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The Effect of Land Use on Soil Carbon Storage Down the Soil Profile

By

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Thesis Submitted for the Doctor of Philosophy in Soil Science

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Dedication

This thesis is dedicated to Alloh SWT, Abah Aos SM and my lovely family.

Declaration of Original Authorship

I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

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Abstract

Soil organic carbon (SOC), although a small component of the soil, is fundamental to delivering the physical, biological, and chemical functions that underpin soil ecosystem goods and services. The loss of SOC causes considerable negative impacts on the global environment. However, our knowledge of SOC is primarily drawn from studies that focus on the topsoil layer (0-30cm) while the majority of SOC stocks are stored in the subsoil layer. The mechanisms responsible for subsoil SOC preservation are far less well understood. This study generally aimed to quantify, compare, and mechanistically explain carbon storage in the top 1 metre of soil under different land uses.

To examine the preservation mechanisms responsible for SOC storage under different land uses down the soil profile in the UK, soil sampling was carried out up to 1 m depth under the three UK dominant land uses (woodland, grassland and arable). The samples were analysed to quantify key soil properties (SOC, pH, C/N ratio, and texture) at 10 cm increments and SOC physical fractionation and ammonium oxalate extractable Al, Fe, and Mn was determined on selected soil layers, representing topsoil and subsoil, to investigate the mechanisms of SOC preservation down the soil profile. The results indicated that woodland soils contain greater SOC, N, and a higher C/N ratio than grassland and arable, while all these properties decreased down the soil profile. SOM fractionation revealed that the mineral-free particulate organic matter (fPOM) fraction was significantly greater in both the topsoil and subsoil under woodland than under grassland or arable. The mineral associated organic carbon (MinOC) fraction was proportionally higher in the subsoil than topsoil under all land uses, indicating that SOM protection in subsoils is primarily regulated by soil organo-mineral interactions, mainly amorphous Fe and Mn concentrations.

Fourier-transform infrared (FTIR) spectroscopy and δ^{13}C analysis of the fPOM fraction of topsoils and subsoils sampled down the soil profile under woodland, grassland, and arable land uses were used to determine the chemical recalcitrance and degree of microbial decomposition of fPOM and attribute this to the isotopic composition and presence of functional groups. The results showed a clear influence of land use on fPOM characteristics where soils under more natural vegetation had higher fPOM, SOC, and N concentrations, more oxygenated functional groups (e.g. carbohydrates and carboxylic acids), and were depleted in ^{13}C due to the absence of C4 crops. Subsoil fPOM was chemically different to the surface layers due to being more microbially decomposed.

The effect of forest conversion to cinnamon plantation on an Indonesian Andosol was investigated by collecting and analysing samples collected down the top 1 m of the soil profile from three different prominent cinnamon producing locations (Lempur, Pungut, Renah Kayu Embun (RKE)) in Kerinci Regency, Sumatera, Indonesia. Soil samples were collected under natural forest vegetation and at 1, 5, and 10 years after clearance of the forest and establishment of a cinnamon plantation. The results revealed that, despite short term increases in SOC stocks due to pyrogenic inputs resulting from slash and burn, SOC stocks were ultimately lower 10 years after forest conversion, reflecting decreases in both topsoil and subsoil layers. FTIR spectroscopy revealed an increase in the degree of decomposition of fPOM down the soil profile 10 years after forest conversion to cinnamon plantation, probably due to less fresh litter input and greater microbial activity.

The findings of this study are that SOC quality and quantity are altered when natural vegetation is converted to an agricultural land use, largely influenced by the lower contribution of plant litter input due as source OM. Natural vegetation have greater OM inputs, with a higher proportion of carbohydrate compounds, than converted land and there is tendency that the SOC quantity decrease as the converted land gets older. Moreover, this study confirmed that mechanisms of SOC protection differ with depth; topsoil is dominated by free particulate organic matter (fPOM) and subsoil dominated by SOM bound to mineral surfaces (amorphous Al, Fe and Mn). Topsoil is provided with direct fresh litter and experienced faster decomposition process while subsoil was dominated by less microbially processed OM. All these observations indicate that SOC, and related physical chemical properties, are clearly influenced by land use and soil depth which is important knowledge to advance SOC preservation.

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Table of Contents

Chapter I - Introduction

1.1 Soils and the global carbon cycle

Human induced increases in atmospheric CO_2 concentrations are of growing concern globally due to their impact on the climate with rising atmospheric concentration of carbon dioxide (IPCC, 2019). Globally, atmospheric CO_2 levels which were 316 ppm in 1958 have continually climbed at 3 ppm per annum increasing to a higher peak of 413 ppm in October 2020 then 409 ppm in October 2019 (NOAA, 2021). Cultivation and management of agricultural soils globally, and the associated liberation of carbon as CO_2, have been cited as significant factors contributing to this atmospheric CO_2 increase (IPCC, 2014; Lal, 2004b).

Globally soils have been estimated to contain approximately 1500 Gt of organic carbon to 1 m depth and represent the largest terrestrial organic carbon pool (Batjes, 1996; Jobbágy and Jackson, 2000). Soil stores some 2-3 times more carbon than in the atmosphere (590 Pg C) and terrestrial vegetation (350-550 Pg C) (Ciais et al., 2013). Soils worldwide have been, and continue to be, intensively exploited, resulting in significant depletion of soil organic matter (SOM). Since the industrial revolution around 1750, global carbon emissions due to land use change and soil cultivation are estimated at 136 ± 55 Pg C (Lal, 2004a). Depletion of soil organic carbon (SOC) due to land use change from natural vegetation to agricultural systems can decrease SOC by 60 to 75 % in temperate and tropical regions, respectively (Lal, 2004b). SOC is known to play a key role in regulating a range of soil physical, chemical, and biological processes, and is a key indicator of soil health and quality (Franzluebbers, 2002).

It is widely acknowledged that soils that are degraded, or carbon depleted, offer the potential to store significant additional carbon with judicious land management practices. There is, therefore, a considerable potential for carbon depleted soils worldwide to store large quantities of extra carbon (Lal, 2005; Whitmore et al., 2015). Knowledge of the carbon storage potential of land-use systems offers the possibility to manage land for enhanced soil carbon storage, improved soil quality, and increased productivity (Lal, 2004b). In addition, knowledge of SOC change resulting from land use or land management changes offers the potential for landowners to access an additional income stream through emerging carbon markets (Perez et al., 2007).

Considerable research has been undertaken internationally relating to soil carbon storage and management (Abson et al., 2014; Bell et al., 2011; Glenk and Colombo, 2011; Gregory et al., 2016). Soil analysis has typically focused on the 0-30 cm soil layers (Bell et al., 2011), but it is now known that as much as 50% of soil carbon can be stored below 30 cm (Rumpel and Kögel-Knabner, 2011). Analysis of carbon stored deeper in soils and an understanding of the mechanisms by which it is protected from decomposition is a key knowledge gap. There is also a need to examine factors affecting soil carbon storage at depth under specific land uses to assess their capacity for soil C sequestration because land use significantly influences soil carbon stocks (Ostle et al., 2009), even though soil carbon is also unevenly spatially distributed naturally because of differences in soil formation factors (climate, geology, organism, topography and time) (Jenny, 1941).

1.2 Land use change in the UK and Indonesia

The area of woodland in the UK is 3.16 million hectares, ~13 % of the land area (Sing et al., 2018). This number has increased compared to 2005 (2.8 million ha) (Rounsevell and Reay, 2009). UK land use is dominated by agriculture, which consists of about 75 % of the total land area of the UK (24 million ha), where 37 % is used for grassland, 30% is rough grazing and the rest ‘crops and bare fallow’ (Rath and Peel, 2005; Rounsevell and Reay, 2009). Grasslands can be broadly grouped into temporary (1.2 million ha), permanent (6.1 million ha) and rough-grazing (5.0 million ha) types (Qi et al., 2017). There is an expectation that forest area in the UK will increase in the future because of declines in agricultural area and the reforestation strategies embedded in rural development policy (Rounsevell and Reay, 2009).

Meanwhile, significant deforestation already started in Indonesia more than a century ago to extract timber and to grow rubber, but during the last few decades, mainly due to the rapid increase in the global demand for vegetable oil, the area planted with oil palm has continued to grow (Bou et al., 2018). In Jambi Province, Sumatera, Indonesia, since the mid-1990s, a significant area of highland forest has been turned into Cinnamon plantation

(Wibowo, 1999). Deforestation remains the main problem in Indonesia, where recent data count more than 800 hectares forest cleared every year for agricultural use and urban expansion (Tölle, 2020).

1.3 General Aim and objectives

This thesis aims to quantify, compare, and mechanistically explain carbon storage in the top 1 m of soil under different land uses. In this study, woodland, grassland, and arable sites were sampled in the UK (chapter 3 and 4), and three chronosequences from natural forest to established cinnamon plantations were sampled in Indonesia (chapter 5).

The objectives of this thesis are:

a. To characterise soil carbon under a range of current land uses in the UK and Indonesia down the soil profile to 1 m and identify preservation mechanisms.
b. To investigate changes in the chemical recalcitrance and degree of decomposition of the free Particulate Organic Matter (fPOM) fraction of SOC down the soil profile under different land uses.
c. To investigate the impact of land use conversion from natural forest vegetation to cinnamon plantation on soil carbon stocks in the top 1 m of the soil profile.

1.4 Outline of the thesis

Chapter 2 explores relevant supporting literature to establish a theoretical framework for the study of subsoil organic carbon under different land uses and introduces recent methodologies and approaches related to this research.

Chapter 3 presents results of soil organic carbon (SOC) concentration and other soil properties to 1 m depth under three significant UK land uses (arable, grassland and woodland). SOM physical fractionation was then conducted from selected layers of topsoil (0-10 cm and 20-30 cm) and subsoil (50-60 cm and 90-100 cm). An ammonium oxalate extraction was also undertaken to quantify the availability of amorphous Al, Fe and Mn oxides in soil minerals and attribute subsoil carbon storage to chemical sorption mechanisms. This chapter's results provided a better understanding of the dynamics of subsoil organic carbon and its stabilisation mechanisms.

Chapter 4 reports the results of FTIR and ^{13}C analysis of the fPOM fraction of selected soil samples from the topsoil (0-10 cm and 20-30 cm) and subsoil (50-60 cm and 90-100 cm) layers described in Chapter 3 to investigate the recalcitrance and the degree of decomposition of fPOM down the soil profile under different land uses.

Chapter 5 shows the result of a forest conversion into cinnamon plantation in Kerinci Regency, Sumatera, Indonesia. SOC stocks were quantified down to 1 m depth under natural forest vegetation and different cinnamon plantation ages (1, 5 and 10 years after conversion). As in Chapter 4, the recalcitrance, and the degree of decomposition of fPOM from selected topsoil (0-10 cm and 20-30 cm) and subsoil (50-60 cm and 90-100 cm) layers were investigated to understand how land use change influences SOC dynamics.

Chapter 6 discusses the key findings of the research undertaken in the thesis in the context of recent literature and makes general conclusions.

1.5 Specific hypothesis addressed in each individual chapter.

Chapter 3: SOC concentration in topsoil is dominated by free particulate OM fractions while subsoil is higher in mineral associated OM related to the influence of mineral sorption as a preservation mechanism.

Chapter 4: The free particulate organic matter (fPOM) in subsoil is more decomposed and more chemically recalcitrant than the topsoil fPOM fraction.

Chapter 5: Soil organic carbon stocks deplete after forest conversion and this continues as the cinnamon plantation get older while the fPOM fraction under forest has a higher degree of decomposition than all ages of cinnamon plantation.

Chapter II-Literature Review

2.1 The soil carbon cycle

Soil organic carbon plays an important role in the soil system and its decline has been a contributing factor to increasing atmospheric CO_2 concenrations. Soil organic carbon is the second largest net source of carbon release to atmosphere after fossil fuel burning (Ciais et al., 2013). The cumulative historic C loss from land use change between 1750 and 2015 has been estimated at 190 ± 65 Pg C (soil+vegetation) compared with 410 ± 20 Pg C that from fossil fuel combustion (Le Quéré et al., 2016). The main pools of actively cycling carbon are the (i) atmosphere, (ii) biota (mostly vegetation), (iii) soil, and (iv) ocean (Janzen, 2004; Lal, 2004a). All these pools are inter-connected and carbon circulates between them (Lal, 2018) (Figure 1).

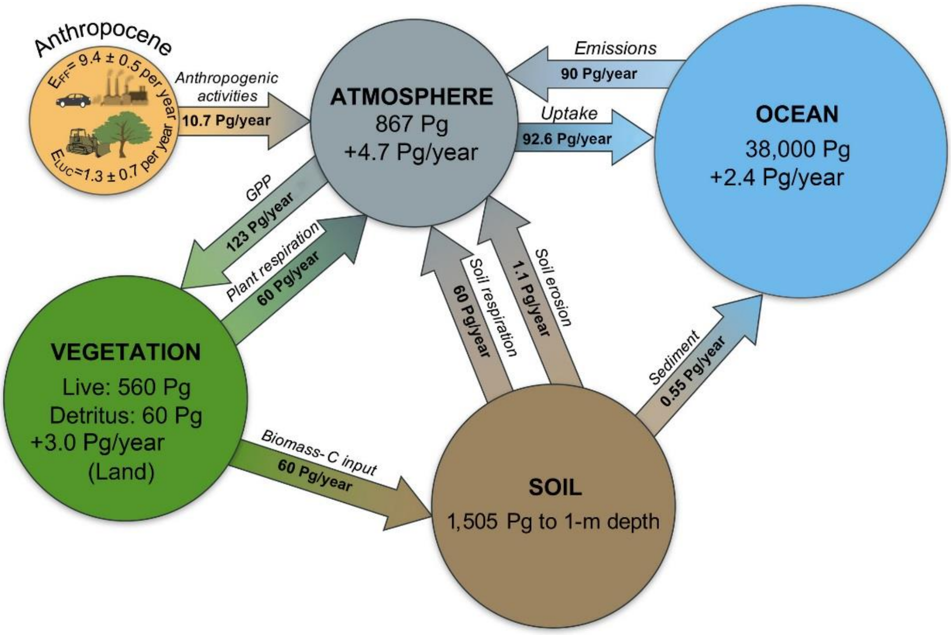


Figure 1. A conceptual diagram of the contemporary global soil carbon cycle identifying the main pools and fluxes. Data within arrows indicate fluxes (Pg C/year), those within circles indicate the magnitude of stock, and the data in circles with + sign indicate the annual rate of change of the stock. Within the circle-labelled Anthropocene, EFF is emissions by fossil fuel and ELUC is the emissions by land use conversion. Atmospheric stock is computed on the basis of 406.29 ppmv of CO_2 on 26 November 2017 (0.040629% by volume) and 0.06122% by mass of atmosphere is 5.148 x 1021 g, containing 3,177 Pg CO_2 or 867 Pg C (Lal, 2017).

Soil organic carbon (SOC), which is generally part of complex compounds in soil organic matter (SOM), plays important roles in soils regulating (i) soil water-holding capacity, (ii) soil structure, (iii) nutrient supply, and (iv) microbial activity (McLauchlan, 2006; Trumbore, 1997). Thus, changes in SOM will have important impacts, particularly on plant productivity (Lal, 2005; Trumbore, 1997).

2.2 How does carbon enter soils?

2.2.1 Photosynthesis

Photosynthesis is the main way in which carbon enters soil. It takes carbon directly from the atmosphere in the form of CO_2 and, together with solar radiation and water, generates organic products (such as glucose) and oxygen (Horwath, 2015). Photosynthesis converts approximately 110 Pg of CO_2-C into organic compounds annually (Houghton, 2007). The overall biochemistry of photosynthesis for the formation of one glucose molecule from six CO_2 molecules may be written as:

$$\mathbf{6\ CO_2 + 2H_2O + 18\ ATP + 12\ NADPH \rightarrow C_6H_{12}O_6 + 18\ ADP + 18\ P_i + 12\ NADP^+ + 12\ H^+ + 6\ O_2\uparrow}$$

Photosynthesis can happen in green plants, algae, cyanobacteria and photosynthetic bacteria where the sunlight is converted into chemical energy (Horwath, 2015; Ke, 2000). The global rate of C fixation through photosynthesis is 120 Pg C/yr (Schlesinger, 1995). Therefore, photosynthesis is the ultimate source of organic matter in soils by plants producing leaf litter, roots, and root exudates (Trumbore, 1997).

2.2.1.1 Photoautotrophic soil microorganisms

Although carbon predominantly enters the soil profile through photosynthesis reaction by plants, autotrophic soil bacteria also provide a small contribution to soil carbon input (Tate, 1987). Moreover, a laboratory experiment conducted by Schmidt, Dyckmans, & Schrader (2016) showed that carbon fixed by photoautotrophic soil microorganisms (Cyanobacteria; coccal cells; Bacillariophyta; Chlorophyta; Euglenophyta) contributed up to 3.0 and 17.0% of the carbon found in endogenic earthworms (*Allolobophora chlorotica*) and hemiedaphic springtails (*Ceratophysella denticulate*), respectively.

2.2.2 Root Exudates

Root exudates are secreted by active roots during plant growth, and they have multiple effects in the plant-soil system (Gregory, 2006a). Root exudation enhances the soil C pool in the rhizosphere and is used as an energy source for microbial activity (Shahzad et al., 2015). However, it also represents a loss of C by the plant (Nguyen, 2003).

Root exudates are a complex mixture, including inorganic ions H^+, OH^-, HCO_3^-, organic anions (e.g. citrate, malate and oxalate) and as well as organic compounds, such as sugars and polysaccharides, acids (amino acids, organic acids and fatty acids), sterols, growth factors, enzymes,and flavonoids (Gregory, 2006b).

Root exudates play important rule in plant growth, especially in rhizosphere. For example, on average, 17% of C taken from all plant photosynthesis is released through root activity (including root exudates) (Nguyen, 2003). Another study demonstrated that nearly 5% to 21% of all photosynthetically fixed carbon is transferred to the rhizosphere through root exudates (Walker et al., 2003). In the case of rice and maize, a study conducted by He et al. (2015) shows that root exudates are rapidly mineralized in soil by microbial activity. Rates of SOM decomposition may increase dramatically (up to 5-fold) in response to root exudates (Stockmann et al., 2013).

2.2.3 Shoot and Root Litter

Plant residues can be from both aboveground biomass (e.g. shoots) and belowground biomass (e.g. roots) (Kögel-Knabner, 2002). Residues of various crops (e.g. maize, sorghum, wheat) are considered a by-product without much value and an impediment (e.g. as a host of plant pathogens) to future production (Bailey and Lazarovits, 2003; Franzluebbers, 2004).

Crop residue quantity and quality (in terms of lignin, hemi-cellulose, and cellulose composition) could vary for each plant, but these are determining characteristics of the response of litter decomposition (Ghidey and Alberts, 1993; Redin et al., 2014). Crop residues, particularly from legume crops, with a low C/N ratio (i.e. below 24:1) can result in net N mineralization, whereas cereal residues with a high C/N ratio (i.e. above 24:1) can temporarily immobilize N during the decomposition process (Turmel et al., 2014).

Therefore, returning crop residues back into the soil benefits soil quality (Aggarwal et al., 1997).

Historically, residue from the plant root system has attracted less attention than the aboveground residues, probably because the plant root system, as sub-surface residue, is often difficult to quantify. However, it can be used to sequester carbon and redistribute it through the soil profile (Reicosky, 1994). A study of winter crops has showed that root residues decompose faster than shoots (Tahir et al., 2016), and are thus an important part of the soil food web in arable soils (Scheunemann et al., 2015). However, another study found that, in forest soil, root litter was more recalcitrant than leaf litter which was responsible for its slower mass loss rate and N release during root decomposition (Fujii and Takeda, 2010). Freschet et al. (2013) also found that root litter had slower decay rate compared to leaves and that roots it contribute more than 30% of annual litter input in grasslands and almost 50% in forest soils.

2.2.4 Organic Fertilizer and Manure

One of the strategies to improve SOM is the use of various types of organic amendments, with the purpose of increasing C and nutrient inputs into soils (Magdoff and Weil, 2004). Amending soil with composted organic waste is often an effective means of increasing SOC and nutrients (Seiter and Horwarth, 2004) and improving soil quality.

Application of animal manures is often presumed to result in higher increases in SOM than compost because it consists of relatively recalcitrant compounds, the most easily oxidized compounds in the original plant tissue having already been broken down by the animal’s digestive system before excretion of the manure (Magdoff and Weil, 2004; Seiter and Horwarth, 2004). However, recent revelations have challenged this view of SOM formation (Lehmann and Kleber, 2015).

Organic mulches made from plant material are decomposed and become a part of the soil. This decomposition adds organic matter to soil and helps to improve the water and nutrient retention capacity of the soil and promotes the growth of healthier plants (Pramanik et al., 2015).

2.2.5 Cover crops

Cover crops are beneficially used in agricultural systems to retain nutrients, increase SOM, and protect soil from erosion (Lal, 2004a). Green manures are a promising way to sequester more carbon in agricultural soil that neither reduces crop yield nor results in carbon losses like other organic manure applications (Poeplau and Don, 2015). Adopting conservation tillage for SOC sequestration is greatly enhanced by growing cover crops in the rotation cycle and then incorporating them as green manure, before planting the cash crop (Lal, 2004a; Lu et al., 2000). Ensinas et al. (2016) found that, under a no till system, the particulate organic carbon and labile carbon fractions were the SOM fractions that increased within the top 20 cm depth of soil due to the cover crops. A review carried out by Poeplau and Don (2015) stated that the cover crop adoption significantly increased SOC stocks compared to the reference croplands with an estimated potential global SOC sequestration of 0.12±0.03 Pg C yr^{-1}.

2.3 How does carbon leave soils?

2.3.1 Respiration

Soil respiration is the process by which carbon is released from the soil. About half of photosynthesized C is lost back into the atmosphere due to respiration by photoautotrophs and heterotrophs (Horwath, 2015). Soil respiratory flux involves the respiration activity of various living organisms in soil such as plant roots, mycorrhizae, and other soil organisms (Boddy et al., 2007; Pregitzer, 2003). The global rate of soil respiration is predicted at approximately 75 Pg C/yr (Schlesinger and Andrews, 2000).

According to Chapin et al (2006), the sum of respiration (CO_2 production) by all living parts of primary producers per unit ground or water area and time is called autotrophic respiration and the respiration of heterotrophic organisms (animals and microbes), summed per unit ground or water area and time, is defined as heterotrophic respiration. Ecosystem respiration is the respiration of all organisms summed per unit ground or water area and time.

Rates of soil respiration depend upon: (i) temperature, (ii) moisture, (iii) nitrogen availability, (iv) amount and availability of organic substrates, (v) root biomass, and (vi) biomass of mycorrhizae, which, together, control the specific rate of respiration per unit time (Pregitzer, 2003). Greater soil temperature will exacerbate the rate of SOM mineralization, leading to a decrease in the SOC pool (Kirschbaum, 1995; Lal, 2004a). A decrease in soil water content affects the diffusion of nutrients in the soil pore space and retards microorganism activity (Yuste et al., 2007). Nitrogen availability, commonly stated as C/N ratio, is an important indicator in C mineralisation (e.g. as energy for microbial growth and proliferation). Hence, N availability often becomes the limiting factor in C mineralisation because the C/N ratio of the decomposing substrate normally narrows progressively with C mineralisation (Wang et al., 2004).

2.3.2 Soil Erosion and Sedimentation

Soil erosion is a process which leads to a loss of organic matter from soils through increased decomposition rates and export of organic matter from field (Doetterl et al., 2016) and erosion-induced soil degradation can impact the global C cycle (Lal, 2017). Olson et al. (2012) reported that soil erosion and transport of C-rich sediments causes release of SOC to streams and to the atmosphere. Soil erosion by water and wind causes a preferential removal of SOC, preferentially removing the light organic fraction with a low density of < 1.8 Mg/m^3 that is concentrated in vicinity of the soil surface (Lal, 2003). The kinetic energy of the agents of erosion (i.e., raindrop, flowing water, blowing wind, gravity) can disrupt aggregates and expose the physically protected (encapsulated) SOC to microbial processes (Lal, 2017). Lal (2003) estimated global C emission by water erosion at 1.1 Pg C yr^{-1}.

2.3.3 Harvest

Removal of biomass through harvesting reduces C input to the soil (McLauchlan, 2006). Harvesting activity also has an impact on plant photosynthesis rate. This activity causes a further decrease of carbon input to soil. Clear cut harvesting in Canadian forests, changes former forest net CO_2 sinks into net sources due to significantly reduced CO_2 uptake through photosynthesis (Paul-Limoges et al., 2015). In arable land, tuber crop harvesting is usually followed by soil loss through erosion that leads to soil nutrients loss, including soil organic carbon (Yu et al., 2016). Carbon loss due to leaching or erosion may be important when considering C balance in soils on long time scales (Trumbore, 1997).

2.4 Differences in the soil carbon cycle under different land uses

2.4.1 Arable

According to FAO (2011), arable land is defined as the part of agricultural land that is temporarily used for agricultural crops, meadows for mowing or pasture, market or kitchen garden and fallow land. Although, in United Kingdom, meadow and pasture are considered to be classified separately as grasslands (Green, 1990).

Sources of organic carbon from arable land could be mainly from (i) crop residues, (ii) organic manures, (iii) root exudates, and (iv) cover crops. Due to the adoption of recommended management practices (e.g., mulch farming, reduced tillage, integrated nutrient management, integrated pest management, and precision farming) SOC can accumulate in soils because tillage-induced soil disturbances are eliminated, erosion losses are minimized, and large quantities of root and above-ground biomass are returned to the soil (Lal, 2004a).

2.4.2 Grassland

Grasslands can be defined as an area dominantly covered by grass with little or even no tree cover (Reynolds, 2005). In more detail, UNESCO defines grassland as “land covered with herbaceous plants with less than 10 percent tree and shrub cover” and wooded grassland as 10-40 percent tree and shrub cover (White, 1983). In the United Kingdom, grasslands are mainly categorized into temporary (1.2 million ha), permanent (6.1 million ha) and rough-grazing (5.0 million ha) types, and they occupy over two thirds of agricultural land area (Qi et al., 2018).

The main sources of OM input into grassland soils are: (i) senescent plant leaves which are not consumed by animals; (ii) plant leaves which escape harvesting; (iii) plant roots and root exudates; (iv) dung and urine of grazing animals; and (v) black carbon in fire affected grasslands (Rumpel, 2011).

In grassland soils a significant carbon source comes from the turnover of root mass and root exudates in the rhizosphere. A study conducted by Boddy et al (2007) in temperate grasslands has shown that root exudate-derived sugars and amino acids, are cycled extremely rapidly by the soil microbial community. This is also the way that the plant stimulates mineralization of the soil organic matter to improve their own nutrient supply (Shahzad et al., 2015).

2.4.2.1 Grazing and manure production

Almost all areas of uncultivated grasslands, globally, are grazed by large mammals (Mcsherry and Ritchie, 2013), while grasslands in the UK also provide forage by cutting grassland for silage or hay (Qi et al., 2017). One of main benefits of grazing is deposition of animal dung and urine through excretion, returning carbon and nutrients back to soil (Rumpel, 2011). For instance, grazing intensity of 700 cow days/ha/year will result an approximately of 6.4% of the grazed area covered by dung patches, which equivalent to ~22.5 t C/ha (Bol et al., 2000). Dung is an important source of labile C as additional substrate for microbial growth and metabolism which may increase soil microbial biomass (Bardgett et al., 1998; Lovell and Jarvis, 1996). Although, It is only deposited in the upper layers of the soil profile (1-5 cm depth) and contributes about 10% of C in grassland ecosystems (Bol et al., 2000), it also can be transported further down the soil profile; i.e. in the form of dissolved organic carbon (Kaiser and Kalbitz, 2012).

2.4.3 Woodland

In woodland or forest systems, there are three main process of organic matter input to the forest soil; through root exudates and root death, forest litter and also deadwood (Pan et al., 2011; Tate, 1987). Soil organic matter inputs to the forest ecosystem happens both continuously and episodically, resulting in an estimated average annual change in the C stock of established forests of 2.41 ± 0.42 Pg C year^{-1} for 1990 to 2007 (Pan et al., 2011). The continuous addition of organic material maintains an endemic decomposer population, but these populations fluctuate rather widely with the episodic addition of large amounts of organic material that occur in most forest soil (Fisher, 1995).

Furthermore, the consequences of increasing in atmospheric CO_2 and global temperatures may also affect soil carbon inputs in woodland soils due to altered photosynthetic rates (Ontl and Schulte, 2012). A field study by Drake et al. (1997) showed that plants growing in elevated CO_2 concentrations fix more carbon through photosynthesis, producing greater biomass, particularly in wood and roots.

Fresh litter from forest plants, mostly originating from leaf litter fall and deadwood (Tate, 1987), contributes large quantities of OM that is decomposed and serves as source of carbon for microflora and fauna (Fisher and Binkley, 2000). The forest floor influences soil properties and changes the microenvironment, leading to alterations in litter decomposition rates and C cycling process (Wang et al., 2021).

2.5 What controls carbon storage in soils?

2.5.1 The nature of soil organic carbon

The soil C pool comprises two components: soil inorganic carbon (SIC) and the soil organic carbon (SOC) pool (Archer, 2010). According to Schumacher (2002), inorganic carbon forms are derived from geologic or soil parent material sources, such as carbonates (e.g.,CaCO3 and $[CaMg(CO_3)_2]$) and organic carbon forms are derived from the decomposition of plants and animals which is commonly known as organic matter.

Plant input plays a main role in SOM decomposition and SOM formation. Soil OM consists of partially decayed plant residues, soil microorganisms, soil fauna, and the microbial products of decomposition (Cotrufo et al., 2013; Horwath, 2015). Lützow et al. (2006) differentiate between the primary recalcitrance of plant litter and rhizodeposits as a function of their indigenous molecular characteristics, and the secondary recalcitrance of microbial products, recalcitrance of humic polymers, and recalcitrance due to production of charred materials.

The recalcitrance of organic matter (OM) has been long accepted as the important factor mediating OM stabilization in the soil (Dungait et al., 2012; Kleber, 2010; Marschner et al., 2008). In general, slow decomposition is observed for plant tissues with higher lignin, polyphenol and wax contents, higher lignin : N and C : N ratios (Kleber, 2010), and more aromatic compounds (Lorenz et al., 2007; Marschner et al., 2008). SOM stabilization was also considered to be enhanced through polymerisation via abiotic or biotic syntheses of original monomers into more complex polymeric molecules (Lorenz et al., 2007). However, contemporary developments have indicated that the chemcial recalcitrance of large molecules, distinct from stabilisation processes like physical protection and chemical sorption in the soil, does not play a major role in SOM.

The traditional view of SOM is that it consists of a complex mixture of (partially) decomposed substances (i.e. organic molecules such as polysaccharides, lignin, aliphatic biopolymers, tannins, lipids, proteins and amino sugars) derived from plant litter as well as faunal and microbial biomass (Janzen, 2006; Stockmann et al., 2013). However, SOM can also be divided according to biological stability (labile, stabile, refractory and inert), decomposition rate (fast-active, slow-intermediate and very slow/passive/inert) and turnover time (short, long, very long) (Stockmann et al., 2013) (Table 1).

Table 1. Forms of soil organic C (Stockmann et al., 2013)

Forms	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 (POM)	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
'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

2.5.2 Physical protection

Soils can protect organic matter from natural decay by forming soil aggregates, particularly microaggregates. Aggregates physically protect SOM by (i) forming physical barriers between microbes, enzymes and substrates; (ii) controlling food web interactions and consequently microbial turnover; and (iii) restricting oxygen diffusion (Plaza et al., 2012; Six et al., 2002, 2000).

SOM protected by physical mechanisms due to aggregate formation can be divided into unprotected C pool (located between aggregates), weakly protected C (occluded within macroaggregates) and strongly protected C (occluded within microaggregates) (Plaza et al., 2012).

Moreover, Baldock & Skjemstad (2000) reviewed the association of SOM with different soil pore sizes (ranging in size from micropores <0.1 mm in diameter through to macro pores >20 mm with an upper size limit on the order of centimetre) and highlighted that pore size distribution plays important role as a site of SOM stabilization. The total amount of pore space and the pore size distribution of the soil matrix controls the availability of water and oxygen and affects the SOM accessibility by decomposer organisms. These soil architectural properties exert a control over decomposition and mineralisation.

2.5.3 Chemical protection

The protection of SOM chemically due to sorption on clay particles and cations in soil such as Ca (as Ca-containing minerals or exchangeable cation), Al or Fe (as amorphous Al and Fe minerals) leads to accumulations of organic C (Krull et al., 2001). Soil minerals (e.g. Al and Fe minerals) are a key regulator in protecting C by forming short range order (SRO) mineral phases which act as ‘nuclei’ for C retention (Yu et al., 2017) due to their high reactive surface areas and capacity for soil C stabilization through sorption or co-precipitation (Coward et al., 2017). Leaching of DOC from subsoils is controlled by retention in B horizons, particularly bound to iron and aluminium (hydr)oxides (Kindler et al., 2011), which are considered to be the most important sorbents for dissolved organic matter in soils (Kaiser et al., 1996).

In soil texture fractions, clay and silt particles play a more important role in protecting C than coarse particles. This is because clay and silt particles have a larger specific surface area to which OM may be adsorbed than other larger soil particles (i.e. sand), but this process depends on pH (Baldock and Skjemstad, 2000). Thus, the capacity of soil to preserve C can be broadly estimated from the percentage of clay and silt content (Hassink, 1997; Hassink et al., 1997).

2.6 Soil organic carbon at depth

2.6.1 How much carbon is stored in the subsoil, compared to the topsoil?

Topsoil (0-30 cm) has been preferentially studied for a long time in soil carbon research because it contains the highest concentration of soil organic matter (Minasny et al., 2017). However, it has been revealed that subsoil (> 30 cm) also stores a significant amount of SOC; more than 50% of the SOC in an average soil profile (Batjes, 1996; Jobbágy and Jackson, 2000).

Using global soil profile data, Batjes (1996) estimated the global SOC content in the upper 30 cm is 684 – 724 Pg C and in the upper 100 cm is 1462 – 1548 Pg C. Another recent estimation stated that SOC in the first meter depth globally is 1502 Pg C (Jobbágy and Jackson, 2000). Furthermore, quantifying the vertical distribution of SOC in the whole soil profile revealed that about 41 – 46 % of the proportion of SOC in the first metre is stored in the topsoil and more than half is located in subsoil (Batjes, 1996; Jobbágy and Jackson, 2000).

SOC density at 20 cm depth (relative to 1 m depth) is also affected by land use type. On a global scale, as reported by Jobbágy & Jackson (2000), in the order from largest to smallest proportion of SOC stored in the topsoil is forests (50%), grasslands (42%), croplands (41%) and shrublands (33%). This report is similar to the study by Wang et al. (2004) that reveals forests (54%) have the highest proportion of SOC stored in the topsoil, followed by shrublands (46%), grasslands (39%), and croplands (37%).

2.6.2 Primary inputs of carbon to the subsoil and the topsoil

The heavy fraction of SOC is the dominant fraction located in the subsoil, naturally bound on mineral and clay surfaces, which may resulted from dissolved organic carbon (DOC) percolation of soil solution (Schrumpf et al., 2013) and microbial products in subsoil horizons (Schmidt et al., 2011).

Root litter input is main source of carbon in deeper soil (Rasse et al., 2005), which is possibly more recalcitrant, chemically, than topsoil litter due to higher amounts of chemically recalcitrant compounds (e.g. lignin, tannin, suberin) (Lorenz and Lal, 2005).

Rumpel et al. (2002) also reported that the carbon stored in forest deep soil layers mainly originates from root contributions (alkyl carbon) and soil forming process (carboxylic carbon as result of carbon leaching).

2.6.3 Are the mechanisms whereby subsoil carbon becomes/remains stable different to the mechanisms whereby topsoil carbon becomes/remains stable?

Both physical and chemical protection of SOC occurs both in topsoil and subsoil layers, but the differences may concern which mechanism is more dominant (Rumpel and Kögel-Knabner, 2011; Six et al., 2002). Physical preservation via soil aggregation is reported to be the main process and the most important mechanism that preserves SOC in topsoil layers (Six et al., 2004). In contrast, SOC in the subsoil is reported to be mainly preserved through the chemical sorption mechanism (Rumpel and Kögel-Knabner, 2011). A study by (Torres-Sallan et al., 2017) revealed that the stable SOC pool stored in micro aggregate and clay plus silt fractions comprised 16% in topsoil and 42% in subsoil, indicating a greater proportion of non-stable SOC in topsoil.

Conversely, Schrumpf et al. (2013) indicated that, generally, based on density fractionation, there is no differences in SOC fractions in topsoil and subsoil layers. Both layers were found to contain fractions in the form of free light, occluded in aggregate, and heavy SOC fractions. However, those fractions were found to have differences in quantity according to the litter source (above or belowground biomass) and decomposition process in soil (microbial activity, mineral binding) (Schrumpf et al., 2013).

Carbon protection in subsoil is attributed to SOC association with clay and mineral surfaces (Schrumpf et al., 2013; Torres-Sallan et al., 2017). Furthermore, in acid subsoil, poorly crystalline mineral (Al and Fe fraction) play significant role (78%) in protecting stable organic C (Kleber et al., 2005) while Amundson et al. (2007) reported that the largest proportion (83%) of organic matter in the subsoil horizon of volcanic soil was associated with minerals in organomineral complexes. However, the chemical composition of SOM in subsoils depends on soil type and is mainly affected by pedogeneses processes (Rumpel and Kögel-Knabner, 2011).

2.6.4 How does the mechanism by which carbon is protected from decomposition down the soil profile vary with land use?

Land use plays a key role in determining the source of organic matter to soils, due to the nature of the aboveground and belowground biomass supplied to soil (Jobbágy and Jackson, 2000; Schrumpf et al., 2013). A study looking at soil carbon storage found differences in C stocks down the soil profile to 1 m, whereby the sequence from largest to smallest stocks in topsoil are stored in forest, grassland and cropland soils whereas the order from highest to lowest in subsoil are grassland, cropland and forest (Dorji et al., 2014; Jobbágy and Jackson, 2000; S. Wang et al., 2004).

Transport of soil organic matter to deep soil layers is also affected by land use. Kindler et al. (2011) stated that SOC moves down the soil profile in dissolved and colloid-associated forms, processes that are more prevalent under grasslands than arable land. Another important aspect that determines soil carbon at deep soil horizons is the plant root contribution (Rumpel and Kögel-Knabner, 2011). Plant roots can penetrate through soil profiles and excrete root exudates and shed root litter into the soil (Jobbágy and Jackson, 2000). For instance, the light fraction distribution in a soil profile has strong relationship with root depth of vegetation (Schrumpf et al., 2013) because the root biomass is a main source of SOM; mainly from root litter and exudation (Rumpel and Kögel-Knabner, 2011). Therefore, land use changes which result in changes to the rooting systems of vegetation will affect the depth distribution of light fraction SOC (Schrumpf et al., 2013).

Furthermore, soil disturbance caused by land cover change (primarily from natural condition to cropland) is another important factor that results in SOC depletion (Lal, 2015; Saha et al., 2012). Regular plowing or harvest is the main reason for significant SOC loss and low cropland SOC stocks (Don et al., 2011; Olson et al., 2012). In addition, in areas with a high slope gradient, soil disturbance can cause erosion due to activities such as cultivation, drainage, road construction, and harvesting (Sing et al., 2018). The soil erosion transports C-rich sediment containing DOC or POC and deposits them at lower landscape positions, with SOC being liberated to rivers or to the air (Lal, 2003; Olson et al., 2012).

Chapter III-The chemical and physical stability of soil organic carbon in the top 1 m of the soil profile under different land uses in England

Abstract

Soils are the largest terrestrial pool of organic carbon and it is known that up to 50% of soil organic carbon (SOC) is stored below 30 cm. Therefore, knowledge of the mechanisms by which SOC is stored in subsoils is critical to developing strategies to mitigate climate change. This study characterised SOC under different land uses in England to determine the mechanisms by which topsoil and subsoil SOC is protected. Samples were collected from a silty-clay loam under three different land uses: arable, grassland and deciduous woodland, and analysed for SOC, pH, C/N ratio, and texture down the top metre of the soil profile. Soil organic matter (SOM) physical fractionation and ammonium oxalate extractable Al, Fe, and Mn were also analysed to elucidate SOM protection mechanisms. Results showed that soil texture was similar between land uses. SOC, N, and C/N ratio decreased down the soil profile and were affected by land use in the order woodland > grassland > arable. SOM fractionation revealed that the mineral-free particulate organic matter (fPOM) fraction was significantly greater in both the topsoil and subsoil under woodland than under grassland or arable. The mineral associated organic carbon (MinOC) fraction was proportionally greater in the subsoil compared to topsoil under all land uses; with arable > grassland > woodland. These findings indicate that land use affects the extent to which SOC is protected, with woodlands showing a higher proportion of carbon that has less protection from decomposition. Subsoil SOC is protected from decomposition by organo-mineral interactions with amorphous Al, Fe and Mn, and may be susceptible to future pH shifts as a result of land use change. This study highlights the need to consider the impact of land use change on SOC, given policy and public interest in woodland planting for climate change mitigation.

3.1 Introduction

Increasing concentrations of atmospheric CO_2 are currently causing global concern due to their propensity to change our climate (Smith et al., 2016). Soils contain approximately 1500 Gt of organic carbon to a depth of 1 m globally and represent the largest terrestrial pool of organic carbon (Batjes, 1996; Jobbágy and Jackson, 2000). Cultivation and management of agricultural soils, and the associated liberation of organic carbon as CO_2, have been cited as major factors contributing to this atmospheric CO_2 increase (Lal, 2018). Recent policy initiatives (e.g. 4 per 1000) have placed a strong focus on the capacity of soils to sequester carbon and mitigate climate change (Minasny et al., 2017). Changes in land use, particularly conversion of agricultural land, both pasture and arable, to woodland have been recommended as a climate change mitigation strategy to capture and store atmospheric carbon on land (Committee on Climate Change, 2018; IPCC, 2019).

Soil science has undergone a revolution in our understanding of the mechanisms by which organic matter becomes stable soil organic matter (SOM) in soils. Soil carbon models (e.g. RothC, CENTURY, DNDC) that are currently used in global biogeochemical simulations base their processes upon the assumption that stable SOM results from the chemical recalcitrance of biopolymers which have a very high mean residence time in soils (Dungait et al., 2012). However, the evidence for the persistence of recalcitrant biopolymers in soils is weak (Lehmann and Kleber, 2015). A new understanding is now developing (Schmidt et al., 2011) that proposes microbial products are the precursors of stable SOM (Cotrufo et al., 2013) and that the primary means by which SOM is stabilised (Schmidt et al., 2011) is due to physical protection through aggregate formation (Six et al., 2000), chemical protection due to sorption on soil surfaces (Kaiser and Guggenberger, 2000), or a combination of both (Hernandez-Soriano et al., 2018).

While observations of decreasing C/N ratio down soil profiles has previously been interpreted as the presence of SOM that has undergone greater microbial processing with increasing soil depth, there is new evidence to suggest that this is actually due to soil mineralogy changing with depth in soils (Kramer et al., 2017). Although there is a well-established relationship between the particle size of soils and the capacity to store soil organic matter (Angst et al., 2018b; Dexter et al., 2008), organo-mineral interactions on soil surfaces of Fe-bearing minerals are also known to play a particularly important role in chemically protecting organic carbon from decomposition (Coward et al., 2018; Torn et al., 1997), especially short-range-ordered minerals that act as ‘nuclei’ for carbon retention in soils (Yu et al., 2017).

Global surveys have typically focused on the 0-30 cm topsoil layer (Bell et al., 2011), but it is now known that as much as 50% of soil carbon is stored below 30 cm (Lal, 2018; Rumpel and Kögel-Knabner, 2011). This is because the volume of subsoil is far greater than the topsoil, even though the concentration of organic carbon in the subsoil is lower than topsoil. Many of the recent insights regarding the stability of organic carbon in soils described above have been inferred due to measurements made on topsoil, and it is not known to what extent these mechanisms underpin the stability of SOM in subsoils. Therefore, knowledge concerning the factors responsible for the stability of organic carbon stored in deeper soils is a key knowledge gap.

The literature contains conflicting reports with respect to the stability of SOM in subsoils and the extent to which it is microbially processed and physically or chemically protected from decomposition (Rumpel and Kögel-Knabner, 2011). Some papers indicate that subsoil SOM is more stable than in the topsoil due to a strong interaction with clay mineral phases and protection in microaggregates (Torres-Sallan et al., 2017), whereas other papers indicate that deep SOM can be easily primed by fresh organic carbon (Fontaine et al., 2007) supplied by earthworm mucus (Hoang et al., 2017) or plant root exudates (Shahzad et al., 2018).

The conversion of land from natural ecosystems to agricultural lands has resulted in the global loss of 133 Pg of C from the soil, and it is widely acknowledged that these degraded, carbon depleted lands offer the greatest potential to store significant additional quantities of carbon by implementing restorative land management practices (Lal, 2018; Sanderman et al., 2017). Thus, there is a need to examine the factors affecting soil carbon storage at depth under different land uses to assess their capacity for further soil C sequestration and prevent unintended priming and loss of soil carbon.

To address the knowledge gaps associated with whether the mechanisms that underpin our recent advances in understanding topsoil SOM dynamics also underpin subsoil SOM dynamics, this paper has three objectives: (i) characterise the organic carbon in soils under woodland, grassland and arable vegetation in England, down the first 1m of the soil profile

(ii) determine the mechanisms of SOC protection in both topsoils and subsoils by employing physical fractionation methods and chemical extractions (iii) evaluate how SOM stabilisation mechanisms alter with depth and whether they are affected by land use. We hypothesised a greater importance of chemical protection mechanisms and lower importance of physical protection mechanisms in the subsoil, compared to the topsoil, assuming that chemical recalcitrance of biopolymers provides only short term protection from SOM decomposition.

3.2 Material and Methods

3.2.1 Soil Sampling

Soil samples were collected in August 2017 from three separate locations within the Loddon Catchment, a tributary of River Thames in the UK (Figure 4.1). At each location soils were collected from a deciduous woodland, a permanent grassland and a long term arable site. All woodland sites were classified as ‘Broadleaved, mixed & yew woodland’ all grassland sites were classified as ‘Improved grassland’ and all arable areas were classified as ‘Arable and horticulture’ on the Centre for Ecology and Hydrology 2015 Land Cover Map (Rowland et al., 2017). Sites were also on the same mudstone geology that is typical of flat low-lying areas of the Thames Valley river terraces (Bloomfield et al., 2011). Two of the locations were the University of Reading’s research farms; Sonning Farm and Hall Farm, and the third was farm and woodlands owned by the The Vyne, National Trust. All soils had similar silty-clay loam surface texture with clay enrichment in subsoils and are affected by groundwater or waterlogging. Under the original Soil Survey of England and Wales classification, Sonning Farm is an argillic brown earth that is typically freely drained by sometimes affected by groundwater (soil series 0571w Hucklesbrook), Hall Farm has argillic gley soils that are permeable soils affected by groundwater (soil series 0841b Hurst), The Vyne has a typical stagnogley soils which are slowly permeable seasonally waterlogged soils (soil series 0711h Wickham) (Cranfield University, 2021). The Soil Survey of England and Wales classifications have been correlated and reclassified using the World Reference Base, 2006 Tier 1 Version as a Luvisol, a Gleysol, and a Planosol, respectively.

Five soil samples were collected from every site using a gouge auger, adopting a stratified random sampling strategy. Each core was sampled down to 1 m depth and divided into 10 cm segments. Samples were then bulked into one composite soil sample for each 10 cm depth per site. Therefore, every site yielded 10 composite soil samples (0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm, 40-50 cm, 50-60 cm, 60-70 cm, 70-80 cm, 80-90 cm, and 90-100 cm). With three different land uses (i.e. three sites per location) and three locations (Sonning farm, Hall farm and The Vyne), 90 composite samples were collected overall from a total of nine sites. Soils were air dried and sieved to <2 mm prior to analysis.

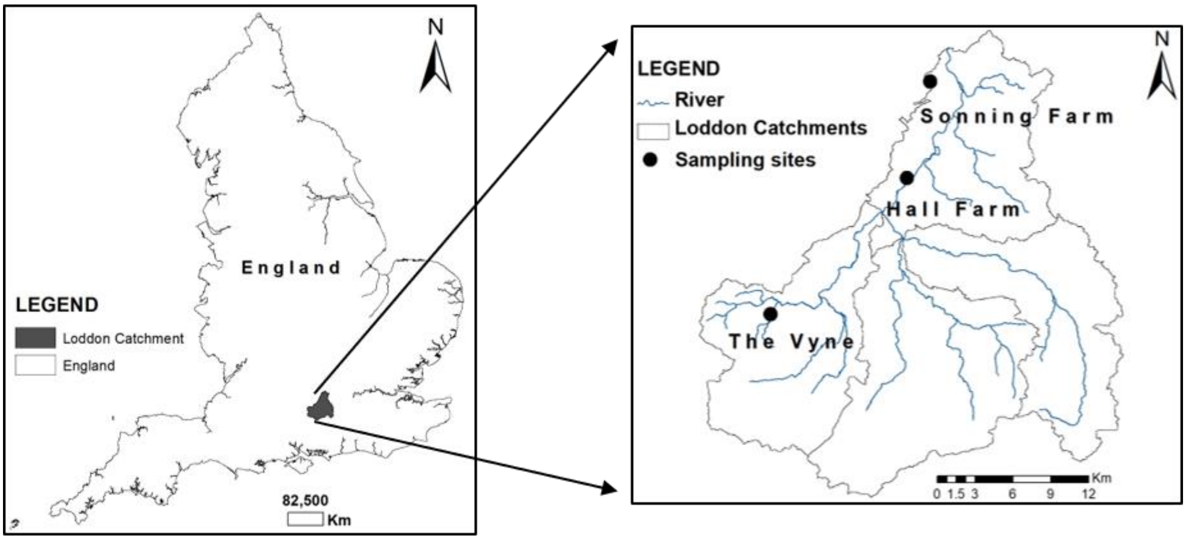


Figure 3.1 Map of soil sampling sites within the Loddon catchment in the UK.

3.2.2 Laboratory methods

3.2.2.1 Soil Carbon and Nitrogen

Soil organic carbon (SOC) and nitrogen were analysed by dry combustion methods using a Thermo Flash 2000 C/N analyzer. A subsample was ground to a fine powder using a ball mill and 10 mg weighed into a tin cup before triplicate analysis. 21 replicates of an in-house QC material that is traceable to GBW07412 (certified for N by State Bureau of Technical Supervision, The People’s Republic of China) and AR-4016 (certified by Alpha Resources Inc. with ISO 17025 accreditation) were run alongside samples with recoveries of 100% ± 0.003 and 98.2% ± 0.022 for N and C, respectively.

3.2.2.2 Soil Texture

The particle size distribution of soil samples was determined using a laser-diffraction method with a Malvern Mastersizer 3000 laser granulometer. A subsample (± 5 mg) of 2 mm sieved air-dried soil was put onto clean plastic disc and a few drops of a dispersing agent (3.3% sodium hexametaphosphate + 0.7% sodium carbonate) were added to aid the dispersion of particles, particularly clay minerals. Disaggregation of the sample was achieved using a rubber pestle for up to 1 minute before analysis. Because the particle size distribution obtained by laser-diffraction methods differ from those achieved using the classic sieve pipette method, we used the following equations reported by Yang et al., (2015) to convert our particle size distribution data from a volume % basis to a mass % basis:

$\text{Estimated Clay}_{\text{SPM}} = 2.17 + 5.76 \exp(0.10 \text{ Measured Clay}_{\text{LDM}})$

$\text{Estimated Sand}_{\text{SPM}} = 6.83 + 0.81 \text{ Measured Sand}_{\text{LDM}}$

$\text{Estimated Silt}_{\text{SPM}} = 100 - \text{Estimated Clay}_{\text{SPM}} - \text{Estimated Sand}_{\text{SPM}}$

Where $\text{Clay}_{\text{SPM,}}$ $\text{Sand}_{\text{SPM,}}$ and Silt_{SPM} are clay, sand and silt content determined with sieve the pipette method, respectively and $\text{Clay}_{\text{LDM,}}$ and $\text{Sand}_{\text{LDM,}}$ are clay and sand content determined with the laser-diffraction method, respectively.

3.2.2.3 Soil pH

Soil pH was determined using a pH electrode, calibrated using pH 4 and 7 buffer solutions. 10 g of 2 mm sieved air-dried soil was weighed into a 50 ml centrifuge tube and then shaken with 25 ml ultrapure (>18.2 MΩ.cm) water for 15 minutes before the measurement was made in the soil suspension.

3.2.2.4 Soil Organic Matter fractionation

Sub-samples of soil at depths representative of topsoil (0-10cm and 20-30cm) and subsoil (50-60 cm and 90-100 cm) underwent organic matter fraction using the method developed by Plaza et al., (2012, 2013) to obtain the following four fractions; mineral-free particulate OM (fPOM) located outside aggregates (i.e. not protected from decomposition by physical or chemical mechanisms), intra macroaggregate organic matter (iMacro), intra micro-aggregate organic matter (iMicro) and mineral-associated organic carbon (MinOC) that is chemically protected from decomposition by adsorption to mineral surfaces.

Air-dried 2 mm sieved soil was mixed with 80 ml of 1.85 g ml^{-1} density sodium polystungstate (SPT) in a 250 ml centrifuge bottle. The mass of soil extracted was different for each sample but amounted to 2 mg soil organic carbon per sample, based on the prior analysis of C described in section 3.2.2.1 and with the details of masses used in Appendix 1 (Table SI-1). Therefore, every tube contained the same ratio (2:80, w/v) of SOC to SPT. This adaptation to the published method was made because subsoils contain much lower SOC than topsoils.

The tubes were shaken for 30 seconds on an end-over-end shaker at 60 rpm and then centrifuged at 2500 g for 30 min. The supernatant containing the fPOM was immediately transferred after centrifugation into a 100 ml polypropylene bottle and filtered, using a Buchner vacuum filtration apparatus through a pre-weighed glass fibre filter (GF/A Whatman, UK) to obtain the fPOM. To obtain the iMacro fraction, the heavy fraction containing macroaggregates remaining in the centrifuge tube were broken up by using a micro aggregate isolator, as depicted by Six et al (2002). The heavy fraction in the centrifuge tube was transferred to the top of a 250 µm sieve by vortex mixing and rinsing with ultrapure water, immersing in deionised water and shaking with 50 silica beads (4 mm diameter) at 150 strokes per minute on a reciprocating shaker under a continuous, steady deionised water flow of about 0.2 L min^{-1} to break up stable macroaggregates, following Six et al (2000, 2002). Microaggregates and other soil components < 250 µm flushed through the sieve were transferred to a beaker. Shaking was stopped after approximately 5 min, while ensuring that the water below the 250 µm sieve had run clear and all macro aggregates were broken. The fraction flushed through the 250 µm sieve and the fraction remaining over the sieve were dried under a heat lamp in a fume cupboard. Both fractions were recombined and gently transferred into a 200 mL polypropylene centrifuge tube together with the filtrate from the first step (SPT solution). The tube was shaken for 30 seconds on an end-over-end shaker at 60 rpm and centrifuged at 2500g for 45 mins. The supernatant containing iMacro fraction was obtained by pipetting and filtering, as described above. To obtain iMicro fraction, the heavy fraction was re-suspended again in the SPT solution (collected from the previous step) and microaggregates dispersed by sonication with an energy input of 1500 J per gram of soil. Again, the tube was shaken for 30 seconds on an end-over-end shaker at 60 rpm and centrifuged at 2500 g for 60 mins. After centrifugation, floating material, representing the iMicro fraction was gently pipetted and filtered, as described above. Lastly, the MinOC fraction was obtained by transferring the heavy fraction (containing MinOC) to a pre-weighed petri dish and dried under a heat lamp in a fume cupboard prior to C and N analysis. At each filtration step, all the pre-dried and pre-weighed GF papers were carefully removed from the Buchner filtration apparatus and dried overnight at 70˚C and then weighed, ball milled and analysed for C and N on a Thermo Flash 2000 C/N analyzer, is as described above. All the dried fractions were also ball milled and analysed for C and N on a Thermo Flash 2000 C/N analyzer, as described above.

3.2.2.5 Mineral availability analysis

The availability of amorphous Al, Fe and Mn oxide minerals in sub-samples of soil that represent surface layer (0-10 cm and 20-30 cm) and subsoil layer (50-60 cm and 90-100 cm) of each land use were analysed using the ammonium oxalate extraction method reported by Loeppert and Inskeep (1996). An ammonium oxalate solution was made by dissolving 49.74 g ammonium oxalate ($(NH_4)_2 C_2O_4 \cdot H_2O$) and 25.22 g oxalic acid ($H_2C_2O_4$) in to 1 L of ultrapure (>18.2 MΩ.cm) water. Because the pH of the solution was 3.01, it was not necessary to adjust to pH 3.0 by addition of dilute ammonia or hydrochloric acid solutions. 0.5 g of ball-milled soil samples were weighed into aluminium foil wrapped 50 ml polypropylene centrifuge tubes, followed by the addition of 30 ml of the ammonium oxalate solution. All samples were then placed on an end-over-end shaker for 2 hours in the dark. Samples were then centrifuged at 3000 rpm for 15 mins and the supernatant carefully decanted into another centrifuge tube. Supernatants were analysed using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) for Fe, Al and Mn after a 100 times dilution.

3.2.3 Statistical Analysis

All statistical analyses were performed with Minitab version 18.0. A Mixed Effects Model (MEM), applying Restricted maximum likelihood (REML) for variance estimation and the Kenward-Roger degrees of freedom approximation. As random factor, farm location was selected whereas land uses and soil depth were chosen as fixed effects. Then followed by a least significant difference (LSD) test ($p<0.05$), was performed to compare effects of land use and soil depth on the measured parameters. Pearson correlation were also conducted to examine relationships between individual soil properties. The influence of land use, soil depth and oxalate extractable Al, Fe, and Mn on mineral associated carbon (MinOC) in the sub soil layers (50-60 cm and 90-100 cm) was also investigated using a Mixed Effects Model, adopting Restricted maximum likelihood (REML) for variance estimation and the Kenward-Roger degrees of freedom approximation. Farm location was selected as a random factor and soil depth, land use, and ammonium oxalate extractable Al, Fe and Mn were selected as fixed effects.

3.3 Results

3.3.1 Differences in soil properties with depth under different land uses

Soil organic carbon decreased with soil depth under all three land uses and at all three locations (Figure 3.2; Appendix 1, Figure SI-1) and was significantly ($p<0.05$) greater in woodland (11.99±1.90 g/kg) and grassland (11.51±1.73 g/kg) soils than arable (8.35±1.03 g/kg) soils (Appendix 1, Table SI-2). Soil organic carbon was also significantly ($p<0.05$) greater in 0-10 cm soils (29.60±3.40 g/kg) than 10-20 cm soils (19.68±1.53 g/kg) which were, in turn, significantly ($p<0.05$) greater than 20-30 cm soils (14.49±0.97 g/kg). Topsoil (0-30 cm) organic carbon was also significantly greater ($p<0.05$) than subsoil (30-100cm) organic carbon content (Appendix 1,Table SI-3).

Similarly to carbon, organic nitrogen decreased down the soil profile (Figure 3.2) and grassland soils (1.27±0.16 g/kg) had significantly ($p<0.05$) greater nitrogen concentrations than woodland (1.08±0.14 g/kg) or arable (1.01±0.20 g/kg) soils (Appendix 1, Table SI-2). Soil organic nitrogen at 0-10 cm (2.64±0.26 g/kg), 10-20 cm (1.89±0.16 g/kg) and 20-30 cm (1.53±0.12 g/kg) were all significantly ($p<0.05$) different from one another (decreasing with depth) and topsoil (0-30 cm) had significantly greater concentrations of organic nitrogen than subsoil (30-100 cm) (Appendix 1,Table SI-3).

C/N ratio significantly ($p<0.05$) decreased down the soil profile (Figure 3.2; Table SI-3) and was significantly ($p<0.05$) different between different land uses in the order woodland (10.46±0.36) > grassland (8.45±0.29) > arable (7.72±0.31) (Appendix 1,Table SI-2).

Statistical analysis revealed that neither the sand, silt, or clay content, nor the median particle size diameter (Figure 3.2) were significantly different between different land uses ($p>0.05$) (Appendix 1, Table SI-2). We can therefore attribute the differences observed under the different land uses to the presence/absence of vegetation types and land management systems and not differences in the soil texture. There were, however, significant ($p<0.05$) differences in soil texture down the soil profile (Figure 3.2; Appendix

1, Table SI-3; Figure SI-1). Overall, soil texture of all sampling sites is dominated by sand (50-2000 µm) in the topsoil and silt (2-50 µm) in the subsoil, while the clay fraction is a minor component and is similar in the topsoils and subsoils (Figure 3.2; Appendix 1, Table SI-3).

Soil pH increased slightly down the soil profile under all land uses, albeit not significantly ($p>0.05$) (Figure 3.2). The average pH, found to be significantly different between land uses ($p<0.05$), was in the order, from lowest to highest; woodland (4.81±0.11) < arable (6.09±0.20) < grassland (6.81±0.12) (Appendix 1, Table SI-2).

Mixed effect model analysis revealed that farm locations has no significant influence ($p>0.05$) on all analysed soil properties (Table SI-5; Table SI-6).

3.3.2 Differences in soil organic matter physical fractionation with depth under different land uses

Physical fractionation of soil organic matter in samples collected from three different land uses, at three different locations revealed that free particulate organic matter (fPOM), intra macro aggregate (iMacro) and intra micro aggregate (iMicro) fractions significantly ($p<0.05$) decreased both in terms of concentration and relative proportion (except iMacro) down the soil profile (Figure 3.3). Whereas the concentration of the mineral associated organic carbon (MinOC) fraction significantly ($p<0.05$) decreased down the 1 m soil profile, the relative proportion of the carbon that was within the MinOC fraction was significantly ($p<0.05$) greater in deeper soil layers compared to other fractions (Figure 3.3). The two topsoil layers (0-10 cm and 20-30 cm) had significantly ($p<0.05$) greater concentrations of C in all SOM fractions than the two subsoil layers (50-60 cm and 90-100 cm) of the soil profile (Appendix 1, Table SI-4).

Generally, the MinOC accounted for the greatest proportion of the total organic carbon under all three (woodland, grassland and arable) land uses (Figure 3.3). Only fPOM concentration was significantly ($p<0.05$) greater in woodland soils than grassland and arable soils (Appendix 1, Table SI-4), with other fractions showing no significant ($p>0.05$) difference. Woodland soils contained considerably greater concentrations of fPOM and iMacro associated C than arable and grassland soils, but grassland soils contained the greatest concentrations of iMicro associated C.

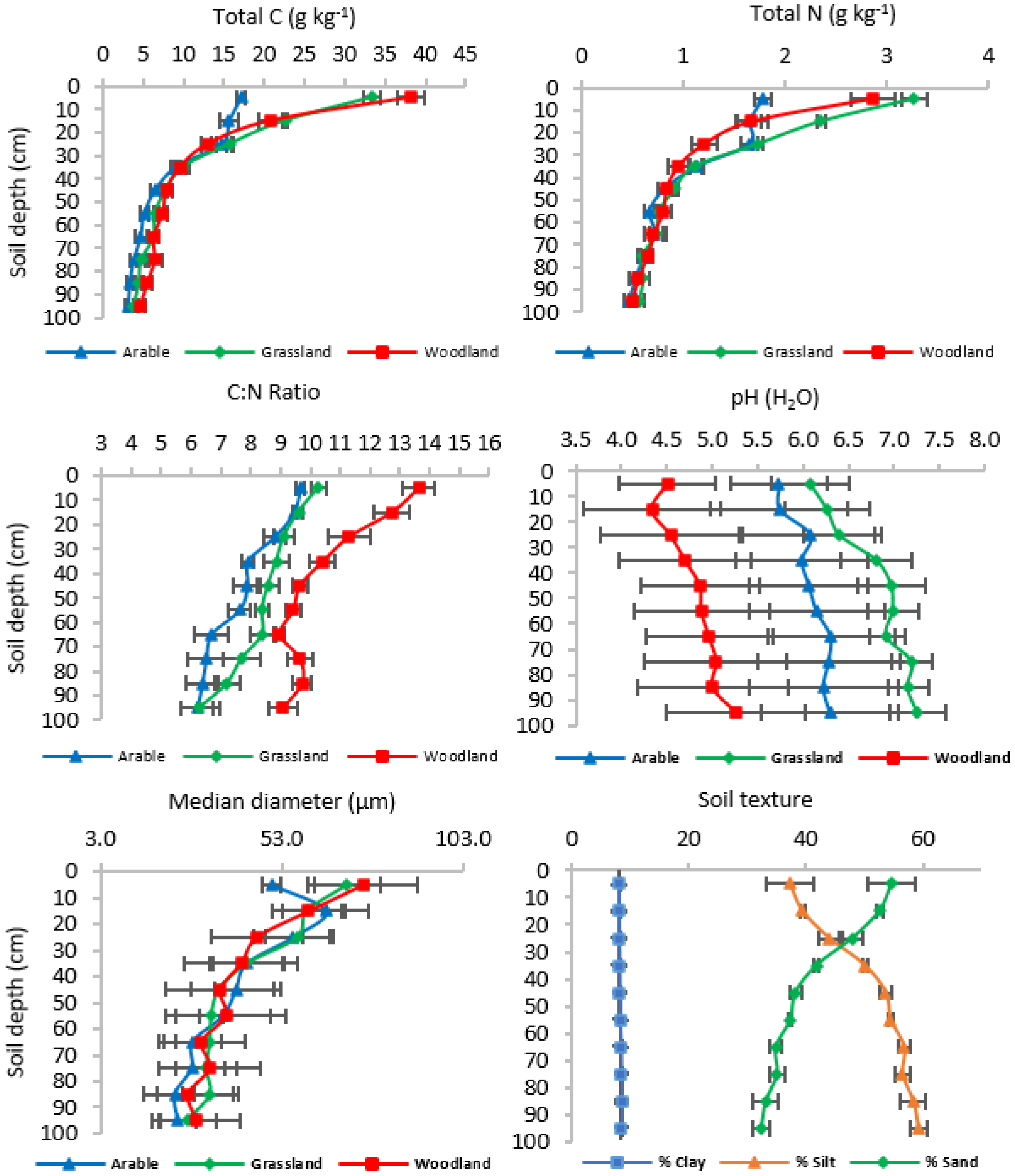


Figure 3.2 Total carbon (g kg^{-1}), total nitrogen (g kg^{-1}), C:N ratio, soil pH (H_2O), median particle size diameter (µm), and soil texture (% clay, silt and sand) at 10 cm depth increments to 1 m under Arable, Grassland, and Woodland land uses at Sonning farm, Hall farm and The Vyne, where points represent mean values from all three locations and error bars represent the standard errors of the mean using the three locations as replicates.

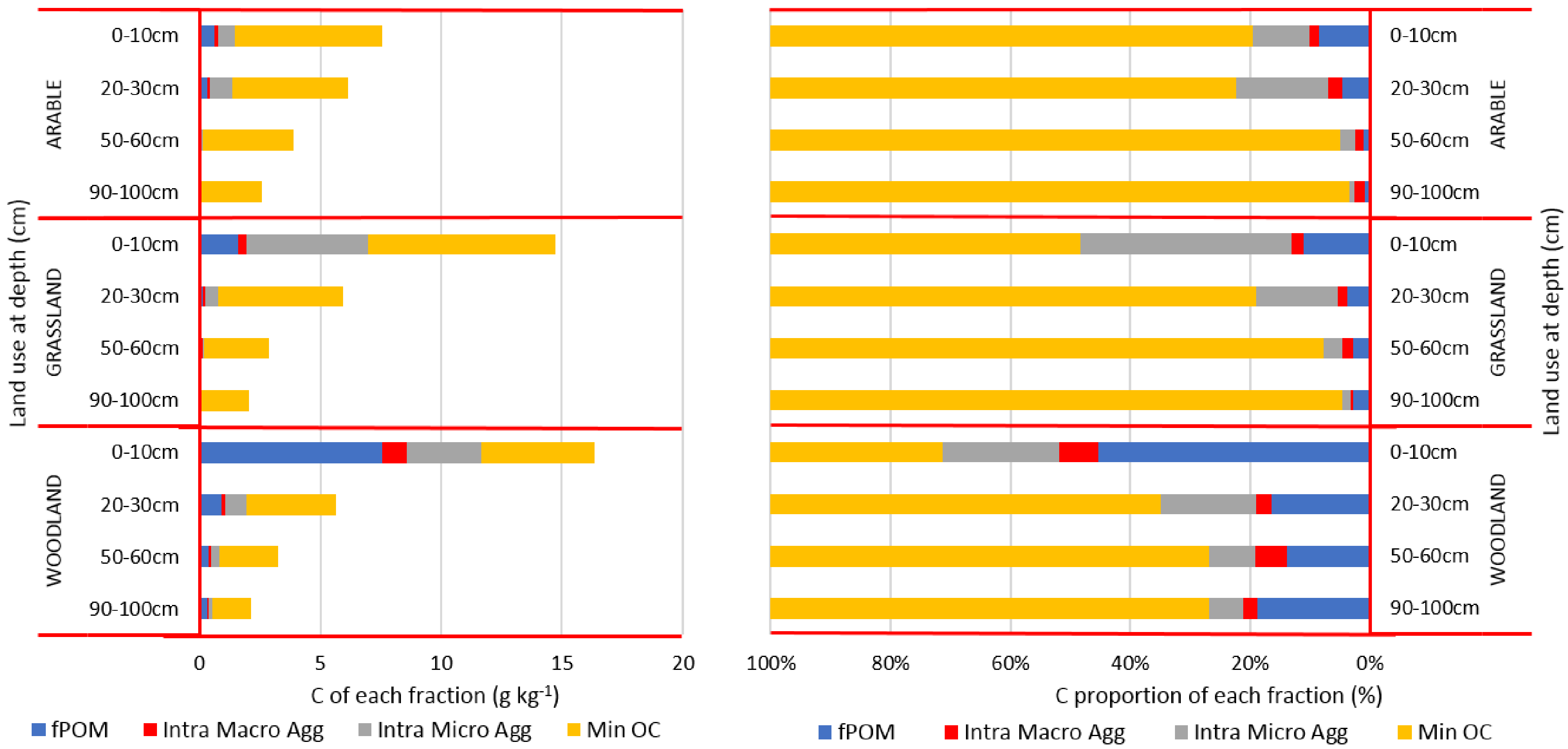
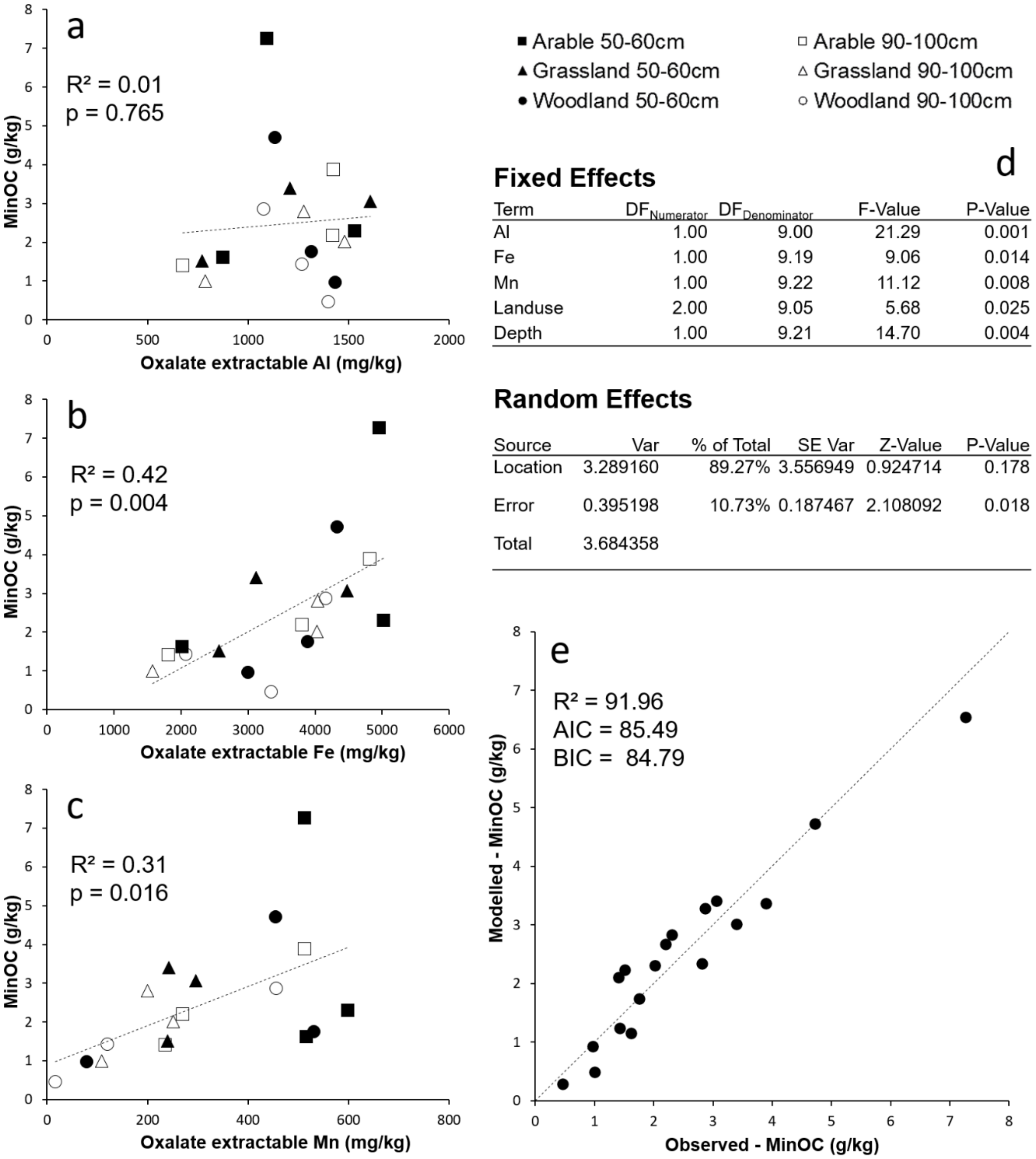


Figure 3.3 Soil organic carbon (C) concentration in g kg^{-1} (left) and relative proportion as a % (right) in each physical fraction of selected soil depths (0-10 cm, 20-30 cm, 50-60 cm and 90-100 cm) in arable, grassland, and woodland soils from three locations (Sonning Farm, Hall Farm and The Vyne) , where bars represent mean values from all three locations.

3.3.3 Relationship between soil mineral availability and mineral associated soil organic carbon (MinOC) in subsoil

Ammonium oxalate extractable Fe and Mn was slightly lower in the two subsoil layers (50-60 cm and 90-100 cm) than the two topsoil layers (0-10 cm and 20-30 cm), while ammonium oxalate extractable Al was greater in the subsoil. Soil from the Vyne had significantly ($p<0.05$) lower concentrations of ammonium oxalate extractable Fe and Mn down the soil profile than soil from Sonning or Hall Farm (Appendix 1, Table SI-5). In subsoils, MinOC was significantly ($p<0.05$) positively correlated with oxides of Fe and Mn, but not with Al (Figure 3.4). Our random mixed effects model indicated that subsoil MinOC concentration was significantly influenced by land use, soil depth (i.e. 50-60 cm or 90-100 cm) and ammonium oxalate extractable Al, Fe, and Mn concentrations (Figure 3.4). More than 90% of the variability in the MinOC concentration in the subsoil layers can be explained using the random (farm location) and these fixed factors used to generate the model (Figure 3.4).



Fixed Effects

Term	$DF_{Numerator}$	$DF_{Denominator}$	F-Value	P-Value
Al	1.00	9.00	21.29	0.001
Fe	1.00	9.19	9.06	0.014
Mn	1.00	9.22	11.12	0.008
Landuse	2.00	9.05	5.68	0.025
Depth	1.00	9.21	14.70	0.004

Random Effects

Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	3.289160	89.27%	3.556949	0.924714	0.178
Error	0.395198	10.73%	0.187467	2.108092	0.018
Total	3.684358				

Figure 3.4. Pearson correlations between subsoil mineral associated organic carbon (MinOC) concentrations and ammonium oxalate extractable Aluminium (a), Iron (b) and Manganese (c), alongside the results of a random mixed effects model (d) that attributes variance in subsoil MinOC concentration to random (farm location) and fixed (oxalate extractable Aluminium, Iron, and Manganese, land use, and soil depth) effects, accompanied by a plot of the observed and modelled concentrations. N = 18. AIC = Akaike's Information Criterion, BIC = Bayesian Information Criterion.

3.4 Discussion

3.4.1 Contrasting soil properties under different land uses

We found significant differences in soil properties between arable, grassland and woodland soils in terms of soil pH, C, N and C/N ratio. The sand fraction decreased down the soil profile, whereas the silt fraction increased down the soil profile. This is an indication that the texture of the soil is becoming finer down the soil profile and thus the soil surface area upon which organic matter can adsorb is likely increasing down the profile. However, neither sand, silt or clay content, nor median particle diameter were significantly different between the three different land uses (Appendix 1, Table SI-2).

This finding indicates that the soils sampled from the three different land uses at each location have a similar soil texture, as was intended when sampling soils from the same soil type at each location. Therefore, comparisons made between arable, grassland and woodland soils can be attributed to their land use, rather than underlying differences in soil type. All three land uses also showed a similar pattern where median particle size decreased with depth in the soil (Figure 3.2). The soil texture was also similar between the three locations (Appendix 1, Figure SI-1 and Table SI-6), despite being classified as belonging to three different World Reference Base Reference Soil Groups. Statistical analysis using mixed effect model (MEM) indicated that location and land use had no significant effect on soil texture Appendix 1, Table SI-6).

On average, SOC concentration in woodland and grassland soils were greater than arable soils (Appendix 1, Table SI-2), in agreement with several other studies conducted in the UK (Bell et al. 2011) and globally (Batjes, 1996; Jobbágy and Jackson, 2000). This difference is most likely due to the higher quantity of litter input into woodland soils due to permanent vegetation (Guo and Gifford, 2002; Li et al., 2016), the livestock manure entering grassland soils (Abdalla et al., 2018), and the tillage of arable soils (Haddaway et al., 2017; Meurer et al., 2018). Woodland soils have a slightly greater concentration of SOC in the top 10 cm, likely due to the presence of a litter layer, whereas grassland soils have a slightly greater concentration at 10-30cm, probably because grasslands have a high root biomass which increases organic matter input to soils, especially in the topsoil. Jobbágy and Jackson (2000) found that 70 % of the root biomass in grasslands was in the topsoil, whereas only 55% of root biomass was in the topsoil of forest soils.

Nitrogen content was significantly greater in grassland soils than in woodland or arable soils (Appendix 1, Table SI-2), probably due to the input from the faeces and urine of grazing livestock (Povirk, Welker, and Vance, 2001). Grazing activity also increases above-belowground biomass by stimulating more photo-synthetically fixed C inputs to belowground roots, leading to increased root exudates and root biomass which eventually further stimulates N inputs into soils (Mcsherry and Ritchie, 2013; Zhou et al., 2017). Some studies also show that root litter is more persistent than leaf litter and serves as a mechanism for N retention in soil (Fujii and Takeda, 2010; Hobbie, 2015). In addition to this, according to global analysis by Jackson et al. (1996), root biomass in grasslands (83%) was higher than temperate deciduous forest (65%).

In agreement with other research (Hobley and Wilson, 2016; Li et al., 2013), C/N ratio was highest in woodland soils, followed by grassland, and then arable soils. This observation is in line with the knowledge that C/N ratio has a close association with vegetation (Jobbágy and Jackson, 2000) as plant litter is the primary source of SOC formation in soil (Li et al., 2016; Lorenz and Lal, 2005) and the distribution of SOC in soil profile has a strong relationship with the root depth of vegetation (Schrumpf et al., 2013). Furthermore, the lowest N concentrations were observed in arable soils, mainly due to leaching of inorganic forms from the profile and repeated growth and harvesting of crops which results in depletion of soil organic matter (and subsequently soil organic nitrogen) in the absence of manures or nitrogen rich crop residues (Pandey et al., 2018).

Soil pH data indicated that soils under woodland were more acidic than arable or grassland soils (Appendix 1, Table SI-2). This observation could be attributed to more organic acids (humus layer) in woodland soils as a result of organic matter decomposition (Falkengren-Grerup, 1987; John et al., 2005). There was no significant difference in soil pH with depth, although soil pH tended to increase (not significantly) down the soil profile. The arable and grassland soil pH display a similar vertical pH distribution to the sigmoidal model defined by Zhang et al., (2017). They explained lower pH in the topsoil may be due to greater SOM, releasing organic acids upon decomposition, or the uptake of bases by plants in the rooting zone, and that higher pH in the subsoil may be due to less SOM, lower disturbance and fluctuating groundwater.

3.4.2 Soil organic matter down the soil profile

Soil organic carbon and nitrogen concentrations decreased down the soil profile under all land uses, in agreement with the observations of multiple other authors (Dorji et al., 2014; Li et al., 2016; Tautges et al., 2019). Whereas topsoil C concentrations were impacted by land use, subsoil concentrations were similar in woodland, grassland, and arable soils, implying that land use change does not considerably alter the concentration of C in the subsoil. This observation is in contrast to the knowledge that the vertical distribution of SOC has a slightly stronger association with vegetation than with climate (Jobbágy and Jackson, 2000; Li et al., 2016).

We also observed a strong correlation between C and N content down the soil profile, in agreement with Tian et al., (2010), but an overall decrease in C/N ratio down the soil profile under all land uses (Figure 2), similar to the findings of other studies (Gregory et al., 2016; Kramer et al., 2017; Lawrence et al., 2015). C/N ratio is a good indicator of the degree of decomposition and quality of the organic matter held in the soil (Batjes, 1996). Organic material with a C/N ratio of approximately 24 is considered optimal for microbial activity, with higher C/N ratios requiring microorganisms to acquire additional N for decomposition to occur (USDA, 2011). Our results indicate that C/N ratios are below 24 in both top and subsoils of all land uses, indicating that the C/N stoichiometry is suitable for organic matter decomposition by microorganisms (Batjes, 1996; Rumpel and Kögel-Knabner, 2011). Therefore, our observation of decreasing C/N ratio down the soil profile is attributed to increased accumulation of more extensively decomposed (or microbially altered) organic compounds in the subsoil (Kramer et al., 2017). Kramer et al. (2017) found that relationships between C/N ratio and soil depth could be driven by N mineral association instead of in situ organic matter decomposition.

3.4.3 The physical and chemical protection of soil organic carbon (SOC) down the soil profile

This study revealed clear differences between topsoil and subsoil in relation to the concentration of labile (fPOM), physically protected (iMacro and iMicro), and chemically protected (MinOC) SOC fractions. The topsoil was dominated by mineral-free particulate organic matter (fPOM) (Figure 3.3) which is composed of fresh material due to the influence of direct plant litter and root input (Dignac et al., 2017; Lal, 2017). This explanation is supported by the finding that deciduous woodland soils, which provide the highest litter inputs, had the greatest fPOM concentration, followed by grassland and arable soils, for which litter inputs are lower (Table SI-4). Our results agree with the findings of others (John et al., 2005; Plaza et al., 2013, 2012) that report MinOC as the major SOC fraction in topsoils. We further confirm that this is also the case in the subsoil and that the proportion of SOC that is MinOC tends to increase down the soil profile (Figure 3.3). This MinOC may have been transported from the topsoil to the subsoil horizon as Dissolved Organic Matter (DOM) with percolating water or exuded at depth by deep pant roots prior to adsorption by soil minerals (Leinemann et al., 2018; Lorenz and Lal, 2005).

Our results imply that the majority of SOC in the subsoil is protected from decomposition because it is chemically associated with mineral surfaces. Fontaine et al., (2007), suggested that SOC in deep soils is protected from decomposition due to a lack of fresh C inputs and that changes in land use can result in priming the decomposition of older SOC. Our findings highlight that the role played by minerals, which act as binding agents for forming organo-mineral complexes, becomes more important down the soil profile (Schrumpf et al., 2013; Torres-Sallan et al., 2017), mainly controlled by geochemical interactions (Cagnarini et al., 2019). Soil metal hydroxides act as binding agents for SOC thus protect SOC from decomposer agents (Angst et al., 2018a; Yu et al., 2017). Indeed, we did observe significant positive correlations between the availability of non-crystalline (amorphous) Fe and Mn in the subsoil layers and the concentration of MinOC (Figure 3.4), in agreement with Rasmussen et al. (2018), and more than 90% of the variability in the subsoil MinOC concentrations can be explained by farm location, land use, soil depth, and amorphous Al, Fe, and Mn concentrations (Figure 3.4).

3.4.4 The importance of organo-mineral interactions for subsoil carbon storage

Our observations highlight the importance of understanding organo-mineral interactions in identifying soils with the greatest potential for storing stable subsoil SOC. It has previously been observed that iron-bearing mineral phases, particularly short-range-order mineral phases are strong drivers of SOC sorption on soils (Coward et al., 2018). The chemical mechanisms proposed for this association is the creation of inner-sphere complexes between the hydrophilic functional groups of amphiphiles (molecules with both polar and non-polar regions) and the mineral surfaces of metal hydroxides (Kleber et al., 2007). The SOC associated with these iron-bearing minerals may not be susceptible to microbial decomposition while adsorbed to the mineral surface, but desorption may occur if a reduction in pH occurs below the point of zero net charge of the hydrophilic functional groups of the amphiphile (Bailey et al., 2019). An example provided by Bailey et al., (2019) is pH 4 as the point of zero charge of carboxyl groups, below which the carboxyl group becomes protonated, positively charged and no longer adsorbs to the mineral surface. We found woodland soils to have lower pH than grassland or arable soils, but this remained, on average, above pH 4 (Figure 3.2). Overall, soil pH is increasing in the topsoils of all UK habitats, especially arable soils, most likely due to decreasing sulphur deposition (Carey et al., 2008). However, further reductions in pH due to land use changes, perhaps due to reversion to acid grassland or heath (Tibbett et al., 2019; Duddigan et al., 2020), or conversion to coniferous plantations, (Reich et al., 2005) may result in pH reductions that cause the desorption.

Lavallee et al., (2019) call for a distinction to be made between particulate and mineral associated organic carbon due to their differences in formation, functioning, and persistence. Similarly, Hoffland et al., (2020) plea for SOM fractions to be better linked to soil functions. Particulate organic carbon has a mean residence time of ‘years’ and is primarily responsible for delivering the soil functions that are characteristic of healthy soils, whereas mineral associated organic carbon has a mean residence time of ‘decades’ and represents the long term store of carbon in soils. Likewise, Tautges et al., (2019) call for greater attention to be paid on subsoil carbon when assessing the impact of land use change on soil carbon stocks, since changes in topsoils may not be reflected in subsoils. We highlight here the need to protect mineral associated soil organic carbon in subsoil layers.

3.5 Conclusion

It is clearly evidenced that total C, total N, and C/N ratio decrease down the soil profile under woodland, grassland and arable land uses. Total C and C/N ratio were significantly different both between land uses (woodland > grassland > arable) and between topsoil and subsoil. In terms of deep SOC stabilisation, SOM physical fractionation found that free particulate organic matter (fPOM) dominated SOC in the topsoil whereas mineral associated organic carbon (MinOC) fraction was proportionally greater in the subsoil under all land uses. Therefore, our hypothesis that chemical protection mechanisms would be of greater importance in the subsoil, compared to the topsoil is supported by this data. Although woodlands contain more fPOM in subsoils than other land uses, SOM protection in subsoils is primarily regulated by soil organo-mineral interactions, particularly amorphous Fe and Mn concentrations and may therefore be susceptible to future changes in soil pH that could occur if land use changes, such as conifer plantation, resulted in subsoil acidification. Our results are novel because they highlight the importance of mineralology in the protection of SOM in subsoils (within which SOM dynamics are poorly understood). Future work should focus on identifying soils that have the greatest capacity for storing additional carbon in subsoils and which are at greatest risk of subsoil carbon losses, based on their mineralogy. These advances will inform strategies for developing site specific land management practices to optimise carbon storage in subsoil horizons.

Chapter IV - Composition of free particulate organic matter (fPOM) in the top 1 m of soil under different land uses

Abstract

Free particulate organic matter (fPOM) is considered as the most labile fraction of soil organic matter and the fraction most easily decomposed by soil microorganisms. The quantity of fPOM in soils decreases with depth and is different between different land uses. However, relatively little is known about whether the chemical composition and quality of fPOM changes down the soil profile and differs between different land uses. We characterised fPOM in topsoils (0-10 cm and 20-30 cm) and subsoils (50-60 cm and 90-100 cm) under arable, grassland, and woodland land uses at three locations in the UK. The fPOM fraction was obtained by density separation and then subjected to analysis for C and N, Fourier-Transformed Infrared (FTIR) spectroscopy, and ^{13}C Isotope Ratio Mass Spectrometry (IRMS). The C and N concentrations of fPOM were significantly higher in woodland than grassland or arable soils, while C/N ratio was similar across all three land uses. FTIR analysis indicated more oxygen-containing functional groups in grassland and arable fPOM than found in woodland soils while, on the contrary, carboxyl acid and carbohydrate groups more abundant in woodland and grassland fPOM than arable fPOM. However, there were no significant differences in the degree of decomposition or recalcitrance of fPOM between the different land uses. Clear differences in the δ^{13}C of fPOM under different land uses reflects the differences in vegetation, with C4 plants grown more recently and frequently in arable soils than woodland or grasslands. We found no significant difference in C concentrations between topsoil and subsoil fPOM, but N concentrations decreased, and C/N ratio increased significantly with depth, while the FTIR analysis indicated that fPOM becomes less recalcitrant with depth, and δ^{13}C of fPOM significantly increased down the soil profile. All these observations indicate that subsoil fPOM is chemically dissimilar to topsoil fPOM and is most likely comprised of more microbially processed organic matter transported from surface layer that is stoichiometrically favourable for further microbial decomposition.

4.1 Introduction

Globally, soils contain a stock of soil organic carbon (SOC) that amounts to approximately 1,505 Pg to 1 m depth, which plays a considerable role in the global carbon cycle, while also providing numerous soil processes and function (Lal, 2018, 2004b). Several factors influence the chemical composition of soil organic matter (SOM) including origin, age, environmental conditions, and land management practices (Parolo et al., 2017). During decomposition and mineralisation, SOM undergoes transformations that result in changes in functional group chemistry, such as the increase in aromatic groups, relative to aliphatic groups, as decomposition progresses (Hsu and Lo, 1999). However, land use and cropping practices have the greatest influence on the composition of soil organic matter (Kaiser and Ellerbrock, 2005) since they dictate the composition and quality of OM input provided by the vegetation and soil amendments (e.g. organic manure) (Yeasmin et al., 2020).

Lavallee et al., (2019) made the distinction between mineral associated organic carbon, which has a long mean residence time in soils and is primarily derived from low molecular weight compounds (largely of microbial origin), and free particulate organic matter (fPOM), which has a much shorter mean residence time. Because the delivery of many soil functions requires the decomposition of SOM by soil organisms, the fPOM fraction of SOM is of great importance for the delivery of soil functions, processes, and services (Hoffland et al., 2020). The fPOM fraction is thought to consist of the undecomposed remnants of plants and animals and is regarded as the most labile component of the soil organic matter (Cerli et al., 2012; Kravchenko et al., 2015). Our previous research has shown that the fPOM fraction of SOC is significantly greater in both topsoils and subsoils under woodland, compared to grassland or arable soils, and that there is proportionally more SOC stored as fPOM in the topsoil, compared to the subsoil (see Chapter 3). However, it is unclear whether (i) the fPOM in the subsoil is of similar chemical composition to fPOM in the topsoil and thus is capable of delivering the same soil functions, processes and services, or if (ii) subsoil fPOM has undergone microbial decomposition to a greater extent than topsoil fPOM.

The use of spectroscopic techniques, such as 13C Nuclear Magnetic Resonance spectroscopy, Fourier-Transformed Infrared (FTIR) spectroscopy, Ultraviolet–Visible spectroscopy, and Fluorescence spectroscopy, has led to considerable advancements in the understanding of SOM structure (Parolo et al., 2017; Savini et al., 2017). FTIR spectroscopy is a method that can be used not only to analyse bulk soil but also to measure the composition of SOM fractions including the fPOM fraction (Margenot et al., 2015a; Yeasmin et al., 2020), intra aggregate fractions (Fultz et al., 2014) and mineral protected SOM (Yeasmin et al., 2020). A small amount of soil is usually sufficient for spectral scanning to obtain representative information whereby the wavelength at which absorption of infrared light occurs can be attributed to the vibrational frequencies of different functional groups. It is a rapid non-destructive method that is capable of screening large collections of samples. FTIR spectroscopy can be used to characterise SOM as it provides information about the relative abundance of different functional groups (Parikh et al., 2014). This allows soil characterisation concerning differences in mineral compositions and organic structures (Xing et al., 2019).

FTIR analysis is particularly helpful in determining the origin and stability of SOM fractions. Decomposition of fresh plant materials initiates with the breakdown the cellulose and carbohydrate compounds, before lignin, tannins, and other recalcitrant plant derived compounds are metabolised, since they are more resistant to microbial biodegradation (Kramer et al., 2012). The fPOM fraction, representing the most physically labile SOC pool, is typically enriched in chemically labile compounds such as carbohydrates (5 to 25% in fPOM), that can be identified by FTIR as aliphatic (C-C/CH/CH_2) and oxygen-containing functional groups (e.g. OH/C-O/CCO), relative to whole soils and heavy fractions. More chemically recalcitrant SOM is identified using FTIR by a greater abundance of aromatic structures due to a high lignin content, relative to alipathic structures, which are associated with SOM that is more easily decomposed (Soucémarianadin et al., 2019).

The natural ^{13}C abundance ($\delta^{13}C$) of SOC is another characteristic of organic matter, which is related mainly to the source of organic carbon, but is also affected by decomposition (Shi et al., 2017) and physical mixing processes (Acton et al., 2013). Additionally, it is well established that gradual increases of $\delta^{13}C$ values with depth, which are partially related to soil OM decomposition processes, are the result of increasing average age of OM with increasing soil depth (Liu et al., 2018). Thus, common understanding dictates that the increase of $\delta^{13}C$ down the soil profile is due to microbial decomposition causing isotopic fractionation of organic carbon (Accoe et al., 2002; Acton et al., 2013).

The objectives of this study were to investigate the evolution of the $\delta^{13}C$ signature of fPOM with increasing depth in soil profiles under different land uses and relate these to the chemical composition and presence of functional groups observed using FTIR spectroscopy to investigate the influence of land use and soil depth on the extent to which subsoil fPOM is microbially decomposed, compared to topsoil fPOM. We hypothesised that fPOM in the subsoil is more microbially decomposed than fPOM in the topsoil.

4.2 Methodology

4.2.1 Field sites

Soil samples were collected in August 2017 from three separate locations within the Loddon Catchment, a tributary of River Thames in the UK (Figure 4.1). At each location soils were collected from a deciduous woodland, a permanent grassland and a long term arable site. All woodland sites were classified as ‘Broadleaved, mixed & yew woodland’ all grassland sites were classified as ‘Improved grassland’ and all arable areas were classified as ‘Arable and horticulture’ on the Centre for Ecology and Hydrology 2015 Land Cover Map (Rowland et al., 2017). Sites were also on the same mudstone geology that is typical of flat low-lying areas of the Thames Valley river terraces (Bloomfield et al., 2011). Two of the locations were the University of Reading’s research farms; Sonning Farm and Hall Farm, and the third was farm and woodlands owned by the The Vyne, National Trust. All soils had similar silty-clay loam surface texture with clay enrichment in subsoils and are affected by groundwater or waterlogging. Under the original Soil Survey of England and Wales classification, Sonning Farm is an argillic brown earth that is typically freely drained by sometimes affected by groundwater (soil series 0571w Hucklesbrook), Hall Farm has argillic gley soils that are permeable soils affected by groundwater (soil series 0841b Hurst), The Vyne has a typical stagnogley soils which are slowly permeable seasonally waterlogged soils (soil series 0711h Wickham) (Cranfield University, 2021). The Soil Survey of England and Wales classifications have been correlated and reclassified using the World Reference Base, 2006 Tier 1 Version as a Luvisol, a Gleysol, and a Planosol, respectively.

4.2.2 Sampling design

We adopted a mixed model approach to our sampling design. Our primary interest was the effect of land use (grassland, arable or woodland) and soil depth on soil properties; thus, soil land use and soil depth are the two main factors in the design. Soils from each land use were collected from each farm. As each farm is on a similar, but slightly different soil type, the effect of soil type and farm are represented in one single random factor called ‘location’ because, although they cannot be separated, they are included because they may have an effect on the overall variation in the data. Within each sampling site, soils were bulked to produce a composite sample, as described in detail below, such that only one composite sample value for each land use for each soil depth for each farm was available, with N = 3 for each land use across the three locations. Therefore, we were able to compare the effect of land use (N = 3) and depth across three different locations and examine whether the location effected any of the variation in soil properties itself.

Details of sample collection are described in Chapter 3. Briefly, five soil samples were collected from every site using a gauge auger, adopting a stratified random sampling strategy. Each core was sampled down to 1 m depth and divided into 10 cm segments. Samples were then bulked into one composite soil sample for each 10 cm depth per site to provide a sampled average. For the purposes of this study, we selected 4 soil depths i.e., 0-10 cm, 20-30 cm (representing the topsoil layer) and 50-60 cm, 90-100 cm (representing the subsoil layer). Because samples were collected from three different locations (Sonning farm, Hall farm and The Vyne), each location contained three different land uses (i.e. three sites per location), and we used 4 depths, a total of 36 composite soil samples were analysed overall. Soil samples were air-dried and sieved to <2 mm before analysis.

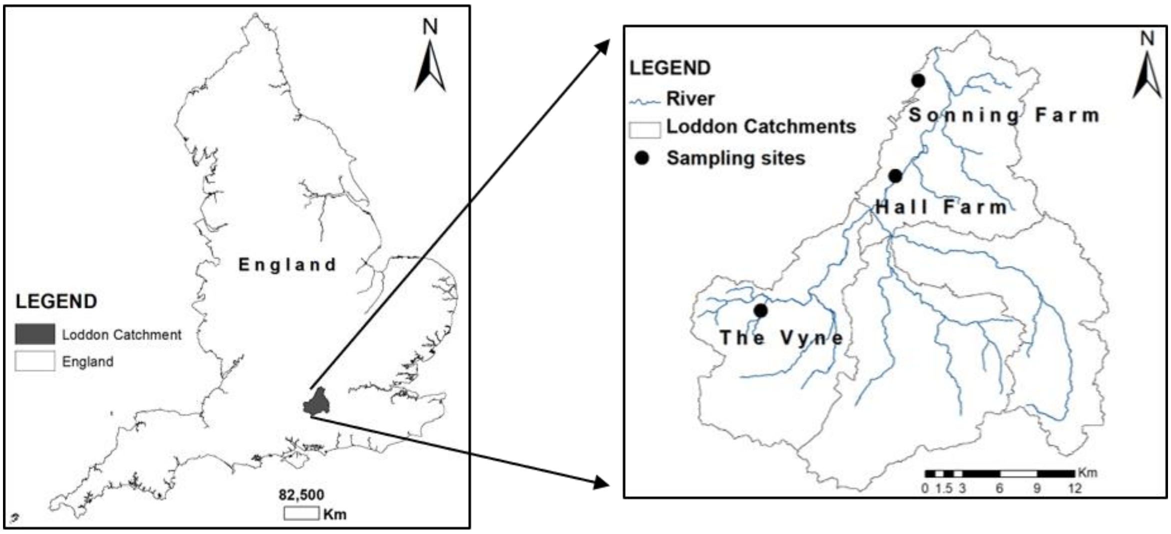


Figure 4.5 Map of soil sampling sites within the Loddon catchment in the UK.

4.2.3 Laboratory analysis

4.2.3.1 Extraction of the free particulate organic matter (fPOM) fraction

Extraction of fPOM was carried out on air-dried 2 mm sieved soil that was mixed with 80 ml of 1.85 g ml^{-1} density sodium polystungstate (SPT) in a 250 ml centrifuge bottle. The mass of soil extracted was different for each sample but amounted to 2 mg of soil organic carbon per sample (see Chapter 3). Therefore, every tube contained the same ratio (2:80, w/v) of SOC to SPT (Appendix 2, Table SI-1). The tubes were shaken for 30 seconds on an end-over-end shaker at 60 rpm and then centrifuged at 2500 g for 30 min. The supernatant containing the fPOM was immediately transferred after centrifugation into a 100 ml polypropylene bottle and filtered, using a Buchner vacuum filtration apparatus, through a pre-weighed glass fibre filter (GF/A Whatman, UK) to obtain the fPOM fraction. The fPOM fraction was brushed off the GF paper and ground to a powder using a mortar and pestle. Ground fPOM samples were then analysed for C and N using a Thermo Flash 2000 C/N analyzer, for molecular structure using fourier transform infrared (FTIR) spectroscopy and for $^{13}C/^{12}C$ ratio using isotope ratio mass spectrometry (IRMS).

4.2.3.2 Fourier Transform Infrared Spectroscopy

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was performed using a Perkin Elmer spectrum 100 FT-IR Spectrometer. The samples were scanned in the infrared region from 4200 to 650 cm^{-1}. 40 scans per spectra were recorded at a resolution of 4 cm^{-1} and then individual peaks were assigned to functional groups as identified in Table SI-2. Spectra observation resulted 11 prominent peaks and shoulders that indicate organic functional groups (Appendix 2, Figure SI-1). FTIR spectra were standardised by z-scoring (mean centring and dividing by the standard deviation), following Hobley et al. (2017), before statistical analysis to quantify the impact of land use and soil depth on relative absorbance of each peak.

Furthermore, to attribute differences in functional group composition to SOM quality, two indices were calculated following (Haberhauer et al., 1998; Margenot et al., 2015a). First, to quantify relative changes in band absorbance, relative absorbance of each of the 11 bands were calculated by dividing the raw (i.e. not z-scored) peak height of a distinct peak (3355, 2921, 2853, 2162, 1621, 1417, 1240, 1029, 930, 874 or 763 cm^{-1}) by the sum of the heights of all these peaks and multiplying by 100 (Haberhauer et al., 1998). The resulting relative absorbance values were then used to calculate the following two indices that use the ratios of bands representing different functional group types (e.g., aliphatic, O-functional group) which in previous studies have been established as indices of relative decomposition and recalcitrance of SOM (Margenot et al., 2015a):

$$\text{Index I} = \frac{1621+930+874+763}{2921+2853+1417}$$

$$\text{Index II} = \frac{2921+2853+1621+1417+930+874+763}{3355+1240+1029+2162}$$

Index I is considered to indicate the degree of decomposition as represented by the ratio of aromatic to aliphatic functional groups because the ratios of bands representing these two functional groups have been shown to increase with increasing degree of decomposition (Hsu and Lo, 1999). Index II represents relative recalcitrance of SOM by determining a ratio of C functionality (aromatic and aliphatic, respectively) to O-functional groups where an increase of which is thought to be associated with greater recalcitrance of SOM (Margenot et al., 2015a; Veum et al., 2014).

4.2.3.3 Isotope Ratio Mass Spectrometry

The measurement of $\delta^{13}C$ of fPOM was performed using a ThermoFisher Scientific Delta V Advantage isotope ratio mass spectrometer (IRMS) connected to a Flash EA 1112 HT elemental analyser, interfaced with Conflo IV device. Samples (0.2 mg) were weighed into tin capsules and lowered into an elemental analyser combustion oven. The measured $^{13}C/^{12}C$ ratios are expressed as $\delta^{13}C$ values (‰) relative to the Pee Dee Belemnite (PDB) standard

$$\delta^{13}C = \left(\frac{R\ Sample - R\ Standard}{R\ Standard} \right) * 1000$$

where R sample and R standard refer to the $^{13}C/^{12}C$ ratio in the sample and the standard (PDB), respectively. The working standards for the measurements were IVA33802174 Urea standard, Silver Spoon Sugar in-house standard, and USGS42 Tibetan Hair certified standard with a $\delta^{13}C$ value of -45.38 ±0.17 ‰, -26.33±0.06 ‰, -21.09±0.1 ‰, respectively.

4.2.4 Statistical analysis

Statistical analysis was performed with Minitab software version 19. A mixed effect model (MEM) was employed to examine the differences between different land uses and soil layers, which were both set as fixed factors, and location was set as random factor. The estimation method used was Restricted Maximum Likelihood (REML), combined with Kenward-Roger as test method for fixed effect, and then followed by a Tukey multiple comparison test ($\alpha = 0.05$) to identify significant differences between individual treatments.

4.3 Results

4.3.1 C and N analysis of free particulate organic matter (fPOM)

Total C and N concentration of the fPOM fractions obtained from woodland soils were significantly ($p<0.05$) higher than fPOM fractions of grassland and arable soils (Table 4.1, Figure 4.2). However, the C/N ratio was not significantly different between land uses. The concentration of fPOM C was not significantly ($p>0.05$) different between different soil depths (Table 4.2) but did appear to decrease down the soil profile of arable and grassland soils and increase down the soil profile of woodland soils (Figure 4.2). The total N concentrations of fPOM revealed the same pattern with land use and depth as the total C concentrations. However, the topsoil layer (0-10 cm) had a significantly greater concentration of N compared to subsoil layers (50-60 cm and 90-100 cm). As a result, the C/N ratio of fPOM was significantly lower ($p<0.05$) in topsoil (0-10 cm) than subsoils (50-60 cm and 90-100 cm). The effect of location was not significantly different among all locations ($p> 0.05$) (Appendix 2, Table SI-3).

Table 4.1 fPOM concentration of Total C (g/kg), Total N (g/kg) and C/N ratio under different land uses (mean ± standard error of the mean, n = 12).

Landuse	Total C (g/kg)	Total N (g/kg)	C/N Ratio
Arable	82.76 ± 12.99 b	3.79±0.67 b	21.28±1.29 a
Grassland	83.61 ± 14.73 b	4.06±0.73 b	19.95±0.80 a
Woodland	149.84 ± 8.28 a	7.99±0.25 a	18.95±1.14 a

Different letters within a column represent statistically significant differences at α = 0.05
Data points are the mean of soil samples collected under the same land use (Arable, Grassland, or Woodland) across three different locations (Sonning, Hall Farm and The Vyne) at four selected depth layers (0-10 cm, 20-30 cm, 50-60 cm, and 90-100 cm).

Table 4.2 fPOM concentration of Total C (g/kg), Total N (g/kg) and C/N ratio for selected soil layers (mean ± standard error of the mean, n = 9)

Soil Depth	Total C (g/kg)	Total N (g/kg)	C/N Ratio
0 – 10 cm	118.19±11.17 a	6.75±0.66 a	17.85±1.26 b
20 – 30 cm	102.76±17.09 a	5.70±0.97 ab	18.17±0.85 ab
50 – 60 cm	98.99±20.82 a	4.70±0.99 b	21.25±1.07 a
90 – 100 cm	109.84±27.49 a	5.37±1.20 b	20.19±1.33 a

Different letters within a column represent statistically significant differences at α = 0.05.
Data points are the mean of soil samples collected at the same depth (0-10 cm, 20-30 cm, 50-60 cm, or 90-100 cm) across three different locations (Sonning, Hall Farm and The Vyne) and three different land uses at eat location (Arable, Grassland, or Woodland).

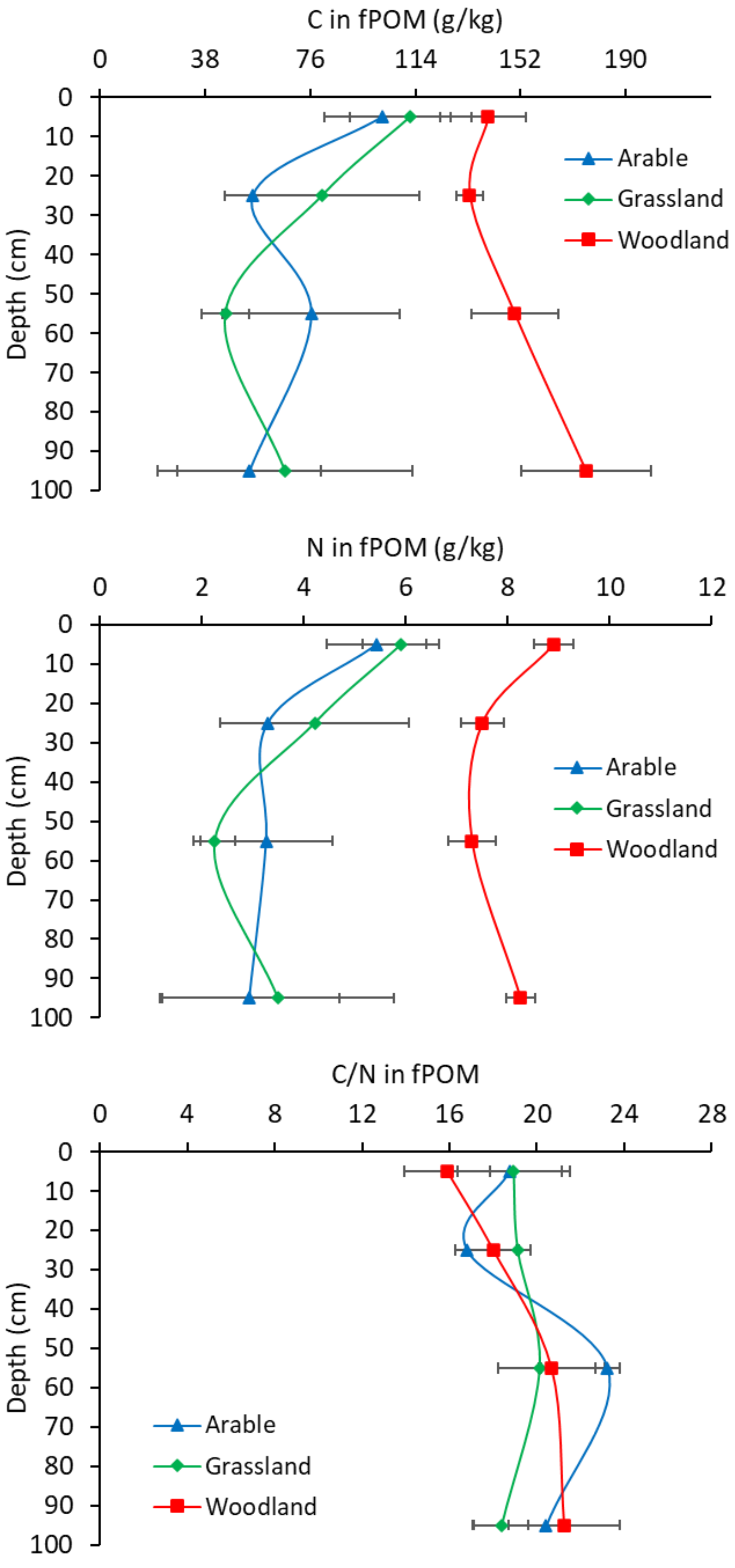


Figure 4.2 Concentration of Total C, Total N (g/kg) and C/N ratio of fPOM under different land use and soil depth, where points represent mean values from all three locations and error bars represent the standard errors of the mean (n = 3) using the three locations as replicates.

4.3.2 Fourier Transform Infrared Spectroscopy of free particulate organic matter (fPOM)

Eleven spectral regions, corresponding to specific C functional groups were identified in the FTIR spectra (Figure 4.3) and these bands were used to characterise fPOM chemistry: (1) the H-bonded hydroxyl (O-H) groups region at 3355 cm^{-1}; (2) the aliphatic (CH_2 and CH_3 stretch) region between 2921, 2853 and 1417 $cm^{−1}$; (3) the carboxyl acid region at 1240 $cm^{−1}$; (4) the aromatic C region between 1621, 930, 874 and 763 $cm^{−1}$ (5) the carbohydrate region at 2162 $cm^{−1}$ (6) C–O stretching vibrations of C-O-C groups at 1029 cm^{-1}. The ratio of aliphatic to and aromatic functional groups was used as the indicator spectra to measure the degree of SOM decomposition, and the ratio of alipathic-aromatic groups to O-funtional groups was used to represent the recalcitrance of the SOM (Margenot et al., 2015b; Veum et al., 2014).

Following peak identification, the Mixed Effects Model (MEM) analysis of the z-score transformed absorbance at identified bands (Appendix 2, Table SI-2) revealed significant ($p<0.05$) differences between land uses in the relative absorbance at 1240, 2162, and 3355 cm^{-1} (Table 4.3; Figure 4.4), each of which are attributed to oxygen-containing functional groups (carboxylic, carbohydrate, and phenolic groups, respectively). However, only the band at 1417 cm^{-1}, attributed to aliphatic (C–H) deformation of CH_2 or CH_3 groups, was found to significantly ($p<0.05$) decrease in relative absorbance with soil depth (Table 4.4; Figure 4.4). Effect of location was not significantly different among all locations ($p> 0.05$) (Appendix 2, Table SI-3).

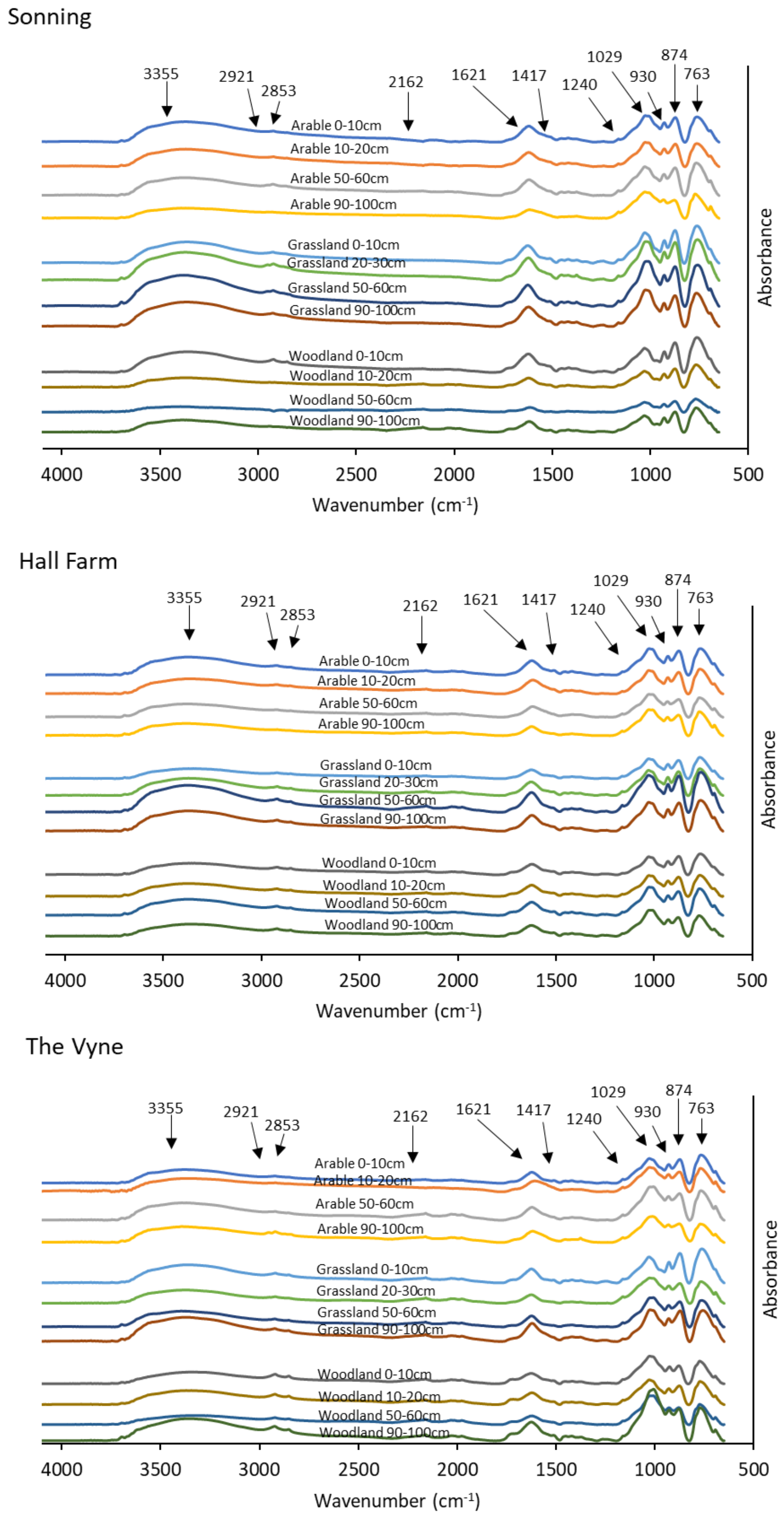


Figure 4.3 ATR-FTIR spectra of fPOM (free particulate organic matter) obtained from different locations (Sonning, Hall Farm and The Vyne) under different land uses (arable, grassland and woodland) and selected soil depths (0-10 cm, 20-30 cm, 50-60 cm and 90-100 cm)

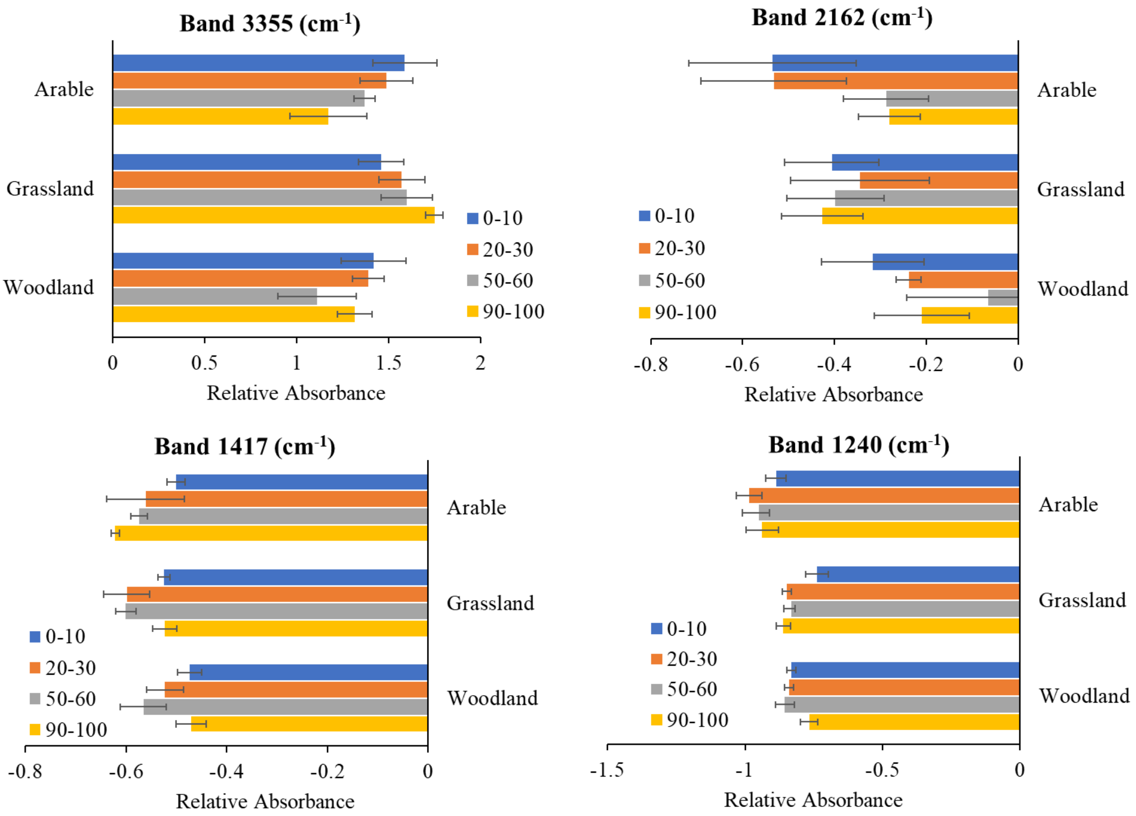


Figure 4.4 Relative absorbance (z-score transformed absorbance in cm^{-1}) of selected bands obtained from Fourier-transform infrared (FTIR) spectra of free particulate organic matter (fPOM) from selected soil layers down the soil profile under arable, grassland and woodland. Bars represent mean values from all three locations and error bars represent the standard errors of the mean using the three locations as replicates (n = 3).

Table 4.3 Relative absorbance (z-score transformed absorbance) of selected bands obtained from Fourier-transform infrared (FTIR) spectra of free particulate organic matter (fPOM) under arable, grassland and woodland (mean ± standard error mean, n = 12)

Band (cm^{-1})	Land use		
	Arable	Grassland	Woodland
3355	1.40±0.08 ab	1.59±0.06 a	1.31±0.07 b
2162	-0.41±0.07 b	-0.39±0.05 b	-0.21±0.06 a
1240	-0.94±0.02 b	-0.82±0.02 a	-0.82±0.02 a

Different letters within a column represent statistically significant differences at the 0.05. Data points are the mean of soil samples collected under the same land use (Arable, Grassland, or Woodland) across three different locations (Sonning, Hall Farm and The Vyne) at four selected depth layers (0-10 cm, 20-30 cm, 50-60 cm, and 90-100 cm).

Table 4.4 Relative absorbance (z-score transformed absorbance) of selected bands obtained from Fourier-transform infrared (FTIR) spectra of free particulate organic matter (fPOM) from selected top soil (0-10 cm and 20-30 cm) and subsoil (50-60 cm and 90-100 cm) layers down the soil profile under arable, grassland and woodland (mean ± standard error mean, n = 9)

Soil layer	Band 1417	Index II
0-10 cm	-0.50 ± 0.01 a	2.07 ± 0.07 a
20-30 cm	-0.56 ± 0.03 ab	1.91 ± 0.04 ab
50-60 cm	-0.58 ± 0.02 b	1.83 ± 0.05 b
90-100 cm	-0.54 ± 0.02 ab	1.80 ± 0.05 b

Different letters within a column represent statistically significant differences at α = 0.05. Data points are the mean of soil samples collected at the same depth (0-10 cm, 20-30 cm, 50-60 cm, or 90-100 cm) across three different locations (Sonning, Hall Farm and The Vyne) and three different land uses at eat location (Arable, Grassland, or Woodland).

The Tukey multiple comparisons test revealed that the relative absorbance of the band at 3355 cm^{-1} was significantly ($p<0.05$) greater for grassland fPOM compared to woodland fPOM, but neither were significantly ($p>0.05$) different to arable fPOM (Table 4.3, Figure 4.4). However, relative absorbance of bands 2162 and 1240 were significantly ($p<0.05$) greater for woodland fPOM than arable fPOM (Table 4.3, Figure. 4.4). While this reveals an inconsistent picture, it can be generally stated that oxygenated functional groups were more prevalent in the fPOM of woodland and grassland soils than arable soils. Down the soil profile, relative absorbance at only band 1417, indicative of aliphatic groups, was found to be significantly greater ($p<0.05$) in topsoil (0-10 cm) fPOM than subsoil (50-60 cm) fPOM (Table 4.4, Figure 4.4). However, the absorbance at this band seems to be very similar at the top of the soil profile (0-10 cm) and at 90-100 cm under grassland and woodland land uses.

The use of FTIR band indices to quantify the degree of fPOM decomposition and recalcitrance revealed no significant ($p>0.05$) differences between land uses (Figure 4.5). Index I (representing the degree of fPOM decomposition) was not significantly different between different land uses or different soil depths (Appendix 2, Table SI-2). However, there is some indication that grassland fPOM, particularly in the top 10 cm, was more decomposed than arable and woodland fPOM at the same depth, as shown by Index I (Figure 4.5). Furthermore, the recalcitrance index (Index II) was found to significantly differ ($p<0.05$) with depth (Table 4.4), but not land use (Appendix 2, Table SI-2). Effect of location was not significantly different among all locations ($p > 0.05$) (Appendix 2, Table SI-3). As shown in Figure 4.5, Index II, under all land uses has a similar decreasing trend with depth, with topsoil (0-10 cm) fPOM significantly ($p<0.05$) more recalcitrant than subsoil (50-60 cm and 90-100 cm) fPOM (Table 4.4).

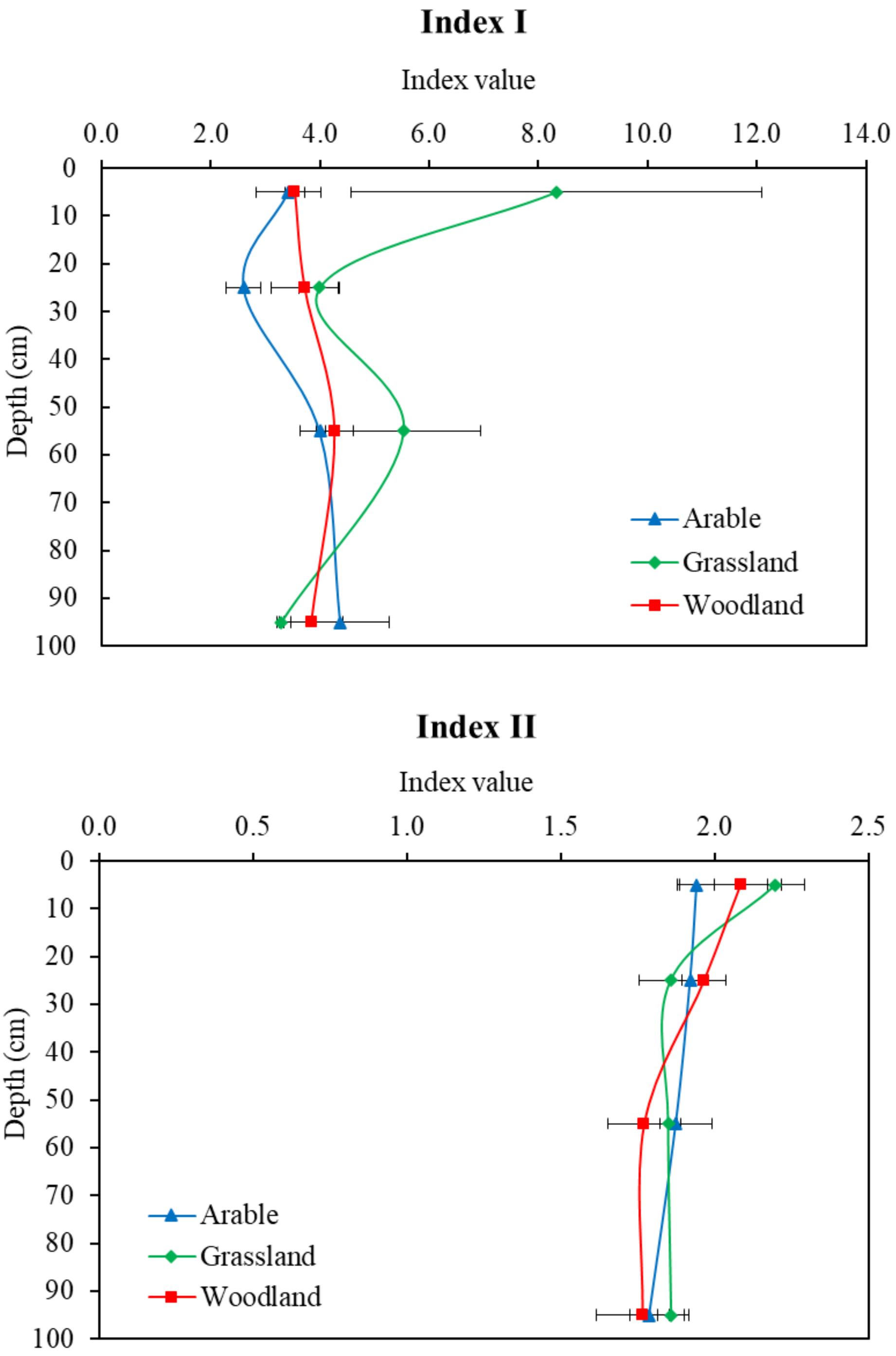


Figure 4.5 Fourier-transform infrared (FTIR) bands indices corresponding to fPOM degree of decomposition (Index I) and recalcitrance (Index II) along with the soil profile under different land use. Error bars are standard errors of the mean, n = 3.

4.3.3 Isotope Ratio Mass Spectrometry of free particulate organic matter (fPOM)

The mean $\delta^{13}C$ of fPOM differed significantly ($p<0.05$) among all land uses (Figure 4.6; Table 4.5) in the order, from the highest to the lowest, arable > woodland > grassland. Down the soil profile, the $\delta^{13}C$ value showed an increasing trend, where topsoil (0-10 cm) fPOM had a significantly ($p<0.05$) lower $\delta^{13}C$ than subsoil (90-100 cm) fPOM (Table 4.6). Grassland fPOM revealed a clear and constant decrease in $\delta^{13}C$ down soil profile at all three farms, but woodland showed little vertical difference. Interestingly, there was a greater $\delta^{13}C$ for fPOM at 20-30 cm at Hall farm and The Vyne than 0-10 cm or 50-60 cm (Figure. 4.6).

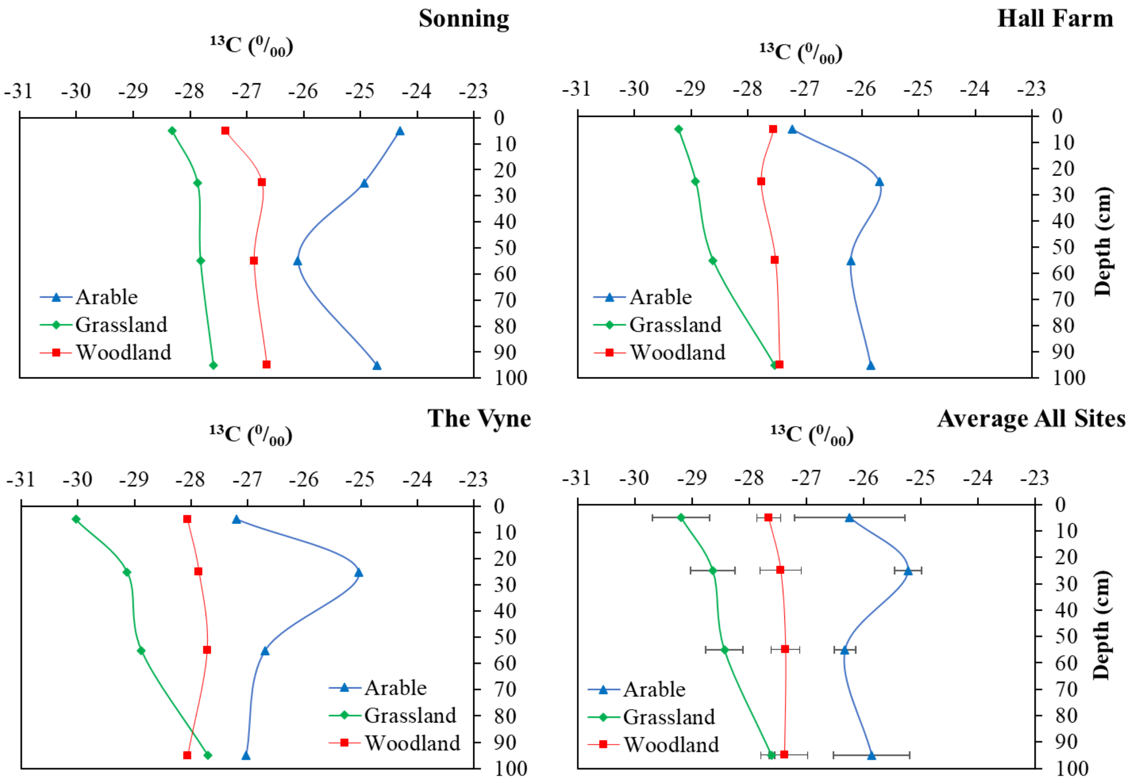


Figure 4.6. $\delta^{13}C$ value of free particulate organic matter (fPOM) with depth for the three sampling locations (Sonning, Hall Farm, and The Vyne) and the average of these three locations, using the three locations as replicates. Error bars on the bottom right graph are standard errors of the mean of the three replicate locations, n = 3.

Table 4.5 δ^{13}C values of the fPOM fractions under different land use (mean ± standard error mean, n = 12)

Land use	δ^{13}C ($^{0}/_{00}$)
Arable	-25.92 ± 0.29 a
Grassland	-28.47 ± 0.23 c
Woodland	-27.47 ± 0.14 b

Different letters within a column represent statistically significant differences at α = 0.05 Data points are the mean of soil samples collected under the same land use (Arable, Grassland, or Woodland) across three different locations (Sonning, Hall Farm and The Vyne) at four selected depth layers (0-10 cm, 20-30 cm, 50-60 cm, and 90-100 cm).

Table 4.6 δ^{13}C values of the fPOM fractions under different land use from selective top soil (0-10 cm and 20-30 cm) and subsoil (50-60 cm and 90-100 cm) layer (mean ± standard error mean, n = 9)

Soil layer	δ^{13}C ($^{0}/_{00}$)
0-10 cm	-27.70 ± 0.53 b
20-30 cm	-27.11 ± 0.53 ab
50-60 cm	-27.38 ± 0.33 ab
90-100 cm	-26.95 ± 0.36 a

Different letters within a column represent statistically significant differences at α = 0.05. Data points are the mean of soil samples collected at the same depth (0-10 cm, 20-30 cm, 50-60 cm, or 90-100 cm) across three different locations (Sonning, Hall Farm and The Vyne) and three different land uses at eat location (Arable, Grassland, or Woodland).

4.4 Discussion

4.4.1 Land use effects on fPOM carbon quality

The concentration of C and N in free particulate organic matter (fPOM) was found to be significantly greater in woodland soils, compared with grassland and arable soils. This is probably because the fPOM brushed off the filter papers and analysed contained larger plant litter particles and is less contaminated by mineral particles. This could indicate that the fPOM from arable and grassland soils is fragmented or biologically mineralised to a greater extent than the fPOM from woodland soils. Yet, the C/N ratio of the fPOM was similar across all three land uses. The low C/N ratio of fPOM obtained in all soils in this study (<

25) indicates faster OM decomposition process than OM accumulation (Li et al., 2016). From previous analysis of these samples, we also know that the woodland soils have a higher quantity of fPOM than the grassland and, in turn, arable soils (see Chapter 3). The greater fPOM content under woodland not only influenced by abundant OM input from plant litter (Hobley et al., 2017a), but also the low pH (see Chapter 3) that limited microorganism activity in decomposing OM (Malik et al., 2018) which is shown by higher content of carbohydrates (band 2162 cm^{-1}) in woodland (Hsu and Lo, 1999; Veum et al., 2014).

According to Chan (2001), the fPOM fraction is the most sensitive to changes in land use. This refers to the common understanding that SOC is lost during the conversion to agriculture (Guo and Gifford, 2002) and depends on vegetation as source of organic matter (Jobbágy and Jackson, 2000). Analysis of the chemical composition of fPOM revealed that land use influences the carbohydrate content (band 2162 cm^{-1}) , which were more prevalent in woodland soils than the other land uses. Carbohydrates are good indicators of fresh plant material input and their lower prevalence in grassland and arable soils (particularly arable topsoils) indicate a greater extent of decomposition (Hsu and Lo, 1999; Veum et al., 2014). Similarly, a greater prevalence of carboxyl/phenoloic/hydroxyl o-containing groups were observed in the woodland and grassland soils than the arable soils, indicating an earlier stages of fPOM decomposition and greater biological reactivity of this fraction in less disturbed (woodland and grassland) soils, compared to the arable soils (Yeasmin et al., 2020). The $\delta^{13}C$ of fPOM was significantly greater in arable soils than grassland or woodland soils. This finding was expected and probably reflects the influence of C4 plants (e.g. maize) that are periodically cropped in arable soils (Fuentes et al., 2010; Shi et al., 2017).

4.4.2 Effects of soil depth on fPOM carbon quality

The C/N ratio of fPOM slightly increases with depth which actually indicates that the fPOM in the subsoil may be decomposed to a lesser extent, or may be more chemically recalcitrant, than the fPOM in the topsoil (Hsu and Lo, 1999). High N contents in the surface layers may reflect the cycling of N within shallow roots and little inputs, as well as surface N inputs from atmospheric deposition (Stevens et al., 2018; Vanguelova and Pitman, 2019) and other amendments applications on arable and grassland (Gerzabek et al., 2006). However, since the C/N ratio of all the fPOM samples analysed were considerably lower than 25, it can be assumed that these residues are favourable for microbial decomposition. Additionally, increasing C/N ratio at depth also revealed that the decomposition process is more intense in topsoils than subsoils (Hsu and Lo, 1999). Moreover, increasing C/N ratio with depth was suggested by Soucémarianadin et al., (2019) to be as a result of higher contribution of roots than leaf litter in the deeper soil layer where C/N ratios of fine roots are closer to 50–60 (Hobbie et al., 2010) while C/N ratios of fresh foliage or humus layers range between 10 and 32 (Cools et al., 2014).

Furthermore, our findings based on C/N ratio of fPOM contradicts evidence from other indicators of the degree to which fPOM is decomposed. For example, we found, in agreement with Hobley et al. (2017), increasing of $\delta^{13}C$ values of fPOM with down the soil profile. The enrichment of ^{13}C with depth signifies that subsoil fPOM consisted of SOM that had undergone more microbial processing than topsoil SOM (Acton et al., 2013; Ehleringer et al., 2000) as a result of ^{13}C-enriched of microbial metabolism during the decomposition process (Zacháry et al., 2020) that was transported down the soil profile (Acton et al., 2013).

The finding that the $\delta^{13}C$ signature of fPOM is greater in arable soils than grassland or forest soils has two possible explanations. Firstly, tillage may have accelerated the decomposition of fPOM due to the physical disruption of soil aggregates and introduction of air that stimulates micobial activity and leads to more microbially processed SOM (Hobley et al., 2017). Secondly, the planting of C4 crops results in plant biomolecules with a greater $\delta^{13}C$ signature because they retain more 13C and less 12C in their tissues. Therefore, inclusion of C4 species (e.g. maize) in arable crop rotations is also likely to increase the $\delta^{13}C$ signature of the fPOM (Fuentes et al., 2010).

We observed a decrease in the prevalence of aliphatic groups in fPOM down the soil profile, also documented by Ding et al. (2002), also significantly decreased of the recalcitrance of fPOM (Index II) with soil depth. This findings indicates that the subsoil layer fPOM was more decomposed than the topsoil layer (Acton et al., 2013; Veum et al., 2014). However, this finding indicated that the fPOM in subsoils contained more microbially processed and less chemically recalcitrant transported from topsoil fPOM but the decomposition process become less than topsoil as evidenced by a higher C/N ratio at subsoil which is indicating slow microbial decomposition (Li et al., 2016).

Additionally, as previously stated, all these soils are affected by waterlogging for part of the year. Oxygen limitation (anaerobic) conditions are commonly understood to supress the SOC decomposition, particularly in the subsoil layer (Huang and Hall, 2017; Jia et al., 2020). However, study from Huang et al. (2020) revealed not only that the effect of anoxia on decomposition supressed total C loss (by 27% to 41%) due to the decrease in litter-C decomposition, but long term anaerobic conditions (over weeks to months) cause decreasing physical protection of mineral-associated SOC as result of the Fe reduction and release of mineral-associated soil C (Huang and Hall, 2017). Litter decomposition in anaerobic conditions also changes the C molecular composition which decreases protein C accumulation and increases carbohydrates and lignin decomposition (Huang et al., 2020). The processes may have possibly affected the dissimilarity of fPOM between topsoil and subsoil layers in this study.

4.5 Conclusion

Our results indicate that both land use and soil depth affect the chemical characteristics of fPOM in terms of C/N ratio and concentration, chemical composition, and δ^{13}C in lowland soils with silty-clay loam topsoils and clay enriched subsoils affected by groundwater and waterlogging. Woodland soils contain fPOM with a high content of carbohydrates and oxygenated functional groups (phenol, carboxyl hydroxyl groups) than grassland and arable soils, indicating the presence of plant litter that is at earlier stages of decomposition. The δ^{13}C of fPOM in arable soils is higher, due to the periodic cropping of C4 plants. The fPOM fraction of the SOM is chemically different in topsoils than subsoils. Deeper soil layers contain fPOM with fewer aliphatic compounds group which are less chemically recalcitrant than topsoil fPOM. The δ^{13}C of fPOM indicates that subsoil contained more microbially decomposed fPOM than topsoil, but the decomposition process become slower in the subsoil as indicated by fPOM C/N ratio increases with soil depth. Therefore, our data supports our hypothesis that fPOM in the subsoil is more microbially decomposed than fPOM in the topsoil. Further study should explore how soil management, mainly arable land management of soil, will affect both quality and quantity of the fPOM, particularly in the subsoil layer. Overall, this study demonstrates that subsoil fPOM is chemically dissimilar to topsoil fPOM. possibly due to the anaerobic effect of waterlogging in study areas and is therefore unlikely to deliver the same soil functions and ecosystem services to the same extent.

Chapter V - Conversion of forest to Cinnamon plantation depletes the carbon stocks in the top 1 metre of the soil profile in the tropical highlands of Kerinci Regency, Jambi Province, Indonesia

Abstract

This study aims to investigate the effect of conversion from natural forest into the cinnamon plantation to top 1 m soil carbon stocks and soil characteristics. The project was conducted in Andosol soil of Kerinci Regency, Sumatera, Indonesia, sampling up to 1 m depth along with the soil profile under forest and different ages of Cinnamon plantation (Cinnamon Year 1, Year 5 and Year 10). Soil organic carbon (SOC) stocks were quantified for the soil whole profile under all land uses, also physical properties (bulk density and soil texture) and chemical properties (Total organic carbon (TOC), total N, C/N ratio) were determined to see the impact of the land conversion. The free particulate organic carbon (fPOM) obtained from SOC fractionation from selected topsoil (0-10 cm and 20-30 cm) and subsoil layer (50-60 cm and 90-100 cm) and then continued to TOC and total N analysis and FTIR analysis. The result showed that there was decreasing bulk density and C:N Ratio and increasing in TOC and total N under 1 year after forest conversion, but as the plantation gets older, TOC, N and C:N ratio decrease significantly under Cinnamon Year 10 (C Y10). Whole soil profile SOC stocks showed increasing under Cinnamon Year 1 (C Y1) but then tend to decrease as the cinnamon plantations get older. FTIR analysis revealed that topsoil fPOM contains greater aromatic band (767 and 878) than subsoil whilst fPOM fraction had decrease in aromatic compound (Band 767, 878, and 931) and carbohydrate (Band 2120) after the conversion, although aromatic and carbohydrate compounds still lower than natural condition, all these compounds rise again at 10 year old cinnamon plantation (C Y10). On the contrary, hydroxyl functional groups (bands 3312) had increase after forest conversion then rise at C Y10 indicating more biological or microorganism activity. Decomposition degree of fPOM (Index I) was higher under forest than all cinnamon plantations but fPOM recalcitrance (Index II) was similar under all land use and depth. We conclude that forest conversion depletes total carbon stocks both in topsoil and subsoil layer and also affected soil characteristics. Our FTIR study suggest that fPOM composition was influenced by land use and soil depth. Post decomposition after forest conversion decrease even though rise

again at year 10 of cinnamon plantation. This finding challenges a need to do better agricultural practice particularly in preserving longer soil organic carbon.

5.1 Introduction

Tropical regions play an important role in the global carbon cycle because tropical soils contain 26% of the 1500 Gt of SOC present in soils globally to a depth of 1 m (Batjes, 1996; Lal, 2017) and 66% (692 Pg C) of atmospheric CO_2 emissions eminate from tropical forests (Jobbágy and Jackson, 2000). Tropical forest are currently experiencing massive deforestration for agriculture and urban development (Tölle, 2020) and are considered the second largest net greenhouse gas emission source (12-20%) (Don et al., 2011). Tropical forest deforestration estimated to release about 0.6 to 1.2 Gt C y^{-1} from topsoils and vegetation (2000–2010) (van Straaten et al., 2015). However, land use change impacts on SOC are not confined to topsoils. Changes are equally high in the subsoil, underscoring the importance of sampling deeper soil layers to deepen our understanding of the magnitude of the SOC losses and their underlying mechanisms (Don et al., 2011; Harrison et al., 2011; Lal, 2018; van Straaten et al., 2015).

Shifting cultivation practices, particularly in South East Asia, have been practised for thousands of years. Still, recent demographic pressures have reduced the fallow period’s duration, decreasing the system's sustainability (Smith et al., 2016). Land use change from native vegetation into cash crop vegetation results in SOC loss (Lal, 2004a) due to greater decomposition rates (Yuste et al., 2007). Land conversion elevates soil temperature by opening soils to sunlight and increases the decomposition rate of both labile and persistent organic matter fractions (Fang et al., 2005; Kirschbaum, 1995). Downward movement of dissolved organic carbon through the soil profile due to precipitation (Kaiser and Kalbitz, 2012) and deep root penetration of new plants releases root exudates that can also prime the decomposition of carbon buried deep within the soil profile by providing microorganisms with a fresh carbon source that they can use to co-metabolise deep SOC (Bernal et al., 2016; Fontaine et al., 2007). The subsoil (below 30 cm) contains the largest SOC pool due to the high capacity of the subsoil to protect SOC from decomposition (Six et al., 2002). Land use, soil depth, and thier interaction significantly affect SOC stocks (Li et al., 2016). However, despite the considerable importance of subsurface SOC, our understanding of the factors influencing subsoil SOC dynamics and how subsoil SOC stocks are altered by changing land use is still limited (Gross and Harrison, 2019; Rumpel and Kögel-Knabner, 2011).

Soils in Indonesia have been, and continue to be, exploited intensively for agriculture, mostly after conversion from natural forest. Around 877,000 acres forest are annually cleared for agricultural use and urban development (Tölle, 2020). However, the true magnitude of SOC depletion caused by this deforestation and the potential to reverse the trend of carbon emissions and increase carbon storage using the available range of land management strategies have not yet been fully and systematically quantified (Minasny et al., 2017). Hairiah et al. (2001) showed that conversion of forest to rubber plantations decreases soil C stocks from 55 to 40 Mg C ha^{-1} and a more recent study by van Straaten et al. (2015) found that conversion of natural forest to rubber, oil palm, and cacao plantation in Jambi Province, Sumatera decreases the topsoil carbon stock by up to 50%.

In Indonesia, particularly in the Kerinci Regency of Jambi Province, Sumatera, shifting cultivation practices now occur less frequently, but there has been an increase in cinnamon (*Cinnamomum burmanii* [Nees & T. Nees] Bl.) agroforestry plantations due to the high economic value of cinnamon on global markets (Hariyadi and Ticktin, 2012). Cinnamon (also called cassiavera or cassia) has become one of the most important agricultural commodities produced in Indonesia. Indonesia contributes 66% of worldwide cinnamon supply. 85% of Indonesian cinnamon originates from Jambi Province, most of which is grown in plantations in Kerinci Regency. Moreover, cinnamon products from Kerinci Regency have a reputation for being high quality (known as *Korintji* Cinamon) because of their many superiorities, including aroma, flavour, colour, size, shape and high essential oil content (Lizawati et al., 2016).

Based on data from the Statistics Office of Kerinci Regency (BPS, 2018), almost all cinnamon plantations in Kerinci Regency are managed by local farmers employing agroforestry cropping systems, which are estimated to cover about 40,762 Ha (12.25% of total regency area). Thus, cinnamon plantations in Kerinci Regency are still managed by smallholder farmers to suppliment their income (Lizawati et al., 2016). However, expansion of these plantations is leading to extensive deforestation within the natural forest area surrounding the Kerinci Seblat National Park (Hariyadi and Ticktin, 2012). The impact of this land conversion from natural forest to cinnamon plantation on the soil carbon stocks is unknown.

We quantified SOC stocks down the soil profile under cinnamon plantations of different ages in three locations in Kerinci Regency, Jambi Province, Indonesia. We collected soil cores at 10 cm intervals down the soil profile (to 1 m) to calculate total stocks of SOC under these land uses and to investigate the effect that natural forest conversion to cinnamon plantation has on topsoil and subsoil carbon. We then investigated whether the chemical composition of soil organic matter (SOM) changes down the soil profile and whether this is different under different land uses. Our aim was to measure topsoil and subsoil carbon stocks in soils under different ages of cinnamon plantation and compare with SOC stocks under native forest. We hypothesised that topsoil and subsoil carbon stocks will decrease with age of cinnamon plantation, and that SOC would decrease with depth. We also hypothesised that SOC would be more degraded in soils after conversion to cinnamon plantation, as reflected in the composition of topsoil and subsoil SOM

5.2 Methodology

5.2.1 Study sites and soil sampling

Our study area was in the Kerinci Regency, Jambi Province of Indonesia, located in the highest elevation land of Jambi Province. The regency is situated between 1° 40' and 2° 4' S, 101° 8' and 101° 50' E, surrounded by Kerinci Seblat National Park and Kerinci Mountain. The regency is known for its high quality horticultural production and some cash crop commodities such as tea, coffee, and cinnamon (BPS, 2019). The elevation of the sampling sites ranged from 1000 to 1500 m above sea level. Mean annual temperature is 22.9 °C (ranging from 28.9 to 18.6 °C) and mean annual precipitation is 2991 mm, with the dry season occurring for less than 2 months per year (BPS, 2019). Three locations were selected following Lizawati et al. (2016) because they were identified as major cinnamon producing areas in Kerinci Regency. These locations were Lempur, Pungut, and Renah Kayu Embun (RKE) villages (Figure 5.1).

The soils present at all three villages where samples were taken for this project are classified as Andosols, as evidenced by the soil map (Figure 5.1). Andosols are soils that are derived from volcanic materials, are rich in organic matter, have high porosity and usually have a low bulk density (McDaniel et al., 2012; Takahashi and Shoji, 2002). Despite andosols, or volcanic ash soils, representing just 0.84% of land globally, they contain approximately 5% of global soil carbon (Eswaran et al., 1993). Andosols contain allophane and imogolite minerals which, besides Al and Fe oxides, are amongst the most effective minerals to bind SOM, thus making andosol the most carbon-rich mineral soil type (Zieger et al., 2018).

At each village soil samples were collected from four sites; a patch of natural forest and three cinnamon plantations that were 1, 5, and 10 years old, adopting a random stratified sampling strategy. Samples were collected by digging a soil pit at each site and collecting a core every 10 cm down the soil profile to 1 m using a 176.63 cm^3 bulk density ring (height = 4 cm, diameter = 7.5 cm), alongside a second sample for chemical analysis.

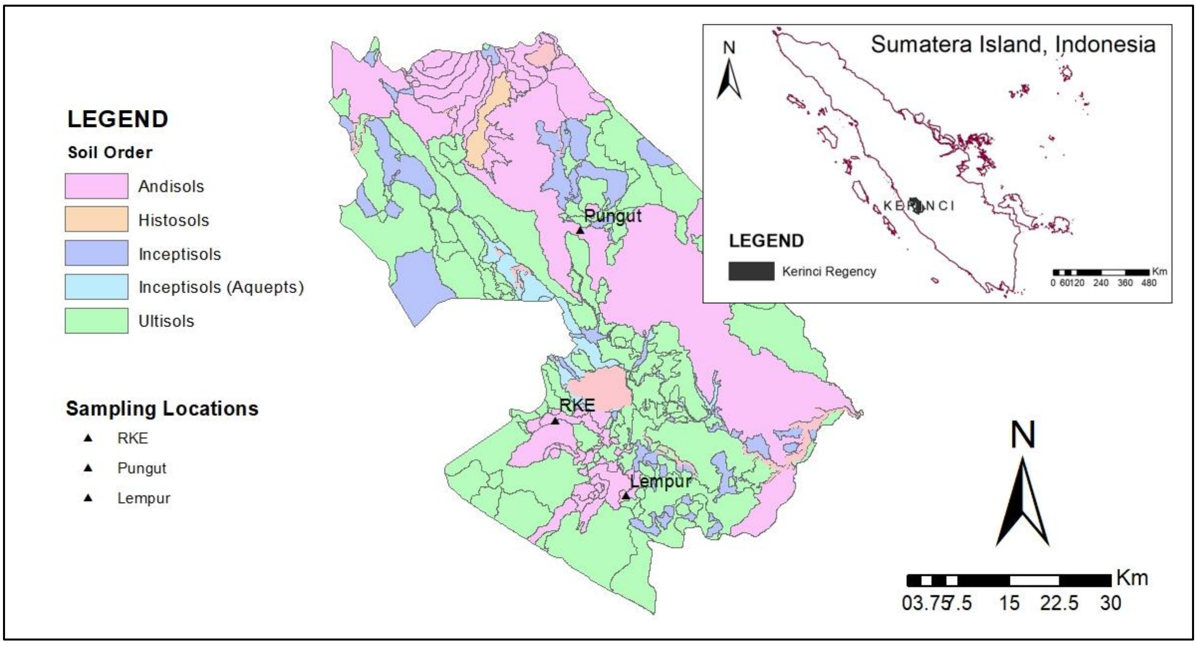


Figure 5.1. The three sampling sites, located in the villages of Lempur, Pungut, and Renah Kayu Embun (RKE), in Kerinci Regency, Jambi Province on the Sumatran island of Indonesia overlain on a soil map of the Regency (source: Department of Agriculture, Indonesia).

5.2.2 Laboratory analysis

5.2.2.1 Bulk density, Carbon, Nitrogen and C Stocks

Bulk density of each soil layer was measured on an oven-dry basis by weighing the contents of each ring after drying at 105°C for 24 hours. Soil samples collected alongside bulk density rings were air dried and sieved through a 2 mm screen prior to further analysis. Total organic carbon (TOC) and nitrogen were analysed by dry combustion methods using a Thermo Flash 2000 C/N analyzer. Each duplicate subsample was ground to a fine powder using a ball mill, and 10 mg weighed into a tin cup before analysis. 24 replicates of an in-house QC material that is traceable to GBW07412 (certified for N by State Bureau of Technical Supervision, The People’s Republic of China) and AR-4016 (certified for C by Alpha Resources Inc. with ISO 17025 accreditation) were run alongside samples with recoveries of 98.15% ± 0.007 and 100.16% ± 0.030 for N and C, respectively.

We calculated SOC stocks in each 10 cm soil layer following Guo and Gifford (2002), using the following equation:

$$\mathrm{Ct} = \mathrm{BD\ x\ Cc\ \%\ x\ D}$$

Where Ct is the SOC stock (Mg ha^{-1}), BD is the soil bulk density (g cm^{-3}), SOC is the soil organic carbon concentration (percentage), and D is the soil sampling thickness (10 cm). The stocks for each 10 cm soil layer were summed to calculate the SOC stock in Mg ha^{-1} to a depth of 1 m.

5.2.2.2 Particulate organic matter extraction

Free particulate organic matter (fPOM) was obtained by extracting a quantity of air-dried 2 mm sieved soil that was mixed with 80 ml of 1.85 g ml^{-1} density sodium polystungstate (SPT) in a 250 ml centrifuge bottle. The mass of soil extracted was different for each sample but amounted to 2 mg soil organic carbon per sample (after SOC analysis, described above). Therefore, every tube contained the same ratio (2:80, w/v) of SOC to SPT (Appendix 3, Table SI-1). The tubes were shaken for 30 seconds on an end-over-end shaker at 60 rpm and then centrifuged at 2500 g for 30 min. The supernatant containing the fPOM was immediately transferred after centrifugation into a 100 ml polypropylene bottle and filtered, using a Buchner vacuum filtration apparatus through a pre-weighed glass fibre filter (GF/A Whatman, UK) to obtain the fPOM and then fPOM was brushed off the GF paper and milled using mortar and pestle prior to fourier transform infrared (FTIR) spectroscopy analysis. fPOM was also analysed for C and N by dry combustion using a Thermo Flash 2000 C/N analyzer, as described above for soil samples. Insufficient sample mass prevented the analysis of all samples.

5.2.2.3 Fourier Transform Infrared Spectroscopy analysis

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy analysis was undertaken on samples from selected soil layers (0-10 cm, 20-30 cm, 50-60 cm and 90-100 cm) at each location and under each land use. Spectra measurement was conducted using a Perkin Elmer Spectrum 100 FTIR Spectrometer in the region from 4200 to 650 cm^{-1} recording 40 scans per spectra at a resolution of 4 cm^{-1}.

Spectra observation identified 11 prominent peaks and shoulders that were present in most samples which indicate organic functional groups. Individual peaks were assigned to functional groups, as outlined in Appendix 3 (Table SI-2). The broad intense band at about 3312 cm^{-1} was assigned to the stretching vibrations of H-bonded hydroxyl (O-H) groups of phenols but may also represent amine (N–H) stretching (Solomon et al., 2005). The weak stretch vibration bands at about 2920 and 2851 cm^{-1} were assigned to vibrations of asymmetric and symmetric aliphatic (CH_3 and CH_2) groups (Ellerbrock and Gerke, 2004; Kaiser and Ellerbrock, 2005; Solomon et al., 2005). The broad band at 1615 cm^{-1} was assigned primarily to aromatic C=O stretching vibrations of the COO^{-} anion to a lesser extent to conjugated carbonyl-C (C O) such as quinones (Ellerbrock and Kaiser, 2005; Solomon et al., 2005), while the band around 1410 cm^{-1} was considered to have originated from aliphatic (C–H) deformation of CH_2 or CH_3 groups (Solomon et al., 2005; Xing et al., 2019). The band which appeared in the 1221 cm^{-1} region was attributed to C–O stretch in carboxylic acid, phenol C–O asymmetric stretch, and OH deformation (Fultz et al., 2014). The strong band at about 1072 cm^{-1} was attributed to C–O stretching vibrations of C-O-C groups (Ellerbrock and Kaiser, 2005). The weak vibrations at band 931 cm^{-1} were considered indicative of bending vibrations of aromatic C-H (Margenot et al., 2015a), while the strong band at 878 cm^{-1} was also attributed to bending vibrations of less substituted aromatic C-H (Margenot et al., 2015a). The strong band at 767 was attributed to aromatic C-H with 3-4 adjacent H deformation (Ascough et al., 2011).

FTIR spectra were then standardised by z-scoring (mean centring and dividing by the standard deviation for each individual spectra) before data analysis (Hobley et al., 2017b). The z-score for each of the 11 prominent peaks were taken forward to determine the impact of plantation age and soil depth on the prevalence of functional groups in fPOM.

Furthermore, to attribute differences in fPOM functional groups to SOM quality, two indices were calculated using the relative absorbance (before Z scoring standardization) of specific bands (Haberhauer et al., 1998; Margenot et al., 2015a). To calculate the relative absorbance of each of the 11 bands used in the indices, we divided the peak height of a distinct peak (e.g., 3312, 2920, 2851, 2120, 1615, 1410, 1221, 1072, 931, 878 or 767 cm^{-1}) by the sum of the heights of all peaks at 3312, 2920, 2851, 2120, 1615, 1410, 1221, 1072, 931, 878 and 767 cm^{-1} and multiplied it by 100 (Haberhauer et al., 1998). The two indices were then calculated as ratios of the relative absorbance of groups of bands representing functional group types (e.g., aliphatic, O-functional group) which in previous studies have been established as indices of relative decomposition and recalcitrance of SOM (Margenot et al., 2015):

$$\text{Index I} = \frac{1615+931+878+767}{2920+2851+1410}$$

$$\text{Index II} = \frac{2920+2851+1615+1410+931+878+767}{3312+1221+1072+2120}$$

Index I is considered to indicate the degree of decomposition as represented by the ratio of aromatic to aliphatic functional groups because the ratios of bands representing these two functional groups have been shown to increase with increasing degree of decomposition (Hsu and Lo, 1999). Index II represents relative recalcitrance of SOM (and hence resistance to decomposition) by determining a ratio of C functionality (aromatic and aliphatic, respectively) to O-functional groups where an increase of which is thought to be associated with greater recalcitrance of SOM (Margenot et al., 2015a; Veum et al., 2014).

5.2.3 Statistical analysis

All statistical analyses were performed using Minitab v. 18. The Johnson transformation was carried out to get data normally distributed prior to running a Mixed effects model (MEM). The Johnson transformation system based on derivation of the moments of the distribution which is appropriate for reducing skewness and to approximate normality (Senvar and Sennaroglu, 2016). The MEM analysis used land use and soil depth as fixed factors, whereas location was a random factor. Response variables were the bulk density, TOC, N, C/N ratio, SOC stocks, FTIR z-scores, and FTIR indices. The estimation method used was the Restricted maximum likelihood (REML) and test method for fixed effects used the Kenward-Roger approximation, followed by a Tukey multiple comparison test ($p<0.05$).

5.3 Results

5.3.1 Soil physico-chemical properties

All soils had a low bulk density which was consistently under 1.0 g cm^{-3}, ranging from 0.48 to 0.68 g cm^{-3} (Table 5.1) and increased down the soil profile, with statistically significant ($p<0.05$) differences observed, particularly between the top and bottom layers (Table 5.2; Figure 5.2). Statistical analysis indicated that forest soil (0.68 ± 0.05 g cm^{-3}) had a significantly ($p<0.05$) greater bulk density than 1 year old cinnamon plantation (0.48 ± 0.03 g cm^{-3}), while no significant ($p>0.05$) differences were observed between the bulk density of 10-year-old (0.60 ± 0.05 g cm^{-3}) and 5-year-old (0.53 ± 0.03 g cm^{-3}) cinnamon plantations (Table 5.1).

Conversion from natural forest to cinnamon plantation altered total organic carbon (TOC) concentrations in soils. The average TOC concentration down the soil profile of the natural forest (54.5 ± 10.2 g kg^{-1}) was significantly lower ($p>0.05$) than the concentration of soils 1 year after conversion to cinnamon plantation (68.61 ± 6.22 g kg^{-1}) but then tended to decrease significantly ($p<0.05$) as the plantation ageed, particularly when the plantation reached 10 years old (39.34 ± 5.59 g kg^{-1}). Topsoil had significantly ($p<0.05$) greater TOC concentrations than subsoils (Table 5.2).

Similar to TOC, N concentration revealed a similar pattern whereby, compared to the natural forest (3.71 ± 0.71 g kg^{-1}), N increased significantly ($p>0.05$) to 4.75 ± 0.40 g kg^{-1} in the 1-year-old plantation, but then decreased as the plantation became 5 (4.04 ± 0.47 g kg^{-1}) and 10 (3.02 ± 0.37 g kg^{-1}) years old. When comparing the 1-year-old plantations with the 10-year-old plantations, average N concentrations were significantly ($p<0.05$) lower in the 10-year-old plantations (Table 5.1). Table 5.2 shows that top layer (0-10 cm) had significantly ($p<0.05$) greater concentrations of N than deeper layers (20-100 cm).

The C/N ratio of the soils significantly ($p<0.05$) decreased with time after conversion to cinnamon plantation (Table 5.1). The C/N ratio of the forest soils (15.54 ± 0.45) were significantly greater ($p<0.05$) than the soils from 5-year-old (13.78 ± 0.32) and 10-year-old (12.61 ± 0.74) cinnamon plantations but were not significantly different ($p>0.05$) to the 1-

year-old (14.13 ± 0.32) plantations. However, there were no significant differences in C/N ratio between any layers down the soil profile (Table 5.2).

Table 5.1. Soil properties in the top 1 m of the soil profile under natural forest and 1-, 5-, and 10-year-old cinnamon plantations from three locations in the Kerinci Regency, Jambi Province of Indonesia (mean ± standard error mean, n = 30)

Land Use	Bulk Density ($g\ cm^{-3}$)	Total Organic Carbon (TOC) ($g\ kg^{-1}$)	Total N ($g\ kg^{-1}$)	C/N ratio
Forest	0.68 ± 0.05 a	54.50 ± 10.2 bc	3.71 ± 0.71 b	15.54 ± 0.45 a
Cinnamon Y1	0.48 ± 0.03 b	68.61 ± 6.22 a	4.75 ± 0.40 a	14.13 ± 0.32 ab
Cinnamon Y5	0.53 ± 0.03 ab	54.36 ± 5.95 ab	4.04 ± 0.47 ab	13.78 ± 0.32 b
Cinnamon Y10	0.60 ± 0.05 ab	39.34 ± 5.59 c	3.02 ± 0.37 b	12.61 ± 0.74 b

Different letters within a column represent statistically significant differences at α = 0.05. Data were averaged across all of 10 depth increments and all three locations (Lempur, RKE and Pungut) for each land use.

Table 5.2. Soil properties in successive 10 cm intervals in the top 1 m of the soil profile in the Kerinci Regency, Jambi Province of Indonesia (mean ± standard error mean, n=12)

Depth (cm)	Bulk Density ($g\ cm^{-3}$)	Total organic carbon (TOC) ($g\ kg^{-1}$)	Total N ($g\ kg^{-1}$)	C/N ratio	C Stock ($Mg\ Ha^{-1}$)
0-10cm	0.44 ± 0.04 b	118.22 ± 12.98 a	8.55 ± 0.87 a	13.69 ± 0.38 a	49.33 ± 5.8 a
10-20cm	0.45 ± 0.04 ab	83.87 ± 12.58 ab	6.18 ± 0.92 ab	13.70 ± 0.51 a	35.42 ± 5.1 ab
20-30cm	0.52 ± 0.05 ab	68.88 ± 8.84 bc	4.93 ± 0.64 bc	14.15 ± 0.63 a	34.24 ± 5.3 ab
30-40cm	0.53 ± 0.06 ab	60.57 ± 9.07 bcd	4.09 ± 0.52 bcd	14.44 ± 0.80 a	27.88 ± 3.7 bc
40-50cm	0.58 ± 0.06 ab	52.44 ± 8.34 bcde	3.59 ± 0.49 bcde	14.37 ± 0.72 a	26.31 ± 3.3 bc
50-60cm	0.62 ± 0.08 ab	42.81 ± 8.08 cdef	2.92 ± 0.47 cdef	14.36 ± 0.77 a	22.13 ± 2.9 bcd
60-70cm	0.62 ± 0.07 ab	37.05 ± 7.50 def	2.67 ± 0.43 cdef	13.96 ± 0.83 a	19.52 ± 2.7 cd
70-80cm	0.64 ± 0.08 ab	31.36 ± 6.29 def	2.34 ± 0.40 def	13.81 ± 0.85 a	15.67 ± 1.8 cd
80-90cm	0.65 ± 0.07 a	25.87 ± 4.42 ef	1.93 ± 0.29 ef	14.52 ± 1.31 a	14.56 ± 2.1 d
90-100cm	0.67 ± 0.07 a	20.96 ± 3.08 f	1.61 ± 0.20 f	13.13 ± 1.20 a	12.27 ± 1.7 d

Different letters within a column represent statistically significant differences at α = 0.05. Data were averaged across all four land uses (Forest and 1, 5, and 10 year old cinnamon plantations) and all three locations (Lempur, RKE and Pungut) at each depth.

5.3.2 Soil carbon stocks

On average, carbon stocks of the 10 cm layers decreased significantly ($p<0.05$) down the soil profile (Figure 5.2; Table 5.2). Statistical analysis revealed significant ($p<0.05$) differences between SOC stocks at the different plantation ages (Table 5.3). Carbon stocks to 1 m soil depth under 1 year old cinnamon plantations (294.83 ± 21.94 Mg Ha^{-1}) were the greatest and were significantly ($p<0.05$) greater than those observed in 10-year-old cinnamon plantations (180.85 ± 22.01 Mg Ha^{-1}), but not significantly ($p>0.05$) different to the forest soils (278.05 ± 42.06 Mg Ha^{-1}) or the 5-year-old cinnamon plantations (275.43 ± 27.13 Mg Ha^{-1}) (Table 5.3).

The impact of soil depth and land use on carbon stocks was further investigated by calculating stocks based on topsoil (0-30cm) and subsoil (30-100cm) layers, as shown in Figure 5.3. In the topsoil layers, forest soils (143.0 ± 37.9 Mg Ha^{-1}) had the greatest stocks, which were significantly ($p<0.05$) greater than the 10-year-old cinnamon plantations (83.1 ± 22.5 Mg Ha^{-1}), but not significantly different ($p>0.05$) to either the 5-year-old (136.6 ± 8.25 Mg Ha^{-1}) or 1-year-old (113.0 ± 21.6 Mg Ha^{-1}) cinnamon plantations (Table 5.3). Interestingly, 1-year-old cinnamon plantations had the largest subsoil C stocks (181.8 ± 12.1 Mg Ha^{-1}), and these were significantly ($p<0.05$) greater than forest subsoil C stocks (135.0 ± 42.9 Mg Ha^{-1}) and 10-year-old cinnamon plantation subsoil C stocks (97.7 ± 33.7 Mg Ha^{-1}), but not significantly ($p>0.05$) different to 5-year-old cinnamon plantation subsoil C stocks (138.8 ± 31.7 Mg Ha^{-1}) (Table 5.3).

Table 5.3. SOC stocks (Mg Ha^{-1}) (mean ± standard error mean, n=3) under different land uses and layers; topsoil (0-30cm), subsoil (30-100cm) and whole 1 m depth.

Land use	C stocks (Mg Ha^{-1})		
	Topsoil	Subsoil	1 m
Forest	143.0 ± 37.9 ab	135.0 ± 42.9 b	278.0 ± 74.1 a
C Y1	113.0 ± 21.6 ab	181.8 ± 12.1 a	294.8 ± 12.2 a
C Y5	136.6 ± 8.25 a	138.8 ± 31.7 ab	275.4 ± 39.9 a
C Y10	83.1 ± 22.5 b	97.7 ± 33.7 b	180.8 ± 55.6 b

Different letters within a column represent statistically significant differences at α = 0.05
Data were averaged across all three locations (Lempur, RKE and Pungut).

5.3.3 TOC, N, CN ratio and Organic carbon functional groups identified in fPOM

TOC, N and C N ratio of fPOM fraction were not significantly different (P>0.05) under all land uses (Table 5.4, Fig. 5.4). Although treatments were not significantly different from one another, the TOC and N of fPOM had a similar pattern to SOC and total N, as shown in Table 5.4. TOC and total N of fPOM increased 1 year after forest conversion but then decreased after 5 and 10 years of plantation (Table 5.4). Meanwhile, the C N ratio of fPOM slghtly increased 1 year after plantation establishment, but then decreased after 5 and 10 years (Table 5.4).

Along the soil profile, we found that fPOM TOC, Total N, and C N ratio were significantly different between topsoil and subsoil (Table 5.5, Fig. 5.4). TOC and Total N of fPOM were greater in topsoil than subsoil whereas C N ratio was lower in topsoil and tended to increase with depth (Table 5.5, Fig. 5.4). Unfortunately, for C Y5, we obtained insufficient fPOM from the SOC fractionation to be analysed for C and N concentration in the subsoil layer, so the graph only shows the trend until 20-30 cm depth. However, we assume the trend would be similar with other land uses that showed decreasing (C and N concentration) and increasing (C N ratio) with depth (Figure 5.4).

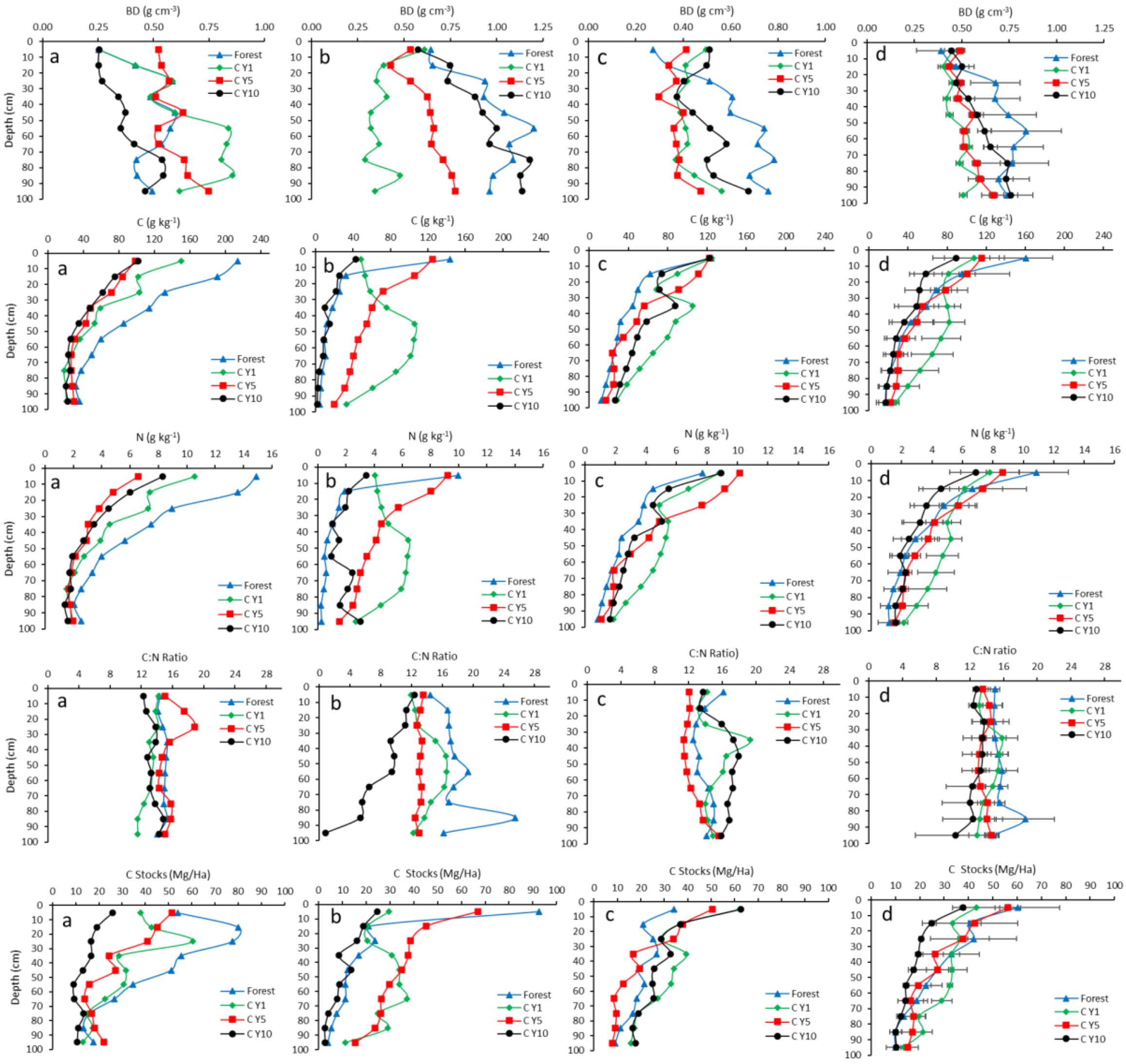


Figure 5.2. Bulk density (g cm^{-3}), Total organic carbon (TOC) (g kg^{-1}), total nitrogen (g kg^{-1}), C/N ratio, and SOC stocks at 10 cm depth increments to 1 m under forest and several different ages of Cinnamon plantation (1, 5, and 10 years old, respectively) at Lempur (a), Pungut (b) and Renah Kayu Embun (c) locations in Kerinci, Jambi Province, Indonesia. Graph (d) of each parameter shows the mean values from all three locations and error bars represent the standard errors of the mean using the three locations as replicates (n = 3).

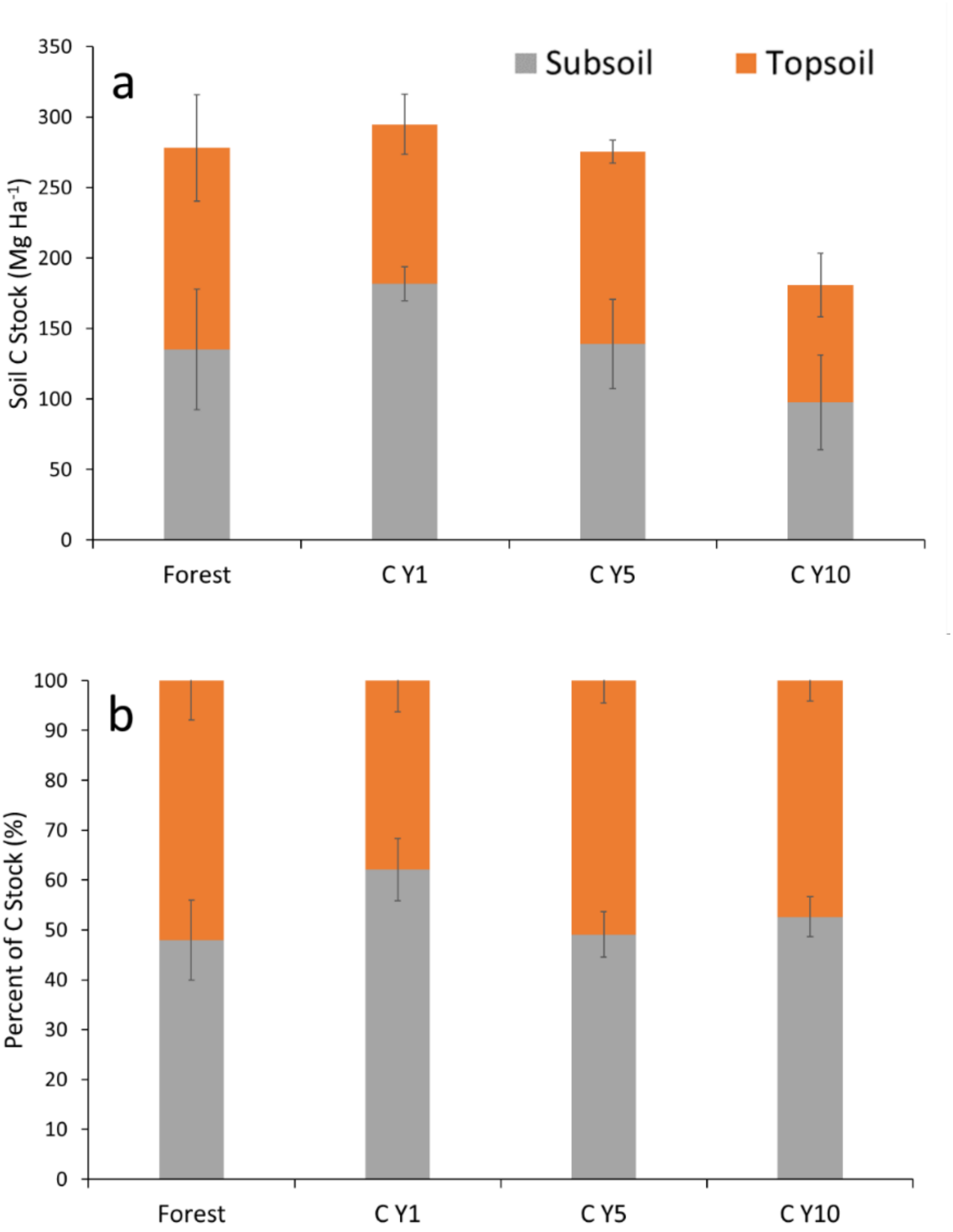


Figure 5.3. Mean SOC stocks in Mg Ha^{-1} (a) and in percentage (b) between topsoil (0-30 cm) and subsoil (30-100 cm) layers under natural forest and three different ages of cinnamon plantation (i.e. at year 1 (C Y1), year 5 (C Y5) and year 10 (C Y10) after conversion from natural forest from three locations (Lempur, RKE and Pungut) in the Kerinci Regency, Jambi Province of Indonesia (n = 3).

Table 5.4 fPOM concentration of Total organic carbon (TOC) (g/kg), Total N (g/kg) and C/N ratio under different land uses (mean ± standard error of the mean).

Landuse	TOC (g/kg)	Total N (g/kg)	C N Ratio
Forest	121.67 ± 11.56 a	7.22 ± 0.89 a	17.46 ± 0.77 a
Cinnamon Y1	133.75 ± 11.68 a	7.64 ± 0.66 a	17.77 ± 0.90 a
Cinnamon Y5	109.39 ± 10.94 a	8.33 ± 1.22 a	13.51 ± 0.65 a
Cinnamon Y10	117.82 ± 8.76 a	7.22 ± 0.89 a	16.20 ± 1.54 a

Different letters within a column represent statistically significant differences at α = 0.05. Data are the mean of four selected depths (0-10 cm, 20-30 cm, 50-60 cm, and 90-100 cm) and three different locations (Lempur, RKE and Pungut) for each land use.

Table 5.5 fPOM concentration of Total organic carbon (TOC) (g/kg), Total N (g/kg) and C/N ratio for selected topsoil (0-10 cm and 20-30 cm) and subsoil (50-60 cm and 90-100 cm) layers (mean ± standard error of the mean)

Soil Depth	TOC (g/kg)	Total N (g/kg)	C N Ratio
0 – 10 cm	135.38 ± 7.60 a	9.24 ± 0.54 a	14.78 ± 0.56 b
20 – 30 cm	123.87 ± 12.21 ab	7.43 ± 0.55 b	16.72 ± 1.06 ab
50 – 60 cm	115.92 ± 12.91 ab	5.88 ± 0.54 b	19.69 ± 0.93 a
90 – 100 cm	93.86 ± 13.96 b	5.52 ± 0.91 b	17.57 ± 1.65 ab

Different letters within a column represent statistically significant differences at α = 0.05. Data were averaged across all four land uses (Forest and 1, 5, and 10 year old cinnamon plantations) and all three locations (Lempur, RKE and Pungut) at each selected depth.

The raw FTIR-ATR spectra of the fPOM fraction (Appendix 3, Figure SI-1) revealed several characteristic major absorbance peaks representing the molecular structure of fPOM in the frequency range of 4000 to 600 cm^{-1}. Although the influence of soil depth and land use on the z-score transformed absorbance of all 11 identified peaks observed in the FTIR spectra of fPOM were analysed using MEM (Table SI-3), only bands attributed to aromatic C-H (bands 767, 878, and 931) and O functional groups (bands 3312) and carbohydrate (2120) significantly differed ($p < 0.05$) with land use (Table 5.6; Figure 5.5). All these bands showed a similar pattern with absorbance intensity in the order Forest > Cinnamon Year 1 > Cinnamon Year 10 > Cinnamon Year 5, except band 3312, which showed the opposite (i.e., Forest < Cinnamon Year 1 < Cinnamon Year 10 < Cinnamon Year 5).

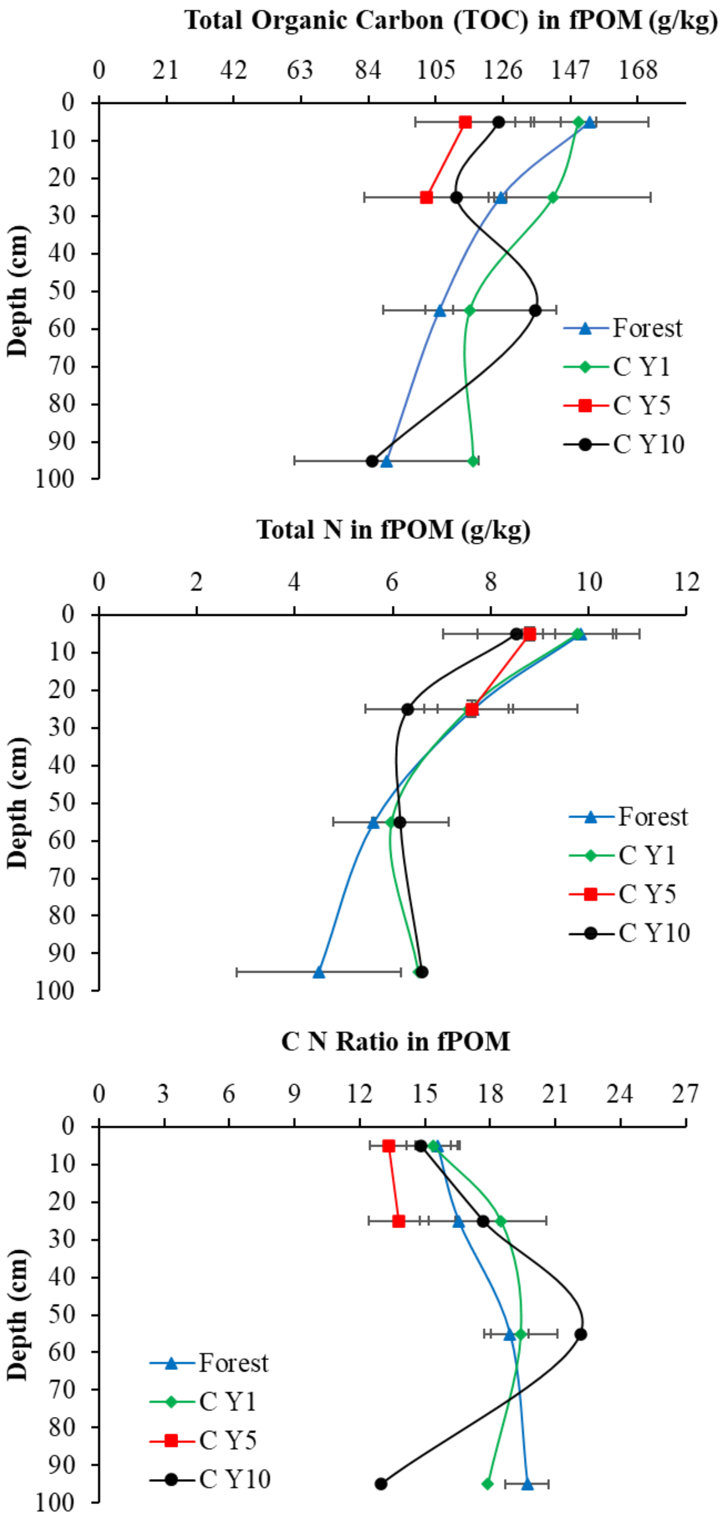


Figure 5.4 Concentration of Total organic carbon (TOC), Total N (g/kg) and C N ratio of fPOM under different forest and various cinnamon plantation ages down the soil profile. Data were averaged across all study locations (Lempur, RKE and Pungut), n = 3.

Table 5.6. Relative absorbance (z-score transformed absorbance) of selected bands obtained from Fourier-transform infrared (FTIR) spectra of free particulate organic matter (fPOM) down the soil profile under natural forest and three different ages of cinnamon plantation; Cinnamon plantation year 1 (C Y1), Cinnamon plantation year 5 (C Y5) and Cinnamon plantation year 10 (C Y10). from three locations in the Kerinci Regency, Jambi Province of Indonesia (mean ± standard error mean, n = 12)

Band (cm^{-1})/	Land use			
Index no.	Forest	Cinnamon Y1	Cinnamon Y5	Cinnamon Y10
767	2.79 ± 0.26 a	2.76 ± 0.47 a	1.65 ± 0.42 b	2.03 ± 0.19 ab
878	2.98 ± 0.12 a	2.38 ± 0.32 ab	1.56 ± 0.29 c	2.25 ± 0.12 b
931	1.81 ± 0.08 a	1.65 ± 0.13 ab	1.22 ± 0.22 b	1.42 ± 0.09 ab
2120	-0.55 ± 0.03 ab	-0.59 ± 0.03 ab	-0.48 ± 0.08 a	-0.68 ± 0.01 b
3312	1.05 ± 0.15 b	1.60 ± 0.10 a	1.80 ± 0.19 a	1.61 ± 0.06 a
Index I	1.78 ± 0.08 a	1.50 ± 0.06 ab	1.41 ± 0.08 b	1.66 ± 0.08 ab

Different letters within a row represent statistically significant differences at α = 0.05. Data are the mean of four selected depths (0-10 cm, 20-30 cm, 50-60 cm, and 90-100 cm) and three different locations (Lempur, RKE and Pungut) for each land use.

Table 5.7. Relative absorbance (z-score transformed absorbance) of selected bands obtained from Fourier-transform infrared (FTIR) spectra of free particulate organic matter (fPOM) from selected topsoil (0-10 cm and 20-30 cm) and subsoil (50-60 cm and 90-100 cm) layers of the soil profile under natural forest and three different ages of cinnamon plantation from three locations in the Kerinci Regency, Jambi Province of Indonesia (mean ± standard error mean, n = 12)

Soil layer	Bands	
	767	878
0-10 cm	3.03 ± 0.35 a	2.70 ± 0.20 a
20-30 cm	2.52 ± 0.31 ab	2.44 ± 0.22 ab
50-60 cm	1.81 ± 0.41 b	2.01 ± 0.33 b
90-100 cm	1.86 ± 0.33 b	2.01 ± 0.28 b

Different letters within a column represent statistically significant differences at α = 0.05. Data were averaged across all four land uses (Forest and 1, 5, and 10 year old cinnamon plantations) and all three locations (Lempur, RKE and Pungut) at each selected depth.

The z-score transformed absorbance at bands 767 and 878 significantly differed ($p < 0.05$) with soil depth (Table 5.7; Figure 5.5). The intensity of absorbance of aromatic C-H (bands 878 and 767) decreased significantly ($p < 0.05$) with depth (Table 5.7), indicating that the aromaticity of fPOM in topsoil is significantly ($p < 0.05$) greater than the fPOM found in the subsoil layer of the soil profile.

MEM analysis of the FTIR band indices of SOM decomposition (Index I) and recalcitrance (Index II) showed that index I significantly differed with land use ($p < 0.05$), but not depth ($p > 0.05$). Despite index II showed no significant difference with either land use or depth, forest had slightly higher value compare with all cinnamon plantations and soil depth (Figure 5.6; Appendix 3, Table SI-3). Index I, which represents the abundance of aromatic C=C and C-H functional groups, relative to aliphatic C-H functional groups, categorised the land uses in the order; Forest > Cinnamon Year 10 > Cinnamon Year 1 > Cinnamon Year 5 (Table 5.6). fPOM from the Forest soils had a significantly higher ($p < 0.05$) index I value than the 5-year-old cinnamon plantation soils but were not significantly different ($p > 0.05$) to 1 year old or 10-year-old cinnamon plantations (Table 5.6). This trend shows that the degree to which fPOM was decomposed decreased after forest conversion until year 5 of cinnamon plantation, but then increased again after 10 years.

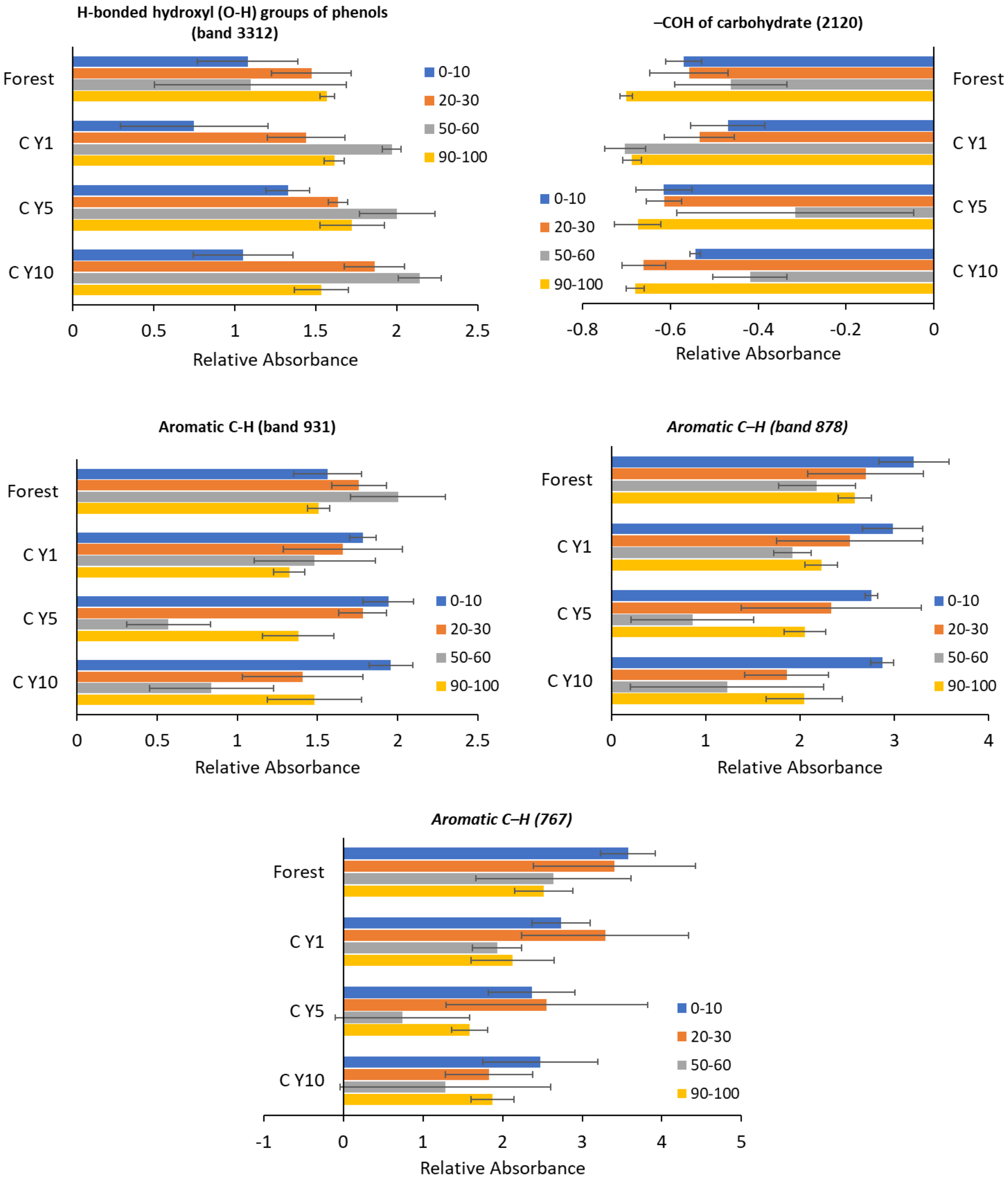


Figure 5.5. Relative absorbance (z-score transformed absorbance) of selected bands obtained from Fourier-transform infrared (FTIR) spectra of free particulate organic matter (fPOM) fraction down the soil profile under natural forest and three different ages of cinnamon plantation; Cinnamon plantation year 1 (C Y1), Cinnamon plantation year 5 (C Y5) and Cinnamon plantation year 10 (C Y10) from three locations in the Kerinci Regency, Jambi Province of Indonesia, which were each used as replicates. (mean ± standard error mean, n = 12).

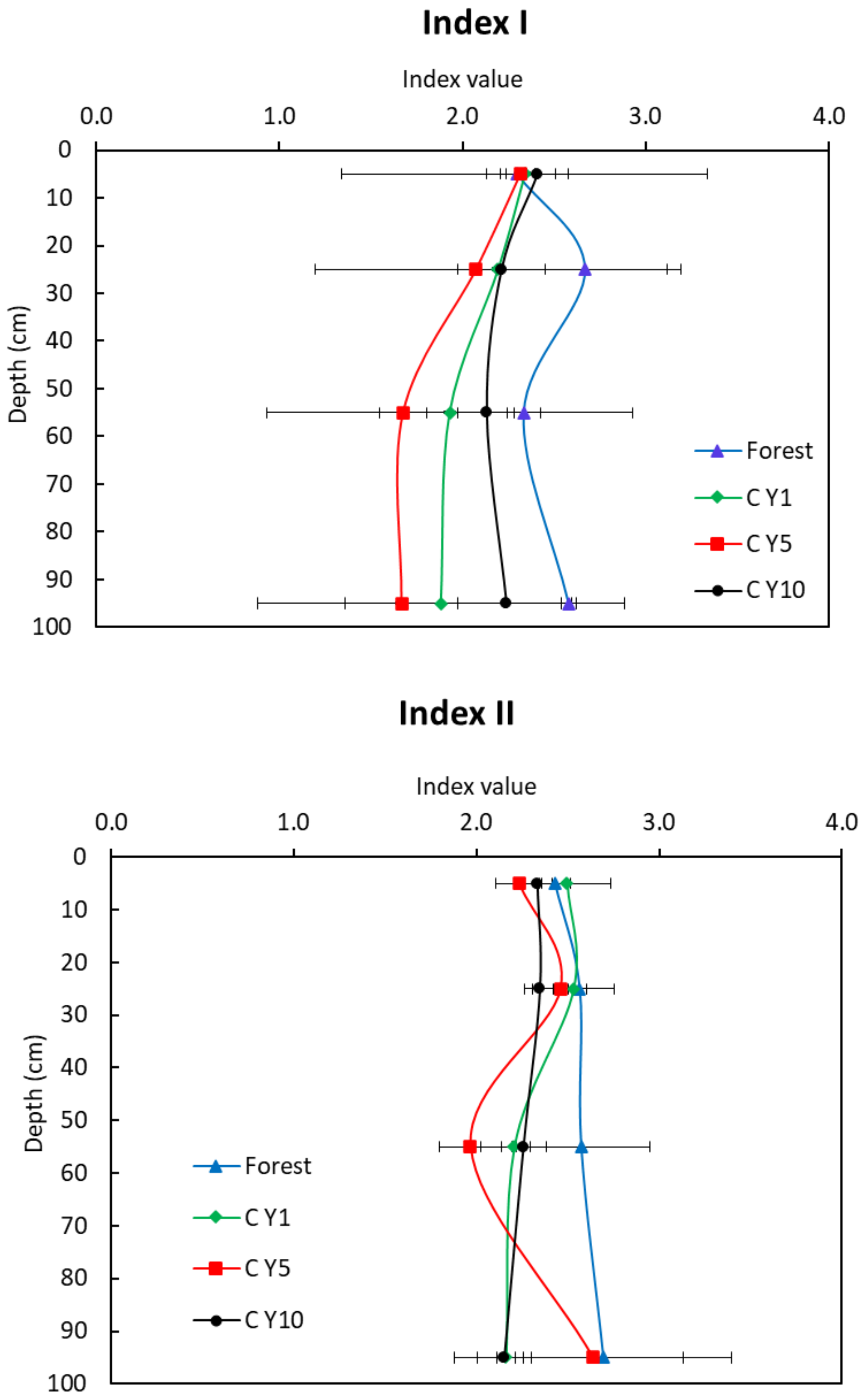


Figure 5.6. Fourier-transform infrared (FTIR) derived indices corresponding to free particulate organic matter (fPOM) degree of decomposition (Index I) and recalcitrance (Index II) down the soil profile under natural forest and three different ages of cinnamon plantation; Cinnamon plantation year 1 (C Y1), Cinnamon plantation year 5 (C Y5) and Cinnamon plantation year 10 (C Y10) from three locations in the Kerinci Regency, Jambi Province of Indonesia. (mean ± standard error mean). Data are the mean of three locations (Lempur, RKE and Pungut).

5.4 Discussion

5.4.1 Topsoil and subsoil carbon stocks in tropical Andosols

The size of the C stock that we measured (Table 5.3) in the top 1 m of soil under the natural rainforest in the Kerinci Regency of Jambi Province in Indonesia (278.0 ± 74.1 Mg Ha^{-1}) was slightly smaller than global average andosol C stocks (290±18 Mg Ha^{-1}) reported by Batjes (1996) and considerably lower than andosol C stocks measured in tropical rain forests in Hawaii (375±83 Mg Ha^{-1}) by Marin-Spiotta et al. (2011), in the Amazon basin (301 Mg Ha^{-1}) by Zieger et al. (2018) and in Ecuadorian forests (530±10 Mg Ha^{-1}) by Tonneijck et al. (2010). In agreement with our observations, about 50% of total C stocks in rainforest soils were observed by Marin-Spiotta et al. (2011) to be stored in subsoil layer. However, global soil data found that subsoils typically contain around 55% C stocks (Batjes, 1996).

5.4.2 Effect of land use change on soil organic matter and carbon stocks

The low soil bulk density that we observed (Table 5.1) under all study sites (0.48 - 0.68 g cm^{-3}) is similar to observations made on other Indonesian andosols (0.37 – 0.9 g cm^{-3}) by Sukarman and Dariah (2014) and within the range of global data (0.28 – 0.99 g cm^{-3}) reported by Batjes (1996). Moreover, our data reveal a significant decrease in bulk density that occurs in the first year after conversion from forest to cinnamon plantation. During the first year of conversion from forest to cinnamon, farmers usually intercrop cinnamon trees with annual crops such as chilli and upland rice (Hariyadi and Ticktin, 2012).

Several other studies undertaken on tropical soils found an increase in bulk density due to the impact of conversion from forest to cultivated land, alongside a decreasing in SOC (Bizuhoraho et al., 2018; Choudhary et al., 2016; Don et al., 2011; Murty et al., 2002). However, in other soils bulk density was even lower in agricultural soil than forest soils (Deng et al., 2016; Murty et al., 2002). We revealed a decrease in bulk density during the initial year of forest conversion, together with an increase in SOC content, but then an increase in bulk density over time as the plantation gets more established. The main factor here is the content of SOC that becomes depleted over time and acts as an important factor in determining the decrease in bulk density (Al-shammary et al., 2018; Chaudhari et al., 2013). Because there are different bulk densities under different ages of plantation, using a fixed depth to quantify soil carbon stocks could result in errors and distort the comparison of carbon stocks between different ages of plantation. To address this issue, stocks could be quantified on an ‘equivalent soil mass’ basis (von Haden et al., 2020).

The significant decrease of bulk density after forest conversion to cinnamon plantation is probably partly due to an increase in pyrogenic soil organic matter (Thomaz, 2017; Thomaz et al., 2014), which has a lower density than mineral soil or fresh SOM, entering the soil due to the slashing and burning of vegetation prior to cultivation (McDaniel et al., 2012). However, we would have expected this explanation to be supported by greater recalcitrance of the fPOM after conversion, but this was not observed in our analysis (Figure 5.6). Studies on the impact of fire associated with shifting cultivation (Ando et al., 2014; Tanaka et al., 2001) found that burning increases soil organic C and N, which we did observe (Figure 5.2). However, the cleared land is only fertile for a couple of years before the nutrients released by slash and burn are exhausted (Sukarman and Dariah, 2014).

After an initial increase during conversion from natural forest to cinnamon plantation, we observed decreasing total C and N concentrations along a chronosequence of cinnamon plantations with increasing age (Table 5.1). The initial increase one year after conversion is likely due to a high input of organic matter from slash and burn activities when clearing the forest. In particular, we observed that the subsoil carbon stock increased 1 year after forest conversion to Cinnamon plantation, although the stock then tends to decrease gradually as the cinnamon plantation get older (Table 5.3; Figure 5.3). We observed a significant decrease in soil bulk density in the first year after conversion from forest vegetation (0.68 ± 0.05 g cm^{-3}) to cinnamon plantation (0.48 ± 0.03 g cm^{-3}). This decrease in bulk density not only directly influences the C stocks, it also causes the soil to become more porous resulting more SOM transported by leaching to the subsoil, leading to an increase in the C and N concentration (Figure 5.2) and carbon stock (Figure 5.3) in the subsoil, as also noted in a review of shifting cultivation systems by Ribeiro Filho et al. (2013). Supporting this interpretation is the observed increase in the proportion of the C stock that is stored in the subsoil layer in the soils converted from forest to cinnamon plantations of all ages. Zieger et al. (2018) revealed that larger C stocks in subsoils of andosols than topsoils, despite high SOC inputs were because of the limited binding capacities of topsoil mineral phases. Therefore, the less strongly bound SOM entering topsoils moves through the soil profile to deeper layers of the soil due to leaching water processes (Kaiser and Kalbitz, 2012) and most likely is largely leached out of the top 1 m within 5 years of conversion.

Our finding that land use change ultimately reduces soil C stocks in the long term (Figure 5.3) is in accordance with several studies on carbon stocks that report SOC losses after land uses conversion from primary forest to agricultural land (Don et al., 2011; Filho et al., 2013; Lal, 2018; van Straaten et al., 2015). However, the approximately 6% increase in C stocks under cinnamon just one year after conversion from forest vegetation is less commonly reported. It probably as a result of an increase in mineral carbon (black carbon) and carbonated matter (Filho et al., 2015). However, the 1 m C stocks decrease gradually as the cinnamon plantation gets older. This finding is supported by the fact declining of carbohydrate groups (Table 5.6) as cinnamon plantation gets older showing less input fresh material (Hsu and Lo, 1999). The low C N ratio (Table 5.4) and increasing hydroxyl groups content (Table 5.6) indicating faster decomposition leading to SOC loss (Hsu and Lo, 1999; Veum et al., 2014; Yeasmin et al., 2020). Losses of soil C, particularly fPOM under regular cultivation are well established in the literature, and usually occur within a few years of starting cultivation (Ashagrie et al., 2007; Murty et al., 2002).

5.4.3 Effect of land use change on soil organic matter quality at depth

While we observed no effect of bulk soil depth on soil C/N ratio, we did observe that C/N ratio decreased significantly with time after conversion to cinnamon plantation, largely because C decreases to a greater extent than N. The decrease in soil C may have been caused by C loss as CO_2 during the decomposition process in the absence of N losses from the soil (Jobbágy and Jackson, 2000). The decreases in soil C/N ratios after conversion may reflect enhanced microbial processing of soils and/or improved quality of organic matter input (van Straaten et al., 2015). We investigated this further by obtaining the fPOM fraction of the SOM since this is the fraction that is most easily accessible by soil organisms and thus drives many soils functions (Hoffland et al., 2020; Lavallee et al., 2019).

In accordance with the study of Guo et al. (2010), we also found that fPOM from different land uses have similar FTIR spectra (Appendix 3, Figure SI-1). Further investigation of the fPOM fractions indicated that the carbon content of fPOM decreases down the soil profile perhaps indicating that a major source of fPOM in subsoils is from leaching of DOC from the topsoil (Marin-Spiotta et al., 2011). Decreasing aromatic C-H groups down the soil profile could imply that there is less fresh plant material (e.g., carbohydrates and lignin) in the subsoil, while a higher C/N ratio of the fPOM indicates that the fPOM in the subsoil is less microbially processed (Veum et al., 2014). Because there are fewer fresh plant inputs, the fPOM in the subsoil may be older and already have undergone microbial processing in the topsoil before it leached. However, greater C/N ratio in subsoils than topsoils is probably also indicator of a different source of fPOM between both layers whereby the subsoil layer mainly consists of carbon from fine root contribution (Soucémarianadin et al., 2019) that has higher C/N ratios (50–60) (Hobbie et al., 2010), compared with C/N ratios of fresh foliage or humus layers which range between 10 and 32 (Cools et al., 2014).

We observed that the degree of decomposition (Index I) of the fPOM fraction of SOM was greatest in the forest soils and that this tends to decrease after conversion to cinnamon plantation, but increases again 10 years after conversion (Table 5.4, Figure 5.5). The differences between land use that we observe here are clearly seen at Table 5.6 where the proportion of aromatic groups (band 767, 878, 931) in the forest soils were greater than soils after conversion indicating more decomposed carbon (Veum et al., 2014). This also arises because of more litter input from vegetation to forest soil, leading to higher decomposition rates by microorganism (Jobbágy and Jackson, 2000). Although the total C stocks of a 10-year-old cinnamon plantation are still the lowest of all the land uses surveyed, the degree of decomposition of the fPOM is higher than freshly converted plantations, which demonstrates the progression of decay of the flush of fresh organic inputs that resulted from the slash and burn activities (Margenot et al., 2015a). Further observation of fPOM quality at depth shows the decreasing content of aromatic-C with depth, indicating less microbial activity happens in the down 1 m depth. All these findings are supported by the study of Soucémarianadin et al. (2019) which revealed that fPOM chemistry variations depending on vegetation and soil depth.

5.5 Conclusion

Subsoils contain approximately half of soil carbon stocks, but fresh organic matter decreases down the soil profile, as evidenced by the reduction in aromatic and carbohydrate groups in subsoil particulate organic matter relative to topsoil particulate organic matter. In the first year after conversion from forest, the slash and burn activities added pyrogenic carbon into the soil, which then leached down the soil profile, as evidenced by an increase in bulk density, higher C and N concentrations but a lower C/N ratio, higher subsoil carbon stocks and more aliphatic groups in the subsoil particulate organic matter, leading to a lower degree of decomposition. These observations, made one year after plantation establishment, do not support our hypothesis that topsoil and subsoil carbon stocks decrease and SOC becomes more degraded with age of cinnamon plantation. However, comparing the forest with the older cinnamon plantations, there is less fresh litter input, as evidenced by topsoil and subsoil carbon stocks decreasing over time, a decrease in the carbohydrate and increase in hydroxyl groups in particulate organic matter of older cinnamon plantation, an increase in bulk density and decrease in the degree of decomposition of particulate soil organic matter. These observations do support our hypothesis and cause us to qualify that these observations only emerge several years after forest conversion to cinnamon plantation. Further research is required related to litter inputs and processes involved in the stabilisation of SOC down the soil profile, since these processes are likely to play a key role in tropical forest soil C sequestration. Future work should include elucidating the underlying mechanisms. Finally, applying good agricultural practices (such as avoiding burning when land clearing, applying cover crops, selective harvesting instead of total cutting down all vegetation at the same time, increasing harvest time up to year 15) are important to mitigate the loss of SOC from the soil and may increase yield for farmers.

Chapter VI – General Discussion

6.1. The dynamics of soil organic carbon under different land use in tropical and temperate soils

It is well known that soil organic carbon (SOC) content depends on vegetation as a source of fresh organic matter (Jobbágy and Jackson, 2000). As discussed in Chapter 3, this thesis confirms that SOC concentration in UK soils is influenced by vegetation, as revealed by the finding that woodland soils have significantly higher SOC concentrations, compared with agricultural land (grassland and arable). Also, in Chapter 5, a study on Indonesian Andosols showed that conversion from native forest to cinnamon plantation resulted the depletion of SOC; exhibited by a decrease in SOC stocks with increasing age of plantation. Both studies in UK and Indonesia revealed that soils under native vegetation contain higher quantities of SOC; as found in numerous other studies (Bradley et al., 2005; Guo and Gifford, 2002; Hendrickson, 2012; Murty et al., 2002; van Straaten et al., 2015). These chapters provide useful data that quantifies the impact of land use change on soil carbon that are of importance to policy makers interested in reducing greenhouse gas emissions.

On average, Indonesian tropical forest soils contain more SOC than UK temperate woodlands. This phenomenon is explained by Blais et al. (2005) who found that the carbon density in the top 1 meter of temperate woodland and tropical forest soil differ between 8.5 and 13.9 kg C/m^2 because tropical forest has very high flora diversity (200-300 tree species per hectare) resulting in around 123 t/ha SOC, compared with around 96 t/Ha in temperate regions (Malhi et al., 1999). Martinelli et al. (1999) revealed that N is relatively abundant in many tropical forest topsoils and subsoils; amounting to N levels almost 8% higher than temperate forest soils.

Overall, SOC concentration was higher in the Indonesian study sites than UK soil. This finding is also related the soil types where the samples were collected for both studies. As discussed in Chapter 3, UK soil samples were collected in seasonally flooded Gleysol, Planosol and Luvisol soil types, which are known to contains lower quantities of carbon compared with Andosol soils in Indonesia (Chapter V) (Batjes, 1996). Based on a global data set reported by Batjes (1996), Andosols contained large stocks of SOC (25.4 kg C m^{-2}) that are explained by the protection process of SOC by allophane and imogolite minerals

(Batjes, 1996; Zieger et al., 2018). It is therefore of critical importance that the forests on Andosols in Indonesia, and other tropical countries, are protected from deforestation.

The fPOM, as a labile SOC fraction which is easily to decompose (Chan, 2001), was found to be more abundant under natural vegetation than under agricultural land uses, both in Indonesian and UK soils. Therefore, changes in fPOM abundance can be used as an early warning indicator that is predictive of changes that we may observe in total SOC concentrations and stocks. Similar to SOC content, the carbon content of fPOM was greater in tropical soils than temperate soils. However, the C/N ratio of fPOM was lower in all tropical soils (13.51 ± 0.65 to 17.77 ± 0.90) which suggests a greater decomposition rate than temperate soils (18.95±1.14 to 21.28±1.29) (Guo et al., 2010).

Generally, the chemical composition of fPOM under different land uses, either in Indonesian or UK soils, were similar. Our observations indicate that fPOM under different land uses are mainly differentiated by relative proportions of carbohydrates and O functional groups; indicating differences in the quantity and quality of fresh organic matter (OM) inputs and rate of decomposition process (Hsu and Lo, 1999), respectively. Significant components of various aromatic carbon structures under all land uses in tropical soils suggested that the fPOM contained more decomposed and less aliphatic material (Wen et al., 2021) as a result of faster decomposition processes in the tropics (Ross, 1993). Conversely, in the temperate region, with slower decomposition rates (Blais et al., 2005), we observed more carboxyl groups indicating less disturbed OM, or plant material in the early stages of decomposition process (Yeasmin et al., 2020). It is therefore likely that the depletion of SOC stocks in tropical soils will proceed at a faster rate than the depletion of SOC stocks in temperate soils.

6.2. The dynamics of soil organic carbon in tropical and temperate region down the soil profile

A key knowledge gap concerning SOC dynamics gave rise to this study mainly because much work still focuses on shallow soil layers (0-30cm) while the majority of SOC stocks are stored in subsoil layers, where the mechanisms responsible for SOC preservation is less well understood (Lal, 2018; Rumpel and Kögel-Knabner, 2011).

Overall, SOC concentration of bulk soil was observed to decrease down the soil profile both in UK soils (Chapter 3) and Indonesian soils (Chapter 5). This finding in accordance with other studies (Dignac et al., 2017; Harrison et al., 2011; Lal, 2017) that confirm that topsoils are enriched with OM directly from plant litter and root input which decreases with soil depth. SOC stock calculations of Indonesian soils also indicated that there were greater carbon stocks, per 10 cm layer, in topsoil layers than subsoil layers. Reductions in SOC stocks after land use change indicate that OM input is lower than carbon release from the soil as result of enhanced decomposition and nutrient mineralisation rates after forest conversion (Ross, 1993). Therefore, this thesis provides valuabe insights into the impact of land management change on subsoil SOC and fPOM dynamics that should be taken into account when calculating the carbon emitted from deforestation.

SOC physical fractionation analysis (Chapter 3) revealed that mineral associated OM (MinOM) was the main fraction in topsoils and its importance increases down the soil profile. This finding indicated that soil minerals associated with OM play important roles in SOC preservation down the whole soil profile (John et al., 2005; Plaza et al., 2013, 2012). Further investigation should highlight soil types that have the greatest potential to store carbon associated with minerals in the subsoil and prioritise these for protection or restoration.

In general, the fPOM carbon concentration was found to decrease down the soil profile both in UK (Chapter 4) and Indonesian soils (Chapter 5) because the importance of fresh litter input as source of SOC is greater in topsoils than subsoils (Hsu and Lo, 1999; Veum et al., 2014). Interestingly, a contrasting pattern that fPOM carbon concentration down the soil profile under natural conditions (forest/woodland) in Indonesia decreased with soil depth whereas UK soils showed increasing down the soil profile. The UK result was probably caused by decreasing SOC turnover with depth because of slow decomposition process in temperate regions (Blais et al., 2005) or anaerobic conditions due to waterlogging (Huang et al., 2020; Huang and Hall, 2017), resulting in higher SOC accumulations per unit of C input in deep soil layers (Jobbágy and Jackson, 2000).

The chemical structure of fPOM in UK subsoils was dominated by aliphatic groups while Indonesian subsoils were dominated by the presence of aromatic groups. As discussed earlier, this difference possibly due to the stage of decomposition process that the fPOM is at. The UK is located in the temperate region, which has slower decomposition rates, resulting more simple material (aliphatic groups) than Indonesian tropical soil with faster decomposition resulting more complex or chemically recalcitrant material (aromatic groups) (Hsu and Lo, 1999; Wen et al., 2021; Yeasmin et al., 2020). However, both aromatic and aliphatic groups showed a similar trend to decrease down the soil profile. This indicates that fPOM material in deeper soil layers are less decomposed due to lower microbial activity (Soucémarianadin et al., 2019).

We found land use change both in Indonesia and UK resulted a decrease of SOC both in topsoils and subsoils. The SOC fractionation of UK soils revealed that all OM fractions were higher under natural vegetation compared to converted land down the soil profile (topsoil and subsoil). This fractionation also found that the topsoil layer was dominated by less protected fraction (fPOM) while subsoils were rich in organo-mineral associated carbon (MinOC) that is considered to be the most protected fraction of OM against decomposers. SOC stocks in Indonesian soil were found to increase after conversion from natural forest into cinnamon plantation, but then tended to decrease with increasing plantation age both in topsoil and subsoil layers. The fPOM quality showed similar spectra from Indonesia and UK soils where natural land use showed higher carbohydrates compounds compared with converted land use which is clearly related to vegetation as source of OM. The deeper the soil layer, the less decomposed fPOM is, due to limited microbial access, particularly in UK soils which are partially protected by waterlogging.

6.3 Contribution of the thesis to knowledge

This research focused on soil organic carbon (SOC), which has been widely aknowledeged as being an important store of carbon and it is critical that it is protected and/or restored to mitigate global warming. However, there are still many aspects related to SOC dynamics that are yet to be explored. Our study investigated the effect of land use change on SOC depletion in the top 1 m of soil profile, and therefore advances our knowledge beyond that acquired by most studies on SOC which still undertake sampling at shallow depths (around 0-30 cm). The locations of the research also enabled us to compare and contrast two regions (i.e., tropical and temperate region) in terms of SOC dynamics down the soil profile.

Although our study confirmed the findings of other studies that document SOC depletion after deforestation and land conversion from natural condition to agriculture, this study goes further by presenting data associated with subsoil layers, whereas most other studis still focus on the topsoil (0-30 cm) layer (Gross and Harrison, 2019; Lal, 2018). Moreover, the experiment undertaken in the tropics (Chapter 5), enriches the literature with rare but essential data regarding SOC loss affected by land use change that is currently underway. According to (Don et al., 2011), there is still limited quantitative data from studies reporting the effect of land use change on SOC from Soth East Asia, particularly Indonesia. This data is therefore important because this region currently contributes the greatest CO_2 emissions due land use changes. Based on this condition, SOC research related to land use change is still needed, particularly in Indonesia, to fill gaps in our knowledge of global soil cabon storage.

The soil organic carbon (SOC) fractionation methodology conducted in this study provides important data related to the status and distribution of SOC in the soil profile under various land uses. Again, because our study sampled up to 1 m depth of soil profile, we were able to see the vertical distribution of each fraction along the soil depth which is currently poorly documented (Rumpel and Kögel-Knabner, 2011; Soucémarianadin et al., 2019). This information is useful because it helps us predict how each SOC fraction may be distributed down the soil profile during and after to land use change. It therefore helps us to identify soils that are most susceptible to SOC loss due to land use change. Moreover, futher exploration through spectroscopy analysis of fPOM fractions reveals that the most labile and easy to decompose SOC fraction, fPOM, exhibits a high degree of similarity in terms of functional groups both in tropical and temperate soils. This study advances our understanding of the ability of soils to store more SOC in the subsoil, particularly under natural conditions. Further research should explore the effect on land management on SOC fractions in deep soil horizon and use it as one indicator of good management practice.

References

Abdalla, M., Hastings, A., Chadwick, D.R., Jones, D.L., Evans, C.D., Jones, M.B., Rees, R.M., Smith, P., 2018. Critical review of the impacts of grazing intensity on soil organic carbon storage and other soil quality indicators in extensively managed grasslands. Agric. Ecosyst. Environ. 253, 62–81.

Abson, D.J., Termansen, M., Pascual, U., Aslam, U., Fezzi, C., Bateman, I., 2014. Valuing Climate Change Effects Upon UK Agricultural GHG Emissions: Spatial Analysis of a Regulating Ecosystem Service. Environ. Resour. Econ. 57, 215–231.

Accoe, F., Boeckx, P., Cleemput, O. V, Hofman, G., Zhang, Y., Li, R.H., Guanxiong, C., 2002. Evolution of the δ13C signature related to total carbon contents and carbon decomposition rate constants in a soil profile under grassland. Rapid Commun. Mass Spectrom. 16, 2184–2189.

Acton, P., Fox, J., Campbell, E., Rowe, H., Wilkinson, M., 2013. Carbon isotopes for estimating soil decomposition and physical mixing in well-drained forest soils. Rapid Commun. Mass Spectrom. 118, 1532–1545.

Aggarwal, R.K., Kumar, P., Power, J.F., 1997. Use of crop residue and manure to conserve water and enhance nutrient availability and pearl millet yields in an arid tropical region. Soil Tillage Res. 41, 43–51.

Al-shammary, A.A.G., Kouzani, A.Z., Kaynak, A., Khoo, S.Y., Norton, M., Gates, W., 2018. Soil Bulk Density Estimation Methods : A Review. Pedosphere 28, 581–596.

Amundson, R., Therapeutics, A., Bottero, J., Masin, F., 2007. Mineral control of carbon pools in a volcanic soil horizon.

Ando, K., Shinjo, H., Noro, Y., Takenaka, S., Miura, R., Sokotela, S.B., Funakawa, S., 2014. Short-term effects of fire intensity on soil organic matter and nutrient release after slash-and-burn in Eastern Province, Zambia. Soil Sci. Plant Nutr. 60, 173–182.

Angst, G., Messinger, J., Greiner, M., Häusler, W., Hertel, D., Kirfel, K., Kögel-knabner, I., Leuschner, C., Rethemeyer, J., Mueller, C.W., 2018a. Soil organic carbon stocks in topsoil and subsoil controlled by parent material , carbon input in the rhizosphere , and microbial-derived compounds. Soil Biol. Biochem. 122, 19–30.

Angst, G., Messinger, J., Greiner, M., Häusler, W., Hertel, D., Kirfel, K., Kögel-Knabner, I., Leuschner, C., Rethemeyer, J., Mueller, C.W., 2018b. Soil organic carbon stocks in topsoil and subsoil controlled by parent material, carbon input in the rhizosphere, and microbial-derived compounds. Soil Biol. Biochem. 122, 19–30.

Archer, D., 2010. The Global Carbon Cycle. Princeton University Press.

Ascough, P.L., Bird, M.I., Francis, S.M., Lebl, T., 2011. Alkali extraction of archaeological and geological charcoal : evidence for diagenetic degradation and formation of humic acids. J. Archaeol. Sci. 38, 69–78.

Ashagrie, Y., Zech, W., Guggenberger, G., Mamo, T., 2007. Soil aggregation , and total and particulate organic matter following conversion of native forests to continuous cultivation in Ethiopia. Soil Tillage Res. 94, 101–108.

Bailey, K.L., Lazarovits, G., 2003. Suppressing soil-borne diseases with residue management and organic amendments. Soil Tillage Res. 72, 169–180.

Bailey, V.L., Pries, C.H., Lajtha, K., 2019. What do we know about soil carbon destabilization? Environ. Res. Lett. 14.

Baldock, J.A., Skjemstad, J.O., 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. Org. Geochem. 31, 697–710.

Bardgett, R.D., Keiller, S., Cook, R., Gilburn, A.S., 1998. Dynamic interactions between soil animals and microorganisms in upland grassland soils amended with sheep dung: A microcosm experiment. Soil Biol. Biochem. 30, 531–539.

Batjes, N.H., 1996. Total carbon and nitrogen in the soils of the world. Eur. J. Soil Sci. 47, 151–163.

Bell, M.J., Worrall, F., Smith, P., Bhogal, A., Black, H., Lilly, A., Barraclough, D., Merrington, G., 2011. UK land-use change and its impact on SOC: 1925-2007. Global Biogeochem. Cycles 25, 1–16.

Bernal, B., McKinley, D.C., Hungate, B.A., White, P.M., Mozdzer, T.J., Megonigal, J.P., 2016. Limits to soil carbon stability; Deep, ancient soil carbon decomposition stimulated by new labile organic inputs. Soil Biol. Biochem. 98, 85–94.

Bizuhoraho, T., Kayiranga, A., Manirakiza, N., Mourad, K.A., 2018. The Effect of Land Use Systems on Soil Properties ; A case study from Rwanda. Sustain. Agric. Res. 7, 30–40.

Blais, A.-M., Lorrain, S., Plourde, Y., Varfalvy, Louis, 2005. Organic Carbon Densities of Soils and Vegetation of Tropical, Temperate and Boreal Forests. In: Tremblay, A., Varfalvy, L, Roehm, C., Garneau, M. (Eds.), Greenhouse Gas Emissions — Fluxes and Processes. Springer, Berlin, Heidelberg, pp. 155–185.

Bloomfield, J.P., Bricker, S.H., Newell, A.J., 2011. Some relationships between lithology, basin form and hydrology : a case study from the Thames basin , UK. Hydrol. Process. 25, 2518–2530.

Boddy, E., Hill, P.W., Farrar, J., Jones, D.L., 2007. Fast turnover of low molecular weight components of the dissolved organic carbon pool of temperate grassland field soils. Soil Biol. Biochem. 39, 827–835.

Bol, R., Amelung, W., Friedrich, C., Ostle, N., 2000. Tracing dung-derived carbon in temperate grassland using 13c natural abundance measurements. Soil Biol. Biochem. 32, 1337–1343.

Bou, J., Krishna, V. V, Qaim, M., 2018. Land-use change and livelihoods of non-farm households : The role of income from employment in oil palm and rubber in rural Indonesia. Land use policy 76, 828–838.

BPS, 2018. Kerinci Regency in figure 2018.

Bradley, R.I., Milne, R., Bell, J., Lilly, A., Jordan, C., Higgins, A., 2005. A soil carbon and land use database for the United Kingdom. Soil Use Manag. 21, 363–369.

Cagnarini, C., Blyth, E., Emmett, B.A., Evans, C.D., Griffiths, R.I., Keith, A., Jones, L., Lebron, I., McNamara, N.P., Puissant, J., Reinsch, S., Robinson, D.A., Rowe, E.C., Thomas, A.R.C., Smart, S.M., Whitaker, J., Cosby, B.J., 2019. Zones of influence for soil organic matter dynamics: a conceptual framework for data and models. Glob. Chang. Biol. 1–12.

Cerli, C., Celi, L., Kalbitz, K., Guggenberger, G., Kaiser, K., 2012. Separation of light and heavy organic matter fractions in soil — Testing for proper density cut-off and dispersion level. Geoderma 170, 403–416.

Chan, K.Y., 2001. Soil particulate organic carbon under different land use and management. Soil Use Manag. 17, 217–221.

Chaudhari, P.R., Ahire, D. V, Ahire, V.D., Chkravarty, M., Maity, S., 2013. Soil Bulk Density as related to Soil Texture , Organic Matter Content and available total Nutrients of. Int. J. Sci. Res. Publ. 3, 1–8.

Choudhary, B.K., Majumdar, K., Datta, B.K., 2016. Effects of Land Use on the Soil Organic Carbon Storage Potentiality and Edaphic Factors in Tripura , Northeast India. Am. J. Clim. Chang. 5, 417–429.

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A., DeFries, R., Galloway, J., Heimann, M., Jones, C., Quéré, C. Le, Myneni, R.B., Piao, S., Thornton, P., 2013. Carbon and Other Biogeochemical Cycles. In: Stocker, T.., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the

Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 465–570.

Coates, J., 2000. Interpretation of Infrared Spectra. A Practical Approach. Encycl. Anal. Chem. 1–23.

Committee on Climate Change, 2018. Land use : Reducing emissions and preparing for climate change.

Cools, N., Vesterdal, L., Vos, B. De, Vanguelova, E., Hansen, K., 2014. Tree species is the major factor explaining C : N ratios in European forest soils. For. Ecol. Manage. 311, 3–16.

Cotrufo, M.F., Wallenstein, M.D., Boot, C.M., Denef, K., Paul, E., 2013. The Microbial Efficiency-Matrix Stabilization (MEMS) framework integrates plant litter decomposition with soil organic matter stabilization: Do labile plant inputs form stable soil organic matter? Glob. Chang. Biol. 19, 988–995.

Coward, E.K., Ohno, T., Plante, A.F., 2018. Adsorption and Molecular Fractionation of Dissolved Organic Matter on Iron-Bearing Mineral Matrices of Varying Crystallinity. Environ. Sci. Technol. 52, 1036–1044.

Coward, E.K., Thompson, A.T., Plante, A.F., 2017. Iron-mediated mineralogical control of organic matter accumulation in tropical soils. Geoderma 306, 206–216.

Cranfield University, 2021. The Soils Guide [WWW Document]. Cranf. Univ. UK. URL www.landis.org.uk. (accessed 2.25.21).

Deng, L., Zhu, G., Tang, Z., Shangguan, Z., 2016. Global patterns of the effects of land-use changes on soil carbon stocks. Glob. Ecol. Conserv. 5, 127–138.

Dexter, A.R., Richard, G., Arrouays, D., Czy, E.A., Jolivet, C., Duval, O., 2008. Complexed organic matter controls soil physical properties. Geoderma 144, 620–627.

Dignac, M., Derrien, D., Barré, P., Barot, S., Cécillon, L., Chenu, C., Chevallier, T., Freschet, G.T., Garnier, P., Guenet, B., Hedde, M., Klumpp, K., 2017. Increasing soil carbon storage : mechanisms , effects of agricultural practices and proxies . A review. Agron. Sustain. Dev.

Ding, G., Novak, J.M., Amarasiriwardena, D., Hunt, P.G., Xing, B., 2002. Soil Organic Matter Characteristics as Affected by Tillage Management. Soil Sci. Soc. Am. J. 66, 421–429.

Doetterl, S., Berhe, A.A., Nadeu, E., Wang, Z., Sommer, M., Fiener, P., 2016. Erosion, deposition and soil carbon: A review of process-level controls, experimental tools and models to address C cycling in dynamic landscapes. Earth-Science Rev. 154, 102–122.

Don, A., Schumacher, J., Freibauer, A., 2011. Impact of tropical land-use change on soil organic carbon stocks – a meta-analysis. Glob. Chang. Biol. 1658–1670.

Dorji, T., Odeh, I., Field, D., 2014. Vertical Distribution of Soil Organic Carbon Density in Relation to Land Use/Cover, Altitude and Slope Aspect in the Eastern Himalayas. Land 3, 1232–1250.

Drake, B.G., Gonzàlez-Meler, M.A., Long, S.P., 1997. More efficient plants: A Consequence of Rising Atmospheric CO2? Annu. Rev. Plant Biol. 48, 609–639.

Dungait, J.A.J., Hopkins, D.W., Gregory, A.S., Whitmore, A.P., 2012. Soil organic matter turnover is governed by accessibility not recalcitrance. Glob. Chang. Biol. 18, 1781–1796.

Ehleringer, J., Buchmann, N., Flanagan, B., 2000. Carbon isotope ratios in belowground carbon cycle processes. Ecol. Appl. 412–422.

Ellerbrock, R.H., Gerke, H.H., 2004. Characterizing organic matter of soil aggregate coatings and biopores by Fourier transform infrared spectroscopy. Eur. J. Soil Sci. 55, 219–228.

Ellerbrock, R.H., Kaiser, M., 2005. Stability and composition of different soluble soil organic matter fractions – evidence from δ13C and FTIR signatures. Geoderma 128, 28–37.

Ensinas, S.C., Serra, A.P., Marchetti, M.E., Da Silva, E.F., Do Prado, E.A.F., Lourente, E.R.P., Altomar, P.H., Potrich, D.C., Martinez, M.A., Do Amaral Conrad, V., Jesus, M.V., El Kadri, T.C., 2016. Cover crops affect on soil organic matter fractions under no till system. Aust. J. Crop Sci. 10, 503–512.

Eswaran, H., Van Den Berg, E., Reich, P., 1993. Organic Carbon in Soils of the World. Soil Sci. Soc. Am. J. 57, 192–194.

Falkengren-Grerup, U., 1987. Long-term changes in pH of forest soils in southern Sweden. Environ. Pollut. 43, 79–90.

Fang, C., Smith, P., Moncrieff, J.B., Smith, J.U., 2005. Similar response of labile and resitant soil organic matter pools to changes in temperature. Nature 433, 57–59.

FAO, 2011. The State of the World’s land and water resources for Food and Agriculture. Managing systems at risk, Food and Agriculture Organization.

Filho, A.A.R., Adams, C., Manfredini, S., Aguilar, R., Neves, W.A., 2015. Dynamics of soil chemical properties in shifting cultivation systems in the tropics: A meta-analysis. Soil Use Manag. 31, 474–482.

Filho, A.A.R., Adams, C., Murrieta, R.S.S., 2013. The impacts of shifting cultivation on tropical forest soil: a review. Bol. do Mus. Para. Emílio Goeldi. Ciências Humanas 8, 693–727.

Fisher, Richard F and Binkley, D., 2000. Ecology and Management of Forest Soil, Third Edit. ed.

Fisher, R.F., 1995. Soil Organic Matter: Clue or Conundrum? In: Carbon Form and Functions in Forest Soil. Soil Science Society of America, pp. 1–12.

Follett, R.F., Kimble, J.M., Lal, R., 2001. The potential of U.S. grazinglands to sequester carbon and mitigate the greenhouse effect.

Fontaine, S., Barot, S., Barré, P., Bdioui, N., Mary, B., Rumpel, C., 2007. Stability of organic carbon in deep soil layers controlled by fresh carbon supply. Nature 450, 277–80.

Franzluebbers, A.J., 2002. Soil organic matter stratification ratio as an indicator of soil quality. Soil Tillage Res. 66, 95–106.

Franzluebbers, A.J., 2004. Tillage and Residue Management Effects on Soil Organic Matter. In: Magdoff, Fred and Weil, R.R. (Ed.), Soil Organic Matter in Sustainable Agriculture. CRC Press, pp. 227–268.

Freschet, T., Cornwell, W.K., Wardle, D.A., Elumeeva, T.G., Liu, W., Jackson, B.G., Onipchenko, V.G., Soudzilovskaia, N.A., Tao, J., Cornelissen, J.H.C., 2013. Linking litter decomposition of above- and below-ground organs to plant – soil feedbacks worldwide. J. Ecol. 101, 943–952.

Fuentes, M., Govaerts, B., Hidalgo, C., Etchevers, J., González-martín, I., Hernández-hierro, J.M., Sayre, K.D., Dendooven, L., 2010. Organic carbon and stable 13C isotope in conservation agriculture and conventional systems. Soil Biol. Biochem. 42, 551–557.

Fujii, S., Takeda, H., 2010. Dominant effects of litter substrate quality on the difference between leaf and root decomposition process above- and belowground. Soil Biol. Biochem. 42, 2224–2230.

Fultz, L.M., Moore-kucera, J., Calderón, F., Acosta-martínez, V., 2014. Using Fourier-Transform Mid-Infrared Spectroscopy to Distinguish Soil Organic Matter Composition Dynamics in Aggregate Fractions of Two Agroecosystems. Soil Sci. Soc. Am. J. 78, 1940–1948.

Gerzabek, M.H., Antil, R., Kogel-Knabner, I., Knicker, H., Kirchmann, H., Haberhauer, G., 2006. How are soil use and management reflected by soil organic matter characteristics : a spectroscopic approach. Eur. J. Soil Sci. 57, 485–494.

Ghidey, F., Alberts, E.E., 1993. Residue type and placement effects on decomposition: field study and model evaluation. Trans. ASAE 36, 1611–1617.

Glenk, K., Colombo, S., 2011. Designing policies to mitigate the agricultural contribution to climate change: An assessment of soil based carbon sequestration and its ancillary effects. Clim. Change 105, 43–66.

Green, B.H., 1990. Agricultural intensification and the loss of habitat, species and amenity in British grasslands: a review of historical change and assessment of future prospects. Grass Forage Sci. 45, 365–372.

Gregory, A.S., Dungait, J.A.J., Watts, C.W., Bol, R., Dixon, E.R., White, R.P., Whitmore, A.P., 2016. Long-term management changes topsoil and subsoil organic carbon and nitrogen dynamics in a temperate agricultural system. Eur. J. Soil Sci. 67, 421–430.

Gregory, P.J., 2006a. Roots, rhizosphere and soil: The route to a better understanding of soil science? Eur. J. Soil Sci. 57, 2–12.

Gregory, P.J., 2006b. Plant Roots: Growth, Activity and Interaction with Soils. Blackwell Publishing, Oxford.

Gross, C.D., Harrison, R.B., 2019. The Case for Digging Deeper : Soil Organic Carbon Storage , Dynamics , and Controls in Our Changing World †. Soil Syst. 3, 1–24.

Guo, L.B., Gifford, R.M., 2002. Soil carbon stocks and land use change: A meta analysis. Glob. Chang. Biol. 8, 345–360.

Guo, X., Luo, L., Ma, Y., Zhang, S., 2010. Sorption of polycyclic aromatic hydrocarbons on particulate organic matters 173, 130–136.

Haberhauer, G., Rafferty, B., Strebl, F., Gerzabek, M.H., 1998. Comparison of the composition of forest soil litter derived from three different sites at various decompositional stages using FTIR spectroscopy. Geoderma 83, 331–342.

Haddaway, N.R., Hedlund, K., Jackson, L.E., Kätterer, T., Lugato, E., Thomsen, I.K., Jørgensen, H.B., Isberg, P.E., 2017. How does tillage intensity affect soil organic carbon ? A systematic review, Environmental Evidence. BioMed Central.

Hairiah, K., Sitompul, S., Noordwijk, M. Van, Cheryl Palm, 2001. Carbon stocks of tropical land use systems as part of the global carbon balance: effects of forest conversion and options for clean development activities.

Hariyadi, B., Ticktin, T., 2012. From Shifting Cultivation to Cinnamon Agroforestry: Changing Agricultural Practices Among the Serampas in the Kerinci Seblat National Park, Indonesia. Hum. Ecol. 40, 315–325.

Harrison, R.B., Footen, P.W., Strahm, B.D., 2011. Deep soil horizons: Contribution and importance to soil carbon pools and in assessing whole-ecosystem response to management and global change. For. Sci. 57, 67–76.

Hassink, J., 1997. The capacity of soils to preserve organic C and N by their association with clay and silt particles. Plant Soil 191, 77–87.

Hassink, J., Whitmore, A., Kubát, J., 1997. Size and density fractionation of soil organic matter and the physical capacity of soils to …. Eur. J. Agron. 7, 189–199.

He, Y., Siemens, J., Amelung, W., Goldbach, H., Wassmann, R., Alberto, M.C.R., Lücke, A., Lehndorff, E., 2015. Carbon release from rice roots under paddy rice and maize-paddy rice cropping. Agric. Ecosyst. Environ. 210, 15–24.

Hendrickson, O., 2012. Influences of global change on carbon sequestration by agricultural and forest soils, Organization Development Journal.

Hernandez-soriano, M., Dalal, R., Warren, F.J., Wang, P., Green, K., Tobin, M.J., Menzies, N.W., Kopittke, P.M., 2018. Soil organic carbon stabilization : Mapping carbon speciation from intact microaggregates. Environ. Sci. Technol.

Hoang, D.T.T., Bauke, S.L., Kuzyakov, Y., Pausch, J., 2017. Soil Biology & Biochemistry Rolling in the deep : Priming effects in earthworm biopores in topsoil and subsoil. Soil Biol. Biochem. 114, 59–71.

Hobbie, S.., Eissenstat, D., Oleksyn, J., Reich, P.B., 2010. Fine root decomposition rates do not mirror those of leaf litter among temperate tree species. Oecologia 162, 505–513.

Hobbie, S.E., 2015. Plant species effects on nutrient cycling: revisiting litter feedbacks. Trends Ecol. Evol. 30, 357–363.

Hobley, E., Baldock, J., Hua, Q., Wilson, B., 2017a. Land-use contrasts reveal instability of subsoil organic carbon. Glob. Chang. Biol. 23, 955–965.

Hobley, E., Brereton, A., Wilson, B., 2017b. Soil charcoal prediction using attenuated total reflectance mid-infrared spectroscopy. Soil Res. 55, 86–92.

Hobley, E.U., Wilson, B., 2016. The depth distribution of organic carbon in the soils of eastern Australia. Ecosphere 7, 1–21.

Hoffland, E., Kuyper, T.W., Comans, R.N.J., Creamer, R.E., 2020. Eco-functionality of organic matter in soils. Plant Soil.

Horwath, W., 2015. Carbon Cycling: The Dynamics and Formation of Organic Matter, 4th ed, Soil Microbiology, Ecology and Biochemistry. Elsevier Inc.

Houghton, R.A., 2007. Balancing the Global Carbon Budget. Annu. Rev. Earth Planet.

Sci. 35, 313–347.

Hsu, J., Lo, S., 1999. Chemical and spectroscopic analysis of organic matter transformations during composting of pig manure. Environ. Pollut. 104, 189–196.

Huang, W., Hall, S., 2017. Elevated moisture stimulates carbon loss from mineral soils by releasing protected organic matter. Nat. Commun. 8.

Huang, W., Ye, C., Hockaday, W., Hall, S., 2020. Trade-offs in soil carbon protection mechanisms under aerobic and anaerobic conditions. Glob. Chang. Biol. 3726–3737.

IPCC, 2019. Climate Change and Land: An IPCC Special Report on climate change, desertification, land degradation, sustainable land management, food security, and greenhouse gas fluxes in terrestrial ecosystems.

Jackson, R.B., Canadell, J., Ehleringer, J.R., Mooney, H. a., Sala, O.E., Schulze, E.D., 1996. A global analysis of root distributions for terrestrial biomes. Oecologia 108, 389–411.

Janzen, H.H., 2004. Carbon cycling in earth systems - A soil science perspective. Agric. Ecosyst. Environ. 104, 399–417.

Janzen, H.H., 2006. The soil carbon dilemma : Shall we hoard it or use it ? Soil Biol. Biochem. 38, 419–424.

Jenny, H., 1941. Factors of soil formation. A system of quantitative pedology, Geoderma. McGraw-Hill, New York.

Jia, B., Niu, Z., Wu, Y., Kuzyakov, Y., Gang, X., 2020. Waterlogging increases organic carbon decomposition in grassland soils. Soil Biol. Biochem. 148, 107927.

Jobbágy, E.G., Jackson, R.B., 2000. The Vertical Distribution of Soil Organic Carbon and Its Relation to Climate and Vegetation. Ecol. Appl. 10, 423–436.

John, B., Yamashita, T., Ludwig, B., Flessa, H., 2005. Storage of organic carbon in aggregate and density fractions of silty soils under different types of land use. Geoderma 128, 63–79.

Kaiser, K., Guggenberger, G., 2000. The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. Org. Geochem. 31, 711–725.

Kaiser, K., Guggenberger, G., Zech, W., 1996. Sorption of DOM and DOM fractions to forest soils. Geoderma 74, 281–303.

Kaiser, K., Kalbitz, K., 2012. Cycling downwards - dissolved organic matter in soils. Soil Biol. Biochem. 52, 29–32.

Kaiser, M., Ellerbrock, R.H., 2005. Functional characterization of soil organic matter fractions different in solubility originating from a long-term field experiment 127, 196–206.

Ke, B., 2000. Chapter 1 Photosynthesis : An Overview. In: Photosynthesis : Photobiochemistry and Photobiophysics. Kluwer Academic Publishers, pp. 1–46.

Kindler, R., Siemens, J., Kaiser, K., Walmsley, D.C., Bernhofer, C., Buchmann, N., Cellier, P., Eugster, W., Gleixner, G., Grunwald, T., Heim, A., Ibrom, A., Jones, S.K., Jones, M., Klumpp, K., Kutsch, W., Larsen, K.S., Lehuger, S., Loubet, B., Mckenzie, R., Moors, E., Osborne, B., Pilegaard, K., Rebmann, C., Saunders, M., Schmidt, M.W.I., Schrumpf, M., Seyfferth, J., Skiba, U., Soussana, J.F., Sutton, M.A., Tefs, C., Vowinckel, B., Zeeman, M.J., Kaupenjohann, M., 2011. Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance. Glob. Chang. Biol. 17, 1167–1185.

Kirschbaum, M.U.F., 1995. The temperature dependence of soil organic matter decomposition, and the effect of global warming on soil organic C storage. Soil Biol. Biochem. 27, 753–760.

Kleber, M., 2010. What is recalcitrant soil organic matter ? Environ. Chem. 7, 320–332.

Kleber, M., Mikutta, R., Torn, M.S., Jahn, R., 2005. Poorly crystalline mineral phases protect organic matter in acid subsoil horizons. Eur. J. Soil Sci. 56, 717–725.

Kleber, M., Sollins, P., Sutton, R., 2007. A conceptual model of organo-mineral interactions in soils : self-assembly of organic molecular fragments into zonal structures on mineral surfaces. Biogeochemistry 85, 9–24.

Kögel-Knabner, I., 2002. The macromolecular organic composition of Plant and microbial residues as inputs to soil organic matter. Soil Biol. Biochem. 34, 139–162.

Kramer, M.G., Lajtha, K., Aufdenkampe, A.K., 2017. Depth trends of soil organic matter C:N and 15N natural abundance controlled by association with minerals. Biogeochemistry 136, 237–248.

Kramer, M.G., Sanderman, J., Chadwick, O.., Chorover, J., Vitousek, P.M., 2012. Long-term carbon storage through retention of dissolved aromatic acids by reactive particles in soil. Glob. Chang. Biol. 18, 2594–2605.

Kravchenko, A.N., Negassa, W.C., Guber, A.K., Rivers, M.L., 2015. Protection of soil carbon within macro-aggregates depends on intra-aggregate pore characteristics. Sci. Rep. 5, 16261.

Krull, E., Baldock, J., Skjemstad, J., 2001. Soil Texture Effects on Decomposition and Soil Carbon Storage. In: NEE Workshop Proceedings. pp. 103–110.

Lal, R., 2003. Soil erosion and the global carbon budget. Environ. Int. 29, 437–450.

Lal, R., 2004a. Soil carbon sequestration to mitigate climate change. Geoderma 123, 1–22.

Lal, R., 2004b. Soil Carbon Sequestration Impacts on Global Climate Change and Food Security. Am. Assoc. Adv. Sci. 304, 1623–7.

Lal, R., 2005. Enhancing crop yields in the developing countries through restoration of the soil organic carbon pool in agricultural lands. L. Degrad. Dev. 17, 197–209.

Lal, R., 2015. Sequestering carbon and increasing productivity by conservation agriculture. J. Soil Water Conserv. 70, 55A-62A.

Lal, R., 2017. Digging Deeper: A Holistic Perspective of Factors Affecting Soil Organic Carbon Sequestration in Agroecosystems. ARPN J. Eng. Appl. Sci. 12, 3218–3221.

Lal, R., 2018. Digging Deeper: A Holistic Perspective of Factors Affecting Soil Organic Carbon Sequestration in Agroecosystems. Glob. Chang. Biol.

Lavallee, J., Soong, J., Cotrufo, M.F., 2019. Conceptualizing soil organic matter into particulate and mineral-associated forms to address global change in the 21st century. Glob. Chang. Biol.

Lawrence, C.R., Harden, J.W., Xu, X., Schulz, M.S., Trumbore, S.E., 2015. Long-term controls on soil organic carbon with depth and time: A case study from the Cowlitz River Chronosequence, WA USA. Geoderma 247–248, 73–87.

Le Quéré, C., Andrew, R.M., Canadell, J.G., Sitch, S., Ivar Korsbakken, J., Peters, G.P., Manning, A.C., Boden, T.A., Tans, P.P., Houghton, R.A., Keeling, R.F., Alin, S., Andrews, O.D., Anthoni, P., Barbero, L., Bopp, L., Chevallier, F., Chini, L.P., Ciais, P., Currie, K., Delire, C., Doney, S.C., Friedlingstein, P., Gkritzalis, T., Harris, I., Hauck, J., Haverd, V., Hoppema, M., Klein Goldewijk, K., Jain, A.K., Kato, E., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lombardozzi, D., Melton, J.R., Metzl, N., Millero, F., Monteiro, P.M.S., Munro, D.R., Nabel, J.E.M.S., Nakaoka, S.I., O'Brien, K., Olsen, A., Omar, A.M., Ono, T., Pierrot, D., Poulter, B., Rödenbeck, C., Salisbury, J., Schuster, U., Schwinger, J., Séférian, R., Skjelvan, I., Stocker, B.D., Sutton, A.J., Takahashi, T., Tian, H., Tilbrook, B., Van Der Laan-Luijkx, I.T., Van Der Werf, G.R., Viovy, N., Walker, A.P., Wiltshire, A.J., Zaehle, S., 2016. Global Carbon Budget 2016. Earth Syst. Sci. Data 8, 605–649.

Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. Nature 528, 60–68.

Leinemann, T., Preusser, S., Mikutta, R., Kalbitz, K., Cerli, C., Höschen, C., Mueller, C.W., Kandeler, E., Guggenberger, G., 2018. Multiple exchange processes on mineral surfaces control the transport of dissolved organic matter through soil profiles. Soil Biol. Biochem. 118, 79–90.

Li, C., Zhao, L., Sun, P., Zhao, F., Kang, D., Yang, G., Han, X., Feng, Y., Ren, G., 2016. Deep soil c, n, and p stocks and stoichiometry in response to land use patterns in the loess hilly region of china. PLoS One 11, 1–15.

Li, M., Zhang, X., Pang, G., Han, F., 2013. Catena The estimation of soil organic carbon distribution and storage in a small catchment area of the Loess Plateau. Catena 101, 11–16.

Liu, Y., Liu, W., Wu, L., Liu, C., Wang, L., Chen, F., Li, Z., 2018. Soil aggregate-associated organic carbon dynamics subjected to di ff erent types of land use : Evidence from 13 C natural abundance. Ecol. Eng. 122, 295–302.

Lizawati, Riduan, A., Neliyati, Alia, Y., 2016. Penyelamatan Plasma Nutfah Kulit Kayu Manis Melalui Teknologi Perbanyakan Vegetatif Dalam Upaya Pengelolaan Sumber Daya Genetik Komoditas Ekspor Unggulan Provinsi Jambi. Jambi, Indonesia.

Loeppert, R.H., Inskeep, W.P., 1996. Chapter 23. Iron. In: Methods of Soil Analysis: Chemical Methods. Part 3. Book Series 5. pp. 639–664.

Lorenz, K., Lal, R., 2005. The Depth Distribution of Soil Organic Carbon in Relation to Land Use and Management and the Potential of Carbon Sequestration in Subsoil Horizons. Adv. Agron. 88, 35–66.

Lorenz, K., Lal, R., Preston, C.M., Nierop, K.G.J., 2007. Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio (macro) molecules. Geoderma 142, 1–10.

Lovell, R.D., Jarvis, S.C., 1996. Effect of cattle dung on soil microbial biomass C and N in a permanent pasture soil. Soil Biol. Biochem. 28, 291–299.

Lu, Y., Watkins, K.B., Teasdale, J.R., Aref, A., 2000. Cover Crops in Sustainable Food Production 16, 121–157.

Lützow, M. V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: Mechanisms and their relevance under different soil conditions - A review. Eur. J. Soil Sci. 57, 426–445.

Madhavan, D.B., Mendham, D., Kitching, M., Weston, C., Baker, T., 2012. Use of mid-infrared spectroscopy to characterise and predict particulate organic carbon and nitrogen in soils after land-use change from agriculture to plantation forestry. In: 5th Joint SSA and NZSSS Soil Science Conference Soil Solutions for Diverse Landscapes.

Magdoff, R., Weil, R., 2004. Soil Organic Matter Management Strategies. In: Magdoff, Red and Weil, R.R. (Ed.), Soil Organic Matter in Sustainable Agriculture. CRC Press, pp. 46–62.

Malhi, Y., Baldocchi, D.D., Jarvis, P.G., 1999. The carbon balance of tropical , temperate and boreal forests. Plant, Cell Environ. 22, 715–740.

Malik, A.A., Puissant, J., Buckeridge, K.M., Goodall, T., Jehmlich, N., Chowdhury, S., Gweon, H.S., Peyton, J.M., Mason, K.E., Agtmaal, M. Van, Blaud, A., Clark, I.M., Whitaker, J., Pywell, R.F., Ostle, N., Gleixner, G., Grif, R.I., 2018. Land use driven change in soil pH affects microbial carbon cycling processes. Nat. Commun. 9, 1–10.

Margenot, A.J., Calderón, F.J., Bowles, T.M., Jackson, L.E., 2015a. Soil Organic Matter Functional Group Composition in Relation to Organic Carbon, Nitrogen, and Phosphorus Fractions in Organically Managed Tomato Fields. Soil Sci. Soc. Am. J. 79, 772–782.

Margenot, A.J., Calderón, F.J., Parikh, S.J., 2015b. Limitations and Potential of Spectral Subtractions in Fourier-Transform Infrared Spectroscopy of Soil Samples. Soil Sci. Soc. Am. J. 80, 10–26.

Marin-Spiotta, E., Chadwick, O.A., Kramer, M., Carbone, M.S., 2011. Carbon delivery to deep mineral horizons in Hawaiian rain forest soils. J. Geophys. Res. Biogeosciences 116, 1–15.

Marschner, B., Brodowski, S., Dreves, A., Gleixner, G., Gude, A., Grootes, P.M., Hamer, U., Heim, A., Jandl, G., Ji, R., Kaiser, K., Kalbitz, K., Kramer, C., Leinweber, P., Rethemeyer, J., Schäffer, A., Schmidt, M.W.I., Schwark, L., Wiesenberg, G.L.B., 2008. How relevant is recalcitrance for the stabilization of organic matter in soils? Plant Nutr. Soil Sci. 1090, 91–110.

Martinelli, L.., Piccolo, M.., Townsend, A.R., Vitousek, P.M., Cuevas, E., McDowell, W., Robertson, G.P., Santos, O., Treseder, K., 1999. Nitrogen stable isotopic composition of leaves and soil : Tropical versus temperate forests. Biogeochemistry 46, 45–65.

McDaniel, P.A., Lowe, D.J., Arnalds, Ó., Ping, C.L., 2012. Andisols. Handb. Soil Sci. Prop. Process. 1, 1–52.

McLauchlan, K., 2006. The nature and longevity of agricultural impacts on soil carbon and nutrients: A review. Ecosystems 9, 1364–1382.

Mcsherry, M.E., Ritchie, M.E., 2013. Effects of grazing on grassland soil carbon: A global review. Glob. Chang. Biol. 19, 1347–1357.

Meurer, K.H.E., Haddaway, N.R., Bolinder, M.A., Kätterer, T., 2018. Earth-Science

Reviews Tillage intensity a ff ects total SOC stocks in boreo-temperate regions only in the topsoil — A systematic review using an ESM approach. Earth-Science Rev. 177, 613–622.

Minasny, B., Malone, B.P., McBratney, A.B., Angers, D.A., Arrouays, D., Chambers, A., Chaplot, V., Chen, Z.-S., Cheng, K., Das, B.S., Field, D.J., Gimona, A., Hedley, C.B., Hong, S.Y., Mandal, B., Marchant, B.P., Martin, M., McConkey, B.G., Mulder, V.L., O'Rourke, S., Richer-de-Forges, A.C., Odeh, I., Padarian, J., Paustian, K., Pan, G., Poggio, L., Savin, I., Stolbovoy, V., Stockmann, U., Sulaeman, Y., Tsui, C.-C., Vågen, T.-G., van Wesemael, B., Winowiecki, L., 2017. Soil carbon 4 per mille. Geoderma 292, 59–86.

Murty, D., Kirschbaum, M.U.F., McMurtrie, R., McGilvray, H., 2002. Does conversion of forest to agricultural land change soil carbon and nitrogen ? a review of the literature. Glob. Chang. Biol. 8, 105–123.

Nguyen, C., 2003. Rhizodeposition of organic C by plants: mechanisms and controls. Ital. J. Agron. 375–396.

NOAA, 2021. Earth System Research Laboratory Website [WWW Document]. Access Febr. 2021. URL https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html

Olson, K.R., Gennadiyev, A.N., Zhidkin, A.P., Markelov, M. V., 2012. Impacts of land-use change, slope, and erosion on soil organic carbon retention and storage. Soil Sci. 177, 269–278.

Ontl, T.A., Schulte, L.A., 2012. Soil Carbon Storage. Nat. Educ. Knowl. 3, 35.

Ostle, N.J., Levy, P.E., Evans, C.D., Smith, P., 2009. UK land use and soil carbon sequestration. Land use policy 26, 274–283.

Pan, Y., Birdsey, R.A., Fang, J., Houghton, R., Kauppi, P.E., Kurz, W.A., Phillips, O.L., Shvidenko, A., Lewis, S.L., Canadell, J.G., Ciais, P., Jackson, R.B., Pacala, S.W., McGuire, A.D., Piao, S., Rautiainen, A., Sitch, S., Hayes, D., 2011. A large and persistent carbon sink in the world's forests. Science (80-.). 333, 988–993.

Pandey, A., Li, F., Askegaard, M., Rasmussen, I.A., Olesen, J.E., 2018. Agriculture , Ecosystems and Environment Nitrogen balances in organic and conventional arable crop rotations and their relations to nitrogen yield and nitrate leaching losses. Agric. Ecosyst. Environ. 265, 350–362.

Parikh, S.J., Goyne, K.W., Margenot, A.J., Mukome, N.D., Calderón, F.J., 2014. Soil Chemical Insights Provided through Vibrational Spectroscopy, Advances in Agronomy. Elsevier.

Parolo, M.E., Savini, C., Loewy, R.M., 2017. Characterization of soil organic matter by FT-IR spectroscopy and its relationship with chlorpyrifos sorption. Environ. Manage. 196, 316–322.

Paul-Limoges, E., Black, T.A., Christen, A., Nesic, Z., Jassal, R.S., 2015. Effect of clearcut harvesting on the carbon balance of a Douglas-fir forest. Agric. For. Meteorol. 203, 30–42.

Peltre, C., Bruun, S., Du, C., Thomsen, I.K., Jensen, L.S., 2014. Assessing soil constituents and labile soil organic carbon by mid- infrared photoacoustic spectroscopy. Soil Biol. Biochem. 77, 41–50.

Perez, C., Roncoli, C., Neely, C., Steiner, J.L., 2007. Can carbon sequestration markets benefit low-income producers in semi-arid Africa? Potentials and challenges. Agric. Syst. 94, 2–12.

Plaza, C., Courtier-Murias, D., Fernández, J.M., Polo, A., Simpson, A.J., 2013. Physical, chemical, and biochemical mechanisms of soil organic matter stabilization under conservation tillage systems: A central role for microbes and microbial by-products in C sequestration. Soil Biol. Biochem. 57, 124–134.

Plaza, C., Fernández, J.M., Pereira, E.I.P., Polo, A., 2012. A comprehensive method for fractionating soil organic matter not protected and protected from decomposition by physical and chemical mechanisms. Clean - Soil, Air, Water 40, 134–139.

Poeplau, C., Don, A., 2015. Carbon sequestration in agricultural soils via cultivation of cover crops - A meta-analysis. Agric. Ecosyst. Environ. 200, 33–41.

Pramanik, P., Bandyopadhyay, K.K., Bhaduri, D., Bhattacharyya, R., Aggarwal, P., 2015. Effect of mulch on soil thermal regimes - A review. Int. J. Agric. Environ. Biotechnol. 8, 645.

Pregitzer, K.S., 2003. Carbon Cycling in Forest Ecosystem with an Emphasis on Belowground Processes. In: Kimble, J.M; Heath, Linda S; Birdsey, R.A.L.R. (Ed.), The Potensial of US Forest Soils to Sequester Carbon and Mitigate the Greenhouse Effect. Lewis Publisher, pp. 93–104.

Qi, A., Holland, R.A., Taylor, G., Richter, G.M., 2018. Grassland futures in Great Britain – Productivity assessment and scenarios for land use change opportunities. Sci. Total Environ. 634, 1108–1118.

Qi, A., Murray, P.J., Richter, G.M., 2017. Modelling productivity and resource use efficiency for grassland ecosystems in the UK. Eur. J. Agron.

Rasmussen, C., Heckman, K., Wieder, W.R., Keiluweit, M., Lawrence, C.R., Asefaw, A., Blankinship, J.C., Crow, S.E., Druhan, J.L., Hicks, C.E., Schimel, J.P., Alain, E.M., Christina, F.P., 2018. Beyond clay : towards an improved set of variables for predicting soil organic matter content 297–306.

Rasse, D.P., Rumpel, C., Dignac, M., 2005. Is soil carbon mostly root carbon ? Mechanisms for a specific stabilisation 341–356.

Rath, M., Peel, S., 2005. Grassland in Ireland and the UK. In: McGilloway, D.A. (Ed.), Grassland: A Global Resource. Wageningen Academic Publishers, The Netherlands.

Redin, M., Recous, S., Aita, C., Dietrich, G., Skolaude, A.C., Ludke, W.H., Schmatz, R., Giacomini, S.J., 2014. How the chemical composition and heterogeneity of crop residue mixtures decomposing at the soil surface affects C and N mineralization. Soil Biol. Biochem. 78, 65–75.

Reich, P.., Oleksyn, J., Modrzynski, J., Mrozinski, P., Hobbie, S.., Eissenstat, D.., Chorover, J., Chadwick, O.., Hale, C.., Tjoelker, M.., 2005. Linking litter calcium , earthworms and soil properties : a common garden test with 14 tree species. Ecol. Lett. 8, 811–818.

Reicosky, D.., 1994. Crop residue management: Soil, Crop, Climate Interaction. In: Hatfield, J.L. and Stewart, B.. (Ed.), Crops Residue Management. Lewis Publisher, pp. 191–210.

Reynolds, S., 2005. Introduction. In: Suttie, J.M., Reynolds, S.G., and Batello, C. (Ed.), Grassland of the World. FAO, Rome.

Ross, S.., 1993. Organic matter in tropical soils: current conditions, concerns and prospects for conservation. Prog. Phys. Geogr. Earth Environ. 17, 265–305.

Rounsevell, M.D.A., Reay, D.S., 2009. Land use and climate change in the UK. Land use policy 26, 160–169.

Rowland, C.., Morton, R.., Carrasco, L., McShane, G., O’Neil, A.., Wood, C.., 2017. Land Cover Map 2015 (1km dominant aggregate class, GB).

Rumpel, C., 2011. Carbon Storage and Organic Matter Dynamics in Grassland Soils. In: Lemaire, Dr. Gilles; Hodgson, Professor John; Chabbi, D.A. (Ed.), Grassland Productivity and Ecosystem Services. CABI, pp. 65–72.

Rumpel, C., Kögel-Knabner, I., 2011. Deep soil organic matter-a key but poorly understood component of terrestrial C cycle. Plant Soil 338, 143–158.

Rumpel, C., Kögel-Knabner, I., Bruhn, F., 2002. Vertical distribution, age, and chemical composition of organic carbon in two forest soils of different pedogenesis. Org. Geochem. 33, 1131–1142.

Saha, D., Kukal, S.S., Bawa, S.S., 2012. Soil organic carbon stock and fractions in relation to land use and soil depth in the degraded Shiwaliks hills of lower Himalayas. L. Degrad. Dev.

Sanderman, J., Hengl, T., Fiske, G.J., 2017. Soil carbon debt of 12,000 years of human land use. Proc. Natl. Acad. Sci. 2017, 9575–9580.

Savini, M.C., Loewy, R.M., Nicotra, V.E., Parolo, M.E., 2017. Contribution of Soil Components on the Sorption of Chlorpyrifos. Water, Air, Soil Pollut. 228.

Scheunemann, N., Digel, C., Scheu, S., Butenschoen, O., 2015. Roots rather than shoot residues drive soil arthropod communities of arable fields. Oecologia 179, 1135–1145.

Schlesinger, W.., 1995. An overview of the carbon cycle. In: Lal, R., Kimble, J., Levine, E., and Stewart, B.. (Ed.), Soils and Global Change. CRC/ Lewis Publisher, Boca Raton FL, pp. 9–26.

Schlesinger, W., Andrews, J., 2000. Soil respiration and the global carbon cycle. Biogeochemistry 48, 7–20.

Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. a., Kleber, M., Kögel-Knabner, I., Lehmann, J., Manning, D. a. C., Nannipieri, P., Rasse, D.P., Weiner, S., Trumbore, S.E., 2011. Persistence of soil organic matter as an ecosystem property. Nature 478, 49–56.

Schmidt, O., Dyckmans, J., Schrader, S., 2016. Photoautotrophic microorganisms as a carbon source for temperate soil invertebrates. Bol. Lett. 12, 20150646.

Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I., Schulze, E.D., 2013. Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates, and attachment to minerals. Biogeosciences 10, 1675–1691.

Schumacher, B.A., 2002. Methods for the Determination of Total Organic Carbon (TOC) in Soils and Sediments 25.

Seiter, S., Horwarth, W.R., 2004. Strategies for Managing Soil Organic Matter to Supply Plant Nutrients. In: Soil Organic Matter in Sustainable Agriculture. pp. 269–287.

Senvar, O., Sennaroglu, B., 2016. Comparing Performances of Clements , Box-Cox , Johnson Methods with Weibull Distributions for Assessing Process Capability. J. Ind. Eng. Manag. 9, 634–656.

Shahzad, T., Chenu, C., Genet, P., Barot, S., Perveen, N., Mougin, C., Fontaine, S., 2015. Contribution of exudates, arbuscular mycorrhizal fungi and litter depositions to the rhizosphere priming effect induced by grassland species. Soil Biol. Biochem. 80, 146–155.

Shahzad, T., Imtiaz, M., Maire, V., Barot, S., 2018. Root penetration in deep soil layers stimulates mineralization of millenniaold organic carbon Root penetration in deep soil layers stimulates mineralization of millennia- old organic carbon. Soil Biol. Biochem. 124, 150–160.

Shi, H., Wang, X., Xu, M., Zhang, H., Luo, Y., 2017. Characteristics of soil C : N ratio and δ 13 C in wheat-maize cropping system of the North China Plain and influences of the Yellow River. Sci. Rep. 7, 1–9.

Sing, L., Metzger, M., Paterson, J., Ray, D., 2018. A review of the effects of forest management intensity on ecosystem services for northern European temperate forests with a focus on the UK. FORESTRY 91, 151–164.

Six, J., Bossuyt, H., Degryze, S., Denef, K., 2004. A history of research on the link between (micro) aggregates , soil biota , and soil organic matter dynamics. Soil Tillage Res. 79, 7–31.

Six, J., Conant, R.T., Paul, E.A., Paustian, K., 2002. Stabilization mechanisms of soil organic matter : Implications for C-saturation of soils. Plant Soil 241, 155–176.

Six, J., Elliot, E.T., Paustian, K., 2000. Soil microaggregate turnover and microaggregate formation: a mechanism for C organic under no-tillage agriculture. Soil Biol. Biochem. 32, 2099–2103.

Smith, P., House, J.I., Bustamante, M., Sobocká, J., Harper, R., Pan, G., West, P.C., Clark, J.M., Adhya, T., Rumpel, C., Paustian, K., Kuikman, P., Cotrufo, M.F., Elliott, J.A., Mcdowell, R., Griffiths, R.I., Asakawa, S., Bondeau, A., Jain, A.K., Meersmans, J., Pugh, T.A.M., 2016. Global change pressures on soils from land use and management. Glob. Chang. Biol. 22, 1008–1028.

Solomon, D., Lehmann, J., Kinyangi, J., Liang, B., Scha, T., 2005. Carbon K-Edge NEXAFS and FTIR-ATR Spectroscopic Investigation of. Soil Sci. Soc. Am. J. 69, 107–119.

Soucémarianadin, L., Cécillon, L., Chenu, C., Baudin, F., Nicolas, M., Girardin, C., Delahaie, A., Barré, P., 2019. Heterogeneity of the chemical composition and thermal stability of particulate organic matter in French forest soils. Geoderma 342, 65–74.

Stevens, C.J., David, T.I., Storkey, J., 2018. Atmospheric nitrogen deposition in terrestrial ecosystems : Its impact on plant communities and consequences across trophic levels. Funct. Ecol. 32, 1757–1769.

Stockmann, U., Adams, M.A., Crawford, J.W., Field, D.J., Henakaarchchi, N., Jenkins, M., Minasny, B., McBratney, A.B., Courcelles, V. de R. de, Singh, K., Wheeler, I., Abbott, L., Angers, D.A., Baldock, J., Bird, M., Brookes, P.C., Chenu, C., Jastrow, J.D., Lal, R., Lehmann, J., O'Donnell, A.G., Parton, W.J., Whitehead, D., Zimmermann, M., 2013. The knowns, known unknowns and unknowns of sequestration of soil organic carbon. Agric. Ecosyst. Environ. 164, 80–99.

Sukarman, Dariah, A., 2014. Tanah Andosol Di Indonesia.

Tahir, M.M., Recous, S., Aita, C., Schmatz, R., Pilecco, G.E., Giacomini, S.J., 2016. In situ roots decompose faster than shoots left on the soil surface under subtropical no-till conditions. Biol. Fertil. Soils 52, 853–865.

Takahashi, T., Shoji, S., 2002. Distribution and classification of volcanic ash soils. Glob. Environ. Res. 6, 83–97.

Tanaka, S., Ando, T., Funakawa, S., Sukhrun, C., Kaewkhongkha, T., Sakurai, K., 2001. Effect of burning on soil organic matter content and N mineralization under shifting cultivation system of Karen people in northern Thailand. Soil Sci. Plant Nutr. 47, 547–558.

Tate, R.L., 1987. Soil Organic Matter: Biological and Ecological Effects. John Wiley & Sons, Inc., United States of America.

Tautges, N.E., Chiartas, J., Gaudin, A.C.M., O'Geen, A.T., Herrera, I., M.Scow, K., 2019. Deep soil inventories reveal that impacts of cover crops and compost on soil carbon sequestration differ in surface and sub-surface soils. Glob. Chang. Biol. 1–14.

Thomaz, E.L., 2017. High fire temperature changes soil aggregate stability in slash-and-burn agricultural systems. Sci. Agric. 157–162.

Thomaz, E.L., Antoneli, V., Doerr, S.H., 2014. Effects of fire on the physicochemical properties of soil in a slash-and-burn agriculture. Catena 122, 209–215.

Tian, H., Chen, G., Zhang, C., Melillo, J.M., Hall, C.A.S., 2010. Pattern and variation of C:N:P ratios in China's soils: A synthesis of observational data. Biogeochemistry 98, 139–151.

Tölle, M.H., 2020. Impact of Deforestation on Land – Atmosphere Coupling Strength and Climate in Southeast Asia.

Tonneijck, F.., Jansen, B., Nierop, K., Verstraten, J., Sevink, J., De Lange, L., 2010. Towards understanding of carbon stocks and stabilization in volcanic ash soils in natural Andean ecosystems of northern Ecuador. Eur. J. Soil Sci. 61, 392–405.

Torn, M.S., Trumbore, S.E., Chadwick, O.., Vitousek, P.M., Hendricks, D.M., 1997.

Mineral control of soil organic carbon storage and turnover. Nature 389, 170–173.

Torres-Sallan, G., Schulte, R.P.O., Lanigan, G.J., Byrne, K.A., Reidy, B., Simó, I., Six, J., Creamer, R.E., 2017. Clay illuviation provides a long-term sink for C sequestration in subsoils. Sci. Rep. 7, 45635.

Trumbore, S.E., 1997. Potential responses of soil organic carbon to global environmental change. Proc. Natl. Acad. Sci. 94, 8284–8291.

Turmel, M.-S., Speratti, A., Baudron, F., Verhulst, N., Govaerts, B., 2014. Crop residue management and soil health: A systems analysis. Agric. Syst. 134, 6–16.

USDA, 2011. Carbon to Nitrogen Ratios in Cropping Systems. USDA Nat. Resour. Conserv. Serv.

van Straaten, O., Corre, M.D., Wolf, K., Tchienkoua, M., Cuellar, E., Matthews, R.B., Veldkamp, E., 2015. Conversion of lowland tropical forests to tree cash crop plantations loses up to one-half of stored soil organic carbon. Proc. Natl. Acad. Sci. 112, 9956–9960.

Vanguelova, E.I., Pitman, R.M., 2019. Nutrient and carbon cycling along nitrogen deposition gradients in broadleaf and conifer forest stands in the east of England. For. Ecol. Manage. 447, 180–194.

Veum, K.S., Goyne, K.W., Kremer, R.J., Miles, R.J., Sudduth, K.A., 2014. Biological indicators of soil quality and soil organic matter characteristics in an agricultural management continuum. Biogeochemistry 117, 81–99.

von Haden, A.C., Yang, W.H., DeLucia, E.H., 2020. Soils’ dirty little secret: Depth-based comparisons can be inadequate for quantifying changes in soil organic carbon and other mineral soil properties. Glob. Chang. Biol. 3759–3770.

Walker, T.S., Bais, H.P., Grotewold, E., Vivanco, J.M., 2003. Root Exudation and Rhizosphere Biology. Plant Physiol. 132, 44–51.

Wang, B., Liu, D., Yang, J., Zhu, Z., Darboux, F., Jiao, J., 2021. Effects of forest floor characteristics on soil labile carbon as varied by topography and vegetation type in the Chinese Loess Plateau. Catena 196, 104825.

Wang, S., Huang, M., Shao, X., Mickler, R.A., Li, K., Ji, J., 2004. Vertical distribution of soil organic carbon in China. Environ. Manage. 33, 200–209.

Wang, W., Baldock, J.A., Dalal, R.C., Moody, P.W., 2004. Decomposition dynamics of plant materials in relation to nitrogen availability and biochemistry determined by NMR and wet-chemical analysis. Soil Biol. Biochem. 36, 2045–2058.

Wen, Y., Wen, J., Wang, Q., Bai, L., Wang, Y., Su, S., Wu, C., Zeng, X., 2021. Organic carbon preservation promoted by aromatic compound-iron complexes through manure fertilization in red soil. Soils and Sediments 21, 295–306.

White, F., 1983. The vegetation of Africa: a descriptive memoir to accompany the UNESCO/AETFAT/UNSO vegetation map of Africa, Natural Resources Research.

Whitmore, A.P., Kirk, G.J.D., Rawlins, B.G., 2015. Technologies for increasing carbon storage in soil to mitigate climate change. Soil Use Manag. 31, 62–71.

Wibowo, D.., 1999. Deforestation, Capital Accumulation and Consumption: Strategic Implications for sustainable Development. In: International Sustainable Development Research Conference. University of Leeds, UK, pp. 394–400.

Xing, Z., Tian, K., Du, C., Li, C., Zhou, J., Chen, Z., 2019. Agricultural soil characterization by FTIR spectroscopy at micrometer scales : Depth profiling by photoacoustic spectroscopy. Geoderma 335, 94–103.

Yang, X., Zhang, Q., Li, X., Jia, X., Wei, X., Shao, M., 2015. Determination of Soil Texture by Laser Diffraction Method. Soil Sci. Soc. Am. J.

Yeasmin, S., Singh, B., Smernik, R.J., Johnston, C.T., 2020. Effect of land use on organic matter composition in density fractions of contrasting soils : A comparative study using 13 C NMR and DRIFT spectroscopy. Sci. Total Environ. 726, 138395.

Yu, G., Xiao, J., Hu, S., Polizzotto, M.L., Zhao, F., Mcgrath, S.P., Li, H., Ran, W., Shen, Q., 2017. Mineral Availability as a Key Regulator of Soil Carbon Storage. Environ. Sci. Technol. 51, 4960−4969.

Yu, H. qing, Li, Y., Zhou, N., Chappell, A., Li, X. yu, Poesen, J., 2016. Soil nutrient loss due to tuber crop harvesting and its environmental impact in the North China Plain. J. Integr. Agric. 15, 1612–1624.

Yuste, J.C., Baldocchi, D.D., Gershenson, A., Goldstein, A., Misson, L., Wong, S., 2007. Microbial soil respiration and its dependency on carbon inputs , soil temperature and moisture. Glob. Chang. Biol. 13, 2018–2035.

Zacháry, D., Filep, T., Jakab, G., Molnár, M., Kertész, T., Király, C., Hegyi, I., Gáspár, L., Szalai, Z., 2020. Carbon isotope measurements to determine the turnover of soil organic matter fractions in a temperate forest soil. Agronomy 10, 1–13.

Zhang, Y., Biswas, A., Adamchuk, V.I., 2017. Implementation of a sigmoid depth function to describe change of soil pH with depth. Geoderma 289, 1–10.

Zhou, G., Zhou, X., He, Y., Shao, J., Hu, Z., Liu, R., Zhou, H., Hosseinibai, S., 2017. Grazing intensity significantly affects belowground carbon and nitrogen cycling in grassland ecosystems: a meta-analysis. Glob. Chang. Biol. 23, 1167–1179.

Zieger, A., Kaiser, K., Guayasamín, R.P., Kaupenjohann, M., 2018. Massive carbon addition to an organic-rich Andosol did not increase the topsoil but the subsoil carbon stock. Biogeosciences 15, 1–30.

Appendices

Appendix 1. Supporting information for Chapter 3

This supporting information contains:

- Table SI-1. The mass of soil used for each sample in the soil organic matter fractionation method in order to obtain a consistent ratio of 2:80 (w/v) of soil organic C to sodium polystungstate (SPT).
- Table SI-2 Soil properties under different land uses
- Table SI-3 Soil properties with depth in successive 10 cm intervals
- Table SI-4 Soil organic C (g kg-1) in the free (fPOM), intra-macro aggregate (iMacro), intra-micro (imicro) aggregate and mineral associated organic matter (MinOM) fractions under different land uses and between selected soil layers
- Table SI-5 Ammonium oxalate extractable Al, Fe, Mn (mg/kg) under different land uses and between selected soil layers
- Figure SI-1 Soil texture (% clay, silt and sand), particle size in median diameter (µm), soil pH (H2O), total organic carbon (TOC) (g kg-1), total nitrogen (g kg-1), and C:N ratio at 10 cm depth increments to 1 m under Arable, Grassland, and Woodland land uses at Sonning farm (a), Hall farm (b) and The Vyne (c), (d) average, where bars represent standard error of the mean of three sub-samples. Graph d of each parameter shows the mean values from all three sites and error bars represent the standard errors of the mean using the three sites as replicates.
- Table SI-6 Soil properties and results of mixed effects model (MEM) analysis where soil depth and land were fixed factors and farm location was a random factor
- Table SI-7 Mixed effect model analysis of TOC, Nitrogen and C N Ratio, soil pH (H_2O) and soil texture (Clay, Silt and Sand) where farm locations as random factor and land use and soil depth as fixed factor

Table SI-1. The mass of soil used for each sample in the soil organic matter fractionation method in order to obtain a consistent ratio of 2:80 (w/v) of soil organic C to sodium polystungstate (SPT).

No	Location	Sample Code	C (mg g^{-1})	SPT (mL)	Soil (g)
1	Hall Farm	Arable (0-10 cm)	17.71	80	9.04
2		Arable (20-30 cm)	17.68	80	9.05
3		Arable (50-60 cm)	6.15	80	26.03
4		Arable (90-100 cm)	4.13	80	38.76
5		Grassland (0-10 cm)	32.98	80	4.85
6		Grassland (20-30 cm)	14.88	80	10.75
7		Grassland (50-60 cm)	6.31	80	25.35
8		Grassland (90-100 cm)	5.37	80	29.78
9		Woodland (0-10 cm)	44.02	80	3.63
10		Woodland (20-30 cm)	16.20	80	9.88
11		Woodland (50-60 cm)	7.59	80	21.07
12		Woodland (90-100 cm)	4.81	80	33.28
13	Sonning Farm	Arable (0-10 cm)	18.58	80	8.61
14		Arable (20-30 cm)	16.44	80	9.73
15		Arable (50-60 cm)	6.19	80	25.84
16		Arable (90-100 cm)	4.20	80	38.06
17		Grassland (0-10 cm)	30.14	80	5.31
18		Grassland (20-30 cm)	17.20	80	9.30
19		Grassland (50-60 cm)	7.13	80	22.44
20		Grassland (90-100 cm)	4.50	80	35.57
21		Woodland (0-10 cm)	38.32	80	4.18
22		Woodland (20-30 cm)	13.03	80	12.28
23		Woodland (50-60 cm)	9.36	80	17.09
24		Woodland (90-100 cm)	6.39	80	25.05
25	The Vyne	Arable (0-10 cm)	15.12	80	10.58
26		Arable (20-30 cm)	10.03	80	15.95
27		Arable (50-60 cm)	3.17	80	50.55
28		Arable (90-100 cm)	1.35	80	118.70
29		Grassland (0-10 cm)	37.19	80	4.30
30		Grassland (20-30 cm)	15.06	80	10.62
31		Grassland (50-60 cm)	5.81	80	27.52
32		Grassland (90-100 cm)	1.51	80	106.14
33		Woodland (0-10 cm)	32.36	80	4.94
34		Woodland (20-30 cm)	9.95	80	16.07
35		Woodland (50-60 cm)	5.34	80	29.98
36		Woodland (90-100 cm)	2.79	80	57.42

Table SI-2 Soil properties under different land uses (mean ± standard error of the mean)

Land Use	%Clay	%Silt	%Sand	Median particle diameter (µm)	pH (H_20)	Total C (g kg^{-1})	Total N (g kg^{-1})	C:N Ratio
Arable	8.23±0.05 a	52.44±2.19 a	39.33±2.24 a	39.69±3.52 a	6.09±0.20 a	8.35±1.03 a	1.01±0.10 a	7.72±0.31 a
Grassland	8.20±0.05 a	50.10±1.87 a	41.71±1.91 a	42.70±3.34 a	6.81±0.12 b	11.51±1.73 b	1.27±0.16 b	8.44±0.28 b
Woodland	8.33±0.07 a	50.34±2.46 a	41.34±2.52 a	41.79±4.48 a	4.81±0.11 c	11.99±1.90 b	1.08±0.14 a	10.46±0.36 c

Different letters within a column represent statistically significant differences at α = 0.05.
Data were averaged across all 10 depth increments and all three locations (Sonning, Hall Farm and The Vyne) for each land use.

Table SI-3 Soil properties with depth (mean ± standard error of the mean) in successive 10 cm intervals

Depth (cm)	%Clay	%Silt	%Sand	Median particle diameter (µm)	pH (H_20)	Total C (g kg^{-1})	Total N (g kg^{-1})	C:N Ratio
0-10cm	8.02±0.02 c	37.33±2.32 d	54.65±2.34 a	65.49±6.43a	5.44±0.32 a	29.60±3.40 a	2.64±0.26 a	11.19±0.71 a
10-20cm	8.01±0.03 c	39.43±2.61 cd	52.56±2.63 ab	61.82±5.29ab	5.45±0.39 a	19.68±1.53 b	1.89±0.16 b	10.59±0.64 ab
20-30cm	8.07±0.06 c	44.00±3.00 bcd	47.93±3.04 abc	53.22±5.73bc	5.68±0.39 a	14.49±0.97 c	1.53±0.12 c	9.75±0.59 bc
30-40cm	8.14±0.07 bc	50.06±3.64 abc	41.80±3.69 bcd	42.87±6.12cd	5.83±0.39 a	9.51±0.73 d	1.07±0.08 d	9.07±0.50 cd
40-50cm	8.19±0.08 bc	53.60±3.63 ab	38.22±3.69 cd	37.39±5.67de	5.97±0.38 a	7.39±0.56 de	0.86±0.06 de	8.70±0.43 cd
50-60cm	8.21±0.07 bc	54.48±3.95 ab	37.31±4.01 cd	36.01±6.13de	6.01±0.40 a	6.34±0.56 ef	0.75±0.06 def	8.48±0.38 cde
60-70cm	8.40±0.10 ab	56.73±3.27 a	34.87±3.36 d	31.22±4.98de	6.06±0.37 a	5.77±0.75 ef	0.72±0.09 ef	8.02±0.51 de
70-80cm	8.46±0.13 ab	56.48±3.41 a	35.07±3.53 d	30.89±5.45de	6.18±0.41 a	5.03±0.75 ef	0.62±0.06 ef	7.94±0.71 de
80-90cm	8.55±0.14 a	58.31±2.97 a	33.14±3.08 d	28.01±4.67e	6.13±0.42 a	4.45±0.56 ef	0.56±0.05 ef	7.77±0.61 de
90-100cm	8.45±0.14 ab	59.17±2.94 a	32.38±3.06 d	27.00±4.47e	6.27±0.42 a	3.89±0.57 f	0.51±0.05 f	7.19±0.72 e

Different letters within a column represent statistically significant differences at α = 0.05
Data were averaged across all landuses (arable, grassland and woodland) and all three locations (Sonning, Hall Farm and The Vyne).

Table SI-4 Soil organic C (g kg^{-1}) in the free (fPOM), intra-macro aggregate (iMacro), intra-micro (imicro) aggregate and mineral associated organic matter (MinOM) fractions under different land uses (mean ± standard error, n = 12) and between selected soil layers (mean ± standard error, n = 9)

Landuse	fPOM_	iMacro	imicro	MinOC
Arable	0.25±0.10 a	0.08±0.02 a	0.43±0.13 a	4.28±0.63 a
Grassland	0.48±0.24 b	0.11±0.04 a	1.43±0.75 a	4.39±1.00 a
Woodland	2.29±0.99 b	0.34±0.16 a	1.11±0.40 a	3.11±0.47 a
Depth	fPOM	iMacro	imicro	MinOC
0-10 cm	3.27±1.20 a	0.48±0.20 a	2.95±0.86 a	6.19±0.79 a
20-30 cm	0.46±0.15 b	0.12±0.02 b	0.78±0.09 b	4.56±0.85 ab
50-60 cm	0.16±0.06 b	0.07±0.02 b	0.15±0.07 b	2.96±0.66 b
90-100 cm	0.14±0.06 b	0.04±0.02 b	0.07±0.04 b	2.01±0.36 b

Different letters within a column represent statistically significant differences at α = 0.05. Data in the top half of the table represent the mean of soil samples collected under the same land use (Arable, Grassland, or Woodland) across three different locations (Sonning, Hall Farm and The Vyne) at four selected depth layers (0-10 cm, 20-30 cm, 50-60 cm, and 90-100 cm). Data in the bottom half of the table represent the mean of soil samples collected at the same depth (0-10 cm, 20-30 cm, 50-60 cm, or 90-100 cm) across three different locations (Sonning, Hall Farm and The Vyne) and three different land uses at eat location (Arable, Grassland, or Woodland).

Tabel SI-5 Ammonium oxalate extractable Al, Fe, Mn (mg/kg) under different land uses (mean ± standard error, n = 12) and between selected soil layers (mean ± standard error, n = 9)

Landuse	Al	Fe	Mn
Arable	1038.05±85.6 a	3919.80±360.0 a	433.99±43.2 a
Grassland	984.33±97.6 a	3673.74±260.1 a	287.51±32.0 b
Woodland	1114.50±63.2 a	3620.18±185.3 a	278.07±47.3 b
Depth	Al	Fe	Mn
0-10 cm	838.42±60.7 b	3894.44±206 a	327.57±43.1 a
20-30 cm	925.96±59.8 ab	4058.27±259 a	378.57±46.2 a
50-60 cm	1218.16±94.7 a	3706.58±360 a	385.55±58.7 a
90-100 cm	1199.97±97.9 a	3292.35±392 a	241.08±53.3 a

Different letters within a column represent statistically significant differences at α = 0.05 Data in the top half of the table represent the mean of soil samples collected under the same land use (Arable, Grassland, or Woodland) across three different locations (Sonning, Hall Farm and The Vyne) at four selected depth layers (0-10 cm, 20-30 cm, 50-60 cm, and 90-100 cm). Data in the bottom half of the table represent the mean of soil samples collected at the same depth (0-10 cm, 20-30 cm, 50-60 cm, or 90-100 cm) across three different locations (Sonning, Hall Farm and The Vyne) and three different land uses at eat location (Arable, Grassland, or Woodland).

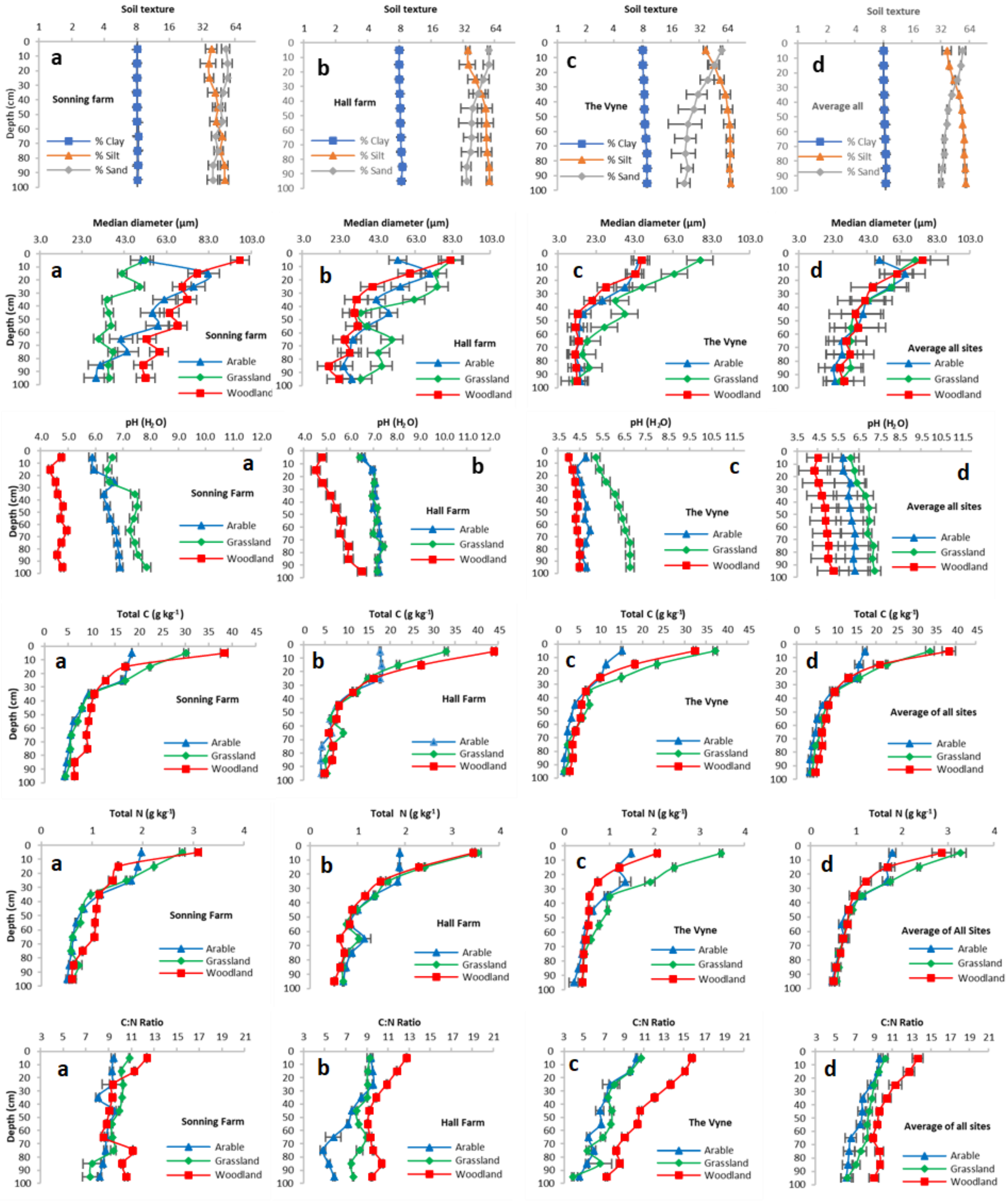


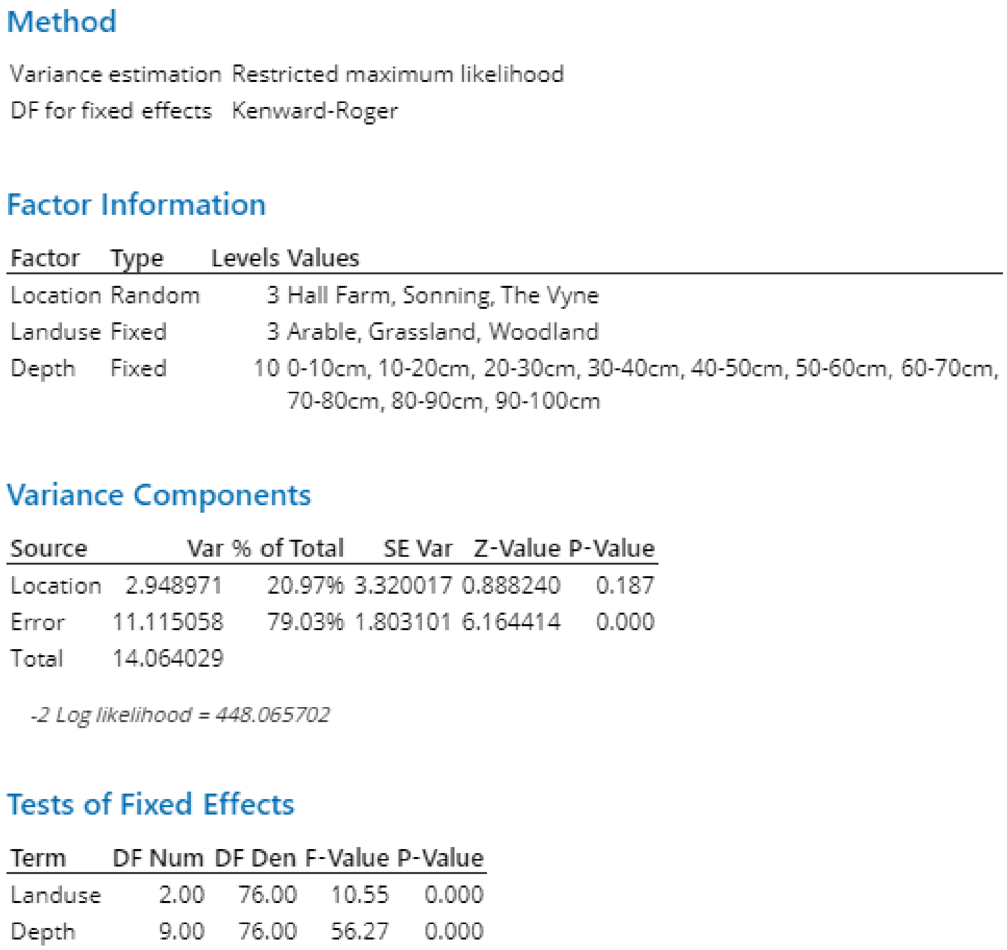
Figure SI-1 Soil texture (% clay, silt and sand), particle size in median diameter (µm), soil pH (H_2O), total organic carbon (TOC) (g kg-1), total nitrogen (g kg-1), and C:N ratio at 10 cm depth increments to 1 m under Arable, Grassland, and Woodland land uses at Sonning farm (a), Hall farm (b) and The Vyne (c), (d) average, where bars represent standard error of the mean of three sub-samples. Graph d of each parameter shows the mean values from all three locations and error bars represent the standard errors of the mean using the three locations as replicates which data were averaged across study sites.

Table SI-6 Soil properties and results of mixed effects model (MEM) analysis where soil depth and land were fixed factors and farm location was a random factor

No	Soil Properties	ANOVA results of MEM		
		Depth	Land use	Location
1	Total C	0.000*	0.000*	0.187 ns
2	Total N	0.000*	0.003*	0.177 ns
3	C N Ratio	0.000*	0.000*	0.209 ns
4	pH (H_2O)	0.000*	0.000*	0.161 ns
5	% Clay	0.000*	0.031*	0.165 ns
6	% Silt	0.000*	0.187 ns	0.164 ns
7	% Sand	0.000*	0.357 ns	0.164 ns
8	Median D50	0.000*	0.614 ns	0.165 ns

Table SI-7 Mixed effect model analysis of TOC, Nitrogen and C N Ratio, soil pH (H_2O) and soil texture (Clay, Silt and Sand) where farm locations as random factor and land use and soil depth as fixed factor

Mixed Effects Model of Total C versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

```
Variance estimation  Restricted maximum likelihood
DF for fixed effects Kenward-Roger
```

Factor Information

```
Factor   Type    Levels Values
Location Random       3 Hall Farm, Sonning, The Vyne
Landuse  Fixed        3 Arable, Grassland, Woodland
Depth    Fixed       10 0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm,
                        70-80cm, 80-90cm, 90-100cm
```

Variance Components

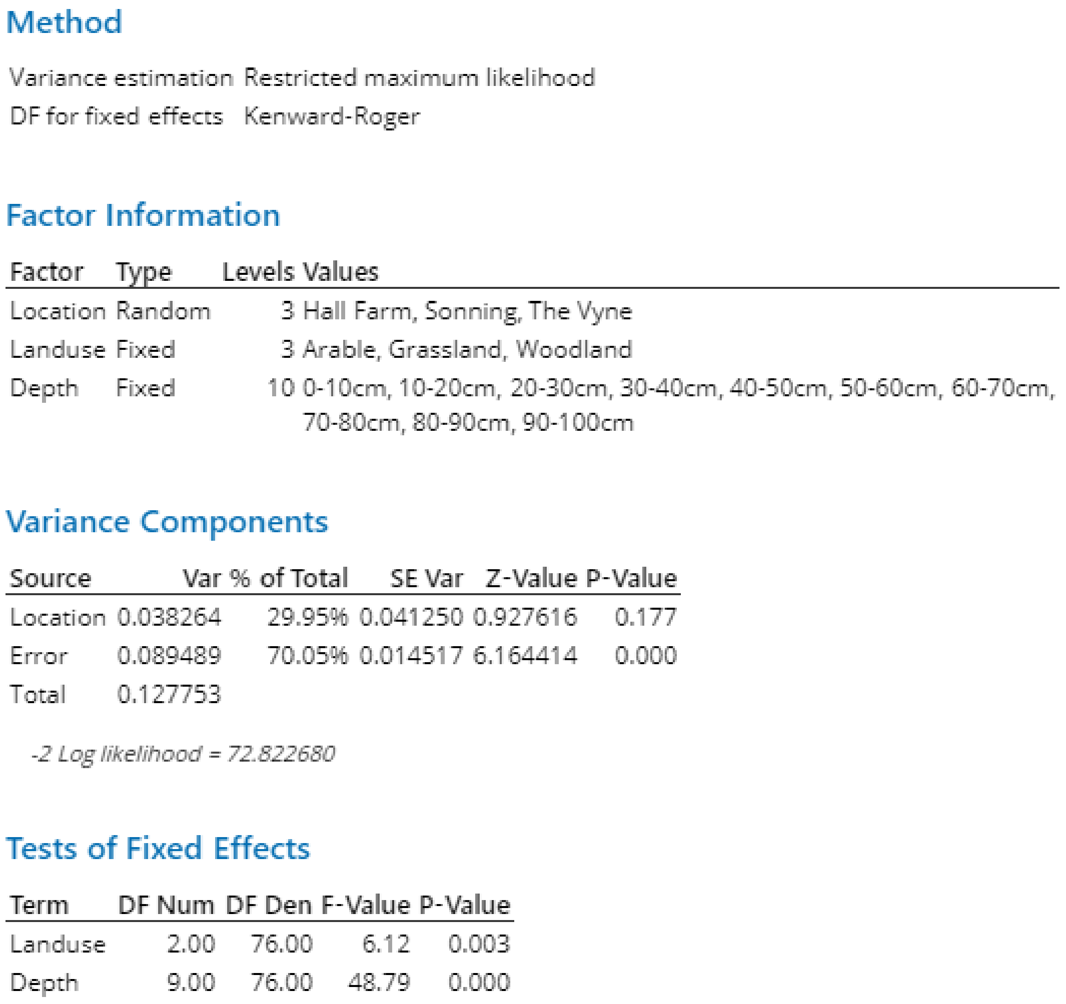
```
Source         Var  % of Total   SE Var  Z-Value P-Value
Location  2.948971      20.97% 3.320017 0.888240   0.187
Error    11.115058      79.03% 1.803101 6.164414   0.000
Total    14.064029

  -2 Log likelihood = 448.065702
```

Tests of Fixed Effects

```
Term     DF Num  DF Den  F-Value P-Value
Landuse    2.00   76.00    10.55   0.000
Depth      9.00   76.00    56.27   0.000
```

Mixed Effects Model of Total N versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Landuse	Fixed	3	Arable, Grassland, Woodland
Depth	Fixed	10	0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm, 70-80cm, 80-90cm, 90-100cm

Variance Components

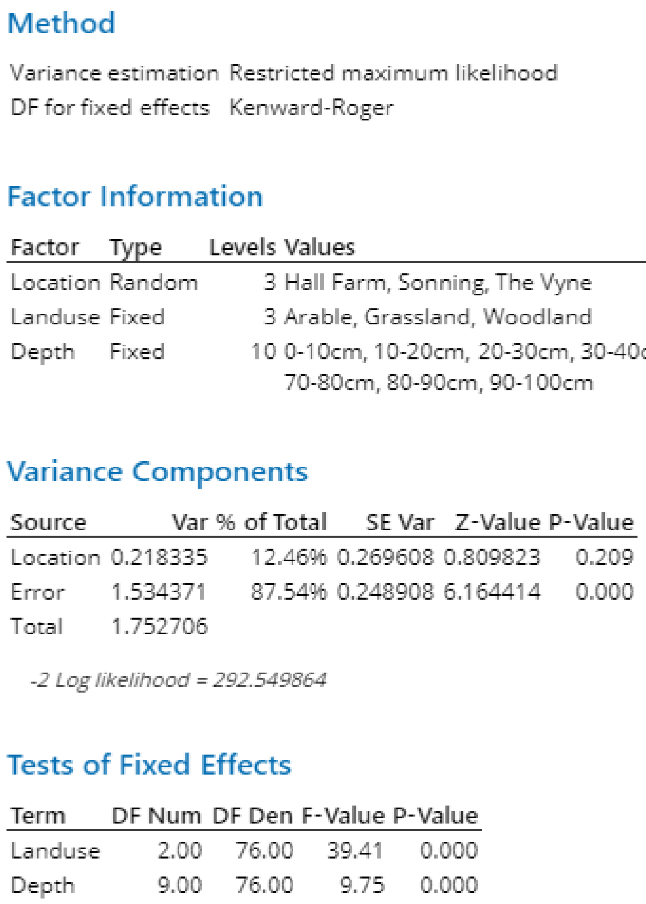
Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	0.038264	29.95%	0.041250	0.927616	0.177
Error	0.089489	70.05%	0.014517	6.164414	0.000
Total	0.127753				

-2 Log likelihood = 72.822680

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Landuse	2.00	76.00	6.12	0.003
Depth	9.00	76.00	48.79	0.000

Mixed Effects Model of C N Ratio versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Landuse	Fixed	3	Arable, Grassland, Woodland
Depth	Fixed	10	0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm, 70-80cm, 80-90cm, 90-100cm

Variance Components

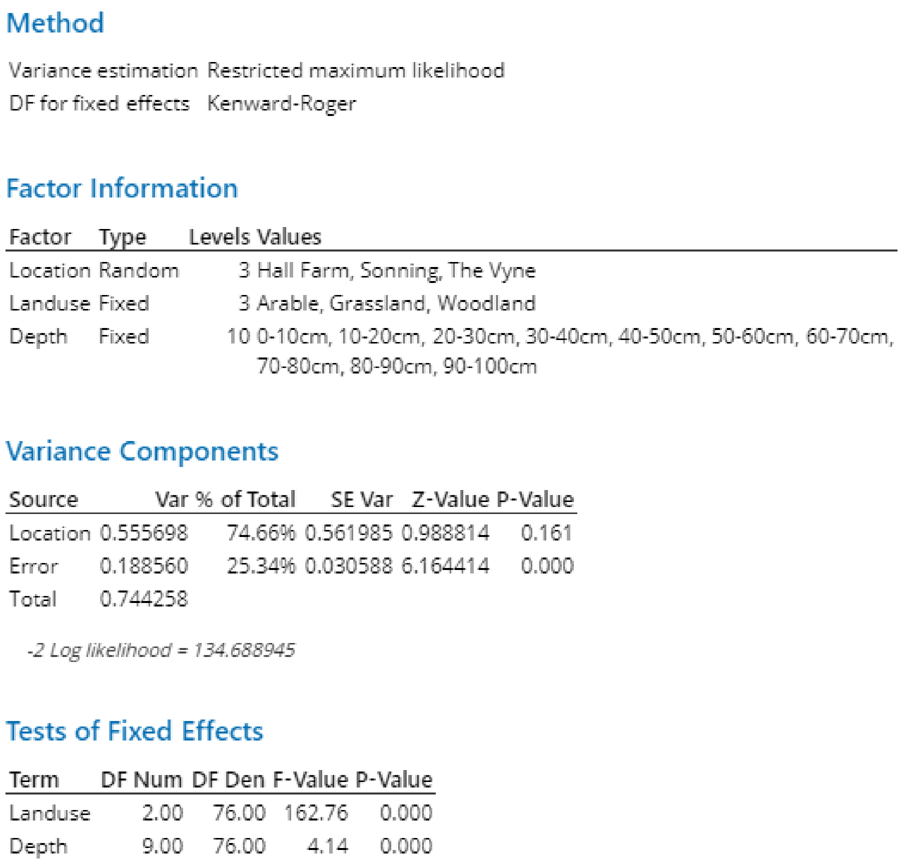
Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	0.218335	12.46%	0.269608	0.809823	0.209
Error	1.534371	87.54%	0.248908	6.164414	0.000
Total	1.752706				

-2 Log likelihood = 292.549864

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Landuse	2.00	76.00	39.41	0.000
Depth	9.00	76.00	9.75	0.000

Mixed Effects Model of soil pH (H_2O) versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Landuse	Fixed	3	Arable, Grassland, Woodland
Depth	Fixed	10	0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm, 70-80cm, 80-90cm, 90-100cm

Variance Components

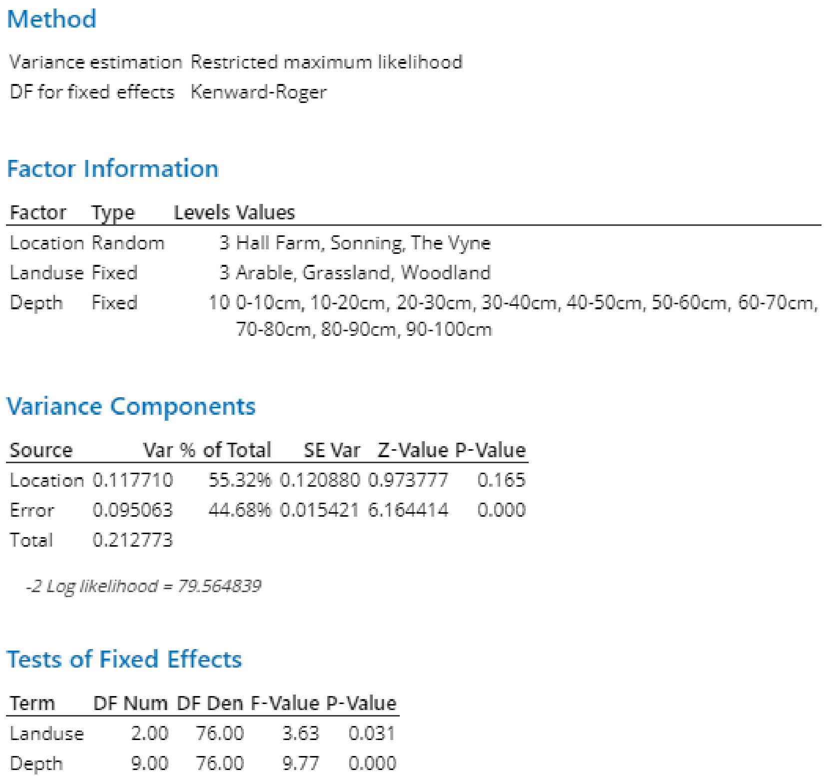
Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	0.555698	74.66%	0.561985	0.988814	0.161
Error	0.188560	25.34%	0.030588	6.164414	0.000
Total	0.744258				

-2 Log likelihood = 134.688945

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Landuse	2.00	76.00	162.76	0.000
Depth	9.00	76.00	4.14	0.000

Mixed Effects Model of % Clay versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Landuse	Fixed	3	Arable, Grassland, Woodland
Depth	Fixed	10	0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm, 70-80cm, 80-90cm, 90-100cm

Variance Components

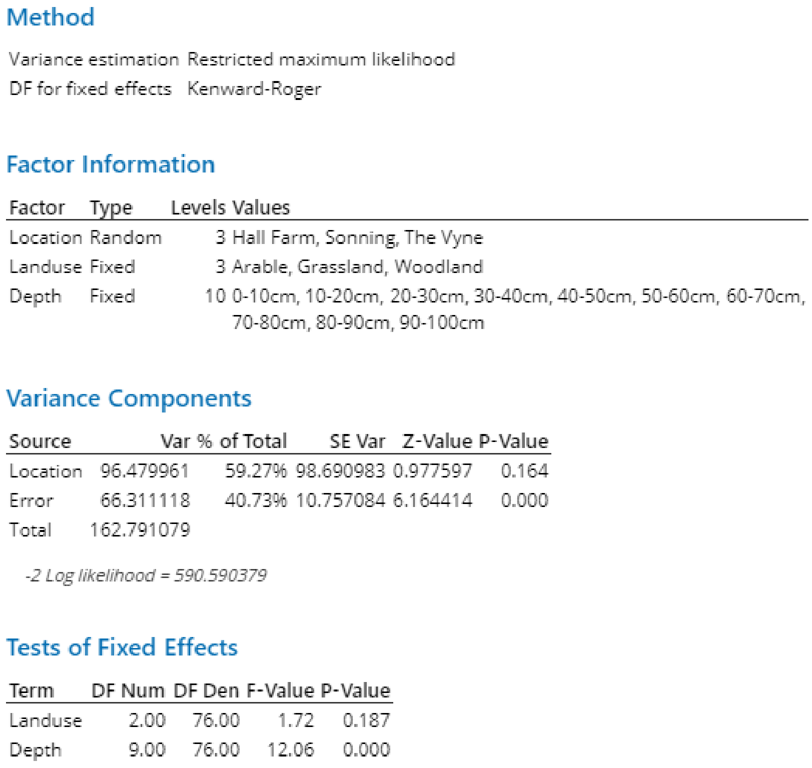
Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	0.117710	55.32%	0.120880	0.973777	0.165
Error	0.095063	44.68%	0.015421	6.164414	0.000
Total	0.212773				

-2 Log likelihood = 79.564839

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Landuse	2.00	76.00	3.63	0.031
Depth	9.00	76.00	9.77	0.000

Mixed Effects Model of % Silt versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Landuse	Fixed	3	Arable, Grassland, Woodland
Depth	Fixed	10	0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm, 70-80cm, 80-90cm, 90-100cm

Variance Components

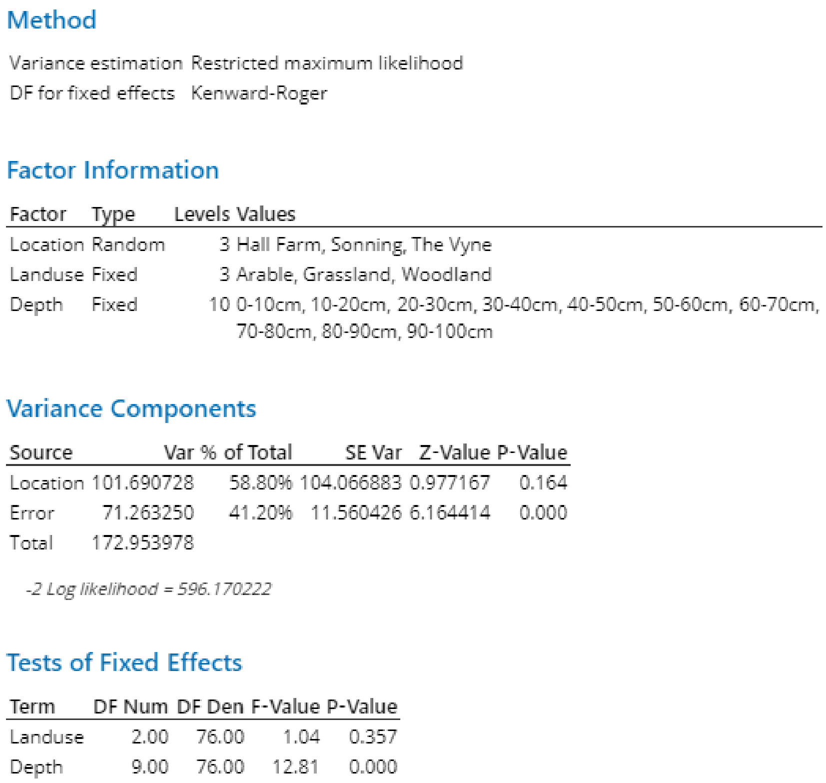
Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	96.479961	59.27%	98.690983	0.977597	0.164
Error	66.311118	40.73%	10.757084	6.164414	0.000
Total	162.791079				

-2 Log likelihood = 590.590379

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Landuse	2.00	76.00	1.72	0.187
Depth	9.00	76.00	12.06	0.000

Mixed Effects Model of % Sand versus Location as random factor and Land use and Layer (soil depth) as fixed factor



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Method

Variance estimation  Restricted maximum likelihood
DF for fixed effects   Kenward-Roger


Factor Information

Factor   Type     Levels Values
Location Random        3 Hall Farm, Sonning, The Vyne
Landuse  Fixed         3 Arable, Grassland, Woodland
Depth    Fixed        10 0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm,
                         70-80cm, 80-90cm, 90-100cm


Variance Components

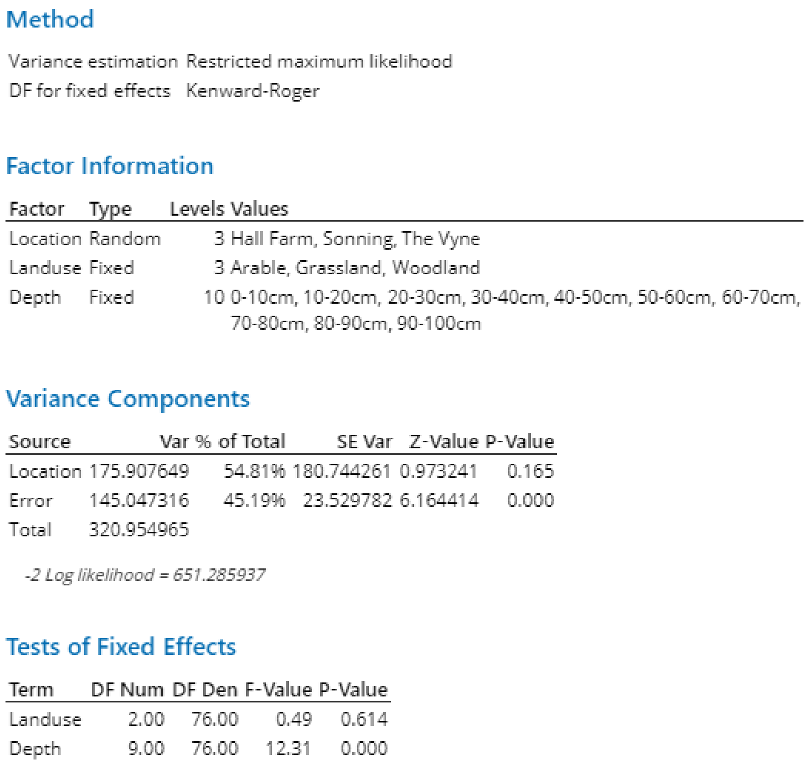
Source          Var  % of Total      SE Var  Z-Value P-Value
Location 101.690728     58.80% 104.066883 0.977167    0.164
Error     71.263250     41.20%  11.560426 6.164414    0.000
Total    172.953978

  -2 Log likelihood = 596.170222


Tests of Fixed Effects

Term     DF Num  DF Den F-Value P-Value
Landuse    2.00   76.00    1.04   0.357
Depth      9.00   76.00   12.81   0.000
```

Mixed Effects Model of Median D50 versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Landuse	Fixed	3	Arable, Grassland, Woodland
Depth	Fixed	10	0-10cm, 10-20cm, 20-30cm, 30-40cm, 40-50cm, 50-60cm, 60-70cm, 70-80cm, 80-90cm, 90-100cm

Variance Components

Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	175.907649	54.81%	180.744261	0.973241	0.165
Error	145.047316	45.19%	23.529782	6.164414	0.000
Total	320.954965				

-2 Log likelihood = 651.285937

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Landuse	2.00	76.00	0.49	0.614
Depth	9.00	76.00	12.31	0.000

Appendix 2. Supporting information for Chapter 4

This supplementary material contains:

- Table SI-1 Mass of soil samples used for each fPOM extraction according to ratio (2:80, w/v) of soil organic matter to sodium polystungstate (SPT), the mass of fPOM recovered from each sample, and the % of the sample that was identified as fPOM.
- Table SI-2. Peak assignment of absorption bands in FTIR spectra of fPOM and results of mixed effects model (MEM) analysis of z-score normalised peaks and decomposability (Index I) and recalcitrance (Index II) indices where soil depth and land were fixed factors and location was a random factor
- Table SI-3 Mixed effect model analysis of SOC, Nitrogen and C N Ratio of fPOM where locations as random factor and land use and soil depth as fixed factor

Table SI-1 Mass of soil samples used for each fPOM extraction according to ratio (2:80, w/v) of soil organic matter to sodium polystungstate (SPT), the mass of fPOM recovered from each sample, and the % of the sample that was identified as fPOM.

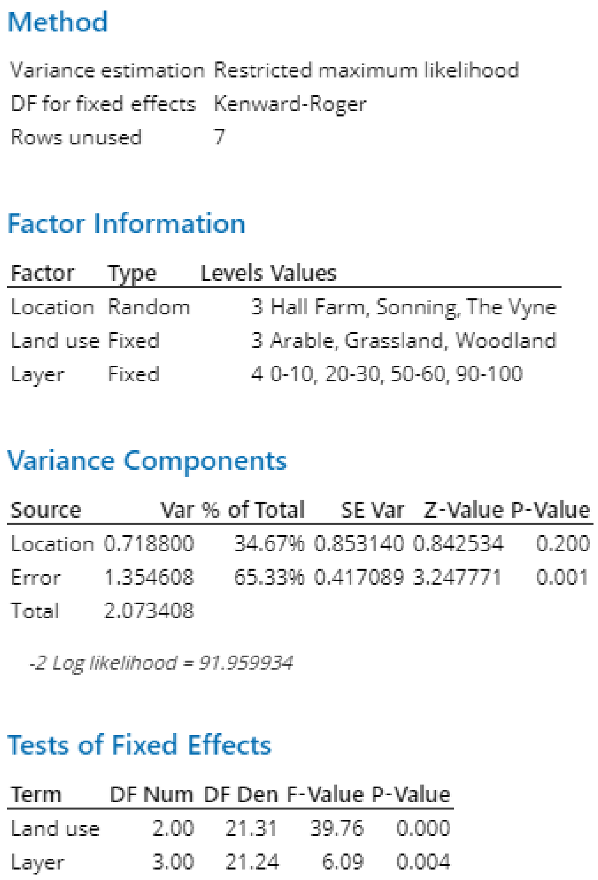
No	Location	Land Use and Depth	C (mg/g)	SPT (mL)	Soil (g)	fPOM (g)	fPOM (%)
1	Sonning	Arable (0-10 cm)	18.58	80	8.61	0.60	6.94
2		Arable (20-30 cm)	16.44	80	9.73	0.57	5.82
3		Arable (50-60 cm)	6.19	80	25.84	0.37	1.45
4		Arable (90-100 cm)	4.20	80	38.06	0.37	0.96
5		Grassland (0-10 cm)	30.14	80	5.31	0.49	9.31
6		Grassland (20-30 cm)	17.20	80	9.30	0.41	4.40
7		Grassland (50-60 cm)	7.13	80	22.44	0.41	1.81
8		Grassland (90-100 cm)	4.50	80	35.57	0.35	0.98
9		Woodland (0-10 cm)	38.32	80	4.18	1.22	29.16
10		Woodland (20-30 cm)	13.03	80	12.28	0.75	6.07
11		Woodland (50-60 cm)	9.36	80	17.09	0.53	3.12
12		Woodland (90-100 cm)	6.39	80	25.05	0.58	2.32
13	Hall Farm	Arable (0-10 cm)	17.71	80	9.04	0.64	7.06
14		Arable (20-30 cm)	17.68	80	9.05	0.44	4.90
15		Arable (50-60 cm)	6.15	80	26.03	0.50	1.91
16		Arable (90-100 cm)	4.13	80	38.76	0.53	1.37
17		Grassland (0-10 cm)	32.98	80	4.85	0.75	15.49
18		Grassland (20-30 cm)	14.88	80	10.75	0.76	7.06
19		Grassland (50-60 cm)	6.31	80	25.35	0.50	1.99
20		Grassland (90-100 cm)	5.37	80	29.78	0.60	2.01
21		Woodland (0-10 cm)	44.02	80	3.63	1.10	30.17
22		Woodland (20-30 cm)	16.20	80	9.88	0.60	6.12
23		Woodland (50-60 cm)	7.59	80	21.07	0.38	1.83
24		Woodland (90-100 cm)	4.81	80	33.28	0.33	0.98
25	The Vyne	Arable (0-10 cm)	15.12	80	10.58	0.74	6.99
26		Arable (20-30 cm)	10.03	80	15.95	0.47	2.98
27		Arable (50-60 cm)	3.17	80	50.55	0.30	0.59
28		Arable (90-100 cm)	1.35	80	118.70	0.33	0.27
29		Grassland (0-10 cm)	37.19	80	4.30	0.86	20.04
30		Grassland (20-30 cm)	15.06	80	10.62	0.73	6.83
31		Grassland (50-60 cm)	5.81	80	27.52	0.53	1.92
32		Grassland (90-100 cm)	1.51	80	106.14	0.57	0.53
33		Woodland (0-10 cm)	32.36	80	4.94	0.48	9.77
34		Woodland (20-30 cm)	9.95	80	16.07	0.42	2.59
35		Woodland (50-60 cm)	5.34	80	29.98	0.31	1.03
36		Woodland (90-100 cm)	2.79	80	57.42	0.38	0.66

Table SI-2 Peak assignment of absorption bands in FTIR spectra of fPOM and results of mixed effects model (MEM) analysis of z-score normalised peaks and decomposability (Index I) and recalcitrance (Index II) indices where soil depth and land were fixed factors and location was a random factor

No	Wavenumber (cm^{-1})/ indices	Peak Assignment	ANOVA results of MEM	
			Depth	Landuse
1	763	Aromatic C-H, 3-4 adjacent H deformation	0.16 ns	0.30 ns
2	874	Aromatic δ(C-H), less substituted	0.21 ns	0.12 ns
3	930	Aromatic δ(C-H)	0.41 ns	0.20 ns
4	1029	C–O stretching vibrations of C–O–C groups	0.18 ns	0.25 ns
5	1240	C–O stretch in carboxylic acid, phenol C–O asymmetric stretch, OH deformation, ester	0.09 ns	0.00*
6	1417	Aliphatic (C–H) deformation of CH2 or CH3 groups aliphatic C-H deformation of CH2 and CH3 groups	0.03*	0.06 ns
7	1621	C=O stretching vibrations of COO$^-$anion aromatic-C (C C) vibrations and to a smaller extent to conjugated carbonyl-C (C O) such as quinones. stretching vibrations of aromatic C=C double bonds conjugated with C=O or COO– bonds or both, i.e. of unsaturated ketones, carboxylic acids or amides	0.05 ns	0.19 ns
8	2162	Carbohydrate overtones of –COH stretching C≡C Terminal alkyne (monosubstituted)	0.22 ns	0.02*
9	2853	Asymmetric and symmetric C–H stretching vibrations of CH3 and CH2 groups	0.08 ns	0.79 ns
10	2921		0.18 ns	0.98 ns
11	3355	stretching vibrations of H-bonded hydroxyl (O-H) groups of phenols with traces of amine (N–H) stretch	0.64 ns	0.02*
12	Index I	fPOM degree of decomposition index	0.37 ns	0.14 ns
13	Index II	fPOM Recalcitrance index	0.00*	0.58 ns

Table SI-3 Mixed effect model analysis of SOC, Nitrogen and C N Ratio of fPOM where locations as random factor and land use and soil depth as fixed factor.

Mixed Effects Model of fPOM N versus Location as random factor and land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger
Rows unused	7

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Land use	Fixed	3	Arable, Grassland, Woodland
Layer	Fixed	4	0-10, 20-30, 50-60, 90-100

Variance Components

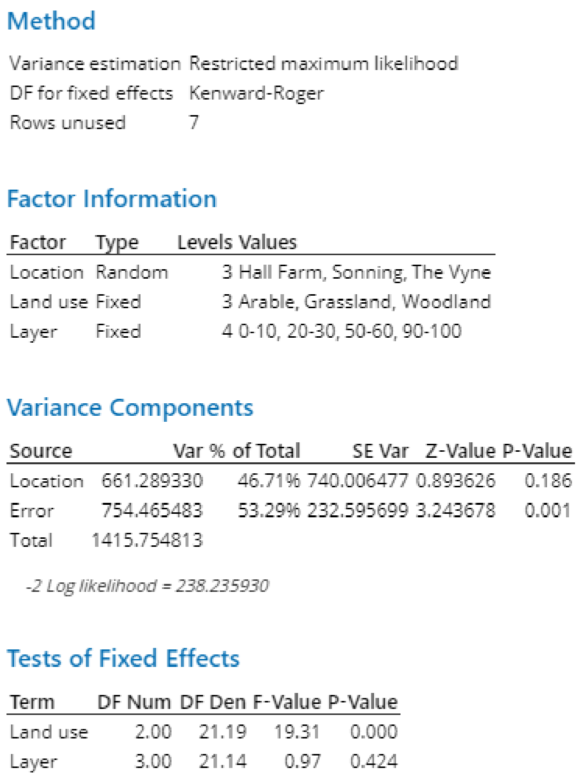
Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	0.718800	34.67%	0.853140	0.842534	0.200
Error	1.354608	65.33%	0.417089	3.247771	0.001
Total	2.073408				

-2 Log likelihood = 91.959934

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Land use	2.00	21.31	39.76	0.000
Layer	3.00	21.24	6.09	0.004

Mixed Effects Model of fPOM C versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger
Rows unused	7

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Land use	Fixed	3	Arable, Grassland, Woodland
Layer	Fixed	4	0-10, 20-30, 50-60, 90-100

Variance Components

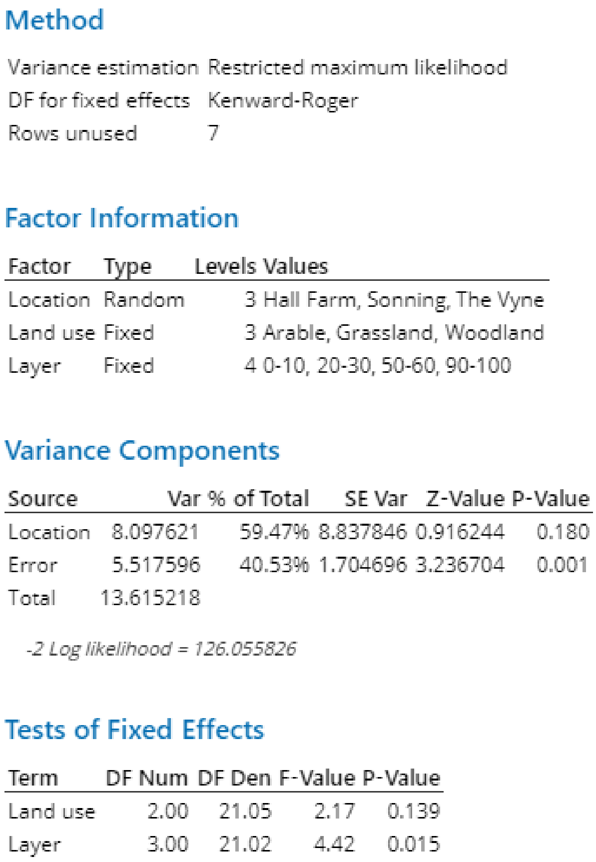
Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	661.289330	46.71%	740.006477	0.893626	0.186
Error	754.465483	53.29%	232.595699	3.243678	0.001
Total	1415.754813				

-2 Log likelihood = 238.235930

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Land use	2.00	21.19	19.31	0.000
Layer	3.00	21.14	0.97	0.424

Mixed Effects Model of fPOM C N ratio versus Location as random factor and Land use and Layer (soil depth) as fixed factor



Method

Variance estimation	Restricted maximum likelihood
DF for fixed effects	Kenward-Roger
Rows unused	7

Factor Information

Factor	Type	Levels	Values
Location	Random	3	Hall Farm, Sonning, The Vyne
Land use	Fixed	3	Arable, Grassland, Woodland
Layer	Fixed	4	0-10, 20-30, 50-60, 90-100

Variance Components

Source	Var	% of Total	SE Var	Z-Value	P-Value
Location	8.097621	59.47%	8.837846	0.916244	0.180
Error	5.517596	40.53%	1.704696	3.236704	0.001
Total	13.615218				

-2 Log likelihood = 126.055826

Tests of Fixed Effects

Term	DF Num	DF Den	F-Value	P-Value
Land use	2.00	21.05	2.17	0.139
Layer	3.00	21.02	4.42	0.015

Appendix 3. Supporting information for Chapter 5

This supplementary material contains:

- Table SI-1 Mass of soil used to extract free particulate organic matter (fPOM) according to ratio (2:80, w/v) of soil organic carbon (SOC) to 1.85 g ml^{-1} density sodium polystungstate (SPT).
- Table SI-2 Assignment of FTIR peaks identified in fPOM in the experiment to functional groups previously attributed to similar peaks in the literature.
- Figure SI-1 FTIR-ATR spectra of fPOM (free particulate organic matter) from selected soil depths (0-10 cm, 20-30 cm, 50-60 cm and 90-100 cm) at different locations (i.e Lempur , Pungut and RKE) under natural forest and three different ages of cinnamon plantation; Cinnamon plantation year 1 (C Y1), Cinnamon plantation year 5 (C Y5) and Cinnamon plantation year 10 (C Y10).
- Table SI-3 Mixed effects model (MEM) analysis of fPOM FTIR identified peaks and fPOM decomposability (Index I) and recalcitrance (Index II) where soil depth and land use as fixed factor and location as random factor.

Table SI-1 Mass of soil used to extract free particulate organic matter (fPOM) according to ratio (2:80, w/v) of soil organic carbon (SOC) to 1.85 g ml^{-1} density sodium polystungstate (SPT).

Sample No	Location	Sample Code	Soil C content (mg/g)	Volume of SPT used(ml)	Mass of soil used (g)
1	Lempur	Forest (0-10 cm)	214.05	80	0.75
2		Forest (10-20 cm)	132.10	80	1.21
3		Forest (50-60 cm)	60.16	80	2.66
4		Forest (90-100 cm)	35.59	80	4.49
5		C Y1 (0-10 cm)	150.13	80	1.07
6		C Y1 (10-20 cm)	102.92	80	1.55
7		C Y1 (50-60 cm)	36.52	80	4.38
8		C Y1 (90-100 cm)	21.24	80	7.53
9		C Y5 (0-10 cm)	98.75	80	1.62
10		C Y5 (10-20 cm)	71.54	80	2.24
11		C Y5 (50-60 cm)	30.37	80	5.27
12		C Y15(90-100 cm)	29.60	80	5.41
13		C Y10 (0-10 cm)	101.68	80	1.57
14		C Y10 (10-20 cm)	61.96	80	2.58
15		C Y10 (50-60 cm)	25.77	80	6.21
16		C Y10 (90-100 cm)	22.79	80	7.02
17	Pungut	Forest (0-10 cm)	143.65	80	1.11
18		Forest (10-20 cm)	25.31	80	6.32
19		Forest (50-60 cm)	9.34	80	17.14
20		Forest (90-100 cm)	4.24	80	37.71
21		C Y1 (0-10 cm)	48.43	80	3.30
22		C Y1 (10-20 cm)	58.13	80	2.75
23		C Y1 (50-60 cm)	105.13	80	1.52
24		C Y1 (90-100 cm)	32.90	80	4.86
25		C Y5 (0-10 cm)	124.69	80	1.28
26		C Y5 (10-20 cm)	72.32	80	2.21
27		C Y5 (50-60 cm)	45.27	80	3.53
28		C Y15(90-100 cm)	19.77	80	8.09
29		C Y10 (0-10 cm)	42.80	80	3.74
30		C Y10 (10-20 cm)	21.90	80	7.31
31		C Y10 (50-60 cm)	8.75	80	18.29
32		C Y10 (90-100 cm)	2.39	80	66.87
33	RKE	Forest (0-10 cm)	124.40	80	1.29
34		Forest (10-20 cm)	49.46	80	3.24
35		Forest (50-60 cm)	28.91	80	5.53
36		Forest (90-100 cm)	11.94	80	13.40
37		C Y1 (0-10 cm)	125.11	80	1.28
38		C Y1 (10-20 cm)	68.55	80	2.33
39		C Y1 (50-60 cm)	79.74	80	2.01
40		C Y1 (90-100 cm)	28.08	80	5.70

41	C Y5 (0-10 cm)	122.36	80	1.31
42	C Y5 (10-20 cm)	90.99	80	1.76
43	C Y5 (50-60 cm)	34.97	80	4.58
44	C Y15(90-100 cm)	16.78	80	9.53
45	C Y10 (0-10 cm)	122.54	80	1.31
46	C Y10 (10-20 cm)	71.36	80	2.24
47	C Y10 (50-60 cm)	48.76	80	3.28
48	C Y10 (90-100 cm)	26.42	80	6.06

Table SI-2 Assignment of FTIR peaks identified in fPOM in the experiment to functional groups previously attributed to similar peaks in the literature.

No	Wavenumber (cm^{-1})		Assignment	Reference
	Experiment	Literature		
1	767	700-900	Aromatic CH, 3-4 adjacent H deformation	(Ascough et al., 2011)
2	878	840	Aromatic δ(C-H), less substituted	(Margenot et al., 2015a)
3	931	920	Aromatic δ(C-H)	(Margenot et al., 2015a)
4	1072	1081	C–O stretching vibrations of C–O–C groups	(Ellerbrock and Kaiser, 2005)
5	1221	1200-1280	C–O stretch in carboxylic acid, phenol C–O asymmetric stretch, OH deformation, ester	(Fultz et al., 2014)
6	1410	About 1410 ~1416	aliphatic (C–H) deformation of CH2 or CH3 groups aliphatic C-H deformation of CH2 and CH3 groups	(Solomon et al., 2005) (Xing et al., 2019)
7	1615	1600-1640 1626 1600-1613	C=O stretching vibrations of COO$^-$ anion aromatic-C (C C) vibrations and to a smaller extent to conjugated carbonyl-C (C O) such as quinones stretching vibrations of aromatic C=C double bonds conjugated with C=O or COO– bonds or both, i.e. of unsaturated ketones, carboxylic acids or amides	(Ellerbrock and Kaiser, 2005) (Solomon et al., 2005) (Ellerbrock and Gerke, 2004)
8	2120	2000-2200 2100-2140	Carbohydrate overtones of –COH stretching C≡C Terminal alkyne (monosubstituted)	(Madhavan et al., 2012; Peltre et al., 2014) (Coates, 2000)
9	2851	2860	Asymmetric and symmetric C–H stretching vibrations of CH3 and CH2 groups	(Ellerbrock and Gerke, 2004; Ellerbrock and Kaiser, 2005; Solomon et al., 2005)
10	2920	2920		
11	3312	About 3374	stretching vibrations of H-bonded hydroxyl (O-H) groups of phenols with traces of amine (N–H) stretch	(Solomon et al., 2005)

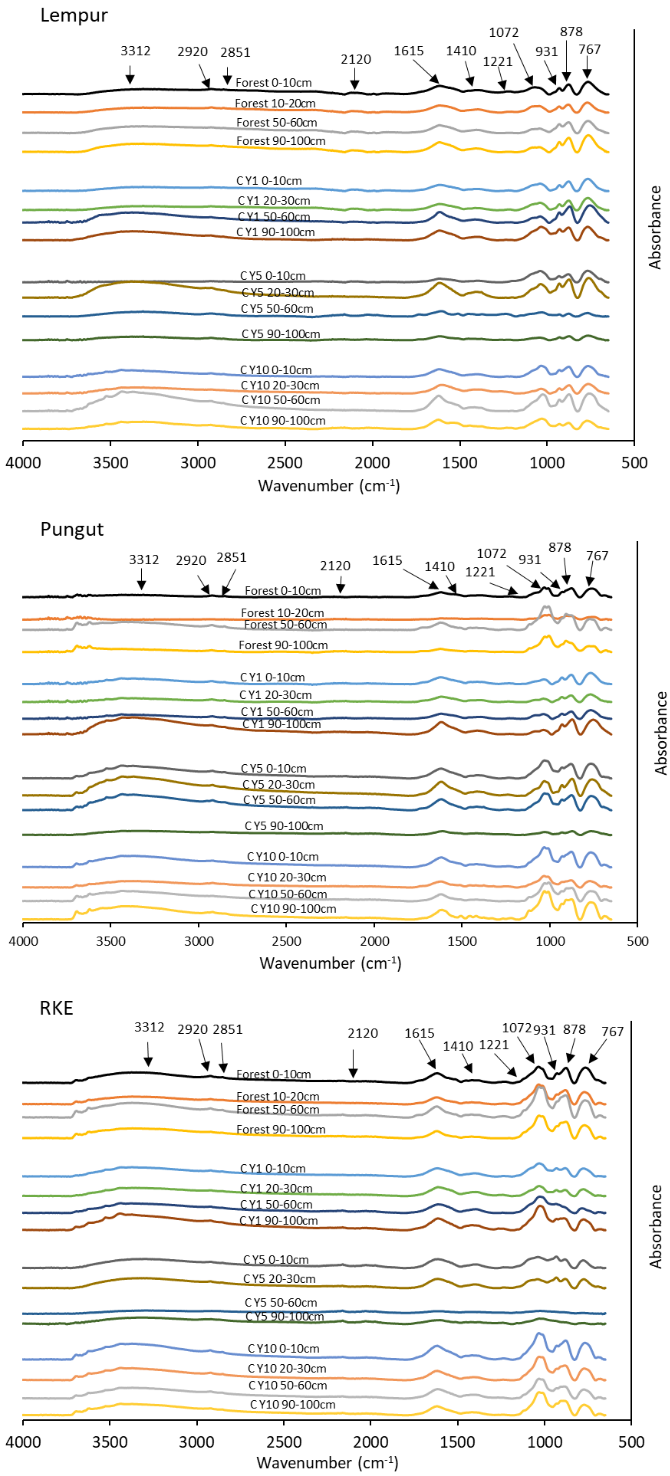


Figure SI-1 FTIR-ATR spectra of fPOM (free particulate organic matter) from selected soil depths (0-10 cm, 20-30 cm, 50-60 cm and 90-100 cm) at different locations (i.e Lempur, Pungut and RKE) under natural forest and three different ages of cinnamon plantation; Cinnamon plantation year 1 (C Y1), Cinnamon plantation year 5 (C Y5) and Cinnamon plantation year 10 (C Y10).

Table SI-3 Mixed effects model (MEM) analysis of fPOM FTIR identified peaks and fPOM decomposability (Index I) and recalcitrance (Index II) where soil depth and land use as fixed factor and location as random factor.

No	Band (cm^{-1})/ Index no.	Assignment	MEM	
			Depth	Landuse
1	767	Aromatic CH. 3-4 adjacent H deformation	0.00*	0.00*
2	878	Aromatic δ(C-H), less substituted	0.02*	0.00*
3	931	Aromatic δ(C-H)	0.42 ns	0.03*
4	1072	C–O stretching vibrations of C–O–C groups	0.054 ns	0.41 ns
5	1221	C–O stretch in carboxylic acid, phenol C–O asymmetric stretch, OH deformation, ester	0.69 ns	0.58 ns
6	1410	aliphatic (C–H) deformation of CH2 or CH3 groups aliphatic C-H deformation of CH2 and CH3 groups	0.18 ns	0.30 ns
7	1615	C=O stretching vibrations of COO^-anion aromatic-C (C C) vibrations and to a smaller extent to conjugated carbonyl-C (C O) such as quinones stretching vibrations of aromatic C=C double bonds conjugated with C=O or COO– bonds or both, i.e. of unsaturated ketones, carboxylic acids or amides	0.25 ns	0.08 ns
8	2120	Carbohydrate overtones of –COH stretching C≡C Terminal alkyne (monosubstituted)	0.94 ns	0.03*
9	2851	Asymmetric and symmetric C–H stretching vibrations of CH3 and CH2 groups	0.26 ns	0.78 ns
10	2920		0.52 ns	0.05 ns
11	3312	stretching vibrations of H-bonded hydroxyl (O-H) groups of phenols with traces of amine (N–H) stretch	0.16 ns	0.00*
12	Index I	fPOM degree of decomposition index	0.27 ns	0.01*
13	Index II	fPOM Recalcitrance index	0.23 ns	0.94 ns

ns : not significant $p > 0.05$; * $p < 0.005$