating organic matter decomposition.

Differences of A+AB horizon thickness of tree and grassland soils when plotted versus HTC for the three U.S. sites and three sites in southern Russia using the same methodology (Chendev et al. 2013) exhibit a linear dependence with R^2 of 0.57 (Fig. 47.3). Thus, the effect of tree planting on grassland soils appears to follow the same rate of organic carbon accumulation in the U.S. Great Plains and Central Russian Upland and this rate is strongly linked to climate. The Reynolds site is an outlier to this trend and two factors may explain this finding. First, the soil under the windbreak had a dense layer of glacial origin coarse stone fragments at 38–56 cm. This restrictive layer could slow down the process of SOC accumulation by inhibiting root growth. Second, the grassland soil may have received external organic inputs from intermittent flooding that would increase SOC accumulation.

Conclusions

Mollisols of the Great Plains respond within decades to changes caused by human activity – changing virgin grasslands to arable lands, or arable lands to windbreaks. Tree cover seems to improve soil quality by increasing of A and A+AB horizons thickness, SOC content and stocks. The maximum effect of this soil development was found in more cool and moist conditions and was consistent with findings at three sites in the Russian steppe. Accumulation of carbon in windbreak biomass and soils indicates that afforestation is an effective measure to assimilate carbon from the atmosphere and convert it into ecosystem components. As such, tree planting in the Great Plains can improve or restore soil quality and is as an effective climate change mitigation practice.

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Chapter 48
Soil Carbon Research Priorities

Alfred E. Hartemink, Martin H. Gerzabek, Rattan Lal, and Kevin McSweeney

Abstract In this book, research on soil C is presented from different parts of the world, and from the fundamental aspects all the way to its management at a range of temporal and spatial scales. Here we summarize a set of priorities and these are loosely grouped in: Research priorities in soil C in space and time; Research priorities in soil C properties and processes, and research priorities in Soil C use and management. A list is presented that focuses on monitoring, assessment and upscaling as well as the biochemistry and role of soil structure in the sequestration of soil C. The effect of fire, black carbon, deep carbon and hydrophobicity as well as depth distribution are important research priorities. The relation between soil C and agronomic productivity are discussed in the context of sustainable intensification for advancing global food security. Lastly, some considerations are discussed how linkages with other disciplines might enhance the impact of the soil science community in soil C research.

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Keywords Soil carbon • Climate change adaptation and mitigation • Soil quality • Crop productivity • Measurement and monitoring of soil carbon • Soil research

Introduction

In 1968, one of the first conferences solely dedicated to organic matter was held in Rome (Pontificiae Academiae Scieniarum Scripta Varia 1968). The book has a combination of chapters that focus on the chemical, physical and biological properties of soil organic matter (SOM) mainly in relation to the fertility of the soil. The role of SOM and greenhouse gases was not discussed, and it was not until the 1980s that the relation between soils and climate change was emphasized and that it was realized that soils played a key role as sink and source of greenhouse gases (Bouwman 1990; Scharpenseel et al. 1990). The role of soil C was quickly discovered and this was followed by the importance of soil management in the sequestration and release of C (Lal 1995; Gerzabek et al. 1997). Although much of that initial research and attention was geared towards priorities in the temperate and boreal zones, research in the tropics was considered as well (Greenland et al. 1992).

Since the mid 1990s, research on soil C expanded greatly as was shown in the first chapter of this book. There are many excellent reviews available (e.g. Lal 2002, 2004; Stockmann et al. 2013) and globally there are numerous research projects in which soil C is a key component. This book, that resulted from the 2013 IUSS Global Soil C Conference, presents the wide array of research that is being conducted on soil C in all parts of the world, and at all scales. The overall purpose of this chapter is to take stock of research priorities that are listed in various chapters and that were discussed during the conference. Although many of us may regard such lists and stocks as somewhat self-serving, in the future it allows us to look back and see what research on soil C has been undertaken and where progress has been made.

Research Priorities in Soil C in Space and Time

Soils are variable and much understanding has been gained in the past decades about what causes variation and how it can be modeled (Heuvelink and Webster 2001). Variation in soil types partly explains variation that is found in soil organic carbon (SOC) levels (Batjes 1996), and the diverse range of factors that affect C levels. Research questions in this area include: measurement and monitoring over the landscape scale, depth distribution of SOC in relation to land use and management to create a positive soil C budget, and upscaling from point or pedon scale to landscape or watershed scale.

Soil monitoring of SOC across landscape units and over time is crucial for the assessment of SOC pools and fluxes. Such monitoring programs should be carefully designed and once started should be conducted for the long-term, that is: over 5 years at least. The Critical Zone Observatory Networks (Banwart et al. 2012), the Long Term Ecological Research Networks (LTER) and the Deep Carbon Observatory yield data that are promising for assessment of SOC changes over time. Sites that include capability for measuring soil gas fluxes and soil solution and redox dynamics will be most valuable for unraveling the role of soil C in earth system processes. Soil chronosequence studies may add to the understanding of long-term changes of soil C (Zehetner et al. 2009).

Methods of sampling and analysis need some standardization but also further refinement. Carbon needs to be expressed on mass per volume basis and not solely in concentrations. Bulk density measurements and extent and representativeness of a given location are therefore important. Too few studies include this. There is a set of proximal soil sensing technologies now available by which the number of measurements can be greatly increased while reducing the cost per sample (McBratney et al. 2006).

Many soils have large pools of SOC below what is generally considered the topsoil. This SOC may have been buried such as in volcanic or alluvial soils or may have washed into the subsoil over time. Although the concentrations of SOC at depth may be small, the sheer volume contributes to a considerable stock that has not been well-quantified (Lorenz and Lal 2005). Also the contribution of inorganic C to C sequestration potential should be further investigated and quantified. Deep placement, away from the zone of anthropogenic perturbation and climatic factors, enhances the mean residence time of SOC.

The upscaling of SOC levels in a soil or across a landscape needs further refinement. That includes upscaling to district or regional, national and to supranational and continental scales. There is a fair amount of data that can be used and global SOC maps show where data deficiencies lie. There is also a rapidly evolving set of techniques to produce SOC maps at a range of scales including predictions of associated uncertainties. Such predictions will guide future sampling, monitoring and modeling efforts. It is clear that land use and its rapid changes has a major impact on SOC, which should be built into prediction of SOC levels at any scale.

Changes in SOC pools are rapid in areas where levels are large. These areas, the global hot spots of SOC, include permafrost soils, and peat soils in wetlands. The warming climate and increased decomposition warrant the need for monitoring and assessing C stocks in soils of these hot spots. Priority areas for SOC research include areas that are subject to rapid land use change, changes in climate, areas from which we have only sparse data, and soils of ecologically sensitive regions. Some base line soil C data may be obtained from soil fertility studies and there is also quite some data available for the tropical regions (Hartemink 2006), where land use changes are large (Hartemink et al. 2008).

Finally, it was identified that site characterization, including soil classification in either of the international systems (WRB or Soil Taxonomy), is essential for cross-site comparisons and extrapolations. Since a portion of SOC research is conducted for example by microbiologists or geochemists, the soil science discipline must make sure that such research properly characterizes sites and soils.

Research Priorities in Soil C Properties and Processes

Soil organic matter (SOM) is one of the key components of soil with respect to rhizospheric processes and its functions. It influences adsorption, pH buffering, soil colour and heat absorption, nutrient storage, soil structure and its stability, infiltration properties, water storage and is the most important substrate for living organisms in soil. Current research activities put considerable emphasis on C sequestration and SOM dynamics and less on its functions and provisioning of essential ecosystem services.

An analysis of the contributions to the 2013 IUSS Global Soil Carbon Conference showed that 18 % of the presentations dealt with C sequestration, 16 % with development of methods for SOC analysis and advancing these techniques, 12 % with effects of land use, land management and climate on SOC levels, 11 % with the formation of aggregates, 6 % with interactions of micro-organisms with SOM and 2 to 5 % each with topics such as sesquioxides – SOM interactions, soil gas emissions, black carbon, humic substances, modeling and simulation, spatial distribution of SOM, SOM impact on soil properties and molecular features of SOM. The different topics reflect the societal importance of soils as sink and source of Greenhouse Gases. However, SOM is also an important basis for production of biomass, soil functions such as "biological heritage" and "gene reserve", as well as the denaturing and transformation of pollutants, filtering and buffering functions of soils.

There is a need for developing time effective, accurate and comparable measurements of SOC, specifically for large sample numbers for monitoring and modeling purposes. Increasing the speed of measurements and taking into account spatial variability of SOC content and soil bulk density are important research topics.

The interaction of SOM with mineral surfaces in soil deserves further investigation. The interaction with iron and aluminium and the impact of redox chemistry are crucial for understanding SOM stabilisation. The effect of clay mineralogy on SOC sequestration by the build-up of micro-aggregates is still debated, and in particular if swelling properties of clays are crucial or if local SOC accumulation on the microscopic scale is more related to physical location than to mineralogical properties. The soil aggregate hierarchy theory needs to be validated in calcareous and non-calcareous soils in terms of encapsulation of SOC within stable micro-aggregates and its impacts on mean residence time.

Another topical theme is the contribution of black carbon to SOM and to the recalcitrant SOM fractions. Hydrophobicity is an additional issue in this context. Hydrophobicity of the soil surface is modified by the surface coverage with hydrophobic layers of organic compounds on minerals. The degree of surface hydrophobicity and its impact on adsorption properties still needs to be investigated. Soil management, especially tillage, has a large impact on location of SOC within soil structure. The formation of organo-mineral associations protecting SOC against decomposition can be crucial for modeling of SOC mineralization and turnover. Clay amendments might contribute to SOC stabilization by formation of additional micro-aggregates and improve soil properties.

Biological processes concerning SOC sequestration and turnover need further attention. Research questions include the quantification of the role of roots to recalcitrant SOC, fungal contribution to SOC sequestration and the impact of elevated CO_2 concentrations on residue decomposition. Soil erosion might significantly modify soil respiration which affects local, regional and even global C balances. The fate of SOC transported by erosional processes (water and wind) is a theme that needs to be studied by interdisciplinary teams on watershed scale. Is carbon transported over the landscape by aeolian and hydrological processes a source or sink of GHGs? Under what biophysical and hydrological conditions is eroded SOC sequestered or emitted as CO_2 or CH_4? Identification of site-specific land use and soil management practices that create a positive SOC budget is important for making soils a net sink of atmospheric CO_2.

Some research questions, which seem to be of specific relevance and are presently less investigated include: (i) the nature of non-extractable SOM on reactive surfaces, (ii) the role of macro- versus micro-aggregates in C stabilization, (iii) the quantitative contribution of micro- meso- and macro- fauna on SOC turnover and stabilization, and (iv) the role of soil structure in SOC sequestration and modeling. Formation of secondary carbonates in soils of arid and semiarid regions, and leaching of bicarbonates in irrigated soils are relevant to C sequestration, but have not been widely addressed. Secondary carbonates play a major role in soil C dynamics in Mollisols, Vertisols, and Aridisols. Application of liming materials, cement and C-rich by-products can affect the formation of secondary carbonates. Some research on weathering of silicate minerals (e.g. olivine) is also being done to assess the rate of sequestration of inorganic C.

Understanding SOC/SOM behavior in soils involves the molecular scale (properties of organic molecules and their molecular interaction with soil minerals) as well as the micro-scale (formation of micro-aggregates, physical protection of SOM, interaction of micro-organisms and their impact on surface properties) and all larger scales such as the bench scale and even the landscape scale (including mass transport and its impact on SOM turnover and stabilisation). Combining information across different scales is a great challenge, for example, combining (i) remote sensing data with plot information as a basis for modeling on the landscape level and (ii) molecular information with micro-and macro structural data to elucidate the accessibility of reactive surfaces and to investigate, if spatial arrangements obscure effects of molecular structure and properties. The prediction of changes of SOC quality and quantity over years and decades remains the largest challenge.

Research Priorities in Soil C Use and Management

Many soils of agroecosystems have been depleted of their antecedent SOC pool. The magnitude of depletion depends on climate, soil properties, depth distribution of SOC, and land use and management. Soils used by extractive farming methods have been severely depleted of their SOC pools, and there is a need to replenish SOC to above a critical level. The latter ranges from 1.2 to 2.0 % depending on the soil type, climate and the farming system. Key questions about replenishment of SOC pool include: the critical level in the root zone, use efficiency of inputs (fertilizer, water etc.), gains in agronomic productivity per unit increase in SOC pool in the root zone, and the impact of management on rate of change of SOC pool in the root zone. The impact of no-till farming or conservation agriculture, especially with

Table 48.1 Some research priorities for soil C research

Main research area	Topics
Soil C in space and time	Monitoring and assessment of C stocks and fluxes
	Standardizing sampling and analytical methods
	Further development of proximal soil sensors for C analysis
	Assessment of SOC at depths below the topsoil
	Contribution of soil inorganic C to C sequestration potential
	Upscaling from pedon and field measurements to regional, national and continental scales
	Increased reporting of uncertainties in measurement, monitoring and modeling of SOC
	Establish list of priority areas that need research: areas of rapid land use change, areas with large C stocks and a rapidly changing climate, areas for which there exists only sparse data or high uncertainties, and ecologically-sensitive ecoregions and global hot spots
Soil C properties and processes	Development of time effective, accurate SOC measurement apparatus such as inelastic neutron scattering and laser induced breakdown spectroscopy
	Increased understanding needed about C interaction with Al and Fe and the impact of redox chemistry
	Interaction between SOC and mineral surfaces and formation of stable microaggregates leading to encapsulation of SOC
	Mean residence time of SOC in relation to light and heavy fractions, aggregation, association with textural separates and depth distribution
	Contribution of black carbon to recalcitrant fractions
	Hydrophobicity and SOC
	Clay additions to sandy soils and SOC
	The nature of non-extractable SOM on reactive surfaces
	Role of macro- versus micro-aggregates in C stabilization
	Quantitative contribution of micro- meso- and macro- fauna on SOC turnover, and the role of microbial biomass C
	Role of soil structure in SOC sequestration and modeling
	The role of fungi in C sequestration
Soil C use and management	Sequestration of SOC in deltas and oceans
	The fate of C transported by erosion
	The effects of fire on SOC in relation to hydrophobicity and black carbon
	Identification of site-specific land use and management practices which create a positive soil C budget
	Threshold level of SOC in the root zone in relation to rhizospheric processes, soil functions and ecosystem services
	Relation between SOC accretion in the root zone and agronomic yield
	Climate resilience of soils of agroecosystems and SOC pool in relation to drought
	Water retention and transmission characteristics in relation to SOC pool
	The mean residence time in the context of land use and management
	Modus operandi of C farming and trading of soil C credits

regards to depth distribution of SOC pool and impact of residue management and its placement in the soil, are important researchable themes which need to be researched under site-specific conditions. There are many technologies that can be used to enhance SOC pool (no-till, mulch, cover crop, agroforestry, deep rooted species) and the choice of specific techniques depend on biophysical, social and economic factors. Whereas use of no–till farming is useful in soils prone to erosion, there are constraints to its adoption especially by the resource-poor and small land holders in developing countries. Competing uses of crop residues (e.g., feed, fodder, fencing and construction material, cooking fuel) are also among major considerations.

Conclusions

In the previous sections, we have highlighted and discussed the main priorities in SOC research. Below is a summary table of the main research priorities as identified in the various chapters in this book and during the 2013 IUSS Global Soil C Conference.

In addition to the ambitious but much needed research on soil C listed in Table 48.1, there is a need to incorporate more detailed soil information in climate models. This is currently lacking in part as data on soil information is not readily available or compatible with model needs, and in part because the climate modeling community is not well-linked to the soil science community. This has improved in recent years but there remains scope for increased interaction and cooperation. There may also be scope for linkages to other disciplines and the microbial scientific community is such an example. Microbes do most of the work in C models and their activity is largely influenced by soil conditions.

The soil science community should take full ownership of the role of soil C in the global issues that confront humanity. Besides the list of possible research areas we need to build stronger models for global C, reach consensus and agree on processes and structures. The risk of creating confusion by diverse and unconnected groups of scientists may affect our impact on policy and decision making. The International Union of Soil Sciences (IUSS) should act as a catalyst in soil C research and a bridge to the broader scientific community and policy makers.

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Subject Index

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