The response of soil quality and carbon cycling to changes in agricultural systems and management practices. Assessing, predicting, and mapping

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Abstract

Changes in agricultural systems, for example from conventional to organic, have the potential to alter a range of ecosystem functions and services, affecting soil quality (SQ) aspects including carbon (C) storage in agricultural soils. Yet, the effects of agricultural systems will not be consistent across agricultural soils, instead likely varying with management practices. Different management practices, such as grazing regime (non-grazed *vs.* grazed), proportions of temporary grass-clover leys in crop rotations (ley time proportion), crop rotation schemes (conventional *vs.* organic) and fertilisation sources (mineral *vs.* compost), bring about changes in inputs and outputs of soil organic matter (SOM), soil biodiversity, nutrient cycling, C distribution within SOM pools, molecular composition of SOM and consequently affect SQ as well as soil organic C stocks (SOC) and stability. In this thesis, the effect of changing the agricultural system from conventional to organic on SQ (using individual and integrated soil quality indicator approaches), SOC stocks (*in situ* and spatially-mapping), and the distribution of soil C among SOM fractions are investigated in a commercial split farm (~50% of the farm area under each system), with fields differing in terms of grazing regimes and with varying ley time proportions. Impacts of conventional *vs.* organic crop rotation schemes and mineral *vs.* compost fertility sources are assessed for SOM composition and SOC stocks and stability over time using a long-term experimental trial. A mechanistic model is used to validate empirical measurements of SOC stocks and to predict long-term effects of each treatment as well as other hypothetical scenarios. The farm-scale study generated the first direct comparison between the conventional and organic system under the same mixed farming system in the north-east of England, UK. The results reflect existing knowledge on the advantages of organic *vs.* conventional systems on SQ and indicated no major differences in SOC stocks between both systems. However, it also showed that in mixed farming systems, i.e. where arable and grazed livestock are present in a rotation, and with an increased ley time proportion, SQ and SOC stocks can be enhanced regardless of the agricultural system. The increased SOC stock appears to be related to increases in labile C of SOM pools, indicating that it might be susceptible to losses. Yet, simulations predicted that the use of mixed farming and/or increasing ley time proportions in crop rotations can result in accumulation of SOC in the long-term and thus they might be useful strategies to mitigate losses of SOC stocks in arable rotations. The results also suggested that future digital soil mapping studies should include agricultural system and management practice information as potential explanatory covariates, particularly for regional-scale mapping of SOC across farm enterprises. The results from the long-term experimental

trial further emphasised that combining organic crop rotation and compost fertilisation can lead to SOC accumulation over time and improve its stabilisation across the whole soil profile (0-0.60 m). Specifically, the organic rotation favoured SOC stability in subsoil layers (0.30-0.60 m), while compost fertilisation played an important role in the top 0-0.30 m. These results are confirmed by the higher relative weight loss and ion intensity for CO_2 (*m/z* 44) at higher temperature levels (350-750 °C), and the observed higher relative abundance of products that are more resistant to degradation, e.g. *n*-Alkenes, aromatics, and polyaromatics. Nevertheless, simulations revealed that increases in SOC stocks (0-0.20 m depth) in the long-term are dependent on both the organic fertilisation inputs as well as crop choice in the rotation. Ultimately, the results from this thesis can contribute to ongoing efforts to attain a more sustainable agriculture sector, which, at least in part, depend on changes in agricultural systems and management practices.

Declaration

This thesis has been composed by myself, Caio Fernandes Zani unless otherwise stated and has not been submitted as part of any previous application for a degree. All sources of information have been acknowledged explicitly by reference.

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Chapter 1. General introduction

In agricultural soils, the provision of ecosystem services such as biomass production, climate regulation, water resources, nutrient cycling, and carbon (C) sequestration are underpinned by both agricultural systems and the management practices implemented. Changes in agricultural systems and management practices are expected to either assist or disrupt the provision of these as well as other ecosystems services (Lal, 2004a). It is, however, still unclear how contrasting agricultural systems, for instance, conventional *vs.* organic, and management practices implemented within each system would affect the provision of ecosystem services from agricultural soils. A particular challenge is the identification of feasible and sensitive indicators for trade-offs and synergies appraisal among various ecosystems services. In this sense, soil quality (SQ) and thus the sustainable agricultural management of soils have become of global interest due to the soil's critical role in providing ecosystem functions and services (Karlen *et al.*, 1997; Doran, 2002; Bünemann *et al.*, 2018). Soil organic matter (SOM) provides the basis for soil quality since it affects physical, chemical, and biological soil properties while controlling its ability to store and release nutrients, water, and air for plant growth (Janzen, 2006). Accordingly, the capacity of soil to function in a way that human societies need, greatly relies on SOM. Since soil organic C (SOC) is the primary component of SOM (Dungait *et al.*, 2012), it is often used as a unifying indicator for SQ assessment (Zornoza *et al.*, 2015). This thesis explores the response of SQ and C cycling to changes in agricultural systems and management practices. Specifically, it considers how conventional and organic systems and components thereof, including crop rotation schemes and fertility sources, as well as distinctive management practices, such as grazing regime (non-grazed *vs.* grazed) and the different proportions of temporary grass-clover leys in crop rotations, affect SQ, SOC stocks and C stability *in situ*, spatially and into the future. The results found here can contribute to ongoing efforts to improve the current agricultural systems and management practices, and delivery of a more sustainable agriculture sector, which might be able to mitigate the expected climate change while contributing to soil health and food security aspects.

1.1 The overall view: Relationship between the agricultural sector, greenhouse gases, climate change and soils

World population is projected to have an exacerbate increase by 2050 leading to a currently estimated 50% increase in the global food supply demand (Alexandratos & Bruinsma, 2012). This has led to an unprecedented increasing pressure on our soils, which is the basis not only for our food production but also for the storage and filtering of our water resources and the largest organic C store (Blum, 2005). Land use changes (LUC) from natural/semi-natural system to agricultural systems, as well as increases in production of current croplands through disruptive management practices (e.g. heavy use of pesticides, synthetic fertilisation, liming, irrigation and tillage events), are the most common paths to meet the food demand rises. However, such practices along with other activities, such as fossil fuel burning, have been often accompanied by increased atmospheric concentration of greenhouse gases (GHGs), overall SQ degradation and depletion of the soil C storage, threatening the ability of soils to deliver important functions and services and driving global climate change (IPCC, 2014; Le Quéré *et al.*, 2018).

According to the Food and Agriculture Organization (FAO, 2015), currently, 1.5 billion hectares, i.e. 36% of the world's land suitable for crop production, is being farmed. It has been estimated that, globally, around 130 Pg (i.e. billion tonnes = 10^{15} g) of C have been already lost due to LUC to agricultural land and its associated cultivation and disturbance practices (Sanderman *et al.*, 2017). The Intergovernmental Panel on Climate Change has indicated that the agricultural sector represents 23% of total net anthropogenic GHG emissions, with this figure potentially increasing to 37% if emissions from pre- and post-food production activities are added (IPCC, 2019). Associated with the potential boost in global climate changes, the continuous intensive cultivation in the agricultural sector may also lead to other environmental risks. Examples are the increase in soil erosion, contamination, sealing, compaction, and salinization, susceptibility to flood and landslide events, reduction in SOM and biodiversity, all of which impact not only the soils *per se* but also other ecosystems, such as marine and terrestrial diversity (Tilman, 1999; European Commission, 2002).

The agricultural sector is thus facing a tipping point with aspects, such as economic and environmental sustainability, already facing a crisis due to soil degradation caused by continuous intensive cultivation. In this scenario, the UK has committed to reducing its GHG emission since the Kyoto Protocol agreement (Kyoto Protocol, 1997), with the 2008 Climate Change Act targeting a reduction of at least 80% by 2050 (from the 1990 base year). One potential option to achieve this national aim could be via improvements in the agricultural sector. In particular, agricultural systems and management practices that can promote SQ have the capacity to regain historically lost SOC and increase nutrient cycling while reducing GHG emissions and ensuring that food production is sustained or even improved (Lal, 2010). Such a strategy would also benefit several Sustainable Development Goals (SDGs) of the United Nations, including goals 2, 6, 13 and 15, i.e. zero hunger, clean water and sanitation, climate action and life on land, respectively (Montanarella & Alva, 2015), as well as initiatives to promote soil C sequestration (e.g. the 4 per 1000 program – launched at COP21 in 2015 http://4p1000.org/understand, the Koronivia workshops in agriculture – launched at COP23 in 2018, and the RECSOIL – launched by FAO in 2019).

Ultimately, it is reasonable to state that the adoption of certain agricultural systems and management practices could help to mitigate the impacts of global climate change as well as several aforementioned soil threats by regulating the delivery of functions and services provided by soils (Smith *et al.*, 2008; Key *et al.*, 2016). However, scientific evidence is still lacking to guide policies and decision-makers towards a sustainable agricultural sector.

1.2 Soil quality

The word quality refers to the degree of excellence of something, the term SQ thus implies a judgment (good or bad) of a soil condition. Discussions on SQ emerged in the 1970s and gained ground when concerns around sustainable agriculture in the mid-1980s attracted public attention. Several definitions for SQ concept have been discussed over the years, with a more recent and theoretical definition describing SQ as the capacity of the soil to deliver key functions so that biological productivity is sustained while simultaneously maintaining or even improving water and air quality and supporting human, plant and animal health (Karlen *et al.*, 1997; Doran, 2002; Bünemann *et al.*, 2018) (Fig. 1.1). Although rather broad and complex, this definition clearly highlights the importance as well as the close relationship between soil functions and ecosystems services. When SQ is under threat, it generally implies that the soil is prone to erosion, contamination, sealing, compaction, biodiversity loss, salinization, flooding, landslides and/or losses of SOM (European Commission, 2002). Therefore, pursuing SQ is a must when it comes to ensuring the long-term sustainability of any given ecosystem (agricultural or natural) or land management.

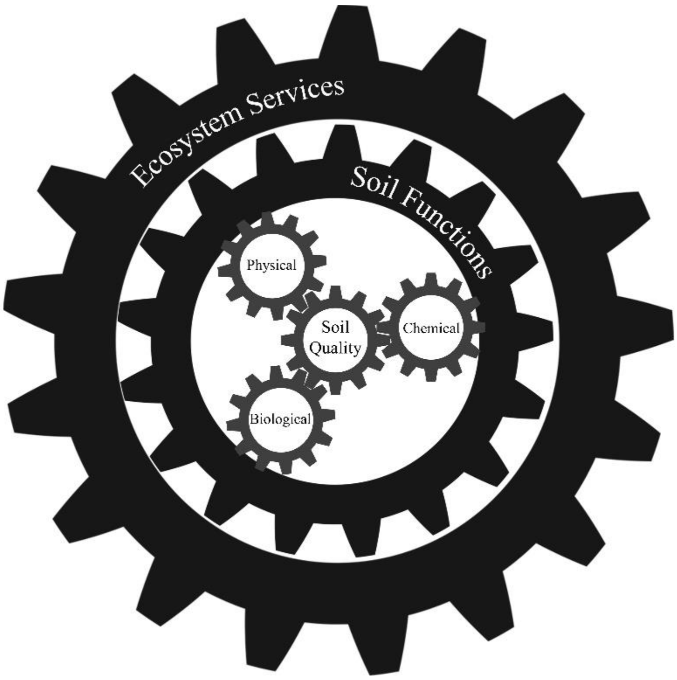

Figure 1.1 The engineering of soil functions and ecosystem services based on soil quality and soil properties.

Several approaches have been used and suggested to evaluate SQ. These approaches include analytical soil analyses (i.e. laboratory-based), scorecards (i.e. visual assessment based on general observation) and test-kit monitoring (i.e. semiquantitative analysis) (Doran & Parkin, 1994; Karlen *et al.*, 1997, 2001; Ball *et al.*, 2007; Guimarães *et al.*, 2011; Romig *et al.*, 2015). Since SQ is dependent on inherent as well as anthropogenic factors, i.e. it encompasses soil-forming aspects (e.g. parental material, climate, topography, etc) as well as dynamic attributes, such as land use and agricultural management, etc (Karlen *et al.*, 1997, 2008), it is impossible to establish global SQ values. Hence, regardless of the approach applied, it is always recommended to use a baseline or a reference value when assessing SQ (Bünemann *et al.*, 2018). Additionally, due to the complexity of the SQ concept, its appraisal in the field or laboratory can only be indirectly inferred through measurement of soil indicators (Andrews *et al.*, 2004). The selection of SQ indicators is a rather important component of SQ assessment. A conceptual condition, particularly when assessing SQ in agroecosystems, is that SQ indicators must be sensitive to anthropogenic activities and linked to soil functions and ecosystem services while being sufficiently diverse to represent soil chemical, physical, and biological soil properties (Bünemann *et al.*, 2018). However, even after many years of discussing SQ, there is still a need to clarify some issues regarding the indicator selection, for instance, the spatial and temporal scales (Halvorson *et al.*, 1997; Wander & Drinkwater, 2000) and the clear relationship between indicators and ecosystem functions (Herrick, 2000).

To overcome such issues, Karlen *et al.* (2003) suggested a holistic SQ assessment framework, which involves the three following steps: i) selection of soil indicators (including chemical, physical, and biological attributes); ii) interpretation of the soil indicators using linear or nonlinear scoring curves and; iii) integration of the chemical, physical, and biological indicators into sectors and to an overall SQ index. Such a framework can help to unify the SQ concept and accommodates the spatial and temporal constraints that are based on inherent soil and/or climatic factors. Another advantage of this framework is that although different approaches might be used in each step, studies can be compared to each other since the values are often expressed as a fraction/percentage of full performance for soil functioning. Finally, the results can be easily understood by farmers, stakeholders, and various policymakers, which is one of the most important goals when assessing SQ.

Acknowledging that the use of several soil indicators may not always be possible because of constraints, such as practicality, sensitivity, reliability, reproducibility and time and costs involved, a reduction to a minimum dataset using only the most relevant indicators has been suggested (Bünemann *et al.*, 2018). This is, however, context-dependent, i.e. it varies according to the target soil functions and ecosystem services of interest, with the most studied ones being soil organic C, pH, available P, water storage and bulk density (BD) (Bünemann *et al.*, 2018). SOC, in particular, stands out among the others as it plays a central role to SQ, providing a plethora of benefits, notably improved soil structure, nutrient availability and cycling, microbial biomass and soil fauna, water retention and resilience as well as fertility (Six *et al.*, 1999; Janzen, 2006; Watts *et al.*, 2006; Powlson *et al.*, 2011b). Consequently, when it comes to SQ assessment through a single indicator, SOC is commonly suggested worldwide (Zornoza *et al.*, 2015).

1.3 Soil carbon dynamics and stabilisation

The C element exists in the earth system in different forms and reservoirs, including the biosphere, geosphere, hydrosphere, and atmosphere of the earth (Lal, 2004a). Carbon cycles between these reservoirs as a result of numerous chemical, physical, geological, and biological processes. Among the terrestrial C pools (i.e. geologic, pedologic and biotic), the pedologic pool (soils) have the largest dynamic reservoir of C on earth, being thus considered one of the most important ecosystems. It has been estimated that the quantity of C in soils is larger than that stored in the atmosphere and terrestrial vegetation pools combined (Schimel, 1995; Batjes, 1996). Figures suggest that globally while the total terrestrial ecosystems C capacity is roughly 3150 Pg, 2500 Pg C are stored into the soil (Lal, 2004a).

The absolute quantity of C held within a soil (i.e. the soil C stock) consists of two major components: soil inorganic C (SIC) and SOC. Soil inorganic C, the smaller portion of C on soils (approximately 950 Pg), is represented mainly by carbonates derived from geologic or soil parent material sources while soil organic C, the most abundant terrestrial C pool (approximately 1550 Pg), comprises SOM components (Trumper *et al.*, 2009). SOC stock is particularly dependent on a long-term net balance between photosynthesis, i.e. the total CO_2 uptake from the atmosphere also referred as the gross primary production (GPP), and terrestrial/soil respiration, where the higher of the first the higher soil C storage potential (Amundson, 2001; Jastrow *et al.*, 2007). In short, the C assimilated into plant biomass flows between a range of pools, at both ground and below ground levels (Fig. 1.2).

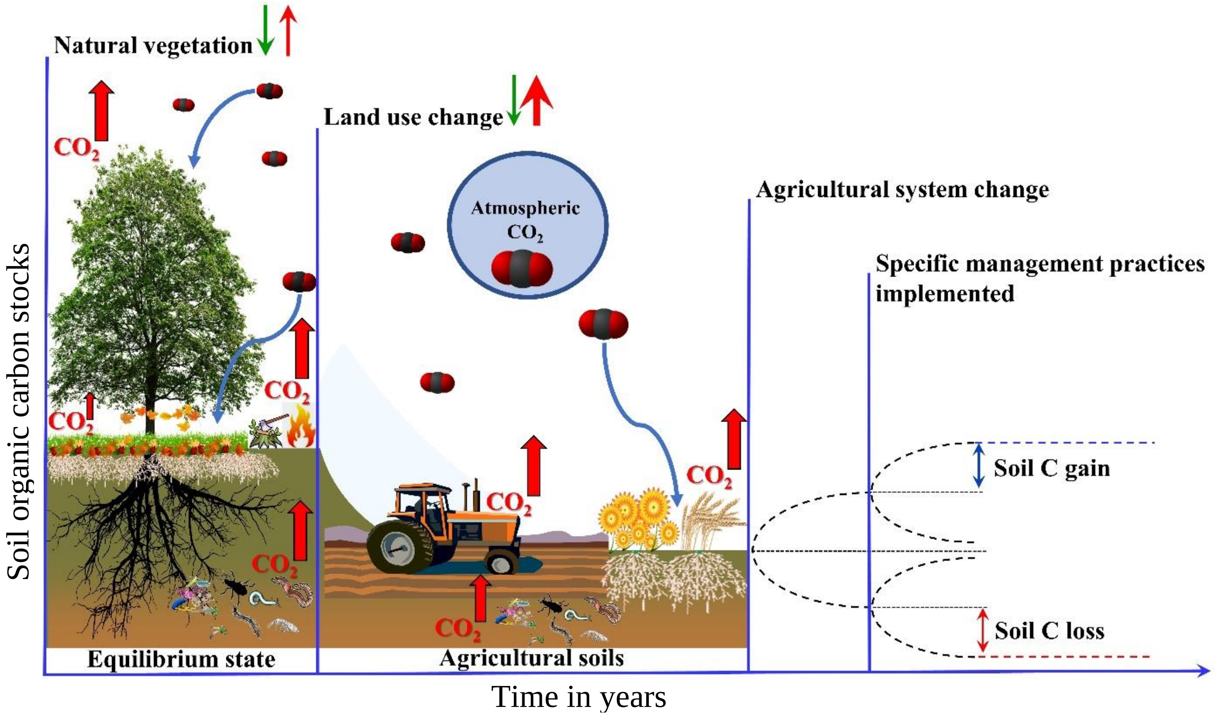

Figure 1.2 The terrestrial carbon (C) cycle and the relationship between soil organic C stocks, land use change, agricultural system change, and specific management practices implemented.

Whilst part of the uptaken CO_2 will constitute a plant's biomass, another part will enter the soil system as SOM through several biochemical and physical mechanisms including, for instance, the decay of root litter, root exudates, and the incorporation of plant residues by both faunal and microbial activities. The C remaining is released back to the atmosphere through autotrophic respiration (i.e. coming from living plant leaves stems and roots), senescence and/or leaching as well as through heterotrophic respiration (i.e. partially decomposition of plant biomass and non-living SOM by soil organisms) (Trumbore, 2006) (Fig. 1.2). Autotrophic and heterotrophic respiration processes are deemed together as ecosystem respiration, which is currently responsible for a global C flux at around 118.7 Pg C a year, i.e. the second largest global C flux after photosynthesis (123 Pg C yr^{-1}) (Bispo *et al.*, 2017). Other non-plant forms of C inputs/outputs also occur, for instance through the animal deposition and in cultivated soils through additions of manures, composts, and paper waste by distinctive management practices (Bardgett & Wardle, 2010). Such inputs are equally important when it comes to SOM quantity and quality.

In a broader definition, SOM is characterised as all the derivatives of plant and animal materials (living and non-living) present in soils, which can be found either incorporated or on the soil surface, alive or at various stages of decomposition (Oades, 1989; Bernoux & Cerri, 2005). These materials are essentially, but not exclusive, crop residues, tissues, intact and decayed detritus, animal remains, as well as living materials such as roots and their exudates, soil organisms (macro, meso and micro fauna) and their metabolites. Overall, SOM contains roughly 58% of organic C (Post *et al.*, 2001), of which the majority is present in the topsoil layer (~0-0.30 m depth) meaning that high-intensity soil management optimises/accelerates SOM decomposition processes.

In fact, SOM can be lost in the form of gases (CO_2 and CH_4) through decomposition/degradation processes, leached through the soil profile into waterways or stabilised into different soil pools, i.e. with different ranges of turnover times. According to González-Pérez *et al.* (2004), natural organic matter decomposition already converts between 60-80% of every 100 units of labile organic matter added to the soil into CO_2. Despite the fact that presumably 20-40% of it remains in the soil, if only a fraction of the solid soil fraction is considered, i.e. excluding porosity, air, and water content, it is estimated that soils have a global average of approximately 5% of SOM content, with this number highly varying under agricultural soils from values < 1%. The SOM is also found at various sizes and different decomposition stages, which may vary from labile to intermediate and stable fractions. Labile C is also referred to as an active fraction, with a relatively rapid turnover rate and mean residence time of days to years (normally <10 years), the intermediate fraction, also referred as slow C, is a more recalcitrant fraction, with a residence time of decades to a hundred years, stable fractions and/or passive C, in turn, are those fractions in which turnover time may reach >1000 years (sometimes it is also referred to as the refractory fraction) (Trumbore, 1997; Lützow *et al.*, 2006; Lorenz *et al.*, 2007).

The decomposition/degradation of the SOM depends on several aspects, such as nature and chemical composition of the material, soil properties, biological activities, and environmental conditions as well as the quantity of the inputs to the given ecosystem (Dixon *et al.*, 1994;

Trumbore, 1997). A historical concept for the formation of stabilised SOM is that the so-called "humic substances" would be characterised by the formation of macromolecules as a result of a gradual condensation of plant molecules and their decomposition products. In addition, it was formerly proposed that the higher the elementary (i.e. high C:N ratio) and biochemical recalcitrance of the input material (i.e. high lignin:N), the higher the formation of stabilised SOM and as such the materials restrict decomposition, i.e. SOM stabilisation would occur through selective preservation due to structural composition of the added material (Piccolo, 2002; Krull *et al.*, 2003). However, both concepts have recently raised some concerns with studies indicating that i) rather than macromolecules, the SOM biotransformation would result in supramolecular products, i.e. a group of small molecules that are interconnected with each other via weak bonds (e.g. hydrogen bonds or hydrophobic interactions), ii) soil microbial communities are able to degrade even the so-called recalcitrant C forms, and iii) labile C forms can contribute to the preservation of more stable fractions (Lützow *et al.*, 2006; Kleber *et al.*, 2011; Lehmann & Kleber, 2015; Basile-Doelsch *et al.*, 2020). As such, SOM stabilisation and thus long-term SOC stocks should occur through other mechanisms, including the physical and chemical protection mechanisms, e.g. the sorption of C into fine soil particles (silt and clay), the occlusion/transformation of the SOM by microbial activities, and especially its ability to link with soil minerals (Amelung *et al.*, 2008; Marschner *et al.*, 2008; Schmidt *et al.*, 2011; Dungait *et al.*, 2012; Lal *et al.*, 2015). In these cases, spatial inaccessibility and interactions with mineral surfaces play an important role in the stabilisation processes (Sollins *et al.*, 1996; Six *et al.*, 2002a; Lützow *et al.*, 2006).

Ultimately, regardless of the mechanisms by which soil C dynamics and stabilisation occur, what is certain is that agricultural soils can act either as a sink or source of C, and this will predominantly depend upon factors such as land uses, agricultural systems, and management practices (Lal, 2004a; Smith *et al.*, 2007, 2008). Monitoring the effects that different agricultural systems and management practices have on SOC stocks becomes an important way to bridge the gaps around the uncertainties of sustainability aspects of current agroecosystems.

1.4 Agricultural sector, soil quality and soil carbon dynamics

Agricultural systems and implemented management practices can significantly affect SQ and soil C dynamics. Agricultural systems and management practices that promote SQ will also sustain SOC storage and are therefore important as potential strategies to tackle the issues of increasing atmospheric GHG concentrations and food security, whilst minimising potential soil threats triggered by the agricultural sector (e.g. erosion, flooding, etc) (Lal, 2010). High-intensity agricultural systems and poor management practices are likely to 'erode' SQ attributes, decrease SOC storage and negatively affect nutrient cycling potential while being a source of GHG emissions (Gregory *et al.*, 2015).

Examples of agricultural systems and management practices that could benefit SQ and promote the delivery of soil functions and services, including soil C sequestration, are particularly those that aim to reduce soil disturbance and synthetic fertiliser inputs while encouraging higher diversity and cover crops in crop rotation schemes and the return of crop residues and organic amendments (Bai *et al.*, 2018; Sandén *et al.*, 2018; Sykes *et al.*, 2020). Such approaches can control key aspects such as the quality and quantity of organic matter entering the soil system, thus regulating the composition of C pools, their stability and/or decomposability as well as nutrient turnover (Dignac *et al.*, 2017). In addition, they influence soil biological activities and root development, which has led to the conclusion that biological, chemical and physical soil features are all shaped by agricultural systems and the management practices implemented (Sandén *et al.*, 2018). Hence, determining how efficient a particular agricultural system and/or management practice operates, within the context of regulating SQ and SOC stocks, is a complex but critical task. This is especially true as even small changes in SOC stocks under agricultural soils may significantly affect regional-scale SOC stocks as agricultural systems occupy large areas in the world (Smith, 2008).

Despite the large body of work, the effects of some agricultural systems and specific management practices on SQ and soil C dynamics, including its stabilisation, remain unclear. Of particular interest is how conventional *vs.* organic systems, their core practices (e.g. crop rotation schemes and fertility sources) and distinctive management practices, including grazing regime (non-grazed *vs.* grazed) and the different proportions of temporary grass-clover leys in crop rotations, would affect SQ and soil C dynamics. A better understanding and quantification of the effects of these agricultural systems and management practices on SQ and C dynamics with clear links to soil functions and services is vital to a more sustainable agricultural sector.

1.4.1 Conventional vs. organic systems

Conventional agriculture, sometimes also referred to as industrial agriculture, is a farming system which is reliant on off-farm resources, e.g. synthetic fertilisers, pesticides, herbicides, genetically modified organism (GMO), as well as characterised by its high-input operations, e.g. irrigation, tillage, monoculture production, and large capital investment. In these production systems, the use of crop rotation, for example, is also often characterised by simplified cereal intensive crops. Through these practices, conventional agriculture has provided an adequate and relatively inexpensive food supply during decades of global population growth. In addition, conventional farming practices have developed considerably over the years, accompanied by important advances in technological innovations. However, the focus on productivity and profitability aspects, as well as the recent increasing pressures for increasing food supply to a growing world population (Alexandratos & Bruinsma, 2012), have brought about concerns regarding the long-term sustainability of the conventional agricultural system. The main negative impacts associated with conventional agriculture include further GHG emissions (Reay *et al.*, 2012a; Stavi & Lal, 2012), decreasing biodiversity (Gomiero *et al.*, 2011; Tsiafouli *et al.*, 2015), increasing pollution of land and water bodies and soil C losses (Houghton, 2003; Lal, 2004a; Godfray *et al.*, 2010; Amundson *et al.*, 2015).

Organic agriculture, in contrast, is a farming system where the use of off-farm resources, including synthetic fertilisers, pesticides, and herbicides, as well as GMO are strictly prohibited. Whilst these are the main distinctions between non-organic 'conventional' and organic systems, there are other differences including, for example, management practices associated with crop rotation, crop protection, and weed control. Internationally, organic agriculture is defined as a system that relies particularly on ecological processes, which strive to support as well as enhance biodiversity and biological cycles, thereby re-establishing ecological harmony (IFOAM, 2012).

Globally, organic agriculture has grown since 1999, backed particularly by a solid increase in farmers interest, markets, and research from the scientific community (Willer *et al.*, 2020). According to the most recent Research Institute of Organic Agriculture (FiBL) data (2018), the total global area under certified organic agriculture has reached 71.5 million hectares, distributed across 186 countries (Willer *et al.*, 2020). Europe alone represents approximately 22% of the total global share, with the UK market had a total area of 485 thousand hectares in 2019 (DEFRA, 2020). Although these figures still represent a small percentage of the total agricultural area in the UK (only ~ 3%), areas under conversion to organic have increased steadily since 2014. Crowder & Reganold, (2015), suggested that organic agriculture should continue to expand, especially when either premiums or ecosystem services are included in profitability. Estimates for the UK agree with this perspective indicating a reduction by roughly £1,127 million yr^{-1} in the external costs of agricultural production with the implementation of organic agriculture (Pretty *et al.*, 2005).

Among the benefits provided by an organic system, an enhanced soil structure and soil microbial biomass are often reported (Maeder *et al.*, 2002; Lori *et al.*, 2017; Cooper *et al.*, 2018;

Loaiza Puerta *et al.*, 2018). Additionally, studies have indicated that when it comes to environmental aspects, organic systems deliver more benefits than conventional systems, including for instance lower GHG emission (Mondelaers *et al.*, 2009; Tuomisto *et al.*, 2012; Meier *et al.*, 2015; Seufert & Ramankutty, 2017). Accordingly, the organic system has been proposed as an attractive agricultural management option to enhance SQ, reduce the impacts of agriculture on the environment and deliver more sustainable agriculture, particularly compared to non-organic 'conventional' systems (Reganold & Wachter, 2016). However, there are also concerns regarding its ability to sustainably meet the current and future global agriculture demands, in particular with regards to food supply potential (Connor, 2008; Seufert *et al.*, 2012; Pickett, 2013). Lower yields would require more land to be converted to agricultural systems, counteracting thus the potential benefits of organic systems (Emsley, 2001; Trewavas, 2001). Other aspects, such as the low nutrient availability (e.g. P and K) and poor weed control (Fess & Benedito, 2018; Möller *et al.*, 2018), are also frequently debate issues.

Whilst comparisons between conventional and organic systems on agronomic, economic, and environmental aspects have mainly demonstrated benefits for the latter, studies comparing conventional and organic system have indicated mixed results for SOC stocks. Some show an increase in topsoil SOC stocks in organic systems (Diacono & Montemurro, 2010; Gattinger *et al.*, 2012; García-Palacios *et al.*, 2018), whereas others indicated no increase or even reductions (Leifeld & Fuhrer, 2010; Leifeld *et al.*, 2013). This disparity may be due to the lack of comparisons considering more than one driver of change, i.e. not only the agricultural system as a whole but also taking into account the interactions between the systems and core practices (e.g. crop rotation schemes and fertility sources). Additionally, information on distinctive management practices, such as the proportion of grass-clover leys in arable rotations, amount of manure applied, and whether ley periods are used for hay meadow cutting or livestock grazing (i.e. non-grazed *vs.* grazed), have seldom been considered in previous studies. Lastly, previous studies comparing conventional *vs.* organic systems have only examined the change in topsoil SOC, but comparable research has demonstrated that SOC in subsoil layers (i.e. > 0.20 m) must be included in any assessment of SOC stocks (Jenkinson *et al.*, 2008; Syswerda *et al.*, 2011; Blanco-Canqui *et al.*, 2017; Börjesson *et al.*, 2018). Therefore, such aspects are essential for a more holistically SOC stocks assessment under different agricultural systems and if they are not taken into account the results can be misleading.

1.4.2 Grass-clover leys in crop rotations and its use under non-grazed vs. grazed regimes

The inclusion of temporary grass-clover leys in crop rotations is a key element of many organic agricultural systems. The main aim of this practice is to increase productivity, nutrient supply, and soil fertility, via both symbiotic N_2 fixation by legumes (Nyfeler *et al.*, 2011; Suter *et al.*, 2015) and increases in SOM (Paustian *et al.*, 1997). Although temporary grass-clover leys in crop rotations is a core practice of the organic systems, its use is also encouraged under conventional systems.

The use of temporary grass-clover leys in crop rotations has shown several benefits to SQ, mainly related to SOM increase, including improved soil structure, biological diversity, SOC accumulation, nutrient cycling and water quality, as well as a controlled weed community, insects and diseases (Franzluebbers *et al.*, 2014; Albizua *et al.*, 2015; Lori *et al.*, 2017; Johnston *et al.*, 2017; Jarvis *et al.*, 2017; Loaiza Puerta *et al.*, 2018; Jensen *et al.*, 2019). Such functions are crucial for the delivery of a sustainable agricultural sector, beyond offering opportunities to reconcile the currently rather broken relationship between productivity and other ecosystem services (Lemaire *et al.*, 2015). However, while the implementation of grass-clover leys in crop rotations is generally associated with an improved agricultural sector, questions remain on whether ley periods should be non-grazed or grazed and the length of time in ley needed to enhance SOC stocks in the top and subsoil layers.

Indeed, management practices performed during ley periods can change C as well as nitrogen (N) cycles and therefore affect SOM decomposition and stabilisation (Conant *et al.*, 2001; Klumpp *et al.*, 2009; Acharya *et al.*, 2012; Lemaire *et al.*, 2015; Rumpel *et al.*, 2015). Recent research showed that non-grazed *vs.* grazed regimes can change nutrient inputs and dynamics, soil microbial community size, diversity, and activities differently (Crème *et al.*, 2018). It has been indicated that if a temporary grass-clover ley is grazed (i.e. if the farm is under a mixed arable/livestock system), then there may be an additional benefit to SOC accumulation, nutrient cycling and utilisation, and consequently improved SQ in the agroecosystem (Chen *et al.*, 2015; Assmann *et al.*, 2017). These effects are particularly explained by extra inputs through forage residues and animal dung, stimulation of root turnover and exudation and changes in plant species and composition (Pineiro *et al.*, 2010; McSherry & Ritchie, 2013; Assmann *et al.*, 2014). It has also been suggested that livestock can transform plant-bound nutrients into readily mineralised substrates improving soil fertility. The reduction in soil disturbance (i.e. under less ploughing) and the increase in plant cover and SOM for the duration of the ley, are further important aspects that are likely to play a role in the SOC accumulation in ley-arable rotation systems (Paustian *et al.*, 1997; Cooper *et al.*, 2016). However, the effects of non-grazed *vs.* grazed regimes, as well as the length of time in ley, may also depend on the interplay between agricultural systems (conventional *vs.* organic) and their core practices (crop rotation schemes and fertility sources).

To date, even though many benefits and drawbacks are well documented regarding the use of grass-clover leys in crop rotations, significant knowledge gaps remain in relation to the effects of length of time in ley periods, grazing regime (non-grazed *vs.* grazed) and their interactions with conventional and organic systems on SQ aspects and SOC stocks.

1.5 Assessing, predicting, and mapping soil C dynamics

Assessment of SOC stocks is normally conducted by measuring the C component of the SOM. A well-planned physical soil sampling is required, ensuring that the sampling method fulfils standard methodology e.g. allowing soil bulk density (BD) or soil mass to be measured. As a guideline, soil samples should be taken horizontally and within a specific soil depth increment, preferably using cores of known volume, which will allow simultaneous determination of BD. Whenever possible it is also recommended to dig trenches as this practice can reveal important soil profile characteristics and help to reduce potential issues, such as soil compression and the collection of coarse organic and/or mineral fragments during soil sampling (Davis *et al.*, 2017). Importantly, in order to reduce uncertainties and avoid bias in SOC stock measurements, especially if assessing SOC stocks at a scale higher than a plot scale, a stratified soil sampling strategy with random locations within each stratum is highly advised (Maillard *et al.*, 2017). After sampling, fine soil fractions should be presented for the measurement of soil C contents ensuring that worldwide operational definition of SOC is followed, i.e. the SOC is the measured C in the soil fraction < 2 mm (Whitehead *et al.*, 2012).

Dry combustion method is usually recommended as an analytical way to measured soil C contents (Nelson & Sommers, 1996). This method simply burns all the C present in the sample in complete combustion, generating CO_2, and quantify it by gas chromatography using a thermal conductivity or a flame ionization detector. Although this method also burns carbonates, nowadays there is equipment designed to measure soil C contents using time and/or programmed temperatures allowing SOC and SIC to be quantified separately (Manning *et al.*, 2005).

After measurement of SOC contents, SOC stocks can be simply calculated following the eqs. 1.1:

eqs. 1.1) $SOC\ stock_i = OC_i \times BD_i \times t_i$

where,

$SOC\ stock_i$ (Mg ha^{-1}) is the soil organic carbon stock of the sample in the depth increment *i*

OC_i (%) is the organic carbon content of the sample in the depth increment *i*

BD_i (g cm^{-3}) is the soil bulk density of the sample in the depth increment *i*

t_i (cm) is the thickness in which the sample was taken of the depth increment *i*.

However, acknowledging that the agricultural system and specific management practices, as well as climate, might alter soil BD and thus soil mass, SOC stock calculation must be adjusted on an equivalent soil mass (ESM) technique (Wendt & Hauser, 2013). Mathematically, the equivalent soil mass is calculated as follows (eqs. 1.2):

eqs. 1.2) $ESM = \frac{1}{n} \times \frac{\Sigma M_{bi}}{\Sigma V_{bi}} \times t_i \times 100$

ESM (Mg soil ha^{-1}) is the equivalent soil mass to be used in eqs. 1.3

n is the number of samples being aggregated

$\sum M_{bi}$ (Mg) is the sum of the masses of all samples being aggregated

$\sum V_{bi}$ (Mg) is the sum of the volumes of all samples being aggregated

t_i (cm) is the thickness of the depth increment *i*.

As a result, adjusted SOC stocks for each sample is calculated according to the following equation (eqs. 1.3):

eqs. 1.3) $SOC\ stock\ adjusted_i = OC_i \times ESM \times (1 - vG_i) \times 100000$

$SOC\ stock\ adjusted_i$ (Mg ha^{-1}) is the adjusted soil organic carbon stock of each aggregated sample *i* that represent a point or area in space

OC_i (g kg^{-1}) is the organic carbon content of the sample *i*

ESM (Mg ha^{-1}) is the equivalent soil mass calculated in the eqs. 1.2

vG_i is the volumetric coarse fragment content of the sample layer of the sample *i*.

Particular attention should be given to the baseline in which SOC stock change will be based on for assessment. There are different ways to define a baseline and this should be determined relative to the main aims of the study (Brander, 2016). The point-in-time measurements against an assumed business-as-usual baseline is an approach often used to compare contrasting management practices at one single time point using the business-as-usual site as a baseline. However, it is important to stress that such an approach can only be applied for cases where the business-as-usual site and the target site can be assumed to be the same prior to the change in management, i.e. they should be the same or as similar as possible in terms of soil type, climate, land use, productivity and most importantly the SOC stocks should preferably be at a steady state.

According to the IPCC, (2003, 2006) reports, a minimum period of 20 years is required to achieve a SOC stock steady state (also referred to as ‘equilibrium’) for any given agricultural system and/or management practices. Nevertheless, whilst an equilibrium in SOC stock can be reached, its distribution among soil pools with varying stability might change constantly. Therefore, a separation of SOC stocks into fractions with contrasting behaviour may serve as a proxy for a better understanding of SOM dynamics as well as soil C stabilisation mechanisms (Poeplau *et al.*, 2018). It has been particularly recommended to separate SOM into an organic fraction (generally referred as particulate organic matter – POM > 53 μm) and a mineral-associated fraction (often associated with the silt and clay fraction – SC < 53 μm), due to their highly contrasting behaviours and therefore stabilisation and mean residence time (Lavallee *et al.*, 2019). It is possible to fractionate SOM through several techniques including physical and/or chemical methods (Christensen, 1992, 2001). Physical fractionation techniques have been particularly advocated as they have been proven to successfully assess soil C stability and quality/characteristics across different land uses as well as agricultural systems (Zani *et al.*, 2018; Poeplau *et al.*, 2018), without changing the original composition of the SOM compounds as chemical separation methods (Lehmann & Kleber, 2015).

As mentioned earlier, the turnover and potential stability of SOM may be dependent on the composition (chemical and physical) of the input material, climate, and soil properties, all of which influence SOM permanent transformation and mineralisation processes. However, the SOM composition aspects have been normally left out of current soil C studies. In recent years, a few techniques have been introduced to fill this knowledge gap, including the use of thermogravimetry-differential scanning calorimetry coupled with quadrupole mass spectrometry and pyrolysis coupled with gas chromatography-mass spectrometry analyses. The former can provide information on the physical as well as chemical properties of a sample

(Langier-Kuźniarowa, 2002) while the latter provides detailed molecular structural information (Meier & Faix, 1992; Leinweber & Schulten, 1993). Overall, further understanding in proportions of C within pools with potential differences in stability aspects, as well as SOM composition, are crucial for the long-term sustainability of agricultural systems as it controls soil-atmosphere C fluxes.

Separation of the soil C into pools is also important for predictions, i.e. for use in systems models that represent soil C dynamics, as most mechanistic models highlight the importance of separating at least labile and stable C pools (Parton *et al.*, 1988; Gulde *et al.*, 2008). Adjusting the distribution of SOC stocks among different pools in mechanistic models, particularly during the initialisation phase, is not a compulsory step but it may greatly improve simulation reliability. Moreover, as models are under continued development, measuring soil C pools can help in the validation process, especially because many mechanistic models partition SOC stocks into conceptual pools (Li *et al.*, 1992; Parton *et al.*, 1993; Zimmermann *et al.*, 2007; Smith *et al.*, 2010). In short, mechanistic models are a type of model that simulates and integrates a variety of different underlying dynamic processes and variables to determine SOC stocks (FAO, 2019). In mechanistic models, predictions are based on the understanding of the functioning of a system of interest, considering also other soil processes that may directly or indirectly impact SOC dynamics (Buck-Sorlin, 2013). Among the mechanistic models, the DayCent is a terrestrial ecosystem model designed to simulate C and N cycles, as well as the dynamics of a range of nutrients, among the atmosphere, vegetation, and soil (Parton *et al.*, 1988; Del Grosso *et al.*, 2001). The DayCent model includes sub-models for the representation of plant productivity, phenology, decomposition of dead plant material and SOM, soil water and temperature dynamics, and GHG fluxes (Fig. 1.3). Its use has proven to be suitable for simulations at a range of temporal and spatial scales depending on its configuration. Although it was originally developed for grassland in the USA (Parton *et al.*, 1987), DayCent has been widely used across the world, including Brazil (Oliveira *et al.*, 2017), China (Cheng *et al.*, 2014; Yue *et al.*, 2019), Canada (Chang *et al.*, 2013; Sansoulet *et al.*, 2014) and Europe (Abdalla *et al.*, 2010; Fitton *et al.*, 2014a; b; Senapati *et al.*, 2016; Begum *et al.*, 2017; Necpalova *et al.*, 2018; Lee *et al.*, 2020), and at a range of ecosystems, e.g. grasslands, cropland, and forests.

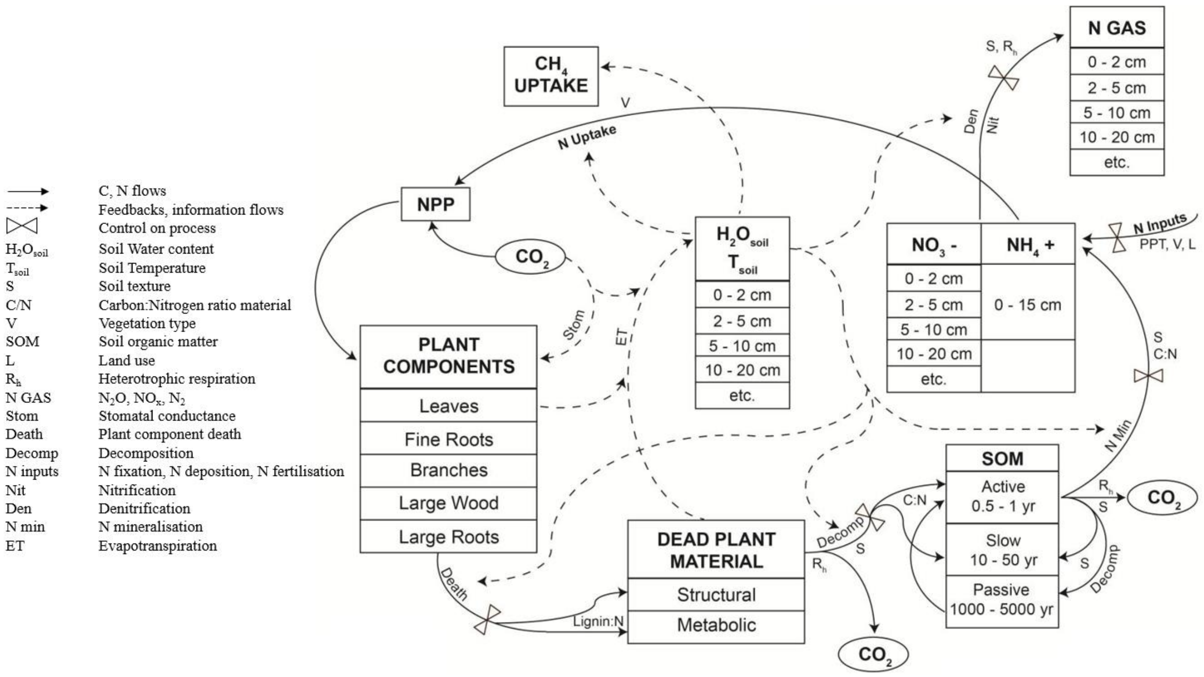

Figure 1.3 Conceptual structure of the DayCent ecosystem model. Adapted from Parton *et al.* (1998); Del Grosso *et al.* (2001).

Since soil C dynamics are highly varied at both spatial and temporal scales, particularly due to the heterogeneous nature of soils, it is also recommended to appraise SOC stocks using a fine resolution approach. In this sense, Digital Soil Mapping (DSM) has emerged as a key tool for soil quality evaluation (including soil C) and sustainable soil management (McBratney *et al.*, 2003). The beginning of DSM can be linked to the wide development of quantitative techniques for soil survey and mapping in the late 1990s. It is currently considered a cost-effective approach that can generate accurate spatial soil information created and populated by statistical tools, which are based on soil observation and knowledge of potentially related environmental variables (Lagacherie & McBratney, 2006). Basically, the DSM approach involves the following steps, soil data collection for the indicator of interest, a compilation of relevant covariates for the target area, calibration and/or training of a spatial prediction function using the observed dataset as a base, and finally, spatial modelling, interpolation and/or extrapolation using the prediction function for the non-sampled locations (Minasny *et al.*, 2013). Based on the concept that soil formation/properties are highly dependent on their position in the landscape, most of the previous DSM studies have relied heavily on environmental data that are correlated to soil properties. This is particularly derived from the well-known SCORPAN framework for DSM, i.e. soil properties (s), climate (c), organisms (o), relief (r), parent materials (p), age/time (a) and space/spatial position (n) (McBratney *et al.*, 2003). Such a framework can be applied using a wide variety of methods from a simple Linear Regression Models (LM) to more complex methods, such as Random Forest Models (RFM) (Thompson *et* *al.*, 2006; Minasny *et al.*, 2013; Were *et al.*, 2015; Wang *et al.*, 2018). With regards to SOC, DSM approaches can contribute towards the identification of both locations where a high and/or low soil C sequestration is likely as well as aspects that control SOC. In this way, promising agricultural systems and management practices can be framed as sequestration strategies as well as monitoring purposes for further understanding and policy.

1.6 Research aims and objectives

The over-arching aim of this thesis was to investigate how SQ and C cycling responds to conventional and organic systems, and how this may depend on specific management practices. Specifically, it examines, *in situ* and spatially, the effect of conventional and organic systems as main drivers as well as their interaction with non-grazed and grazed regimes and different proportions of temporary grass-clover leys in crop rotations on SQ, SOC stocks and C distribution within SOM pools using a mixed commercial farm (i.e. arable/livestock) enterprise in the UK. A long-term field experimental trial was used to evaluate the effects of conventional and organic crop rotation schemes and mineral and compost fertilisation sources on SOM composition and SOC stocks and stability over time. Finally, a mechanistic DayCent model was used to validate empirical measurements of SOC stocks from both the farm-scale and the long-term experimental trial studies, and to explore the long-term effects of each situation as well as other hypothetical scenarios.

The thesis was sub-divided into five data chapters characterised by smaller objectives, which are described below as questions to help to fill the identified gaps in the current knowledge:

Chapter 2: How do contrasting agricultural system (conventional *vs.* organic), grazing regime (non-grazed *vs.* grazed) and different proportions of temporary grass-clover leys in crop rotations affect SQ within a mixed commercial farm?

The intensification of conventional agricultural activity has negatively impacted SQ and consequently the delivery of functions and services provided by agricultural soils. Some agricultural systems and management practices have been proposed as options to counteract such a scenario. This chapter investigates whether the adoption of organic over non-organic (conventional system) and specific management practices (i.e. grazing regime and grass-clover leys) and their interaction would affect SQ using individual physical, chemical and biological measured indicators as well as scoring curves and an integration approach. The latter was conducted by using the Soil Management Assessment Framework (SMAF) approach, which to the best of our knowledge has never been used in the UK. Therefore, a secondary aim of this chapter was to evaluate the predictive abilities of SMAF for monitoring SQ in cool temperate agricultural landscapes. The SMAF was also used to identify a potential relationship between integrated overall SQ status and measured SOC stocks.

This study tests the overall hypothesis that agricultural system and management practices which ameliorate the soil capacity to function properly regarding its chemical, physical, and biological characteristics would also improve SQ status. Specifically, it was hypothesised that the adoption of the organic system, grazed regime and increases in proportions of temporary grass-clover leys in crop rotations would lead to improvements in SQ, due to the presumably higher SOM supply, nutrient addition, and minimal soil disturbance that they exert. As a result, a strong correlation between integrated overall SQ and measured SOC stocks would be identified, also indicating that the SMAF would be a suitable approach to assess changes SQ.

Chapter 3: What are the responses to contrasting agricultural systems (conventional *vs.* organic), grazing regimes (non-grazed *vs.* grazed) and different proportions of temporary grass-clover leys in crop rotations for SOC stocks and SOM fractions?

In addition to the negative effect on SQ, the intensification of crop production has brought about substantial C losses from agricultural soils. However, the response of contrasting agricultural systems, grazing regime and temporary grass-clover leys and their interaction to SOC stocks and SOM fractions, particularly in subsoil layers, is still unknown. This chapter explores the effects of conversion from a conventional to the organic system, differences in grazing regime (non-grazed *vs.* grazed) and different proportions of temporary grass-clover leys in crop rotations on SOC stocks and C distribution among SOM fractions down to 0.60 m soil depth. The comparison was conducted under a mixed commercial farm where both conventional and organic systems co-exist. To the best of our knowledge, this was the first direct comparison between the conventional and organic system under the same mixed farming system in the north-east of England, UK.

In line with chapter 2, this study tests the hypothesis that agricultural systems and management practices that improve SQ status would also lead to higher SOC stocks. Accordingly, it was hypothesised that the organic system, grazed regime and increases in the proportions of temporary grass-clover leys in crop rotations would increase SOC stocks. The assessment of soil C in the SOM fractions would shed some light on soil C stabilisation mechanisms and rates of turnover. In addition, the separation of SOM into three discrete fractions could also be related to the conceptual pools of the mechanistic DayCent model, which will be used in chapter 6.

Chapter 4: Does the information on agricultural systems and management practices improve the accuracy of digital soil mapping in predicting SOC stocks at a farm-scale level?

The pressure for soil C sequestration has brought about a higher demand for rapid and cost-effective approaches that can deliver a reliable spatial resolution of SOC stocks. Digital soil mapping is an important tool already widely used, particularly for soil surveys, but previous studies have rarely included agricultural systems and management practices information in the mapping approach. This chapter aimed to use a digital elevation model and its topography covariates and high-resolution soil sensing data (i.e. more typical covariates used for digital soil mapping) in association with agricultural systems and management practices information to derive a potential alternative and more reliable digital soil mapping of SOC stocks at the farm-scale level.

Based on the findings of chapters 2 and 3, it was hypothesised that the inclusion of agricultural systems and management practices information as potential explanatory covariates would contribute to a more reliable digital soil mapping of SOC stocks at the farm-scale level.

Chapter 5: Which are the components of conventional and organic agricultural systems that may drive SOC accumulation and stability over time?

A diverse crop rotation scheme (including longer periods under grass-clover leys in the crop rotations) and application of compost/organic fertilisation sources have been posited as effective ways to increase SOM inputs and therefore SOC stocks. However, comparisons between the core practices of organic and conventional systems (i.e. crop rotation schemes and fertilisation sources) on SOM composition and stabilisation are either inconsistent and/or scarce. This chapter uses a long-term experimental trial to evaluate the effects of conventional and organic crop rotation schemes and mineral and compost fertilisation sources and their interactions on quantitative (SOC stocks) and qualitative (size separation of SOM into fractions and chemical and molecular SOM composition) SOM data. In this sense, it was expected the magnitudes of SOC storage, degradation and stability would be better understood.

Physical SOM separation into organic and mineral-associated fractions, thermogravimetry-differential scanning calorimetry coupled with quadrupole mass spectrometry and pyrolysis coupled with gas chromatography-mass spectrometry were all used to test the hypothesis that the higher the SOC stocks the higher SOM stability.

Chapter 6: Does the DayCent model realistically simulate temporal SOC stock changes under different agricultural systems and management practices?

Mechanistic models are often suggested as a reliable, feasible and cost-effective alternative to appraise long-term effects on SOC stocks. Such an approach can also provide the chance to perform predictions where measurements are impractical. In this last data chapter, empirical measurements collected under both a farm-scale study (Chapter 3) and from a long-term experimental trial study (Chapter 5) were used to assess the reliability and the sensitivity of the DayCent model. Furthermore, the model was used for predicting long-term effects of contrasting agricultural systems (conventional *vs.* organic), grazing regime (non-grazed *vs.* grazed), arable systems with ley phases, mineral *vs.* compost fertility sources and conventional *vs.* organic crop rotation schemes on SOC stocks.

It was hypothesised that the DayCent model would be able to realistically simulate SOC stocks. Ultimately, the outcomes from this chapter would demonstrate how climatic conditions (rainfall and temperature), soil characteristics, duration of contrasting agricultural systems and specific management practices impact SOC stocks in the long-term.

A final chapter (**Chapter 7 – General Discussion**) is provided at the end of this thesis synthesising the main findings, limitations, lessons learnt followed by conclusions and recommendations for future research.

Chapter 2. Grazed temporary grass-clover leys in crop rotations can have a positive impact on soil quality under both conventional and organic agricultural systems. An assessment using individual and integrated soil quality indicators

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Notes

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Declaration of contribution

The data collection in this chapter consists of original work undertaken by myself, Caio Fernandes Zani. The soil sampling was also carried out by myself, Caio Fernandes Zani, with assistance from Gavin Hall and Rachel Chapman. Some soil analyses were conducted with the contributions of some MSc students at Newcastle University. The aggregate stability was performed by Pengliang Shang while P and K contents were analysed by Ayobami. The microbial respiration measurements were taken by Sarah A. Wyld. Mauricio R. Cherubin helped in the understanding and implementation of the SMAF approach. The other soil analyses, as well as statistical analyses of all data, were made by myself, Caio Fernandes Zani. Caio Fernandes Zani led the writing of the chapter and the published paper, with contribution from all co-authors. Specifically, Julia Cooper, Elisa Lopez-Capel, James A. Taylor and Geoffrey D. Abbott provided Ph.D. supervision and detailed comments on the chapter. John Gowing contributed significantly to the discussion and understanding of the chapter.

2.1 Introduction

While intensification of agricultural activity in the last century has supported rapid growth in the global population, it has also contributed to significant environmental impacts. Soil quality (SQ) and thus sustainable agricultural management of soils have become of global interest due to the soil's critical role in providing ecosystem functions and services (Karlen *et al.*, 1997; Doran, 2002; Bünemann *et al.*, 2018). However, there are uncertainties as to how changes in agricultural systems (e.g. from conventional to organic) and the implementation of mixed farming systems (i.e. arable/livestock), with temporary grass-clover leys in crop rotations, affect the SQ of agroecosystems and consequently the environment.

Discussions on SQ emerged in the 1970s and gained ground when concerns around sustainable agriculture in the mid-1980s attracted public attention. In short, SQ encompasses the capacity of the soil to deliver key functions within a particular ecosystem/land use and to sustain biological productivity whilst maintaining or even improving water and air quality and human, plant and animal health (Karlen *et al.*, 1997; Doran, 2002; Bünemann *et al.*, 2018). Based on this definition, it is impossible to directly measure SQ due to its complexity, but it is possible to pursue SQ to ensure sustainability in any given ecosystem. The SQ status of a given ecosystem takes into account inherent and anthropogenic synergies, with the former related to the process of soil-forming and the latter attributed to land use and agricultural management (Karlen *et al.*, 1997, 2008). Soil indicators are measured soil properties that are sensitive to anthropogenic activities and linked to soil functions and ecosystem services. Therefore, they are normally used to indirectly assess the SQ (Andrews *et al.*, 2004). The selection of soil quality indicators is crucial, and they should be sufficiently diverse to represent chemical, physical and biological soil properties; the most studied ones being, soil organic carbon (SOC), pH, phosphorus (P), water storage and bulk density (BD) (Bünemann *et al.*, 2018).

The organic system has been proposed as an attractive agricultural management option to enhance SQ, particularly when compared to non-organic 'conventional' systems (Reganold & Wachter, 2016). Organic systems rely mainly on ecological processes, which strive to support as well as enhance biodiversity and biological cycles, thereby re-establishing ecological harmony (IFOAM, 2012). National organic guidelines include practices that may improve SQ, such as diverse crop rotations, mixed farming systems with high animal welfare standards and genetically diverse animal and plant communities, and limited use of all synthetic input sources. This has been confirmed by studies which have shown positive effects on several soil indicators normally used to assess SQ, such as SOC, soil structure and soil microbial biomass (Maeder *et al.*, 2002; Gattinger *et al.*, 2012; Lori *et al.*, 2017; Cooper *et al.*, 2018; Loaiza Puerta *et al.*, 2018). Other studies have also indicated that when it comes to environmental aspects, organic systems deliver more benefits than conventional systems (Mondelaers *et al.*, 2009; Tuomisto *et al.*, 2012; Meier *et al.*, 2015; Seufert & Ramankutty, 2017). However, organic systems could potentially negatively affect some aspects of SQ, which has led to critics claiming that organic systems will be incapable of feeding the projected global population (Connor, 2008; Pickett, 2013). One of the main concerns is that essential nutrients, such as P and potassium (K), may become deficient under long-term organic systems due to restrictions on sources of imported crop nutrients (Möller *et al.*, 2018). On the other hand, conventional systems are recognised as having negative impacts on the environment including contributing to greenhouse gas (GHG) emissions (Reay *et al.*, 2012b; Stavi & Lal, 2012), decreasing biodiversity (Gomiero *et al.*, 2011; Tsiafouli *et al.*, 2015), increasing pollution of land and water bodies and degrading SOC (Lal, 2004a, 2007; Godfray *et al.*, 2010; Amundson *et al.*, 2015), all of which can be linked to declines in SQ.

It has been recognised that no single approach will solve the challenge of achieving future food security (Reganold & Wachter, 2016). Rather, it may be necessary to adopt some farming practices in combination with other strategies. The inclusion of temporary grass-clover leys in crop rotations (a practice usually implemented in organic systems but also currently encouraged under conventional systems) could help to enhanced SQ by regulating the quality and quantity of soil organic matter (SOM) entering the soil system (Paustian *et al.*, 1997). The use of temporary grass-clover leys in crop rotations has also been suggested to improve soil biodiversity, SOC accumulation and nutrient cycling among many other benefits (Lori *et al.*, 2017; Johnston *et al.*, 2017). Recent research has further stressed that if temporary grass-clover leys are grazed (i.e. if the farm is under a mixed arable/livestock system), then there may be an additional benefit to SOC accumulation and enhanced nutrient cycling and utilisation, and consequently improved SQ in the agroecosystem (Chen *et al.*, 2015; Assmann *et al.*, 2017).

The use of individual soil indicators has been widely used to infer SQ in agricultural systems, however, it usually relies on either reference values, for instance, from a native soil, which is often not suitable for agricultural production, or a soil that represents a maximum production and/or environmental performance (Bünemann *et al.*, 2018). In addition, the use of individual indicators occasionally does not represent the bigger picture for SQ, since it does not always include soil indicators that represent the three main groups i.e. chemical, physical and biological. A holistic SQ assessment has been proposed instead, involving three main steps (Karlen *et al.*, 2003):

1) selection of indicator variables (including chemical, physical and biological attributes),

2) interpretation of the soil indicator using linear or nonlinear scoring curves and,

3) integration into chemical, physical and biological sectors as well as into an overall SQ index (SQI).

This theoretical SQ assessment framework has been well accepted and widely used worldwide, but often using different approaches for each step (Andrews *et al.*, 2004; Mukherjee & Lal, 2014; Cherubin *et al.*, 2016a). A clear advantage of the framework is that different approaches are usually comparable since the use of SQI scores is often expressed as a fraction/percentage of full performance for soil functioning. Additionally, the results can be easily understood by farmers, stakeholders, and various policymakers. The soil management assessment framework (SMAF) has emerged among the options as a promising tool for SQ appraisal (Andrews *et al.*, 2004). SMAF uses nonlinear scoring functions that were built on a combination of literature values and expert judgements. It has been reported to provide reliable results under different land uses and management from both experimental to regional scales all across the globe (Andrews *et al.*, 2004; Stott *et al.*, 2013; Cherubin *et al.*, 2016b; Gura & Mnkeni, 2019).

Despite the potential benefits of mixed farming systems, there are still uncertainties regarding two key points: (1) the impact of interactive effects between different agricultural systems (conventional *vs.* organic) and specific practices (e.g. grazing regime: non-grazed *vs.* grazed) on SQ indicators and; (2) the effect of the length of temporary grass-clover leys in crop rotations on SQ. In addition, to the best of our knowledge, there are no published studies evaluating SQ using SMAF in the UK. To address these current gaps in knowledge, this study used a mixed commercial farm, where conventional and organic agricultural systems co-exist, to evaluate the impacts of agricultural systems, grazing regimes and temporary grass-clover leys on SQ. The overarching aims of this study were (1) to evaluate the effects of agricultural systems (conventional *vs.* organic), grazing regimes (non-grazed *vs.* grazed) and their interaction on individual and integrated SQ indicators and, (2) to assess the effects of different proportions of temporary grass-clover leys in crop rotations on SQ indicators. The null hypotheses are ultimately that (i) the adoption of the organic system, grazed regime and increases in the proportions of temporary grass-clover leys do not lead to improvements in any SQ indicators, and (ii) the SMAF is not suitable to assess SQ in northern UK agricultural systems.

2.2 Materials and Methods

2.2.1 Farm description

The study was performed at Newcastle University's Nafferton Farm, a mixed (arable/livestock system) commercial farm located 12 miles west of Newcastle upon Tyne in north-east England (54º59'09''N; 1º43'56''W, 60 m a.s.l.) where both conventional and organic agricultural systems co-exist in a split farm comparison. According to the Köppen classification, the site experiences a marine west coast climatic condition. From 1981 to 2018, the average annual temperature and total annual precipitation were 8.6 ºC and 638.6 mm respectively, with a maximum monthly temperature of 22 ºC and a minimum of 0 ºC (https://www.metoffice.gov.uk). The soil is classified predominantly as a Eutric Stagnosol (WRB, 2015); slowly permeable, seasonally wet, acidic loamy to clayey soil that is naturally low in fertility (Farewell *et al.*, 2011; Cranfield University, 2020). The terrain across Nafferton farm is generally flat with elevation ranging from 64 to 153 m. Particle-size distribution analysis across the farm indicated an average of 13%, 44% and 43% of clay, silt, and sand, respectively (sandy silt loam) in the top 0.30 m soil layer, and 20%, 40% and 30% of clay, silt, and sand, respectively (clay loam) in the 0.30-0.60 m soil layer (Table A1.1, Appendix 1).

Historically, Nafferton farm was a conventional mixed commercial system, with the main activities being a dairy herd, with associated pastoral production, intermixed with a conventional arable cropping system. In 2001, there was a management change from conventional to an organic system across approximately 50% of the farm area (~ 160 ha), while maintaining the mixed (arable and livestock) production system on both the conventional and organic parts of the farm. For the past 14 years, the farm has been run with a mixed conventional and a mixed organic agricultural system side-by-side. Conventional enterprises are operated to current UK best practices (Red Tractor Assurance, 2015) and the organic enterprises to Soil Association (2019) standards. As conventional was the default system for the preceding 50+ years at Nafferton farm, the comparison between the two agricultural systems (conventional and organic) was made using conventional as the baseline. The study fields were deemed suitable since they had similar soil types and experienced similar climatic conditions.

2.2.2 Study fields selection

Fifteen commercial-sized representative agricultural fields (~ 120 ha of the total 320 ha of the farm) were selected across the farm, but for this study twelve fields were considered (Fig. 2.1). Criteria used when selecting the study fields were recent (2008-2017) agricultural system (S) (conventional-CONV *vs.* organic-ORG), grazing regime (G) (non-grazed-NG *vs.* grazed-GG), and crop rotations, i.e. the inclusion of temporary grass-clover leys in crop rotations. In general, agricultural systems (conventional *vs.* organic) were tested using all the twelve study fields, six under conventional and six under organic, which were considered as replicates for each agricultural system. Grazing regime (non-grazed *vs.* grazed), was tested using four non-grazed and eight grazed study fields (two non-grazed and four grazed study fields within each agricultural system, respectively). The stocking rate on the farm is 1-1.5 livestock units ha^{-1}, which was considered to be light to moderate (Soil Association, 2019). Rotations for the organic and conventional agricultural systems did differ slightly, mainly due to the need to have a nitrogen-fixing component within the organic system to support arable production. In addition, ley rotations tended to be longer within the organic system to assist with weed and disease control. As such, it was not possible to have directly paired fields with the same rotational history under the conventional and organic system. Therefore, study fields were deliberately chosen based on the percentage (0 to 100%) of time as temporary grass-clover leys (hereafter referred to as ley time proportion-LTP), during the previous 10 years and selected within each agricultural system to have a similar spread of LTP, being 4.83 ± 0.83 and 5.50 ± 0.46 years, for the CONV and ORG systems respectively. In general, mineral and organic fertilisers were applied in the CONV system, while the ORG system was subjected to organic amendments only. The main arable crops grown in the conventional rotation were winter cereals, including winter wheat (*Triticum aestivum*), winter barley (*Hordeum vulgare*) and oilseed rape (*Brassica napus*). Organic rotations included mainly spring wheat and barley and field beans (*Phaseolus vulgaris*). Grass-clover ley periods, in both conventional and organic systems, used a mixture of white and red clover (*Trifolium repens* and *Trifolium pratense*) with perennial ryegrass (*Lolium perenne*). Ley periods in both grazed and non-grazed fields were subjected to two to three harvests for silage per year, depending on their productivity and timing of grazing in the paddock. Further details of management practices in each study field, such as tillage and manure and fertiliser applications, are given in Table 2.1. Crop history details are given in Table A1.2 (Appendix 1).

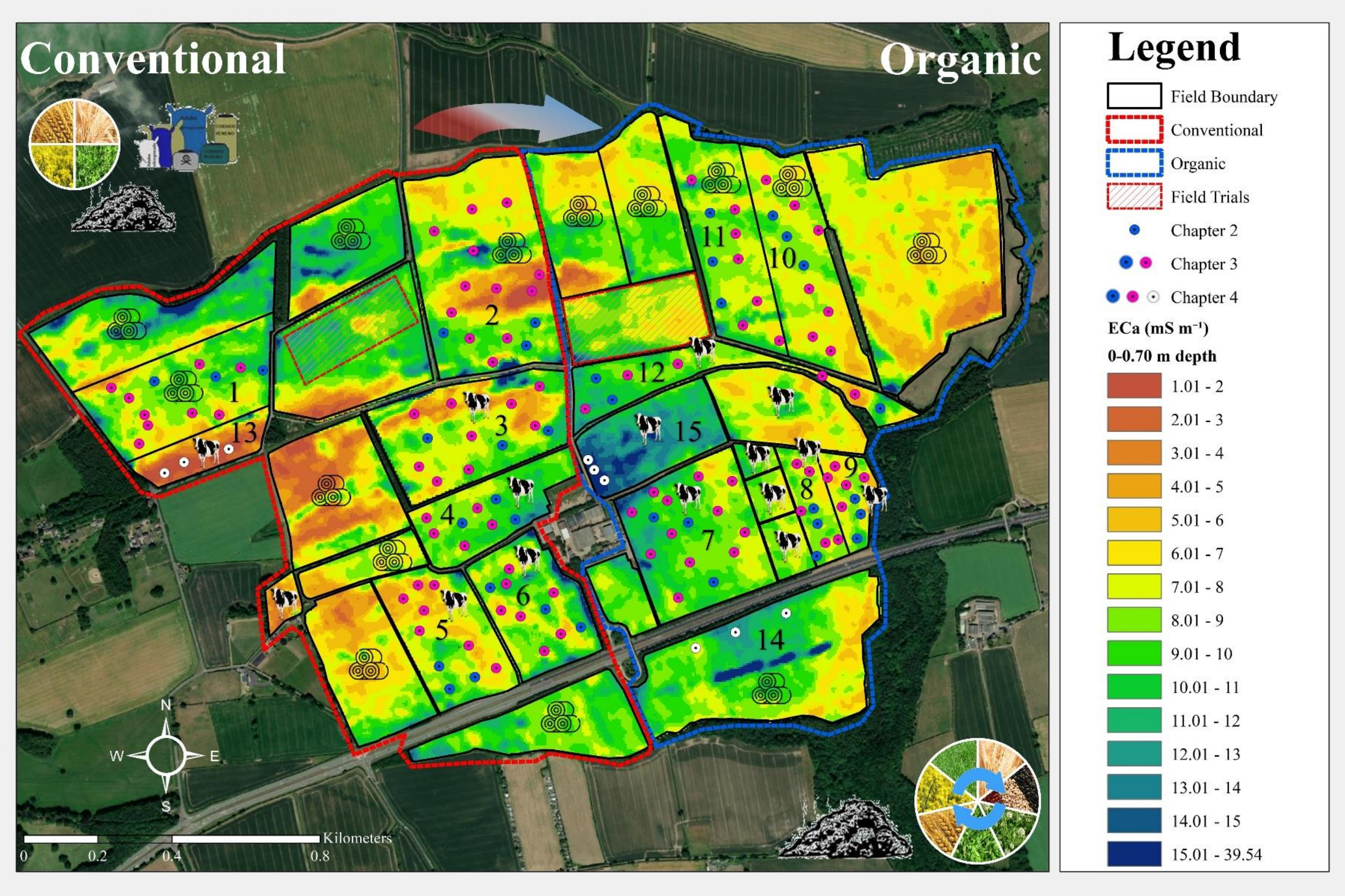


Figure 2.1 Map of spatial variability of apparent soil electrical conductivity (ECa) 0-0.70 m depth at Nafferton farm showing the locations (blue, pink and white points) where the soil cores were taken. Numbers from 1 to 15 refer to the study fields selected across the farm. Non-grazed and grazed study sites are denoted by hay bales or a cow, respectively.

Table 2.1 Details of management practices on the 12 study fields at Nafferton Farm over 10 years (2008-2017) indicating agricultural system, grazing regime, ley time proportions (LTP) (% years under ley prior sampling) and manure application proportions (MAP) (% years with manure applied prior sampling), and further details including main crops grown, fertilisation and tillage occurrence that accounted for any activity that turned the soil over for at least 0.15 m soil depth.

Study field nº in the map	Agricultural system	Grazing regime	LTP %	MAP %	Further details
1	Conventional	Non-grazed	0	10	Continuous arable rotation of wheat, barley and oilseed rape crops for the last ten years, eight tillage occurrences. Annual fertilisation (mineral and organic forms) of roughly 89, 78 and 156 kg ha^{-1} yr^{-1} for N, P and K, respectively.
2	Conventional	Non-grazed	10	10	Previously cultivated with ley-arable rotation but became a continuous arable rotation of wheat, barley and oilseed rape crops in which the field is for the last nine years, five tillage occurrences. Annual fertilisation (mineral and organic forms) of roughly 69, 56 and 111 kg ha^{-1} yr^{-1} for N, P and K, respectively.
3	Conventional	Grazed	70	60	Ley-arable rotation of wheat, barley, three tillage occurrences, and ley in which the field is for the last seven years. Annual fertilisation (mineral and organic forms) of roughly 148, 46 and 93 kg ha^{-1} yr^{-1} for N, P and K, respectively.
4	Conventional	Grazed	50	40	Ley-arable rotation of wheat, barley in which the field is for the last four years, four tillage occurrences. Before that, ley was used for five years in a row with one previous year under barley. Annual fertilisation (mineral and organic forms) of roughly 89, 31 and 43 kg ha^{-1} yr^{-1} for N, P and K, respectively.
5	Conventional	Grazed	100	50	Ley-arable rotation field but under ley for the last ten years, no tillage occurrence. Annual fertilisation (mineral and organic forms) of roughly 130, 28 and 57 kg ha^{-1} yr^{-1} for N, P and K, respectively.
6	Conventional	Grazed	60	40	Ley-arable rotation of wheat, barley, three tillage occurrences, and ley in which the field is for the last four years. Before the ley, the field had three years under arable rotation with the previous three years under ley. Annual fertilisation (mineral and organic forms) of roughly 190, 79 and 140 kg ha^{-1} yr^{-1} for N, P and K, respectively.
7	Organic	Grazed	80	60	Ley-arable rotation of wheat, barley, two tillage occurrences, and ley in which the field is for the last seven years. Before the ley, the field had two years under arable rotation and one previous year under ley. Annual fertilisation (only organic forms) of roughly 48, 52 and 141 kg ha^{-1} yr^{-1} for N, P and K, respectively.
8	Organic	Grazed	60	70	Ley-arable rotation of wheat, barley, beans, four tillage occurrences, and ley in which the field is for the last four years. Before the ley, the field had three years under arable rotation with the previous two years under ley and one year under beans. Annual fertilisation (only organic forms) of roughly 59, 61 and 150 kg ha^{-1} yr^{-1} for N, P and K, respectively.
9	Organic	Grazed	60	20	Ley-arable rotation of barley, beans, potatoes, three tillage occurrences, and ley, which occurred in an interval of every two years of arable crop. Currently, the field is under ley for the last three years. Annual fertilisation (only organic forms) of roughly 59, 65 and 170 kg ha^{-1} yr^{-1} for N, P and K, respectively.
10	Organic	Non-grazed	30	70	Ley-arable rotation of wheat, barley and beans in which the field is for the last five years in a row, seven tillage occurrences, and with ley before that for three years in a row with two previous arable rotation. Annual fertilisation (only organic forms) of roughly 67, 74 and 200 kg ha^{-1} yr^{-1} for N, P and K, respectively.
11	Organic	Non-grazed	30	60	Ley-arable rotation of wheat, barley and beans in which the field is for the last six years in a row, five tillage occurrences. Before that, ley was used for three years in a row with one previous year under arable. Annual fertilisation (only organic forms) of roughly 71, 79 and 200 kg ha^{-1} yr^{-1} for N, P and K, respectively.
12	Organic	Grazed	70	40	Ley-arable rotation of wheat, barley, beans, and ley in which the field is for six years in a row before the three years of arable crops, three tillage occurrences. Annual fertilisation (only organic forms) of roughly 65, 46 and 96 kg ha^{-1} yr^{-1} for N, P and K, respectively.

2.2.3 Sampling strategy and methods

The experimental design and the selection of sampling points in each study field were based on *an a priori* apparent soil electrical conductivity (EC_a) (0-0.70 m depth) map (Fig. 2.1). This was derived from an on-the-go survey conducted in 2014 using a global navigation satellite system (GNSS) enabled DualEM-1s sensor (Milton, ON, Canada). For consistency and to remove variability between the samples due to textural variation and relative EC_a signal response, three sampling points per field were selected under the following criteria:

- The location had an EC_a value of between 8-10 mS m^{-1},
- The location was at least 50 m away from another within field sample site,
- It was not located near the field border (> 20 m from a field boundary), and
- It was not located in an area likely to be disproportionately affected by compaction from either machinery or animal activity.

Across the 12 selected study fields, there were 36 sampling points (2 agricultural systems: 6 fields per system: 3 replicates per study field) (Fig. 2.1). At each point, two undisturbed soil cores (1 m length, 0.03 m inner core diameter) were collected using a hydraulic soil sampler (Atlas Copco Ltd., Hemel Hempstead, Hertfordshire, UK) and a metallic tube (1 m length, 0.03 m inner diameter), totalling 72 sampled cores across the farm. The soil cores were manually cut during sampling into 0-0.15, 0.15-0.30 and 0.30-0.60 m depths resulting in a total of 216 undisturbed soil core sections. In addition, three disturbed samples (0-0.15 m) were also taken using an auger near each of the 36 sample points to provide 108 disturbed soil samples. Soil sampling was conducted in February-March 2017 and the position of each sampled point was geo-referenced with an EGNOS-enabled handheld GPS receiver (Garmin eTrex® 30x). Particle-size distribution analysis for the 36 sampled points indicated that the soil samples used in this study had an average of 14%, 45% and 41% of clay, silt, and sand, respectively (sandy silt loam) in the top 0.30 m soil layer, and 21%, 41% and 38% of clay, silt, and sand, respectively (clay loam) in the 0.30-0.60 m soil layer.

2.2.4 SQ indicators, soil preparation and analyses

The following seven SQ indicators were analysed: chemical - active acidity (pH), Olsen's phosphorus (P) and ammonium nitrate-extractable potassium (K); physical - aggregate stability (AS) and bulk density (BD); and biological - SOC concentration and microbial biomass carbon (MBC). These SQ indicators were chosen based on productivity and environmental protection management goals and their influence on critical/supporting soil functions and potential threats. The productivity and environmental protection goals are related to the capacity of the system to enhance or maintain the production quantity, quality and stability as well as its efficiency to improve or maintain soil, air and water quality (Andrews *et al.*, 2004).

Each of the 216 fresh undisturbed samples was gently mixed and passed through a 4 mm sieve; large stones were removed and weighed plant remains were discarded. The weight of the sieved, fresh soil was then recorded. A subsample of the sieved soil (5 g) was used for determination of gravimetric water content. BD was calculated using the core method adjusting for the weight and volume of large stones (Blake & Hartge, 1986). Thereafter, the duplicate core samples taken at the same georeferenced location and same depth interval were merged and sieved through a 2 mm sieve. This resulted in 108 merged samples, which were then air-dried before being used for particle-size distribution (PSD), pH, P, K, and SOC.

PSD was determined in triplicate by a low angle laser light scattering technique (Laser diffraction). Briefly, 5 g of air-dried soil was suspended in a sodium hexametaphosphate solution (35.7 g in 1 L). The solution was stirred at 3000 rpm and, the laser obscuration observed until complete dispersion had taken place. Analysis of clay, silt and sand was then performed using a Malvern Mastersizer 2000 optical bench with recirculating wet cell enhancement and a Hydro 2000MU sample introduction unit, which can provide accurate particles measurements from 0.02 to 2000 μm. Three analyses of each sample were performed, if they provided an acceptable degree of variance then the average results were employed for interpretation. Soil available P concentration was measured by Olsen's P method (Olsen & Sommers, 1982) followed by a spectrophotometer analysis of P concentration in the extract. Soil available K was analysed by extraction with NH_4NO_3 at a soil extractant ratio of 1:5 w/v (Anon, 1986) and measurement of K concentrations using a flame photometer. Soil pH was measured in H_2O (1:2.5 soil:solution) with analytical procedures described in Mc Lean, (1982). SOC concentration was determined by dry combustion, post-combustion and reduction tube in an Elementary Vario Macro Cube analyser (furnace at 960 °C in pure oxygen). For this, a small portion (0.05 g) of each sample was ground to a fine powder, using an agate mortar and pestle, and sieved to 150 μm prior to determination. Post combustion (900 ºC) and reduction (830 ºC) tubes used helium to carry off the oxygen used to burn the sample to the detectors housed within the analyser. In order to ensure that the analyser was working properly, a set of standards were tested before and in the middle of each run. Thermal analysis (Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry) conducted in Chapter 5, Section 5.3.3, of this thesis, showed that there was an absence or very low presence of low carbonate minerals in the samples (Chapter 5, Fig 5.7), therefore, total soil C concentration can be assumed to be total SOC.

All 108 disturbed soil samples were used for AS and MBC measurements. First, the three samples from the same location point were combined and sieved through a 4 mm mesh to make a composite sample. MBC was assessed using the D glucose respiration rate derived from the MicroResp™ rapid microtiter plate method (Campbell *et al.*, 2003). MBC was calculated from the biomass respiration measurements following procedures described in West & Sparling (1986). The remaining portion of each sample was air-dried and sieved through a 2 mm sieve above a 1 mm sieve. The aggregates collected on the 1 mm sieve (1-2 mm diameter) were used to determine soil AS using a wet-sieving procedure, which measured the effective resistance of the soil structure against either mechanical or physicochemical collapsing forces (Bourget & Kemp, 1957). Briefly, 4 g sample of 2 mm air dried soil from each of the sampled points was placed into the eight 0.25 mm sieves (60 Mesh screen). The samples were placed in a can, which was cover using distilled water. At first, the wet sieving apparatus was set for 3 minutes (stroke =1.3 cm, at about 34 times/min). It moves up and downward breaking the unstable aggregates, which passed through the sieves. The cans were then removed and the aggregates that had passed through were placed in a tray. The remaining sample (i.e. macro-aggregates > 0.25 mm), was then exposed to a dispersion solution (2 g per L of NaOH) instead of distilled water and sieved using the apparatus in order to destroy all remaining aggregates and determine the sand content. The samples were then dried for 24 h at 110 ºC, weighed, and both stable and unstable aggregate mass determined. The soil AS was calculated as the aggregate mass remaining after wet sieving as a percent of the total mass of the soil without sand.

2.2.5 Soil Management Assessment Framework (SMAF) approach

The SMAF approach was used to convert individual soil indicator measurements into a soil quality index (SQI) score. The latest version of SMAF has nonlinear scoring curves for 13 soil indicators, which are represented by five chemical, four physical and four biological soil indicators. Karlen *et al.* (2008) recommend a minimum data set of five indicators, including at least one for each sector group i.e. chemical, physical, and biological. In this study, the seven indicators, pH, P and K (chemical); BD and AS (physical); and SOC and MBC (biological) were used for 0-0.15 m depth interval whereas five of them (pH, P, K, BD, and SOC) were considered for 0.15-0.30 and 0.30-0.60 m depth. The SQI score for each soil indicator was obtained through previously published scoring algorithms that converted the measured soil indicator values into scores between 0 and 1, where a 0 score is considered the poorest and 1 the best (Andrews *et al.*, 2004; Wienhold *et al.*, 2009). The shape of the curves used specific algorithm’s equations for each individual indicator as recommended by Andrews *et al.* (2004)

i.e. more-is-better (upper asymptotic sigmoid curve), less-is-better (lower asymptotic) and mid-point optima (Gaussian function).

The SMAF scoring curves mirror ecosystem functions as well as societal interest, for instance, if soil P concentration is above the optimum value for crop production it will receive a lower score, especially if it is on sloping land, due to the risk of runoff and consequently water contamination. Hence, defined threshold values (primarily developed and validated using datasets from North America), controlling factors (site-specific) and potential environmental risk are always considered. Here, we did not change the defined threshold values used to calculate the SQI scores by the nonlinear scoring curves as it is consistent with the Department for Environment, Food & Rural Affairs (Defra - UK) manual recommendations (RB 209). We did, however, consider site-specific features in order to get a precise SQI score, including: organic matter factor (based on soil classification) was defined as class 3 (medium organic matter content), texture factor (based on our particle-size distribution analysis) varied for some points from class 2 (sandy loam with clay content >8%) to class 3 (silt loam, with clay content around 13%). The climate factor was taken as class 3 (<170 °C and ≥ 550 mm of mean annual precipitation) and the Fe_2O_3 factor was chosen as class 2 (other soil that is not a ultisol soil suborder). As soil sampling occurred at the beginning of March 2017, the seasonal factor was settled as class 1 (sampling in spring, pre-planting). Clay mineralogy factor used class 3 (1:1 clay and Fe and Al oxides), while slope and weathering factors were set as class 2 (2-5% slope) and class 3 (slightly weathering) respectively. The input factor in relation to the specific method used to extract P is also required and was chosen as class 4 (Olsen P method). SMAF also requires details regarding the crops used in the field. In this sense, specific crop codes (provided by the SMAF), were selected for each field in accordance with the crop history details (Table A1.2, Appendix 1).

The SQI scores obtained for each individual measured indicator were then added up and divided by the number of soil indicators for each soil depth interval (0-0.15, 0.15-0.30 and 0.30-0.60 m) in order to calculate an overall SQI. The overall SQI was also subdivided into sectors (chemical, physical and biological). The relationship between overall SQI scores, provided by the SMAF approach, and SOC stock data was verified in order to provide evidence that the SMAF approach is suitable for monitoring SQ within a commercial farming enterprise in cool temperate agricultural landscapes. Briefly, SOC stocks per unit of area (Mg ha^{-1}) were calculated for each sampled point by multiplying its SOC concentration (g kg^{-1}) by its BD measurement (g cm^{-3}) and soil depth thickness (i.e. 0.15 m for 0-0.15 and 0.15-0.30 m and 0.30 m for the 0.30-0.60 m depth interval). As agricultural management, as well as specific practices, might alter soil BD, SOC stocks were adjusted on an equivalent soil mass basis as described by Wendt & Hauser, (2013). More details about the calculations of SOC stocks and equivalent soil mass adjustments can be found in Chapter 1, Section 1.5.

2.2.6 Statistical analyses

Boxplots and scatterplots were used as part of an exploratory analysis to study potential relationships between dependent and independent variables. Since the study was carried out on a commercial farm with a stratified selection of the sampling points, spatial autocorrelation and heterogeneity were tested computing the Moran's I index and via a likelihood ratio test (LRT) comparing the null model (an intercept-only model) and the additional, nested model containing a random effect associated with each study field. The latter was confirmed and therefore, linear mixed-effects models (LME) were fitted to each individual SQ indicator (pH, P, K, BD, AS, SOC, and MBC) to test the effects of agricultural systems (S) (conventional-CONV *vs.* organic-ORG), grazing regime (G) (non-grazed-NG *vs.* grazed-GG) and their interaction (S*G). The model structure used S and G, as fixed effects while the random effect was defined as the study field to account for the heterogeneity of the experimental design. The analyses were conducted separately for each depth interval. The same approach was also carried out for each individual SQI score as well as for the integrated SQI sectors (i.e. chemical, physical, and biological) and overall SQI. Finally, linear regression between overall SQI scores and SOC stocks was conducted.

LME models were also used to test the effects of ley time proportion (LTP) (i.e. % years under temporary grass-clover leys in 10 years) on each individual indicator (pH, P, K, BD, AS, SOC, and MBC). In this case, LTP was used as a continuous variable and as a fixed effect, with study fields as a random effect and analysis being performed separately by depth interval. Although not within the objectives of the study, the same approach was performed to assess potential effects of manure application proportion (MAP) (i.e. % years with manure application in 10 years prior to sampling) on each individual SQ indicator.

For all LME models, assumptions were checked for normality and equal variances by examining the QQ plots of residuals (for both fixed and random effects compartments of the model) and scatterplots of standardised against fitted values. The data were Tukey's Ladder of Powers transformed when visual breakdowns in LME model assumptions were revealed by residual plots. The significance of the fixed effects was determined by comparing models with and without the factor of interest using LRT. When the interaction term in the model was significant, Tukey's HSD post-hoc test was carried out and a significant effect was determined at $p < 0.05$. All statistical analysis was carried out in the R programming language 3.4.3 (R Development Core Team, 2019) using the additional packages, ape (Paradis *et al.*, 2004), nlme (Pinheiro. *et al.*, 2018), plyr (Wickham, 2011), ggplot2 (Wickham, 2009), and multcomp (Hothorn *et al.*, 2008).

2.3 Results

2.3.1 Individual measured SQ indicators

The data did not show spatial autocorrelation for any of the SQ indicators measured or depth intervals ($p > 0.05$), indicating that the sampling strategy based on EC_a analysis (0-0.70 m depth) (Fig. 2.1) was effective. Agricultural systems (S) (conventional-CONV *vs.* organic-ORG) associated with grazing regimes (G) (non-grazed-NG *vs.* grazed-GG) and LTP (i.e. % years under temporary grass-clover leys in 10 years) affected soil indicator measurements differently at each depth interval (Table 2.2, Fig. 2.2 and 2.3).

In terms of chemical indicators, pH was not affected by S or G at any soil depth interval ($p > 0.05$). For the 0-0.15 m depth, the ORG system showed lower soil P concentration compared to the CONV system (LRT = 10.53; $p = 0.001$, Table 2.2), while the GG regime significantly increased soil P concentration under both S (LRT= 5.18; $p = 0.02$, Table 2.2). For the 0.15-0.30 and 0.30-0.60 m depth intervals, there was no significant statistical effect of S or G on P concentration (Table 2.2, $p > 0.05$). In the topsoil (0-0.15 m), S and G interacted, resulting in an increased soil K concentration with the combination of the ORG system and the GG regime (LRT = 4.25; $p = 0.04$, Fig. 2.2a), while the GG regime had no effect on soil K concentration under the CONV system. Soil K concentration was lower under the GG regimes at 0.15-0.30 m soil depth (LRT = 10.35; $p = 0.001$, Table 2.2) and was higher in the CONV system at 0.30-0.60 m soil depth (LRT = 5.00; $p = 0.02$, Table 2.2).

For the physical indicators, an interactive effect between S and G was found for soil BD in the 0-0.15 and 0.30-0.60 m layers. The GG regime under the CONV system decreased BD at 0-0.15m (LRT = 5.66; $p = 0.02$, Fig. 2.2b), while the GG regime under the ORG system increased BD at 0.30-0.60 m (LRT = 4.04; $p = 0.04$, Fig. 2.2c) relative to NG. The S and G did not affect AS ($p > 0.05$), even though the GG fields showed approximately 10% higher AS on average relative to the NG fields for the 0-0.15 m depth.

For the biological indicators, SOC concentration was higher under the GG regime in the 0-0.15 m depth (LRT = 9.10; $p = 0.003$, Table 2.2). There was an interaction between S and G, indicating that the GG regime increased SOC concentration under the CONV system in the 0.15-0.30 m depth interval (LRT = 4.89; $p = 0.03$, Fig. 2.2d), but had no effect in the ORG system. The CONV system showed higher SOC concentration in the deeper soil layers (0.30-0.60 m) compared to the ORG system (LRT = 6.48; $p = 0.01$). The ORG system showed higher soil MBC concentration compared to the CONV system (LRT = 4.23; $p = 0.04$). The GG regime also significantly increased MBC concentration for the 0-0.15 m depth interval under both S (LRT = 4.19; $p = 0.04$).

Table 2.2 Effects of agricultural system (S) (conventional – CONV and organic – ORG), grazing regime (G) (non-grazed – NG and grazed – GG) and their interaction on individual measured soil quality indicators: active acidity (pH), Olsen's phosphorus (P), extractable potassium (K), bulk density (BD), aggregate stability (AS), soil organic carbon (SOC) concentration and microbial biomass carbon (MBC) at three soil depth intervals.

		Chemical indicators			Physical indicators		Biological indicators	
Depth (m)		pH	P	K	BD	AS	SOC	MBC
		H_2O	mg kg^{-1}	mg kg^{-1}	Mg m^{-3}	%	g kg^{-1}	mg kg^{-1}
0-0.15	CONV	6.22 (0.09)	29.42 (2.99)	183.08 (37.12)	1.09 (0.02)	73.62 (2.84)	27.68 (1.11)	181.56 (18.33)
	ORG	6.36 (0.08)	12.25 (2.54)	226.25 (55.32)	1.08 (0.02)	69.16 (2.70)	25.72 (0.92)	236.52 (16.34)
	NG	6.36 (0.08)	13.97 (3.46)	135.74 (35.44)	1.12 (0.03)	65.31 (3.44)	23.24 (0.59)	170.37 (22.59)
	GG	6.25 (0.08)	24.27 (2.99)	239.13 (45.11)	1.06 (0.02)	74.43 (2.19)	28.43 (0.86)	228.37 (14.58)
	S	LRT=0.87; p=0.35	LRT=10.5; **p<0.01**	LRT=0.11; p=0.92	LRT=0.06; p=0.81	LRT=0.95; p=0.33	LRT=1.63; p=0.20	LRT=4.23; **p=0.04**
	G	LRT=0.49; p=0.48	LRT=5.18; **p=0.02**	LRT=1.95; p=0.16	LRT=1.77; p=0.18	LRT=2.86; p=0.09	LRT=9.10; **p<0.01**	LRT=4.19; **p=0.04**
	S*G	LRT=1.44; p=0.23	LRT=0.99; p=0.31	LRT=4.25; **p=0.04**	LRT=5.66; **p=0.02**	LRT=0.02; p=0.88	LRT=1.38; p=0.24	LRT=0.57; p=0.45
0.15-0.30	CONV	6.59 (0.12)	8.72 (0.50)	83.94 (8.03)	1.21 (0.07)	-	20.22 (1.21)	-
	ORG	6.66 (0.10)	9.61 (0.99)	88.44 (15.02)	1.19 (0.07)	-	19.67 (0.59)	-
	NG	6.78 (0.09)	11.00 (1.11)	120.00 (16.36)	1.20 (0.02)	-	18.78 (0.84)	-
	GG	6.54 (0.10)	8.25 (0.54)	69.29 (7.75)	1.20 (0.01)	-	20.53 (0.89)	-
	S	LRT=0.20; p=0.65	LRT=0.21; p=0.64	LRT=0.38; p=0.53	LRT=0.89; p=0.34	-	LRT=0.01 p=0.92	-
	G	LRT=2.17; p=0.14	LRT=3.76; p=0.05	LRT=10.3; **p<0.01**	LRT=0.00; p=0.97	-	LRT=1.60; p=0.23	-
	S*G	LRT=0.65; p=0.42	LRT=2.72; p=0.10	LRT=0.46; p=0.50	LRT=0.36; p=0.55	-	LRT=4.89; **p=0.03**	-
0.30-0.60	CONV	7.12 (0.09)	1.39 (0.14)	58.33 (2.62)	1.29 (0.01)	-	13.20 (1.17)	-
	ORG	7.09 (0.07)	1.78 (0.17)	49.72 (2.61)	1.24 (0.02)	-	10.18 (0.59)	-
	NG	7.14 (0.12)	1.58 (0.23)	54.83 (1.86)	1.24 (0.02)	-	11.88 (1.29)	-
	GG	7.08 (0.06)	1.58 (0.13)	53.63 (2.82)	1.28 (0.01)	-	11.60 (0.84)	-
	S	LRT=0.04; p=0.83	LRT=2.99; p=0.08	LRT=5.00; **p=0.02**	LRT=2.68; p=0.10	-	LRT=6.48; **p=0.01**	-
	G	LRT=0.17; p=0.68	LRT=0.00; p=1.00	LRT=0.10; p=0.75	LRT=1.63; p=0.20	-	LRT=0.01; p=0.91	-
	S*G	LRT=0.70; p=0.40	LRT=2.14; p=0.14	LRT=0.20; p=0.65	LRT=4.04; **p=0.04**	-	LRT=0.50; p=0.47	-

Data are measured mean values (n=18 for each S, n=24 for grazed and n=12 for non-grazed). The standard error of the mean in parentheses. Significance tests using likelihood ratio test (LRT), are compared models with or without the parameter of interest. Significant effects ($p < 0.05$) are shown in bold.

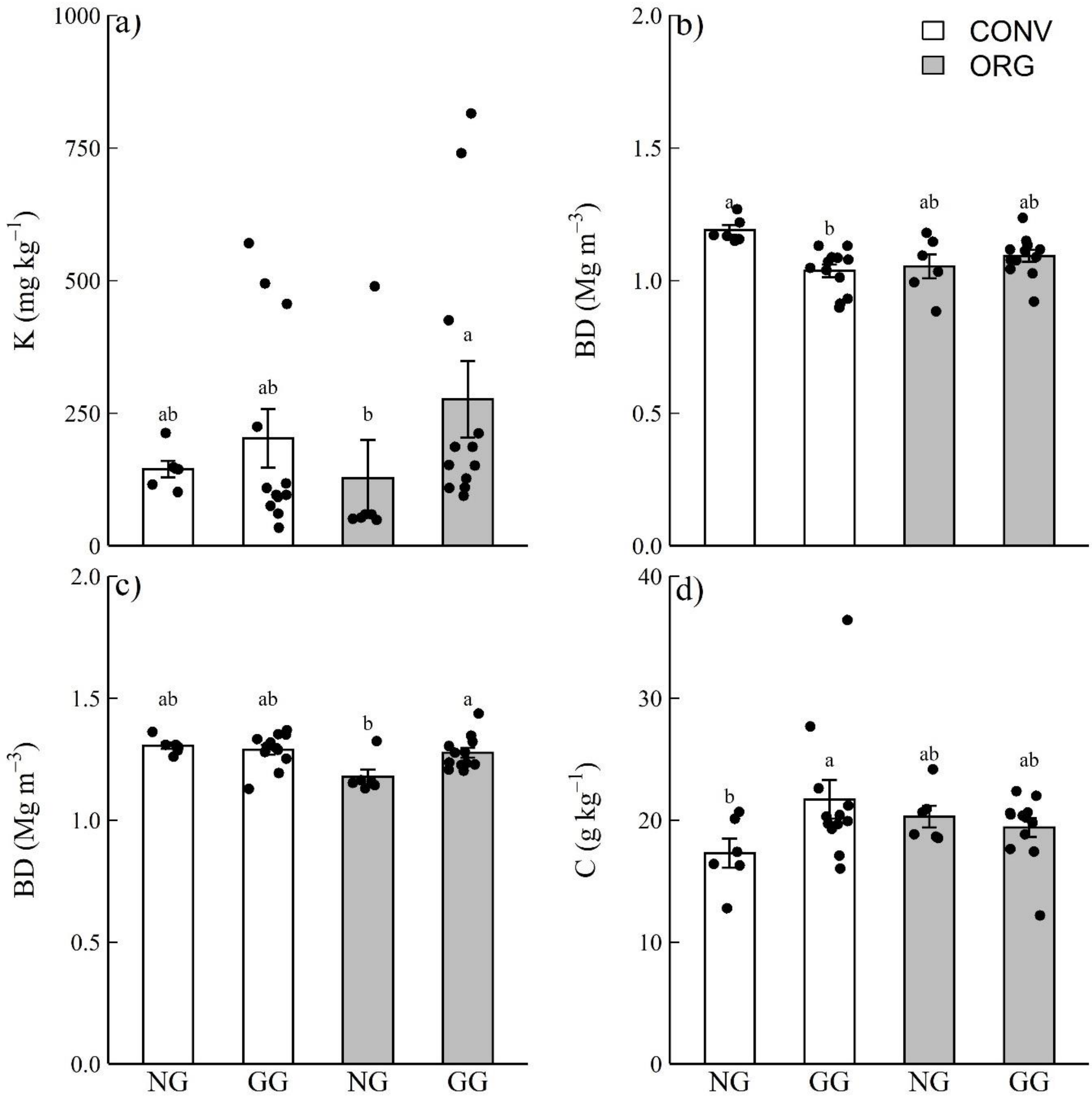


Figure 2.2 Interactive effects between agricultural system (conventional – CONV and organic – ORG) and grazing regime (non-grazed – NG and grazed – GG) on the following individual measured soil quality indicators and soil depth intervals: a) extractable potassium (K) for 0-0.15 m; b) bulk density (BD) for 0-0.15 m, c) bulk density for 0.30-0.60 m and d) soil organic carbon (C) concentration for 0.15-0.30 m. Data are measured mean values ± SE (black dots represent individual sample values, n=12 for conventional and organic grazed and n=6 for conventional and organic non-grazed). Significance tests using likelihood ratio test (LRT) comparing models with or without parameter of interest. Mean measured indicator values followed by the same letter do not significantly differ according to Tukey's test ($p < 0.05$).

The effects of S (CONV *vs.* ORG), G (NG *vs.* GG) and their interactions (S*G) were also assessed on SQ indicators across the whole soil profile (0-0.60 m) (Table 2.3). Most of the findings reflected those found for the top 0-0.15 m depth interval, except for the soil K and SOC concentrations that showed no S or G effects when the whole soil profile was considered. This demonstrates the benefit of individually assessing separate depth intervals as some effects might be masked when soil layers are combined.

Increased LTP did not affect soil pH, P, BD and MBC at any depth interval studied ($p > 0.05$, Fig. 2.3). There was a trend towards increased topsoil K and MBC concentration (0-0.15 m) as LTP increased. An increased LTP significantly increased AS in the 0-0.15 m depth ($p = 0.05$) and SOC concentration in the 0-0.15 m and 0.15-0.30 m depth ($p = 0.002$, $p = 0.05$, respectively). In contrast, as LTP increased, soil K concentration decreased in the 0.15-0.30 m depth ($p = 0.007$ (Fig. 2.3). MAP (i.e. % years with manure application in 10 years) did not affect any of the soil indicators measured (pH, P, K, BD, AS, C and MBC) at any of the three depth intervals (0-0.15; 0.15-0.30 and 0.30-0.60 m) assessed.

Table 2.3 Effects of agricultural system (S) (conventional – CONV and organic – ORG), grazing regime (G) (non-grazed – NG and grazed – GG) and their interaction on individual measured soil quality indicators: active acidity (pH), Olsen's phosphorus (P), extractable potassium (K), bulk density (BD) and soil organic carbon (SOC) concentration for 0-0.60 m depth.

Depth (m)		Chemical indicators			Physical indicator	Biological indicator
		pH	P	K	BD	SOC
		H_2O	mg kg^{-1}		Mg m^{-3}	g kg^{-1}
0-0.60	CONV	6.64 (0.08)	13.18 (1.91)	108.45 (14.48)	1.20 (0.02)	20.37 (1.04)
	ORG	6.70 (0.06)	7.88 (1.08)	121.47 (21.45)	1.17 (0.01)	18.53 (0.97)
	NG	6.63 (0.06)	11.37 (1.51)	120.68 (18.07)	1.18 (0.01)	20.19 (0.95)
	GG	6.76 (0.08)	8.85 (1.48)	103.53 (13.96)	1.19 (0.02)	17.96 (0.95)
	S	LRT=0.22; p=0.64	LRT=5.76; **p=0.02**	LRT=0.26; p=0.61	LRT=1.40; p=0.81	LRT=1.70; p=0.19
	G	LRT=0.94; p=0.33	LRT=2.20; **p=0.04**	LRT=0.40; p=0.53	LRT=0.06; p=0.18	LRT=1.99; p=0.16
	S*G	LRT=1.19; p=0.27	LRT=0.38; p=0.84	LRT=0.09; p=0.76	LRT=6.51; **p=0.01**	LRT=0.43; p=0.51

Data are measured mean values (n=54 for each S, n=72 for grazed and n=36 for non-grazed) calculated from weighted values for each layer: 0-0.15, 0.15-0.30, 0.30-0.60 m. The standard error of the mean in parentheses. Significance tests using likelihood ratio test (LRT), are compared models with or without the parameter of interest. Significant effects ($p < 0.05$) are shown in bold.

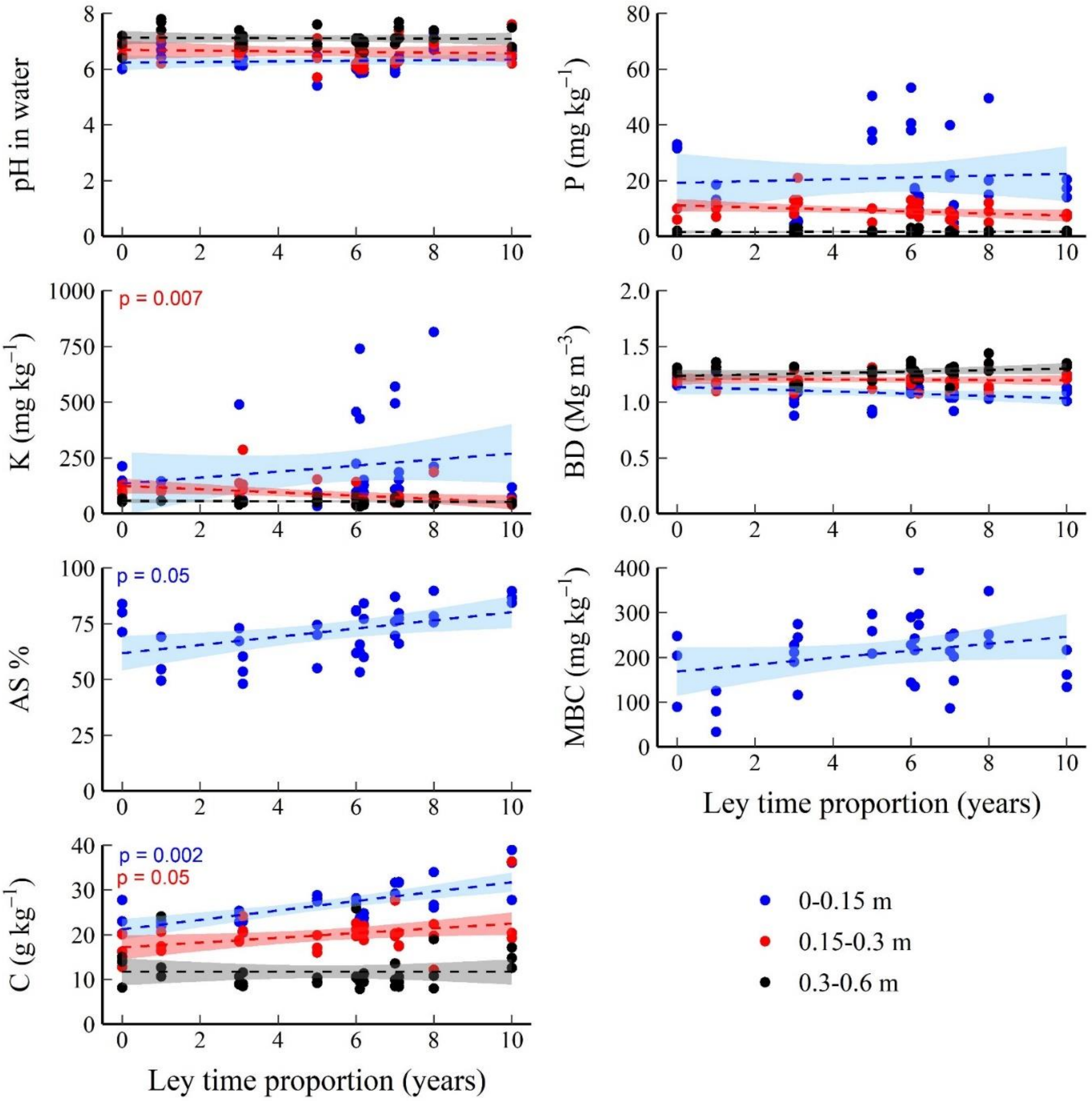


Figure 2.3 Relationship between individual measured soil quality indicators: active acidity (pH), Olsen's phosphorus (P), extractable potassium (K), bulk density (BD), aggregate stability (AS), microbial biomass carbon (MBC) and soil organic carbon (C) concentration, and ley time proportion (years). Data are measured indicator values (n=36 for each indicator in each soil depth interval 0-0.15, 0.15-0.30 and 0.30-0.60 m). Significance tests using a linear mixed effect model (LME). Significant effect ($p < 0.05$) is shown in the specific soil indicator figure by depth: blue (0-0.15 m), red (0.15-0.30 m) and black (0.30-0.60 m).

2.3.2 Individual and integrated SQI scores

Individual SQI scores showed similar findings of those observed for the individual measured SQ indicators (Table 2.4). The only exceptions were the SQI scores for soil P concentration (0.15-0.30 m), BD (0.30-0.60 m) and AS (0-0.15 m). While measured soil P concentration did not indicate significant changes for the 0.15-0.30 m depth, its assigned SQI score was significantly higher under NG regime for both S. Conversely, the measured BD (0.30-0.60 m) indicated an interaction between S and G, but its SQI score did not indicate any significant effect. For the AS (0-0.15 m), the measured indicator appears to be more sensitive to changes than the SQI scores, which were assigned as 1.0 for all AS measurements (Table 2.4). Overall SQI scores and the contribution of each sector for the main effects of S (CONV and ORG) and G (NG and GG) only are shown in Fig. 2.4. Interactive effects between S and G are presented in Fig. 2.5. In general, individual SQI scores, sector scores (chemical, physical and biological) and overall SQI were higher in the topsoil (0-0.15 and 0.15-0.30 m) compared to the subsoil (0.30-0.60 m), regardless of the S and G (Table 2.4 and Fig. 2.4 and 2.5).

In the chemical sector and 0-0.15 m depth, there was an interaction between S and G (LRT = 6.19; $p = 0.01$). The GG regime under ORG system increased the chemical sector SQI score from 0.72 ± 0.05 to 0.91 ± 0.02 (i.e. functioning at 72 and 91% of its potential capacity, respectively), while GG regime under CONV system slightly decreased (non-significant; $p > 0.05$) chemical SQI score from 0.93 ± 0.03 to 0.89 ± 0.02 (functioning at 93 and 89%, respectively) relative to CONV system under NG (Fig. 2.5a). For 0.15-0.30 m depth, the results indicated that GG under both S decreased chemical SQI score (LRT = 7.72; $p < 0.01$, Fig. 2.4b). CONV and ORG system under GG regime were functioning at 77 and 71% of their chemical potential capacity respectively, while CONV and ORG systems under NG regime were functioning at 83 and 89%, respectively (LRT = 7.72; $p = 0.005$) (Fig. 2.5b). For the 0.30-0.60 m depth, the chemical sector was not significantly affected by S or G (Fig. 2.4c and 2.5c).

The physical sector was affected by G in the first depth interval (0-0.15 m) (LRT = 6.14; $p = 0.01$, Fig. 2.4a). The GG regime increased physical SQI score under CONV and ORG system from 0.91 and 0.98 respectively (i.e. 91 to 98% of physical soil functioning capacity) to 1.0 (i.e. functioning at its full potential capacity) (Fig. 2.5a). Although CONV and ORG systems under GG regime (functioning at 93 and 96%, respectively) have had higher physical SQI score at 0.15-0.30 m depth compared to CONV and ORG systems under NG regime (functioning at 84 and 92%, respectively), there was no significant effect due to G (Fig. 2.4b and 2.5b, $p > 0.05$). The only significant difference found for the 0.15-0.30 m depth was between ORG system under GG regime (96%) and the CONV system under NG regime (84%) (Fig. 2.5b). For the 0.30-0.60 m depth, the physical sector was not affected by S or G ($p > 0.05$). The results, however, indicated that the NG regime under CONV system can lead to lower SQI scores, differing particularly from the ORG system under NG regime (functioning capacity of 56% and 86%, respectively) (Fig. 2.5c).

The biological sector followed the same trends observed in the chemical and physical sectors. The GG regime led to higher biological SQI score at the 0-0.15 m depth in both S (LRT = 9.85; $p < 0.01$, Fig. 2.4). The lowest biological SQI score was found for the CONV system under NG regime and the highest for the ORG system under GG regime, which were functioning at 56 and 85% of capacity respectively (Fig. 2.5a). For the 0.15-0.30 m depth, an interactive effect between S and G was observed, where the GG regime under CONV system lead to a significant improvement in the biological SQI scores (from 49% to 70%), while it did not change the functioning biological capacity under the ORG system (LRT = 4.62; $p = 0.03$, Fig. 2.5b). For the 0.30-0.60 m depth, the CONV system was the main factor enhancing biological functioning capacity compared to ORG system (LRT = 5.58 $p = 0.02$, Fig. 2.4). At this particular depth interval, the highest biological scores were observed for the CONV system under NG regime (functioning at 32% of capacity) and the lowest were assigned to the ORG system under NG regime, which were functioning at only 14% of capacity (Fig. 2.5c).

In relation to the overall SQI, our results showed that GG regime increased the scores under both S for the 0-0.15 m depth (LRT = 15.95; $p < 0.01$, Fig. 2.4a). The highest overall SQI for this depth was found under CONV and ORG systems under GG regime (functioning capacity of 91 and 92% respectively), which were significantly higher than CONV and ORG systems under NG regime (functioning capacity of 82 and 80% respectively) (Fig. 2.5a). For the 0.15-0.30 m depth, an interaction was found indicating that GG regime under ORG system improved overall SQI (increasing its functioning capacity from 74% to 85%), while it did not greatly affected fields under CONV system (functioning at 76% and 79%, NG and GG regimes respectively) (LRT = 4.73; $p = 0.03$, Fig. 2.5b). For the 0.30-0.60 m depth, there was no significant effect of S or G on overall SQI scores (Fig. 2.4c). Linear regression between overall SQI scores and measured SOC stocks showed that this individual soil indicator alone explained 66% of its variation (Fig. 2.6).

Table 2.4 Effects of agricultural system (S) (conventional – CONV and organic – ORG), grazing regime (G) (non-grazed – NG and grazed – GG) and their interaction on individual soil quality index (SQI) scores: active acidity (pH), Olsen's phosphorus (P), extractable potassium (K), bulk density (BD), aggregate stability (AS), soil organic carbon (SOC) concentration and microbial biomass carbon (MBC) at three soil depth intervals.

		Chemical indicators			Physical indicators		Biological indicators	
Depth (m)		pH	P	K	BD	AS	SOC	MBC
0-0.15	CONV	0.90 (0.03)	0.99 (0.01)	0.82 (0.04)	0.93 (0.04)	1.00 (0.01)	0.89 (0.02)	0.61 (0.08)
	ORG	0.90 (0.04)	0.82 (0.06)	0.82 (0.05)	0.98 (0.01)	1.00 (0.01)	0.85 (0.02)	0.79 (0.05)
	NG	0.92 (0.03)	0.79 (0.08)	0.77 (0.06)	0.89 (0.06)	1.00 (0.01)	0.77 (0.02)	0.54 (0.09)
	GG	0.90 (0.03)	0.96 (0.02)	0.85 (0.04)	0.99 (0.01)	1.00 (0.01)	0.91 (0.01)	0.78 (0.05)
	S	LRT=0.01; p=0.91	LRT=10.24; **p<0.01**	LRT=0.01; p=0.95	LRT=0.68; p=0.19	LRT=1.11; p=0.29	LRT=1.99; p=0.20	LRT=3.93; **p=0.04**
	G	LRT=0.02; p=0.88	LRT=6.06; **p=0.01**	LRT=1.14; p=0.28	LRT=6.00; **p=0.01**	LRT=2.18; p=0.14	LRT=13.43; **p<0.01**	LRT=5.93; **p=0.01**
	S*G	LRT=0.07; p=0.79	LRT=5.49; p=0.06	LRT=7.56; **p=0.01**	LRT=4.15; **p=0.04**	LRT=2.32; p=0.13	LRT=1.98; p=0.16	LRT=2.37; p=0.12
0.15-0.30	CONV	0.81 (0.06)	0.87 (0.02)	0.68 (0.04)	0.90 (0.03)	-	0.63 (0.04)	-
	ORG	0.81 (0.05)	0.83 (0.06)	0.66 (0.04)	0.94 (0.01)	-	0.63 (0.03)	-
	NG	0.82 (0.06)	0.93 (0.02)	0.82 (0.03)	0.88 (0.04)	-	0.57 (0.04)	-
	GG	0.80 (0.05)	0.81 (0.04)	0.60 (0.03)	0.94 (0.02)	-	0.66 (0.03)	-
	S	LRT=0.59; p=0.44	LRT=0.52; p=0.47	LRT=0.18; p=0.67	LRT=1.54; p=0.21	-	LRT=0.01 p=0.96	-
	G	LRT=0.56; p=0.45	LRT=6.02; **p=0.01**	LRT=11.27; **p<0.01**	LRT=3.25; p=0.07	-	LRT=2.48; p=0.12	-
	S*G	LRT=0.45; p=0.50	LRT=3.24; p=0.07	LRT=0.33; p=0.56	LRT=0.75; p=0.38	-	LRT=4.62; **p=0.03**	-
0.30-0.60	CONV	0.56 (0.06)	0.05 (0.01)	0.58 (0.70)	0.63 (0.03)	-	0.29 (0.05)	-
	ORG	0.57 (0.05)	0.09 (0.02)	0.52 (0.71)	0.76 (0.050	-	0.17 (0.02)	-
	NG	0.59 (0.09)	0.09 (0.03)	0.56 (0.01)	0.71 (0.06)	-	0.23 (0.05)	-
	GG	0.55 (0.04)	0.06 (0.01)	0.54 (0.02)	0.69 (0.04)	-	0.23 (0.04)	-
	S	LRT=0.01; p=0.95	LRT=2.68; p=0.10	LRT=5.03; **p=0.02**	LRT=2.83; p=0.09	-	LRT=5.58; **p=0.02**	-
	G	LRT=0.27; p=0.60	LRT=0.14; p=0.70	LRT=0.34; p=0.56	LRT=0.44; p=0.73	-	LRT=0.01; p=0.99	-
	S*G	LRT=0.24; p=0.62	LRT=2.76; p=0.10	LRT=0.22; p=0.64	LRT=3.59; p=0.06	-	LRT=0.67; p=0.41	-

Data are measured mean values (n=18 for each S, n=24 for grazed and n=12 for non-grazed). The standard error of the mean in parentheses. Significance tests using likelihood ratio test (LRT), are compared models with or without the parameter of interest. Significant effects ($p < 0.05$) are shown in bold.

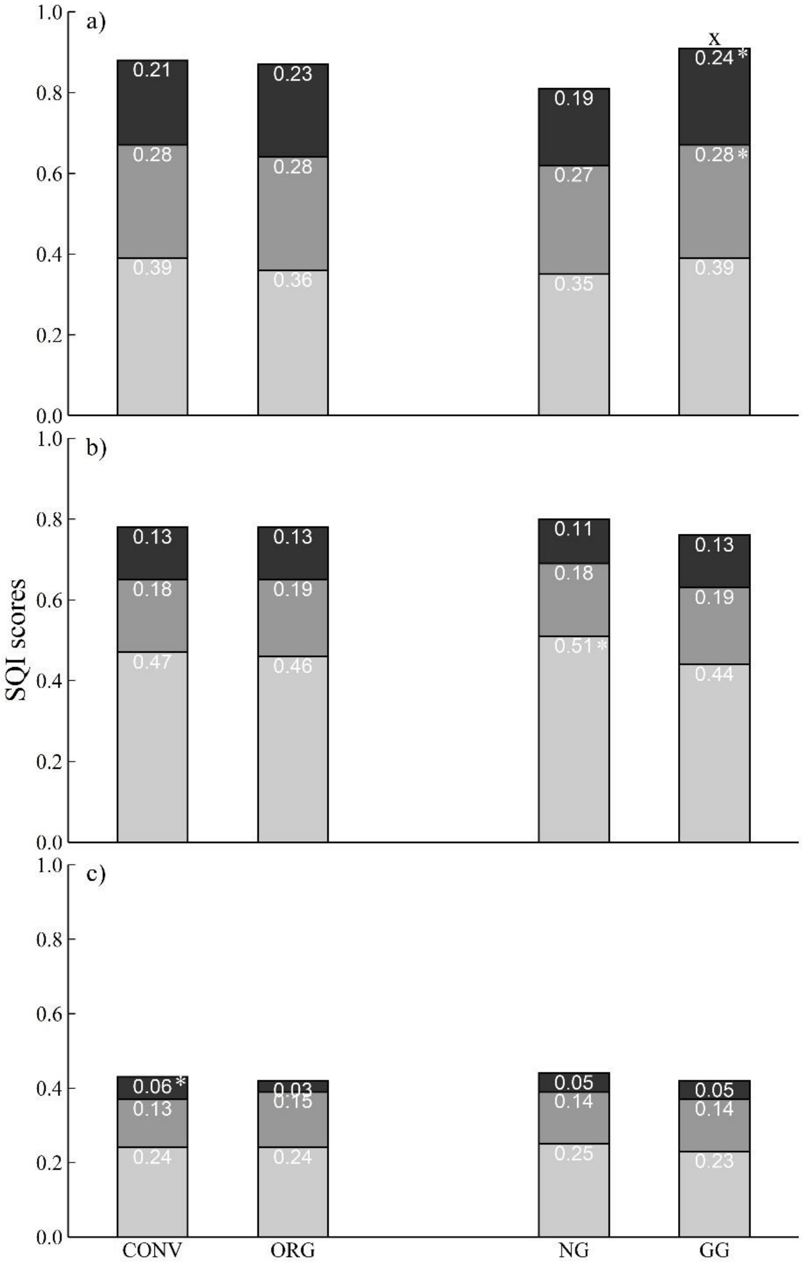
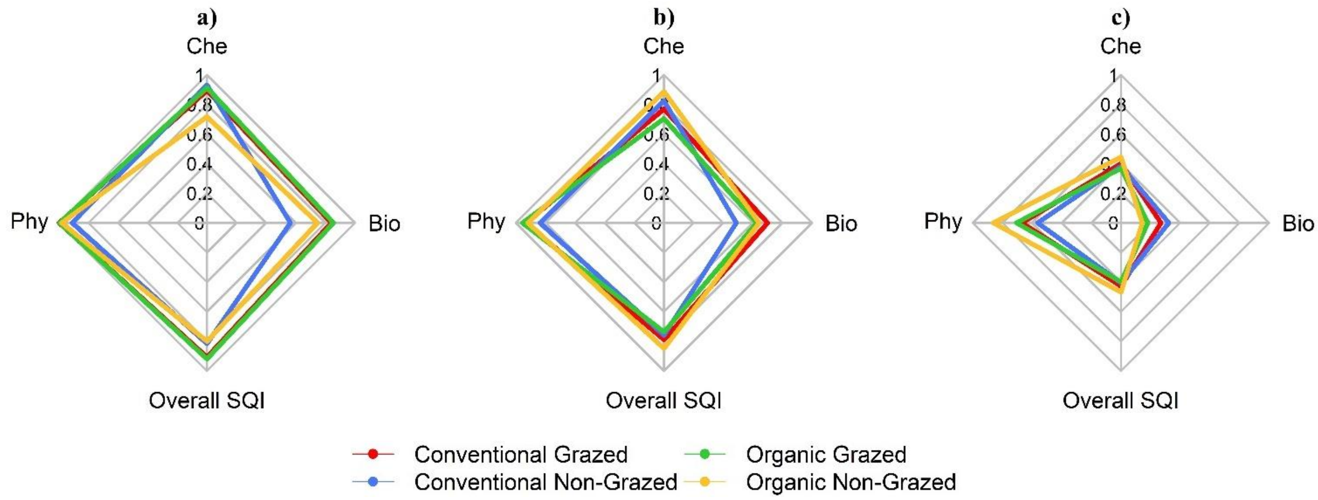


Figure 2.4 Effects of agricultural system (conventional – CONV and organic – ORG) and grazing regime (non-grazed – NG and grazed – GG) on overall soil quality index (SQI) scores and the contribution of the chemical, physical and biological sectors at three soil depth intervals: a) 0-0.15; b) 0.15-0.30 and c) 0.30-0.60 m. Overall SQI data and contribution of each sector are score mean values (n=18 for CONV and ORG, n=24 for GG and n=12 for NG). Significance tests using likelihood ratio test (LRT) comparing models with or without parameter of interest. Significant effects ($p < 0.05$) between the contribution of each sector to the overall SQI scores are represented by a star (*), while differences between overall SQI scores are represented by the letter “x”.



Depth (m)		Che	Phy	Bio	Overall SQI
0-0.15	Conventional Grazed	a	a	a	a
	Conventional Non-Grazed	a	b	b	b
	Organic Grazed	a	a	a	a
	Organic Non-Grazed	b	a	a	b
0.15-0.30	Conventional Grazed	ab	ab	a	ab
	Conventional Non-Grazed	ab	b	b	ab
	Organic Grazed	b	a	ab	b
	Organic Non-Grazed	a	ab	ab	a
0.30-0.60	Conventional Grazed	a	ab	ab	a
	Conventional Non-Grazed	a	b	a	a
	Organic Grazed	a	ab	ab	a
	Organic Non-Grazed	a	a	b	a

Figure 2.5 Interactive effects between agricultural system (conventional – CONV and organic – ORG) and grazing regime (non-grazed – NG and grazed – GG) on overall soil quality index (SQI) scores and chemical (Che), physical (Phy) and biological (Bio) sectors at three soil depth intervals: a) 0-0.15; b) 0.15-0.30 and c) 0.30-0.60 m. Overall SQI and sector data are score mean values (n=12 for conventional and organic grazed and n=6 for conventional and organic non-grazed). The same letter within overall SQI and/or sector and depth interval followed by the same letter are not significantly different by Tukey's honestly significant difference test ($p < 0.05$).

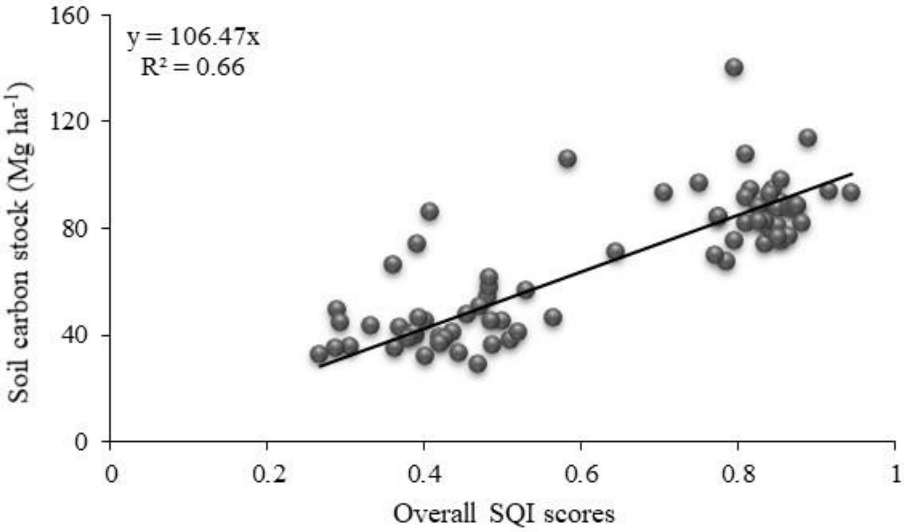


Figure 2.6 Relationship between overall soil quality index (SQI) scores and soil organic carbon stocks (0-0.60 m depth) under a mix of conventional and organic systems and grazed and non-grazed regimes.

2.4 Discussion

2.4.1 Effects of an organic system on individual measured SQ indicators

The lower soil available P concentration in the topsoil (0-0.15 m) in the organic system reflected other studies which have reported challenges with maintaining topsoil available P in organic cropping systems (Goulding *et al.*, 2009; Løes & Ebbesvik, 2017; Cooper *et al.*, 2018). Løes & Ebbesvik, (2017) reported that topsoil available P concentration (0-0.20 m) can decrease by half after conversion from a conventional to an organic system. Cooper *et al*. (2018), in a recent survey across Europe, found a declining trend in the soil available P concentrations under organic systems. The decrease in soil available P in organic systems is often associated with an imbalance between the export of P in products and the import of nutrients in livestock feed or approved fertilisers. This imbalance can jeopardise nutrient cycling function and reduce the capacity of the organic systems to deliver ecosystem services, such as biomass production in the long-term (Goulding *et al.*, 2009; Cooper *et al.*, 2018). However, it is also possible that the Olsen's P test does not accurately assess the pool of available P in the organically managed soils (Kratz *et al.*, 2016; Cooper *et al.*, 2018). The broad range of elements provided by organic amendments might have caused sorption of P or immobilization in microbial biomass; these forms of P may be slowly available to crops but not reflected in the results of the Olsen's P test (Möller *et al.*, 2018). In addition, the significantly higher MBC in the organic system should reflect a higher level of microbial activity with increased capacity to mobilise nutrients from inaccessible pools including organic P and sorbed P (Maeder *et al.*, 2002).

The absence of a difference between the conventional and organic system in the topsoil (0-0.30 m) K concentration can be explained by the fact that FYM, used as a source of K fertiliser in the organic system, is providing an equivalent supply of K to conventional K fertilisers (Fortune *et al.*, 2006). Nonetheless, differences in soil K concentrations deeper in the soil profile (> 0.30 m) between conventional and organic systems are rarely examined in the literature. Alfaro *et al.* (2006) investigated the effects of N application and drainage of K in grasslands and found higher K leaching as N application was increased. This was attributed to the acidification of the topsoil by synthetic N fertilisers and displacement of cations (including K) on the exchange complex, leading to K leaching down the profile. This could be a mechanism to explain the elevated concentration of K in the conventionally managed subsoils (0.30-0.60 m) and the lower values in the topsoil, relative to the organic. The sustained levels of K in the topsoil in organically managed soils indicate effective nutrient retention, possibly on the cation exchange complex which may be enhanced by the FYM additions.

The higher MBC under the organic system is in agreement with a recent global meta-analysis conducted by Lori *et al*. (2017), who observed a positive effect on soil microbial community abundance and activities when fields are managed organically. The authors pointed out that organic amendments and a more diverse rotation, particularly with the inclusion of legumes, increased the abundance of the microbial community. In this study, conventional and organic inputs and to a certain extent rotation system were alike, but only the organic part of the farm had the inclusion of nitrogen-fixing beans, whereas oilseed rape was only cropped in the conventional system. Although the conventional part of the farm also received organic fertiliser application (FYM), it was used together with mineral fertilisation, which might have affected the efficiency and/or community composition of the microbial biomass (García-Palacios *et al.*, 2018). This theory is also confirmed by the results of Maeder *et al*. (2002), who found enhanced microbial biomass in organically managed soils even when compared to the conventional system that used mineral fertiliser plus FYM.

Previous research has reported that organic systems can also increase topsoil (< 0.20 m depth) SOC concentrations (Marriott & Wander, 2006; Scialabba & Müller-Lindenlauf, 2010; Gattinger *et al.*, 2012), with very limited studies assessing deeper layers (Blanco-Canqui *et al.*, 2017). In this study, SOC concentrations in the topsoil layers (i.e. 0-0.15 m and 0.15-0.30 m) were not affected while concentrations were lower under the organic system at the 0.30-0.60 m depth interval. Previous research has attributed higher SOC concentrations in organic systems to higher C inputs (through manure, slurry and/or compost application) (Leifeld & Fuhrer, 2010; Gattinger *et al.*, 2012; Kirchmann *et al.*, 2016), but in this study, both conventional and organic systems had regular applications of FYM, as well as ley periods in the rotation, which might have limited differences between the two systems in the topsoil layers. Moreover, it is worth noting that changes in SOC occur slowly (Smith *et al.*, 2020), and therefore the short period since conversion to the organic system (~ 15 years) may have not allowed for detectable changes.

The significantly higher SOC concentration at 0.30-0.60 m depth under the conventional system contradicted previous work. Blanco-Canqui *et al*. (2017), in a long-term experiment (+20 years), did not find significant differences in SOC concentrations between a conventional and an organic system below 0.15 m depth, but they highlighted that in the organic system there was a trend towards higher SOC concentrations with the implementation of a more diversified rotation treatment and deep-rooting crops. However, studies comparing soil properties in deeper soil profiles between organic and non-organic systems are limited. In this study, the typically large aboveground biomass in the conventional system should equate to larger belowground biomass (Bilsborrow *et al.*, 2013). This could have resulted in a larger, deeper rooting system under the conventionally managed soils that enhanced SOC concentrations in the deeper (0.30-0.60 m) layer. This finding has implications for the climate regulation function of soils. While organic systems are commonly reported to have less of an impact on climate due to lower emissions from fertiliser manufacture (Smith *et al.,* 2019), increasing SOC concentrations in deeper soil layers could result in increased SOC sequestration at depth, which may partially offset GHG emissions from conventional systems (Tautges *et al.*, 2019).

Organic systems have been reported to trigger beneficial feedback loops between plants and microbial biomass that ultimately stimulates the plant to promote its own microbial population to increase nutrient availability and utilisation from organic material (Hamilton & Frank, 2001; Stockdale *et al.*, 2006). This is facilitated by microbial exudates, which would also bring further long-term benefits to soil aggregation and to SOC quantity and stability (Tisdall & Oades, 1982; Loaiza Puerta *et al.,* 2018). In this regard, it was expected that soil physical properties (i.e. BD and AS) would be enhanced in organic systems. Where soil type is the same, differences in physical properties such as BD and AS are largely driven by SOC contents. In this study, since soil type and SOC contents were similar for both systems, it is not surprising that AS and BD were also not significantly different when comparing the two systems. This suggests that the soil functions linked to soil structure, including regulation of the water cycle and provision of physically stable aggregates, do not differ between conventional and organic systems.

Overall, the potentially higher organic and microbial forms of P, similar topsoil (0-0.30 m) K, BD, AS and SOC concentration and the higher MBC under the organic system indicate that agricultural systems receiving only organic amendments and including nitrogen-fixing plants in the rotation can generate analogous SQ with fewer external inputs than conventional systems.

2.4.2 Effects of the grazing regime and its interaction with agricultural systems on individual measured SQ indicators

The higher topsoil (0-0.15 m) available P, SOC and MBC under grazed regimes (compared to non-grazed) were likely to be associated with the higher nutrient returns and enhanced nutrient cycling provided by animals, ley periods and residues left in the soil.

Topsoil (0-0.15 m) available P was 40% and 240% higher under conventional and organic grazed regimes respectively, when compared with non-grazed counterparts (Table 2.2). According to Nash *et al.* (2014), up to 85% of the P applied and taken up by plants is returned to the soil via animal dung in a grazed system. Since animals in a grazed regime act as a nutrient cycling agent (Carvalho *et al.*, 2010), it is likely that they modify both the biochemical form of the nutrients and their spatial distribution, and consequently influence local availability in the soil solution. Moreover, grazing can change plant population dynamics and species diversity, resulting in a different plant ecology system compared to a non-grazed regime (Assmann *et al.*, 2017). This increased soil P availability effect can be found even under light grazing intensities (Assmann *et al.*, 2017) and has been observed across varying mixed (arable/livestock) production systems in Europe (Cooper *et al.*, 2018). However, studies directly comparing conventional and organic mixed farming systems in association with non-grazed and grazed regimes, as compared in this study, are rare (Jackson *et al.*, 2019). This finding on soil available P merits particular attention for future discussions on sustainable agriculture strategies as mineral P (as rock phosphate) is a finite resource. Increased available P under organic grazed regimes suggests that grazing residues (urine and dung) and organic amendments are complementary strategies (Assmann *et al.*, 2017) which may be beneficial for cropping systems at a lower level of P supply.

The grazed regime also increased topsoil (0-0.15 m) SOC concentration and MBC under both agricultural systems (Table 2.2). Previous studies have also found that implementing grazing can increase topsoil SOC concentration (Abdalla *et al.*, 2018), indicating that the SOC gains may be limited to the surface layers where the root systems dominate (Medina-Roldán *et al.*, 2008; Chen *et al.*, 2015). Increased MBC in grazed fields might be related to interlinked mechanisms regarding the effects of grazing on the microbial community, including changes in biomass production and resource allocation, resource inputs to the decomposers and the plant community itself (Bardgett & Wardle, 2003). Together, these suggest that grazing could be driving SOC accumulation and MBC in the top 0-0.15 m depth due to greater deposition of easily available C inputs and nutrients, which indirectly stimulates below-ground biomass (e.g. root growth), followed by greater root turnover and exudations (McSherry & Ritchie, 2013; Chen *et al.*, 2015).

Grazing intensity may influence SOC concentration and MBC positively or negatively by changing individual plant species and plant cover as well as processes that fix C during photosynthesis as a function of microclimate (McSherry & Ritchie, 2013; Abdalla *et al.*, 2018). Since in our study grazing intensity was relatively low and climate parameters were similar for all study fields, the residue amount left in the soil by animals and root growth are likely to be the primary causes of the higher SOC concentration and MBC in the grazed regimes. We hypothesise that animal trampling may have incorporated part of the residues deposited on the soil surface into the topsoil, whilst also stimulating greater root growth and turnover. These mechanisms could be especially important for the 0.15-0.30 m depth in the conventional system, which showed the lowest SOC concentration in non-grazed fields but a significant increase in grazed regimes (Table 2.2 and Fig. 2.2). Lower SOC concentration in conventional non-grazed study fields may also be related to the use of more mineral N fertiliser and an increase in residue decomposability (García-Palacios *et al.*, 2018). While grazed regimes have increased topsoil (0-0.15 m) SOC concentration and MBC, grazing ruminants on leys results in GHG emissions and reduces land available for cereal crop production. This illustrates the complexity of decision making about land management practices once the multiple ecosystem services provided by agricultural landscapes are considered. Further research is required to assess the trade-offs between the SOC sequestration benefits of grazed leys and the wider impacts on the food system.

The grazed regime also interacted with agricultural system enhancing topsoil (0-0.15 m) K concentration under the organic system (Table 2.2 and Fig. 2.2). Grazed organic systems experience a high degree of recycling of K through the return of dung, especially urine, since only a small portion of K is retained in animal products (e.g. milk and meat) (Haynes & Williams, 1993; Assmann *et al.*, 2017). This cycling of K, in combination with higher rates of FYM inputs on organic fields (averages of 100 and 166 kg K ha^{-1} yr^{-1}, for the conventional and organic system in the last 10 years, respectively) could result in high levels of available K in grazed organic fields.

In contrast, the non-grazed regime showed nearly twice as much available K in the 0.15-0.30 m compared to the grazed fields regardless of the agricultural system. This corresponds to results from a review conducted in Brazil by de Faccio Carvalho *et al.* (2010) who found that non-grazed fields have higher K concentrations in the soil profile, in particular from 0.10 to 0.30 m soil depth. The main hypothesis for the higher K concentration in the non-grazed field at depth is that grazed fields possess a denser root system in the topsoil that mines subsurface K reserves (0.15-0.30 m) and recycles and deposits this K onto the soil surface (0-0.15 m). However, more research on the morphology of ley root systems under non-grazed and grazed regime is required to further elucidate these mechanisms.

Changes in root growth quantity and dynamics might also explain the interactive effect found in soil BD. The decrease in topsoil (0-0.15 m) BD in conventional grazed fields, compared to conventional non-grazed fields, may be linked to the stimulation of root growth resulting in an increase in the root exudation and microbial activities (confirmed by our MBC results and also by Hamilton & Frank, 2001). In organic systems, the higher nutrient availability in the surface layers under grazed fields (Table 2.2) may have discouraged the need for root development into the deeper soil layers, resulting in a higher BD for 0.30-0.60 m depth. A potential stimulation of surface below-ground biomass production by grazing is an important feature as it can amplify the formation of soil aggregates and reduce soil compaction (Dominy & Haynes, 2002). Although not significant ($p = 0.09$, Table 2.2), soil aggregate stability was 10% higher in the topsoil of grazed fields compared to non-grazed fields and appeared to be linked to the length of time that a field was in the ley phase (see section 4.3). This indicates that important soil functions, including mitigation of GHG emissions (Ball, 2013), resistance to soil erosion (Barthès & Roose, 2002), and improved water infiltration and retention, may all be enhanced by grazed ley periods. Our results, therefore, indicate an enhanced SQ from mixed farming systems that could have potential policy implications for the design of multifunctional landscapes.

2.4.3 Effects of ley time proportion (LTP) on individual measured SQ indicators

Increasing LTP in the crop rotation increased AS (0-0.15 m) and SOC concentration (0-0.15 and 0.15-0.30 m) under both agricultural systems, while it decreased K concentration in the 0.15-0.30 m depth (Fig. 2.3). The decreased soil K concentration at this intermediate-depth interval with increased LTP supports the notion that a more extensive root system might be mining K from the 0.15-0.30 m depth and depositing it onto the soil surface (0-0.15 m); the trend (non-significant) towards increased topsoil K (0-0.15 m) as LTP increased further supports this hypothesis. The development of a dense root system may also lead to improved soil aggregate stability (i.e. soil structure), and favour the protection and stabilisation of SOM as well as associated nutrients (Six *et al.*, 2002b). This is supported by the observed increased AS (0-0.15 m) and SOC concentration (0-0.15 and 0.15-0.30 m) with increased LTP.

The results of this study agree with findings from other studies assessing the effects of LTP on soil structure and SOC concentration (Jarvis *et al.*, 2017; Loaiza Puerta *et al.*, 2018; Crème *et al.*, 2018). Jarvis *et al.* (2017) compared varying proportions of ley (1, 2, 3 or 5 years) in a long-term field trial (60 years) and found that higher proportions of ley time in a rotation improved both topsoil structure and SOC concentration. Similarly, Loaiza Puerta *et al.* (2018) reported improved soil aggregate stability and SOC concentration after two years following four years of arable cropping. Crème *et al.* (2018) assessed the legacy effect of 3 and 6 years of grassland ley periods after 3 years arable cropping and found that even under short periods (i.e. 3 years) the SOC concentration increased with the implementation of ley periods compared to continuous arable production.

Most previous studies have indicated higher soil aggregate stability and SOC concentration in a ley-arable rotation compared to continuous arable in the topsoil layers (max. 0.20 m soil depth). This study supports these findings but also reported increased SOC concentration for intermediate soil layers (i.e. 0.15-0.30 m), which is a significant outcome. In one of the few studies assessing the effects of ley-arable rotations on SOC below 0.20 m, Blanco-Canqui *et al.* (2017) found no significant effect below 0.15 m soil depth. The authors considered two-year ley periods in a four-year crop rotation, concluding that the time under ley (i.e. two years) was insufficient to develop an extensive and deep root system to build SOC concentration in the subsoil. Our results suggest that grass-clover ley for approximately 30-40% of the crop rotation (i.e. 3-4 years in a 10-year period) may be required to increase SOC concentration at 0.15-0.30 m depth. This is particularly relevant for future policies relating to climate change mitigation since building SOC in deeper layers can result in slower rates of decomposition and improve C protection and sequestration in the soil (Lorenz & Lal, 2005). Increasing LTP has increased AS (0-0.15 m) and SOC concentration (0-0.15 and 0.15-0.30 m) and its wide adoption to improve SQ could result in a return to mixed farming systems and less specialisation of crop or livestock farms. This could have GHG implications if total ruminant numbers increased, something that would need investigation using a life-cycle assessment approach to point out the real benefits and/or drawbacks of different scenarios.

2.4.4 Effects of agricultural systems, grazing regime, and their interaction on individual and integrated SQI scores

The SMAF has been primarily designed to assess changes for the near-surface soil (0-0.15 m depth), but it was also capable of identifying differences at the depth intervals 0.15-0.30 and 0.30-0.60 m (Table 2.4). The findings at these soil depths, however, should be carefully judged as the algorithms used in the SMAF approach were based on optimum levels for topsoil chemical, physical and biological aspects. For each individual soil indicator measurement, the calculation of the SQI scores considered site-specific inherent features, including climate, soil type and slope, among others. Although it thus might represent a distinct case study, the use of the SQI scores rather than actual measurements might also be representative of a more realistic soil functionality, since it considered the influence of all these other aspects (Andrews *et al.*, 2004).

The use of SQI scores showed a few significant differences that were not observed using the soil indicator measurements only. For example, grazing regime under either conventional or organic system significantly decreased soil P scores for the 0.15-0.30 m depth interval. The measured soil available P concentration, on the other hand, did not indicate a significant effect at this depth interval ($p > 0.05$). The use of SQI scores for soil available P concentration (mid-point optima Gaussian function) indicated that the decreased soil available P under grazing might be detrimental for the 0.15-0.30 m layer. According to Andrews *et al.* (2004), significant effects found for the SQI scores, but not for the measured indicator, can occur when most of the measured values for one of the treatments receive scores that fell into the ascendant and/or descendant portion of the curve with only a few points in the finest range, as occurred in our grazed study fields. It is important to also stress that the scoring curves for P considered critical limits to sustain plant growth without being detrimental to the environment, in particular, the water resources. This means that if the soil available P concentration increased more than was necessary for plant growth, then its SQI scores actually decreased. The use of SQI scores for soil available P concentration can therefore provide a more valuable evaluation of the effects of agricultural systems and grazing regime compared to the actual measurement of soil available P concentration. This finding also confirms our previously discussed assumption for the measured soil available P and K indicators, that the returns from animal grazing (e.g. dung) would only benefit the topsoil (0-0.15 m) as a source of available P and K (Nash *et al.*, 2014).

By contrast, the use of SQI scores, instead of the measured values for soil aggregate stability, which uses the more-is-better upper asymptotic sigmoid curve shape, prevented us seeing the potential of the grazed regime to enhancement soil structure. Although not statistically different, grazed fields showed higher soil aggregate stability (average of ~ 75%) compared to non-grazed fields (average of ~ 65%). The use of SMAF approach, however, ascribed a maximum score (1.0) to values higher than 50% (Table 2.4), i.e. for all the measurements in this study. The same behaviour was reported in a previous study conducted under tropical soils in Brazil using the SMAF approach (Cherubin *et al.*, 2016b). Differently than this study, the authors assessed contrasting land uses (native vegetation – pasture – sugarcane) rather than agricultural systems and management practices as assessed here. While the authors found some significant differences in the actual soil aggregate stability measurement, the soil aggregate stability scores provided by the SMAF approach were unable to detect any difference. Based on our and Cherubin's et al. (2016b) findings, we underpin the conclusions that other scoring curve functions need to be implemented in the SMAF approach for the assessment of soil aggregate stability, including also temperate soils.

Apart from these two indicators (i.e. soil available P concentration and soil aggregate stability), the use of SMAF appears to show essentially the same results as the measurements, indicating thus that the scores could simply stand alone in any monitoring assessment. This represents an advantage for the use of scores, especially with regard to interpretation and comparison with other studies. Besides, it allows the integration of indicator scores into sectors (chemical, physical and biological) as well as in an overall SQI, which seems to be an attractive approach for summarising information and planning future management decisions. For example, even though organic system and the non-grazed regime had shown significantly lower topsoil (0-0.15 m) soil P availability and SQI scores than conventional system and grazed regime, the chemical sector, i.e. integrating pH, P, and K, was only lower under organic non-grazed fields. The lower chemical SQI score under organic non-grazed fields indicate that only this situation needs more attention regarding to a potential imbalance of nutrients. It is important to highlight that pH, P and K (i.e. the chemical SQ indicators used in this study) are crucial indicators in an SQ assessment, particularly because they represent soil nutrient storage, availability and cycling status, and are widely used to guide soil fertility (Karlen & Stott, 1994). Besides, they are relatively low-cost analyses, often available in soil analysis laboratories and are considered easy to sample and interpret (Doran & Parkin, 1994; Cherubin *et al.*, 2016a). For the same depth interval (0-0.15 m), the integrated approach also revealed that non-grazed regime in both agricultural systems (conventional and organic) led to the lowest functioning capacity for the physical and biological sectors. A decreased SQ in these sectors can be detrimental to some key soil functions, such as water infiltration, structural ability, biological activities and plant growth (Karlen & Stott, 1994). In contrast to the top 0-0.15 m depth, grazed regime did not improve soil functionality at the 0.15-0.30 m depth interval, although it led to numerically better SQI scores in the physical and biological sectors under the organic and conventional system. The overall SQI indicated that organic non-grazed fields could deliver an improved SQ at this depth interval, driven particularly by improvements in the chemical sector. For deeper soil layers (0.30-0.60 m) grazed regimes did not result in any further difference within sectors nor in the overall SQI. The decreased SQI scores with an increase in soil depth highlighted the better soil quality aspects in the top centimetres, particularly as a function of higher inputs (including fertilisation), better soil structure and physical resistance as well as greater chemical and biological activities. This result, however, highlighted the need to develop algorithms for the subsoil which, possibly have different functions.

Overall, the results using SQI scores supported the hypothesis that grazed regimes can be important for the balance and functionality of topsoil (0-0.15 m) chemical, physical and biological attributes in both conventional and organic system. However, it does not appear that a grazed regime would be beneficial for any agricultural systems (i.e. conventional or organic) below 0.15 m depth, in fact, it can lead to a decrease overall SQI at 0-15-0.30 m under the organic system. While there is room for improvement in all indicator scoring curves, special attention should be given to soil aggregate stability, which seems to be non-sensible in both tropical and temperate soils. Such improvements would make the SMAF a more sensitive tool, capable of detecting smaller changes caused by different land uses and management interventions. We conclude that while some tailoring is still required, the SMAF approach is suitable to capture SQ information under contrasting agricultural system and grazing regime in northern UK agricultural systems. The SMAF approach could help farmers and stakeholders to make important decisions regarding improved management and practices.

2.5 Conclusions

This research was performed in a commercial mixed (arable/livestock) farm in northern England to investigate the impacts of organic and non-organic (conventional) agricultural systems on individual and integrated soil quality (SQ) indicators in both the topsoil and subsoil. More specifically, it investigated how changes from a conventional to an organic system and the presence (or absence) of grazing regimes (non-grazed *vs.* grazed) and pasture leys in rotation, and their interactions, influenced chemical, physical, and biological soil quality indicators. For the topsoil, the findings reflected existing knowledge on the advantages of organic *vs.* conventional systems on SQ indicators. When grazing was included, both agricultural systems benefited from a greatly enhanced SQ, in particular the grazed conventional system. The grazed organic system had a much smaller benefit compared to the non-grazed organic system. The length of pasture leys in the rotation was positively related to SQ regardless of the type of agricultural system, and a grass-clover ley period length equivalent to 30-40% of the full crop rotation is needed to increase aggregate stability and soil organic C concentration in a linear fashion. Subsoil conditions (below 0.30 m) showed a different pattern for SQ to the topsoil. Bulk density and SOC accumulation were favoured under the conventional system, which is hypothesised to be due to a larger and deeper rooting system. Studies into subsoil SQ indicators are less common and the results here show that the agricultural system effects are probably more complex than in the topsoil. However, including grazing and pasture leys in management systems has positive benefits throughout the profile on SQ indicators regardless of whether the system is conventionally or organically managed. The use of SMAF for the very first time in northern UK agricultural systems confirmed our predictions of its suitability for the assessment of SQ. The use of SQI scores revealed that the framework was sensitive enough to detect most of the variations observed within single indicators measurements. In addition, the use of SMAF approach for integration of the SQI scores into sectors (chemical, physical and biological) and overall SQI was advantageous as it facilitates the identification of sectors that require priority actions and the effects of agricultural systems and management practices to SQ in general. The strong positive correlation between overall SQI scores and SOC stocks confirms the use of the latter as a potential universal indicator of SQ and validate the SMAF as a tool for scoring and integration approach. Ultimately, reviving mixed farming systems may be a key factor for delivering multi-functional agroecosystems that maintain SQ and optimise ecosystem services including nutrient recycling/release and utilisation. This still needs more research, particularly in furthering knowledge of how subsoil SQ indicators respond to management and also on economic considerations of any proposed changes in management.

Chapter 3. Mixed arable-livestock farming system and temporary grass-clover leys in crop rotations increase soil carbon and nitrogen stocks and affect carbon in particulate and mineral-associated fractions under both conventional and organic agricultural systems

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Notes

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Declaration of contribution

The experiment was planned by myself, Caio Fernandes Zani with advice from Geoffrey D. Abbott, James A. Taylor, Elisa Lopez-Capel and Julia Cooper. The soil sampling was carried out by myself, Caio Fernandes Zani, with assistance from Gavin Hall and Rachel Chapman. Caio Fernandes Zani also carried out all soil analyses and data analysis. Caio Fernandes Zani led the writing of the chapter and potential paper, with contribution from all co-authors. Specifically, Geoffrey D. Abbott, James A. Taylor, Elisa Lopez-Capel and Julia Cooper provided PhD supervision and detailed comments on the chapter.

3.1 Introduction

The intensification of crop production has led to substantial organic carbon (C) losses from agricultural soils (Lal, 2004a). Soil organic C (SOC) accumulation is possible within the agricultural sector, especially via improved management practices (Smith *et al.*, 2007, 2008). In particular, it has been suggested that significant increases in SOC stocks may be achieved with the adoption of organic over non-organic 'conventional' system, as well as through mixed arable-livestock farming system and through including grass-clover leys in arable crop rotations (Conant *et al.*, 2001; Gattinger *et al.*, 2012; Chen *et al.*, 2015; Li *et al.*, 2018; Börjesson *et al.*, 2018). However, there are concerns that previous studies have only considered one driver of change (i.e. the agricultural system or grazing regime or ley periods), have evaluated SOC content instead of stocks, were limited to the topsoil (<0.20 m), used only short-term grass-clover ley periods and have rarely assessed the distribution of soil C among soil organic matter (SOM) fractions. Therefore, uncertainties remain on whether changing the agricultural system from conventional to organic, implementing non-grazed or grazed grass-clover leys in crop rotations and the length of time in ley for enhancing SOC and nitrogen (N) stocks in the top and subsoil layers and to what extent these practices affect the distribution of C between SOM fractions. An improved understanding of these effects could inform future land management policies designed to mitigate climate change through C sequestration.

Organic systems aim to supply high-quality food with minimal environmental impact using a sustainable production approach that relies on closed nutrient cycles (Reganold & Wachter, 2016). General organic system guidelines include the return of plant and animal residues as organic fertilisers, limiting any synthetic input sources and the implementation of an extended rotation, which includes legumes and grass-clover ley periods (IFOAM, 2012). Many studies have indicated that the core practices of organic systems can promote SOC accumulation in agricultural soils (Diacono & Montemurro, 2010; Gattinger *et al.*, 2012; Panettieri *et al.*, 2017; Conant *et al.*, 2017). For instance, Gattinger *et al.* (2012) found that two main practices of organic systems, external C inputs (i.e. manure) and diversity in crop rotation, significantly increased SOC stocks.

The implementation of temporary grass-clover leys in crop rotations is another practice that might enhance SOC stocks. The main aim of grass-clover ley periods in an organic system is to increase productivity, nutrient supply and soil fertility, via both symbiotic N_2 fixation by legumes (Nyfeler *et al.*, 2011; Suter *et al.*, 2015) and increases in SOM (Paustian *et al.*, 1997). However, an increase in SOM inputs and the relatively undisturbed soils under ley periods (i.e. no cultivation) can also directly benefit SOC and N stocks (Paustian *et al.*, 1997; Cooper *et al.*, 2016). Other factors, such as improved soil structure and biodiversity, can indirectly contribute to SOC accumulation and have been associated with grass-clover ley periods and general organic practices (e.g. manure application) (Jarvis *et al.*, 2017; Loaiza Puerta *et al.*, 2018; Jensen *et al.*, 2019).

Whilst comparisons between conventional and organic systems on agronomic, and environmental aspects have demonstrated benefits for the latter (Mondelaers *et al.*, 2009; Tuomisto *et al.*, 2012; Meier *et al.*, 2015; Seufert & Ramankutty, 2017), the potential for organic systems to act as C sinks is still contentious. Contrasting results for SOC stocks could be due to a lack of consideration for specific factors, such as the proportions of temporary grass-clover leys in crop rotations, beyond differences in the amount of manure applied under organic systems (Leifeld & Fuhrer, 2010; Gomiero *et al.*, 2011; Gattinger *et al.*, 2012, 2013; Leifeld *et al.*, 2013; Kirchmann *et al.*, 2016). Another potential confounding factor could be differences in specific management practices during ley periods. For instance, whether a ley is used for hay meadow cutting or livestock grazing (i.e. non-grazed *vs.* grazed) can change its nutrient inputs and dynamics (Zani *et al.*, 2020), soil microbial community size, diversity and activities (Crème *et al.*, 2018) and is therefore likely to affect SOC and N stocks. Under a grazed regime, extra inputs through forage residues and animal dung, stimulation of root turnover and exudation and changes in plant species and composition, as well as in root growth quantity and dynamics, could enhance soil C stocks throughout the profile, although this is also dependent on several aspects e.g. climate, soil type, grass species and/or grazing intensity/management (Pineiro *et al.*, 2010; McSherry & Ritchie, 2013; Assmann *et al.*, 2014; Chen *et al.*, 2015).

Contrasting results in different agricultural systems and uncertainty about the impacts of specific practices on SOC stocks indicate the need for advanced techniques to identify optimum management practices. The separation of soil C into fractions with contrasting behaviour can be used to better understand SOM dynamics. The assessment of C in different SOM fractions may also serve as a proxy for better understanding of SOC stabilisation mechanisms and rates of turnover (Poeplau *et al.*, 2018). In this sense, it has been recommended to separate SOM into an organic fraction (particulate organic matter – POM > 53 μm) and mineral-associated fraction ((heavy fraction – HF > 53 μm, consisting of primarily coarse and sand particles, and silt and clay fraction – SC < 53 μm) (Christensen, 1992, 2001), as they have highly contrasting behaviours and therefore stabilisation and mean residence time (Lavallee *et al.*, 2019). Due to its nature (readily available), the POM fraction has been suggested as an early and sensitive indicator in the evaluation of management practices impacts, while the mineral-associated fraction has been associated with long-term SOM sequestration (von Lützow *et al.*, 2007;

Lavallee *et al.*, 2019). Whilst mineral-associated C is considered more stable than C in the POM fraction, the turnover time of both may vary. According to Feng *et al.* (2016), C turnover times may range from 0.5 to 374 years for the sand fraction, 8 to 1660 years for the silt fraction and from 33 to 4409 years for the clay fraction. The organic fraction (often termed as POM), in turn, is often linked to input quality, meaning that depolymerisation might be required prior to assimilation in cases where inputs contain large, insoluble molecules (Kleber *et al.*, 2015). Ultimately, the assessment of soil C in the SOM fractions is important as, whilst an equilibrium in SOC stock can be reached, its distribution among SOM fractions with varying stability might change constantly, meaning that the C stored can be either stable or susceptible to losses.

In this context, the aims of this study were to compare SOC and N stocks and C distribution in SOM fractions down to 0.60 m soil depth in conventional and organic mixed farming systems, with both non-grazed and grazed regimes, and to explore the influence of different proportions of temporary grass-clover leys in crop rotations. The comparison was conducted under the same mixed-farm condition, where both conventional and organic systems co-exist. It was hypothesised that (i) the organic system would lead to higher SOC and N stocks; (ii) integrating grass-clover leys with livestock in crop rotations (i.e. mixed farming system) would increase SOC and N stocks in both agricultural systems; (iii) increases in the proportions of temporary grass-clover leys in crop rotations would increase SOC and N stocks regardless of the agricultural system or grazing regime; and (iv) POM will be the fraction most sensitive to differences in management followed by the heavy (HF) and SC fractions..

3.2 Materials and Methods

3.2.1 Farm description

The study was conducted at Newcastle University's Nafferton farm, a mixed (arable/livestock system) commercial farm located 12 miles west of Newcastle upon Tyne in north-east England (54º59'09''N; 1º43'56''W, 60 m a.s.l.). A detailed description of the farm can be found in Chapter 2, section 2.2.1. In this study, the comparison between the two agricultural systems (conventional and organic) was also made using the first as a baseline, on the premise that SOC was already at an equilibrium stage since it had been in place for the preceding 50+ years. In addition, the study fields were deemed suitable since they had similar soil types and experienced similar climatic conditions.

3.2.2 Study fields selection

This chapter used the same twelve commercial-size agricultural study fields selected for Chapter 2. Criteria for selection and more details of each study field can be found in Chapter 2, Section 2.2.2 and Table 2.1. Briefly, there were six study fields under conventional (CONV) and six under organic (ORG) system, of which four were under non-grazed (NG) and eight were under grazed (GG) regime (two non-grazed and four grazed study fields within each agricultural system, respectively). The selected twelve study fields were also deliberately chosen on the basis of the percentage (0 to 100%) of time as temporary grass-clover leys in 10 years prior sampling (hereafter referred to as ley time proportion-LTP). General characteristics of the soil properties and other management histories, including LTP, manure application proportion (MAP) (i.e. % years with manure application in 10 years prior sampling) and tillage event proportion (TEP) (i.e. % years with activities that turned the soil over for at least 0.15 m depth in 10 years prior sampling), under both agricultural systems and grazing regimes are given in Table 3.1. Crop history details are given in Table A1.2 (Appendix 1).

Table 3.1 Overall soil properties [a] and other management histories [b] across the Nafferton farm by treatments assessed [c].

	Sand	Silt	Clay	pH	Bulk density	LTP	MAP	TEP
	g kg^{-1}			H_2O	Mg m^{-3}	Years		
CONV	417.83 (5.67)	426.76 (4.00)	155.41 (3.17)	6.35 (0.06)	1.21 (0.01)	4.83 (0.83)	3.50 (0.46)	3.83 (0.58)
ORG	427.39 (5.16)	419.99 (3.69)	152.62 (3.10)	6.66 (0.05)	1.17 (0.01)	5.50 (0.46)	5.33 (0.43)	4.00 (0.40)
NG	399.62 (5.40)	436.45 (4.77)	163.93 (3.35)	6.64 (0.06)	1.20 (0.01)	1.75 (0.39)	3.75 (0.84)	6.25 (0.39)
GG	435.80 (5.07)	415.94 (3.24)	148.26 (2.87)	6.43 (0.05)	1.19 (0.01)	6.88 (0.30)	4.75 (0.31)	2.75 (0.25)

[a] Soil properties data are measured mean values for the 0-0.60 m depth (n=201 for conventional, n=177 for organic, n=141 for non-grazed and n=237 for grazed).
[b] LTP, ley time proportion; MAP, manure application proportion; TEP, tillage event proportion. LTP, MAP and TEP are shown as the average number of years under ley, manure applied and tillage events occurrence over the 10 years (2008-2017) prior sampling. Since conversion from conventional to the organic system across 50% of the farm area (i.e. from 2001 onwards), tillage practice was conducted using ploughing and disking practices to a maximum depth of 0.15 m at both sides of the farm.
[c] CONV, conventional; ORG organic; NG, non-grazed; GG, grazed.

3.2.3 Sampling strategy and methods

Sampling location points were laid out using a quasi-random stratified design based on an *a priori* soil apparent electrical conductivity (EC_a) (0-0.70 m depth) map (Chapter 2, Fig 2.1). More details about the methods and equipment's used for EC_a survey can be found in Chapter 2, Section 2.2.3. The use of this design was to ensure samples were taken across a range of EC_a values (the likely soil texture range) and covered the entire field while maintaining some element of randomisation to avoid user-bias in the site selection.

For each study field, a different number of sampling points (ranging from eight to 15) were selected based on the size of the field and observed variability in the measured EC_a. To identify the location and the number of sampling points in a study field, the 0-0.70 m depth EC_a distribution was separated into quartiles. The JMP statistical program (JMP, 2019) and ArcGIS software (Esri, 2018) were used to select two randomly sampling points from each quartile, ensuring a minimum of eight sampling points per study field, with the constraints that i) it could not be located within 20 m of a field boundary and, ii) it could not be located within 50 m of another sampling point in the study field. For larger study fields (based on area) and more variable fields (higher variance in the EC_a), additional sampling points were randomly selected using the same two constraints. The quartile selection process was not used in this stage. The number of additional sampling points was determined arbitrarily, using local expert knowledge, but they were distributed evenly between both agricultural systems (ORG and CONV). A nearby site was selected during the survey if the sampling point was deemed likely to be disproportionately affected by compaction from either machinery or animal trampling.

There were 126 sampling points selected across the farm (2 agricultural system: 6 study fields per system: 8-15 replicate sampled points per study field) (Chapter 2, Fig. 2.1). Two undisturbed soil cores (1 m length, 0.03 m inner core diameter) were taken at each selected point using a hydraulic soil sampler (Atlas Copco Ltd., Hemel Hempstead, Hertfordshire, UK). Each soil core was separated into three distinct depth intervals 0-0.15; 0.15-0.30 and 0.30-0.60 m, resulting in 756 soil samples. Soil sampling was conducted in February-March 2017 and the position of each sample point was georeferenced with an EGNOS-enabled handheld GPS receiver (Garmin eTrex ® 30x).

3.2.4 Soil preparation and analyses

Each of the 756 fresh undisturbed samples was gently mixed and passed through a 4 mm sieve; large stones were removed and weighed plant remains were discarded. The weight of the sieved, fresh soil was then recorded. A subsample of the sieved soil (5 g) was used for determination of gravimetric water content. Soil bulk density (BD) was calculated using the core method adjusting for the weight and volume of large stones (Blake & Hartge, 1986). Thereafter, the duplicate core samples taken at the same georeferenced location and same depth interval were merged and sieved through a 2 mm sieve. This resulted in 378 merged samples, which were then air-dried before being used for particle-size distribution (PSD), SOC and N concentration and physical fractionation analysis.

PSD of each merged sample was determined in triplicate by a low angle laser light scattering technique (Laser diffraction) as described in Chapter 2, Section 2.2.4. Likewise, analytical procedures for SOC and N concentration, determined by dry combustion method, can be found in Chapter 2, Section 2.2.4. Thermal analysis (Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry) conducted in Chapter 5, Section 5.3.3, of this thesis, showed that there was an absence or very low presence of carbonate minerals in the samples (Chapter 5, Fig 5.7), therefore, total soil C concentration can be assumed to be total SOC. SOC and N stocks per unit of area (Mg ha^{-1}) were calculated for each depth interval (i.e. 0-0.15; 0.15-0.30 and 0.30-0.60 m) on an equivalent soil mass basis (Wendt & Hauser, 2013) using the CONV and NG as a reference. More details about the calculations and equivalent soil mass adjustments can be found in Chapter 1, Section 1.5.

Physical fractionation of SOM was accomplished according to Christensen (1992) (Fig. 3.1). The method is known as granulometric physical fractionation and is distinguished from the densimetric physical fractionation that often uses high-density liquids. A recent comparison between different physical fractionation methods has showed that the use of high-density liquids or water did not significantly influence the recovery and reproducibility of the total C in the fractions (Poeplau *et al.*, 2018). As such, the method chosen in this study did not use any chemical to separate the soil particles into organic and mineral-associated fractions (Christensen, 1992, 2001), helping to preserve as much as possible the original composition of the SOM compounds, unlike chemical separation methods (Lehmann & Kleber, 2015). The use of water also helped to avoid potential contamination by chemical compounds. A potential disadvantage of such an approach might be that the soil particles are not fully dispersed resulting an inconsequential retention of mass and/or C in fractions that it does not belong (von Lützow *et al.*, 2007; Lavallee *et al.*, 2019). In this study, the organic fraction, i.e. the intermediate free and/or occluded SOM particles that are loose or located between stable soil aggregates, was denoted as particulate organic matter fraction (POM > 53 μm). The other fractions were a heavy fraction (HF > 53 μm), which consisted primarily of coarse and sand particles, and a mineral-associated fraction represented mainly by silt and clay fraction (SC < 53 μm).

A subset of 36 soil-sampling points (three replicates per study fields, the same samples used in Chapter 2, Fig. 2.1) was selected for physical fractionation, resulting in a total 108 soil samples (considering the three depth intervals). The subset was selected based on EC_a analysis, focussing on the green map zone (medium conductivity from 8 to 10 mS m^{-1}). This approach was made for consistency and to minimise variability due to potential textural variation. For each soil sample, 20 g of air-dried soil was added to 70 mL of Milli-Q water and sonicated at 500 W for 15 minutes using an ultrasonic processor (Model VC-505; Sonics Vibra Cell). This provides approximately 13 J per sample or 144 J mL^{-1}, which capable of total dispersion of aggregates, breaking down bonds and exposing the POM, HF and SC fractions. To avoid overheating during sonication, soil samples were previously stored for 24 hours at 4 ºC and sonicated in an ice water bath. After sonication, the sample was wet sieved through a 53 μm sieve using Milli-Q water. The HF and POM fractions were retained in the sieve and were separated by flotation and sedimentation using Milli-Q water (1 g cm^{-3}). To ensure that no POM fraction was retained in the HF fraction, samples were thoroughly and successively rinsed with Milli-Q water (Fig. 3.1). This procedure resulted in 324 fraction samples (36 points X 3 depths X 3 fractions). Each fraction was oven-dried at 40 ºC and their weights recorded. Soil C concentration of each fraction was determined following the same preparation and dry combustion methods described in Chapter 2, Section 2.2.4. For quality assurance, the final recovery of the soil mass was checked against the original 20 g and the recovery of the elemental analysis for the fractions were checked against SOC concentrations from the < 2 mm samples (Table 3.2 and Fig. 3.2). Soil C concentration and the masses of each fraction was used for the calculation of SOC in each fraction and the results were reported on a per-kilogram-bulk-soil-basis (g C kg^{-1}). SOC concentrations of the individual fractions and their recovery soil masses are given in Table A2.1 (Appendix 2).

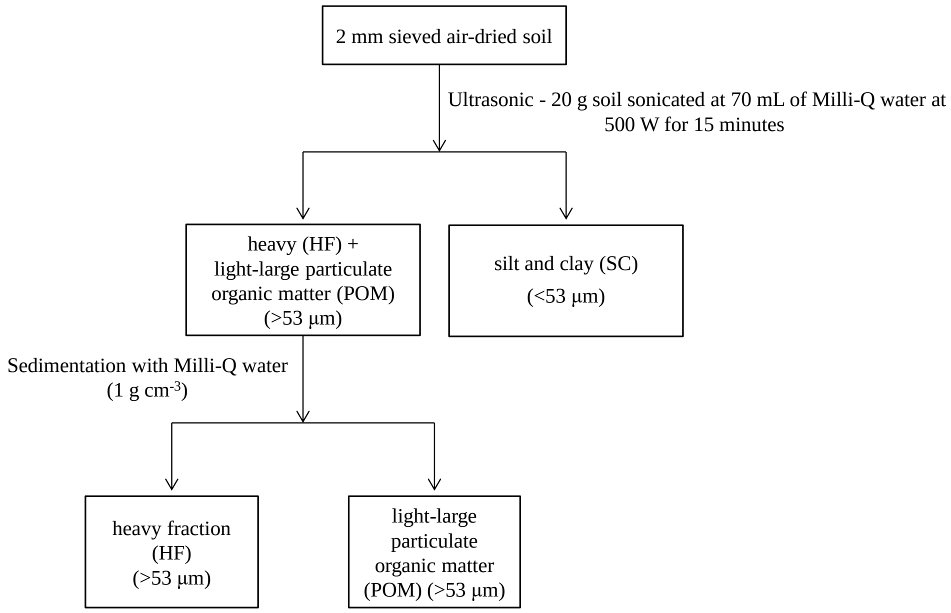

Figure 3.1 Flow diagram schematic to represent different stages of the physical and sedimentation soil fractionation to obtain the three soil organic matter fractions: Particulate organic matter (POM > 53 µm), and mineral-associated fractions, the heavy fraction (HF > 53 µm) and silt and clay fraction (SC < 53 µm). (Adapted from Christensen 1985 and 1992).

Table 3.2 Summary of the mean fractional soil mass recovery (g fraction kg^{-1} soil) under conventional (CONV) and organic (ORG) agricultural system, and non-grazed (NG) and grazed (GG) regime, by soil organic matter fractions, particulate organic matter (POM > 53 μm), the heavy fraction (HF > 53 μm) and silt clay fraction (SC < 53 μm) and soil depth intervals, 0-0.15, 0.15-0.30 and 0.30-0.60 m.

Depth m		POM (> 53 μm)	HF (> 53 μm)	SC (< 53 μm)	Mean Recovery %
			g kg^{-1}		
0-0.15	CONV	22.37 (1.99)	641.48 (14.27)	336.16 (15.16)	98.27 (0.29)
	ORG	29.83 (1.82)	673.65 (10.39)	296.52 (10.65)	98.69 (0.08)
	NG	23.53 (3.16)	626.75 (15.31)	349.72 (17.34)	98.43 (0.26)
	GG	27.38 (1.53)	672.97 (10.12)	299.65 (10.38)	98.51 (0.19)
0.15-0.30	CONV	19.11 (1.58)	701.02 (12.45)	279.87 (12.98)	98.56 (0.23)
	ORG	13.82 (0.64)	736.43 (9.69)	249.75 (9.47)	98.64 (0.11)
	NG	16.31 (0.79)	689.26 (16.21)	294.44 (16.31)	98.57 (0.27)
	GG	16.55 (1.38)	733.46 (8.20)	250.00 (8.11)	98.61 (0.14)
0.30-0.60	CONV	5.86 (0.44)	590.74 (17.05)	403.41 (17.17)	98.39 (0.27)
	ORG	6.08 (0.77)	558.41 (15.42)	435.51 (15.66)	98.35 (0.20)
	NG	5.60 (1.14)	553.11 (19.48)	441.29 (19.83)	98.75 (0.20)
	GG	6.15 (0.35)	585.31 (14.29)	408.54 (14.37)	98.18 (0.22)

Data are measured mean values (n=18 for conventional, n=18 for organic, n=12 for non-grazed and n=24 for grazed within individual soil depth intervals). Standard error of the mean in parentheses.

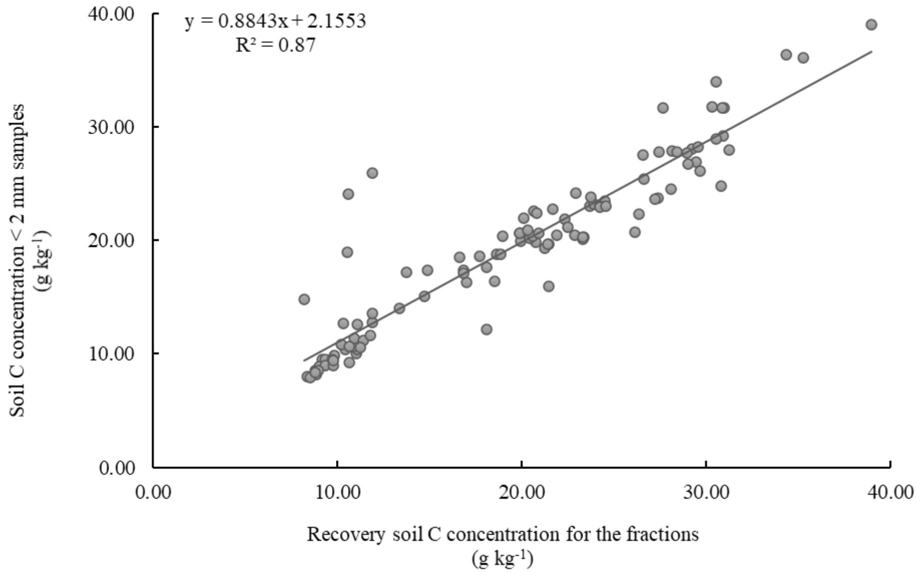

Figure 3.2 Relationship between soil organic carbon (C) concentration of each < 2 mm soil sample used in the physical fractionation and their recovery of the elemental analysis for the fractions, i.e. sum of the soil organic C concentration of the fractions related to their mass fraction.

3.2.5 Statistical analyses

Exploratory analyses were initially conducted using boxplots and scatterplots to assess potential relationships between dependent and independent variables. Spatial autocorrelation and heterogeneity were suspected due to the schematic selection of the sampling points. Spatial autocorrelation was formally tested by computing the Moran's I index (Paradis *et al.*, 2004). Essentially, this approach calculates whether the measured values in the same depth interval tend to cluster spatially. The null hypothesis of the Moran's I index assumes that elemental composition is randomly distributed among the features (i.e. coordinates) in the study sites. If the p value given by the Moran's I test is not statistically significant (i.e. $p > 0.05$), the null hypothesis cannot be rejected, whilst the opposite state potential spatial distribution between the measurements. The Moran's I index results did not confirm spatial autocorrelation for elemental composition measurements, and therefore it was not considered in the model.

Heterogeneity arising from differences between the study sites was also suspected and it was examined via a likelihood ratio test (LRT) comparing the null model (an intercept-only model) and the additional, nested model containing a random effect associated with each study field. This test provided evidence against the null model ($p < 0.05$) and thus confirmed the presence of heterogeneity. Hence, Linear mixed-effects (LME) models were fitted to test the effects of agricultural systems (S) (conventional-CONV *vs.* organic-ORG), grazing regime (G) (non-grazed-NG *vs.* grazed-GG) and their two-way interaction (S*G) on SOC and N concentration, SOC and N stocks and C in the SOM fractions (POM > 53 μm, HF > 53 μm and SC < 53 μm). In general, the agricultural system was tested using all twelve-study fields, six under CONV and six under ORG, which were considered as replicates. The grazing factor was verified using four NG and eight GG study fields (two NG and four GG study fields within each agricultural system, respectively). Even though differences in soil BD and clay content were not the focus of the study, they were explored due to the experimental design conducted and acknowledging that it can directly influence SOC and N accumulation. For all cases, the model was structured using the agricultural system and grazing regime and as fixed effects. The random effect was defined as the study field to account for the heterogeneity of the experimental design. The analyses were conducted separately by depth interval.

To assess the effects of ley time proportion (LTP) (i.e. % years under temporary grass-clover leys in 10 years prior sampling) on the measurements (i.e. BD, clay, SOC and N concentration, SOC and N stocks and C in the SOM fractions), the LME models followed the same structure and approach aforementioned but using LTP as a continuous variable and as a fixed effect.

Although not within the objectives of the study, the same approach was used to assess potential effects of manure application proportion (MAP) (i.e. % years with manure application in 10 years prior sampling) and tillage event proportion (TEP) (i.e. % years with activities that turned the soil over for at least 0.15 m depth in 10 years prior sampling).

For all LME models, data were analysed for normality and equal variances by examining the QQ plots of residuals (for fixed and random effects compartments of the model) and scatterplots of standardised against fitted values. The data were Tukey's Ladder of Powers transformed when visual breakdowns in the LME model assumptions were revealed by residual plots. Data were back-transformed to be presented throughout the chapter in order to aid interpretation. To test the significance of the fixed effects on the dependent variables, models were compared with and without the factor of interest using the LRT approach. When the interaction term in the model was significant, Tukey’s HSD post-hoc test was carried out and a significant effect was determined at $p < 0.05$. All statistical analyses were conducted using R programming language 3.4.3 (R Development Core Team, 2019) and the additional packages, ape (Paradis *et al.*, 2004), nlme (Pinheiro. *et al.*, 2018), plyr (Wickham, 2011), ggplot2 (Wickham, 2009) and multcomp (Hothorn *et al.*, 2008).

3.3 Results

3.3.1 Soil BD, SOC and N concentrations and stocks

3.3.1.1 Effects of agricultural systems (S) (conventional-CONV vs. organic-ORG) associated with grazing regimes (G) (non-grazed-NG vs. grazed-GG)

Spatial autocorrelation was not confirmed for any of the measurements or depth intervals ($p > 0.05$), confirming the effectiveness of the sampling strategy based on EC_a analysis (Chapter 2, Fig 2.1).

For the 0-0.15 m depth, an interactive effect between S and G was found to affect soil BD while GG regime alone was the main factor affecting SOC and N concentration and stocks (Table 3.3). CONV managed fields that were under GG regime showed lower soil BD (1.18 ± 0.01) than CONV fields under NG regime (1.05 ± 0.01 Mg m^{-3}) whilst under ORG systems, the soil BD was not affected by G (LRT = 5.12; p = 0.02) (Fig. 3.3). The GG study fields showed higher SOC and N concentration and stocks than NG study fields (Table 3.3).

For the 0.15-0.30 m depth, the CONV system showed a significantly higher soil BD compared to the ORG system (LRT = 5.20; $p = 0.02$) (Table 3.3). Similarly to the topsoil layer (0-0-15 m), SOC and N concentration and stocks were markedly affected by G, where study fields under the GG regime were significantly higher in SOC and N concentrations and stocks compared to the NG study fields ($p < 0.01$) (Table 3.3).

For deeper soil layers (0.30-0.60 m), there was no significant difference in soil BD (Table 3.3). However, once again, study fields under GG regime were significantly higher in SOC and N concentrations and stocks under either CONV or ORG system, compared to the NG study fields. The only exception was the SOC stocks, which although numerically higher for the GG study fields, did not reveal any statistically significant difference (Table 3.3).

Table 3.3 Effects of agricultural system (S) (conventional-CONV and organic-ORG), grazing regime (G) (non-grazed-NG and grazed-GG) and their interaction on soil bulk density (BD), soil organic carbon (SOC) and soil nitrogen (N) concentrations, and SOC and N stocks at 0-0.15, 0.15-0.30 and 0.30-0.60 m soil depth intervals.

Depth		BD	SOC	N	SOC stock	N stock
m		Mg m^{-3}	g kg^{-1}		Mg ha^{-1}	
0-0.15	CONV	1.10 (0.01)	25.91 (0.55)	2.30 (0.04)	38.99 (0.84)	3.46 (0.07)
	ORG	1.07 (0.01)	25.57 (0.63)	2.29 (0.05)	38.28 (0.91)	3.43 (0.07)
	NG	1.13 (0.01)	22.14 (0.30)	1.98 (0.03)	33.27 (0.48)	2.98 (0.04)
	GG	1.06 (0.01)	27.90 (0.50)	2.48 (0.03)	41.86 (0.73)	3.72 (0.05)
	S	LRT=0.38; p=0.54	LRT=0.90; p=0.34	LRT=0.65; p=0.42	LRT=1.03; p=0.31	LRT=0.88; p=0.35
	G	LRT=3.30; p=0.07	LRT=11.02; **p<0.01**	LRT=13.54; **p<0.01**	LRT=11.04; **p<0.01**	LRT=13.16; **p<0.01**
	S*G	LRT=5.12; **p=0.02**	LRT=1.25; p=0.26	LRT=1.72; p=0.19	LRT=0.96; p=0.33	LRT=1.19; p=0.27
0.15-0.30	CONV	1.22 (0.01)	19.35 (0.45)	1.72 (0.04)	30.47 (0.68)	2.71 (0.06)
	ORG	1.18 (0.01)	19.88 (0.40)	1.81 (0.04)	30.64 (0.56)	2.79 (0.05)
	NG	1.21 (0.01)	18.28 (0.47)	1.64 (0.04)	28.44 (0.68)	2.56 (0.06)
	GG	1.20 (0.01)	20.38 (0.38)	1.84 (0.03)	31.81 (0.54)	2.86 (0.04)
	S	LRT=5.20; **p=0.02**	LRT=0.53; p=0.47	LRT=2.11; p=0.15	LRT=0.01; p=0.97	LRT=0.60; p=0.44
	G	LRT=0.02; p=0.89	LRT=8.29; **p<0.01**	LRT=9.91; **p<0.01**	LRT=7.78; **p<0.01**	LRT=10.38; **p<0.01**
	S*G	LRT=1.79; p=0.18	LRT=1.85; p=0.17	LRT=1.22; p=0.27	LRT=0.77; p=0.38	LRT=0.52; p=0.47
0.30-0.60	CONV	1.30 (0.01)	10.84 (0.51)	1.01 (0.04)	37.25 (1.29)	3.41 (0.11)
	ORG	1.26 (0.01)	10.73 (0.50)	1.00 (0.05)	36.65 (1.31)	3.39 (0.12)
	NG	1.25 (0.01)	10.26 (0.49)	0.92 (0.04)	34.96 (1.24)	3.14 (0.10)
	GG	1.30 (0.01)	11.11 (0.48)	1.06 (0.05)	38.17 (1.25)	3.56 (0.12)
	S	LRT=2.21; p=0.14	LRT=0.00; p=0.99	LRT=0.03; p=0.86	LRT=0.11; p=0.74	LRT=0.05; p=0.83
	G	LRT=2.39; p=0.12	LRT=1.19; **p=0.03**	LRT=4.56; **p=0.03**	LRT=2.52; p=0.11	LRT=6.18; **p=0.01**
	S*G	LRT=2.30; p=0.12	LRT=0.65; p=0.42	LRT=0.01; p=0.92	LRT=1.31; p=0.25	LRT=0.37; p=0.54

Data are measured mean values (n=67 for conventional, n=59 for organic, n=47 for non-grazed and n=79 for grazed within individual soil depth intervals). The standard error of the mean is in parentheses. Significance tests, using likelihood ratio test (LRT), are comparing models with or without the parameter of interest. Significant effects (p < 0.05) are shown in bold.

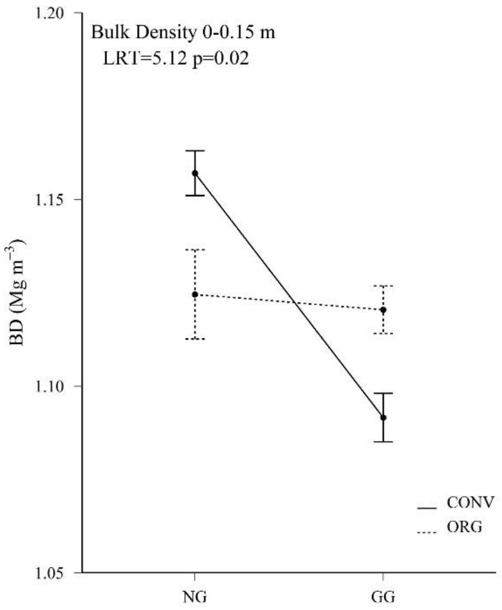

Figure 3.3 Interactive effects between agricultural system (conventional-CONV and organic-ORG) and grazing regime (non-grazed-NG and grazed-GG) on soil bulk density (BD) at 0-0.15 m depth. Data are measured mean values (n=27 for conventional non-grazed, n=40 for conventional grazed, n=20 for organic non-grazed and n=39 for organic grazed). Significance tests, using likelihood ratio test (LRT), are comparing models with or without the parameter of interest.

3.3.1.2 Ley time proportion (LTP), manure application proportion (MAP) and tillage event proportion (TEP)

Increasing the LTP led to a significant increase in SOC and N stocks for the 0-0.15 and 0.15-0.30 m depth, irrespective of the agricultural system (Fig. 3.4a, b and Fig.3.5a, b). For the subsoil (0.30-0.60 m), LTP did not affect SOC stocks ($p = 0.10$) (Fig. 3.4c) but N stocks continued to significantly increase as a function of higher LTP ($p = 0.03$) (Fig. 3.5c). LTP did not significantly affect soil BD in any of the depth intervals assessed (0-0.15, 0.15-0.30 and 0.30-0.60 m). There was also no significant effect of MAP or TEP on soil BD, SOC and N concentrations and/or stocks in any of the three depth intervals assessed.

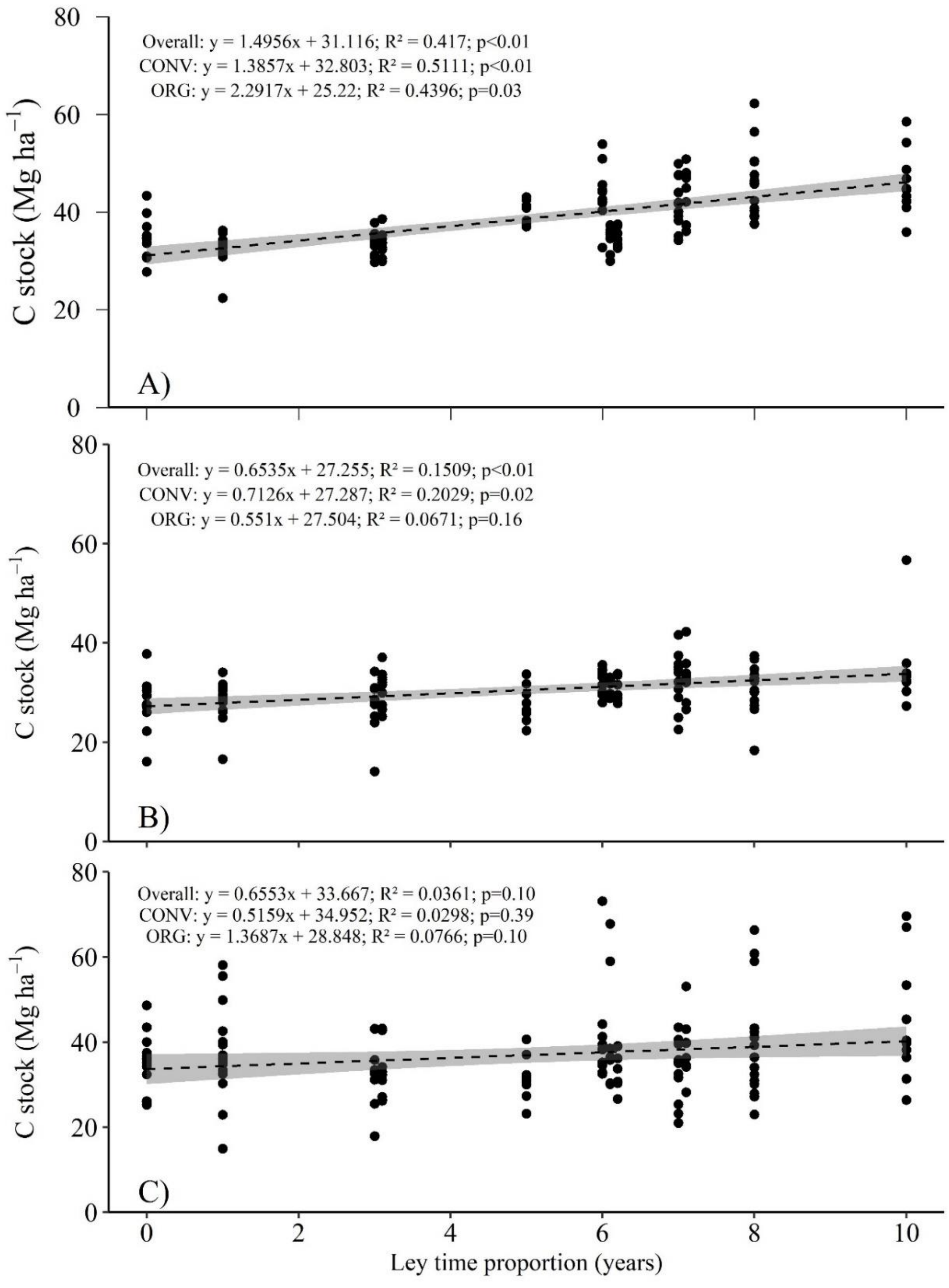

Figure 3.4 Soil organic carbon (C) stock in response to ley time proportion (years) at 0-0.15 m (A), 0.15-0.30 m (B) and 0.30-0.60 m (C) soil depth intervals. Points are measured soil organic C stock values (n=126 for each depth interval). Dashed lines are fitting the overall data. Shaded areas represent standard error of the mean. Significance tests performed using ley time proportion as a continuous variable and as a fixed effect in a linear mixed effect model (LME). Overall data represent both agricultural systems together (conventional-CONV and organic-ORG).

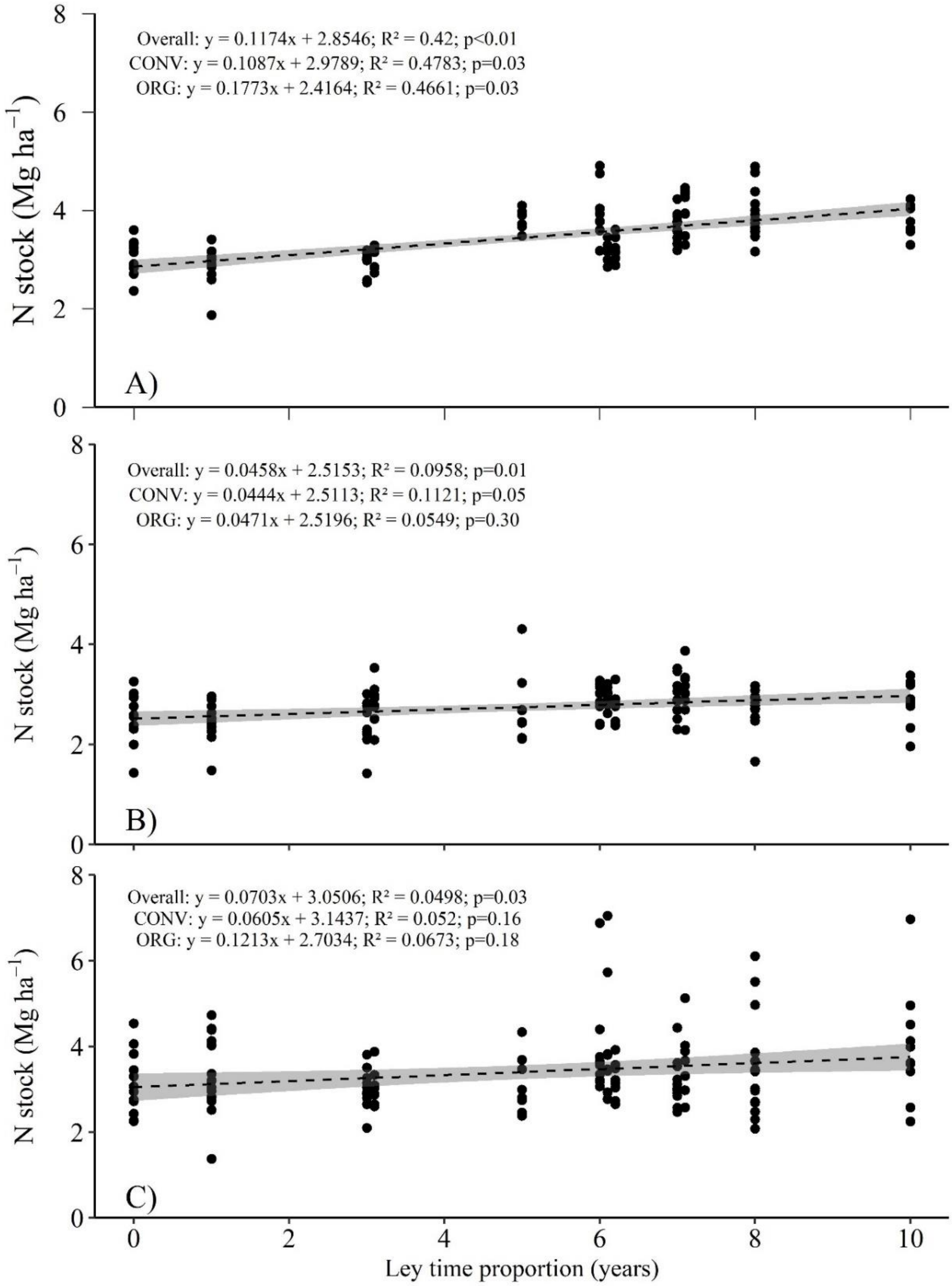

Figure 3.5 Soil nitrogen (N) stock in response to ley time proportion (years) at 0-0.15 m (A), 0.15-0.30 m (B) and 0.30-0.60 m (C) soil depth intervals. Points are measured soil N stock values (n=126 for each depth interval). Dashed lines are fitting the overall data. Shaded areas represent standard error of the mean. Significance tests performed using ley time proportion as a continuous variable and as a fixed effect in a linear mixed effect model (LME). Overall data represent both agricultural systems together (conventional-CONV and organic-ORG).

3.3.2 Soil carbon (C) distribution in soil organic matter (SOM) physical fractions

3.3.2.1 Effects of agricultural systems (S) (conventional-CONV vs. organic-ORG) associated with grazing regimes (G) (non-grazed-NG vs. grazed-GG)

The physical fractionation procedure resulted in an average recovery of 98% (Table 3.2), indicating that it was a reliable technique for the assessment of soil C distribution within SOM fractions. The use of different S and G affected the distribution of soil C concentrations within the SOM fractions assessed (Table 3.4). This is also reflected in the soil C stock in the SOM fractions (Fig. A2.2) (Appendix 2).

Regarding the POM fraction (> 53 μm), an interactive effect between S and G was observed in the 0-0.15 and 0.15-0.30 m soil depth intervals (LRT = 4.65; $p = 0.03$ and LRT = 6.85; $p < 0.01$, respectively). In both cases, the combination of a CONV system and GG resulted in higher soil C concentration in the POM, whilst under an ORG system, it did not change (Fig. 3.6a, b). For the 0.30-0.60 m depth interval, the GG regime showed higher soil C concentrations in the POM fraction, irrespective of the S carried out (LRT = 5.34; $p = 0.02$) (Table 3.4).

For the HF (> 53 μm) fraction, another interaction between S and G was observed in the topsoil (0-0.15 m) (LRT = 7.43; $p < 0.01$) (Table 3.4). More specifically, this result indicated that the combination of a CONV system and GG regime led to higher soil C concentrations in the HF fraction, whereas under an ORG system the GG regime increased soil C concentration in the HF fraction to a lesser degree, which was not statistically significant (Fig. 3.6c). For the 0.15-0.30 m depth interval, the GG regime increased soil C concentrations in the HF fraction from 7.95 ± 1.52 to 11.40 ± 0.71 g C kg^{-1} under CONV system and from 7.79 ± 0.62 to 9.78 ± 0.66 g C kg^{-1} under ORG system (LRT = 8.45; $p = 0.004$) (Table 3.4). For the subsoil layer (0.30-0.60 m), CONV managed soils showed higher soil C concentrations in the HF fraction compared to ORG managed soils (LRT = 11.10; $p < 0.01$) (Table 3.4).

Unlike other fractions, only one difference was observed for the SC (< 53 μm) fraction (Table 3.4). Soil C concentration in the SC fraction was significantly higher under the CONV system than the ORG system at 0-0.15 m soil depth (LRT = 5.34; $p = 0.02$). For the other soil depth intervals (0.15-0.30 and 0.30-0.60 m) there was no effect of S or G in the soil C concentration of the SC fraction.

Table 3.4 Effects of agricultural system (S) (conventional-CONV and organic-ORG), grazing regime (G) (non-grazed-NG and grazed-GG) and their interaction on soil carbon (C) concentrations (g per kg^{-1} soil) in the organic fraction (particulate organic matter-POM > 53 µm), heavy fraction (HF > 53 µm) and mineral-associated fraction (silt and clay fraction-SC < 53 µm) at 0-0.15, 0.15-0.30 and 0.30-0.60 m soil depth intervals.

Depth m		POM (> 53 µm)	HF (> 53 µm)	SC (< 53 µm)
		C concentration in g kg^{-1} soil		
0-0.15	CONV	2.95 (0.28)	11.53 (1.87)	16.11 (0.49)
	ORG	3.46 (0.28)	9.86 (0.69)	14.30 (0.54)
	NG	2.77 (0.37)	7.39 (0.96)	15.29 (0.53)
	GG	3.42 (0.23)	12.34 (1.29)	15.16 (0.53)
	S	LRT=1.01; p=0.31	LRT=0.06; p=0.81	LRT=5.34; **p=0.02**
	G	LRT=1.43; p=0.23	LRT=6.86; **p<0.01**	LRT=0.03; p=0.86
	S*G	LRT=4.65; **p=0.03**	LRT=7.43; **p<0.01**	LRT=0.02; p=0.88
0.15-0.30	CONV	1.99 (0.08)	10.25 (0.77)	8.84 (0.38)
	ORG	1.50 (0.09)	9.12 (0.53)	9.29 (0.46)
	NG	1.74 (0.12)	7.87 (0.78)	9.55 (0.42)
	GG	1.75 (0.15)	10.59 (0.50)	8.82 (0.39)
	S	LRT=2.34; p=0.13	LRT=1.93; p=0.16	LRT=0.64; p=0.42
	G	LRT=0.19; p=0.66	LRT=8.45; **p<0.01**	LRT=1.90; p=0.17
	S*G	LRT=6.85; **p<0.01**	LRT=0.75; p=0.39	LRT=0.004; p=0.95
0.30-0.60	CONV	0.65 (0.08)	3.63 (0.37)	6.46 (0.29)
	ORG	0.57 (0.04)	2.08 (0.26)	7.17 (0.26)
	NG	0.49 (0.04)	2.74 (0.28)	7.10 (0.45)
	GG	0.67 (0.06)	2.91 (0.56)	6.67 (0.20)
	S	LRT=0.35; p=0.56	LRT=11.10; **p<0.01**	LRT=3.32; p=0.07
	G	LRT=5.34; **p=0.02**	LRT=0.53; p=0.47	LRT=0.95; p=0.33
	S*G	LRT=0.58; p=0.44	LRT=0.08; p=0.77	LRT=0.03; p=0.85

Data are measured mean values (n=18 for conventional, n=18 for organic, n=12 for non-grazed and n=24 for grazed within individual soil depth intervals). Standard error of the mean is in parentheses. Significance tests, using likelihood ratio tests (LRT), are comparing models with or without the parameter of interest. Significant effects (p < 0.05) are shown in bold.

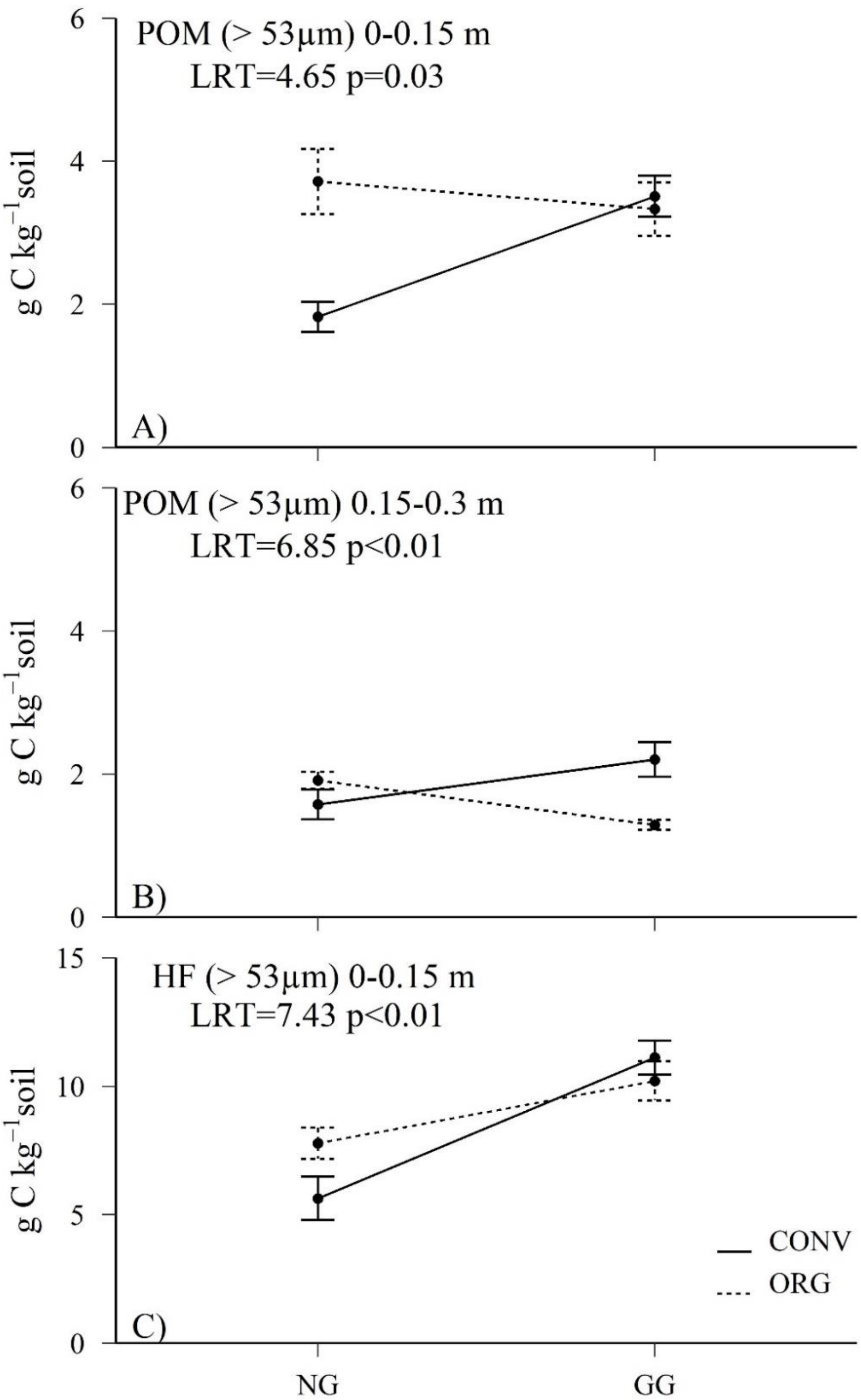

Figure 3.6 Interactive effects between agricultural system (conventional-CONV and organic-ORG) and grazing regime (non-grazed-NG and grazed-GG) on: A) particulate organic matter fraction (POM > 53 μm) in the 0-0.15 m; B) particulate organic matter fraction (POM > 53 μm) in the 0.15-0.30 m and; C) heavy sand (HF > 53 μm) in the 0-0.15 m. Data are measured mean values (n=6 for conventional and organic non-grazed and n=12 for conventional and organic grazed within individual soil depth intervals). Significance tests, using likelihood ratio test (LRT), are comparing models with or without the parameter of interest.

3.3.2.2 Ley time proportion (LTP), manure application proportion (MAP) and tillage event proportion (TEP)

Increased LTP increased soil C concentrations in the POM fraction for the 0-0.15 and 0.30-0.60 m depth interval ($p = 0.05$ and 0.02, respectively) (Fig. 3.7a and c). Similarly, increased LTP increased soil C concentrations in the HF fraction for the 0-0.15 ($p < 0.01$) (Fig. 3.7a). It was also observed that more frequent applications of manure (i.e. increasing MAP) contributed to an increase in soil C concentrations in the POM fraction at 0-0.15 m depth (Fig. 3.8a).

There was no effect of TEP on the distribution of C within SOM fractions in any of the soil depth intervals assessed (0-0.15; 0.15-0.30 and 0.30-0.60 m).

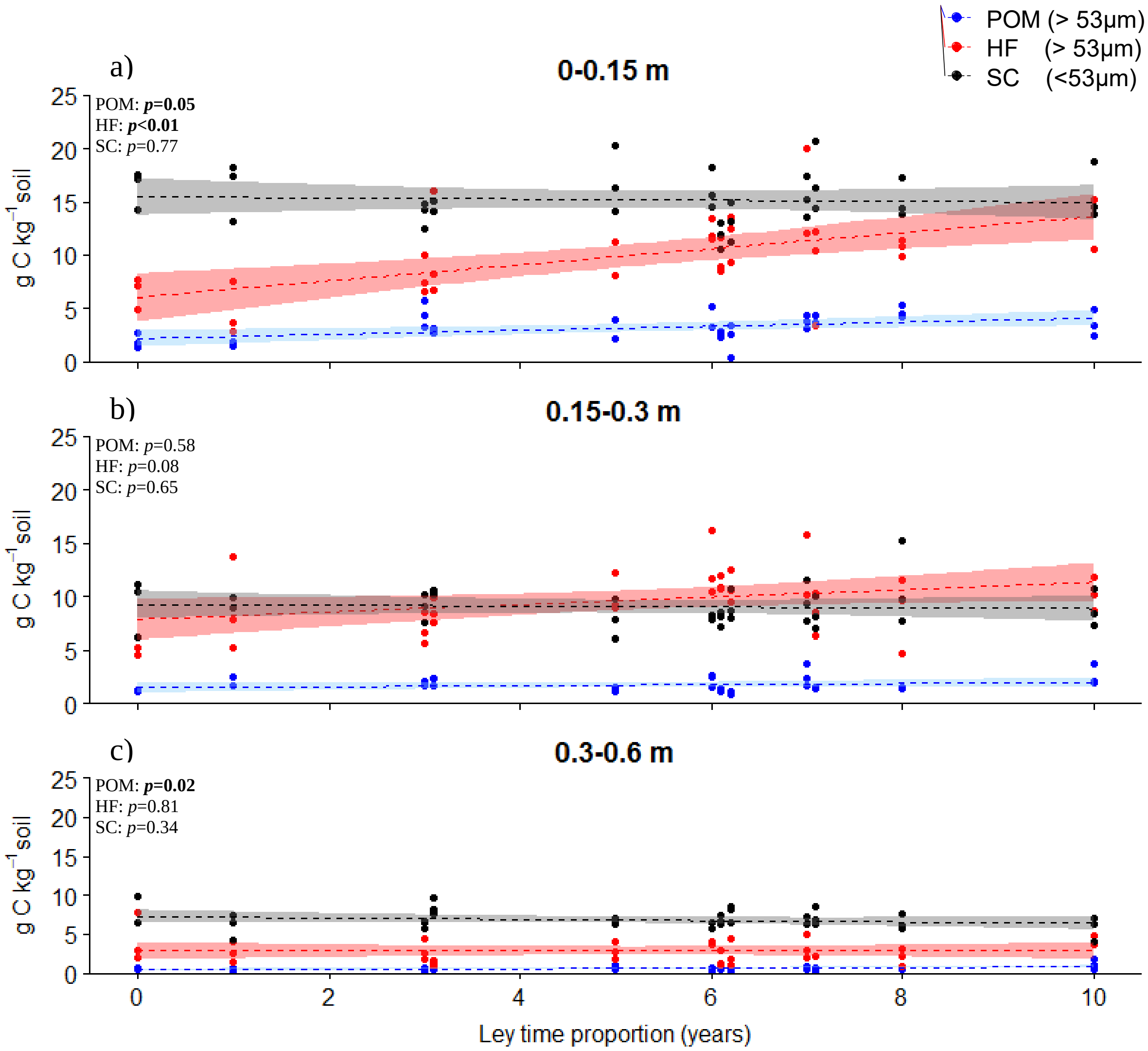

Figure 3.7 Soil organic carbon concentration of particulate organic matter (POM > 53 µm), heavy fraction (HF > 53 µm) and silt clay fraction (SC < 53 µm) in response to ley time proportion (years) at 0-0.15 m (a), 0.15-0.30 m (b) and 0.30-0.60 m (c) soil depth intervals. Points are measured values (n=36 for each fraction in each depth interval). Dashed lines are fitting the overall data. Shaded areas represent standard error of the mean. Significance tests performed using ley time proportion (years) as a continuous variable and as a fixed effect in a linear mixed effect model (LME). Significant effects (p < 0.05) are shown in bold within each depth interval.

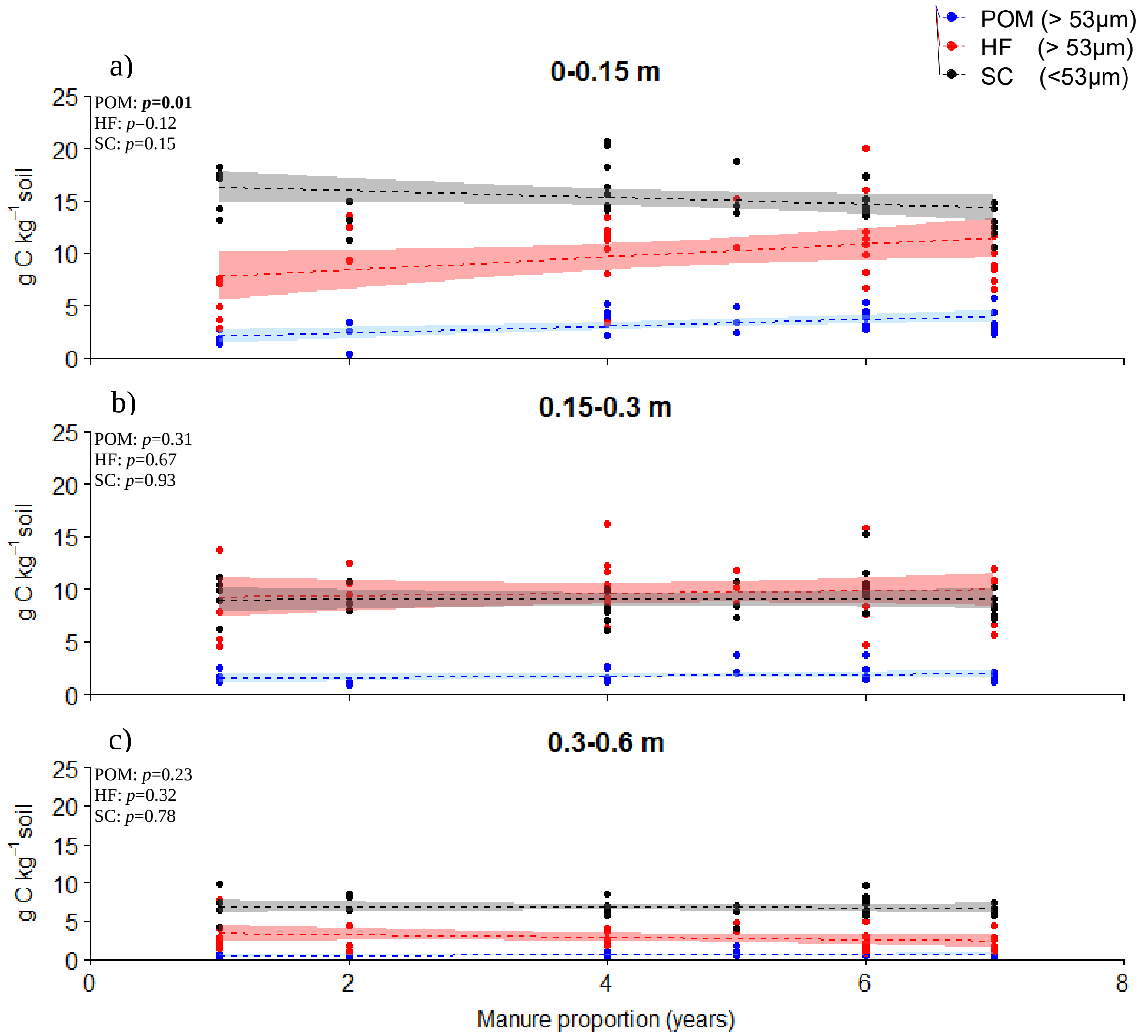

Figure 3.8 Soil organic carbon concentration of particulate organic matter (POM > 53 μm), heavy fraction (HF > 53 μm) and silt clay fraction (SC < 53 μm) in response to manure application proportion (years) at 0-0.15 m (a), 0.15-0.30 m (b) and 0.30-0.60 m (c) soil depth intervals. Points are measured values (n=36 for each fraction in each depth interval). Dashed lines are fitting the overall data. Shaded areas represent standard error of the mean. Significance tests performed using manure proportion (years) as a continuous variable and as a fixed effect in a linear mixed effect model (LME). Significant effects ($p < 0.05$) are shown in bold within each depth interval.

3.4 Discussion

3.4.1 Changes in soil organic carbon and nitrogen stocks

The results of this study suggested that the inclusion of grass-clover ley periods in the crop rotation increased SOC (0-0.15 and 0.15-0.30 m) and N stocks (0-0.15; 0.15-0.30 and 0.30-0.60 m) (Figs. 3.4 and 3.5). This result confirmed the hypothesis that an increasing proportion of grass-clover ley period in crop rotations would increase SOC and N stocks regardless of the agricultural system or grazing regime adopted. Although a great effort was made when selecting the study fields, the grazing regime was confounded by the length of ley periods (Table 3.1). Therefore, this study cannot fully test the hypothesis that the integration of grass-clover leys with livestock in crop rotations (i.e. ICL system) by itself would increase soil C stocks in both agricultural systems. As a result, the effects of grazing are discussed throughout this section as a secondary factor that could not be effectively controlled or investigated but nevertheless is of interest. Since outcomes for SOC and N concentrations and stocks were similar, this discussion focusses only on the stocks.

The positive effect of grass-clover ley periods also matched previous research where it had been recognised as a practice that can increase SOC and N stocks (Lemaire *et al.*, 2015; Johnston *et al.*, 2017; Börjesson *et al.*, 2018). SOC stocks are usually higher with longer ley periods given the development of an extensive, more fibrous and deep rooted system (Johnston *et al.*, 2017). Even if a short-term ley (3 years) is inserted into an arable rotation system, a legacy effect on SOC concentration is likely for the top 0-0.10 m depth (Crème *et al.*, 2018). Although it may be limited to when soil C equilibrium is reached, it has been suggested that the repeated implementation of three-years of ley after five-years arable rotation, would significantly increase SOC concentrations in the top 0.20 m soil depth over a period of 30-40 years (Johnston *et al.*, 2017).

The stimulation of below-ground biomass, as well as extra inputs of C and N through forage residues and animal dung, were previously proposed as the main factors increasing SOC and N stocks (Pineiro *et al.*, 2010; McSherry & Ritchie, 2013; Assmann *et al.*, 2014; Chen *et al.*, 2015). Assmann *et al.* (2014) quantified the main soil C and N inputs in a 10-year trial under a mixed farming system with non-grazed and grazed treatments. They found that forage residues (above and below-ground) at the end of the cycle are the main C inputs under the grazed, which implies that there were more C inputs in the grazed fields compared to harvested systems. Increases in N stocks, in turn, can be related to the inputs of manure and urine deposition, which return N to the soil at a rate of approximately 90% (Haynes & Williams, 1993) whereas under non-grazed systems the N is exported in harvested products.

Other grazing factors that might have affected topsoil SOC and N stocks under longer ley are defoliation, which might change species abundance and proportions, and grazing methods (frequency/intensity). Whilst herbivores consume a portion of aboveground biomass, they also remove standing dead biomass that may shade green leaves, promoting photosynthesis, greater root turnover and exudations (Pavlů *et al.*, 2007; Lemaire *et al.*, 2009). Pavlů *et al.* (2007) also found that defoliation by grazing could enable co-existence of plant species leading to a change in plant species and composition. This effect on plant species and composition, as well as species abundance proportions as previously mentioned, might lead to a change of quantity and quality of the litter inputs, as evidenced by the results of the SOM fractions (discussed in the section 3.4.2). This in turn will affect decomposition actions by soil microbes and fauna and consequently affecting SOC and N stocks.

The increased SOC stocks for intermediate soil layers (i.e. 0.15-0.30 m) was a significant outcome as most of the previous studies in ley-arable rotations have only reported results for topsoil layers (max. 0.20 m depth). Blanco-Canqui *et al.* (2017), in one of the very few studies assessing the effects of ley-arable rotation on SOC stocks below 0.20 m, suggested that two-years leys after four-year arable rotations could only increase SOC stocks up to 0.15 m depth. Based on these previous studies, the increased SOC and N stocks here in the intermediate soil layers (i.e. 0.15-0.30 m) may be tied to both the presence of legumes (clover) and the time under ley. Clover possesses more fibrous, longer root growth periods altering root turnover and exudation (Tracy & Zhang, 2008; Johnston *et al.*, 2017), which might have enhanced C and N cycling and increased inputs below 0.15 m depth. The average grass-clover ley period in this study was 3-4 years in a 10-year period (i.e. approximately 30-40% of LTP), which was slightly higher than previous studies (approximately 20-30% of LTP). Other factors that can to build up SOC and N in the top 0-0.30 m depth during ley phases are the slower rates of decomposition processes, via altered evapotranspiration and lower soil temperature (Kätterer & Andrén, 2009) and the reduction in soil disturbance by ploughing (Johnston *et al.*, 2017).

Although it was expected that deeper rooting systems would increase SOC stocks also in the subsoil layers (> 0.30 m), this specific case study at Nafferton, showed no change. A possible reason could be the increase in soil bulk density at depth, which although not above concerning threshold value (i.e. it was not > 1.5 Mg m^{-3}) may still have restricted root growth in the subsoil layers. This result can also be explained by the characteristics of the soil at Nafferton farm (stagnosol), which are recognised for their temporary anoxic conditions (confirmed in the subsoil by the presence of mottles) and potential restriction in root growth (Soil Series Brickfield) (Cranfield University, 2021).

Another point that merits attention is the fact that there are usually many different management practices between conventional and organic systems, including manure use, crop varieties in the rotation, the inclusion of livestock, etc. Results here demonstrated that in this specific situation, where the amount of manure applied, rotation and the implementation of the grazed regime and ley periods were fairly similar between both the conventional and organic systems (Table 3.1), the SOC and N stocks did not differ in the topsoil (0-0.30 m depth) or the subsoil layers (i.e. > 0.30 m depth). However, further studies are required to verify if this outcome would be translated to other sites/locations. Additionally, this study was relatively short-term (about 15 years), and differences between conventional and organic systems may need longer periods to show significant differences.

Overall, whilst grazed regime may have a positive effect on SOC and N stocks, the results of this study can only conclude that this was a secondary effect of the longer ley periods. Without considering the potential effects of livestock grazing, the results of this study suggested that in order to improve SOC and N stocks in arable systems, the fields need to have grass-clover ley periods for at least 30-40% of the time in the crop rotation. It is important to stress that the potential increase in soil C with grass-clover leys will also depend on site-specific properties and conditions, as well as the initial C storage. In addition, increases in soil C should attenuate with time as a new equilibrium is reach. In these cases, or where soil C stocks are already high, increased proportion of grass-clover ley periods would only help to maintain the high levels of soil C stocks, which normally is not the case of arable fields. Although promoting these practices might be an obvious first step to mitigate losses of SOC and N stocks in arable rotations, a cost-benefit analysis between soil C and N storage and productivity trade-off would be needed to confirm their applicability.

3.4.2 Changes in soil C distribution in SOM fractions

Understanding changes in SOC stocks can be challenging due to the complex nature of SOM. Separation of SOM into multiple components with contrasting behaviours can help to elucidate some effects, such as soil C turnover and its residence time (Lavallee *et al.*, 2019). For instance, particulate organic matter (POM > 53 μm) is vulnerable/accessible to soil biota and decomposition while mineral-associated fractions (silt and clay fraction; SC < 53 μm) are less accessible and thus considered more stable or long-lived SOM (von Lützow *et al.*, 2007). This study supported these findings with changes in soil C distribution among SOM fractions occurring mainly in the POM fraction, which was affected by agricultural systems, ley time and manure proportions and possibly grazing regimes. Similar behaviour was observed in the HF fraction, a fraction that is often classified as transitional between active and passive pool (von Lützow *et al.*, 2007), except that it was unaffected by manure proportions. The SC fraction, in turn, was only affected by agricultural systems. These results confirmed the hypothesis that differences in management would lead to changes in the distribution of soil C among SOM fractions particularly in the following order POM > HF > SC.

Regarding the POM fraction, the implementation of a higher proportion of ley time in a rotation, which was also associated with livestock grazing, increased POM-C (Table 3.4 and Fig. 3.7a). Increases in POM-C fractions under longer ley periods that were also often grazed suggested that there were higher inputs of above- (forage and manure) and belowground (root biomass) residues compared to the shorter non-grazed ley periods (McSherry & Ritchie, 2013; Assmann *et al.*, 2014; Chen *et al.*, 2015), supporting the results found for SOC and N stocks. The significantly lower POM (0-0.15 and 0.15-0.30 m; Fig. 3.6) only in the conventional non-grazed fields indicated lower levels of residue deposition in the topsoil (0-0.30 m soil depth), which in this study was an effect of the short ley periods (LTP averages of 5% *vs.* 70% for conventional non-grazed and grazed study fields, respectively, Table A1.2, Appendix 1). In addition, the conventional system received higher inputs of total N (120 *vs.* 62 kg ha^{-1} yr^{-1} under conventional and organic system, respectively), which can increase POM decomposition by ensuring microbial breakdown of C was less affected by any N limitation. This was confirmed by the results of Kirkby *et al.* (2014) and Bradford *et al.* (2008), who found higher POM decomposition when comparing treatments with and without N additions. Kirkby *et al.* (2014) also highlighted that the lower the quality of the litter input (i.e. higher recalcitrance) the higher the formation of POM. Ultimately, these results suggested that the implementation of longer ley periods that were also grazed may have played a key role in the increased POM-C of conventional, short ley periods with non-grazed study fields because of the extra associated inputs through forage residues, animal dung and below-ground biomass. On the other hand, in the organic system, applications of manure (i.e. high-quality residue) and low ready available N additions were able to maintain high POM-C when a three year non-grazed ley period was adopted.

The quality of the residues is a crucial aspect when assessing SOM fractions because this correlates with its persistence in the soil. The two broad mechanisms that affect SOM fraction decomposition are spatial constraints and microbial inhibition, where the first refers to the physical separation between decomposers/enzymes and substrates and the latter to the absence of oxygen under freezing temperatures and waterlogging conditions (Lavallee *et al.*, 2019). Since the POM fraction is primarily made up of undecomposed plant and animal fragments (von Lützow *et al.*, 2007), this was taken as an uncomplexed/transitory pool, that is a fraction that is not yet incorporated into primary organomineral complexes and consequently readily available to decomposers (Christensen, 2001). However, POM decomposition rates can vary as it may require a depolymerisation process due to the presence of larger, insoluble molecules (Kleber *et al.*, 2015). A longer time to decomposition might allow for the POM fraction to be occluded within aggregates, playing an important role in soil C accumulation and its stabilisation (Six *et al.*, 2002a). The increase in the POM-C with an increased grazed ley time proportion (0-0.15 m) were in line with increases in soil aggregation for the same study sites where the same treatment was implemented (Zani *et al.*, 2020). Even though Zani *et al.* (2020) have also reported increased microbial biomass C with the implementation of grazing, these results altogether suggested that at least part of this POM-C is not being decomposed, potentially because of spatial constraints (i.e. POM-C is being occluded within soil aggregates). The higher C inputs through above- and below-ground residues under an increased grazed ley time proportion associated with a likely microbial inhibition, might be the main mechanism that led to increased POM-C in the subsoil layer (0.30-0.60 m) (Table 3.4).

Since SOM fractions are highly heterogeneity, all soil fractions were acknowledged to not be completely uniform, regardless of the methodological fractionation scheme deployed (von Lützow *et al.*, 2007; Lavallee *et al.*, 2019). On this basis, changes in the POM fraction may have indirectly influenced the changes in the mineral-associated fractions. Cotrufo *et al.* (2015) confirmed this by pointing out that a more recalcitrant part of the POM fraction is likely to be found in other fractions, mainly in the HF fraction. In fact, the authors even suggest combining the POM with the heavy/sand-sized fraction (i.e. the HF fraction in this study) to understand overall POM dynamics. In a recent contextualisation of SOM fractions, Lavallee *et al.* (2019) defined POM as both, lighter and heavier than 1.6-1.85 1 g cm^{-3} (i.e. light and heavy POM, respectively) but always larger than 53 μm. Although in this study it has been used 1 g cm^{-3} instead of high-density liquids to separate POM and HF, a recent comparison between different methods showed that these differences did not significantly influence in the recovery and reproducibility of the total C in the fractions (Poeplau *et al.*, 2018). The results found for the HF fraction were in line with these statements, showing that the same behaviour observed for POM, i.e. higher proportion of ley time (0-0.15 m) in arable rotations that are grazed increased HF-C. As for the POM fraction, this was particularly important in the topsoil (0-0.15 m) in the conventional system (Fig. 3.6c). The main reasons for this result should, therefore, be the same as for the POM-C fraction, i.e. higher residue inputs through forage, manure and root biomass under longer grazed ley fields. Conversely, conventional short non-grazed ley fields, beyond these limitations, might have also experienced high decomposition rates as a result of a decrease in N limitations (Bradford *et al.*, 2008; Kirkby *et al.*, 2014).

High decomposition rates and potential inputs of lower quality residues (i.e. higher recalcitrant nature) might have indirectly led to the higher HF-C (0.30-0.60 m) and SC-C (0-0.15 m) under the conventional system (Table 3.4). According to Cotrufo *et al.* (2013), N additions could shift SOM formation from POM to mineral-associated fractions as a result of microbial products of decomposition. Kirkby *et al.* (2014) confirmed this theory by showing that augmenting straw residues, a higher recalcitrant and thus low-quality litter, in combination with supplementary nutrients additions (including N) could result in an increased mineral-associated fraction. Those are important mechanisms as mineral-associated fractions, particularly the clay-silt sized particles (e.g. sesquioxides, layer silicates bonding), are held by strong interaction mechanisms, including ligand exchange and polyvalent cation bridges, representing a potentially more stabilised soil C (Sposito *et al.*, 1999; Christensen, 2001). However, it is important to emphasise this does not mean that organic system will not have stabilised C. In fact, this result might suggest that the conventional system only accelerates the transformation of C into more stabilised pools whilst organic system might require more time for this to happen. The results of this study also contradicted the expected greater proportion of soil C into a mineral-associate fraction with higher ley time proportions. This is, however, consistent with recent study conduct by Paterson *et al.* (2020), who found no relationship between sward age and mineral-associated carbon across grassland fields in the UK. Further investigations of the effects of the conventional and organic system on stabilised C are needed, particularly allowing long-term experiment comparisons, which might elucidate shifts between SOM fractions.

The separation of SOM into multiple components provided insights about the distribution of C among fractions. This provides information on the characteristics of the soil C, which helps in the understanding of soil C stock formation and inferences about its stability and functional aspects that are not possible based on soil C and N stocks (Baldock *et al.*, 2013; Cotrufo *et al.*, 2015). In short, although the higher proportion of grass-clover ley periods that are grazed was beneficial management practice for SOC and N stocks under both conventional and organic systems, it did not lead to a more stabilised C. More specifically, the assessment of soil C in SOM fractions rather than stocks, indicated that longer grazed ley periods could be particularly beneficial in conventional system but not essential for organic; in this study, an average LTP of

30% showed comparable results to an average LTP of ~70% under the organic system. Conventional systems also appeared to transform C into more stabilised pools, which could be due to stimulation of microbial process by the addition of N fertiliser.

3.5 Conclusions

The results of this study have shown that integrating an extended grass-clover ley phase with livestock into farming systems can build soil C and N stocks under both organic and conventional systems. The separation of SOM into fractions indicated that an extended grazed ley period can be particularly beneficial for improving SOC and N in conventional system. The study provided evidence to suggest that the higher total inputs of N as soluble fertiliser under conventional systems could lead to higher proportions of more stable C (i.e. at SC < 53 μm fraction). Physical methods for fractionation of SOM offer useful insights into the stability of C pools that could be complemented by chemical characterisation methods at the molecular level and investigation of interactions with mineral components of the soil. These approaches would provide a more complete understanding of the impacts of management practices on soil C sequestration, in both the short and long-term. We concluded that mixed farming system with increasing proportions of grass-clover leys compared to short non-grazed ley periods in crop rotations can play an important role in reaching a net C benefit, particularly in the topsoil layers, regardless of whether the agricultural system is conventional or organic.

Chapter 4. Mapping soil carbon stocks at the farm scale level using the digital elevation model and its derivatives in association with high-resolution soil sensing data and agricultural land management information

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Notes

This chapter has been prepared for submission to the peer reviewed Geoderma Journal.

Declaration of contribution

This chapter consists of original digital soil mapping undertaken by myself, Caio Fernandes Zani, using measured data collected in Chapters 2 and 3. Caio Fernandes Zani carried out all soil analyses and data analysis, except for soil sensing and elevation layers, which were obtained from NU Farms. Caio Fernandes Zani also led the writing of the chapter and potential paper, with contribution from all co-authors. Specifically, the contribution of co-authors is such: James A. Taylor provided practical training, involving the approach, interpretation, and assessment, for using digital soil mapping as well as the application of the linear and nonlinear models (Linear model and Random forest model); Geoffrey D. Abbott, Julia Cooper and Elisa Lopez-Capel provided PhD supervision and detailed comments on the chapter. I would like to also thank Dr Philippe Lagacherie (INRAE), who is not listed as an author here but substantially help with his valuable advice and R coding.

4.1 Introduction

In the Paris Climate Agreement, COP21, the goal was set such that by the end of the century the global temperature rise should be limited to 2 °C above pre-industrial levels. It has been pointed out that soils can play a fundamental role in achieving this aim by sequestering carbon (C) present in the atmosphere as CO_2 and accumulating it into soil C pools (Lal, 2004a; Paustian *et al.*, 2016). Soils are long recognised as one of the largest C reservoirs in the globe, containing more C than the atmosphere and plant biomass compartments combined (Schimel, 1995; Batjes, 1996). However, the absolute quantity of C held within a soil (i.e. soil C stocks) is not inert, meaning that the misuse of soils can turn them into a source rather than a sink of C, impacting the climate as well as other soil properties severely (Lal, 2004a). Whilst, agricultural intensification has supported rapid population growth, over the last century it has also raised concerns regarding agricultures contribution to soil organic C (SOC) losses and therefore the increased atmospheric concentration of greenhouse gases (GHG). In agricultural soils, several factors can change soil C dynamics, including land uses, agricultural systems and management practices (Le Quéré *et al.*, 2018), all of which are particularly important for SOC stocks (Smith *et al.*, 2007, 2008).

Worldwide institutions and international treaties have already recognised the importance of precise estimation of SOC stocks (IPCC, 2000, 2003; Stolbovoy *et al.*, 2007). Alongside several initiatives to promote soil C sequestration (e.g. the 4 per 1000 program – launched at COP21 in 2015 http://4p1000.org/understand, the Koronivia workshops in agriculture – launched at COP23 in 2018 and the RECSOIL – launched by FAO in 2019) and the need for more fine resolution and accurate data, Digital Soil Mapping (DSM) has emerged as a key tool for soil quality evaluation (including SOC) and sustainable soil management (McBratney *et al.*, 2003). As a general definition, DSM can be referred to as the mapping and modelling of spatial and temporal soil properties created and populated by statistical tools, which are based on soil observation and knowledge of potentially related environmental variables (Lagacherie & McBratney, 2006). DSM has been demonstrated to be a reliable approach for mapping some soil classes and properties, including SOC content and stocks (Minasny *et al.*, 2013; Zhang *et al.*, 2017). Based on the concept that soil formation/properties are highly dependent on their position in the landscape, most of the previous DSM studies to spatially predict SOC (content and stocks) have relied heavily on information from soil sensing systems, such as electromagnetic induction (EMI) sensors together with spatial environmental data layers that are correlated to soil properties. This is underpinned by a well-known framework for DSM that considers soil properties (s), climate (c), organisms (o), relief (r), parent material (p), age/time

(a) and space (n) (SCORPAN) as the key factors needed for soil mapping (McBratney *et al.*, 2003). Environmental data widely applied in DSM includes Digital Elevation Model (DEM) and derived topographic or terrain attributes/covariates (e.g. slope, curvature, etc), remotely sensing imagery of the soil surface or biomass and/or climate data as these data have been shown to have a close relationship with spatially implicit soil-forming factors (Behrens *et al.*, 2010). More specifically, these commonly chosen covariates will directly affect the quantity and quality of soil organic matter (SOM) inputs as well as decomposition rates under uncultivated soils (Minasny *et al.*, 2013).

Although a DEM and its derivative covariates are undeniably important parameters, previous studies have indicated that depending on the scale of the study, different parameters should be considered. For instance, when assessing SOC content and stocks in a global/regional scale, the inclusion of climate (rainfall and temperature) and position parameters are important parameters to be considered as they play a key role in SOC storage due to their direct effect on decomposition, erosion and leaching (Guo & Gifford, 2002; Badgery *et al.*, 2013). On the other hand, at a smaller scale (resolution <100 m), the main predictors used are local attributes, including DEM and its derivatives (Minasny *et al.*, 2013) as micro/meso-climate is assumed to be uniform across the study area. Most previous studies have shown a reasonable prediction for SOC content and stocks; however, the majority have not included agricultural system and management practices information, and therefore it is still unknown to what extent that information could improve the accuracy of DSM in predicting SOC stocks at the local scale (field/farm/regional).

When assessing SOC stocks under agricultural soils, especially at a farm-scale level, it is expected that the direct effect of the agricultural system and management practice decisions on the quantity, quality and stabilisation of the SOM (Six *et al.*, 1999, 2002a) might be as important as topographic/terrain and climate covariates in modelling and mapping SOC. In a recent study, Singh & Whelan, (2020) examined the influence of agricultural land management on spatial variability of SOC. The authors concluded that land management was important for SOC on certain farms in Australia, however, they did not attempt to find out whether such information would improve DSM products for SOC stocks. According to the review carried out by Minasny *et al.* (2013), only ‘snapshots’ of land use and/or land cover, and not directly the longer-term agricultural system and management practice approach, have been considered as anthropogenic information in previous DSM studies that assessed SOC stocks.

Another shortcoming observed in previous studies using DSM for SOC stocks is the lack of data for subsoil layers (> 0.30 m) (Grunwald, 2009). Typically, lower organic-derived soil C stocks are found in the subsoil layers (i.e. below 0.30 m depth), and there is a higher potential for soil C sequestration in these sub-soil layers (Lorenz & Lal, 2005). In addition, SOC stocks at subsoil layers are constituted by intermediate and passive SOM pools (von Lützow *et al.*, 2008), which makes it even more important to be included in any agricultural management sustainability assessment (Jenkinson *et al.*, 2008; Syswerda *et al.*, 2011; Blanco-Canqui *et al.*, 2017; Börjesson *et al.*, 2018). The use of subsoil layers in DSM for SOC stocks appears to be limited particularly because the use of environmental covariates largely explains conditions in the topsoil. Therefore, a DSM approach to mapping SOC stocks at a farm-scale level should benefit from the inclusion of information about agricultural land management and subsoil layers in the model.

The prediction of spatially SOC stocks has been successfully carried out using several statistical prediction approaches including simple Linear Regression Models (LM) as well as more complex machine learning methods like Random Forest Models (RFM) (Thompson *et al.*, 2006; Minasny *et al.*, 2013; Were *et al.*, 2015; Wang *et al.*, 2018). Both LM and RFM have benefits and drawbacks. While LMs are straightforward to apply, use and understand (Thompson *et al.*, 2006), RFMs have the ability to investigate relationships between the predictors and the response in a non-linear and in a hierarchical way, permitting the identification of potential outliers and anomalies in the data (Breiman, 2001). One of the disadvantages of the LM is its assumption of a linear relationship between soil properties and environmental variables, even though these relationships are known to sometimes be complex and non-linear (Wang *et al.*, 2018). On the other hand, RFM is limited by the fact that it does not consider spatial autocorrelation of neighbouring observed data, considering only the relationship between the soil properties of interest (e.g. SOC stocks) and covariates, such as environmental factors (Takata *et al.*, 2007).

The objective of this study was therefore to understand if incorporating the agricultural system and management practice information into both simple (LM) and complex (RFM) models provide more reliable DSM products for SOC stocks. Specifically, the aims of this study were i) to test LM and RFM models, which are generated with typical DSM covariates (DEM derivatives and soil sensor data), with and without agricultural system and management practice information to assess its effect on predicting and mapping the variability of cumulative SOC stocks in the top and subsoil layers across a northern UK farm, and ii) use the best fitted LM and RFM models to produce high-resolution maps of SOC stocks at the farm-scale for three cumulative depth intervals (0-0.15, 0-0.30 and 0-0.60 m).

4.2 Materials and Methods

4.2.1 Farm description

This study was conducted at Newcastle University's Nafferton farm, situated 12 miles west of Newcastle upon Tyne in north-east England, UK (54º59'09''N; 1º43'56''W, 60 m a.s.l.). A detailed description of the farm can be found in Chapter 2, section 2.2.1.

4.2.2 Study fields selection

Fifteen commercial-sized representative agricultural fields (~ 120 ha of the total 320 ha of the farm) were selected across the farm, based on agricultural system and management practice information for the previous 10-year period (2008-2017) (Chapter 2, Fig. 2.1). It was stratified on i) conventional (CONV) *vs.* organic (ORG) agricultural system, and ii) by considering specific management practices within each system, in particular, grazing regime i.e. non-grazed (NG) or grazed (GG) fields and the history of cropping rotation, i.e. taking into account the inclusion of grass-clover ley periods in the crop rotation (hereafter referred to as ley time proportion-LTP). Criteria for selection and more details of each study field can be found in Chapter 2, Section 2.2.2 and Table 2.1 while details regarding general characteristics of the soil properties and other management histories are given in Chapter 3, Section 3.2.2 and Table 3.1. Crop history details are given in Table A1.2 (Appendix 1).

4.2.3 Sampling strategy and methods

The sampling strategy is described in detail in Chapter 3, Section 3.2.3. Chapter 2, Figure 2.1, shows the exact location of each sampling point within each selected field, which were chosen using a quasi-random stratified design based on an *a priori* soil apparent electrical conductivity (EC_a) map (0-0.70 m depth; Figure 4.11 and 4.12). Details about the methods and equipment's used for EC_a survey can also be found in Chapter 2, Section 2.2.3. The only exception for this chapter is that three additional fields (one under CONV and two under ORG system, study fields number 13, 14 and 15) were also sampled (3 sampling points in each) due to their high contrasting EC_a values compared to the other study fields (Chapter 2, Fig. 2.1). The reason for the selection of these extra nine sampling location points was to ensure samples were taken across the range of EC_a values (the likely soil texture range) that covered the entire farm.

In total there were 135 sampling points selected across the farm (2 agricultural systems: 7 study fields under CONV system and 8 fields under ORG system: 8-15 replicate sampled points per study field), except for the three additional fields where only three sampling points were sampled. Two undisturbed soil cores (1 m length, 0.03 m inner core diameter) were taken at each selected point using a hydraulic soil sampler (Atlas Copco Ltd., Hemel Hempstead, Hertfordshire, UK). Each soil core was separated into three distinct depth intervals 0-0.15; 0.15-0.30 and 0.30-0.60 m, resulting in 810 soil samples. Soil sampling was conducted in February-March 2017 and the position of each sample point was georeferenced with an EGNOS-enabled handheld GPS receiver (Garmin eTrex ® 30x).

4.2.4 Soil preparation and analyses

In the laboratory, each of the 810 soil samples was processed individually. Fresh soil samples were gently mixed and passed through a 4 mm sieve; large stones were removed and weighed, and plant remains were discarded. The weight of the sieved, fresh soil was then recorded. A subsample of the sieved soil (5 g) was used for determination of gravimetric water content. Soil bulk density (BD) was calculated using the core method adjusting for the weight and volume of large stones (Blake & Hartge, 1986). Thereafter, the duplicate core samples taken at the same georeferenced location and same depth interval were merged and sieved through a 2 mm sieve. This resulted in 405 merged samples, which were then air-dried before being used for particle-size distribution (PSD), pH and SOC concentrations.

PSD of each merged sample was determined in triplicate by a low angle laser light scattering technique (Laser diffraction) as described in Chapter 2, Section 2.2.4. Likewise, analytical procedures for soil pH and SOC concentration, measured in H_2O (1:2.5 soil:solution) and determined by dry combustion method, respectively, can be found in Chapter 2, Section 2.2.4. Thermal analysis (Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry) conducted in Chapter 5, Section 5.3.3, of this thesis, showed that there was an absence or very low presence of carbonate minerals in the samples (Chapter 5, Fig 5.7), therefore, total soil C concentration can be assumed to be total SOC. SOC stocks per unit of area (Mg ha^{-1}) were calculated for each depth interval (i.e. 0-0.15; 0.15-0.30 and 0.30-0.60 m) on an equivalent soil mass basis (Wendt & Hauser, 2013) using the CONV and NG as a reference. More details about the calculations and equivalent soil mass adjustments can be found in Chapter 1, Section 1.5. Cumulative SOC stocks in the 0-0.30 and 0-0.60 m depth were calculated by summing the average SOC stocks in each individual soil depth interval.

4.2.5 Digital soil mapping approach

In total 15 covariates were considered as potential predictors for mapping SOC stocks (Table 4.1). The Digital Elevation Model (DEM) at 5 m resolution for the catchment area, within which Nafferton farm is located, was download from the Digimap dataset (Ordnance Survey (GB), 2019). The catchment area for deriving terrain attributes was considered to avoid boundary effects. Topography/terrain predictor covariates were derived from the DEM map for the whole catchment area surrounding Nafferton farm using functions available in ArcGIS (version 10.6.1 Environmental Systems Research Institute, Inc., Redlands, CA, USA) (Esri, 2018). Topography/terrain covariates included slope (degree), flow direction, flow accumulation, basin, aspect, curvature, hillshade as well as the computed Topographic Wetness Index and Topographic Position Index (TWI and TPI, respectively). The TWI, a predictor for zones of soil saturation, was calculated based on the following equation (eqs. 4.1) (Moore *et al.*, 1993):

$$\text{eqs. 4.1)} \qquad \text{TWI} = \ln(\alpha/\tan\beta)$$

where α is the flow accumulation of the area computed with the D8 algorithm, and β is the local slope.

The TPI provides information relative to the topographic position (i.e. valleys, slopes and ridges), which can expose the soil to different microclimates (wind, temperature and radiation). TPI was calculated based on the following equation (eqs. 4.2):

$$\text{eqs. 4.2)} \qquad TPI = DEM - \mu DEM$$

where DEM is the actual digital elevation of the area and μ is its mean values.

It is important to highlight that although all these topography/terrain attributes were considered, it was not expected that all of them will be useful for mapping SOC stocks, but the modelling allows for redundant and/or non-useful variables to be removed.

In addition to the above covariates, data from a high-resolution soil sensor survey (~10 m transects) of EC_a using the DualEM1s (shallow 0-0.70 m and deeper 0-1.5 m depth), was interpolated to the 5 m DEM grid over the entire farm area. The interpolation was a performed using local block kriging with the VESPER freeware (Minasny *et al.*, 2005) following the protocol in Taylor *et al.* (2007). The resulting two EC_a layers (shallow and deep) were included as potential covariates in the modelling approach. Finally, agricultural system (i.e. conventional or organic) and management practice information, including grazing regime (i.e. non-grazed or grazed practices) and ley time proportion varying from 0 to a maximum of 10 years i.e. number of years under grass-clover mix in the crop rotation at both agricultural systems in the last 10 years period (from 2008 to 2017) were also considered as potential SOC stock predictor covariates. These data were available at the field level but downscaled to the 5 m DEM grid so that all covariate data layers were available on the 5 m grid over the entire farm area. Topography/terrain covariates were resampled into 20 x 20 m resolution raster cells using the nearest neighbour interpolation to smooth local effects and remove very short-range noise in the terrain data, before values were extracted to the measured soil points. The EC_a maps were kept in a 5 m resolution raster (Fig. 4.1-4.12).

All the covariates chosen in this study are related to factors including soil properties, topography, climate, organisms (including human activities, management practices), which are consistent to the SCORPAN approach for DSM (McBratney *et al.*, 2003) (Table 4.1). The SCORPAN approach is based on the premise that there is a direct relationship between soil properties and environmental factors. The SCORPAN function is described as (eqs 4.3):

$$\text{eqs. 4.3)} \qquad \mathrm{S} = f(\mathrm{s}, \mathrm{c}, \mathrm{o}, \mathrm{r}, \mathrm{p}, \mathrm{a}, \mathrm{n})$$

where S is soil classes or attributes (to be modelled), “s” refers to the soil (other or previously measured properties of the soil at a point), “c” is climatic properties of the environment at a point, “o” refers to organisms, including land cover and natural vegetation or fauna or human activity, “r” is the relief, topography, landscape attributes, “p” is the parent material/lithology, “a” refers to the age, i.e. the time factor and finally, “n” is the spatial or geographic position.

Table 4.1 Covariates used to predict soil organic carbon stocks at Nafferton farm.

Covariate	Scorpan Factor	Description	Resolution (m)
Topography / Terrain			
Elevation	R	The height of a location above the Earth's sea level	20
Slope	R	The inclination of the land surface from the horizontal	20
Flow Direction	R	Direction of water flow in a given cell based on its steepest descent drop	20
Flow Accumulation	R	Accumulated flow determined by accumulating the weight for all cells that flow into each downslope cell	20
Basin	N	Connected cells belonging to the same drainage basin defined by the flow direction	20
Aspect	R, N	The direction in which a land surface slope face	20
Curvature	R	The shape or curvature of the slope i.e. concave or convex	20
Hillshade	C	Representation of the surface considering the sun position for shading	20
Topographic Wetness Index (TWI)	C, R	The relative wetness within moist catchments, but is more commonly used as a measure of position on the slope with larger values indicating a lower slope position	20
Topographic Position Index (TPI)	R	Topographic position classification identifying upper, middle and lower parts of the landscape	20
Anthropogenic factors			
Agricultural Systems	O	Organic system in accordance with the Soil Association Organic Standards or Conventional system (UK best practices recommendations)	-
Grazing Regime	O	Non-grazed or grazed by cattle. Under grazed fields stock rates (i.e. grazing intensity) were considered light to moderate	-
Ley Time Proportion (LTP)	O	Number of years (proportion) that the field was under grass-clover mix in the crop rotation in the last 10 years period (from 2008 to 2017)	-
High Resolution Soil Sensing			
Horizontal Electrical Conductivity (Shallow EC_a)	S	Soil apparent electrical conductivity (EC_a) analysis (0-0.7 m depth), using a DualEM-1s sensor (Milton, ON, Canada)	5
Vertical Electrical Conductivity (Deeper EC_a)	S	Soil apparent electrical conductivity (EC_a) analysis (0-1.5 m depth), using a DualEM-1s sensor (Milton, ON, Canada)	5

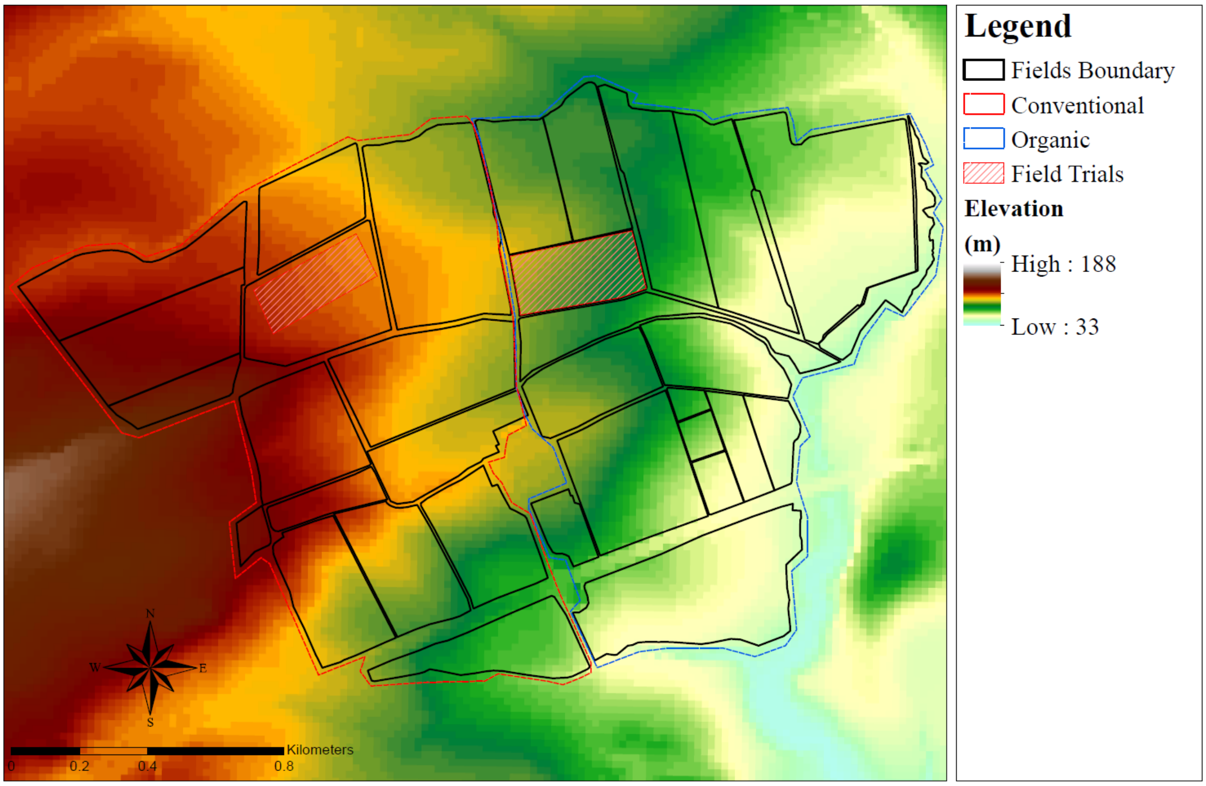

Figure 4.1 Elevation map of Nafferton farm.

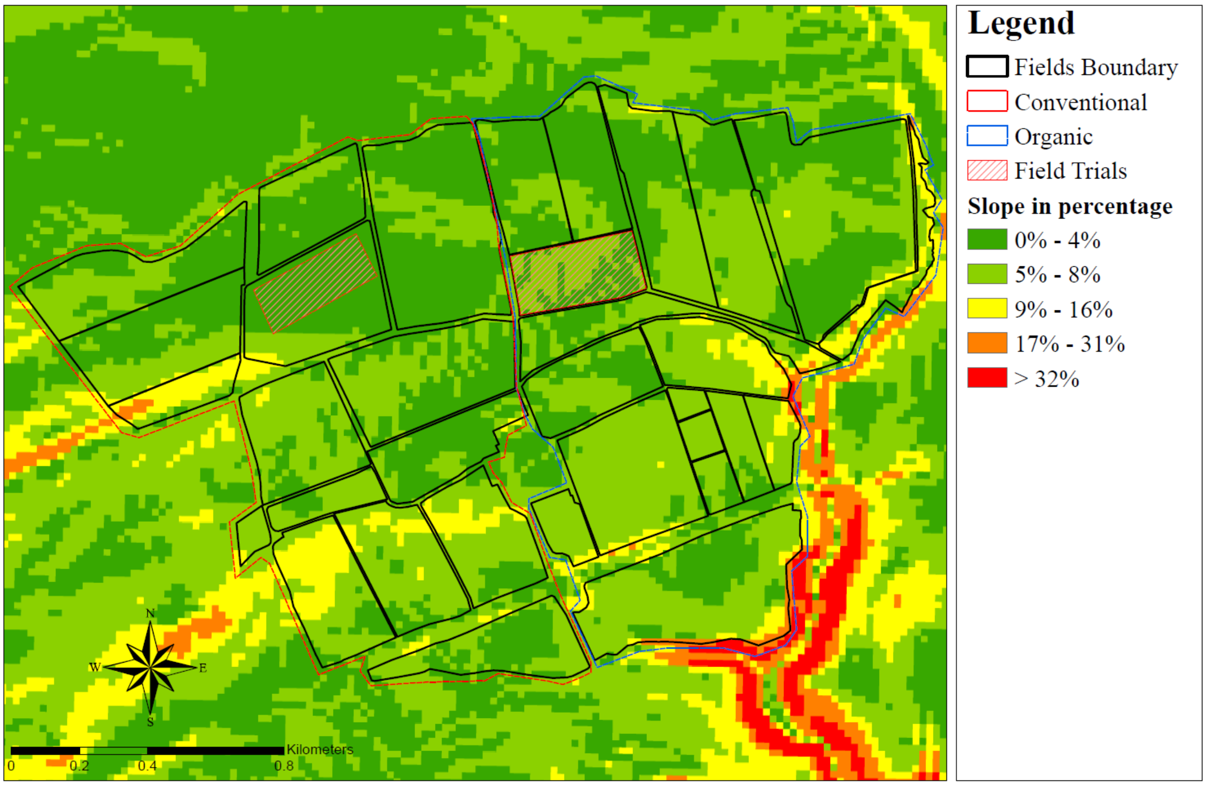

Figure 4.2 Slope map of Nafferton farm.

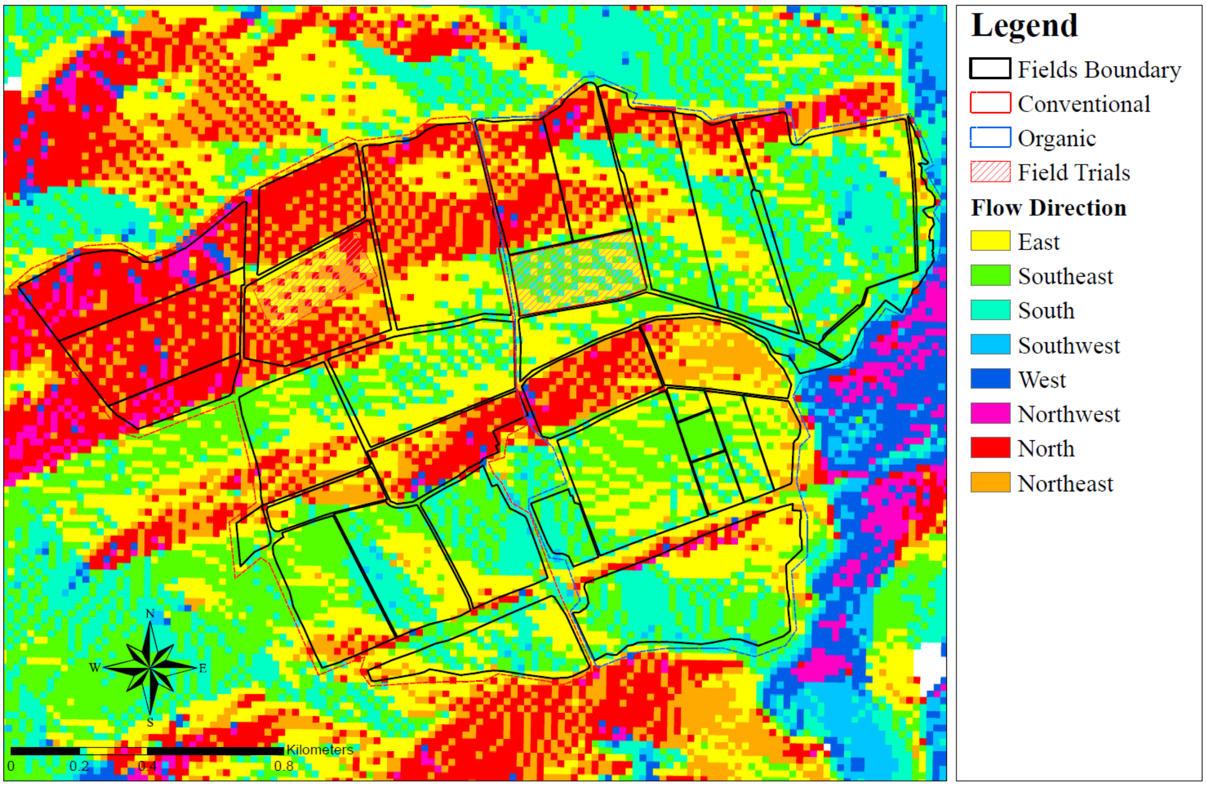

Figure 4.3 Flow direction map of Nafferton farm.

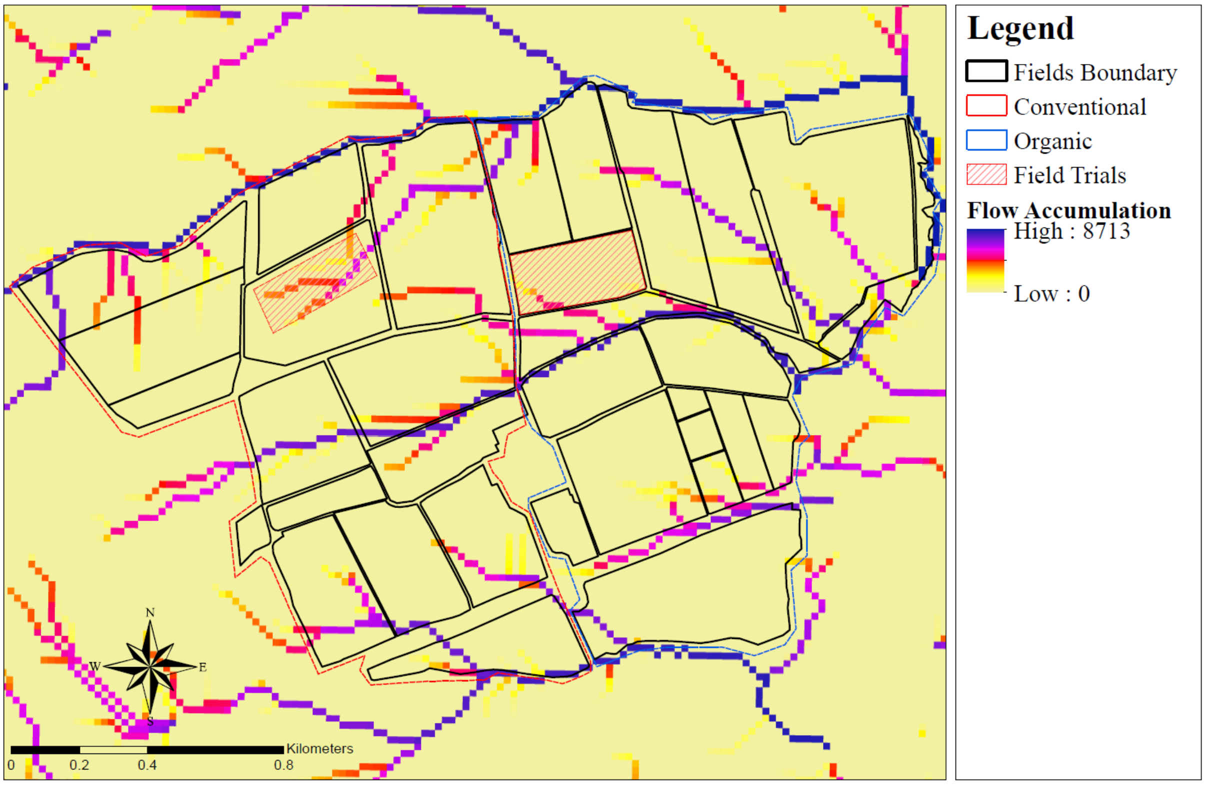

Figure 4.4 Flow accumulation map of Nafferton farm.

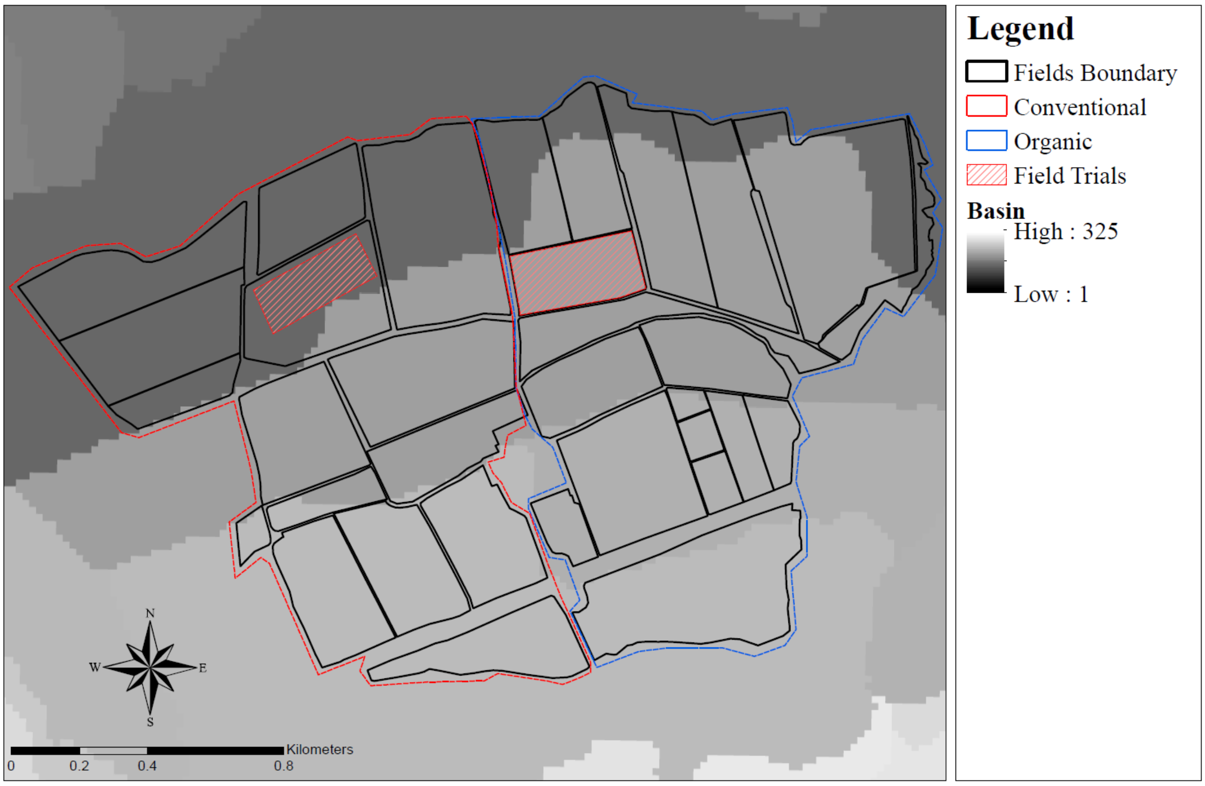

Figure 4.5 Basin map of Nafferton farm.

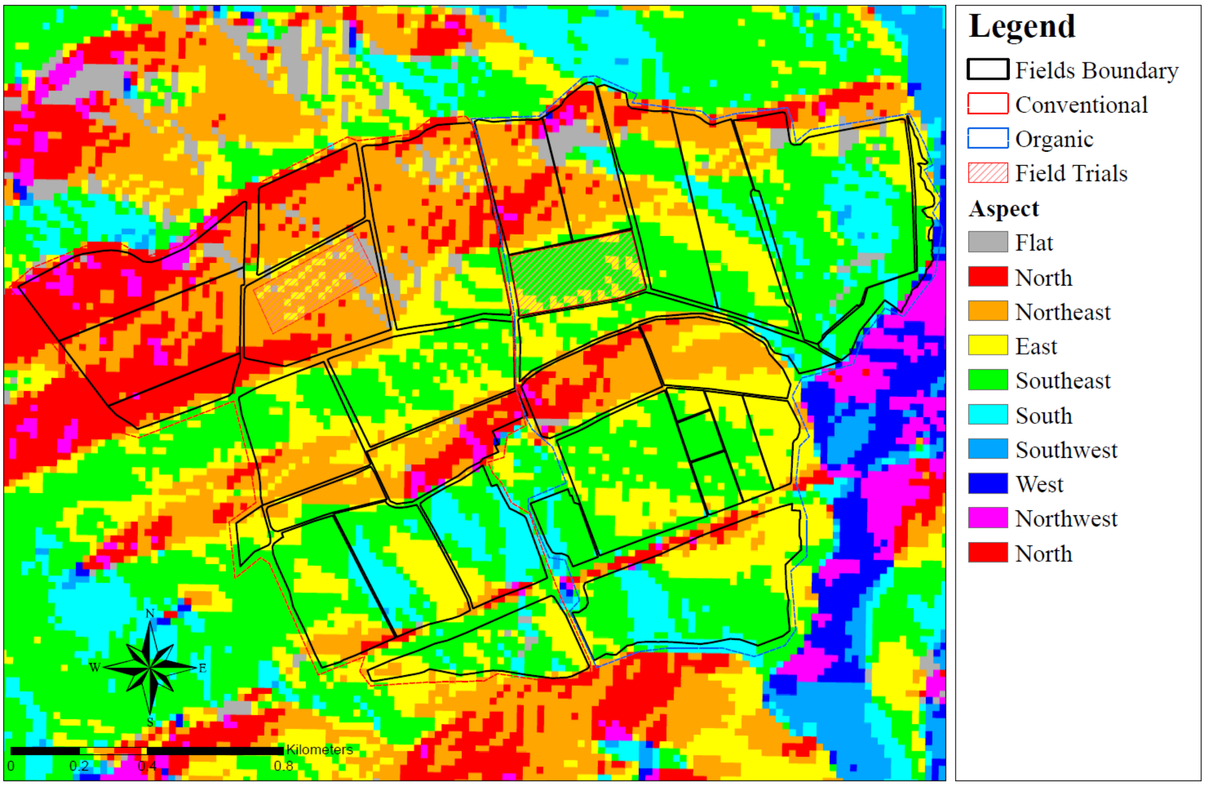

Figure 4.6 Aspect map of Nafferton farm.

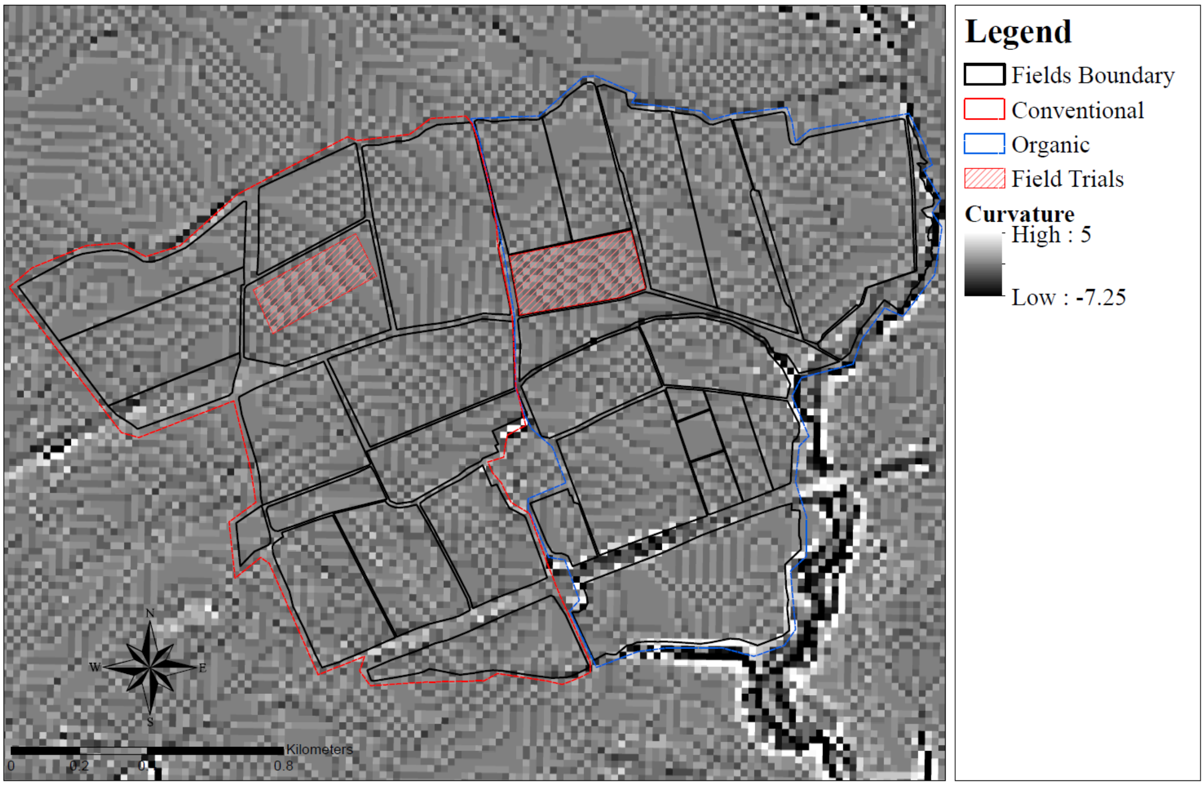

Figure 4.7 Curvature map of Nafferton farm.

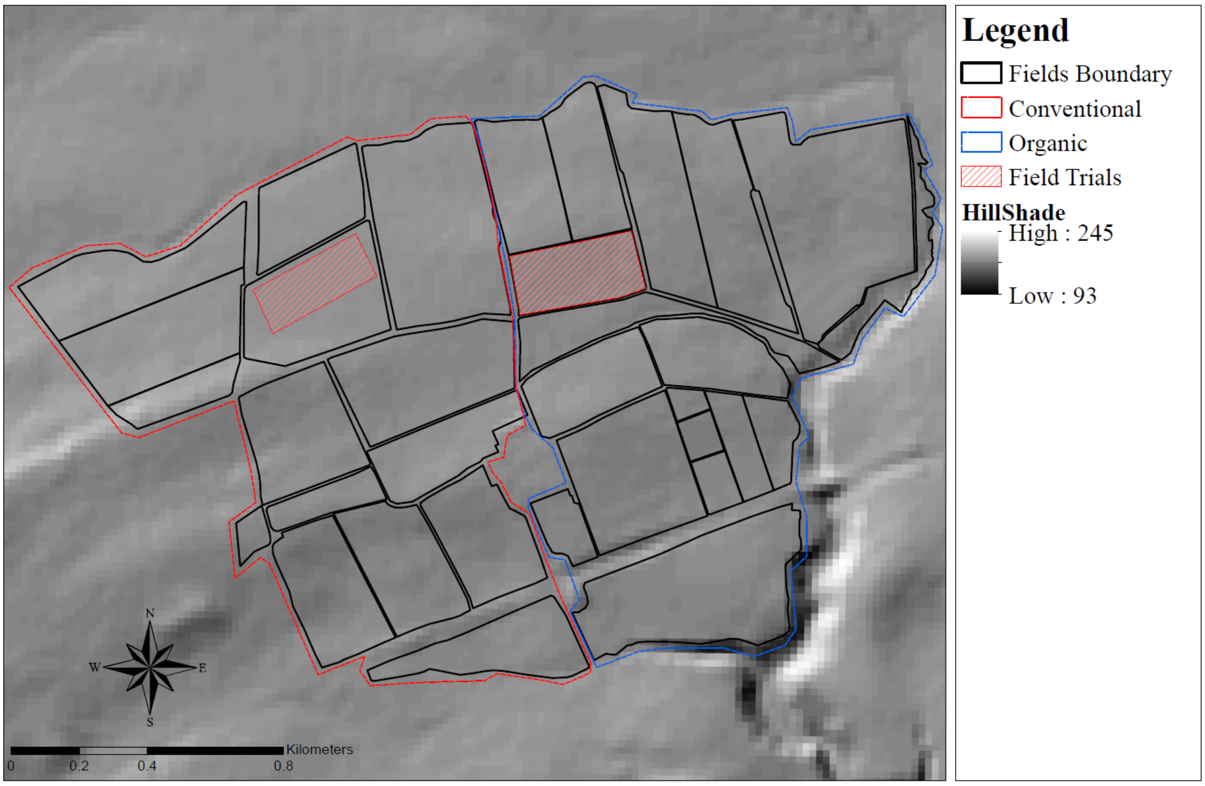

Figure 4.8 Hillshade map of Nafferton farm.

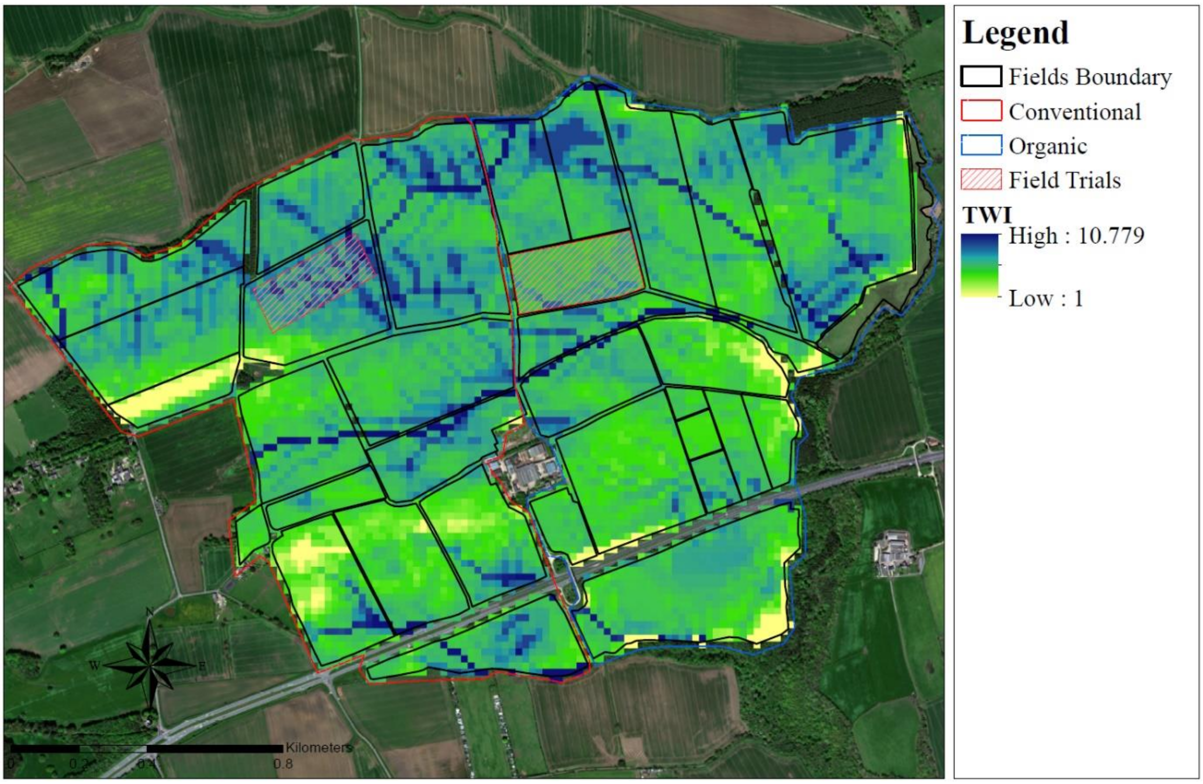

Figure 4.9 Topographic Wetness Index (TWI) map of Nafferton farm.

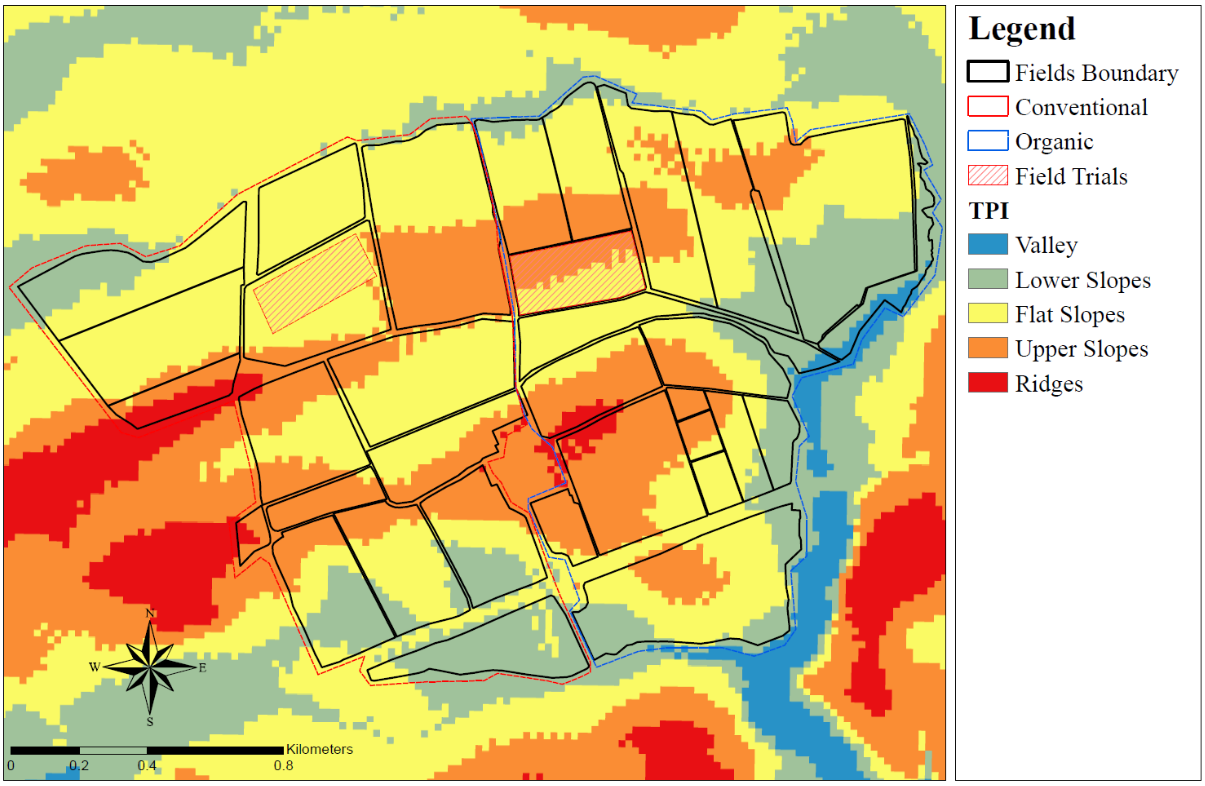

Figure 4.10 Topographic Position Index (TPI) map of Nafferton farm.

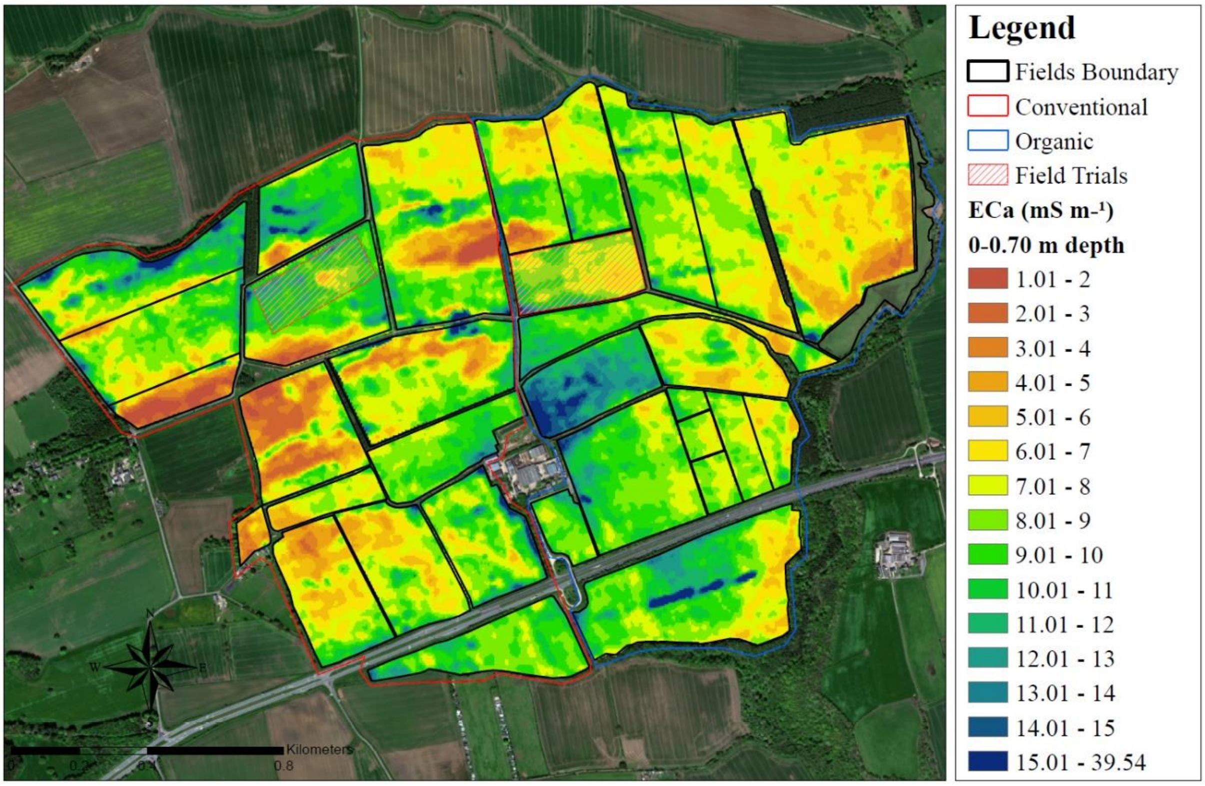

Figure 4.11 Shallow (0-0.70 m) soil apparent electrical conductivity (EC_a) map of Nafferton farm.

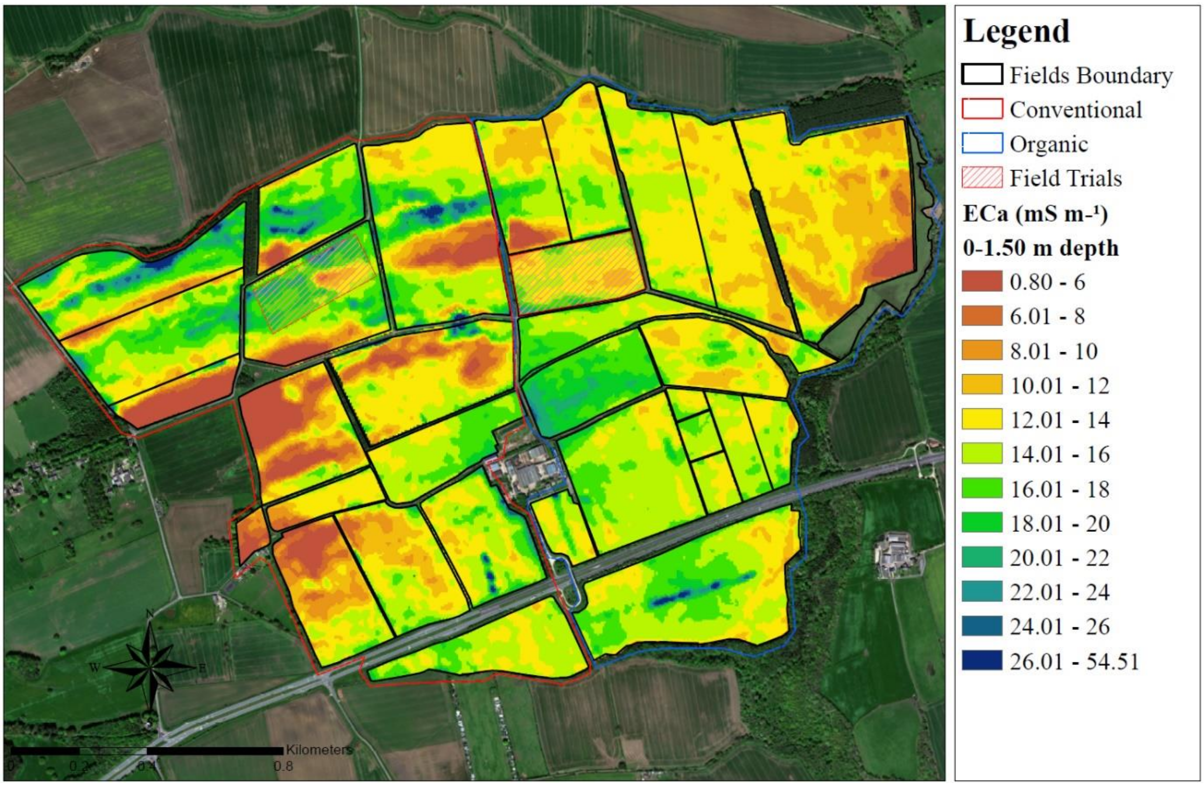

Figure 4.12 Deeper (0-1.50 m) soil apparent electrical conductivity (EC_a) map of Nafferton farm.

4.2.6 Modelling SOC stocks

Two fitting methods were tested to construct the spatial predictive model for SOC stocks, a Linear Model (LM) and an ensemble learning method Random Forest Model (RFM). Both models were structured in three different ways in order to i) assess the effect of agricultural systems and management practices and ii) reduce bias and eliminate potentially correlated covariates. Firstly, a base model was created with no pre-selection of the available covariates from DEM/terrain and soil sensor information, i.e. considering a total of 12 covariates excluding agricultural system and management practice information (Table 4.1). Secondly, a pre-selection was conducted among the 12 covariates used in the previous model and only the selected covariates were considered in the model structure, i.e. disregarding once again agricultural system and management practice information. Finally, the third approach for the model construction involved a pre-selection among all the 15 covariates (Table 4.1), i.e. including agricultural system and management practice information.

In the LM approach, and for the second and the third model structure described above, a combination of forward and backward stepwise regression was carried out aiming to select the best subset of predictor covariates on the bases of an F probability of 0.05. The RFM, in turn, used a nonlinear approach to rank the potentially most informative predictor variables (Huang & Wang, 2006; Taghizadeh-Mehrjardi *et al.*, 2016). The RFM is a tree-based method, which was developed with a clear aim to improve regression accuracy (Breiman, 2001). It consists of multiple trees generated by a combination of bagging and random selection of features applied at each split of the trees, which is considered a rather favourable model as it is robust to noise and irrelevant features. In short, the RFM is a nonparametric method, where many individual tree models are trained from bootstrap samples of the data (Breiman, 2001). The bootstrap sampling method approach conducted by RFM helps to avoid a potential over-fitting of the variables compared to standard decision tree models. A single prediction is obtained from the aggregation of the results of all individual trees. The predictions acquired from the regression prediction error out-of-bag (OOB) are used to rank the importance of each predictor variable (Taghizadeh-Mehrjardi *et al.*, 2016). RFM requires two main parameters: 1) number of regression tress (n_{tree}), and 2) the number of randomly available variables for selection in each split/node (*mtry*) (Houborg & McCabe, 2018). Specifically, the *mtry* value was adjusted in accordance with the depth interval and fixing n_{tree} value was set as 500. The potential advantages of using RFM model are that it normally includes fewer parameters with the power to investigate nonlinear and hierarchical relationships between the predictors and the response (Everingham *et al.*, 2016).

LM and RFM were developed individually for each of the cumulative depth intervals (0-0.15, 0-0.30 and 0-0.60 m). All the tested models were trained using a random selection of 80% (n = 108 for each cumulative depth interval) of the samples, while the remaining 20% (n = 27 for each cumulative depth interval) were used to evaluate the performance of the model using the cross-validation approach. LM was implemented using JMP Pro 13 statistical program (JMP, 2019). Descriptive statistics and RFM was performed using the packages *ranger*, *tuneRanger* (Probst *et al.*, 2019), *mlr* (Bischl *et al.*, 2016) and *cvTools* (Alfons, 2012) in R programming language 3.4.3 (R Development Core Team, 2019). The accuracy of the models was tested using the coefficient of determination (R^2) and the root mean square error (RMSE) statistical criteria. The R^2 gives the relationship between the predicted and measured values (i.e. it explains the percentage of variation explained by the model) while the RMSE measures the goodness-of-fit relevant to high values (i.e. model accuracy). The best models were chosen to spatially map SOC stocks across Nafferton farm using ArGIS 10.6.1 (Environmental Systems Research Institute, Inc., Redlands, CA, USA).

4.3 Results and Discussion

4.3.1 Exploratory data analysis

Table 4.2 shows the descriptive statistics of measured SOC stocks at Nafferton farm. Measured SOC stocks ranged from 22.36 to 62.22; 43.85 to 115.18 and 62.72 to 182.27 Mg ha^{-1}, with means of 39.74, 69.71 and 106.54 Mg ha^{-1} for the cumulative 0-0.15, 0-0.30 and 0-0.60 m depth intervals, respectively (Table 4.2). The variability observed in all cumulative depth intervals was a consequence of the sampling design that encompassed different agricultural systems, management practices and soil textures. On average, SOC stocks decreased with depth while the standard error (SE) of the mean increased when deeper soil layers were considered. It is important to highlight that the 0.30-0.60 m soil layer had double the thickness of the other layers (0-0.15 and 0.15-0.30 m) and hence its SOC stocks were increased by a factor of 2.

The summary statistics of the predicted SOC stocks for each model tested is presented in Table 4.3. In general, the predicted SOC stocks of the three models tested, i.e. using LM and RFM with different covariates in the model structure, were similar to the mean SOC stocks measured. However, both model types slightly overestimated minimum and underestimated the maximum values. The model that best described the measured SOC stocks was the stepwise LM that included agricultural system and management practice information. In this specific model, predicted SOC stocks ranged from 24.09 to 64.28; 51.02 to 99.62 and 79.29 to 161.75 Mg ha^{-}

^{1}, with means of 36.23, 65.66 and 101.83 Mg ha^{-1} for the cumulative 0-0.15, 0-0.30 and 0-0.60 m depth intervals, respectively (Table 4.3). Differences observed for the minimum and maximum between predicted values and the measured SOC stocks, especially by RFM, are likely caused as a result of the algorithms dealing with these data point as outliers. These differences between predicted and measured minimum and maximum values were also observed in previous studies using RFM approach (Were *et al.*, 2015).

Table 4.2 Descriptive statistics of the measured soil organic carbon (SOC) stocks by cumulative depth intervals at Nafferton farm study fields.

Property	Depth interval (m)	Min	Max	Mean	SD	SE	Median	Skewness	Kurtosis
SOC stock	0-0.15	22.36	62.22	39.24	7.38	0.64	37.45	0.84	0.50
(Mg ha^{-1})	0-0.30	43.85	115.18	69.71	10.35	0.89	68.13	0.88	2.34
(n=135)	0-0.60	62.72	182.27	106.54	17.14	1.47	104.14	0.92	2.21

n: number of samples, Min: minimum, Max: maximum, SD: standard deviation, SE: standard error of the mean.

Table 4.3 Descriptive statistics of the linear model (LM) and random forest model (RFM) in three different structures in predicting soil organic carbon stocks by cumulative depth intervals at Nafferton farm study fields. Values presented in Mg of carbon per ha^{-1}.

Depth interval (m)	Min	Max	Mean	SD	SE	Median	Skewness	Kurtosis
	LM							
All covariates without agricultural system and management practice information								
0-0.15	17.56	75.25	38.28	5.83	0.01	38.35	0.17	0.90
0-0.30	31.28	121.47	68.36	7.75	0.02	68.48	-0.10	0.56
0-0.60	20.03	168.25	104.16	11.30	0.03	105.01	-0.60	1.79
Selected covariates without agricultural system and management practice information								
0-0.15	17.10	60.93	38.21	5.56	0.01	38.48	-0.18	0.48
0-0.30	38.24	126.08	70.03	4.15	0.01	69.66	1.38	8.67
0-0.60	78.40	157.54	105.24	7.18	0.02	106.60	-0.41	0.91
Selected covariates including agricultural system and management practice information								
0-0.15	24.09	64.28	36.23	6.03	0.02	34.49	0.89	0.06
0-0.30	51.02	99.62	65.66	7.73	0.02	62.91	0.77	-0.47
0-0.60	79.29	161.75	101.83	9.98	0.03	99.09	0.58	-0.16
	RFM							
All covariates without agricultural system and management practice information								
0-0.15	31.72	47.58	38.52	4.42	0.01	36.97	0.33	1.37
0-0.30	59.67	86.48	67.77	4.72	0.01	66.11	0.74	-0.27
0-0.60	94.24	121.52	103.31	5.99	0.01	101.45	0.51	-0.96
Selected covariates without agricultural system and management practice information								
0-0.15	31.72	52.20	38.46	4.34	0.01	37.51	0.40	-1.14
0-0.30	60.44	80.31	68.12	4.67	0.01	66.33	0.61	-0.77
0-0.60	94.59	121.50	103.45	6.17	0.02	101.45	0.60	-0.84
Selected covariates including agricultural system and management practice information								
0-0.15	31.05	48.69	36.82	4.83	0.01	34.69	1.01	-0.25
0-0.30	60.76	85.55	66.04	5.66	0.02	63.78	1.13	0.22
0-0.60	94.59	115.26	101.14	6.07	0.01	98.90	0.69	-0.90

Min: minimum, Max: maximum, SD: standard deviation, SE: standard error of the mean.

4.3.2 Accuracy of the models and importance of the predictor covariates

The performance of the LM and RFM in predicting cumulative SOC stocks at 0-0.15, 0-0.30 and 0-0.60 m depth intervals are shown in Table 4.4. LM prediction showed slightly lower performance in the training data (80%) than in the validation data (20%) whilst RFM showed the opposite. In the LM, the full model without agricultural system and management practice information showed a reasonable performance for all cumulative intervals (capturing 30 to 42% of the variation in SOC stocks), however, it generated noisier maps (Figure 4.13a, d, g). This indicates potential overfitting of the model, which can be related to the inclusion of correlated (confounding) covariates. Conversely, the stepwise LM models resulted in less noisy maps (Figure 4.13b, e, h) but captured only 17 to 36% of the variation in SOC stocks across the farm. In the RFM, the full model structure showed the poorest performance (capturing 20 to 42% of the variation in SOC stocks) while the stepwise model that included only main covariates without agricultural system and management practice information indicated reasonable performance (capturing 22 to 48% of the variation in SOC stocks). It is important to stress that only the best performed of the LM and RFM are presented in Table 4.4, which included only significant covariates (Table 4.5 and 4.6). These differences between the LM and RFM models and among the fitting method approaches, highlighted the importance of comparing different models and methods before carrying out spatially SOC stock mapping at a farm-scale level.

For both models (LM and RFM), the highest R^2 and lower RMSE (i.e. overall best performance), were observed when agricultural system and management practice information were considered (Table 4.4). In these models, the LM prediction was able to capture up to 62, 49 and 30% of SOC stock variability for the 0-0.15, 0-0.30 and 0-0.60 m depth, respectively. The RFM, in turn, capture up to 60, 44, and 27% of SOC stock variability for the 0-0.15, 0-0.30 and 0-0.60 m depth, respectively. Although the LM performed slightly better than the RFM models, both models were similar, showing a particular strength to capture higher variation in SOC stocks when shallower layers were considered (i.e. in the cumulative 0-0.15 m and 0-0.30 m layers). The R^2 range (~0.3–0.6) found in this study was similar to other DSM studies of SOC stocks where the authors also carried out an internal validation approach (Minasny *et al.*, 2013; Adhikari *et al.*, 2014). The decrease in the R^2 values as depth increased was expected as most of the information used as covariates in the model explain mainly surface phenomena (Minasny *et al.*, 2006).

When comparing the most important covariates (all 15 covariates) for predicting SOC stocks, it was observed that both models ranked similar covariates (Table 4.5 and 4.6). Stepwise regression selected in the following order, ley time proportion, shallow EC_a, elevation and grazing regime as the most important predictors of topsoil (0-0.15 and 0-0.30 m) cumulative SOC stocks for the LM approach. Similarly, but in a different order, the RFM approach selected, ley time proportion, grazing regime, elevation and shallow EC_a as the most important covariates for predicting topsoil (0-0.15 and 0-0.30 m) cumulative SOC stocks. When considering subsoil layers (i.e. the cumulative 0-0.60 m), flow accumulation replaced grazing regime, while deeper EC_a substituted shallow EC_a among the top four most important predictors of SOC stocks for LM and RFM, respectively. In short, these results emphasised that ley time proportion, shallow EC_a (0-0.70 m depth), grazing regime and elevation are central covariates to predict SOC stocks regardless of the model used (i.e. LM or RFM) or depth interval assessed (i.e. 0-0.15, 0-0.30 and 0-0.60 m). In previous studies, elevation, as well as electrical conductivity were also shown to be highly correlated with SOC stocks (Vasques *et al.*, 2010; Minasny *et al.*, 2013; Ross *et al.*, 2013), but the influence of different agricultural systems and management practices appears to be a new finding.

The slightly better performance of the LM is a surprising result as previous studies have found RFM to be better for predicting SOC stocks (Akpa *et al.*, 2016; Wang *et al.*, 2018). RFM is often preferred due to its capacity to reduce over-fitting and manage the hierarchical non-linear relationship between the predictor covariates and SOC stocks. It is important to highlight, however, that the best model for predicting SOC stocks can vary from site to site (Were *et al.*, 2015; Ließ *et al.*, 2016; Yang *et al.*, 2016) and, as shown in this study, may also vary at different depth intervals. Several factors might play a role in these disparities, for instance, differences in data sources, the scale of prediction as well as different types of predictor covariates available (Miller *et al.*, 2015; Wang *et al.*, 2018). Ultimately, based on these and other findings, it was concluded that covariate selection and model choice for estimating SOC stocks at a farm-scale level will vary with depth, and there is no global preferred best prediction model. However, including information relating to land use management is useful for modelling and estimating SOC stocks across at the farm-scale.

Table 4.4 Performance of the linear model (LM) and random forest model (RFM) in three different structures in predicting soil organic carbon stocks by cumulative depth intervals at Nafferton farm study fields.

Soil depth (m)	Training data				Validation data			
	LM		RFM		LM		RFM	
	R^2	RMSE	R^2	RMSE	R^2	RMSE	R^2	RMSE
All covariates without agricultural system and management practice information								
0-0.15	0.42	5.87	0.42	5.73	0.71	5.12	0.39	5.75
0-0.30	0.37	8.56	0.32	8.72	0.67	10.33	0.22	11.60
0-0.60	0.30	15.06	0.20	15.54	0.57	19.68	0.15	20.94
Selected covariates without agricultural system and management practice information								
0-0.15	0.36	5.98	0.48	5.40	0.58	4.93	0.47	5.19
0-0.30	0.16	9.61	0.30	8.82	0.36	11.14	0.27	11.26
0-0.60	0.17	15.80	0.22	15.49	0.33	19.35	0.16	20.71
Selected covariates including agricultural system and management practice information								
0-0.15	0.62	4.66	0.60	4.74	0.76	3.73	0.60	4.08
0-0.30	0.49	7.51	0.44	7.97	0.59	8.85	0.37	10.84
0-0.60	0.30	14.45	0.27	15.30	0.40	18.31	0.19	20.51

RMSE: root mean square error.

Table 4.5 Relative importance rank of the total 15 covariates by cumulative depth intervals (0-0.15, 0-0.30 and 0-0.60 m) selected by stepwise regression analysis prior Linear Model (LM) approach.

Covariate	p Value	Covariate	p Value	Covariate	p Value
0-0.15		0-0.30		0-0.60	
Ley time proportion	<0.01	Ley time proportion	<0.01	Ley time proportion	<0.01
Shallow EC_a	0.01	Shallow EC_a	0.01	Shallow EC_a	0.12
Elevation	0.06	Elevation	0.17	Elevation	0.19
Grazing regime	0.26	Grazing regime	0.18	Flow accumulation	0.21
Slope	0.27	TPI	0.25	Grazing regime	0.21
TWI	0.31	Deeper EC_a	0.26	TPI	0.29
Deeper EC_a	0.32	HillShade	0.40	Basin	0.42
Basin	0.33	Flow accumulation	0.43	TWI	0.42
Management practices	0.35	TWI	0.43	Management practices	0.43
Curvature	0.40	Management practices	0.57	HillShade	0.47
TPI	0.62	Curvature	0.65	Flow direction	0.58
Flow accumulation	0.83	Aspect	0.71	Aspect	0.66
Aspect	0.94	Flow direction	0.73	Curvature	0.81
HillShade	0.95	Slope	0.76	Deeper EC_a	0.82
Flow direction	0.95	Basin	0.96	Slope	0.88

EC_a: soil apparent electrical conductivity, TWI: topographic wetness index, TPI: topographic position index.

Table 4.6 Relative importance rank of the total 15 covariates by cumulative depth intervals (0-0.15, 0-0.30 and 0-0.60 m) selected by Random Forest Model (RFM) approach.

Covariate	p Value	Covariate	p Value	Covariate	p Value
0-0.15		0-0.30		0-0.60	
Ley time proportion	0.01	Ley time proportion	0.01	Ley time proportion	0.01
Grazing regime	0.01	Grazing regime	0.01	Grazing regime	0.03
Elevation	0.02	Elevation	0.02	Elevation	0.03
Shallow EC_a	0.02	Shallow EC_a	0.09	Deeper EC_a	0.15
TPI	0.05	TPI	0.23	Management practices	0.29
Management practices	0.08	Management practices	0.25	Aspect	0.29
Basin	0.08	Deeper EC_a	0.26	Flow direction	0.37
HillShade	0.20	Basin	0.43	Shallow EC_a	0.39
Deeper EC_a	0.20	Flow direction	0.47	HillShade	0.59
Slope	0.22	Flow accumulation	0.54	TWI	0.63
Aspect	0.25	Aspect	0.54	Curvature	0.64
TWI	0.29	Curvature	0.54	TPI	0.69
Flow direction	0.45	HillShade	0.62	Flow accumulation	0.74
Curvature	0.46	Slope	0.75	Basin	0.85
Flow accumulation	0.70	TWI	0.76	Slope	0.93

EC_a: soil apparent electrical conductivity, TWI: Topographic Wetness Index, TPI: Topographic Position Index.

4.3.3 Spatial prediction and mapping SOC stocks

Output maps of predicted SOC stock (5 m resolution) by LM and RFM models using three different fitting method structures (i.e. all covariates without agricultural system and management practice information, selected covariates without agricultural system and management practice information and selected covariates including agricultural system and management practice information) are presented for the 0-0.15; 0-0.30 and 0-0.60 m depth layers in Fig. 4.13 and Fig. 4.14. Despite the differences in maximum and minimum values, it is possible to observe spatial similarities between the two models. At both, SOC stocks varied significantly across the farm regardless of the cumulative soil depth assessed. In particular, it was observed that SOC stocks varied spatially between study fields according to the agricultural system and management practices deployed at each study field. The highest cumulative SOC stocks were observed in the study fields with higher ley time proportions and the lowest SOC stocks were found in the fields where a more continuous arable-crop rotation was implemented over the preceding 10 years. Intensive agricultural land management (i.e. represented here by the use of a more continuous arable-crop rotation and lower ley time proportions) can lead to lower SOC stock as a result of the highest level of disturbance, particularly through tillage, which breaks up soil aggregates and boosts microbial decomposition and oxidation of the SOM (Six *et al.*, 2010). The lower SOC stocks found in this study under more continuous arable-crop rotation study fields can also be linked to the removal of crop residues and reduced vegetation cover, which can lead to a re-distribution and/or mineralisation of organic matter at depth (Six *et al.*, 1998; Balesdent *et al.*, 2000; Stoate *et al.*, 2001; Hamza & Anderson, 2005).

The differences in SOC stocks between fields with more continuous arable-crop rotation and others with higher ley time proportions were also observed when subsoil layers were considered (i.e. > 0.30 m). This may be related to potential changes in rooting depths as discussed in Chapter 3. It was hypothesised that some grassland species used in the fields with high ley time proportions might have led to deep SOM input via higher root-shoot ratio and net primary productivity (Jobbágy & Jackson, 2000; Rumpel & Kögel-Knabner, 2010). In addition, the presence of herbivores in grazed fields can promote root and shoot growth, which in turn may have boosted subsoil SOC accumulation (Pineiro *et al.*, 2010; McSherry & Ritchie, 2013; Assmann *et al.*, 2014; Chen *et al.*, 2015). This is important since significant amounts of SOC stocks were present in the deeper layers (~ 35%, Table 4.2). Such finding also helps in understanding the relationship between land use and SOC accumulation and distribution patterns across the farm. Even though elevation had a strong influence in prediction of the spatial distribution of SOC stocks across Nafferton farm, for this particular case, it might be related to the land use. At Nafferton farm, the valley fields are characterised by more intensive agricultural land management (continuous arable-crop rotation) whereas hilly areas (upper slopes) are dominated by grassland. These findings are also in agreement with the global meta-analysis conducted by Guo and Gifford, (2002) who indicated that SOC trends can to some extent be explained by land use.

The results of this study indicated that the reliability to predict and map spatially SOC stocks (at the top and subsoil layers) under agricultural soils and at the farm level was particularly improved when ley time proportion and grazing regime information were included as covariates in both LM and RFM models. Including agricultural land management information improved model fit in the validation data by 12-13% in the topsoil (0-0.15 m) and 10% in the 0 – 0.30 m layer. The effect was less pronounced (4 - 7%) when the subsoil was included (0 – 0.60 m) but the R^2 was always higher and the RMSE lower in all layers when agricultural systems and management practices were incorporated. For Nafferton farm, the spatial information of SOC stocks can be used to identify fields where a lower or higher allocation of resources and fertility management deserves more attention. Although this study has focussed on a single farm, understanding the spatial and distribution of SOC stocks could help other farms to better formulate their strategy for a more sustainable agricultural land management, and therefore climate change mitigation.

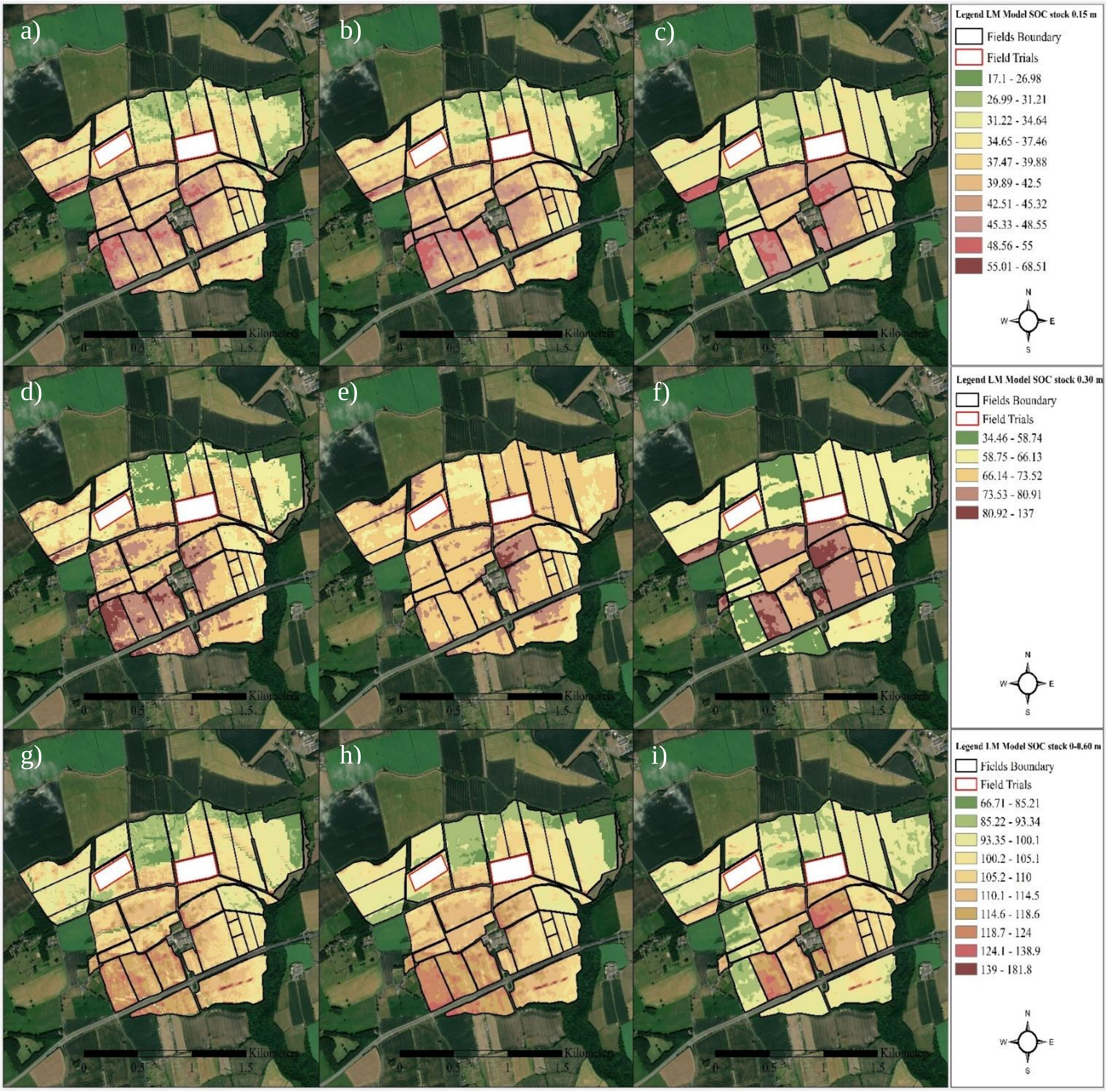

Figure 4.13 Spatial variability output maps of soil organic carbon (SOC) stocks obtained by three different linear model (LM) structures (all covariates without agricultural system and management practice information: a, d, g; selected covariates without agricultural system and management practice information: b, e, h; selected covariates including agricultural system and management practice information: c, f, i) at different cumulative depth intervals (0-0.15 m: a, b, c; 0-0.30 m: d, e, f and 0-0.60 m: g, h, i) at Nafferton farm (5 m resolution).

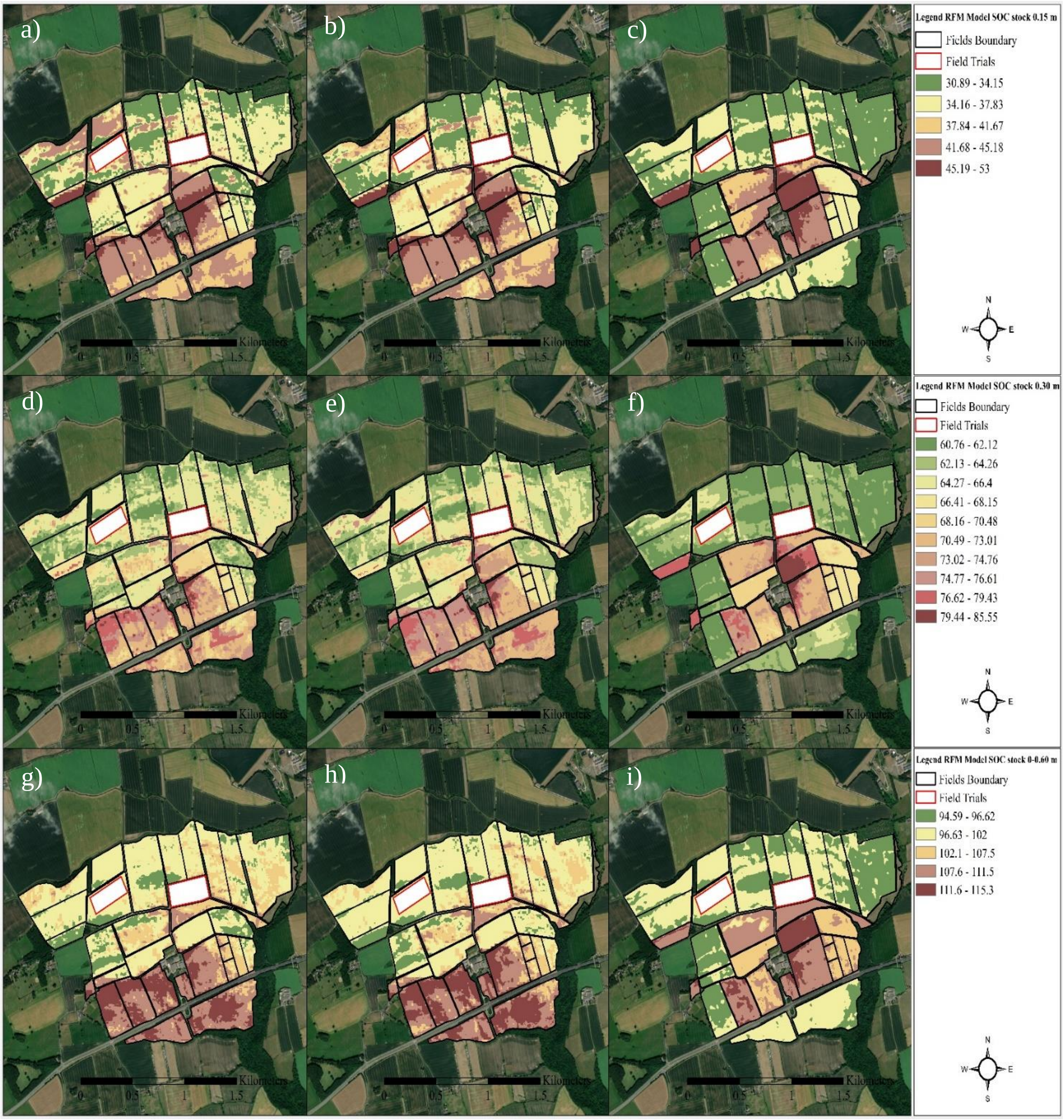

Figure 4.14 Spatial variability output maps of soil organic carbon (SOC) stocks obtained by three different random forest model (RFM) structures (all covariates without agricultural system and management practice information: a, d, g; selected covariates without agricultural system and management practice information: b, e, h; selected covariates including agricultural system and management practice information: c, f, i) at different cumulative depth intervals (0-0.15 m: a, b, c; 0-0.30 m: d, e, f and 0-0.60 m: g, h, i) at Nafferton farm (5 m resolution).

4.4 Conclusions

Overall, this study showed that the best fitting method approach for DSM of SOC stock at the farm-scale level should encompass agricultural system and management practice information as one the main covariates into the model structure. For both models tested (LM and RFM), the model structure contained ley time proportions, grazing regimes, elevation and soil apparent electrical conductivity as important covariates to map spatially SOC stock at the three cumulative soil depth intervals (0-0.15, 0-0.30 and 0-0.60 m). Even though the study also showed the typical trend of decreasing SOC stocks with depth, the results highlighted the importance of subsoil horizons for total cumulative SOC stocks down the soil profile. Among the models used to spatially map SOC stocks across Nafferton farm, and regardless of the cumulative depth interval assessed (0-0.15, 0-0.30 and 0-0.60 m), LM showed a slightly better performance than RFM. Future studies to calibrate soil C models should include agricultural land management information as potential explanatory covariates. This certainly can deliver a more reliable DSM prediction of top and subsoil SOC stocks at the farm-scale level. Its inclusion in regional and global evaluations could and should be also tested. For the Nafferton farm study case, the maps can be used to identify locations with higher potential to sequester C by altering management, such as where continuous arable-crop rotation has been deployed in the last 10 years period. The knowledge acquired by the high-resolution maps of SOC stocks produced for Nafferton farm at three depth interval 0-0.15, 0-0.30 and 0-0.60 m can be vital for framing appropriate agricultural land management practices and future environmental monitoring purposes.

Chapter 5. Individual and combined role of crop rotation scheme and fertility source in soil carbon stocks and stabilisation

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Notes

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Declaration of contribution

This chapter was conducted in an established long-term experimental trial. Soil analyses and evaluation of this chapter was developed by myself, Caio Fernandes Zani with advice from Geoffrey D. Abbott, James A. Taylor, Julia Cooper and Elisa Lopez-Capel. The 2018 soil sampling was carried out by Caio Fernandes Zani with assistance from Gavin Hall and Rachel Chapman. The 2011 soil sampling was carried out by Gavin Hall and Rachel Chapman as a part of a previous project. Caio Fernandes Zani carried out all soil analyses (including samples from 2011 and 2018) as well as data analysis. Caio Fernandes Zani also led the writing of the chapter and potential paper, with contribution from all co-authors. Specifically, Geoffrey D. Abbott, James A. Taylor, Julia Cooper and Elisa Lopez-Capel provided PhD supervision and detailed comments on the chapter. David Manning provided full assistance with the run, interpretation, and discussion of the TG-DSC-QMS analysis as well as many helpful comments and discussion of the chapter.

5.1 Introduction

Accumulation of soil organic carbon (SOC) has been pointed out as one of the solutions for the increasing atmospheric CO_2 and its associated climate change effects (Paustian *et al.*, 2016). Plant-soil interactions play a key role in the global C cycle as they represent the biggest reservoir of terrestrial C in the biosphere (Lal, 2004b). In agricultural soils, the adoption of the organic system, characterised by a diverse crop rotation scheme (including higher periods under grass-clover leys in the crop rotations) and application of compost/organic fertilisation sources, has been posited as an effective way to increase soil organic matter (SOM) inputs. This increment in SOM inputs can lead to improvements in soil quality, including its chemical, biological and physical properties, as well as to promote SOC accumulation (Zani *et al.*, 2020) (Chapter 2, 3 and 4). While chapters 2, 3 and 4 of this thesis and previous studies have confirmed the notion that the higher SOM inputs the higher SOC stocks, further evidence is needed to investigate whether these practices also affect SOM quality, i.e. its composition and stability.

SOM stability can be simply defined as the resistance of the SOC to decomposition/degradation. The decomposition/degradation of the SOC is affected by nature and composition (chemical and physical) of the input material, soil properties, biological activities, environmental conditions as well as the quantity of the inputs to the given ecosystem (Dixon *et al.*, 1994; Trumbore, 1997). The resistance of SOC to decomposition/degradation can be controlled by various biological, physicochemical and structural factors including its disconnection from microbes, soil aggregation and physical protection as well as chemical recalcitrance, where the SOC-mineral association is considered a significant factor controlling SOM stability (Lützow *et al.*, 2006; Schmidt *et al.*, 2011; Keil & Mayer, 2013; Cloy *et al.*, 2014; Basile-Doelsch *et al.*, 2020). Overall, it has been suggested that if SOM consists of easily degradable material (e.g. straw) its decomposition rate is high because microorganisms decompose it relatively rapidly (Powlson *et al.*, 2011a). On the other hand, if SOM consists of stabilised material (e.g. farmyard manure), its decomposition rate is lower and therefore it has longer turnover rates in soil environments (Li *et al.*, 2018). In agricultural soils with different crop rotation schemes and fertilisation sources (e.g. conventional and organic systems), changes in the inputs (i.e. the amount of SOM) and outputs of SOM (through decomposition/degradation processes) are expected and thus knock-on effects on SOC stocks and stabilisation. Understanding such changes in proportions of SOC within pools with differing stability is crucial for the sustainability of agricultural systems as it controls soil-atmosphere C fluxes. However, although a relatively high amount of data exists comparing conventional *vs.* organic systems (Leifeld &

Fuhrer, 2010; Gomiero *et al.*, 2011; Gattinger *et al.*, 2012, 2013; Leifeld *et al.*, 2013; Kirchmann *et al.*, 2016), the results are often contradictory and do not consider SOM composition and stabilisation. This can be mostly because of both the complexity structure/composition and the high variability of SOM in the environment, which makes its stability assessment challenging.

Several methods have been developed to assess SOM composition and stability. A few examples of analytical techniques used to this aim are i) physical fractionation of SOM into organic and mineral-associated fractions, ii) thermogravimetry-differential scanning calorimetry coupled with quadrupole mass spectrometry (TG-DSC-QMS) and iii) pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC-MS). Nuclear magnetic resonance (NMR) spectroscopy and radiocarbon dating are other good examples of methods that have been also critical to understanding SOM composition and turnover times over the years. The quantification of organic and mineral-associated fractions through ultrasonication process and density separation is a technique used for the understanding of the soil C dynamics, turnover and stability (Christensen, 1992). In this particular approach, SOM fractions can be associated with either a cellulosic material (composed of polysaccharides) or to a lignin-like material (composed of a mixture of aromatic, cross-linked phenolic C compounds) (Ranalli *et al.*, 2001; Vane *et al.*, 2001; Dell'Abate *et al.*, 2002; Strezov *et al.*, 2004). Particulate organic matter fractions (POM) (i.e. the more readily/labile available component for decomposition) represents the former, while the latter is composed of a more refractory (stable to decomposition) material characterised by mineral-associated organic matter fraction (Manning *et al.*, 2005). The use of thermal analytical techniques (i.e. TG-DSC-QMS), in turn, use time and/or programmed temperature to monitor physical and/or chemical properties of a sample (Langier-Kuźniarowa, 2002). In this sense, SOM stability can be defined as a function of its chemical composition and the degree of humification and mineral association of the SOM (Plante *et al.*, 2009). As for the fractionation approach, this technique can provide insight into the proportions of active and more stable SOM components (Lopez-Capel *et al.*, 2005). Coupling TG-DSC into a QMS allows the chemical identification, characterisation and proportions of major evolved gas species (Lopez-Capel *et al.*, 2006). In short, the thermal decomposition before 200 ºC can be associated with the content of physically absorbed water, changes from 200 ºC to approximately 350 ºC will release relatively volatile and labile forms of C whilst temperatures at around 350-650 ºC will release more recalcitrant and refractory C forms, which are related to lignin and related biopolymers (Plante *et al.*, 2009). Soil carbonate minerals, if any, will be decomposed at 750-900 ºC. Variability in shape, area, and temperature of TG-DSC-QMS can reveal differences in thermal stability and chemical structure of the sample. As stated before by Manning et al. (2005), this technique allows the determination of all the C present within a sample in a single heating analysis. Lastly, the use of Py-GC-MS can provide detailed molecular structural information, which is not provided by the other two techniques, in a simple and rapid manner. In short, it aims to degrade macromolecules into small fragments (representative to the large macromolecules) and simultaneously identify structural information (Meier & Faix, 1992; Leinweber & Schulten, 1993). Whilst Py-GC-MS has allowed comparison of SOM produced under different environments and land uses (Buurman & Roscoe, 2011; Oliveira *et al.*, 2016), the highly polar pyrolysis products from biopolymers can be either difficult or impossible to detect by Py-GC-MS analysis (Challinor, 1989; Kaal & Janssen, 2008). In this sense, on-line thermally assisted hydrolysis and methylation (THM) in the presence of tetramethylammonium hydroxide (TMAH) has been used together with Py-GC-MS. Accordingly, phenolic compounds formed from the TMAH-induced cleavage of ether and ester bonds, which are present in soils by plant-derived macromolecular organic C, can be also characterised (Mason *et al.*, 2012).

In this context, in order to fully understand the fate of SOC upon different agricultural systems (e.g. conventional *vs.* organic), qualitative (size separation of SOM into fractions and chemical composition of SOM) and quantitative (SOC stocks) data must be investigated. Combining qualitative and quantitative data could provide novel insights about the underlying mechanisms for SOC stabilisation that are not fully understood. It could also help to elucidate the largely unknown processes in subsoil layers (i.e. > 0.30 m depth), which might represent more stable and long SOC turnovers as a result of reduced microbial activities, suboptimal environmental conditions, energy scarcity and less accessibility to the SOM (Rumpel & Kögel-Knabner, 2010). However, to the best of our knowledge, there are no investigations of SOM composition and stability comparing the components of conventional and organic agricultural systems (e.g. crop rotation schemes and fertility sources) that included both qualitative and quantitative data, especially considering long-term experiments and subsoil layers.

The objectives of this study were to i) assess SOC and nitrogen (N) stock changes in the top- (0-0.30 m) and subsoil layers (0.30-0.60 m) after one complete cycle under conventional and organic rotation scheme associated with different fertilisation sources (mineral *vs.* compost), and ii) characterise the SOM composition and stabilisation by using SOM physical fractionation, TG-DSC-QMS and Py-GC/MS-TMAH analyses.

5.2 Materials and Methods

5.2.1 Field site, experimental design, and treatments

The study was conducted at the Nafferton Factorial Systems Comparison (NFSC) trial based at Newcastle University's Nafferton Farm, located 12 miles west of Newcastle upon Tyne in north-east England (54º59'09''N; 1º43'56''W, 60 m a.s.l). A detailed description of the farm can be found in Chapter 2, section 2.2.1.

The NFSC is a long-term field experimental trial established in 2001. Likewise for the other fields of the farm, the soil in the NFSC is classified predominantly as a Dystric Stagnosol (WRB, 2015), slowly permeable, seasonally wet, acidic loamy and clayey soil that is naturally low in fertility (Farewell *et al.*, 2011; Cranfield University, 2021). Analysis of SOM at the start of the experiment indicated an average SOC content of ~3% (Cooper *et al.*, 2011; Bilsborrow *et al.*, 2013). The soil mineralogy composition across the farm is predominantly composed of 1:1 clay mineral (Kaolinite) and residual accumulation of Quartz, with also a few occurrences of Illite, Nacaphite, and other Feldspars, particularly in subsoil layers (> 0.30 m) (Table A3.1, Appendix 3). According to the Köppen classification system, the site experiences a marine west coast climatic condition, with the average annual temperature and total annual precipitation were 8.6 ºC and 638.6 mm respectively, with a maximum monthly temperature of 22 ºC and a minimum of 0 ºC (https://www.metoffice.gov.uk).

The NFSC trial was settled after two years of grass-clover ley in order to achieve uniformity in the area and a baseline for each system. The trial compares crop rotation schemes, fertility sources and crop protection in an 8-year rotation, which is based on the guidelines of the current UK conventional farming best practices (Red Tractor Assurance, 2015) and requirements for certified organic production (Soil Association, 2019). There are two levels of crop rotation schemes (RS) i) conventional rotation (CONV-RT), characterised by cereal intensive crops with 2 years of grass-clover ley period at the end of the cycle and ii) organic rotation (ORG-RT), which is based on a more diverse and legume-rich cycle with 3 years of grass-clover ley period at the end of the rotation. Likewise, fertility sources (FS) are divided into two levels, mineral (MINE) *vs.* compost (COMP) fertilisation, where the first is based on inorganic NPK fertiliser and the latter use only composted dairy manure as a fertility amendment to give the recommended rate of N for each crop. Crop protection is compared by the application of herbicides, fungicides and insecticides typical of conventional agriculture against those methods that are permitted in the standard organic guidelines (e.g. control of weeds by tractormounted hoes, inter-row cultivators/ridges, tine-weeders, and occasionally hand weeding). In short, the experimental trial consists of four replicated main blocks (122 x 122 m^2), each of which is comprised of four sub-blocks (24 x 112 m^2), which are further divided into eight plots of 12 x 24 m^2 size totalling 32 plots per block. The position of treatments within each sub-block and plot of the four main blocks was randomised and the crop rotation was staggered at the beginning of the experiment so that each phase of the rotation was replicated in time. Accordingly, each sub-block consists of a different experiment. To avoid contamination between the treatments, grass-clover strips of 10 m are used in the edges of the main blocks as well as in between the blocks, whilst a strip of 2 metres separates the plots. Figure 5.1 shows one main block of the experimental trial and the split of crop rotation scheme, fertility source and crop protection.

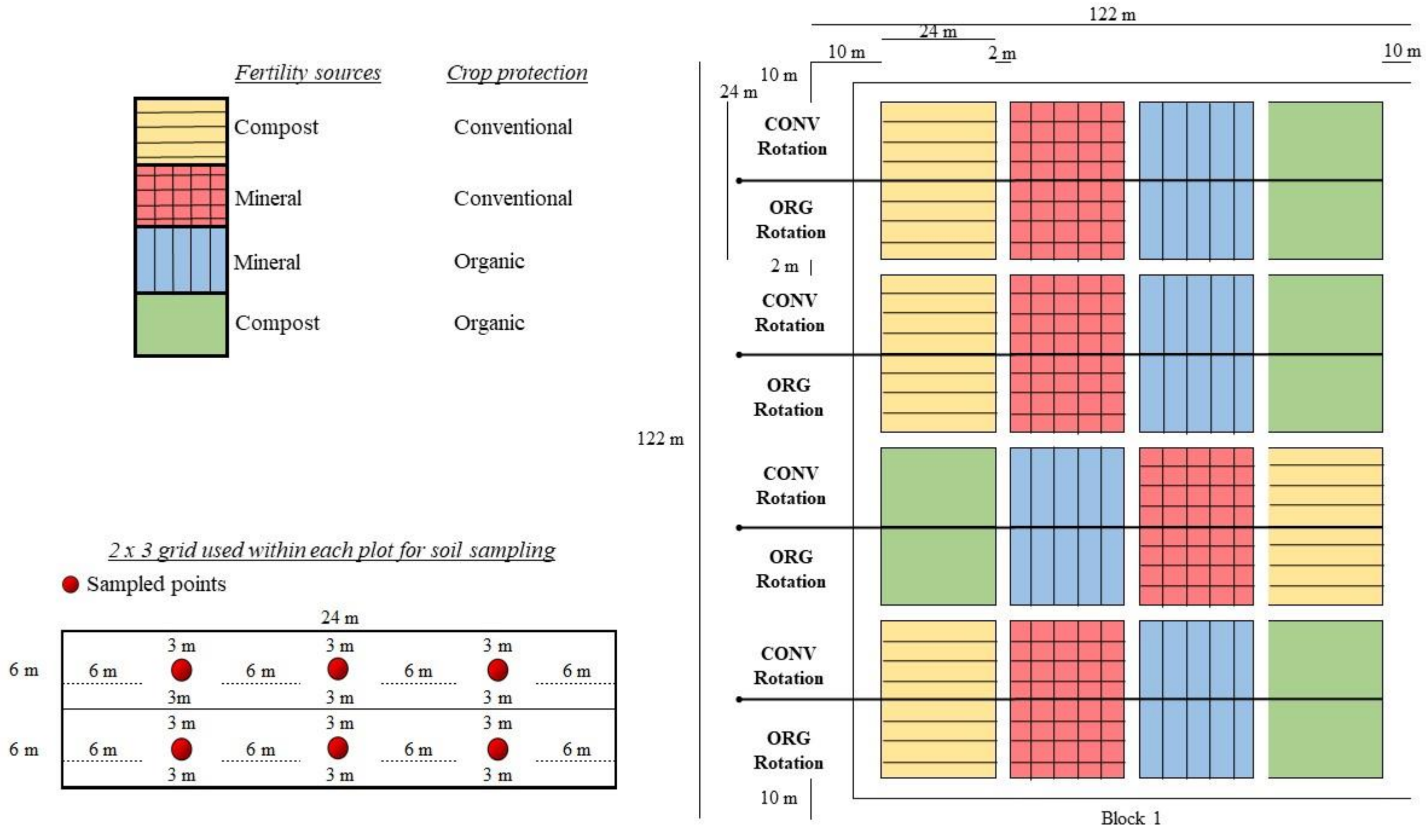

Figure 5.1 Nafferton Factorial Systems Comparison (NFSC) block layout and experimental design used for soil sampling. The 2 x 3 grid is zoomed in for one plot layout (12 x 24 m). Schematic soil sampling location within each plot is represented by red points. Crop rotation scheme is divided into conventional (CONV) and organic (ORG) rotation levels.

In this study, RS (CONV-RT *vs.* ORG-RT) and FS (MINE *vs.* COMP) were tested within the same crop protection (conventional) regime. The design of the NFSC trial allowed the comparison of the main treatments (i.e. crop rotation scheme and fertility source) as well as four combination of treatment factors: conventional crop rotation scheme with mineral fertilisation source (CONV-M), conventional crop rotation scheme with compost fertilisation source (CONV-C), organic crop rotation scheme with mineral fertilisation source (ORG-M) and organic crop rotation scheme with compost fertilisation source (ORG-C). As the comparison was made considering one completed cycle of rotation, the year was also considered a factor and therefore all treatments and combination are replicated into two years (2011, first year of the rotation and 2018, last year of the rotation). Further details of treatments including crop grown in the rotation cycle are given in Table 5.1.

Table 5.1 Historical summary of crop sequence grown at Nafferton Factorial Systems Comparison (NFSC) trial 2008-2018 for the crop rotation scheme (RS) (conventional-CONV-RT *vs.* organic-ORG-RT) and fertility source (FS) (mineral-MINE *vs.* compost-COMP) treatment plots, and further details including crop varieties, fertilisation sources, crop protection and specific information on management practices.

RS	FS	2008	2009	2010	2011*	2012	2013	2014	2015	2016	2017	2018*	Further details
CONV-RT	MINE	W. Barley	Grass / Clover	Grass / Clover	Sp. Wheat	W. Wheat	W. Barley	Potato	W. Wheat	Spelt / Rye	Grass / Clover	Grass / Clover	Crop varieties: Winter Barley (*Hordeum vulgare*), Grass and Clover (*Trifolium repens and Trifolium pratense*), Spring and Winter Wheat (*Triticum aestivum*), Potato (*Sante*), Spelt (*Triticum spelta*) and Ryegrass (*Lolium perenne*). Annual fertilisation was conducted using ammonium nitrate, superphosphate and chloride, for N, P, K respectively. Conventional crop protection carried out using conventional herbicides, fungicides, and insecticides to weed control as well as seeds that were coated with commercial insecticide and fungicide dressing. Under wheat growing season, straw was baled and removed from the plots following harvest. Under grass and clover growing season, plots were subjected to harvest for silage three times. Under potato growing season, plots were cut prior to harvest and residues incorporated into the soil. Soil preparation before a new crop used ploughing and disking practices.
CONV-RT	COMP	W. Barley	Grass / Clover	Grass / Clover	Sp. Wheat	W. Wheat	W. Barley	Potato	W. Wheat	Spelt / Rye	Grass / Clover	Grass / Clover	The same RS, varieties and management practices as the CONV+MINE treatment but changing annual FS from inorganic NPK fertiliser to organic fertilisation sources, particularly by applying composted dairy manure and slurry.
ORG-RT	MINE	Grass / Clover	Grass / Clover	Grass / Clover	Sp. Wheat	Potato / Veg.	Peas / Beans	Potato / Veg	S. Barley	Grass / Clover	Grass / Clover	Grass / Clover	The same management practices and sources of fertilisation as the CONV+MINE treatment but changing RS from CONV to ORG with a more diverse and legume-rich cycle including vegetables such as cabbages (*Brassica oleracea*), lettuces (*Lactuca sativa*), onions (*Allium cepa*), carrots (*Daucus carota*), peas (*Pisum sativum*) and beans (*Phaseolus vulgaris*) as well as 3 years of grass-clover ley period at the end of the rotation instead of only 2 years.
ORG-RT	COMP	Grass / Clover	Grass / Clover	Grass / Clover	Sp. Wheat	Potato / Veg.	Peas / Beans	Potato / Veg	S. Barley	Grass / Clover	Grass / Clover	Grass / Clover	The same management practices and sources of fertilisation as the CONV+COMP treatment but changing RS as the same as ORG+MINE treatment.

*years in which soil samples were taken.

5.2.2 Soil sampling and sample preparation for soil analyses

Soil sampling was conducted in one experiment (i.e. one sub-block per main block, four replication) at the beginning of the rotation (March 2011) and at the last year of the rotation (March 2018). At both years, soil sampling was conducted in the plots during the grass-clover ley periods (i.e. in 2011, first year of the rotation, it was carried out just before planting and in 2018, last year of the rotation, just before harvest). In each one of the target treatments plots, six intact soil cores (0-0.90 m depth) were taken in 2 x 3 grid spaced at 6 m apart. This approach was carried out to encompass potential variability within the plots, and thus to avoid over- or under-estimate values. The soil cores were collected using a hydraulic soil sampler (Atlas Copco Ltd., Hemel Hempstead, Hertfordshire, UK) and a metallic tube (1 m length, 0.30 m inner diameter). In 2011, the collected cores were separated into two soil depth intervals (0-0.30 and 0.30-0.60 m) totalling 192 soil samples, whilst in 2018 collected cores were separated into three soil depth intervals (0-0.15; 0.15-0.30 and 0.30-0.60 m) totalling 288 samples. Each of the 480 soil samples was gently mixed and passed through a 4 mm sieve; large stones were removed and weighed plant remains were discarded. The weight of the sieved, fresh soil was then recorded. A subsample of the sieved soil (5 g) was used for determination of gravimetric water content. The soil bulk density (BD) was calculated using the core method adjusting for the weight and volume of large stones (Blake & Hartge, 1986). In order to equate the same number of samples between two-sampling year, the six soil samples from the same treatment plot, sampling year and depth interval were then combined into a composite sample. The 2018 samples from the depth intervals of 0-0.15 and 0.15-0.30 m were also combined in order to match the same depth intervals of 2011 (i.e. 0-0.30 and 0.30-0.60 m depth). This resulted in 64 composite soil samples, 32 for each sampled year, which were wet sieved through a 2 mm sieve and air-dried to a constant weight at a room temperature before further analyses. It is important to highlight that soil samples from 2011 were kept frozen before analysis while the 2018 samples were analysed as fresh samples. Whilst it is not expected that this difference in storage and process would major impact the chemical composition of the samples, this might result in minor differences in the results that cannot be avoided and therefore must be acknowledged by the reader of this thesis. Soil pH of composite samples was measured in H_2O (1:2.5 soil:solution), following analytical procedures described in Mc Lean, (1982).

5.2.3 Total carbon and nitrogen quantification and stocks calculation

For each composite sample, a subsample of approximately 0.05 g of dry soil was ground to a fine powder, using an agate mortar and pestle, sieved through a 150 μm sieve and then analysed for total carbon (C) and nitrogen (N) concentration by dry combustion method (Nelson & Sommers, 1996), post combustion and reduction tubes in an Elementary Vario Macro Cube analyser (furnace at 960 °C in pure oxygen). Helium gas was used during post combustion (900 ºC) and reduction (830 ºC) processes to carry off the oxygen used to burn the sample to the detectors. After every tenth sample, a set of standards of known C and N values was measured to ensure instrument calibration. Thermal analysis (Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry) described in detail in the Section 5.3.3, of the present chapter, showed that there was an absence or very low presence of carbonate minerals in the samples (Fig 5.7), therefore, total soil C concentration can be assumed to be total SOC.

SOC and N stocks per unit of area (Mg ha^{-1}) was calculated for each depth interval (i.e. 0-0.30 and 0.30-0.60 m) on an equivalent soil mass basis (Wendt & Hauser, 2013) using the 2011 samples as a reference. More details about the calculations and equivalent soil mass adjustments can be found in Chapter 1, Section 1.5. The difference in SOC and N stocks between 2011 and 2018 samples were used to calculate accumulation or reduction rate during one rotation cycle (i.e. in the 8-year period).

5.2.4 Physical fractionation of SOM

Physical fractionation of SOM was accomplished according to Christensen (1992) as described in Chapter 3, Section 3.2.4. The method distinguishes the soil particles into organic (particulate organic matter; POM > 53 μm) and mineral-associated fractions (heavy fraction and silt and clay fraction; HF > 53 μm and SC < 53 μm, respectively) by dispersion, wet sieving, flotation and sedimentation, followed by a subsequent mass balance check (Christensen, 1992, 2001). Briefly, 20 g of air-dried soil was sonicated in 70 mL of Milli-Q water at 500 W for 15 minutes (providing approximatelly13 J per sample or 144 J mL^{-1}) using an ultrasonic processor (Model VC-505; Sonics Vibra Cell). After sonication, the sample was wet sieved through a 53 μm sieve using Milli-Q water. The HF and POM fractions were retained in the sieve and were separated by flotation and sedimentation using Milli-Q water (1 g cm^{-3}).

This procedure generated 192 fraction samples (64 samples x 3 fractions). Each fraction was oven-dried at 40 ºC and their weights recorded. SOC concentration of each fraction was determined following the same preparation and dry combustion methods described in section 5.2.3 and Chapter 2, Section 2.2.4. For quality assurance, the final recovery of the soil mass was checked against the original 20 g and the recovery of the elemental analysis for the fractions were checked against SOC concentrations from the < 2 mm samples (Table 5.2 and Fig. 5.2). SOC concentration and the masses of each fraction was used for the calculation of SOC in each fraction and the results were reported on a per-kilogram-bulk-soil-basis (g C kg^{-1}). SOC concentrations of the individual fractions and their recovery soil masses are given in Table A3.2 (Appendix 3).

Table 5.2 Summary of the mean fractional soil mass recovery (g fraction kg^{-1} soil) under conventional and organic crop rotation schemes (CONV-RT and ORG-RT, respectively), mineral and compost fertilisation (MINE and COMP, respectively) and years of sampling (2011 and 2018), by organic matter fractions, particulate organic matter (POM > 53 μm), the heavy fraction (HF > 53 μm) and silt clay fraction (SC < 53 μm) and soil depth intervals, 0-0.30 and 0.30-0.60 m.

Depth m		POM (> 53 μm)	HF (> 53 μm) g kg^{-1}	SC (< 53 μm)	Mean Recovery %
0-0.30	CONV-RT	11.08 (0.54)	752.50 (8.05)	236.41 (8.03)	97.80 (0.16)
	ORG-RT	10.62 (0.43)	747.26 (6.25)	242.12 (6.34)	97.73 (0.16)
	MINE	11.14 (0.45)	758.18 (6.65)	230.68 (6.68)	97.71 (0.17)
	COMP	10.56 (0.52)	741.58 (7.17)	247.85 (7.18)	97.82 (0.15)
	2011	11.15 (0.54)	760.50 (7.56)	228.35 (7.52)	97.53 (0.17)
	2018	10.55 (0.43)	739.26 (5.72)	250.19 (5.79)	98.00 (0.13)
0.30-0.60	CONV-RT	5.03 (0.46)	644.03 (14.06)	350.93 (13.94)	98.08 (0.14)
	ORG-RT	4.46 (0.47)	643.05 (8.94)	352.48 (8.80)	97.89 (0.19)
	MINE	4.57 (0.38)	649.42 (11.49)	346.01 (11.41)	98.13 (0.14)
	COMP	4.92 (0.54)	637.67 (11.88)	357.40 (11.72)	97.84 (0.18)
	2011	4.05 (0.19)	650.55 (13.64)	345.41 (13.62)	97.83 (0.16)
	2018	5.45 (0.58)	636.55 (9.22)	358.00 (9.00)	98.14 (0.16)

Data are measured mean values (n=32 for crop rotation schemes, fertility sources and years of sampling within individual fractions and soil depth intervals). Standard error of the mean in parentheses.

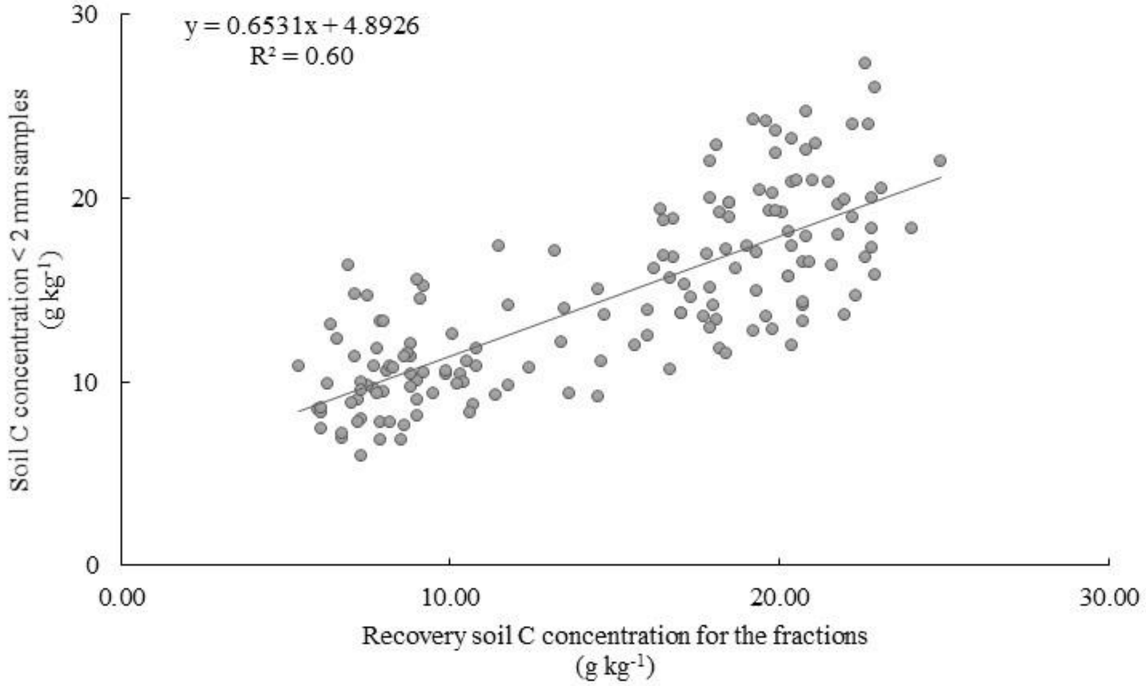

Figure 5.2 Relationship between soil organic carbon (C) concentration of each < 2 mm soil sample used in the physical fractionation and their recovery of the elemental analysis for the fractions, i.e. sum of the C concentration of the fractions related to their mass fraction.

5.2.5 Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry (TG-DSC-QMS)

Thermal analysis was used to examine the relative proportions of different 'fractions' of C in the soil samples, termed the labile, recalcitrant and refractory fractions following the methods described by Lopez-Capel *et al*, (2005) and Fernández *et al*, (2012). The samples were analysed using thermogravimetry (TG) and differential scanning calorimetry (DSC), combined with quadrupole mass spectrometry (QMS) analysis of the gas evolved during thermal decomposition. While TG and DSC data quantifies the weight change and the gain/loss in energy of the sample during heating, QMS analysis provides data on the chemical composition of the gaseous combustion products, which can be used to characterise the sample in terms of its organic and inorganic components.

Sixteen soil samples were selected for TG-DSC-QMS analysis, one composite soil sample per treatment per depth per year (i.e. considering the combination of treatment factors, i) conventional crop rotation scheme with mineral fertilisation source (CONV-M); ii) conventional crop rotation scheme with compost fertilisation source (CONV-C); iii) organic crop rotation scheme with mineral fertilisation source (ORG-M); and iv) organic crop rotation scheme with compost fertilisation source (ORG-C). The samples were selected with reference to the mean total C (TC) content obtained by the dry combustion method such that the sample selected for analysis had a TC content closest to the mean (Table 5.3). The selected samples were air-dried at ambient temperature, ground to a fine powder, using an agate mortar and pestle, and sieved through a 150 µm sieve prior to analysis.

An aliquot of the sample (ca. 50 mg) was weighed accurately into an alumina crucible and analysed using a Netzsch Jupiter STA 449C thermogravimetry-differential scanning calorimetry (TG-DSC) analyser. Samples were heated from 25 °C to 1000 °C at a rate of 10 °C min^{-1} in an (oxidizing) atmosphere of 20% oxygen in helium (purge gas, flow rate 30 mL min^{-1}). The protective gas was helium (flow rate of 20 mL min^{-1}). TG and DSC data were acquired and processed using Netzsch Proteus 61 software and then converted into Excel format for further processing. Variation of the TG-DSC analysis was less than ±5% for calcium oxalate. For mass spectrometric analysis, the evolved gas stream was sampled continuously through a fused silica capillary transfer line connected to a Netzsch Aeolos 403C quadrupole mass spectrometer (QMS). Adapter heads and the transfer line (between the Jupiter and Aeolos) were at 150 °C. The QMS was operated in full scan mode over the range *m/z* 10-160 and the dwell time was 0.2 s, giving a sampling rate of ca. 1 scan per 5 °C increase in temperature. Mass spectrometric data were acquired and processed using Aeolos software.

In short, TG-DSC was used to determine the relative proportions of labile, recalcitrant and refractory C fractions by comparing the total weight loss over the temperature range 200-750 °C (Exotot) with its relative proportions from the defined intervals: i) 200-350 ℃ (Exo 1), ii) 350-500 ℃ (Exo 2) and iii) 500-750 ℃ (Exo 3). These temperatures were established based on the first derivatives of the DSC traces (i.e. distinct exothermic reactions), which also agreed with the methods described by Dell'Abate *et al*, (2000), (2002). The curves of the gas evolution (i.e. the QMS system) were interpreted in order to assess the contribution of individual peaks into the overall trace (Arenillas *et al.*, 1999). The main ion of interest in the QMS analysis was *m/z* 44 (carbon dioxide). Quantitative data for the abundance of *m/z* 44 in the evolved gas during heating of the sample was converted into ASCII format and then into Excel format for further processing. For each sample, the QMS data for the selected ion (*m/z* 44) were normalised to the total ion intensity to allow comparison of different samples (Arenillas *et al.*, 1999). The corresponding variation in abundance of the *m/z* 44 with the variation in TG and DSC curves was used to verify the organic origin of the three fractions and differentiate these from the decomposition of inorganic carbon. The same intervals considered in the TG-DSC approach (200-350 ℃, 350-500 ℃, 500-750 ℃) were used to seek CO_2 peaks and to calculate the area under the peaks, representing the exact amount of C released. Additionally, we have used *m/z* 18 (water) to distinguish the different organic matter pools (Fig. 5.3).

Table 5.3 Mean soil organic carbon concentration (Mean SOC) for 0-0.30 and 0.30-0.60 m soil depth intervals at both 2011 and 2018 sampled years by the combination of treatment factors (conventional crop rotation scheme with mineral fertilisation source-CONV-M; conventional crop rotation scheme with compost fertilisation source-CONV-C; organic crop rotation scheme with mineral fertilisation source-ORG-M; and organic crop rotation scheme with compost fertilisation source-ORG-C) and the soil organic C concentration of each selected sample used for the Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry and the Pyrolysis-Gas Chromatography-Mass Spectrometry analyses.

Year		Mean SOC 0-0.30 m	Mean SOC 0.30-0.60 m	SOC chosen samples 0-0.30 m	SOC chosen samples 0.30-0.60 m
		g kg^{-1}			
2011	CONV-M	18.40 (0.69)	8.82 (0.60)	17.96	8.81
	CONV-C	16.82 (0.54)	8.37 (0.90)	17.00	7.78
	ORG-M	18.42 (1.16)	8.37 (0.39)	18.09	8.50
	ORG-C	18.00 (1.02)	7.62 (0.74)	18.41	7.35
2018	CONV-M	19.65 (0.42)	8.82 (0.48)	20.01	8.39
	CONV-C	19.10 (0.43)	9.05 (1.24)	18.77	10.8
	ORG-M	19.22 (0.82)	8.10 (0.43)	19.17	8.06
	ORG-C	19.72 (0.58)	8.82 (0.54)	19.58	8.28

Measured mean soil organic C concentration values for each year of sampling and depth intervals (n=4).

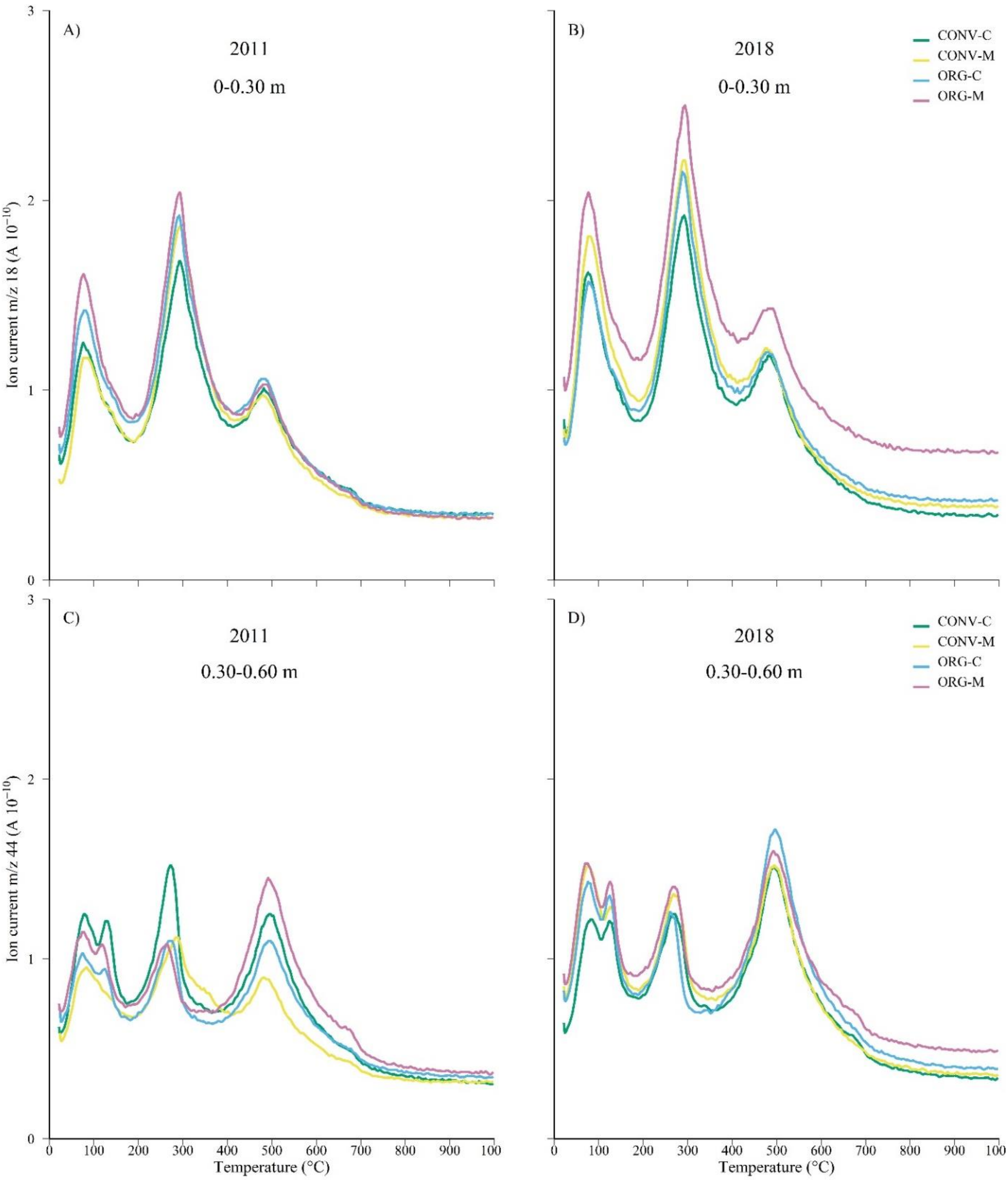

Figure 5.3 Ion current intensity for water (*m/z* 18) from the soil samples of combined treatment factors: conventional rotation with mineral fertilisation (CONV-M), conventional rotation with compost fertilisation (CONV-C), organic rotation with mineral fertilisation (ORG-M) and organic rotation with compost fertilisation (ORG-C) at 0-0.30 (A and B) and 0.30-0.60 m (C and D) soil depth intervals and different years of sampling 2011 (A and C) and 2018 (B and D).

5.2.6 Chemical extraction and analysis of soil samples by Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

The same sixteen soil samples used for TG-DSC-QMS were submitted to Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) analysis (Table 5.3). Prior to Py-GC-MS, the organic-soluble SOM was extracted. This organic extract was obtained from the soil using a Soxhlet extractor apparatus with a mixture of dichloromethane (DCM)/methanol (MeOH) (93:7, v/v). Briefly, 100 g of soil (in a thimble) and 450 mL of the DCM/MeOH mixture were extracted for 24 h. As the solvent is heated it vapours up to a distillation arm and floods into the thimble with the soil. The condensed warm solvent passes through the soil and the non-volatile compounds are dissolved into the solvent.

The solvent extracted solid residue remaining in the thimble was air-dried at room temperature and then subjected to Py-GC-MS together with on-line thermally assisted hydrolysis and methylation (THM) in the presence of tetramethylammonium hydroxide (TMAH) following adapted analytical procedures described by Abbott *et al*, (2013). For this, a sub-sample of ca. 13 mg of soil was accurately weighed into a deactivated stainless steel 50 μL 'Eco-cup' and a known amount of internal standard (5α-androstane) was added. Immediately prior to analysis, 5 μL of an aqueous solution of TMAH (25% w/w, Sigma-Aldrich) was added and the sample cup was loaded into the pyrolyser.

Pyrolysis was performed using a Frontier Laboratories Single-shot Pyrolyser Model PY-3030s. The pyrolyser was connected to an HP 6890 gas chromatograph (GC) and interfaced to an HP 5973 MSD. The pyrolysis temperature and time were 610 °C and 1 minute, respectively. The GC inlet was heated at 320 °C and the sample was injected in split mode with a split ratio of 30:1. Gas chromatographic separation of compounds was performed using a Phenomenex ZB-5MS (Torrance, CA, USA) fused silica capillary column (60 m x 0.25 mm i.D. x 0.25 μm film thickness). The GC oven temperature program was 50 °C (initial hold time 1 min.) then 4 °C min^{-1} to 320 °C (final hold time 10 min). Helium was used as carrier gas at a constant flow rate of 1 mL min^{-1}. The GC-MS was operated in full scan mode, scanning the range *m/z* 50-650. Operating conditions were; electron voltage 70 eV, emission current 35 μA, source temperature 230 °C, quadrupole temperature 150 °C, multiplier voltage 2200 V and interface temperature 320 °C. This analytical process was conducted in triplicate for each sample so that analytical reproducibility could be checked.

Data acquisition and processing were performed using Agilent Chemstation software and pyrolysis products were identified using the Chemstation NIST05 library of mass spectra. All prominent, identifiable products of each sample were quantified relative to the internal standard and reported as a proportion of the total peak area of the identified characteristic ions (i.e. *m/z* values). The identified products were grouped into *n*-alkanes, *n*-alkenes, aromatics, benzofurans, carbohydrates, fatty acids, lignin phenols, N containing compounds, phenols and polycyclic aromatic hydrocarbons (polyaromatics). These groups were defined based on the origin and chemical similarity of the identifiable products.

5.2.7 Statistical analyses

Linear mixed-effects models (LME) were fitted to test the effects of crop rotation schemes (RS) (conventional-CONV-RT *vs.* organic-ORG-RT), fertility sources (FS) (mineral-MINE *vs.* compost-COMP), year of sampling (YR) (2011 and 2018) and their interaction (RS*FS*YR) on active acidity (pH), soil bulk density (BD), soil organic C concentration (SOC), soil N concentration (N), soil organic C stocks (SOC stock), soil N stocks (N stocks) and C in the SOM fractions (POM > 53 μm, HF > 53 μm and SC < 53 μm). Results from the Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry (TG-DSC-QMS) and the Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) analyses were only used for description and therefore not statistically assessed.

For all LME models, fixed effects were crop rotation schemes, fertility sources, year of sampling and their three-way interaction. The random effect was defined as block, crop rotation schemes and year of sampling due to the nested structure of the NFSC trial. The analyses were conducted separately for each depth interval (i.e. 0-0.30 and 0.30-0.60 m). Assumptions were checked for normality and equal variances by examining the QQ plots of residuals (for both fixed and random effects compartments of the model) and scatterplots of standardised against fitted values. The data were Tukey's Ladder of Powers transformed when visual breakdowns in LME model assumptions were revealed by residual plots. To test the significance of the fixed effects on the dependent variables, models were compared with and without the factor of interest using the likelihood ratio tests (LRT) approach. When the interaction term in the model was significant, Tukey’s HSD post-hoc test was carried out and a significant effect was determined at $p < 0.05$. All statistical analysis was carried out in the R programming language 3.4.3 (R Development Core Team, 2019) using the additional packages, ape (Paradis *et al.*, 2004), nlme (Pinheiro. *et al.*, 2018), plyr (Wickham, 2011), ggplot2 (Wickham, 2009), and multcomp (Hothorn *et al.*, 2008).

5.3 Results

5.3.1 Soil pH, BD and SOC and N concentrations and stocks

For the 0-0.30 m depth, soil pH was not affected by any of the treatments (RS, FS and/or YR). Soil BD was higher under ORG-RT compared to CONV-RT (LRT = 29.96; $p < 0.01$) (Table 5.4). There was an interactive effect between FS and YR affecting SOC concentrations and stocks (LRT = 4.70; p=0.03 and LRT = 5.19; p = 0.02, respectively) (Table 5.4 and 5.5). In both cases, COMP fertilisation significantly increased SOC concentration and stocks over time (i.e. from 2011 to 2018) from 17.41 ± 0.58 to 19.41 ± 0.35 g kg^{-1} and from 54.81 ± 1.98 to 60.86 ± 1.11 Mg ha^{-1}, respectively. This result suggests SOC stock accumulation mean of 11% at 0-0.30 m soil depth every 8-year under COMP fertilisation, which translates into SOC accumulation rate of 0.76 Mg ha yr^{-1}. MINE fertilisation, on the other hand, increased SOC concentrations and stocks over the years from 18.41 ± 0.92 to 19.44 ± 0.62 g kg^{-1} and from 57.74 ± 2.03 to 60.42 ± 1.48 Mg ha^{-1}, respectively (i.e. SOC stock accumulation mean of approximately 5% and C accumulation rate of 0.33 Mg ha yr^{-1}), which was not statistically verified (Fig. 5.4A, C). SOC stocks were also higher in the ORG-RT compared with CONV-RT (approximately 5%), regardless of the FS (MINE or COMP) or YR (2011 or 2018) (LRT = 4.45; p = 0.03) (Table 5.5). In an 8-year rotation, this translates into a SOC accumulation rate of 0.31 Mg ha yr^{-1}. In turn, soil N concentration and stocks at 0-0.30 m soil depth were only affected by YR, indicating that irrespective of RS (CONV-RT or ORG-RT) or FS (MINE or COMP fertilisation), soil N concentrations and stocks in the 2018 samples outperformed the 2011 samples (LRT = 19.71; $p < 0.01$ and LRT = 17.56; $p < 0.01$, for soil N concentration and stocks, respectively) (Table 5.4 and 5.5).

For deeper soil layers (0.30-0.60 m), pH was not affected by RS or FS or YR. There was an interaction between RS and FS altering soil BD (Table 5.4). Overall, soil BD was always higher under ORG-RT regardless of the FS applied. However, the combination of CONV-RT and COMP fertilisation significantly increased soil BD, whereas under ORG-RT the use of COMP fertilisation slightly decreased soil BD (LRT = 4.27; p = 0.04) (Fig. 5.4D). Likewise, in the topsoil (i.e. 0-0.30 m), an interactive effect between FS and YR was found affecting SOC concentrations (LRT = 4.47; p = 0.03) (Table 5.4). In this case, however, whilst COMP fertilisation increased SOC concentrations over time (from 2011 to 2018) from 8.00 ± 0.27 to 8.94 ± 0.33 g kg^{-1}, MINE fertilisation slightly decreased it from 8.60 ± 0.34 to 8.46 ± 0.33 g kg^{-1} (Fig. 5.4C). SOC stocks were only affected by RS (LRT = 6.41; p = 0.01), where ORG-RT showed higher SOC stocks than CONV-RT regardless of the FS or YR (Table 5.5). As for the topsoil layer (0-0.30 m), soil N concentration and stocks were significant higher in 2018 compared to 2011 (LRT = 23.23; $p < 0.01$ and LRT = 15.32; $p < 0.01$ for soil N concentration and stocks, respectively) (Tables 5.4 and 5.5).

Table 5.4 Effects of crop rotation scheme (RS) (conventional-CONV-RT *vs.* organic-ORG-RT), fertility sources (FS) (mineral-MINE *vs.* compost-COMP) and years of sampling (YR) (2011 and 2018) and their interaction on active acidity (pH), soil bulk density (BD), soil organic carbon (SOC) concentration and soil nitrogen (N) concentration at 0-0.30 and 0.30-0.60 m soil depth intervals.

Depth m		pH H_2O	BD Mg m^{-3}	SOC g kg^{-1}	N g kg^{-1}
0-0.30	CONV-RT	6.30 (0.04)	1.21 (0.02)	18.49 (0.36)	1.59 (0.07)
	ORG-RT	6.37 (0.03)	1.34 (0.02)	18.84 (0.45)	1.50 (0.05)
	MINE	6.34 (0.05)	1.27 (0.03)	18.93 (0.39)	1.60 (0.07)
	COMP	6.33 (0.04)	1.29 (0.02)	18.41 (0.42)	1.49 (0.06)
	2011	6.33 (0.05)	1.27 (0.02)	17.91 (0.43)	1.41 (0.05)
	2018	6.32 (0.03)	1.28 (0.03)	19.43 (0.27)	1.68 (0.06)
	RS	LRT=1.83; p=0.18	LRT=29.96; **p<0.01**	LRT=3.05; p=0.08	LRT=0.53; p=0.47
	FS	LRT=0.02; p=0.88	LRT=1.91; p=0.17	LRT=7.91; **p<0.01**	LRT=2.90; p=0.09
	YR	LRT=0.03; p=0.87	LRT=0.11; p=0.73	LRT=24.79; **p<0.01**	LRT=19.71; **p<0.01**
	RS*FS	LRT=1.79; p=0.18	LRT=0.21; p=0.64	LRT=2.56; p=0.11	LRT=1.05; p=0.31
	RS*YR	LRT=0.01; p=0.99	LRT=0.10; p=0.75	LRT=0.83; p=0.36	LRT=0.08; p=0.78
	FS*YR	LRT=3.55; p=0.06	LRT=0.15; p=0.70	LRT=4.70; **p=0.03**	LRT=0.74; p=0.39
	RS*FS*YR	LRT=0.30; p=0.58	LRT=0.01; p=0.94	LRT=0.01; p=0.94	LRT=0.01; p=0.94
0.30-0.60	CONV-RT	7.11 (0.02)	1.35 (0.01)	8.77 (0.39)	0.61 (0.03)
	ORG-RT	7.12 (0.02)	1.50 (0.03)	8.23 (0.27)	0.56 (0.02)
	MINE	7.10 (0.03)	1.42 (0.03)	8.53 (0.23)	0.60 (0.02)
	COMP	7.11 (0.02)	1.43 (0.03)	8.47 (0.42)	0.57 (0.03)
	2011	7.08 (0.02)	1.42 (0.03)	8.30 (0.32)	0.53 (0.02)
	2018	7.13 (0.02)	1.43 (0.03)	8.70 (0.35)	0.64 (0.01)
	RS	LRT=0.01; p=0.95	LRT=20.33; **p<0.01**	LRT=2.09; p=0.15	LRT=2.70; p=0.10
	FS	LRT=0.02; p=0.89	LRT=0.39; p=0.53	LRT=0.23; p=0.63	LRT=0.10; p=0.75
	YR	LRT=2.11; p=0.15	LRT=0.04; p=0.84	LRT=1.74; p=0.19	LRT=23.23; **p<0.01**
	RS*FS	LRT=1.21; p=0.27	LRT=4.27; **p=0.04**	LRT=0.08; p=0.78	LRT=3.11; p=0.08
	RS*YR	LRT=0.62; p=0.43	LRT=0.10; p=0.76	LRT=0.12; p=0.72	LRT=0.01; p=0.94
	FS*YR	LRT=0.61; p=0.43	LRT=0.09; p=0.77	LRT=4.47; **p=0.03**	LRT=1.64; p=0.20
	RS*FS*YR	LRT=0.01; p=0.97	LRT=0.05; p=0.82	LRT=0.72; p=0.40	LRT=4.13 p=0.06

Data are measured mean values (n=32 for crop rotation schemes, fertility sources and years of sampling within individual soil depth intervals). The standard error of the mean is in parentheses. Significance tests, using likelihood ratio test (LRT), are comparing models with or without the parameter of interest. Significant effects ($p < 0.05$) are shown in bold.

Table 5.5 Effects of crop rotation schemes (RS) (conventional-CONV-RT *vs.* organic-ORG-RT), fertility sources (FS) (mineral-MINE *vs.* compost-COMP), years of sampling (YR) (2011 and 2018) and their interaction on soil organic carbon (SOC) and soil nitrogen (N) stocks at 0-0.30 and 0.30-0.60 m soil depth intervals.

Depth m		SOC stock	N stock
		Mg ha^{-1}	
0-0.30	CONV-RT	57.20 (1.08)	4.98 (0.24)
	ORG-RT	59.71 (1.44)	4.79 (0.16)
	MINE	59.08 (1.26)	5.05 (0.23)
	COMP	57.83 (1.35)	4.71 (0.17)
	2011	56.27 (1.42)	4.46 (0.16)
	2018	60.64 (0.90)	5.30 (0.19)
	RS	LRT=4.45; **p=0.03**	LRT=0.02; p=0.88
	FS	LRT=5.02; **p=0.02**	LRT=2.14; p=0.14
	YR	LRT=16.95; **p<0.01**	LRT=17.56; **p<0.01**
	RS*FS	LRT=2.24; p=0.13	LRT=1.09; p=0.29
	RS*YR	LRT=0.14; p=0.71	LRT=0.03; p=0.86
	FS*YR	LRT=5.19; **p=0.02**	LRT=0.79; p=0.37
	RS*FS*YR	LRT=0.05; p=0.83	LRT=0.02; p=0.89
0.30-0.60	CONV-RT	33.84 (1.46)	2.69 (0.16)
	ORG-RT	36.70 (1.28)	2.81 (0.12)
	MINE	35.47 (1.17)	2.85 (0.15)
	COMP	35.06 (1.64)	2.64 (0.13)
	2011	34.23 (1.31)	2.44 (0.10)
	2018	36.30 (1.48)	3.05 (0.13)
	RS	LRT=6.41**; p=0.01**	LRT=1.55; p=0.21
	FS	LRT=0.14; p=0.71	LRT=1.79; p=0.18
	YR	LRT=3.47; p=0.06	LRT=15.32; **p<0.01**
	RS*FS	LRT=0.42; p=0.52	LRT=1.51; p=0.22
	RS*YR	LRT=0.04; p=0.85	LRT=0.31; p=0.58
	FS*YR	LRT=0.62; p=0.43	LRT=0.02; p=0.87
	RS*FS*YR	LRT=0.57; p=0.45	LRT=0.25; p=0.61

Data are measured mean values (n=32 for crop rotation schemes, fertility sources and years of sampling within individual soil depth intervals). The standard error of the mean is in parentheses. Significance tests, using likelihood ratio tests (LRT), are comparing models with or without the parameter of interest. Significant effects ($p < 0.05$) are shown in bold.

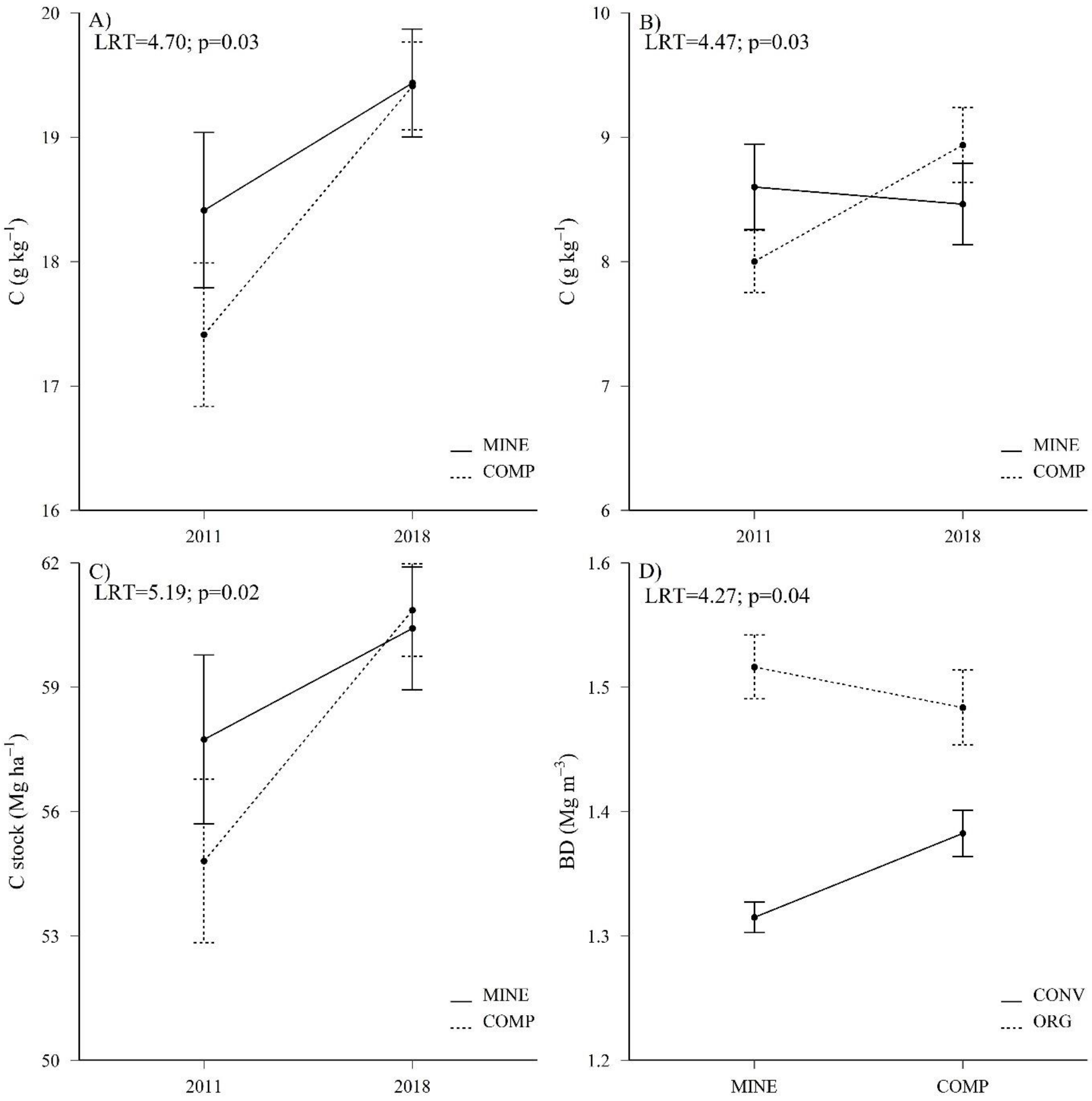

Figure 5.4 Interactive effects between fertility source (mineral-MINE and compost-COMP) and year of sampling (2011 and 2018) on: A) soil organic carbon (C) concentration in the 0-0.30 m; B) soil organic carbon concentration in the 0.30-0.60 m; C) soil organic carbon stocks in the 0-0.30 m and; D) interaction effect between fertility source and crop rotation scheme (conventional-CONV-RT and organic-ORG-RT) on soil bulk density (BD) in the 0.30-0.60 m. Data are measured mean values ± SE (n=8 for crop rotation schemes, fertility sources and years of sampling). Significance tests, using likelihood ratio test (LRT), are comparing models with or without the parameter of interest.

5.3.2 Soil organic carbon (C) distribution in soil organic matter (SOM) physical fractions

The average mass balance recovery of physical fractionation ranged between 97% and 98% (Table 5.2). Most of the soil mass was found in the HF (> 53 μm) fraction ranging from 63.6% to 76.0%. The total soil mass in the other two SOM fractions (i.e. POM and SC) ranged from 0.4% to 1.1% in the POM and from 22.8% to 35.8% in the SC fraction. Whilst the mass of HF fraction was higher than POM or SC fractions, higher SOC concentration was found in the SC (< 53 μm) than either of the other > 53 μm fractions (i.e. POM and HF), regardless of soil depth interval (0-0.30 or 0.30-0.60 m), RS, FS or YR (Table 5.6). For all SOM fractions and treatments, there was an overall decrease in SOC concentrations with an increase in the soil depth.

For the 0-0.30 m depth, although POM-C was numerically higher in 2011 than in 2018 samples, indicating thus a potential trend towards decreased POM-C, it was not statistically significant (LRT = 0.37, p = 0.54). The MINE fertilisation had higher SOC concentration in the HF (> 53 μm) fraction compared to the COMP fertilisation (LRT = 3.71; p = 0.05). In 2018, SOC concentration was higher in the SC fraction compared to 2011 (LRT = 4.63; p = 0.03) (Table 5.6).

For the 0.30-0.60 m depth, POM was not affected by RS, FS or YR (p > 0.05). The HF (> 53 μm) fraction was affected by YR, showing that in 2011 HF-C was higher compared to 2018 (LRT = 4.20; p = 0.04) irrespective of the RS and FS. In the same depth interval (i.e. 0.30-0.60 m), FS and YR interacted resulting in an increased SC-C over time (i.e. from 2011 to 2018) from 5.60 ± 0.48 to 6.26 ± 0.27 g C kg^{-1}under MINE fertilisation, whilst under COMP fertilisation SC-C decreased over time from 6.22 ± 0.53 to 5.77 ± 0.65 g C kg^{-1} (LRT = 3.96; p = 0.04) (Fig. 5.5).

Table 5.6 Effects of crop rotation schemes (RS) (conventional-CONV-RT *vs.* organic-ORG-RT), fertility sources (FS) (mineral-MINE *vs.* compost-COMP), years of sampling (YR) (2011 and 2018) and their interaction on soil organic carbon concentrations (g per kg^{-1} soil) in the organic fraction (particulate organic matter-POM > 53 μm), the heavy fraction (HF > 53 μm) and a mineral-associated fraction (silt and clay fraction-SC < 53 μm) at 0-0.30 and 0.30-0.60 m soil depth intervals.

Depth m		POM (> 53 μm)	HF (> 53 μm)	SC (< 53 μm)
			g kg^{-1}	
0-0.30	CONV-RT	1.24 (0.05)	6.68 (1.03)	9.59 (0.55)
	ORG-RT	1.34 (0.09)	6.78 (0.95)	9.14 (0.37)
	MINE	1.28 (0.06)	7.86 (1.17)	9.22 (0.42)
	COMP	1.30 (0.08)	5.60 (0.64)	9.51 (0.52)
	2011	1.34 (0.09)	6.27 (1.06)	8.86 (0.53)
	2018	1.23 (0.04)	7.19 (0.90)	9.87 (0.37)
	RS	LRT=0.44; p=0.50	LRT=0.12; p=0.73	LRT=1.05; p=0.30
	FS	LRT=0.01; p=0.95	LRT=3.71; **p=0.05**	LRT=0.39; p=0.53
	YR	LRT=0.37; p=0.54	LRT=1.05; p=0.30	LRT=4.63; **p=0.03**
	RS*FS	LRT=0.27; p=0.60	LRT=1.27; p=0.26	LRT=3.00; p=0.08
	RS*YR	LRT=0.01; p=0.98	LRT=0.01; p=0.93	LRT=0.74; p=0.39
	FS*YR	LRT=0.01; p=0.95	LRT=0.73; p=0.39	LRT=3.04; p=0.08
	RS*FS*YR	LRT=0.20; p=0.66	LRT=2.40; p=0.12	LRT=1.81; p=0.18
0.30-0.60	CONV-RT	0.61 (0.11)	5.41 (1.00)	6.10 (0.30)
	ORG-RT	0.44 (0.03)	4.24 (0.47)	5.83 (0.19)
	MINE	0.45 (0.03)	5.69 (0.98)	5.93 (0.20)
	COMP	0.61 (0.11)	3.96 (0.45)	5.99 (0.29)
	2011	0.47 (0.04)	5.66 (0.98)	5.91 (0.26)
	2018	0.58 (0.10)	3.99 (0.45)	6.01 (0.24)
	RS	LRT=2.19; p=0.14	LRT=0.10; p=0.75	LRT=1.42; p=0.23
	FS	LRT=1.36; p=0.24	LRT=2.51; p=0.11	LRT=0.17; p=0.68
	YR	LRT=0.60; p=0.44	LRT=4.20; **p=0.04**	LRT=1.36; p=0.24
	RS*FS	LRT=0.02; p=0.88	LRT=2.68; p=0.10	LRT=0.03; p=0.86
	RS*YR	LRT=1.08; p=0.30	LRT=1.34; p=0.25	LRT=1.90; p=0.17
	FS*YR	LRT=2.35; p=0.12	LRT=2.05; p=0.15	LRT=3.96; **p=0.04**
	RS*FS*YR	LRT=0.07; p=0.79	LRT=3.80; p=0.06	LRT=2.03; p=0.15

Data are measured mean values (n=32 for crop rotation schemes, fertility sources and years of sampling within individual fractions and soil depth intervals). Standard error of the mean is in parentheses. Significance tests, using likelihood ratio tests (LRT), are comparing models with or without the parameter of interest. Significant effects (p < 0.05) are shown in bold.

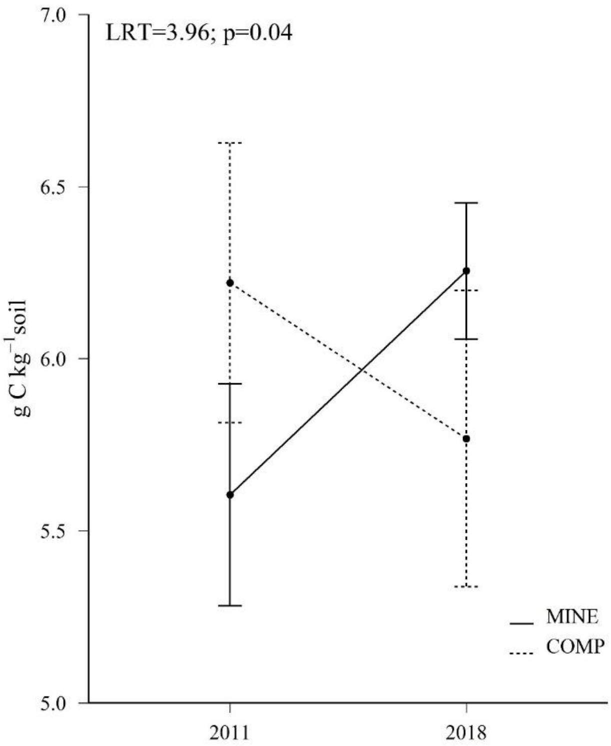

Figure 5.5 Interactive effects between fertility source (mineral-MINE and compost-COMP) and year of sampling (2011 and 2018) on silt and clay fraction (SC < 53 μm) at 0.30-0.60 m soil depth interval. Data are measured mean values ± SE (n=8 for fertility sources and years of sampling). Significance tests, using likelihood ratio test (LRT), are comparing models with or without the parameter of interest.

5.3.3 Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry (TG-DSC-QMS)

Total weight loss and relative weight loss from different temperature intervals (Exo 1 – 200-350 °C; Exo 2 – 350-500 °C; and Exo 3 – 500-750 °C), which represent material loss during heating (e.g. labile, recalcitrant and refractory), are given in Table 5.7. For the 0-0.30 m depth, soil samples showed discrete weight loss variability between the treatments, with labile (Exo 1) and recalcitrant/refractory (i.e. the sum of Exo 2 + Exo 3) fractions being evenly distributed within the samples (approximately 50/50). In general, the order of total weight loss (Exotot) from the higher to the lower was CONV-M 2018 > ORG-C 2018 > ORG-M 2011 > ORG-M 2018 > CONV-C 2018 > ORG-C 2011 > CONV-M 2011 > CONV-C 2011. More specifically, ORG-RT, MINE fertilisation and samples collected in 2018 showed a slightly more labile organic matter compared to their counterparts CONV-RT, COMP fertilisation and samples collected in 2011 (Exo 1). Likewise, ORG-RT and samples collected in 2018 showed a slightly more refractory organic matter compared to their counterparts CONV-RT and samples collected in 2011 (i.e. Exo 2 + Exo 3), while COMP fertilisation outperformed MINE fertilisation at the same temperature intervals (i.e. Exo 2 + Exo 3) (Table 5.7).

For deeper soil layers (0.30-0.60 m), more disparity in weight loss was observed between the treatments, with recalcitrant and refractory fractions (Exo 2 + Exo 3) dominating over the labile fractions (Exo 1) (Table 5.7). Total weight loss (Exotot) order, from the higher to the lower, between 200-750 °C was ORG-C 2011 > CONV-M 2011 > ORG-M 2011 > ORG-M 2018 > CONV-C 2011 > ORG-C 2018 > CONV-M 2018 > CONV-C 2018. Specifically, CONV-RT, MINE fertilisation and samples collected in 2011 showed more labile organic matter compared to their counterparts ORG-RT, COMP fertilisation and samples collected in 2018 (Exo 1). The opposite was observed for the refractory organic matter (Exo 2 + Exo 3), i.e. ORG-RT, COMP fertilisation and samples collected in 2018 showing more refractory organic matter than CONV-RT, MINE fertilisation and samples collected in 2011 (Table 5.7).

These differences are highlighted by the differential scanning calorimetry analysis (DSC traces), which showed three exothermic peaks between 200 and 600 °C in the topsoil (0-0.30 m), characterised by a distinct peak at 300-350 °C and two other broad peaks, one at 400-450 °C and another at 500-550 °C (Fig. 5.6 A, B). Subsoil (0.30-0.60 m) samples also showed three exothermic peaks characterised by a distinct peak at 400-450 °C and two other broad peaks, one at 300-350 °C and another at 500-550 °C (Fig. 5.6 C, D). Regardless of the RS, FS or YR, all samples showed an endothermic peak at approximately 570-580 °C for both depth intervals assessed (Fig. 5.6).

Changes in the relative ion intensity for CO_2 (*m/z* 44) resemble those observed in the relative weight loss and DSC traces and are shown in Figure 5.7. For the 0-0.30 m depth, regardless of the YR, all samples showed a similar pattern with *m/z* 44 reaching a maximum at around 300-350 °C and with two minor shoulders at 400-450 °C and 500-550 °C (Fig. 5.7 A, B). Except for the ORG-M treatment, all the other treatments showed a slightly increased in the C released, particularly in the first temperature interval (Exo 1 – 200-350 °C), in 2018 compared to 2011. The other two temperature intervals (Exo 2 + Exo 3 – 350-500 °C and 500-750 °C), which represent recalcitrant and refractory fractions, showed a similar release of C with the ORG-RT, COMP fertilisation and samples collected in 2018 being slightly predominant than their counterparts (i.e. CONV-RT, MINE fertilisation and 2011 samples) (Fig. 5.7 A, B). These results are especially highlighted when the amount of C released within each temperature interval was calculated using the *m/z* 44 peak areas (Table 5.8). In general, there was a little variability between the treatments in the topsoil (0-0.30 m), with labile (Exo 1 – 200-350 °C) and recalcitrant/refractory (Exo 2 + Exo 3 – 350-500 °C and 500-750 °C, respectively) fractions showing similar C amounts (approximately 50/50). The only major difference observed was regarding the YR, where 2018 samples had higher soil C amounts than 2011 samples (Table 5.8).

For deeper soil layers (0.30-0.60 m), in both years (2011 and 2018), the *m/z* 44 reached a maximum at around 400-450 °C, with two other shoulders observed at 300-350 °C and 500-550 °C (Fig. 5.7 C, D). Under CONV-RT, there was a shift from 2011 to 2018 in C released to higher temperatures, particularly with the combination of CONV-RT and COMP fertilisation (i.e. CONV-C treatment), which resulted in the highest peak observed under the subsoil layer (Fig. 5.7 C, D). Under the ORG-RT, similar peaks were observed between the two years of sampling (2011 and 2018). However, it appears that the combination of ORG-RT and COMP fertilisation (i.e. ORG-C treatment) slightly shifted the release of C to higher temperatures resulting in a higher peak at 400-450 °C whereas the peaks remained unchanged in the combination of ORG-RT and MINE fertilisation (Fig. 5.7 C, D). These results were confirmed by the amount of C released within each temperature interval using the *m/z* 44 peak areas (Table 5.8). The CONV-RT, MINE fertilisation and samples collected in 2011 showed a higher release of C at the first interval (Exo 1 – 200-350 °C) compared to ORG-RT, COMP fertilisation and samples collected in 2018. For the recalcitrant and refractory fractions (Exo 2 + Exo 3), 2018 samples showed higher soil C than 2011 samples (Table 5.8).

For both top- (0-0.30 m) and subsoil layers (0.30-0.60 m), there were no peaks between the 750-900 ºC temperature range, indicating that there were none or low soil carbonate minerals present in the samples, therefore, total soil C concentration can be assumed to be total SOC (Fig. 5.7).

Table 5.7 Changes in total weight loss (50-800 °C), weight loss for the temperature interval 200-750 °C (Exotot) and relative weight losses of temperature intervals 200-350 °C (Exo 1), 350-500 °C (Exo 2) and 500-750 °C (Exo 3) as a result of different crop rotation schemes (conventional-CONV-RT *or* organic-ORG-RT), fertility sources (mineral-MINE *or* compost-COMP) and years of sampling (YR) (2011 and 2018).

Depth m		Total weight loss (50-800 °C)	Exotot (200-750 °C)	Exo 1 (200-350 °C)	Exo 2 (350-500 °C)	Exo 3 (500-750 °C)
		%				
0-0.30	CONV-RT	5.58 (0.26)	4.69 (0.19)	46.79 (0.51)	36.85 (0.38)	15.63 (0.28)
	ORG-RT	5.82 (0.12)	4.87 (0.09)	47.52 (0.34)	37.15 (0.27)	16.06 (0.71)
	MINE	5.85 (0.18)	4.89 (0.12)	47.79 (0.33)	36.97 (0.42)	15.24 (0.43)
	COMP	5.55 (0.21)	4.67 (0.16)	46.52 (0.28)	37.03 (0.24)	16.45 (0.44)
	2011	5.44 (0.21)	4.59 (0.15)	46.95 (0.50)	36.63 (0.36)	16.41 (0.44)
	2018	5.96 (0.07)	4.97 (0.05)	47.35 (0.43)	37.37 (0.10)	15.28 (0.46)
0.30-0.60	CONV-RT	4.29 (0.33)	3.48 (0.25)	34.80 (2.70)	38.76 (1.01)	26.43 (1.90)
	ORG-RT	3.98 (0.26)	3.25 (0.18)	27.26 (1.74)	41.04 (0.72)	31.69 (1.05)
	MINE	4.04 (0.29)	3.28 (0.20)	31.97 (3.37)	39.88 (0.93)	28.15 (2.51)
	COMP	4.23 (0.32)	3.44 (0.24)	30.09 (2.79)	39.93 (1.24)	29.97 (1.57)
	2011	3.74 (0.28)	3.07 (0.20)	33.62 (3.48)	38.97 (1.18)	27.40 (2.43)
	2018	4.54 (0.09)	3.65 (0.09)	28.44 (1.78)	40.83 (0.65)	30.72 (1.25)

Data are measured mean values (n=8 for crop rotation schemes, fertility sources and years of sampling within soil depth intervals). Standard error of the mean is in parentheses.

Table 5.8 Changes in carbon (C) released calculated from the *m/z* 44 (CO_2) peak areas in the temperature intervals 200-350 °C (Exo 1), 350-500 °C (Exo 2) and 500-750 °C (Exo 3) as a result of different crop rotation schemes (conventional-CONV-RT *or* organic-ORG-RT), fertility sources (mineral-MINE *or* compost-COMP) and years of sampling (YR) (2011 and 2018).

Depth m		Exo 1 (200-350 °C)	Exo 2 (350-500 °C)	Exo 3 (500-750 °C)
			g C kg	
0-0.30	CONV	9.03 (0.37)	7.44 (0.25)	1.93 (0.05)
	ORG	9.01 (0.10)	7.75 (0.18)	1.99 (0.12)
	MINE	9.13 (0.30)	7.57 (0.26)	1.91 (0.11)
	COMP	8.90 (0.22)	7.62 (0.21)	2.00 (0.06)
	2011	8.66 (0.13)	7.30 (0.21)	1.86 (0.06)
	2018	9.37 (0.21)	7.89 (0.09)	2.06 (0.08)
0.30-0.60	CONV	3.60 (0.32)	4.34 (0.53)	0.96 (0.17)
	ORG	2.50 (0.17)	4.53 (0.28)	0.97 (0.07)
	MINE	3.21 (0.43)	4.32 (0.29)	0.87 (0.04)
	COMP	2.89 (0.36)	4.55 (0.52)	1.06 (0.16)
	2011	3.29 (0.44)	3.98 (0.34)	0.80 (0.04)
	2018	2.81 (0.32)	4.89 (0.34)	1.12 (0.12)

Data are measured mean values (n=8 for crop rotation schemes, fertility sources and years of sampling within soil depth intervals). Standard error of the mean is in parentheses

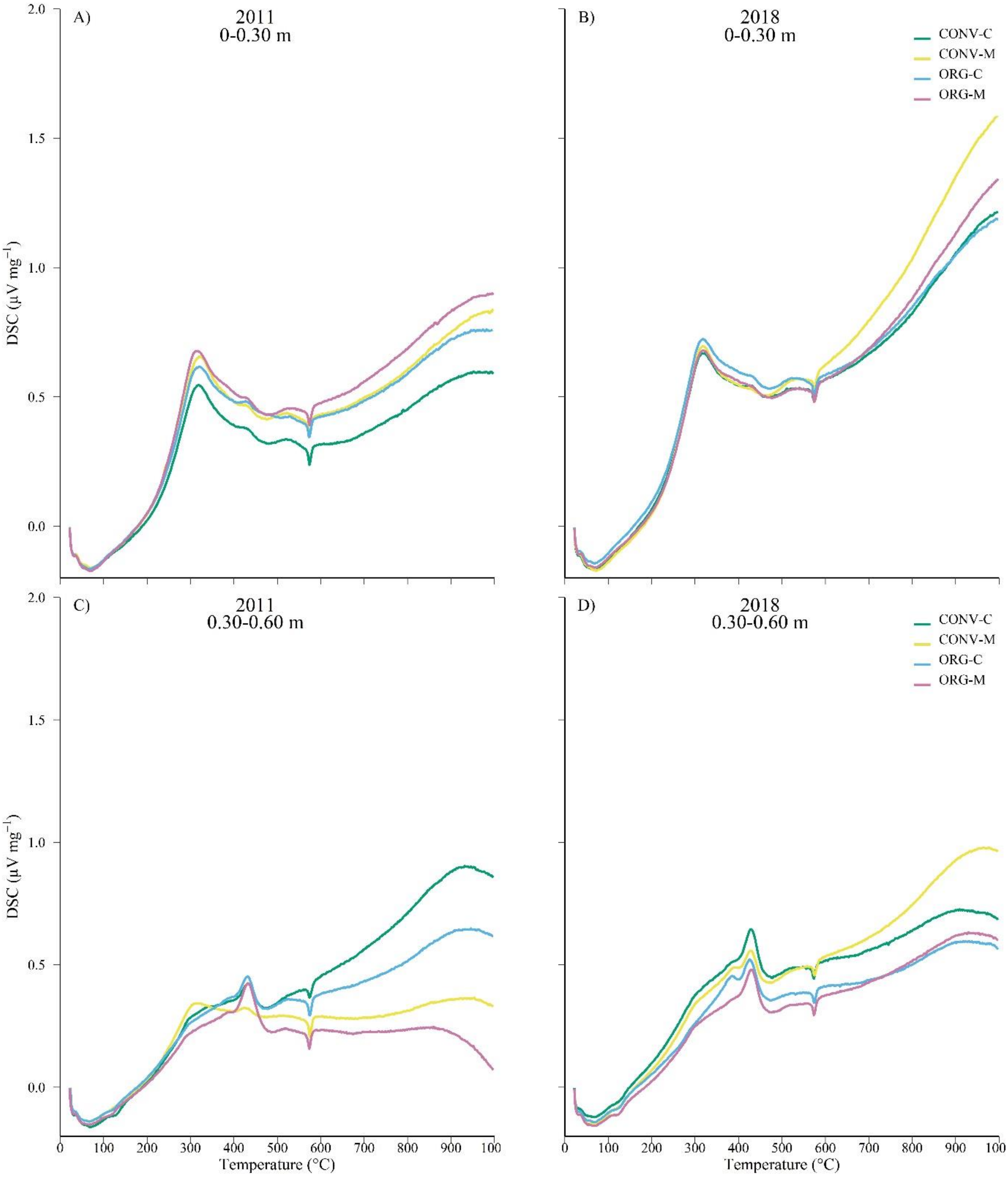

Figure 5.6 Differential scanning calorimetric (DSC) traces from the soil samples of combined treatment factors: conventional rotation with mineral fertilisation (CONV-M), conventional rotation with compost fertilisation (CONV-C), organic rotation with mineral fertilisation (ORG-M) and organic rotation with compost fertilisation (ORG-C) at 0-0.30 (A and B) and 0.30-0.60 m (C and D) soil depth intervals and different years of sampling 2011 (A and C) and 2018 (B and D).

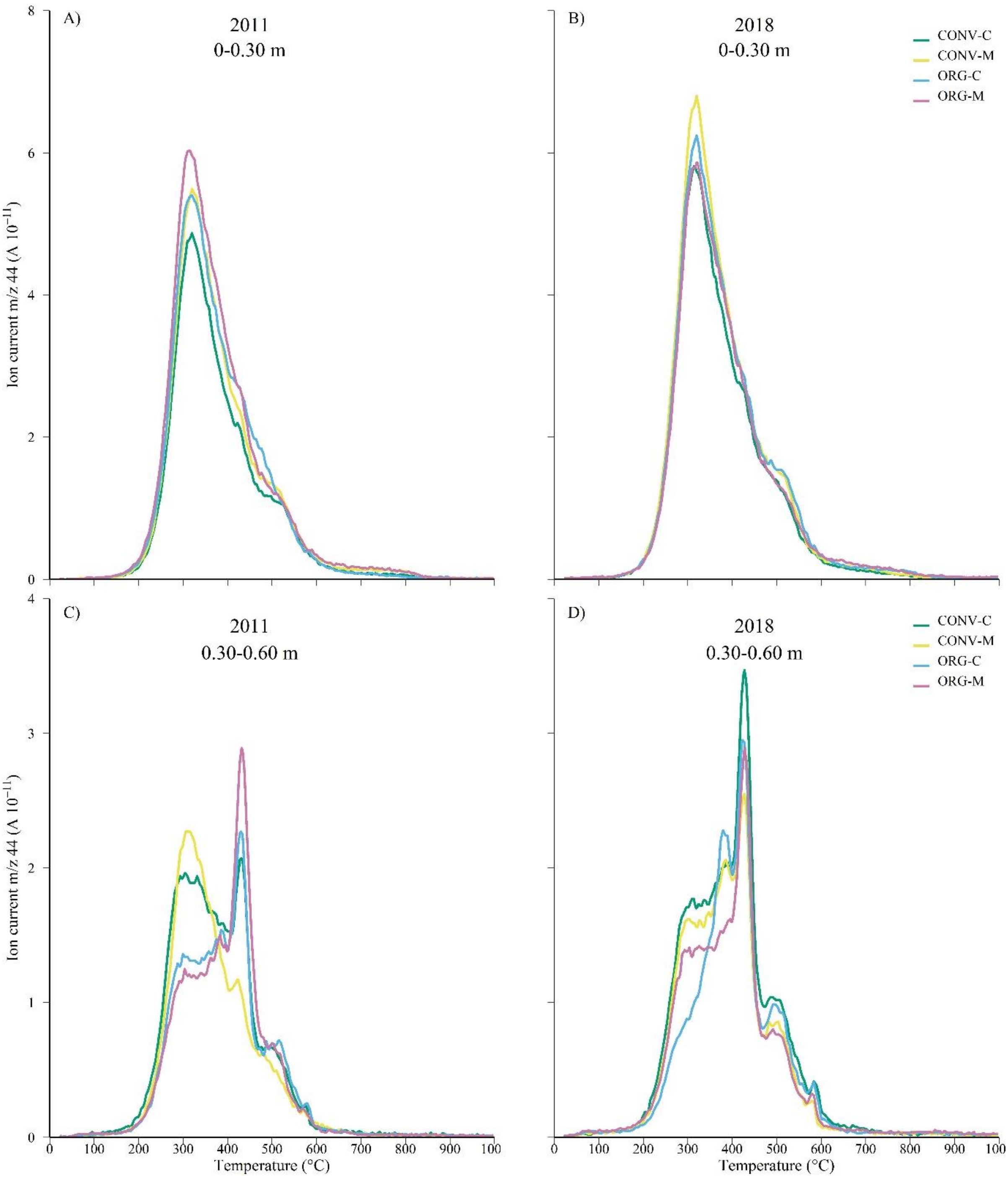

Figure 5.7 Ion current intensity for CO_2 (*m/z* 44) from the soil samples of combined treatment factors: conventional rotation with mineral fertilisation (CONV-M), conventional rotation with compost fertilisation (CONV-C), organic rotation with mineral fertilisation (ORG-M) and organic rotation with compost fertilisation (ORG-C) at 0-0.30 (A and B) and 0.30-0.60 m (C and D) soil depth intervals and different years of sampling 2011 (A and C) and 2018 (B and D).

5.3.4 Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) coupled with on-line thermally assisted hydrolysis and methylation (THM) in the presence of tetramethylammonium hydroxide (TMAH)

More than 300 pyrolysis product compounds were released from the extracted solid residue of which 184 dominant product compounds were selected and quantified. All the quantified product compounds are listed in Table A3.3 (Appendix 3), with their position in the chromatogram indicated by retention time (RT). Table A3.3 (Appendix 3) also provides information about the chemical group of the quantified product compounds and in which soil depth interval (0-0.30 and 0.30-0.60 m) they were found. Table 5.9 provides the relative abundance of the quantified pyrolysis product compounds by chemical groups. The chromatograms shown in figures A3.4 and A3.5 (Appendix 3) are from the extracted solid residue samples. Whilst figure A3.4 (Appendix 3) shows examples of representative chromatograms showing labelled pyrolysis product compounds identified as listed in Table A3.3 (Appendix 3), figure A3.5 (Appendix 3) shows the inter-relationships between the samples from the combined treatments i.e. conventional rotation with mineral fertilisation (CONV-M), conventional rotation with compost fertilisation (CONV-C), organic rotation with mineral fertilisation (ORG-M) and organic rotation with compost fertilisation (ORG-C).

For the 0-0.30 m soil depth, 161 quantified compounds were observed of the total 184 detected (Table A3.3, Appendix 3). In general, the order of relative abundance of groups of quantified pyrolysis product compounds, from the higher to the lower was lignin phenols > fatty acids > N compounds > aromatics > phenols > carbohydrates > polyaromatics > benzofurans > *n*-alkenes > *n* alkanes, regardless of the RS, FS or YR (Table 5.9). More specifically, ORG-RT showed a higher relative abundance of benzofurans, carbohydrates, lignin phenols, phenols, and polyaromatics compared to the CONV-RT. The CONV-RT, on the other hand, showed a higher relative abundance of *n*-alkanes, *n*-alkenes, aromatics, fatty acids, and N compounds compared to ORG-RT. In terms of FS, COMP fertilisation showed a higher relative abundance of *n*-alkanes, *n*-alkenes, aromatics and polyaromatics compared to MINE fertilisation. The MINE fertilisation, on the other hand, showed a higher relative abundance of benzofurans, carbohydrates, fatty acids, lignin phenols, N compounds, and phenols compared to the COMP fertilisation (Table 5.9). In relation of YR, samples collected in 2018 showed a higher relative abundance of almost all groups expected for the benzofurans, phenols and polyaromatics than the samples collected in 2011 (Table 5.9).

For deeper soil layers (0.30-0.60 m), 72 quantified compounds were observed of the total 184 detected (Table A3.3, Appendix 3). In terms of relative abundance, it was observed an increased contribution from aromatics, benzofurans, carbohydrates and polyaromatics whereas *n*-alkenes, fatty acids, and lignin phenols decreased their contribution compared to the topsoil layer (0-0.30 m) and regardless of the RS, FS or YR (Table 5.9). The *n*-alkanes were not detected in the deeper soil layers (0.30-0.60 m). For the other two remaining chemical groups (i.e. N compounds and phenols), there was an increasing contribution from N compounds under CONV-RT, MINE fertilisation and in the samples collected in 2011 whilst under ORG-RT, COMP fertilisation and samples collected in 2018, their contribution decreased compared to the topsoil layer (0-0.30 m). For the phenol group, the CONV-RT also increased its contribution compared to the topsoil layer (0-0.30 m) while the ORG-RT showed the opposite. The MINE fertilisation and samples collected in 2011 showed a decreased in phenol content in deepest soil layers (0.30-0.60 m) whilst it increased in relative abundance under COMP fertilisation and samples collected in 2018 at the same soil depth interval (Table 5.9). Comparison between the treatments in deeper soil layers (0.30-0.60 m), showed ORG-RT with a higher relative abundance of *n*-alkenes, aromatics, benzofurans, and polyaromatics compared to the CONV-RT. Consequently, the CONV-RT showed a higher relative abundance of carbohydrates, fatty acids, lignin phenols, N compounds and phenols. The COMP fertilisation showed a higher relative abundance of *n*-alkenes, benzofurans and phenols while the MINE fertilisation showed a higher relative abundance of aromatics, carbohydrates, fatty acids, lignin phenols, N compounds, and polyaromatics (Table 5.9). In relation of YR, samples collected in 2018 showed a higher relative abundance of *n*-alkenes, aromatics, carbohydrates, phenols and polyaromatics while samples collected in 2011 showed a higher relative abundance of benzofurans, fatty acids, lignin phenols and N compound (Table 5.9).

Table 5.9 Relative abundance of groups of pyrolysed product compounds released after Py-GC-MS-TMAH analytical procedures from the extracted solid residue as a result of different crop rotation schemes (conventional-CONV-RT *or* organic-ORG-RT), fertility sources (mineral-MINE *or* compost-COMP) and years of sampling (YR) (2011 and 2018).

Depth m		*n*-Alkanes	*n*-Alkenes	Aromatics	Benzofurans	Carbohydrates	Fatty Acids	Lignin Phenols	N compounds	Phenols	Polyaromatics
		%									
0-0.30	CONV-RT	1.31 (0.02)	2.34 (0.04)	8.80 (0.06)	1.97 (0.05)	3.40 (0.04)	23.30 (0.02)	40.17 (0.04)	9.61 (0.04)	7.30 (0.08)	2.12 (0.04)
	ORG-RT	0.46 (0.01)	1.49 (0.04)	6.50 (0.12)	2.59 (0.04)	4.49 (0.07)	17.64 (0.02)	46.73 (0.05)	9.28 (0.03)	7.36 (0.08)	3.13 (0.03)
	MINE	0.48 (0.01)	1.14 (0.05)	7.53 (0.08)	2.61 (0.05)	4.08 (0.04)	22.48 (0.02)	44.17 (0.05)	9.71 (0.03)	9.01 (0.10)	2.31 (0.03)
	COMP	1.33 (0.02)	2.65 (0.04)	8.04 (0.08)	1.93 (0.04)	3.61 (0.06)	18.89 (0.02)	42.02 (0.04)	9.19 (0.03)	5.97 (0.07)	2.86 (0.04)
	2011	0.56 (0.04)	2.50 (0.05)	6.47 (0.09)	3.35 (0.04)	3.52 (0.05)	20.60 (0.02)	42.77 (0.04)	9.18 (0.03)	8.08 (0.08)	2.97 (0.04)
	2018	1.39 (0.03)	1.39 (0.03)	9.32 (0.08)	0.98 (0.04)	4.25 (0.05)	21.19 (0.02)	43.22 (0.04)	9.69 (0.03)	6.48 (0.06)	2.09 (0.03)
0.30-0.60	CONV-RT	0.00 (0.00)	0.81 (0.01)	19.92 (0.39)	7.25 (0.04)	7.70 (0.10)	2.72 (0.06)	19.29 (0.11)	19.82 (0.28)	9.08 (0.11)	13.41 (0.08)
	ORG-RT	0.00 (0.00)	1.05 (0.01)	39.11 (0.51)	27.82 (0.99)	5.25 (0.03)	0.00 (0.00)	5.91 (0.06)	4.16 (0.19)	1.08 (0.08)	15.62 (0.10)
	MINE	0.00 (0.00)	0.00 (0.00)	30.30 (0.48)	2.24 (0.11)	7.86 (0.16)	3.00 (0.09)	20.19 (0.17)	20.72 (0.54)	4.98 (0.26)	17.59 (0.08)
	COMP	0.00 (0.00)	1.73 (0.05)	25.34 (0.39)	27.79 (0.41)	5.66 (0.08)	0.36 (0.01)	8.08 (0.07)	6.84 (0.06)	6.61 (0.61)	10.71 (0.09)
	2011	0.00 (0.00)	0.59 (0.01)	23.71 (0.30)	18.09 (0.37)	6.48 (0.09)	2.24 (0.05)	16.26 (0.08)	15.72 (0.26)	5.29 (0.12)	11.61 (0.05)
	2018	0.00 (0.00)	1.73 (0.01)	38.08 (0.74)	9.12 (0.10)	7.29 (0.13)	0.00 (0.00)	7.61 (0.24)	7.60 (0.19)	7.25 (0.43)	21.32 (0.20)

Data are measured mean values (n=8 for crop rotation schemes, fertility sources and years of sampling within soil depth intervals). Standard error of the mean is in parentheses.

5.4 Discussion

Organic rotation and compost fertilisation led to SOC accumulation reflecting findings from previous studies (Gattinger *et al.*, 2012; Triberti *et al.*, 2016; Jian *et al.*, 2020). However, while organic rotation showed higher SOC stocks than the conventional rotation under both sampled years (i.e. 2011 and 2018) and soil depth intervals (i.e. 0-0.30 m and 0.30-0.60 m) irrespective of the fertility sources (i.e. mineral or compost), compost fertilisation led to topsoil SOC accumulation (0-0.30 m) over year (i.e. from 2011 to 2018) under both crop rotation schemes. These results suggested that these two core practices of the organic systems are playing a strategic role in SOC accumulation but the means for that might be potentially different, which may influence soil SOC stabilisation.

In terms of the crop rotation schemes, the effect may be partially ascribed to both the incorporation of legumes and the longer length of ley periods into the organic rotation (3 years *vs.* 2 years under organic and conventional rotation, respectively). Previous research has indicated that the mixture of grasses and leguminous (e.g. grass-clover) on ley periods can provide additional yield benefits and thus increase SOC stocks via higher crop residue deposition to the soil surface (Persson *et al.*, 2008; O'Dea *et al.*, 2013). Greater above-ground biomass can also lead to greater below-ground biomass along with more rhizo-deposition, and soil microbial activities (Araujo *et al.*, 2012; Balakrishna *et al.*, 2017), all of which can further benefit SOC accumulation even at deeper soil layers. According to a recent meta-analysis conducted by Jian *et al.* (2020), a greater mass and activity of root biomass, rhizo-deposits, and soil microbes could enhance the availability of essential nutrients to plant growth (e.g. N, phosphorus and potassium), which can be a mechanism explaining the positive effect in SOC stocks at both soil depth intervals. In a longer length of grass-clover ley periods (i.e. under the organic rotation), it is presumed that all these effects would be amplified, contributing to a higher SOC accumulation potential. The positive effect of both the incorporation of legumes and the longer length of ley periods on SOC stocks is also in line with results found in Chapter 3 (farm-scale assessment) and 6 (modelling approach) as well as previous research that suggested a minimum period of three-years ley after five-years arable rotation to promote a significant increase in SOC concentration in topsoil layers (Johnston *et al.*, 2017).

In turn, the topsoil SOC accumulation (0-0.30 m) in both crop rotation schemes over the years (2011-2018) under compost fertilisation can be attributed to the highest and direct supply of SOM to the soil (Aguilera *et al.*, 2013). Previous research also reported significant SOC stock increase under fields receiving organic amendments such as composted dairy manure due to the direct supply of organic C (Christensen, 1988; Gerzabek *et al.*, 2001; Gattinger *et al.*, 2012). Another important factor that may have favoured SOC accumulation under compost fertilisation is its potential to enhance soil aggregate stability (Haynes & Naidu, 1998; Whalen & Chang, 2002). Organic amendments were previous acknowledge by its positive effects on soil biological activity (Maeder *et al.*, 2002; Lori *et al.*, 2017), which can foster the physical protection of C against decomposition through chemical-physical bindings processes (Six *et al.*, 2002b).

Whilst the mixture of grasses and leguminous and the use of organic amendments often result in an increased SOC stock (Sainju *et al.*, 2006; Jian *et al.*, 2020), mixed results have been reported due to the use of grass or legume during the ley period phases as well as due to the application of different organic amendments sources (Mazzoncini *et al.*, 2011; Aguilera *et al.*, 2013; O'Dea *et al.*, 2013). This might be due to differences in biomass production, C:N ratios and lignin content of the crops in the rotation as well persistence of the organic amendments sources to degradability in soils (Tokarski *et al.*, 2019; Zhou *et al.*, 2019). In the organic rotation, along with the grass-clover ley periods, other legumes (e.g. peas and beans) and vegetables (e.g. cabbage, lettuces, onions and carrots) were cultivated in an 8-year period (2011-2018), which might have provided the finest balance between biomass production and optimal C:N ratio inputs. While legumes (usually low C:N ratios) provide soil N to plants by fixing atmospheric N, the grass provides high biomass with high C:N ratios (Jian *et al.*, 2020). In turn, organic amendments such as farmyard manure can increase SOC stocks as it is a C source that offers strong resistance to microbial decomposition (Nardi *et al.*, 2004; Li *et al.*, 2018). In this sense, the combination of grass-clover ley periods, other legumes and vegetables, and compost fertilisation is presumed to be the prime for long-lasting SOC stocks benefit. However, it is important to highlight that the amount of biomass and the characteristics of residues (i.e. C:N ratios, lignin content, as well as other molecular compounds) play a key role in SOM mineralisation (Tian *et al.*, 1992; Triberti *et al.*, 2016). Accordingly, crop choice in the rotation and organic amendment sources can either increase or decrease SOC stocks through effects not only related to residue deposition but also due to potential changes in soil properties, including chemical (nutrient availability), physical (soil structure) and biological (microbial biomass) properties (Campbell *et al.*, 1991; Bandick & Dick, 1999; Sainju *et al.*, 2006).

In this study, crop straw and debris have been always removed from the field under both crop rotation schemes while organic amendments were applied mainly using composted dairy manure. In terms of organic rotation, this indicates that the increased SOC stock in both top- and deeper soil layers was a function of a more diverse rotation system, which supplied higher

C inputs from root biomasses and crop stubbles; materials acknowledged for their relevant amount of stable SOM (Triberti *et al.*, 2016). In addition to the high C:N ratios of grasses (Jian *et al.*, 2020), studies from Martens (2000) and Lorenz & Lal (2005) indicated that cereal roots and stubbles are slowly decomposed materials as they are composed of high C:N ratios, lignin and phenols content. This could be a mechanism to explain the enhanced SOC accumulation under the organic rotation, as legumes, grasses and cereal were all inserted into this crop rotation scheme. On the other hand, as compost fertilisation such as farmyard manure *per se* offers a resistance option to biodegradability in soils (Nardi *et al.*, 2004; Li *et al.*, 2018), it might have benefit SOC accumulation, irrespective of the crop rotation scheme, due to the presence of more stabilised C forms. This was confirmed by a meta-analysis study conducted by Aguilera *et al.* (2013), where the authors found that raw organic amendments materials have a lower capability to increase soil C sequestration than organic composted materials. We also speculate that both organic rotation and compost fertilisation resulted in enhanced faunal activity, particularly worms, whose promote stability of organomineral aggregates and consequently SOC stabilisation (Coq *et al.*, 2007).

Such assumptions were partially validated by our physical fractionation of the SOM, TG-DSC-QMS and Py-GC-MS analyses. Regarding crop rotation schemes, organic rotation showed a slightly higher relative weight loss and ion intensity for CO_2 (*m/z* 44) in the temperature intervals between 350-500 °C and 500-750 °C (Exo 2 and Exo 3) at both soil layers. Likewise, compost fertilisation also resulted in a slightly higher relative weight loss and ion intensity for CO_2 (*m/z* 44) in the same temperature intervals at both soil layers. The endothermic peak at approximately 570-580 °C in all DSC traces is due to a well-established phase change from the α-quartz to β-quartz at 573 °C (Bartenfelder & Karathanasis, 1989), while the peak at 500 °C for the *m/z* 18 (water) refers to the water loss typical of kaolinite. As such, these two results from TG-DSC-QMS analysis are in line with mineralogical analyses, which showed the farm soils were dominated by kaolinite and quartz, and thus indicate that TG-DSC-QMS analysis was effective and reliable. The results of the present study are also in agreement with a recent study conducted by Tokarski *et al.* (2019), who observed that farmyard manure results in thermal mass losses mainly around 450 °C. Previous studies using thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis hinted that exothermic peaks up to 350 °C are related to labile aliphatic and carboxyl groups, whereas identified peaks up to approximately 500 °C are stable aromatic component classes. However, although these findings may indicate high amounts of recalcitrant and refractory C fractions and therefore a potential SOC stabilisation under both organic rotation and compost fertilisation (Lopez-Capel *et al.*, 2005, 2006; Manning *et al.*, 2005; Plante *et al.*, 2009), some considerations should be carefully taken into account.

Under organic rotation and both soil depth intervals, there was a trend (non-significant) towards a decreased SOC in the mineral-associated fractions (silt and clay fraction; SC < 53 μm), i.e. less accessible to decomposers and thus more stable and long-lived SOM (von Lützow *et al.*, 2007). Although not statistically proven, this potential disparity with the TG-DSC-QMS results might be due to either the similarity between the two rotation schemes in terms of SOC associated with this fraction (also observed in the TG-DSC-QMS analysis) as well as potential discrepancies between the temperature intervals and soil fractions (Schiedung *et al.*, 2017). At a molecular level, the organic rotation has shown a slightly higher relative abundance of benzofurans, carbohydrates, lignin-phenols, phenols, and polyaromatics in the top 0-0.30 m depth, in comparison to the conventional rotation. Conversely, in deeper soil layers (0.30-0.60 m), organic rotation showed a higher relative abundance of *n*-alkenes, aromatics, benzofurans, and polyaromatics as well as a much lower relative abundance of carbohydrates, fatty acids, lignin-phenols, N compounds, and phenols. Benzofurans, carbohydrates, lignin-phenols and phenols are products from relatively fresh plant materials while aromatics and polyaromatics compounds are products originate from different sources, including lignin, carbohydrates proteins and charred plant material (González-Pérez *et al.*, 2004; Kaal *et al.*, 2008; Mazzetto *et al.*, 2019). Pyrolysis products from cutan and suberin result in *n*-alkanes and *n*-alkenes compounds, which are more resistant against degradation than lignin (Tegelaar *et al.*, 1995; Klotzbücher *et al.*, 2011). Overall, such findings indicate thus that while the organic rotation has increased SOC stocks in the topsoil layers, it might be susceptible to loses, as there is a high contribution from fresh organic materials. This is most likely related to the potential higher yields under such crop rotation scheme and hence a higher amount of fresh crop residue deposition to the soil surface (Persson *et al.*, 2008; O'Dea *et al.*, 2013). On the other hand, increased SOC stocks in deeper soil layers under organic rotation may be attributed to other factors rather than crop residue deposition. In particular, it can be attributed to the fact that organic rotation is more diversified with a completely different set of crops and rooting patterns, including deep-rooting crops, compared to the conventional rotation (Blanco-Canqui *et al.*, 2017). Kutsch *et al.* (2010), highlighted the importance of root biomass, rhizo-deposits, and microbes as sources of belowground C. The high relative abundance of *n*-alkenes, aromatics, and polyaromatics in deeper soil layers (i.e. > 0.30 m) under organic rotation is an important finding as it implies that SOC stabilisation may be occurring (Mazzetto *et al.*, 2019).

Concerning the fertility sources, a significant higher SOC in the heavy fraction (HF > 53 μm), i.e. a more labile fraction than the mineral-associated fraction due to its weaker association with clay mineral matrix (Hassink, 1997), was observed in the topsoil layers under the mineral fertilisation in comparison to compost fertilisation treatment. Whereas, at the same soil depth interval, a trend (also non-significant) towards increased SOC in the mineral-associated fractions (silt and clay fraction; SC < 53 μm) was observed under the compost fertilisation treatment in comparison to mineral fertilisation. In subsoil layers (0.30-0.60 m), mineral fertilisation significant increased SOC in the mineral-associated fractions (silt and clay fraction; SC < 53 μm) over time, while compost fertilisation decreased it. These results suggest that the observed increased topsoil SOC stocks (0-0.30 m) over 8 years (2011-2018) under compost fertilisation can potentially lead to a SOC stabilisation, but this effect might be limited to the top 0-0.30 m depth. In contrast, mineral fertilisation might have a positive effect on SOC stabilisation in subsoil layers. The mechanisms for this could be the same of those discussed under organic rotation, i.e. higher yields followed by a higher amount of fresh crop residue deposits, which are potentially incorporated to the soil through tillage events (Bilsborrow *et al.*, 2013; Schellekens *et al.*, 2013) and greater below-ground biomass followed by greater rhizo-deposition, and soil microbial activities (Araujo *et al.*, 2012; Balakrishna *et al.*, 2017). The Py-GC-MS results reflected such assumptions. For the 0-0.30 m depth, mineral fertilisation showed a higher relative abundance of products originated from fresh plant materials, including lignin-phenols and phenols (i.e. relatively easy to decompose), while compost fertilisation showed a higher relative abundance of compounds that are relatively difficult to decompose including aliphatic compounds (*n*-alkanes and *n*-alkenes), aromatics, and polyaromatics. For the 0.30-0.60 m depth, although the mineral fertilisation continued to show the higher relative abundance of products originated from fresh plant materials, it also showed the higher relative abundance of recalcitrant products in comparison to the compost fertilisation treatment (e.g. aromatics and polyaromatics). In this thesis, the Py-GC-MS was mainly used here to quantify the relative abundance of groups of pyrolysed product compounds. However, it is worth noting that this technique has also shown some potential to detailed sources and/or processes of the chemical composition of the SOM (Nierop *et al.*, 2001; De la Rosa *et al.*, 2008; Oliveira *et al.*, 2016; Mazzetto *et al.*, 2019). Since this was outside the scope of this study, it would be worth being investigated by future research.

Lastly, it is also worth noting a few further points: 1) the significant increase in N concentration and stocks after a full rotation cycle (i.e. 8 years) at both soil depth intervals assessed (i.e. 0-0.30 m and 0.30-0.60 m) and regardless of the crop rotation scheme or fertility source. This is a striking finding as it indicates that even under the combined organic rotation and compost fertilisation (i.e. fully organic system), fertilisation requirements, in particular for N, are being alike to conventional systems (i.e. conventional rotation and mineral fertilisation). This is key as meeting crop nutrient demand can narrow the yield gap often reported between conventional and organic systems (Seufert *et al.*, 2012; Bilsborrow *et al.*, 2013; Ponisio *et al.*, 2015); 2) similarly to the N stocks, there was a significant increase in the mineral-associated SOC fractions (SC < 53 μm) after a full rotation cycle, at topsoil layer (0-0.30 m) and irrespective of the crop rotation scheme or fertility source. This is an important outcome as it indicates a potential stabilisation by the interaction of clay minerals and SOC. Previous studies have observed that the thermal behaviour of SOC stocks was affected by the interaction of clay minerals interactions (Leinweber & Schulten, 1992; Plante *et al.*, 2005). In particular, high clay content soils have a greater potential to stabilise SOC compared to sandy soils (Lützow *et al.*, 2006; Schrumpf *et al.*, 2013; Brandani *et al.*, 2016). It is very unlikely, however, that clay content and soil mineralogy have changed over an 8-year crop rotation period, which ultimately suggests that both crop rotation schemes and fertility sources are somehow stabilising SOC over-time at the 0-0.30 m depth. Although some disparities have been observed between physical fractionation of SOM and TG-DSC-QMS analysis regarding the treatments (i.e. crop rotation schemes and fertility sources), the results of both agreed with each other in relation to years of sampling (e.g. higher mineral-associated C fractions and higher mass losses and soil C released in 2018 in the Exo 2); 3) at a molecular level, it was observed a substantial decrease in subsoil layers (0.30-0.60 m) of *n*-alkenes, *n*-alkanes, fatty acids, and lignin-phenols, whilst aromatics, benzofurans, carbohydrates, and polyaromatics increased for all treatments in topsoil layers (0-0.30 m). In addition, an increasing contribution from N compounds was observed under conventional rotation, mineral fertilisation and samples collected in 2011. The decreased in *n*-alkenes, *n*-alkanes, fatty acids, and lignin-phenols at depth as well as the high contribution from polyaromatics are acceptable findings as they are pyrolysis products from plant biopolymers/biological origin and black carbon, respectively (Ralph & Hatfield, 1991; Nierop *et al.*, 2001; González-Pérez *et al.*, 2014). However, the higher relative abundance of carbohydrates at this depth interval regardless of the treatment as well as the high contribution from N containing compounds under the conventional system practices (i.e. conventional rotation and mineral fertilisation) deserves particular attention. Upon pyrolysis, these are the main products of microbial activities (Derenne & Quéné, 2015) and thus it may suggest an enhanced SOM decomposition (Rumpel & Kögel-Knabner, 2010); and 4) It is possible that SOC stabilisation at 0-0.30 m depth was also an artefact of the characteristics of the soil at Nafferton farm (stagnosol), which was previously recognised for its potential of SOC stabilisation via chemical interactions with Fe and Al oxide minerals (Cloy *et al.*, 2014). Further research is still required to fully understand the impacts of management practices on SOM decomposition, in particular in subsoil layers (i.e. > 0.30 m depth).

Along with the positive effect to soil C sequestration, it is important to underscore that the use of the leguminous and longer period of grass-clover leys in the rotation are widely acknowledged for their benefits on weed control, disease break crop as well as production. However, despite its potential critical role in agroecosystem functioning, crop rotations have been broadly simplified in the modern agricultural systems, jeopardising the provision of ecosystem services (Tilman *et al.*, 2002; Lamy *et al.*, 2016). In this study, the increased topsoil SOC stock accumulation under organic rotation (approximately 5%) and the increased SOC stock accumulation under compost fertilisation (11%), can play a significant role, especially if combined, in recovering approximately one-quarter of the overall soil C losses due to conversion from natural vegetation to cropland (estimated to range from -25% to -36%) (Poeplau & Don, 2015). These results should be considered carefully under different climate, specific managements, soil texture and type than those tested here, as all these factors can either assist or hinder towards physical protection of SOM and thus affect decomposition and stabilisation of SOC stocks. The use of physical fractionation of SOM, TG-DSC-QMS and Py-GC/MS-TMAH analyses proved to be reliable approaches to assess SOM composition and stabilisation under different crop rotation schemes and fertility sources. Importantly, specific soil types and site characteristics need consideration.

5.5 Conclusions

This study has shown that SOC stocks, as well as soil organic matter (SOM) composition, differ between conventional and organic crop rotation schemes and mineral and compost fertilisation sources with potential implications to stabilisation. More specifically, the organic rotation has shown higher SOC stocks than the conventional rotation in both the topsoil and subsoil (i.e. 0-0.30 m and 0.30-0.60 m) regardless of the sampled year (i.e. 2011 and 2018) and fertility sources (mineral or compost). In turn, compost fertilisation increased topsoil SOC stocks over years (i.e. from 2011 to 2018) under both crop rotation schemes. The unique combination of SOM physical fractionation, TG-DSC-QMS and Py-GC/MS-TMAH analyses helped to better understanding the potential shifts in the composition of SOM and consequently stability when components of conventional and organic agricultural systems (e.g. crop rotation schemes and fertility sources) were implemented. In particular, the findings of this study suggested that the increased topsoil SOC stocks under organic rotation might be susceptible to loses since it occurs through a high contribution from fresh organic materials in the soil surface. On the other hand, the increased subsoil SOC stocks under organic rotation have occurred through a higher contribution of more stable compounds, probably related to the set of crops grown, and thus different rooting patterns, implying for a potential SOC stabilisation. Likewise, the increased topsoil SOC stocks over years under compost fertilisation showed a larger contribution from more stable compounds (aliphatics, aromatics and polyaromatics). These findings ultimately suggested that combining these two core practices of the organic systems can play a significant role in recovering historical soil C losses (e.g. due to land use changes from natural vegetation to cropland as well as due to the intensification of crop production). Further data collection from this long-term trial will help to confirm these effects of crop rotation schemes and fertility sources on SOC stocks and stabilisation as well as to further elucidate its relationship with other factors as for instance changes in environmental variables.

Chapter 6. Predicting long-term effects of alternative management practices in conventional and organic agricultural systems on soil carbon stocks using the DayCent model

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Notes

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Declaration of contribution

This chapter consists of an original simulation undertaken by myself, Caio Fernandes Zani, using measured data collected in 2011, 2017 and 2018 (Chapters 2, 3 and 5). Caio Fernandes Zani carried out all simulations and data analysis. Caio Fernandes Zani also led the writing of the chapter and potential paper, with contribution from all co-authors. Specifically, the contribution of co-authors is such: Marcelo V. Galdos provided practical training, involving running, interpretation and assessment, using the DayCent model; Geoffrey D. Abbott, James A. Taylor, Julia Cooper and Elisa Lopez-Capel provided PhD supervision and detailed comments on the chapter.

6.1 Introduction

Continuous changes in soil carbon (C) storage have contributed to the increased atmospheric concentration of greenhouse gases (GHG), exacerbating global concerns about its impact on climate change (Lal, 2004a). According to the IPCC (Intergovernmental Panel on Climate Change, 2014), the agricultural sector comprises 14% of total GHG emissions, including 56% of the anthropogenic non-CO_2 emission. In order to design a sustainable agricultural sector and informing land use policy, it is therefore vital that mitigation strategies are identified.

Soil C accumulation in agricultural soils has been posited as a strategy for climate change mitigation, particularly through the adoption of the so-called sustainable recommended management practices (Lal, 2004b). These include, but are not limited to, the adoption of the organic system and its associated practices, e.g. the return of plant and animal residues as organic fertilisers and the implementation of an extended rotation with the inclusion of legumes and grass-clover ley periods (IFOAM, 2012), as well as the use of mixed (arable/livestock) farming systems. Both have been particularly suggested as strategies to achieve efficient nutrient cycling and preserving natural resources and the environment (Zani *et al.*, 2020; Chapter 2). However, the relative impacts of those systems and management practices on soil C stocks, i.e. the absolute quantity of C held within the soil, is still contentious, raising uncertainties regarding their sustainability (Gattinger *et al.*, 2012). Part of this uncertainty is due to the limited availability of reliable long-term field data.

Soil C stocks are closely linked and dependent on farming practices, including, for instance, the length of temporary grass-clover ley in crop rotation (referred to in this study as ley time proportion) and whether the ley is used for hay meadow cutting (non-grazed) or livestock grazing (Chapter 3). Furthermore, it has been noted that rotation schemes, conventional *vs.* organic, with the former characterised by cereal intensive crops and the latter based on a more diverse and legume-rich cycle, and fertilisation sources (mineral *vs.* compost), are likely to play a key role in soil C stocks and stabilisation (Chapter 5). Depending on the magnitude of nutrient cycling into and out of a given agricultural system and considering interactions with climate (temperature and rainfall) and different management practices applied, an agroecosystem can either be a sink or a source of C. Therefore before wide-scale deployment of such practices is undertaken, it is important to understand long-term soil C stocks changes not only due to conventional and organic systems as a whole but also due to the specific management practices implemented within these systems.

Previous empirical studies have shown that intensive crop production systems have led to soil C losses (Houghton, 2003), while management practices that add high amounts of biomass to the soil with minimal soil disturbance resulted in soil C gains (Lal, 2004a; Six *et al.*, 2004; Gattinger *et al.*, 2012; Skinner *et al.*, 2014; Cooper *et al.*, 2016; Quemada *et al.*, 2020). However, changes in soil C stocks, particularly the accrual of C into the soil, can take decades to occur and are difficulted to be noted by empirical research of soil C dynamics, which only provides a single snapshot in time, unless carried out over many years. In this sense, long-term experiments are key but although efforts have been made to maintain long-term experiments and measurement intensity, there is still a discrepancy on soil C stocks findings. This is particularly true for the comparison between conventional and organic systems, with empirical studies showing mixed results: some show an increase in topsoil C stocks (Diacono & Montemurro, 2010; Gattinger *et al.*, 2012; García-Palacios *et al.*, 2018), whereas others indicated no increase or even reductions (Leifeld & Fuhrer, 2010; Leifeld *et al.*, 2013) (Chapter 3). It is also important to highlight that soil C cycling is highly complex and dependent on interactions among many factors, including management practices, plant growth processes, soil water dynamics, climate, etc, which makes the interpretation of results from empirical studies challenging. In this sense, complementing empirical measurements with simulation models is placed as a reliable, feasible and cost-effective alternative to appraisal of the long-term effects of agricultural systems and alternative management practices on soil C stocks.

There are two types of models; the empirical models, in which the predictions are based on a fitted mathematical formula that aims to reproduce the available data for similar environmental conditions (Lawson & Tabor, 2001; Hillier *et al.*, 2015) (i.e. there is no attempt to understand the nature of the relationship between the dependent and independent variables), and the mechanistic models, in which several processes are considered based on an understanding of underlying functions of a system of interest (Buck-Sorlin, 2013). In general, mechanistic models that were developed to predict quantities of C in soil, consider similar regulating factors (soil physics, decomposition, plant growth, soil organic matter (SOM) dynamics, among others), but with varying levels of complexity and in some cases, using different algorithms to represent such factors (Dondini *et al.*, 2018). Soil C dynamics is indeed complex, but such mechanistic models represent a powerful option for understanding processes responsible for production, consumption, and transport of soil C over long time scales (Powlson, 1996). Moreover, they can be used to predict soil C changes from current management practices to future alternative scenarios, including different agricultural systems and management practices in different soil types, rotation schemes, fertility sources, etc (Smith *et al.*, 2016). Such a tool can also be applied in different ways including at site and regional scale, and it can be used to extrapolate results from experimental plots spatially and temporally, and to look at past and future time periods (Smith *et al.*, 2012a). Ultimately, mechanistic models can help to address uncertainties regarding the long-term effects of the adoption of alternative management practices within conventional and organic systems on soil C stocks, thus contributing to policies and decision-makers on the long-term ultimate goal of achieving a sustainable agricultural system.

Among the mechanistic models, the DayCent is a terrestrial ecosystem model designed to simulate C and N cycles, as well as the dynamics of a range of nutrients, among the atmosphere, vegetation, and soil (Parton *et al.*, 1998; Del Grosso *et al.*, 2001). The DayCent model includes submodels for the representation of plant productivity, phenology, decomposition of dead plant material and SOM, soil water and temperature dynamics, and GHG fluxes. The model requires reasonable data inputs including soil properties (soil texture, field capacity, wilting point, bulk density, and pH), climate (temperature and rainfall), and land use/management information (grazing intensity, fire, tillage, fertiliser inputs, irrigation and sowing and harvest dates). Its use has proven to be suitable for simulations at a range of temporal and spatial scales depending on its configuration. Although it was originally developed for grassland in the USA (Parton *et al.*, 1987), DayCent has been widely used across the world, including Brazil (Oliveira *et al.*, 2017), China (Cheng *et al.*, 2014; Yue *et al.*, 2019), Canada (Smith *et al.*, 2012b; Chang *et al.*, 2013; Sansoulet *et al.*, 2014) and Europe (Parton *et al.*, 1988; Abdalla *et al.*, 2010; Fitton *et al.*, 2014b; a; Senapati *et al.*, 2016; Begum *et al.*, 2017; Necpalova *et al.*, 2018; Lee *et al.*, 2020), across a range of ecosystems, e.g. grasslands, cropland, and forests. Nevertheless, when using a model for a region different than where it was originally developed, it is always important to take some precautions (Smith & Smith, 2007). One of the main recommended procedures is to carry out a sensitivity analysis so that potential critical parameters that may cause a direct effect on the outcomes might be identified. The identification of such parameters can also help to reduce uncertainties in the model simulations by careful consideration of those parameters and ultimately deliver a better understanding of the model that will improve future model applications.

This study was designed with the following aims: i) to simulate soil C stocks under alternative management practices, including conventional *vs.* organic systems, non-grazed *vs.* grazed regimes, arable systems with ley phases, mineral *vs.* compost fertility sources and conventional *vs.* organic crop rotation schemes using the DayCent model; ii) to assess the reliability and the sensitivity of the DayCent model using empirical measurements collected under both a farm-scale study (Chapter 3) and from a long-term experimental trial study (Chapter 5); and iii) to explore long-term effects of alternative management practices in the conventional and organic system on soil C stocks up to 2050.

6.2 Materials and Methods

6.2.1 Experimental farm site and treatments

The data used in this study was obtained from the farm-scale study (Chapter 3) and the experimental trial comparison (Chapter 5). Briefly, the farm-scale study was conducted at Newcastle University's Nafferton farm, a mixed (arable/livestock system) commercial farm located 12 miles west of Newcastle upon Tyne in north-east England (54º59'09''N; 1º43'56''W, 60 m a.s.l.), where the total farm area (~320 ha) was divided in 2001 into 50% conventional system (CONV), operated to current UK best practices (Red Tractor Assurance, 2015), and 50% organic system (ORG), following (Soil Association, 2019) standards. In turn, the experimental trial, namely Nafferton Factorial Systems Comparison (NFSC), is a long-term experimental field located at Nafferton Farm, where the components of conventional and organic agricultural systems (e.g. crop rotation schemes, fertility sources and crop protection) are studied in a split-plot factorial design. A full detailed description of the farm and the NFSC trial can be found in Chapter 2, section 2.2.1 and Chapter 5, section 5.2.1, respectively.

For the farm-scale study, twelve commercial-sized representative agricultural fields (6 study fields under CONV system and 6 under ORG system) were sampled in February-March 2017, where alternative management practices, including grazing regimes (non-grazed-NG *vs.* grazed-GG) and different proportions (0 to 100%) of temporary grass-clover leys in arable rotations (referred to in this study as ley time proportion; LTP), were implemented within each agricultural system. Further details of the study fields are given in Zani *et al.* (2020) and Chapter 2, section 2.2.2, whilst soil sampling strategy and methods can be found in Chapter 3, section 3.2.3. Table A1.2 (Appendix 1) shows the crop history details of each study over 10 years (2008-2017).

For the NFSC trial, the effects of crop rotation schemes (conventional rotation-CONV-RT and organic rotation-ORG-RT) and fertility sources (mineral-MINE and compost-COMP) were considered within the same crop protection (conventional) regime and over one complete crop rotation cycle (i.e. 8 years). Additional information about the treatments used in this study including crop growth in the rotation cycle, rates of fertilisation as well as sampling, preparation and laboratory procedures are given in Chapter 5, sections, 5.2.1 and 5.2.2.

6.2.2 The DayCent model

The DayCent model (Parton *et al.*, 1998; Del Grosso *et al.*, 2001) was built based on the biochemical ecosystem Century model (Parton *et al.*, 1987). Like the Century model, DayCent simulates C, nitrogen (N), phosphorus (P), and sulfur (S) cycles among the atmosphere, vegetation, and soil, but operating on a daily rather than a monthly timestep. The DayCent model also differs from Century in the processes regulating GHG emissions, particularly N gas fluxes, where processes such as nitrification and denitrification are explicitly represented. Due to the finer time-scale resolution and because of its rapid response to abiotic factors, the DayCent model is generally considered more precise in its performance compared to the Century Model.

The DayCent model can be used to evaluate the C dynamics of different ecosystems (e.g. grassland, agricultural crop, forest, or savanna) in response to changes in climate as well as type and timing of management practices such as tillage, fire, plant harvest (including variable residue removal), grazing intensity, cultivation, irrigation, and organic matter or fertiliser additions. Overall, simulations in DayCent are based on species-specific measured/estimated data for phenology, net primary production (NPP), shoot:root ratio and biomass C:N ratio of plant components. The model consists of different submodels including SOM formation and decomposition, mineralisation of nutrients, soil water and temperature dynamics, plant production and allocation of NPP as well as N gas fluxes (Chapter 1, Fig 1.3). Soil water and temperature are simulated for each horizon by the land surface submodel. In the soil water submodel, water content and fluxes, including runoff, leaching, evaporation, and transpiration, are simulated as a function of water inputs through rainfall, irrigation or snowmelt, that can either lead to saturated or unsaturated water flows in the soil profile. Plant growth is estimated by DayCent according to species-specific data, soil/air temperature, soil water availability and actual plant-specific nutrient requirements and availability. Based on the plant type and phenology, NPP is partitioned into leaves, branches, large wood, fine roots, and large root compartments. The shoot:root ratio of the NPP is calculated as a function of soil water content and nutrient availability and dead plant materials are divided into structural (high C:N ratio) and metabolic (low C:N ratio) components. The DayCent model uses all these plant partitions and processes to determine the quantity and quality of plant residue added to the litter and soil pools, meaning that plant production submodels are directly linked to the SOM submodel. This interaction between plant production routines and soil modules leads to allocation, transfer, and partitioning of the SOM into three conceptual pools with different turnover times controlled by specific decomposition rates (1. active, fast turnover, 2. intermediate, medium turnover, 3.

passive, slow turnover). In this sense, soil C, N and nutrient fluxes are controlled by the amounts in these conceptual pools as well as by the abiotic temperature and soil water factors and soil physical properties e.g. texture. Soil C, in particular, is simulated for the upper 0-0.20 m layer based on the sum of the dead plant matter and SOM pools while considering the mineralisation of the litter and the SOM. Litter and SOM mineralisation are controlled by several factors including substrate availability, substrate quality (lignin content, C:N ratio), water and temperature stress, soil texture and tillage intensity. In terms of GHG emission, N gasses fluxes (N_2O, NOx, N_2) are driven by soil NH_4^+ and NO_3^-, water content, temperature, soil physical properties (e.g. texture, density) and labile C availability (Parton *et al.*, 2001), whilst CH_4 oxidation is mainly governed by C substrate availability for methanogens and the impact of environmental variables (soil texture, pH, temperature, climate and agricultural practices).

The main required inputs parameters for simulation are soil data (including soil texture, bulk density (BD) and pH), current and historical land use, and daily maximum and minimum temperature and precipitation. A full description of the DayCent model can be found in Del Grosso *et al.* (2001) and Parton *et al.* (1998). In this study, a previously parameterised and calibrated version of the DayCent model for the UK conditions was considered (Fitton *et al.*, 2014b; a; Begum *et al.*, 2017).

6.2.3 Model set-up, initialisation, simulation, and validation

The DayCent model was initialised using an average of the measured/estimated site-specific features viz. soil texture, BD, pH, field capacity (FC), wilting point (WP), and hydraulic conductivity (HC), between all the study fields in the farm-scale study (sampled in 2017) and the treatments in the NFSC trial (sampled in 2018) (Table 6.1). Briefly, soil texture was determined by a low angle laser light scattering technique (Laser diffraction), BD was measured using the core method and a volumetric steel ring of 0.03 m inner diameter (Blake & Hartge, 1986) and pH was measured in H_2O (1:2.5 soil:solution). A full description of soil preparation, laboratory procedures and analyses are given in Chapter 3, section 3.2.4 and Chapter 5, section 5.2.2. Estimation of FC, WP, and HC was calculated from texture and organic matter using the algorithms developed by Saxton & Rawls, (2006). Long-term meteorological measurements including daily maximum and minimum average temperature and precipitation for the period between 1900-2020 were taken from the combination of three different weather stations. From 1900 to 2002 data were collected from the historical weather stations of Durham and Albemarle, ~30 and 4 km away from Nafferton farm respectively (https://www.metoffice.gov.uk). On site weather measurements were used for the period from 2003 to 2020, taken from a weather station located at Nafferton farm (Fig. 6.1).

Table 6.1 Summary of the input parameters entered in the DayCent model including climate data and general soil properties (0-0.20 m depth) encompassing the farm-scale study and the Nafferton Factorial Systems Comparison (NFSC) trial.

Input parameters	Unit	Value
Climate data [a]		
Latitude (only used as information, not an input)	degree	54.9857 N
Longitude (only used as information, not an input)	degree	1.8990 W
Yearly maximum of average daily temperature	ºC	12.1
Yearly minimum of average daily temperature	ºC	4.7
Yearly maximum accumulated precipitation	mm	1048
Atmospheric CO_2 concentrations	ppm	418
Soil properties [b]		
Soil texture (sand, silt, clay)	%	40, 43, 17
Bulk density	Mg m^{-3}	1.15
pH (H_2O)	-	6.3
Field capacity	%	28.09
Wilting point	%	10.64
Hydraulic conductivity	cm sec^{-1}	0.001
Initial total carbon stock [c]	Mg ha^{-1}	60

[a] Taken from a combination of the MetOffice database and site-specific inputs.
[b] Average of the measured/estimated site-specific features considering all the study fields in the farm-scale study (sampled in 2017) and the treatments in the NFSC trial (sampled in 2018).
[c] Based on published data for the arable system for the whole UK (Tipping *et al.,* 2012, 2017; Davies *et al.,* 2016; Muhammed *et al.,* 2018)

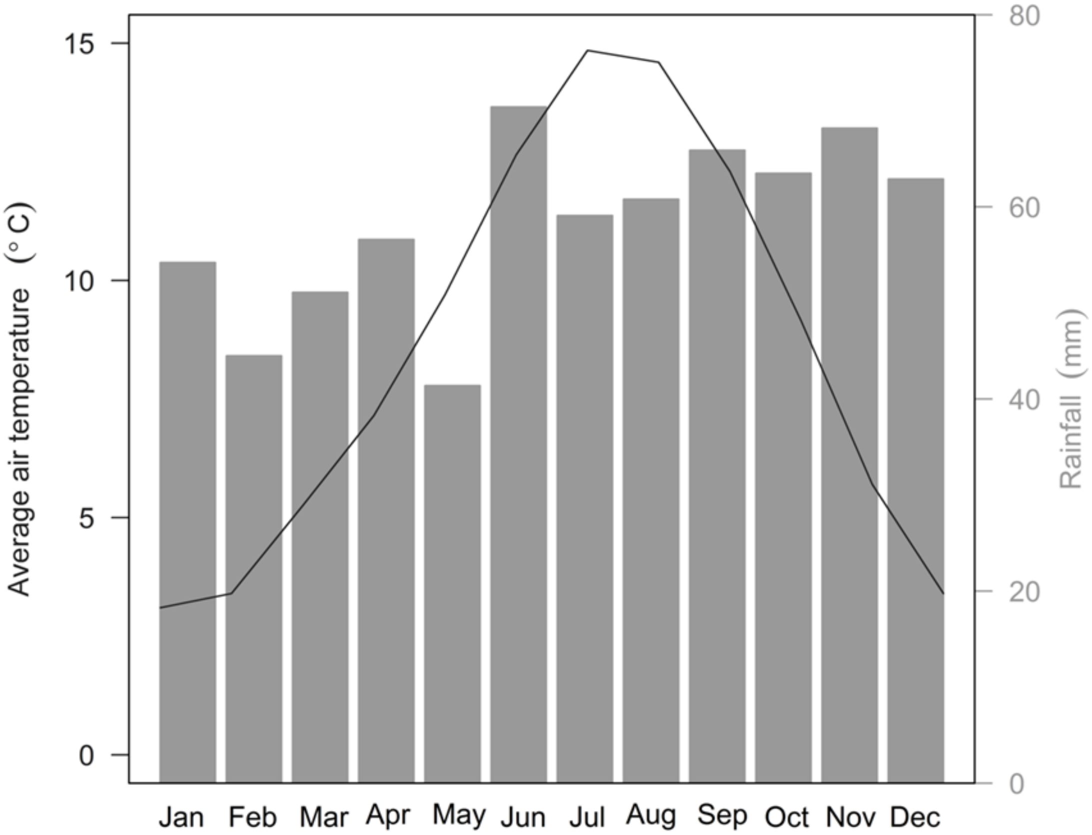

Figure 6.1 Average monthly air temperature (line) and rainfall (bars) at Nafferton farm, Stocksfield, Northumberland, north-east of England, UK, between 1900-2020.

Since there were no historical data of the SOM pools for Nafferton farm, historical land uses were first run to establish a modern-day baseline (Del Grosso *et al.*, 2006, 2011). The initial soil C stock (~ 60 Mg ha^{-1}) was set using previously published data for the arable system for the whole UK (Tipping *et al.*, 2012, 2017; Davies *et al.*, 2016; Muhammed *et al.*, 2018), distributing the total value into the three different SOM pools according to the DayCent manual. This initialisation approach was performed following procedures described in Nemo *et al.* (2017). The modern-day baseline was simulated based on historical records of the UK, and whenever possible local records, by interviewing local experts, and consulting published literature (Avery & Bullock, 1969; Research Rothamsted, 2006; Pullan, 2011). In this sense, the following approach was conducted: i) "three-field rotation system" based on carbohydrates, protein and grazed fallow with no artificial fertilisers application; simulated rotation of wheat/peas/grazed fallow (years 1 to 1850); ii) "Norfolk four-course rotation", a four-field rotation system with also no artificial fertiliser application but including a fertility building phase, simulated rotation of wheat/barley/potatoes/grazed grass-clover (years 1851 to 1950); and iii) "intensification and simplification", a post-war period characterised by the use of agricultural systems with a more cash crop-based system and replacing the fertility building phase and livestock by artificial fertiliser applications (50 kg N ha^{-1} and maintaining minimum residues), simulated rotation of wheat/wheat/barley/potato (years 1951 to 1980). Due to a scarcity of site-specific data, this approach was assumed to be identical for all study sites up to 1980.

From 1981 onwards a slightly different approach was conducted for the farm-scale study and for the NFSC trial. For the farm-scale study, for the period between 1981-2007, we have attempted to use more specific land uses of the Northumberland region based on Pullan, (2011), along with historical land cover maps of Nafferton farm available in Digimap dataset (EDINA Digimap, 2020a; b). In this case, the rotation system of each study field was either still focused on cash crop but also including a compulsory set-aside practice and oilseed rape as a break crop (simulated rotation of barley/set-aside grass-clover/wheat/oilseed rape/wheat) (Pullan, 2011) or it was converted to permanent grassland. For the NFSC trial, the same approach was conducted but only for the period between 1981-2000. For both cases, nitrogen and phosphorus fertiliser application rates were based on historical data reported in Archer (1985); DEFRA (2011) and Naden *et al.* (2016) whilst the cattle stocking rates were estimated based on census data for the UK available at Britain (2020).

From 2008 to 2018 (for the farm-scale study) and from 2001 to 2018 (for the NFSC trial) simulations were scheduled according to the site-specific land uses and type and timing of management practices implemented, including the exact day and rates of fertiliser application, tillage operations, grazing or silage (non-grazed) events and organic amendments application (manure, farmyard manure and/or slurry). For these periods, simulations were based on Nafferton farm records (as described in Chapter 3 and Chapter 5).

For all simulation periods, default parameterised values specified in the DayCent model along with a few previously parameterised and calibrated values for the UK conditions (Fitton *et al.*, 2014b; a; Begum *et al.*, 2017) were employed. Whenever necessary crop production levels were further calibrated by adjusting the biomass production PRDX crop parameter following procedures described in Del Grosso *et al.* (2011) to reflect national yield figures reported by Defra every year since the 1890s. Once adjusted, the PRDX crop parameter was left unchanged across all simulations, so that differences in the model outputs were only due to changes in the agricultural system and/or management practices (Fitton *et al.*, 2014b; a). Soil texture, BD, pH, FC, WP and HC were kept constant across all the study fields considered in the farm-scale study and treatments assessed in the NFSC trial (Table 5.1).

Soil C stock measurements in three different years (2011, 2017 and 2018), which were not used in the initialisation phase, were used for model validation. Soil C concentration was determined by dry combustion method (Nelson & Sommers, 1996) using an Elementary Vario Macro Cube analyser (see details in Chapter 2, Section 2.2.4). Thermal analysis (Thermogravimetry-Differential Scanning Calorimetry-Quadrupole Mass Spectrometry) conducted in Chapter 5, Section 5.3.3, of this thesis showed that there were low carbonates present in the samples (Chapter 5, Fig 5.7), therefore, total soil C concentration can be assumed to be total soil organic C (hereafter referred to as SOC). SOC stocks per unit of area (Mg ha^{-1}) were calculated on an equivalent soil mass basis (see Chapter 1, Section 1.5 for details about the calculations and equivalent soil mass adjustments). Since measured and simulated SOC stocks were evaluated in different depth intervals (0-0.15 and 0.15-0.30 m in 2017 and 2018; 0-0.30 m in 2011; 0-0.20 m in the model output), the 0-0.20 m SOC stocks were calculated by an average of 75% of the accumulate 0-0.30 m depth (Senapati *et al.*, 2016). Subsequent checks were also performed to ensure that simulated yields were in line with measured data from other published studies (Marks, 1989; Glendining *et al.*, 1998).

6.2.4 Statistical analyses

Model simulation performance for SOC stocks was undertaken following the statistical methods described in Smith *et al.* (1997) by using the MODEVAL worksheet. This involved several statistical metrics including correlation coefficient (*r*), root mean square error (*RMSE*), mean difference (*M*), relative error (*E*), and lack of fit (*LOFIT*), shown below as equation 6.1, 6.2, 6.3, 6.4 and 6.5.

eqs. 6.1) $$r = \frac{\sum_{i=1}^{n}(O_i - \bar{O})\,(P_i - \bar{P})}{\sqrt{[\sum_{i=1}^{n}(O_i - \bar{O})^2]}\sqrt{[\sum_{i=1}^{n}(P_i - \bar{P})^2]}}$$

eqs. 6.2) $$RMSE = \frac{100}{\bar{O}} \times \sqrt{\frac{\sum_{i=1}^{n}(O_i - P_i)^2}{n}}$$

eqs. 6.3) $$M = \frac{\sum_{i=1}^{n}(O_i - P_i)}{n}$$

eqs. 6.4) $$E = \frac{100}{\bar{O}}\frac{\sum_{i=1}^{n}(O_i - P_i)}{n}$$

eqs. 6.5) $$LOFIT = \sum_{i=1}^{n} m_i(O_i - P_i)^2$$

where $\bar{O}$, $\bar{P}$, O_i, P_i, m_i and n is the average of all measured values, the average of all simulated values, the measured value, the simulated value, the number of replicates of the measurement and the number of the measurements, respectively.

The *r* test represents the correlation between measured and simulated values and therefore it evaluates the overall performance of the model to capture potential variabilities; *RMSE, M*, *E* and *LOFIT* are tests that are correlated to the coincidence or differences between measured and simulated values. The significance of these tests was evaluated as follows: *r* was tested using *F-value at p = 0.05*; *RMSE* and *E* were tested at 95% confidence limit (*RMSE95%* and *E95%* respectively); *M* was evaluated using Student's t test (two-tailed, critical at 2.5%); *LOFIT* was evaluated by *F* critical at 5%. All these metrics were carried out between measured and simulated SOC stocks separately for the farm-scale study (sampled in 2017) and the NFSC trial (sampled in 2011 and 2018).

6.2.5 Sensitivity analysis

A systematic model sensitivity analysis was conducted for a total of five input parameters: two climatic (daily air temperature and precipitation) and three soil properties (soil clay content, BD and pH). Sensitivity analysis was performed aiming to identify which model input parameter might exert the most influence on the model results. In this study, it also helps to capture how sensitive the model is to variations in environmental covariates and soil characteristics as well as to identify potential critical parameters that might need special attention and/or site-specific calibration for effective simulation of SOC stocks (Smith & Smith, 2007). Since in our simulations an overall average of soil clay content, BD and pH were used for all cases (see section 6.2.3, "*Model set-up, initialisation, simulation, and validation*" for more details), the sensitivity analysis also helps to identify potential variability in our predictions, i.e. detect potential sensitivity of the model to these input variables. All the target input parameters were tested by changing one-at-a-time while the other parameters were kept with their original values. Daily air temperature and pH were checked by changing the target input parameter by a factor of ± 1, i.e. ± 1 °C and ± 1 pH unit respectively, whereas daily precipitation, soil clay content and BD were examined by changing the target input parameter by a factor ± 10%. Sensitivity analysis results were presented as a percentage change in SOC stocks compared to its original base simulation over the last simulation period i.e. from 2008 to 2018.

6.2.6 Long-term scenarios

Validated simulations from all the farm-scale study fields and treatments assessed in the NFSC trial (for details of scenarios see Chapter 3 and Chapter 5) were extended beyond the 2017/18 measurement date up to 2050. This approach was conducted in order to allow enough time for each study field situation and treatments in the NFSC trial to show potential differences in SOC stocks that were not captured by the empirical measurements in 2017/18 (i.e. the year of measurements).

Furthermore, 11 additional scenarios were simulated for each agricultural system (CONV and ORG), totalling 22 long-term hypothetical scenarios as follows:

- Scenario 1: a four-year arable rotation
- Scenario 2: a four-year arable rotation plus two years of non-grazed grass-clover
- Scenario 3: a four-year arable rotation plus four years of non-grazed grass-clover
- Scenario 4: a four-year arable rotation plus six years of non-grazed grass-clover
- Scenario 5: a four-year arable rotation plus eight years of non-grazed grass-clover
- Scenario 6: a four-year arable rotation plus two years of grazed grass-clover
- Scenario 7: a four-year arable rotation plus four years of grazed grass-clover
- Scenario 8: a four-year arable rotation plus six years of grazed grass-clover
- Scenario 9: a four-year arable rotation plus eight years of grazed grass-clover
- Scenario 10: a permanent non-grazed grass-clover
- Scenario 11: a permanent grazed grass-clover

These hypothetical scenarios were created with the aim to capture solely the effects of the implementation of alternative management practices (grazing regimes, length of grass-clover ley periods in crop rotations) in the conventional and organic agricultural system.

In this procedure, the four main arable crops grown in each agricultural system at Nafferton farm in the last 10-year period were used to create hypothetical scenarios. The conventional system was characterised by a hypothetical rotation of winter wheat (*Triticum aestivum*), winter barley (*Hordeum vulgare*), oilseed rape (*Brassica napus*) and potatoes (*Solanum tuberosum*), whereas the hypothetical organic rotation was composed of spring wheat, spring barley, beans (*Phaseolus vulgaris*) and potatoes. For the scenarios where grass-clover leys were grown, white and red clover (*Trifolium repens* and *Trifolium pratense*) as well as perennial ryegrass (*Lolium perenne*), were considered regardless of the agricultural system. Ley periods in the non-grazed scenarios were simulated with three harvests for silage events per year while the grazed scenarios were simulated with light cattle stocking rates (1-1.5 livestock units ha^{-1}) grazing from the beginning of May to end August. For simplicity, typical tillage operations (ploughing and disking) were simulated between each arable crop in both agricultural systems.

For all long-term hypothetical scenarios, the average of soil texture, BD, pH, FC, WP and HC across the whole farm was used (40, 43 and 17% for sand, silt, and clay, respectively and 1.15 Mg m^{-3} BD and pH 6.3). Further, the historical (1900-2020) average of meteorological data condition was considered, assuming thus no climate change or variation in atmospheric CO_2 concentrations. The initial SOC stock for the hypothetical long-term scenarios was set based on the average of the actual empirical measured (2017) SOC stock (0-0.20 m) across each agricultural system; 51.01 and 48.81 Mg ha^{-1} for the conventional and organic system, respectively.

6.3 Results

6.3.1 DayCent performance and sensitivity in simulating SOC stocks

DayCent simulations showed a good fit between measured and simulated values of SOC stocks (0-0.20 m depth) for both the farm-scale study and the NFSC trial (Table 6.2 and Fig. 6.2). In the farm-scale study, the measured SOC stock differences between agricultural systems (conventional-CONV *vs.* organic-ORG) and grazing regimes (non-grazed-NG *vs.* grazed-GG) were also observed in the model simulations. Both, measured and simulated SOC stocks of the CONV system and GG regime were higher compared to the ORG system and NG regime. Nevertheless, the model tended to slightly underestimate SOC stocks in the ORG system and the GG regime by 3.13 ± 1.32 and 3.50 ± 1.11%, respectively. Conversely, the model tended to marginally overestimate simulated values of the CONV system and NG regimes by 0.46 ± 1.59 and 1.13 ± 0.39%, respectively (Table 6.2). The model simulations also reflected measured SOC stocks in terms of different proportions of temporary grass-clover leys in crop rotations (LTP). An increased LTP to approximately 40% of the crop rotation (i.e. 3-4 years in a 10-year period) positively increased SOC stocks regardless of whether the system is conventionally or organically managed (Fig. 6.3).

In the NFSC trial, the differences between measured and simulated values were even lower compared to the farm-scale (less than 2%) (Table 6.2). Nonetheless, not all the differences in the measured SOC stocks between the treatments were reflected in the simulated values. The exception was for the fertility source treatment, which showed higher measured values for the MINE compared to the COMP (41.19 ± 0.69 and 40.59 ± 0.85 Mg ha^{-1}, respectively), but an opposite trend for the simulated values (40.67 ± 0.54 and 41.26 ± 0.66 Mg ha^{-1}, respectively). Higher SOC stocks for the MINE compared to the COMP was also observed in an earlier chapter of this thesis for the 0-0.30 m depth (Chapter 5, Table 5.5) (non-significant; $p > 0.05$). For the crop rotation schemes and year of sampling, both measured and simulated SOC stocks of the ORG-RT and 2018 samples were higher than CONV-RT and 2011 samples (Table 6.2).

Overall, despite the few differences between measured and simulated values, statistical metrics indicated that the DayCent model simulated SOC stock changes under alternative management practices and agricultural systems with good accuracy (Table 6.3). For both cases (farm-scale study and NFSC trial), the model showed good association (indicated by a significant correlation coefficient i.e. *F* value calculated from the *r* greater than the critical *F-value at p = 0.05*), *RMSE* within the 95% confidence limit (i.e. non-significant differences between measured and simulated values), lack of significant bias in the simulated values (represented by the values of *M* and *E*), and a good fit and degree of coincidence (indicated by the non-significant error of *LOFIT* values, that is, the model error is not greater than the error in the measurements) between measured and simulate SOC stocks (Table 6.3).

Table 6.2 Measured and simulated soil organic carbon (SOC) stocks at 0-0.20 m depth for the farm-scale study, encompassing agricultural system (conventional – CONV and organic – ORG) and grazing regime (non-grazed – NG and grazed – GG), and for the Nafferton Factorial Systems Comparison (NFSC) trial treatments, including crop rotation scheme (conventional-CONV-RT and organic-ORG-RT), fertility source (mineral-MINE and compost-COMP) and year of sampling (2011 and 2018).

Treatments	SOC stock			Deviation between measured and simulated
	Measured	Simulated	difference	
Farm-scale	Mg ha^{-1}			%
Agricultural system				
CONV	50.24 (1.03)	50.47 (2.64)	-0.23 (0.81)	0.46 (1.59)
ORG	49.51 (1.05)	47.96 (2.28)	1.55 (0.62)	-3.13 (1.32)
Grazing regime				
GG	53.72 (0.86)	51.84 (1.98)	1.88 (0.56)	-3.50 (1.11)
NG	43.48 (0.60)	43.97 (0.26)	-0.49 (0.17)	1.13 (0.39)
NFSC trial				
Rotation Scheme				
CONV-RT	39.78 (0.71)	40.39 (0.65)	-0.61 (0.03)	1.53 (0.09)
ORG-RT	41.99 (0.63)	41.55 (0.36)	0.44 (0.14)	-1.05 (0.32)
Fertility source				
MINE	41.19 (0.69)	40.67 (0.54)	0.52 (0.07)	-1.26 (0.17)
COMP	40.59 (0.85)	41.26 (0.66)	-0.67 (0.09)	1.65 (0.25)
Year				
2011	39.60 (0.86)	40.27 (0.39)	-0.67 (0.24)	1.69 (0.60)
2018	42.18 (0.50)	41.67 (0.55)	0.51 (0.03)	-1.21 (0.07)

Data are measured mean values (for the farm-scale study, n = 67 for conventional system, n = 59 for organic system, n = 47 for non-grazed regime and n = 79 for grazed regime, for the NFSC trial, n = 32 for rotation scheme, fertility source and year of sampling). The standard error of the mean is in parentheses.

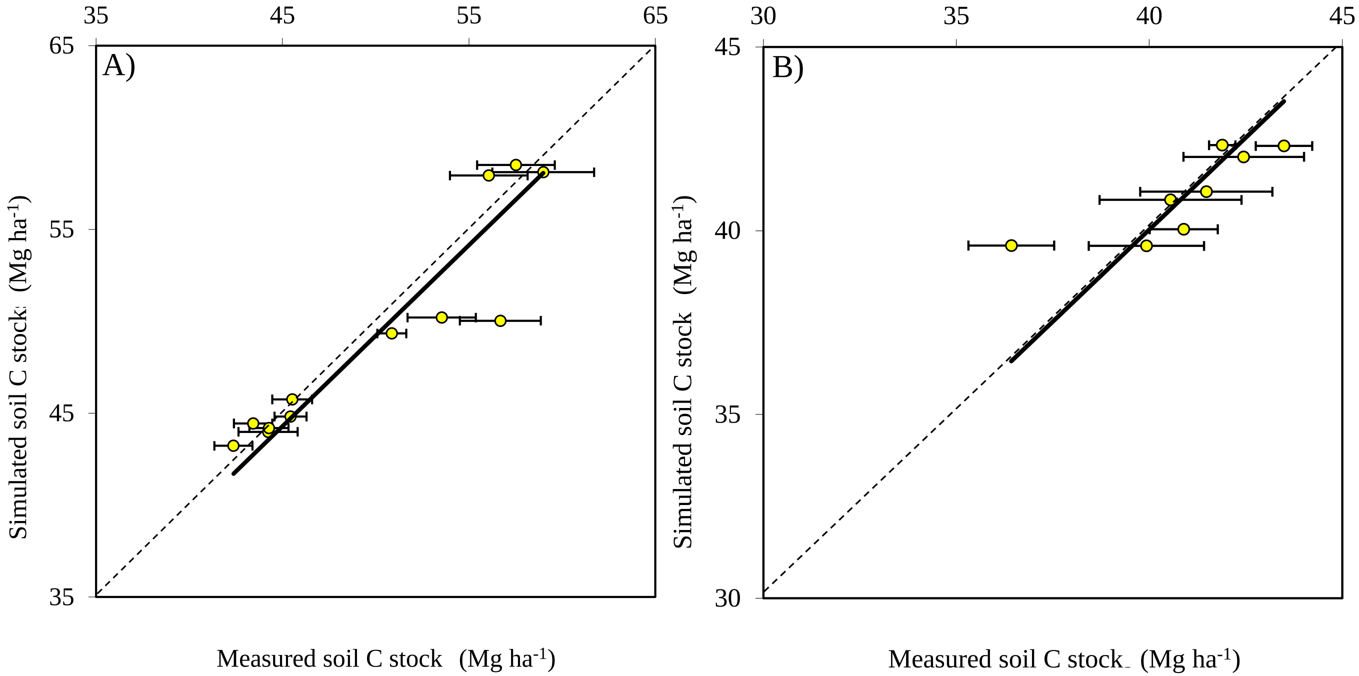

Figure 6.2 Relationship between measured and simulated soil organic carbon (C) stocks at 0-0.20 m depth for the (A) farm-scale study; and (B) for the Nafferton Factorial Systems Comparison (NFSC) trial. Each yellow point represents a study site soil organic C stock mean of a minimum of four and a maximum of 15 spatial replication. The horizontal bars represent standard errors around the mean measured soil organic C stocks due to spatial replication (n = 8-15 for the farm-scale study and n = 4 for the NFSC trial). The dashed line is the 1:1 line and the solid line is the linear regression line.

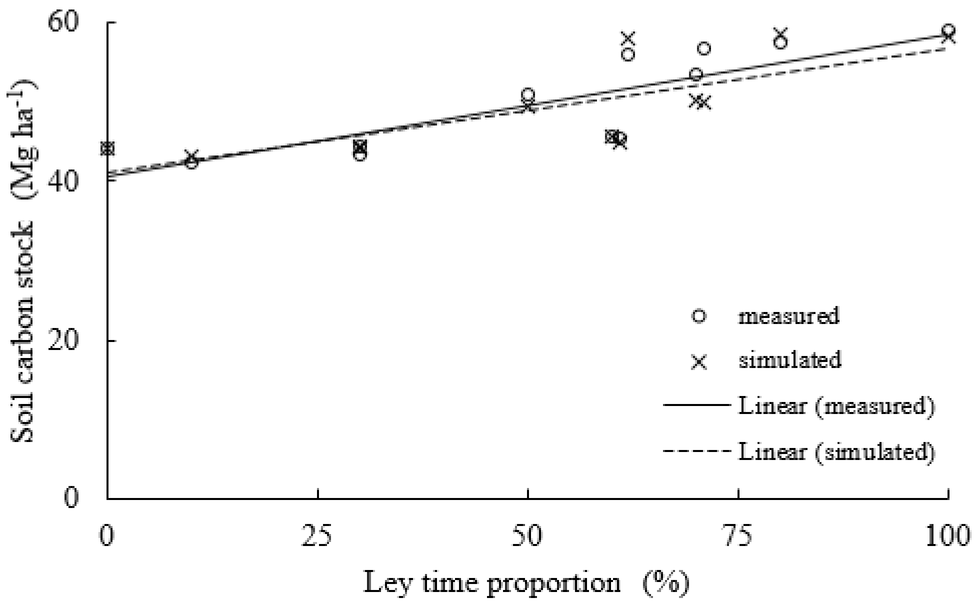

Figure 6.3 Relationship between measured and simulated soil organic carbon stocks at 0-0.20 m depth due to changes in ley time proportions (%). Each (○) symbol represents a study site soil organic carbon stock mean of a minimum of eight and a maximum of 15 spatial replication. Each (x) symbol represents the simulated soil organic carbon stock of the study site. The solid line is the linear regression line around the measured values, while the dashed line is the linear regression line around the simulated values.

Table 6.3 Statistical metrics, including correlation coefficient (*r*), root mean square error (*RMSE*), mean difference (*M*), relative error (*E*), and lack of fit (*LOFIT*), applied for the validation between measured and DayCent model-simulated soil organic carbon stocks (0-0.20 m) for the farm-scale study and the Nafferton Factorial Systems Comparison (NFSC) trial.

Statistical metrics	*Farm-scale*	*NFSC trial*
r = Correlation coefficient	0.93	0.81
$F = ((n-2)\ r^2) / (1-r^2)$	64.14	11.79
F value at p = 0.05	4.96	5.99
RMSE = Root mean square error of model	0.05	0.03
RMSE95% (Confidence limit)	0.08	0.14
M = Mean Difference	0.70	-0.08
t = Student's *t* of *M*	1.05	0.17
t value critical at 2.5% (Two-tailed)	2.23	2.45
E = Relative Error	1.40	-0.20
E95% (Confidence limit).	7.04	12.72
LOFIT = Lack of Fit	588.77	51.76
F = MSLOFIT/MSE*	1.57	0.95
F critical at 5%	1.91	2.42

* MS = mean squared; MSE = mean squared error.

Model simulations of SOC stocks showed an overall low sensitivity to the five input parameters tested (Table 6.4). In general, the model showed the same pattern of sensitivity for the same parameters both for the farm-scale study and the NFSC trial. Among the five parameters tested, simulations of SOC stocks showed sensitivity higher than 1% for changes in daily precipitation, pH and clay contents, whereas sensitivity was lower than 1% for changes in daily air temperature and BD. A change in pH by -1 unit, clay content by +10%, and daily precipitation by -10% resulted in an increase in simulated SOC stocks on average by 7, 3 and 2%, respectively. On the other hand, changing pH by +1 unit, clay content by -10% and daily precipitation by +10%, negatively affected SOC stocks by 2% on average for all cases relative to its original base simulation. Changing in daily air temperature ± 1 °C and soil BD ± 10% showed a negligible effect on simulated SOC stocks for all the treatments, change averages of 0.3, -0.2, -0.1 and 0.3, respectively (Table 6.4).

Table 6.4 Model sensitivity in the simulation of soil organic carbon stocks for the farm-scale study, encompassing agricultural systems (conventional – CONV and organic – ORG) and grazing regimes (non-grazed – NG and grazed – GG), and for the Nafferton Factorial Systems Comparison (NFSC) trial treatments, including crop rotation schemes (conventional-CONV-RT and organic-ORG-RT), fertility sources (mineral-MINE and compost-COMP) and years of sampling (2011 and 2018), to different input parameters.

	Variables/Parameters									
Treatments	Daily air temperature		Daily precipitation		pH		Clay content		Bulk density	
	-1 °C	+1 °C	-10%	+10%	-1 unit	+1 unit	-10%	+10%	-10%	+10%
Farm-scale	% change									
Agricultural system										
CONV	-0.97 (0.91)	0.95 (0.77)	1.88 (0.17)	-1.40 (0.18)	6.48 (0.25)	-1.76 (0.06)	-2.90 (0.13)	3.85 (0.11)	0.09 (0.06)	0.06 (0.02)
ORG	-0.86 (1.05)	0.97 (0.59)	1.52 (0.04)	-1.35 (0.02)	6.51 (0.20)	-1.76 (0.05)	-2.87 (0.13)	3.99 (0.13)	0.44 (0.07)	-0.09 (0.03)
Grazing regime										
GG	-1.86 (0.54)	1.71 (0.49)	1.55 (0.04)	-1.38 (0.07)	6.23 (0.15)	-1.70 (0.03)	-3.05 (0.08)	3.84 (0.12)	0.25 (0.04)	-0.06 (0.02)
NG	0.99 (0.45)	-0.53 (0.33)	2.00 (0.23)	-1.37 (0.25)	7.03 (0.09)	-1.90 (0.02)	-2.57 (0.06)	4.07 (0.06)	0.29 (0.21)	-0.03 (0.08)
NFSC trial										
Rotation Scheme										
CONV-RT	1.41 (0.08)	-1.11 (0.09)	3.41 (0.22)	-3.15 (0.12)	8.23 (0.09)	-2.29 (0.03)	-2.01 (0.06)	2.39 (0.05)	0.20 (0.02)	0.07 (0.02)
ORG-RT	0.25 (0.18)	-0.28 (0.19)	3.29 (0.07)	-2.63 (0.08)	7.91 (0.08)	-2.20 (0.01)	-1.71 (0.11)	2.32 (0.05)	0.52 (0.04)	-0.10 (0.03)
Fertility source										
MINE	0.85 (0.41)	-0.69 (0.32)	3.63 (0.16)	-2.94 (0.16)	8.16 (0.11)	-2.27 (0.03)	-1.75 (0.11)	2.36 (0.04)	0.40 (0.09)	-0.04 (0.05)
COMP	0.81 (0.31)	-0.70 (0.24)	3.06 (0.82)	-2.84 (0.19)	7.98 (0.13)	-2.22 (0.03)	-1.97 (0.08)	2.36 (0.07)	0.31 (0.10)	0.01 (0.02)
Year										
2011	1.02 (0.27)	-0.92 (0.19)	3.85 (0.73)	-3.04 (0.16)	8.10 (0.09)	-2.25 (0.03)	-1.84 (0.07)	2.28 (0.07)	0.39 (0.11)	-0.06 (0.06)
2018	0.64 (0.41)	-0.46 (0.29)	3.84 (0.56)	-2.74 (0.15)	8.05 (0.15)	-2.24 (0.04)	-1.88 (0.15)	2.43 (0.04)	0.32 (0.08)	0.02 (0.05)

6.3.2 SOC stock changes from the historical period up to the measurement date

Model simulations, considering the initial SOC stock of ~ 60 Mg ha^{-1}, indicated that the use of the "three-field rotation system" for a 50-year period led to soil C loss at a rate of 0.30 Mg ha^{-1} yr^{-1} (Fig. 6.4). Subsequently, the model estimated that the use of "Norfolk four-course rotation" for a 100-year period kept SOC stocks relatively stable with a partial recovery rate of 0.01 Mg ha^{-1} yr^{-1}. The third period (referred to as "intensification and simplification"), simulated from 1951 to 1980, led to SOC stocks loss at a rate of 0.05 Mg ha^{-1} yr^{-1}. Overall, the model predicted that SOC stocks after the 180-year period of modelled for historical land use would be approximately 72% of the initial 60 Mg ha^{-1} (Fig. 6.4).

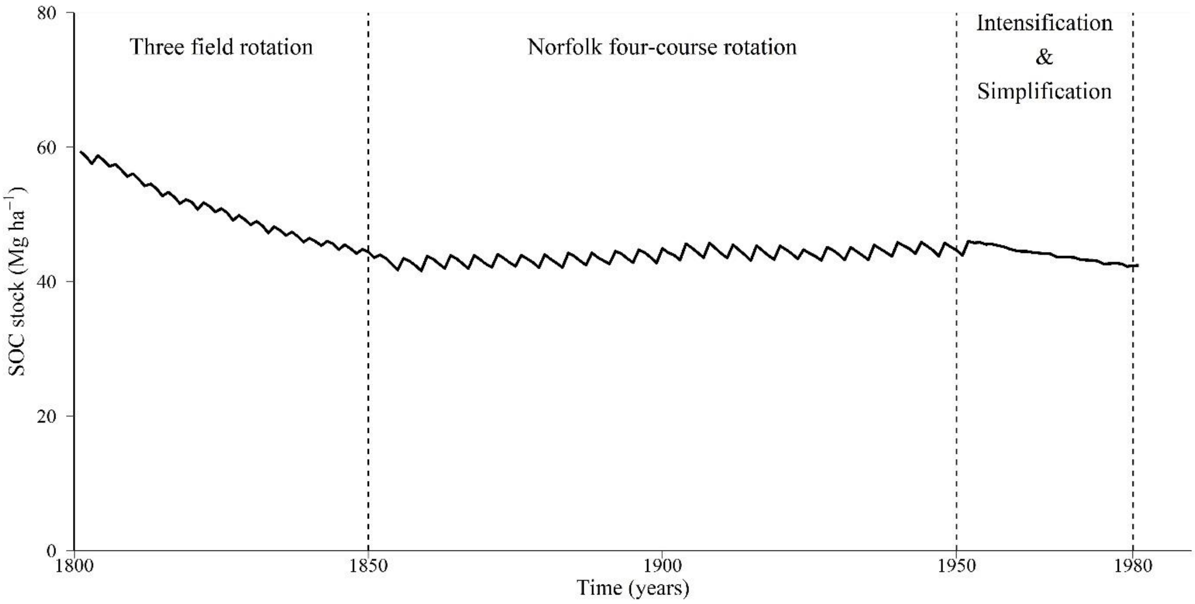

Figure 6.4 Equilibrium to modern-day baseline simulation of soil organic carbon (SOC) stocks at 0-0.20 m depth.

Between 1981 and 2000, both sides of the farm (conventional and organic) were simulated without site-specific details (Fig. 6.5 A, B). However, the few resources available, including publications, maps, and land use history from the farm archives, indicated that the study fields were divided into two distinctive land use groups: a cash crop-based system and another in permanent grassland. Study fields under the cash crop-based system resulted in SOC stock gains of only 0.06 Mg ha^{-1} yr^{-1}, whereas study fields converted to a permanent grassland increased SOC stocks at a rate of 0.31 Mg ha^{-1} yr^{-1}.

Simulations for the farm-scale study fields from 2001 (year of agricultural management change across half of the farm area) to 2017 (year of the measurements) showed a similar overall trend under conventional and organic study fields. In general, study fields under the GG regime and higher LTP ($\geq$ 40%, e.g. study fields n° 3, 4, 5, 6, 7, 8, 9 and 12) increased SOC stocks at an average of 0.35 ± 0.04 and 0.25 ± 0.10 Mg ha^{-1} yr^{-1} in the CONV and ORG system, respectively (Fig. 6.5 A, B). The opposite response was observed when the study fields were under a NG regime with lower LTP (< 40%, e.g. study fields n° 1, 2, 10 and 11), with SOC stock losses of 0.08 ± 0.02 and 0.03 ± 0.01 Mg ha^{-1} yr^{-1} in the CONV and ORG system, respectively (Fig. 6.5 A, B). The variations observed in the measured SOC stocks between the study fields within each agricultural system were also reflected in the model simulations (Fig. 6.5 A, B). For the same period (i.e. 2001-2017), and taking into consideration the agricultural systems only (conventional *vs.* organic), SOC stocks in the conventionally managed soils were enhanced at a rate of 0.21 ± 0.10 Mg ha^{-1} yr^{-1} while under the organically managed soils showed SOC stock gains of 0.17 ± 0.08 Mg ha^{-1} yr^{-1}.

In the NFSC trial, simulations from 2001 (year of the establishment of the experiment) to 2011 and 2018 (years of measurements) confirmed the variations observed in the measured SOC stocks for the treatments assessed (Fig. 6.5 C). From the establishment of the experiment (2001) to the last measurement date (2018), simulations predicted SOC stock losses of ~0.20 ± 0.03 Mg ha^{-1} yr^{-1} for all treatments assessed. However, it was observed that from 2011 to 2018, i.e. the second cycle of the rotation, there was a consistent increase in SOC stocks in all treatments. This increase in SOC stocks was observed to be modest when MINE fertility sources were applied in either CONV-RT or ORG-RT schemes; soil C gains of 0.02 and 0.07 Mg ha^{-1} yr^{-1}, respectively. Whereas the COMP fertiliser application led to SOC stock gains of 0.25 and 0.15 Mg ha^{-1} yr^{-1} under CONV-RT and ORG-RT schemes, respectively (Fig. 6.5C).

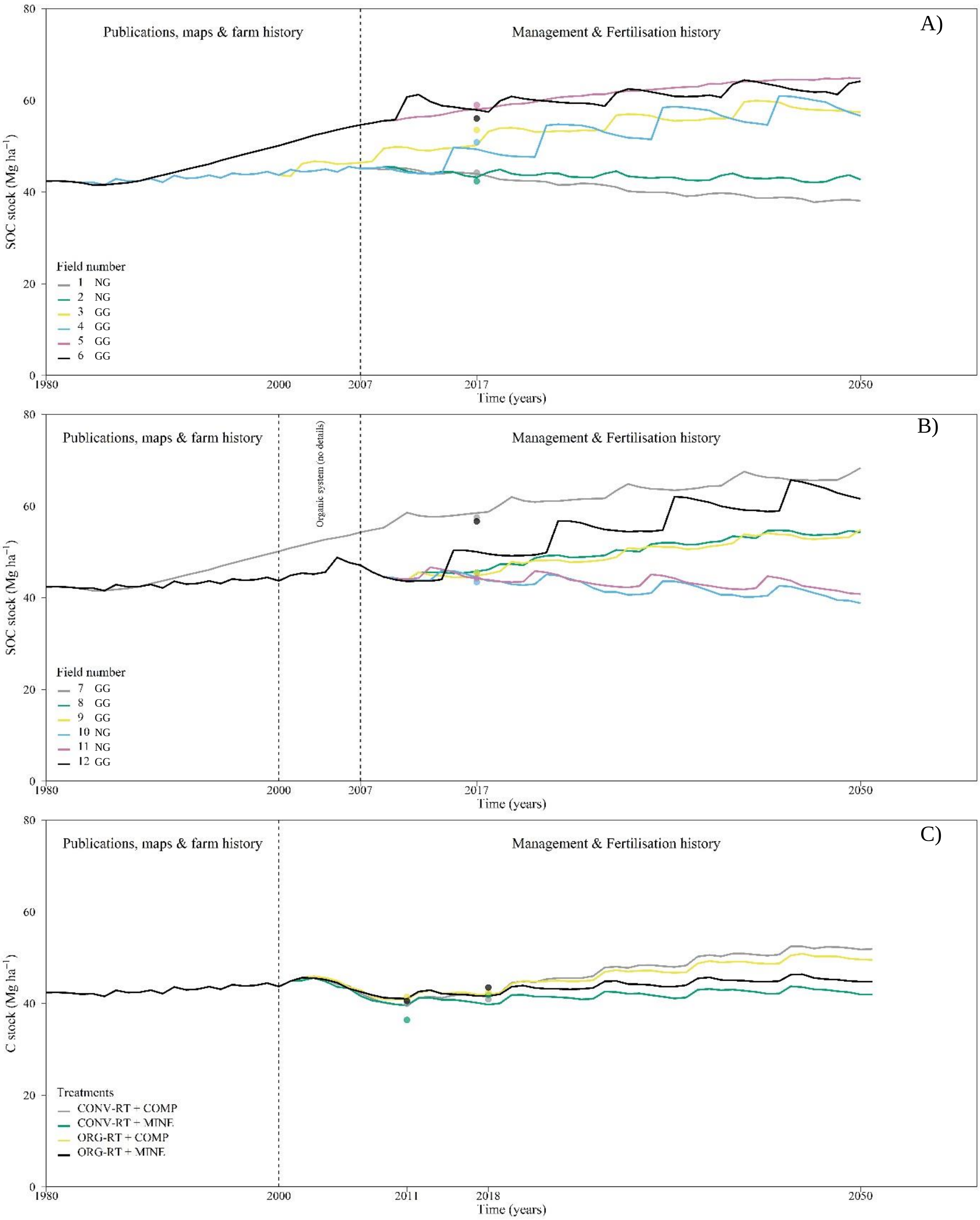

Figure 6.5 Long-term simulations of soil organic carbon (C) stocks at 0-0.20 m depth of the farm-scale study in A) conventional system, B) organic system, and C) for the Nafferton Factorial Systems Comparison (NFSC) trial. Grazing regime represented by non-grazed-NG and/or grazed-GG. Treatments in the NFSC trial includes crop rotation schemes (conventional-CONV-RT and organic-ORG-RT) and fertility sources (mineral-MINE and compost-COMP). Dots represent measured mean soil organic C stock values in 2017 for A and B and 2011 and 2018 for C.

6.3.3 SOC stock changes in the long-term simulations and hypothetical scenarios

The 33-year projection from 2017-2050 for each study field in the farm-scale study confirmed the differences observed in the year of the measurement (Fig. 6.5). Long-term projections have shown that regardless of the agricultural system, study fields under the GG regime and with higher LTP will continue to increase SOC stocks for another 33 years before it attenuates and towards a new equilibrium state (study fields n° 3, 4, 5, 6, 7, 8, 9 and 12; average of 0.25 ± 0.02 Mg ha^{-1} yr^{-1}). Although differences in SOC stocks were still evident between the study fields in the farm-scale and treatments in the NFSC trial in 2050, the rate of increase suggests that it will be minimal between study fields with LTP ≥ 40% (average rates of increase of 0.23 ± 0.01 and 0.28 ± 0.02 Mg ha^{-1} yr^{-1} in the CONV and ORG system, respectively) (Fig. 6.5 A, B). For the same period, the NG regime and lower LTP (< 40%) fields continued to decrease SOC stocks by an average of 0.11 ± 0.03 Mg ha^{-1} yr^{-1} regardless of whether the system is conventionally or organically managed. The use of NG regime and lower LTP also appeared to rapidly reach a near-equilibrium state, but at a slower pace in study fields with a minimum of 10% of LTP.

Extending simulations for an additional 32-years (from 2018 to 2050) in the NFSC trial have also shown a continuous increase in SOC stocks for all treatments (Fig. 6.5 C). As noted for the results up to the year of the measurement (2018), there was a modest rate of increase in SOC stocks for the period between 2018-2050 when MINE fertility sources were applied (0.06 and 0.08 Mg ha^{-1} yr^{-1} in the CONV-RT and ORG-RT schemes respectively), while the use of COMP for the same period led to higher gains under both CONV-RT and ORG-RT schemes (0.29 and 0.22 Mg ha^{-1} yr^{-1} respectively). Overall, the combination of CONV-RT scheme and MINE fertility sources resulted in the lowest simulated SOC stocks (41.95 Mg ha^{-1}), while COMP application in the same rotation scheme showed the highest simulated SOC stocks in 2050 (51.89 Mg ha^{-1}). The differences in simulated SOC stocks for the period between 2018-2050 were 1.91, 9.56, 2.79, 7.22 Mg ha^{-1} for the CONV-RT+MINE, CONV-RT+COMP, ORG-RT+MINE, and ORG-RT+COMP, respectively (Fig. 6.5 C).

The 11 hypothetical scenarios run under both agricultural systems (conventional *vs.* organic) indicated that the use of a four-year arable rotation (scenario 1) sharply decreases SOC stocks (0.50 and 0.32 Mg ha^{-1} yr^{-1} in the CONV and ORG system respectively), while the permanent grazed grass-clover (scenario 11) would result in the higher SOC stocks than all other scenarios by 2050 (increase rate of 0.36 and 0.42 Mg ha^{-1} yr^{-1} in the CONV and ORG system, respectively) (Fig. 6.6 and 6.7). Nearly all scenarios under CONV system have indicated an overall decrease in SOC stocks between 2018 and 2050, except for scenarios 9, 10 and 11 (Fig.

6.6). Comparing rates of increase between the hypothetical scenarios where different years of grass-clover were introduced into a four-year arable rotation, but excluding the effects of the latter, it was noted that both systems were alike (average rates of increase of 0.44 ± 0.03 and 0.48 ± 0.02 Mg ha^{-1} yr^{-1} in the CONV and ORG system, respectively). For both systems, it was observed that the implementation of a minimum of four years grass-clover may prevent SOC stock losses caused by the use of a four-year arable rotation alone. Adding further years of grass-clover ley (i.e. 6 and 8 years, scenarios 4, 5, 8 and 9) in a four-year arable rotation resulted in a similar SOC stock for 2050 (Fig. 6.6 and 6.7). The results further indicated that whilst both non-grazed and grazed grass-clover have had a positive effect on SOC stocks, grass-clover periods under grazed would be slightly higher than the non-grazed regimes (Fig. 6.6 B and 6.7 B).

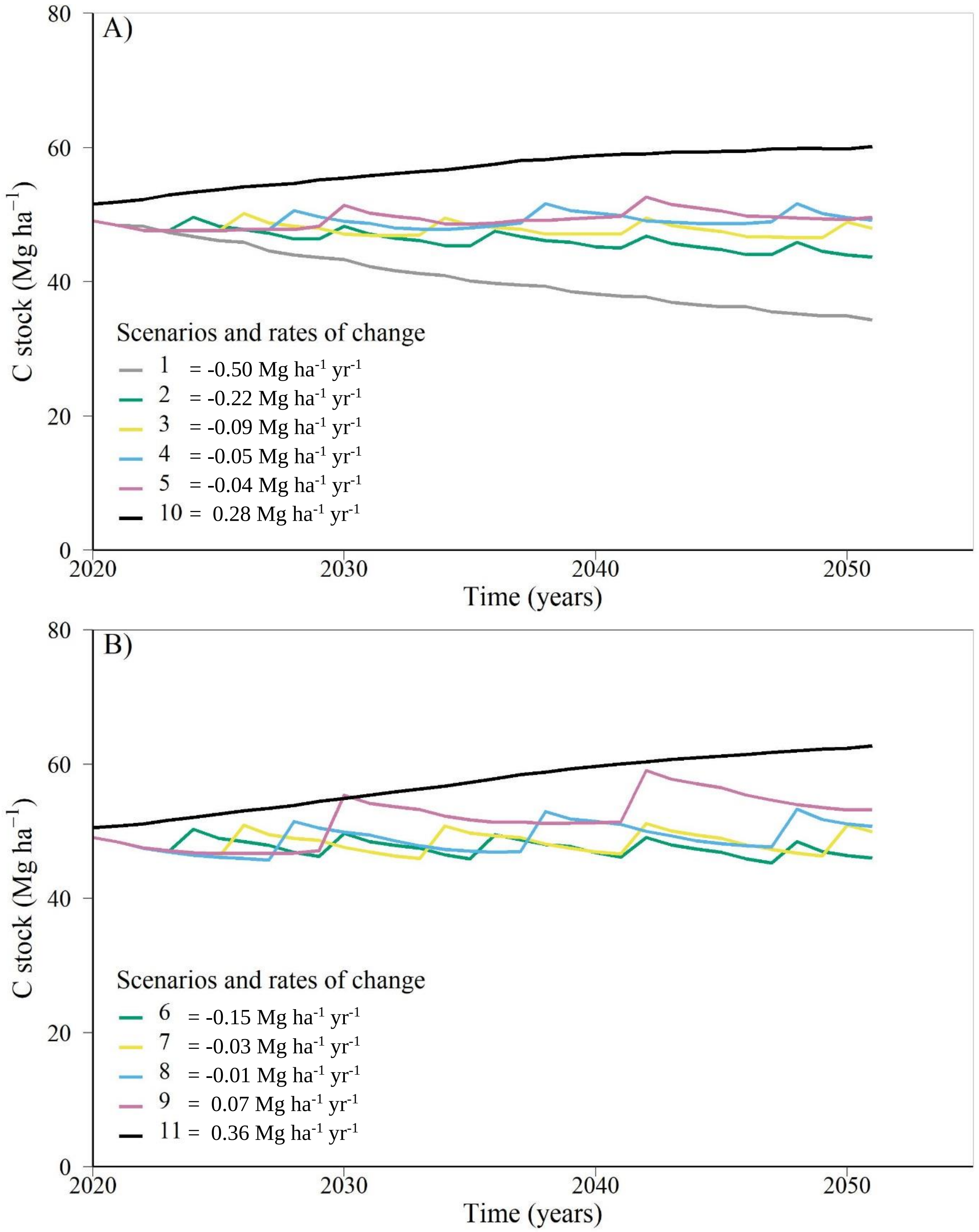

Figure 6.6 Long-term simulations of soil organic carbon (C) stocks at 0-0.20 m depth of the hypothetical scenarios under the conventional system. (A) non-grazed, (B) grazed. The reference for rates of soil organic C stock changes is the average of the measured (2017) soil organic C stock in the conventional system, 51.01 Mg ha^{-1} (n=6). The numbers 1-11 represent hypothetical scenarios as described in the "Long-term scenarios" section (Materials and Methods, section 6.2.6).

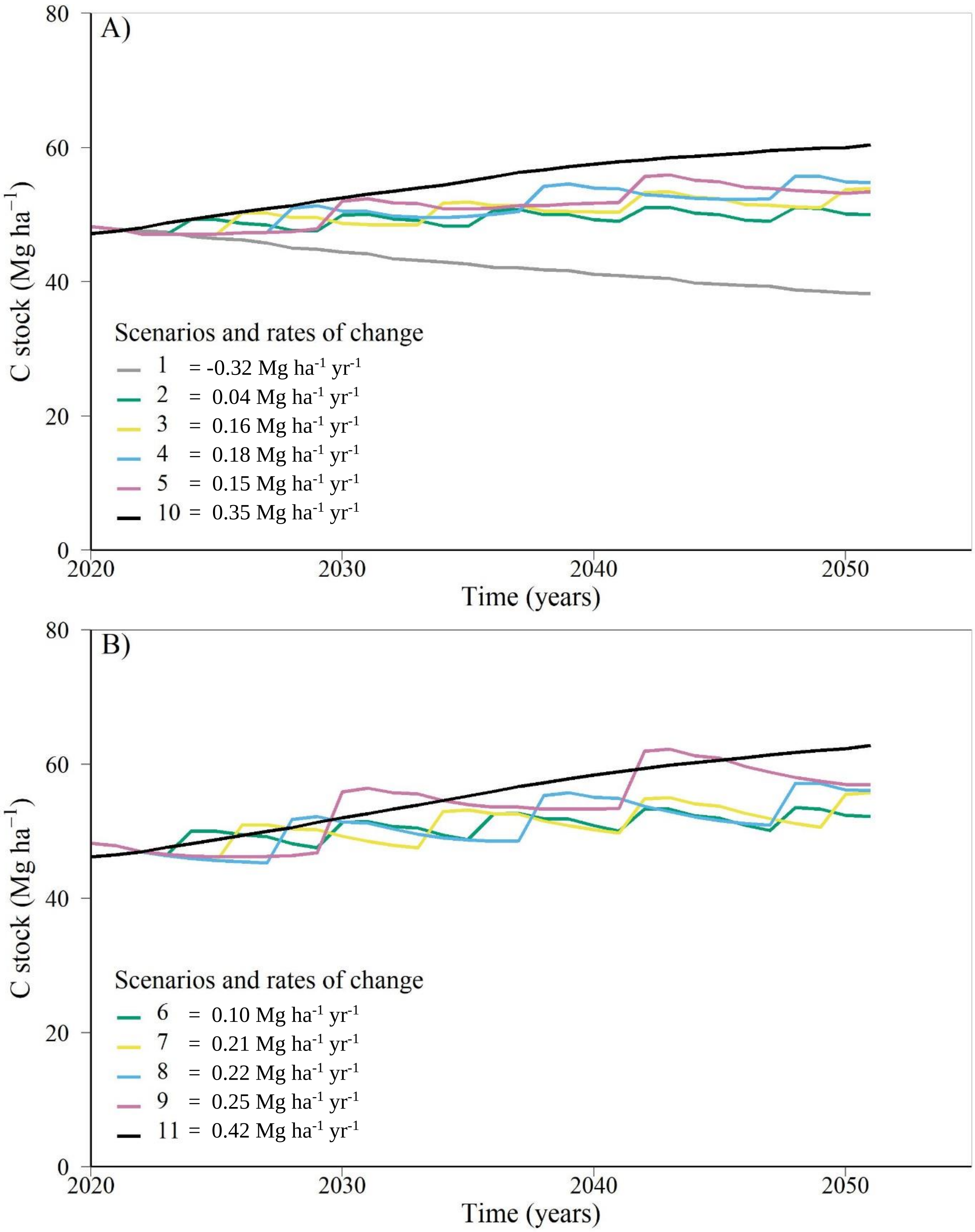

Figure 6.7 Long-term simulations of soil organic carbon (C) stocks at 0-0.20 m depth of the hypothetical scenarios under the organic system. (A) non-grazed, (B) grazed. The reference for rates of soil organic C stock changes is the average of the measured (2017) soil organic C stock in the organic system, 48.81 Mg ha^{-1} (n=6). The numbers 1-11 represent hypothetical scenarios as described in the "Long-term scenarios" section (Materials and Methods, section 6.2.6).

6.4 Discussion

6.4.1 Simulating SOC stocks with DayCent model

The ability of the DayCent model to simulate SOC stock changes under conventional and organic systems and the impacts of alternative management practices within these agricultural systems appeared to be reasonable as the simulated results reflected the main trends observed in the empirical measurements. The only exception was for the compost fertiliser-based treatment in the NFSC trial, which showed slightly higher simulated SOC stocks compared to the mineral fertiliser-based treatment in contrast to the empirical measurements. This is probably because, in the experimental trial study, high rates of compost were applied to match the N rates applied in the mineral treatment, which in the model resulted in accumulation of C mainly in the slow pool. However, it is not expected that all the C additions through compost fertilisation would go into the slow pool (even though empirical results in Chapter 5 have indicated larger contribution from more stable compounds under compost fertilisation). Despite this, all the simulated values were within the measured variability and clearly demonstrate that the simulations follow the measured trend.

The findings of this study are indeed promising as the overall predictions were reasonably accurate with a minimal need for model parameterisation. In this study, the model was not substantially changed (i.e. fully parameterised), instead small tunings were performed. This is also consistent with previous studies which indicated DayCent as a reliable model for simulating SOC stocks even without full site-specific parameterisation (Fitton *et al.*, 2014b; a; Congreves *et al.*, 2015; Bista *et al.*, 2016; Senapati *et al.*, 2016; Begum *et al.*, 2017; Lee *et al.*, 2020). Begum *et al.* (2017), similarly to this study, adjusted only plant production parameters for an appraisal of different fertiliser and manure additions on the long-term Broadbalk experiment (Rothamsted, UK). The authors reported a high degree of association of the DayCent simulated values and the empirical measurements collected between 1843-2014. However, the authors stressed that a slight over-prediction could occur under mineral fertilisation treatments as the model simulates higher yields and therefore also higher C additions. This is also in agreement with another recent study conducted by Senapati *et al.* (2016), who tested the sensitivity of the DayCent model and highlighted that it did not simulate low input regimes very well. These may also be the reasons for the marginally overestimated simulated SOC stocks in the conventional system and non-grazed regimes and the underestimated values in the organic system and the grazed regime (non-significant; $p > 0.05$). Spatial variations, and therefore factors such as pests, weeds, diseases, micronutrient deficiencies, topography, (i.e. factors not considered in the simulations) could also explain the very slight differences observed between measured and simulated SOC stocks in the farm-scale study. Conversely, the smaller number of replicates in the NFSC trial compared to the farm-scale study may have generated a higher measurement uncertainty that also led to slight variations between measured and simulated SOC stocks.

Small variations observed between the study fields and treatments with similar historic management, might also be associated with differences in productivity and therefore soil C inputs. Although the simulated yields were consistent with measurements reported elsewhere in the UK, site-specific yields could help for a more detailed analysis of the relationship between SOC stocks and yields for this specific case of Nafferton farm. As emphasised in the material and methods, section 6.2.3 ("Model set-up, initialisation, simulation, and validation"), in this study, net primary productivity, i.e. crop production levels, were adjusted following procedures described in Del Grosso *et al.* (2011) in order to reflect national yield figures reported by Defra every year since the 1890s. Moreover, soil properties, such as soil texture, bulk density, pH, field capacity, wilting point and hydraulic conductivity were standardised for all simulations in order to focus on the impacts of agricultural systems and alternative management practices alone. However, other studies stressed that soil properties interact with managements and therefore they should be considered in a case by case scenario (Brandani *et al.*, 2015). Although we recognise that this approach may have driven some of the differences between measured and simulated values, the overall findings have shown this was a valid approach since DayCent was capable of capturing most of the variation in measured SOC stocks.

The finer time scale (daily time-steps) that the DayCent model operates in comparison with other models (e.g. Century and/or Roth C, monthly time-steps), provides a detailed representation of processes such as plant growth, decomposition of litter and soil C, nutrient flows, soil water, and soil temperature, allowing the model to simulate SOC stocks under a range of scenarios (Del Grosso *et al.*, 2011, 2012). In particular, the close relationship between plant and soil represented by the model has placed DayCent as one of the most comprehensive mechanistic models for soil C dynamics (Robertson *et al.*, 2015). Sensitivity analysis of the model highlights this close relationship as changes in parameters such as pH, clay content, and daily precipitation directly affected SOC stocks. Specifically, decreasing soil pH by 1 unit and daily precipitation by 10% and increasing clay content by 10%, enhanced SOC stocks by 2-8%. These results are most likely associated with a decrease in the rate of decomposition and an increase in physical protection of SOM without negatively affecting net primary productivity i.e. crop production. Conversely, increasing pH by 1 unit and daily precipitation by 10%, and decreasing clay content by 10%, diminished SOC stocks between 2-3%, which might be due to both the negative effects on crop production and stimulation of SOM decomposition. In agreement with the study conducted by Begum *et al.* (2017), SOC stocks in both the farm-scale study and the NFSC trial were less sensitive to changes in daily air temperature (± 1 °C) and soil bulk density (± 10%). The latter particularly suggests that by using a fixed soil bulk density value for all simulations, as was conducted in this study, did not affect simulated SOC stocks. Although it was expected that temperature would be one of the main driving factors affecting SOC stocks due to its direct effect on both plant growth and microbial activity (Jabro *et al.*, 2008; Wieder *et al.*, 2013), the timespan tested here for the sensitivity analysis (from 2008 to 2018) may not have been enough for the expected increase in plant growth to offset the short-term soil C loss through soil respiration (Zak *et al.*, 2000; Deng *et al.*, 2010). It was further speculated that changing temperature by only ± 1 °C was not large enough to cause a significant change in plant growth.

Ultimately, the DayCent model has shown accurately and precisely simulations of SOC stocks for all study field cases in the farm-scale study as well as for all treatments in the NFSC trial. The results hence confirm the good performance of the initialisation approach and the efficiency of the DayCent model in simulating SOC stocks under different agricultural systems and alternative management practices. Whilst accurate simulation of present SOC stocks is important, the main goal of using a biogeochemical model is to simulate the impacts of C-management practices in the future, which is discussed in detail in the next section.

6.4.2 Historical SOC stock changes and the effects of alternative management practices in the conventional and organic agricultural system now and into the future

The DayCent simulations showed that the intensification of crop production over 180 years (i.e. from 1800 to 1980) resulted in a decrease in SOC stocks of approximately 30%. This amount of C lost and the annual decrease rate predicted by the DayCent model were consistent with previous studies conducted across Europe and in the UK (Murty *et al.*, 2002; Bellamy *et al.*, 2005; Poeplau *et al.*, 2011). Similar reductions in SOC stocks after a land use change from semi-natural systems to cropland were also reported by other studies conducted in the UK but using other soil C models (Muhammed *et al.*, 2018). It is well-known that the historical soil C losses after conversion from a natural/semi-natural system to agricultural systems are primarily associated with increased oxidation of organic matter and often the occurrence of soil erosion.

After the historical period, simulations for the period between 1981-2007 for the farm-scale study and from 1981 to 2000 for the NFSC trial, indicated that study fields used as permanent grassland resulted in higher SOC stocks compared to study fields used as cropland, which reflected existing knowledge in the literature. Permanent grassland generally accumulates SOC stocks due to higher soil C inputs through litter deposition and enhanced soil aggregation and SOM protection as a result of the abundant fine root system with fast turnover (Conant *et al.*, 2001; Six *et al.*, 2002a). This is especially true for well-managed grassland, i.e. not over-grazed and receiving regular applications of fertilisers and/or manure, as is the case at Nafferton farm. In contrast, cropland systems are associated with factors such as the lower return of plant residues (above and belowground) to the soil, increase in mineralisation rates and soil disturbance through tillage and consequently a decrease in physical protection of the SOM (Franzluebbers *et al.*, 2000; Six *et al.*, 2002a). Muhammed *et al.* (2018) using an integrated modelling approach for the whole UK for the period between 1800 and 2010, confirmed that, under arable lands, soil C outputs through decomposition were always higher than soil C inputs by plant residues. This trend was also observed in the long-term simulations of the present study. However, it seems to change when alternative management practices were implemented. Specifically, the DayCent model indicated an overall similar trend for all simulated cases, where the implementation of alternative management practices led to an increase in SOC stocks in the long-term simulations (0-0.20 m depth) (Fig. 6.5).

At the farm-scale, the implementation of grazed regimes and higher ley time proportions showed an upward trend in SOC stocks over 33 years (2017-2050) of simulations, regardless of the agricultural system. There are a lack of studies comparing the implementation of non-grazed *vs.* grazed regime and ley time proportions within conventional and organic systems, especially over longer-term periods. However, it is reasonable that increasing ley time proportions in crop rotation would enhance soil C accumulation since this practice results in higher C inputs and it is often combined with reduced-tillage events (Lee *et al.*, 2020) (Chapter 3). Jarvis *et al.* (2017), in a long-term field trial in Sweden (60 years), measured topsoil soil C concentrations (0-0.10 m) in a varying proportion of grass-clover leys (1, 2, 3 or 5 years) in 6-years rotation. Likewise the simulations of this study, the authors observed that increases in ley time proportions increased soil C concentrations and attributed this to the growth of root systems predominantly in the topsoil. Another recent empirical study conducted by Quemada *et al.* (2020) also indicated that ley periods have the potential to maximise SOC stocks. The authors particularly attribute this finding to the increase in yields of the subsequent cash crop, which occurs especially when ley periods are composed of legumes and maintained for longer periods. Increases in topsoil root growth and in cash crop yields due to increases in ley time proportions may be also the main drivers for soil C accumulation over the 33 years (2017-2050) of our simulations. Whilst ley periods have the potential to increase SOC stocks, they may also either increase or decrease GHG emissions due to interactions between soil N availability and the type of ley growth (e.g. legumes *vs.* non-leguminous species) (Barneze *et al.*, 2020). This is crucial and indicates that further research is required to assess the trade-offs between the C accumulation benefits of leys and the impacts on GHG emissions, not only regarding the length of the ley period but also the type of ley used in the rotation. Ultimately, even though DayCent has shown good performance in simulating different proportions of ley periods with promising potential for soil C accumulation, these predictions should be considered with caution, since GHG emissions were outside the scope of this thesis and thus not examined.

In relation to the grazed regime, as discussed in Chapter 3, the stimulation of belowground biomass and the extra inputs of C through forage residues and animal dung are probably the greatest driving forces of C accumulation (Pineiro *et al.*, 2010; McSherry & Ritchie, 2013; Assmann *et al.*, 2014; Chen *et al.*, 2015). In DayCent model these factors are included in the simulation. Whenever a grazing event is scheduled in the simulation, it directly affects aboveground biomass (live and standing dead) by removing a fraction of it, the return of nutrients to the soil by urine and faeces deposition (including C, N, P and S in organic forms), the lignin content of the faeces and the root:shoot ratios, all of which will depend on the grazing intensity. Although these are arguably the main mechanisms that influence SOC stocks under a grazing regime, there may be also other factors, e.g. individual plant species and plant cover as well as processes that fix C during photosynthesis (McSherry & Ritchie, 2013; Abdalla *et al.*, 2018). However, these factors are not currently accounted as possible extra C inputs by the DayCent model. The simulated soil C accumulation for the study fields under grazed regimes, therefore, resulted mainly from a potential boosted productivity and stimulation of belowground biomass as well as the excreted C in dung and urine. While dung and urine deposition may have some benefits to increase SOC stocks, other issues need to be considered, for example, GHG emission (Barneze *et al.*, 2014; Chadwick *et al.*, 2018). A further important finding is that differences in simulated SOC stocks between study fields in the farm-scale study were minimal in 2050, particularly when a ley time proportion was ≥ 40% and under the grazed regime (Fig. 6.5 A, B). This ultimately suggests that the implementation of grazed ley periods for less than half of the period of the rotation could offset an arable associated decline in SOC stocks.

Previous research, as observed in Chapter 5, has highlighted that changes in SOC stocks are mainly driven by differences in soil C input in the form of fertilisers and crop residues (Leifeld *et al.*, 2005; Oberholzer *et al.*, 2014). In this study, DayCent simulations in the NFSC trial has shown positive effects to SOC stocks under compost fertiliser application while crop rotation schemes showed contrasted findings conditional to the fertilisation source applied (Fig. 6.5 C). Over a projected 32 year period (2018-2050), the increase of SOC stock under compost fertiliser treatments was estimated to be approximately 0.3 Mg ha^{-1} yr^{-1}, which exactly matches the rate of SOC stock gains reported by Begum *et al.* (2017) in a simulation conducted in the Broadbalk experiment, one of the oldest of its kind in the world (Research Rothamsted, 2006). The increased rate found in our study also agrees with Smith *et al.* (2008) who reported a range of C accumulation rates from 0.002 to a maximum of 0.30 Mg ha^{-1} yr^{-1} for cool moist croplands. We hypothesised that the SOC stocks increase was driven by increasing the amount of total C inputs as well as by the low C:N in manure as reported elsewhere (Leifeld & Fuhrer, 2010; Bista *et al.*, 2016). Although organic amendments are widely recognised for their capacity to enhance soil C, it is important to emphasise that it is also dependent on their decomposability (Paustian *et al.*, 1992; Brandani *et al.*, 2015; Begum *et al.*, 2017) (Chapter 5), meaning that this finding should be considered carefully.

Regarding the crop rotation schemes, the conventional rotation showed the highest and the lowest SOC stocks when combined with compost and mineral fertiliser, respectively after 32 years of simulations (difference of approximately 10 Mg ha^{-1}). Similar results were observed under organic rotation schemes but with intermediate SOC stocks and differences of only ~ 4 Mg ha^{-1} between compost and mineral fertiliser after the same period (2018-2050). These results are in line with the simulations reported by Lee *et al.* (2020) who compared conventional and organic systems in Switzerland at the regional scale also using the DayCent model. Their study suggests that the adoption of the organic systems with compost fertiliser has a higher potential to increase SOC stocks relative to conventional systems with only mineral fertiliser. However, the authors used a conventional system without cover crops in the rotation as a baseline for their comparison. In this study, although grown with different length of years (two- and three-years), both conventional and organic systems had grass-clover ley periods inserted into the rotation, which might have limited differences between the two rotations. Moreover, the conventional rotation was characterised by cereal intensive crops while the organic rotation was based on a more diverse and legume-rich cycle. Ultimately, these results suggest that the magnitude of changes in SOC stocks may also be crop-specific. In the DayCent model, crops differ in terms of C allocation fraction, root biomass C, aboveground live C, crop residues, among others, thus affecting soil C accumulation.

The positive influence of grazed regime, ley time proportions and compost fertiliser, as well as the effect of crop choice in rotation, on SOC stocks were all further emphasised under the hypothetical scenarios. It was notable that higher ley time proportions resulted in a higher potential for SOC stocks to increase, albeit at a lower rate when adding more than four years of grass-clover ley periods in a four-year arable rotation and/or under the non-grazed regime (Fig. 6.6 and Fig 6.7). These results were observed under both conventional and organic systems, but the crop choice in the rotation of the former led to higher soil C loss compared to the latter. According to Lee *et al.* (2020), crop choice in rotation, rates of mineral fertilisation and/or organic amendments and tillage events play a key role in simulating SOC stocks by DayCent model. Crop choice in rotation, in particular, help to justify the slight SOC stock differences between the conventional and organic system in the hypothetical scenarios, since all the other parameters (e.g. soil C inputs through fertilisation and tillage events), were kept identical during the simulations. The four-year conventional arable rotation exerts a higher decrease rate compared to the four-year organic arable rotation as a function of different crop-specific parameters defined by the DayCent model as aforementioned. Lastly, it is worth noting that the potential SOC stock accumulation is a function of both the previous management and the initial SOC stocks condition. Accordingly, the DayCent model simulations indicated that implementation of alternative management practices in study fields with an initial depleted soil C storage (e.g. study fields previously under a cropland-based system) increased soil C at higher rates compared to study fields with a high initial soil C storage (e.g. study fields previously under a permanent grassland system). Yet, soil C accumulation is finite and reversible when the land use or management practice is changed. Since these aspects and other such as crop varieties, climatic variation and interactions between other management option will all impact the future performance of the alternative management practices tested here, long-term perspectives should be considered as scenarios only.

Overall, the DayCent model can be used to identify the quantity and the effective period that a management practice can be used for soil C accumulation, thus mitigation efforts could be targeted. The results found in this study support its use to study the effects of conventional and organic systems and the implementation of alternative management practices on SOC stocks in northern England agricultural systems.

6.5 Conclusions

In this study, historical, current, and future soil management were explicitly simulated for SOC stock changes (0-0.20 m depth) by DayCent model. The model was able to capture the trends of decreased SOC stocks due to the historical intensification of crop production followed by recovery when more sustainable agricultural systems and management practices were implemented. The simulations also confirmed empirical findings showing that there are benefits to SOC stocks when implementing management practices such as the grazed regime and higher ley time proportions (especially as combined practices) regardless of whether the system is conventionally or organically managed. Furthermore, model simulations showed that compost fertiliser application promotes soil C accumulation, although the magnitude of changes in SOC stocks may be determined by the choice of the crops in rotation. Changes in pH, clay content, and daily precipitation seems to be sensitive parameters when simulating SOC stocks by DayCent model. Conversely, the lack of sensitivity to parameters such as daily air temperature and soil bulk density implied that the use of the model for other regions may need further refining. Long-term simulations suggested that the grazed regime, higher ley time proportions and/or compost fertiliser application can increase SOC stock for a period of at least 30 years. The implementation of pasture leys with a proportion higher than 40% and/or four years of grass-clover of the full crop rotation would not deliver in significant further soil C accumulation. Apart from the length of the ley period, further studies could be done to evaluate the effects of different types of leys (e.g. legumes *vs.* non-leguminous species) and its interaction with crops choice in the rotation. Overall, the DayCent model demonstrated adequate ability to simulate SOC stock changes from agricultural soils under the conventional and organic systems and the implementation of alternative management practices. Ultimately it means that the model can be used as a tool to better understand the effects of different agricultural systems and interactions with management practices and policies on SOC stocks.

Chapter 7. General discussion

The pressure to feed rapid global population growth has brought about unprecedented pressure on soils. Accordingly, direct implications on soil quality (SQ), including physical, chemical, and biological indicators, and thus on ecosystem functions and services have been reported. This has also raised concerns regarding the sustainability of the current agricultural systems and management practices deployed in the agricultural sector. The organic system has been postulated as a promising sustainable agricultural management option (Reganold & Wachter, 2016). However, whilst studies have shown environmental benefits to the use of organic systems compared to conventional systems (Mondelaers *et al.*, 2009; Tuomisto *et al.*, 2012; Meier *et al.*, 2015; Seufert & Ramankutty, 2017), mixed findings have been reported for other aspects, for example, for soil organic carbon (SOC) stocks. SOC stocks comparison between conventional and organic systems, considering specific management practices within each system, is vital to a better understanding of SQ (Zornoza *et al.*, 2015) as well as to help to shape the agricultural sector against climate change.

This thesis was carried out to assess the response of SQ and C cycling to changes in agricultural systems and management practices. More specifically, the aims were to i) define the SQ status, SOC stocks (*in situ* and spatially) and C distribution among soil organic matter (SOM) fractions under conventional and organic systems, ii) understand how these would be affected by the interaction between agricultural systems and management practices, including the use of non-grazed or grazed regimes and varying proportions of temporary grass-clover leys in crop rotations (referred to as LTP), iii) evaluate the effects of core practices from the conventional and organic system, such as crop rotation schemes and fertilisation sources on SOM composition and SOC stocks and stability over time, and iv) validate and use the mechanistic DayCent model to predict the long-term effects of contrasting agricultural systems (conventional *vs.* organic), grazing regime (non-grazed *vs.* grazed), arable systems with ley phases, conventional *vs.* organic crop rotation schemes and mineral *vs.* compost fertility sources on SOC stocks.

This thesis is composed of five data chapters, which were designed to evaluate different aspects of these aims but in a way that separate chapters are interconnected. Four overarching findings emerged from this research. First, in mixed farming systems, i.e. where arable and grazed livestock are present in a rotation, there was an enhanced SQ and SOC stocks regardless of the agricultural system. Second, increasing LTP in crop rotation brought about increases in SOC stocks under both conventional and organic systems. Third, organic crop rotation and compost fertilisation are important practices for SOC accumulation over time. Fourth, combining these two core practices of the organic system can lead to higher SOC stabilisation across the whole soil profile (0-0.60 m).

7.1 Mixed (arable/livestock) farming systems can enhance SQ and SOC stocks

This thesis found that mixed farming systems can enhance the SQ of commercial farms located in northern England. Overall, this finding was observed in both individual and integrated SQ indicators and regardless of whether the system was conventionally or organically managed (Chapter 2). In addition, and as hypothesised, the results showed that an improved SQ brings beneficial consequences for SOC stocks, leading to the conclusion that the mixed farming system will also play an important role in reaching a net C benefit under both conventional and organic systems (Chapter 3). For a few SQ indicators and specific soil depth intervals, it was also observed that the positive effects of the grazed regime (i.e. mixed farming systems) can be agricultural systems-specific. In particular, when grazing was included then both agricultural systems (conventional and organic) showed higher topsoil (0-0.15 m) available phosphorus (P), SOC concentration and microbial biomass C (MBC), whereas grazing only positively affected topsoil potassium (K) in organic systems and topsoil bulk density (BD) and SOC concentrations (0.15-0.30 m) in conventional systems. All of these findings merit particular attention because there is a lack of studies comparing conventional and organic systems in association with non-grazed and grazed regimes, as carried out in this study (Jackson *et al.*, 2019). Overall, these findings can be related to both the higher nutrient returns and improved nutrient cycling provided by livestock as well as changes in root growth quantity and dynamics. According to Carvalho *et al.* (2010) livestock act as a nutrient cycling agent, modifying both the biochemical form of the nutrients and their spatial distribution and consequently influencing local availability in the soil solution. In this sense, grazing residues (urine and dung) should play a pivotal role particularly in increasing topsoil available P, K and partially in SOC concentration. In turn, the higher MBC may be related to livestock altering biomass production and resource allocation, resource inputs to the decomposers and the composition of thelocal plant community as proposed by Bardgett & Wardle (2003). Conversely, non-grazed regimes showed higher soil K concentration in the 0.15-0.30 m compared to the grazed regime. This might have occurred due to the presence of a denser root system in the topsoil of the grazed regime, which possibly mined subsurface K reserves, recycling and depositing this K onto the soil surface (0-0.15 m).

The positive effect of the grazed regime on SOC stocks as well as soil nitrogen (N) stocks under both conventional and organic systems (Chapter 3) can also be considered in part due to both the dominance/stimulus of root growth as well as the residue amount left in the soil by animals, which is later incorporated by trampling (Pineiro *et al.*, 2010; McSherry & Ritchie, 2013; Assmann *et al.*, 2014; Chen *et al.*, 2015). Increases in SOC stocks are predominantly related to the higher forage residues (above and below-ground) (Assmann *et al.*, 2014), while inputs via manure and urine deposition reflect increases in N stocks (Haynes & Williams, 1993). Such mechanisms were particularly important for intermediate soil layer (i.e. 0.15-0.30 m) SOC concentrations in the conventional system (Chapter 2, Table 2.2 and Fig. 2.2). The absence of a difference in SOC stocks and an increase in N stocks in deeper soil layers (0.30-0.60 m) under the grazed regime is related to both defoliation by grazing that changes plant species and composition (Pavlů *et al.*, 2007), which affects the quantity and the quality of the litter inputs, and the lower C:N ratio of below-ground residues under grazed fields (Heyburn *et al.*, 2017). Although these mechanisms explain most of the differences in SOC and N stocks between non-grazed and grazed regimes of the present study, it is important to highlight that variation in frequency/intensity of the grazing as well as in climate conditions and soil type might lead to different conclusions (Pineiro *et al.*, 2010; McSherry & Ritchie, 2013; Assmann *et al.*, 2014; Abdalla *et al.*, 2018).

Increases in SOC stocks under the mixed farming system were not only observed *in situ* but also spatially, further emphasising that specific management practices, such as grazing regimes, within conventional and organic systems should be taken into account when comparing both systems at a farm-scale resolution (Chapter 4). While there was a considerable increase in SOC stocks under the grazed regime, the physical fractionation of the SOM indicated that the majority of it occurred into particulate organic matter (POM) and heavy (HF) fractions (both > 53 μm), i.e. not into the most stable or long-lived SOM form (von Lützow *et al.*, 2007) (Chapter 3). Nevertheless, simulations predicted that the use of the grazed regime presents a useful long-term potential to SOC accumulation in comparison to non-grazed regimes, i.e. mixed farming *vs.* arable farming, respectively (Chapter 6). Specifically, the results indicated that grazed regimes could lead to a SOC stock accumulation of 0.25 ± 0.02 Mg ha^{-1} yr^{-1} over 33 years for the top 0-0.20 m soil depth. Given the results in this thesis, this SOC increase might be related to a potential improvement in the physical protection of the soil C by soil aggregates as indicated by the comparison between grazed and non-grazed fields (Chapter 2, Table 2.2). Such a mechanism should be particularly important under conventional mixed farming systems, as high decomposition rates and low residue inputs were suggested in the conventional non-grazed fields (Chapter 3). Finally, it must be emphasised that the relative importance of grazed regimes to SOC sequestration should be considered carefully as aspects such as greenhouse gases (GHG) were not considered in our long-term predictions.

7.2 Increasing LTP in crop rotation increases SOC stocks

Empirical measurements (Chapter 3) and simulations (Chapter 6) showed that increasing LTP in crop rotation increased SOC stocks under both conventional and organic systems. The main explanation to this result is the development of an extensive, more fibrous and deep-rooting system which, in addition to increasing C inputs (Johnston *et al.*, 2017), may also enhance soil structure and the protection of SOM against decomposition (Six *et al.*, 2002b). This is in line with results from chapter 2, which suggested improvement in soil aggregate stability with an increased LTP (Chapter 2, Fig. 2.3). Moreover, according to Quemada *et al.* (2020), longer ley periods that are based on legumes can increase crop yields of the subsequent cash crop, leading to higher C inputs and subsequently SOC stocks. The use of grass-clover ley periods can also change evapotranspiration and soil temperature, limiting decomposition processes and consequently benefiting SOC stocks (Kätterer & Andrén, 2009). For topsoil layers (i.e. max. 0.20 m depth), the reduced occurrences of ploughing was also a key factor helping to justify the accrual of SOC stocks with increased LTP (Johnston *et al.*, 2017; Lee *et al.*, 2020). However, while these are well-accepted mechanisms to explain increases in empirical and simulated SOC stocks, there is a growing interest within the scientific community to find out how long ley periods should be used in a crop rotation. For instance, for SOC stocks it might be limited to when saturation of sequestration potential is reached. Studies on this subject are lacking in the current scientific literature. Another bottleneck in current knowledge is about the effects of ley periods on SOC stocks in deeper soil profiles (i.e. > 0.20 m depth).

This thesis was able to give a verdict on both of these aspects within conventional and organic systems in the north-east of England, UK. Regarding the length of time in ley, the empirical findings of this study suggested that in a 10-year rotational period, grass-clover leys should be used for at least 3-4 years (i.e. roughly 30-40% of LTP) in order to enhance SOC stocks up to 0.30 m depth, with positive benefits also to soil N stocks up to 0.60 m depth. For this specific case study, increases in deeper soil layers might be particularly related to the use of clover (i.e. a legume) and increased inputs below 0.15 m depth due to its more fibrous, longer root growth periods (Tracy & Zhang, 2008; Johnston *et al.*, 2017). This result was also confirmed by long-term simulations (33-years projection), with the predictions showing reduced rates of SOC increase when adding more than four years of grass-clover ley periods into a four-year arable rotation and/or non-grazed ley periods (Chapter 6, Fig. 6.6 and Fig 6.7). However, it must be stressed that the DayCent model only simulates SOC stocks in the upper 0-0.20 m layer. As for the grazing regimes, empirical measurements suggested that increases in topsoil and subsoil SOC stocks with an increased LTP occurred in the labile SOM fractions (i.e. POM and HF >

53 μm) (Chapter 3, Fig 3.7 and 3.8). It was concluded that to define the broad benefits of grass-clover leys in crop rotation, more work is needed, particularly for considering a cost-benefit between soil C and N storage and productivity trade-off. Even so, it appears that together with the grazed regime, increasing LTP might be the most available first step to mitigate losses of SOC and N stocks in arable rotations.

7.3 Both organic crop rotation and compost fertilisation were important practices for SOC accumulation over time

A long-term experimental trial was used to assess the effects of the core practices of conventional and organic systems, including crop rotation schemes and fertility sources, on SOC stocks over one complete rotation cycle (8-year period) (Chapter 5). Empirical results suggested higher SOC stocks in the organic rotation in topsoil (0-0.30 m) and subsoil (0.30-0.60 m) layers compared to the conventional rotation. Compost fertilisation, in turn, led to topsoil SOC accumulation under both crop rotation schemes after one complete rotation cycle (Chapter 5, Table 5.5). These support the general findings that a more diverse crop rotation, including legumes and longer length of ley periods (3 years *vs.* 2 years under organic and conventional rotation, respectively), and the direct supply of C through compost fertilisation can increase SOC stocks (Gattinger *et al.*, 2012; Triberti *et al.*, 2016; Jian *et al.*, 2020) (Chapter 3).

Previous research has shown that the effects of the inclusion of legumes and longer length of ley periods into the rotation on SOC stocks are mediated via the high yield potential that they offer to subsequent crops (Persson *et al.*, 2008; O'Dea *et al.*, 2013; Quemada *et al.*, 2020). Higher yields, i.e. greater above-ground biomass, also imply greater below-ground biomass with subsequently higher residue deposition at both the soil surface and in deeper soil layers along with more microbial activity (Araujo *et al.*, 2012; Balakrishna *et al.*, 2017). Since in this particular long-term experimental trial the crop straw and debris were always removed from the field, increases in SOC stocks should reflect the higher C inputs from root biomasses and crop stubbles. As discussed in the previous section, in addition to the direct organic C input supply, such a mechanism has ancillary effects on other important soil properties (e.g. soil structure) that help to increase SOC stocks (Six *et al.*, 2002b). Besides this, a greater mass and activity of root biomass, rhizo-deposits, and soil microbes are described as important processes to the availability of nutrients, such as N, P and K (Jian *et al.*, 2020), helping to justify the enhanced yields under such management practices. While empirical measurements have indicated the positive effects of organic crop rotation on SOC stocks (Chapter 5), simulations predicted that in the longer-term (32-years projection) for the upper 0-0.20 m layer this was conditional on organic fertilisation (i.e. SOC stocks increased in both crop rotation schemes under compost fertilisation) as well as crop-specific activities (i.e. crop choice in the rotation was a strong determinant of SOC stocks) (Chapter 6).

Empirical findings in this thesis confirmed the positive effect of compost fertilisation to topsoil SOC stocks over time (8-year period), regardless of crop rotation schemes (Chapter 5, Table 5.5 and Fig. 5.4 C). The compost fertilisation source represents a direct supply of organic C (Christensen, 1988; Gerzabek *et al.*, 2001; Gattinger *et al.*, 2012), which, however, might represent a transfer of existing C to the soil C pool rather than removal from the atmosphere. Nevertheless, similarly to the crop rotation schemes, organic amendments are also associated with improved crop primary productivity, through the supplement of nutrients and labile C fractions, as well as additional positive effects to soil physical structure (aggregate stability) (Haynes & Naidu, 1998; Whalen & Chang, 2002) and biological activities (Maeder *et al.*, 2002; Lori *et al.*, 2017). As such, compost fertilisation may also indirectly minimise soil C loss via erosion or mineralisation of existing C storage, while influencing net atmospheric C removal. In addition, if the organic amendments are either produced "*on-site*", rather than transferred in from elsewhere, or would have been lost by other practices (e.g. burning), then this practice can be considered a genuine soil C sequestration. Conversely, the addition of a portion of labile C may induce a priming effect (i.e. the stimulation of an increase in the decomposition of older soil C due to new C additions), resulting in a potential soil C loss due to reductions in the longevity of SOC stocks (Kuzyakov *et al.*, 2000; Fontaine *et al.*, 2004, 2007). However, since previous studies have implied that this is a short-term and context-specific effect (Kuzyakov *et al.*, 2000; Kuzyakov, 2010), it is presumed that additions would exceed losses and so long-term compost application results in positive SOC stocks. Simulations confirmed such an assumption, indicating that compost fertilisation would increase SOC over a 32-years period (2018-2050) at a rate of approximately 0.30 Mg ha^{-1} yr^{-1} under both conventional and organic crop rotation schemes (Chapter 6, Fig. 6.5). The relative importance of crop rotation schemes (conventional *vs.* organic) and fertility sources (mineral *vs.* compost) on long-term SOC stocks in deeper soil layers is still unclear, as the DayCent model only predicts changes in topsoil layers (0.20 m depth).

7.4 Organic rotation and compost fertilisation were strong determinants of SOC stabilisation

The stability of SOC is just as important as its accumulation, particularly regarding the long-term sustainability of management practices. This thesis used three different techniques, physical fractionation of SOM into organic and mineral-associated fractions, thermogravimetry-differential scanning calorimetry coupled with quadrupole mass spectrometry (TG-DSC-QMS) and pyrolysis coupled with gas chromatography-mass spectrometry (Py-GC-MS), in an attempt to provide an insight into SOC stability under the core practices of conventional and organic systems. In short, it was found that the combination of organic rotation, i.e. the use of grass-clover ley periods, legumes and vegetables as well as cereals, and compost fertilisation (mainly composted dairy manure) would be the best for long-lasting SOC stocks across the whole soil profile (0-0.60 m).

In this thesis, the positive effect of the organic rotation to SOC stability, mainly observed in subsoil layers (0.30-0.60 m), was attributed due to the balance between biomass production and optimal C:N ratio inputs provided in particular by the use legumes (high N inputs) and grasses (high biomass inputs) in the rotation (Jian *et al.*, 2020). As highlighted in section 7.3, C inputs occurred mainly through root biomass and crop stubbles, i.e. slowly decomposed materials with high C:N ratios, lignin, and phenols content (Martens, 2000; Lorenz & Lal, 2005), which *per se* already explain part of SOC stability due to their relatively high amount of stable SOM (Triberti *et al.*, 2016). It is important to emphasise that there was a presumed higher microbial activity under the organic rotation, confirmed at the farm-scale level where conventional and organic systems differed mainly on the crop rotation schemes (Chapter 2, Table 2.2). The higher microorganism activity in the soil and, therefore, the higher amount of compounds of microbial origin are recognised for their effect on long-term stabilised C products (Amelung *et al.*, 2008), which might have further favoured SOC stability. This should also be the case for the positive effect of compost fertilisation on SOC stability at the 0-0.30 m depth. Whereas organic amendments offer a more stabilised source of C with strong resistance to microbial decomposition (Nardi *et al.*, 2004; Li *et al.*, 2018), this is also applied at the surface level and likely to enhance biological activities and their products (Maeder *et al.*, 2002; Lori *et al.*, 2017), positively affecting SOC stability through the same mechanisms previously described. Another factor that might have influenced SOC stability with both organic rotation and compost fertilisation is an enhanced biological action of soil fauna (mainly earthworms). Earthworms are recognised for their essential role in transferring SOM within the soil profile, contributing to SOC stabilisation throughout the whole soil profile by improvements in organomineral aggregates (Coq *et al.*, 2007).

These effects were supported to some degree by the results from the physical fractionation of the SOM, TG-DSC-QMS and Py-GC-MS analyses. The organic rotation (0.30-0.60 m) and compost fertilisation (0-0.30 m) showed higher relative weight loss and ion intensity for CO_2 (*m/z* 44) in the temperature intervals between 350-500 °C and 500-750 °C (Chapter 5, Table 5.7 and 5.8), i.e. related to recalcitrant and refractory C fractions (Lopez-Capel *et al.*, 2005, 2006; Manning *et al.*, 2005; Plante *et al.*, 2009). The Py-GC-MS analysis also indicated that at a molecular level, there was a higher relative abundance of products that were more resistant to degradation, e.g. *n*-Alkenes, aromatics, and polyaromatics (Mazzetto *et al.*, 2019), in the subsoil under the organic rotation and with topsoil compost fertilisation (Chapter 5, Table 5.9). However, these results were only partially confirmed using the physical fractionation of the SOM. Whilst compost fertilisation showed a trend toward higher topsoil SOC in the mineral associated fraction, i.e. the most stable SOM forms, that confirmed previous findings, for subsoil layers it was noted that there was a decreasing trend under the organic rotation for the same fraction, that was contrasting to previous findings (Chapter 5, Table 5.6). That said, and while it is important to note that most of our results indicated a SOC stabilisation across the profile with the use of organic rotation and compost fertilisation, more studies comparing those three techniques are needed to elucidate potential disparity between them.

7.5 Conclusions & Future research

The conventional and organic systems did not greatly differ for SQ, SOC stocks and SOM stability. However, core practices of the organic system and the implementation of specific management practices, such as the presence of grazing regimes (i.e. mixed farming system) and longer length of temporary grass-clover leys in crop rotations, do have a potential to improve SQ, SOC stocks and SOM stability. In terms of SQ and SOC stocks, the results from this thesis indicate that mixed farming systems with a grass-clover ley period length equivalent to 30-40% of the full crop rotation are critical, *in situ* and spatially, for the provision of many ecosystem services, including nutrient recycling/release and utilisation as well as potential C sequestration through SOC accrued. Both management practices were perceived to accumulate SOC into relatively fast decomposition fractions (> 53 μm). Yet, SOC stock simulation using the DayCent model continuously increased over 33 years when the fields were livestock grazed and/or leys comprised 30-40% of the full crop rotation. Furthermore, this thesis found that a diverse crop rotation scheme and fertilisation with organic amendments, i.e. core practices from the organic system, can play an important role in SOC accumulation both over time and in the long-term as well as SOM stabilisation across the soil profile (0-0.60 m). From the understanding gained and lessons learnt through this research it was concluded that specific management practices within both conventional and organic systems can have a considerable positive potential to affect SQ and C cycling.

While the results of this thesis have brought important new knowledge to aspects of sustainable agriculture, it is important to stress that it represents a particular UK farm. Further research would therefore be needed to determine the impacts of such agricultural systems and management practices on sites with different characteristics to the study area (e.g. climate, soil type, grazing regimes, crop rotation schemes, etc). Moreover, many outcomes of this research raise key questions and challenges that deserve attention in future studies. First, soil depth assessed here (0-0.60 m) appears to be important to both SQ and SOC stocks, but there is a lack of published research and especially mechanistic models that consider depths below 0-0.30 m. Second, there is an urgent need to holistically consider the cost-benefit of the specific management practices assessed in this thesis, particularly between SQ and SOC storage and productivity trade-off. Third, although the potential for SOM stabilisation has been noted under the organic rotation and compost fertilisation based on the thermal (TG-DSC-QMS), pyrolysis followed by molecular (Py-GC-MS), and to a lesser extent the particle size (physical fractionation) analyses, some results from these three techniques appeared to slightly disagree with each other, suggesting that a comparison study might be required. Fourth, GHG emissions and root system morphology of these agricultural systems and management practices will ascertain whether they represent a reliable mitigation option. Finally, while adaptations of the agriculture sector by altering the agricultural system and management practices are not the ‘silver bullet’ for the agricultural sector issues, it is an approach that is readily available and could be implemented with immediate effect across the globe that contributes positively to soil quality/health, food security, and climate change until more solutions come into play.

References

Abbott, G.D., Swain, E.Y., Muhammad, A.B., Allton, K., Belyea, L.R., Laing, C.G., Cowie, G.L. & Cowie, G. 2013. Effect of water-table fluctuations on the degradation of Sphagnum phenols in surficial peats. *Geochimica et Cosmochimica Acta*, **106**, 177–191.

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. *Agriculture, Ecosystems & Environment*, **253**, 62–81.

Abdalla, M., Jones, M., Yeluripati, J., Smith, P., Burke, J. & Williams, M. 2010. Testing DayCent and DNDC model simulations of N2O fluxes and assessing the impacts of climate change on the gas flux and biomass production from a humid pasture. *Atmospheric Environment*.

Acharya, B.S., Rasmussen, J. & Eriksen, J. 2012. Grassland carbon sequestration and emissions following cultivation in a mixed crop rotation. *Agriculture, Ecosystems and Environment*.

Adhikari, K., Hartemink, A.E., Minasny, B., Bou Kheir, R., Greve, M.B. & Greve, M.H. 2014. Digital Mapping of Soil Organic Carbon Contents and Stocks in Denmark. *PLOS ONE*, **9**, e105519.

Aguilera, E., Lassaletta, L., Gattinger, A. & Gimeno, B.S. 2013. Managing soil carbon for climate change mitigation and adaptation in Mediterranean cropping systems: A meta-analysis. *Agriculture, Ecosystems and Environment*.

Akpa, S.I.C., Odeh, I.O.A., Bishop, T.F.A., Hartemink, A.E. & Amapu, I.Y. 2016. Total soil organic carbon and carbon sequestration potential in Nigeria. *Geoderma*, **271**, 202–215.

Albizua, A., Williams, A., Hedlund, K. & Pascual, U. 2015. Crop rotations including ley and manure can promote ecosystem services in conventional farming systems. *Applied Soil Ecology*.

Alexandratos, N. & Bruinsma, J. 2012. *World agriculture towards 2030/2050: the 2012 revision*. ESA Working paper Rome, FAO.

Alfaro, M.A., Jarvis, S.C. & Gregory, P.J. 2006. Potassium budgets in grassland systems as affected by nitrogen and drainage. *Soil Use and Management*, **19**, 89–95.

Alfons, A. 2012. Cross-validation tools for regression models. (At: https://cran.r-project.org/package=cvTools.).

Amelung, W., Brodowski, S., Sandhage-Hofmann, A. & Bol, R. 2008. Chapter 6 Combining Biomarker with Stable Isotope Analyses for Assessing the Transformation and Turnover of Soil Organic Matter. *Advances in Agronomy*.

Amundson, R. 2001. The carbon budget in soils. *Annual Review of Earth and Planetary Sciences*.

Amundson, R., Berhe, A.A., Hopmans, J.W., Olson, C., Sztein, A.E. & Sparks, D.L. 2015. Soil science. Soil and human security in the 21st century. *Science*, **348**, 1261071.

Andrews, S.S., karlen, D.L. & Cambardella, C.A. 2004. The Soil Management Assessment Framework: A quantitative soil quality evvaluation method. *Soil Science Society of America Journal*, **68**, 1945–1962.

Anon. 1986. The analysis of agricultural materials. Ministry of Agriculture Fisheries and Food Reference Book 427, HMSO London.

Araujo, A.S.F., Leite, L.F.C., De Freitas Iwata, B., De Andrade Lira, M., Xavier, G.R. & Do Vale Barreto Figueiredo, M. 2012. Microbiological process in agroforestry systems. A review. *Agronomy for Sustainable Development*.

Archer, J. 1985. Crop Nutrition and Fertiliser Use. *Farming Press Ltd., Wharfedale Road, Ipswitch, Suffolk.*

Arenillas, A., Rubiera, F. & Pis, J.J. 1999. Simultaneous thermogravimetric-mass spectrometric study on the pyrolysis behaviour of different rank coals. *Journal of Analytical and Applied Pyrolysis*.

Assmann, J.M., Anghinoni, I., Martins, A.P., Costa, S.E.V.G. de A., Cecagno, D., Carlos, F.S. & Carvalho, P.C. de F. 2014. Soil carbon and nitrogen stocks and fractions in a long-term integrated crop–livestock system under no-tillage in southern Brazil. *Agriculture, Ecosystems & Environment*, **190**, 52–59.

Assmann, J.M., Martins, A.P., Anghinoni, I., de Oliveira Denardin, L.G., de Holanda Nichel, G., de Andrade Costa, S.E.V.G., Pereira e Silva, R.A., Balerini, F., de Faccio Carvalho, P.C. & Franzluebbers, A.J. 2017. Phosphorus and potassium cycling in a long-term no-till integrated soybean-beef cattle production system under different grazing intensities insubtropics. *Nutrient Cycling in Agroecosystems*, **108**, 21–33.

Avery, B.W. & Bullock, P. 1969. The soils of Broadbalk: morphology and classification of Broadbalk soils. Rothamsted Experimental Station Report for 1968 (part 2). pp. 63–81.

Badgery, W.B., Simmons, A.T., Murphy, B.M., Rawson, A., Andersson, K.O., Lonergan, V.E. & Van De Ven, R. 2013. Relationship between environmental and land-use variables on soil carbon levels at the regional scale in central New South Wales, Australia. *Soil Research*.

Bai, Z., Caspari, T., Gonzalez, M.R., Batjes, N.H., Mäder, P., Bünemann, E.K., de Goede, R., Brussaard, L., Xu, M., Ferreira, C.S.S., Reintam, E., Fan, H., Mihelič, R., Glavan, M. & Tóth, Z. 2018. Effects of agricultural management practices on soil quality: A review of long-term experiments for Europe and China. *Agriculture, Ecosystems and Environment*.

Balakrishna, A.N., Lakshmipathy, R., Bagyaraj, D.J. & Ashwin, R. 2017. Influence of alley copping system on AM fungi, microbial biomass C and yield of finger millet, peanut and pigeon pea. *Agroforestry Systems*.

Baldock, J.A., Sanderman, J., Macdonald, L.M., Puccini, A., Hawke, B., Szarvas, S. & McGowan, J. 2013. Quantifying the allocation of soil organic carbon to biologically significant fractions. *Soil Research*, **51**, 561–576.

Balesdent, J., Chenu, C. & Balabane, M. 2000. Relationship of soil organic matter dynamics to physical protection and tillage. *Soil and Tillage Research*, **53**, 215–230.

Ball, B.C. 2013. Soil structure and greenhouse gas emissions: A synthesis of 20 years of experimentation. *European Journal of Soil Science*, **64**, 357–373.

Ball, B.C., Batey, T. & Munkholm, L.J. 2007. Field assessment of soil structural quality - A development of the Peerlkamp test. *Soil Use and Management*.

Bandick, A.K. & Dick, R.P. 1999. Field management effects on soil enzyme activities. *Soil Biology and Biochemistry*.

Bardgett, R.D. & Wardle, D.A. 2003. Herbivore-Mediated Linkages between Aboveground and Belowground Communities. *Ecology*, **84**, 2258–2268.

Bardgett, R.D. & Wardle, D.A. 2010. *Aboveground-belowground linkages: biotic interactions, ecosystem processes, and global change*. Oxford University Press, Oxford, UK.

Barneze, A.S., Mazzetto, A.M., Zani, C.F., Misselbrook, T. & Cerri, C.C. 2014. Nitrous oxide emissions from soil due to urine deposition by grazing cattle in Brazil. *Atmospheric Environment*, **92**, 394–397.

Barneze, A.S., Whitaker, J., McNamara, N.P. & Ostle, N.J. 2020. Legumes increase grassland productivity with no effect on nitrous oxide emissions. *Plant and Soil*.

Bartenfelder, D.C. & Karathanasis, A.D. 1989. A Differential Scanning Calorimetry Evaluation of Quartz Status in Geogenic and Pedogenic Environments. *Soil Science Society of America Journal*.

Barthès, B. & Roose, E. 2002. Aggregate stability as an indicator of soil susceptibility to runoff and erosion; validation at several levels. *Catena*, **47**, 133–149.

Basile-Doelsch, I., Balesdent, J. & Pellerin, S. 2020. Reviews and syntheses: The mechanisms underlying carbon storage in soil. *Biogeosciences Discussions*.

Batjes, N.H. 1996. Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science*.

Begum, K., Kuhnert, M., Yeluripati, J., Glendining, M. & Smith, P. 2017. Simulating soil carbon sequestration from long term fertilizer and manure additions under continuous wheat using the DailyDayCent model. *Nutrient Cycling in Agroecosystems*.

Behrens, T., Zhu, A.-X., Schmidt, K. & Scholten, T. 2010. Multi-scale digital terrain analysis and feature selection for digital soil mapping. *Geoderma*, **155**, 175–185.

Bellamy, P.H., Loveland, P.J., Bradley, R.I., Lark, R.M. & Kirk, G.J.D. 2005. Carbon losses from all soils across England and Wales 1978-2003. *Nature*.

Bernoux, M. & Cerri, C.E.P. 2005. GEOCHEMISTRY | Soil, Organic Components. In: (eds. Worsfold, P., Townshend, A. & Poole, C.B.T.-E. of A.S. (Second E.), pp. 203–208. Elsevier, Oxford.

Bilsborrow, P., Cooper, J., Tétard-Jones, C., Średnicka-Tober, D., Barański, M., Eyre, M., Schmidt, C., Shotton, P., Volakakis, N., Cakmak, I., Ozturk, L., Leifert, C. & Wilcockson, S. 2013. The effect of organic and conventional management on the yield and quality of wheat grown in a long-term field trial. *European Journal of Agronomy*, **51**, 71–80.

Bischl, B., Lang, M., Kotthoff, L., Schiffner, J., Richter, J., Studerus, E., Casalicchio, G. & Jones, Z.M. 2016. Mlr: Machine learning in R. *Journal of Machine Learning Research*, **17**.

Bispo, A., Andersen, L., Angers, D.A., Bernoux, M., Brossard, M., Cécillon, L., Comans, R.N.J., Harmsen, J., Jonassen, K., Lamé, F., Lhuillery, C., Maly, S., Martin, E., Mcelnea, A.E., Sakai, H., Watabe, Y. & Eglin, T.K. 2017. Accounting for carbon stocks in soils and measuring GHGs emission fluxes from soils: Do we have the necessary standards? *Frontiers in Environmental Science*.

Bista, P., Machado, S., Ghimire, R., Del Grosso, S.J. & Reyes-Fox, M. 2016. Simulating soil organic carbon in a wheat–fallow system using the DAYCENT model. *Agronomy Journal*.

Blake, G.H. & Hartge, K.H. 1986. *"Bulk density", in Methods of soil analysis.* (A Klute, Ed.). 2nd ed. The American Society of Agronomy.

Blanco-Canqui, H., Francis, C.A. & Galusha, T.D. 2017. Does organic farming accumulate carbon in deeper soil profiles in the long term? *Geoderma*, **288**, 213–221.

Blum, W.E.H. 2005. Functions of soil for society and the environment. *Reviews in Environmental Science and Biotechnology*.

Börjesson, G., Bolinder, M.A., Kirchmann, H. & Kätterer, T. 2018. Organic carbon stocks in topsoil and subsoil in long-term ley and cereal monoculture rotations. *Biology and Fertility of Soils*, **54**, 549–558.

Bourget, S.J. & Kemp, J.G. 1957. Wet sieving apparatus for stability analysis of soil aggregates. *Canadian Journal of Soil Science*, **37**, 60–61.

Bradford, M.A., Fierer, N. & Reynolds, J.F. 2008. Soil carbon stocks in experimental mesocosms are dependent on the rate of labile carbon, nitrogen and phosphorus inputs to soils. *Functional Ecology*, **22**, 964–974.

Brandani, C.B., Abbruzzini, T.F., Conant, R.T. & Cerri, C.E.P. 2016. Soil organic and organomineral fractions as indicators of the effects of land management in conventional and organic sugar cane systems. *Soil Research*.

Brandani, C.B., Abbruzzini, T.F., Williams, S., Easter, M., Pellegrino Cerri, C.E. & Paustian, K. 2015. Simulation of management and soil interactions impacting SOC dynamics in sugarcane using the CENTURY Model. *GCB Bioenergy*, **7**, 646–657.

Brander, M. 2016. Conceptualising attributional LCA is necessary for resolving methodological issues such as the appropriate form of land use baseline. *International Journal of Life Cycle Assessment*.

Breiman, L. 2001. Random Forests. *Machine Learning*, **45**, 5–32.

Britain. 2020. Agriculture and Land Use. (At: https://www.visionofbritain.org.uk/data/dds_entity_page.jsp?ent=T_LAND. Accessed:

20/4/2020).

Buck-Sorlin, G. 2013. Process-based Model. In: *Encyclopedia of Systems Biology* (eds. Dubitzky, W., Wolkenhauer, O., Cho, K.H. & Yokota, H.). Springer, New York, NY.

Bünemann, E.K., Bongiorno, G., Bai, Z., Creamer, R.E., De Deyn, G., de Goede, R., Fleskens, L., Geissen, V., Kuyper, T.W., Mäder, P., Pulleman, M., Sukkel, W., van Groenigen, J.W. & Brussaard, L. 2018. Soil quality – A critical review. *Soil Biology and Biochemistry*, **120**, 105–125.

Buurman, P. & Roscoe, R. 2011. Different chemical composition of free light, occluded light and extractable SOM fractions in soils of Cerrado and tilled and untilled fields, Minas Gerais, Brazil: A pyrolysis-GC/MS study. *European Journal of Soil Science*.

Campbell, C.A., Biederbeck, V.O., Zentner, R.P. & Lafond, G.P. 1991. Effect of crop rotations and cultural practices on soil organic matter, microbial biomass and respiration in a thin Black Chernozem. *Canadian Journal of Soil Science*.

Campbell, C.D., Chapman, S.J., Cameron, C.M., Davidson, M.S. & Potts, J.M. 2003. A Rapid Microtiter Plate Method To Measure Carbon Dioxide Evolved from Carbon Substrate Amendments so as To Determine the Physiological Profiles of Soil Microbial Communities by Using Whole Soil. *Applied and Environmental Microbiology*, **69**, 3593–3599.

Carvalho, J.L.N., Raucci, G.S., Cerri, C.E.P., Bernoux, M., Feigl, B.J., Wruck, F.J. & Cerri, C.C. 2010. Impact of pasture, agriculture and crop-livestock systems on soil C stocks in Brazil. *Soil and Tillage Research*, **110**, 175–186.

Chadwick, D.R., Cardenas, L.M., Dhanoa, M.S., Donovan, N., Misselbrook, T., Williams, J.R., Thorman, R.E., McGeough, K.L., Watson, C.J., Bell, M., Anthony, S.G. & Rees, R.M. 2018. The contribution of cattle urine and dung to nitrous oxide emissions: Quantification of country specific emission factors and implications for national inventories. *Science of the Total Environment*.

Challinor, J.M. 1989. A pyrolysis-derivatisation-gas chromatography technique for the structural elucidation of some synthetic polymers. *Journal of Analytical and Applied Pyrolysis*.

Chang, K.-H., Warland, J., Voroney, P., Bartlett, P. & Wagner-Riddle, C. 2013. Using DayCENT to Simulate Carbon Dynamics in Conventional and No-Till Agriculture. *Soil Science Society of America Journal*.

Chen, W., Huang, D., Liu, N., Zhang, Y., Badgery, W.B., Wang, X. & Shen, Y. 2015. Improved grazing management may increase soil carbon sequestration in temperate steppe. *Scientific Reports*, **5**, 10892.

Cheng, K., Ogle, S.M., Parton, W.J. & Pan, G. 2014. Simulating greenhouse gas mitigation potentials for Chinese Croplands using the DAYCENT ecosystem model. *Global Change Biology*.

Cherubin, M.R., Karlen, D.L., Cerri, C.E., Franco, A.L., Tormena, C.A., Davies, C.A. & Cerri, C.C. 2016a. Soil Quality Indexing Strategies for Evaluating Sugarcane Expansion in Brazil. *PLoS One*, **11**, e0150860.

Cherubin, M.R., Karlen, D.L., Franco, A.L.C., Cerri, C.E.P., Tormena, C.A. & Cerri, C.C. 2016b. A Soil Management Assessment Framework (SMAF) Evaluation of Brazilian Sugarcane Expansion on Soil Quality. *Soil Science Society of America Journal*, **80**, 215.

Christensen, B.T. 1988. Effects of animal manure and mineral fertilizer on the total carbon and nitrogen contents of soil size fractions. *Biology and Fertility of Soils*.

Christensen, B.T. 1992. Physical fractionation of soil and organic matter in primary particle size and density separates. *Advances in Soil Science*, **20**.

Christensen, B.T. 2001. Physical fractionation of soil and structural and functional complexity in organic matter turnover. *European Journal of Soil Science*, **52**, 345–353.

Cloy, J.M., Wilson, C.A. & Graham, M.C. 2014. Stabilization of organic carbon via chemical interactions with fe and al oxides in gley soils. *Soil Science*.

Conant, R.T., Cerri, C.E.P., Osborne, B.B. & Paustian, K. 2017. Grassland management impacts on soil carbon stocks: a new synthesis. *Ecological Applications*, **27**, 662–668.

Conant, R.T., Paustian, K. & Elliott, E.T. 2001. Grassland management and conversion into grassland: effects on soil carbon. *Ecological Applications*, **11**, 343–355.

Congreves, K.A., Grant, B.B., Campbell, C.A., Smith, W.N., Vandenbygaart, A.J., Kröbel, R., Lemke, R.L. & Desjardins, R.L. 2015. Measuring and modeling the long-term impact of crop management on soil carbon sequestration in the semiarid canadian prairies. *Agronomy Journal*.

Connor, D.J. 2008. Organic agriculture cannot feed the world. *Field Crops Research*, **106**, 187–190.

Cooper, J., Baranski, M., Stewart, G., Nobel-de Lange, M., Bàrberi, P., Fließbach, A., Peigné, J., Berner, A., Brock, C., Casagrande, M., Crowley, O., David, C., De Vliegher, A., Döring, T.F., Dupont, A., Entz, M., Grosse, M., Haase, T., Halde, C., Hammerl, V., Huiting, H., Leithold, G., Messmer, M., Schloter, M., Sukkel, W., van der Heijden, M.G.A., Willekens, K., Wittwer, R. & Mäder, P. 2016. Shallow non-inversion tillage in organic farming maintains crop yields and increases soil C stocks: a meta-analysis. *Agronomy for Sustainable Development*, **36**, 22.

Cooper, J., Reed, E.Y., Hörtenhuber, S., Lindenthal, T., Løes, A.-K., Mäder, P., Magid, J., Oberson, A., Kolbe, H. & Möller, K. 2018. Phosphorus availability on many organically managed farms in Europe. *Nutrient Cycling in Agroecosystems*, **110**, 227–239.

Cooper, J., Sanderson, R., Cakmak, I., Ozturk, L., Shotton, P., Carmichael, A., Haghighi, R.S., Tetard-Jones, C., Volakakis, N., Eyre, M. & Leifert, C. 2011. Effect of organic and conventional crop rotation, fertilization, and crop protection practices on metal contents in wheat (triticum aestivum). *Journal of Agricultural and Food Chemistry*.

Coq, S., Barthès, B.G., Oliver, R., Rabary, B. & Blanchart, E. 2007. Earthworm activity affects soil aggregation and organic matter dynamics according to the quality and localization of crop residues-An experimental study (Madagascar). *Soil Biology and Biochemistry*.

Cotrufo, M.F., Soong, J.L., Horton, A.J., Campbell, E.E., Haddix, M.L., Wall, D.H. & Parton, W.J. 2015. Formation of soil organic matter via biochemical and physical pathways of litter mass loss. *Nature Geoscience*, **8**, 776.

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? *Global Change Biology*, **19**, 988–995.

Cranfield University. 2021. The Soils Guide. *Cranfield University, UK.*, (At: www.landis.org.uk. Accessed: 30/5/2021).

Crème, A., Rumpel, C., Le Roux, X., Romian, A., Lan, T. & Chabbi, A. 2018. Ley grassland under temperate climate had a legacy effect on soil organic matter quantity, biogeochemical signature and microbial activities. *Soil Biology and Biochemistry*, **122**, 203–210.

Crowder, D.W. & Reganold, J.P. 2015. Financial competitiveness of organic agriculture on a global scale. *Proceedings of the National Academy of Sciences*, **112**, 7611–7616.

Davies, J.A.C., Tipping, E., Rowe, E.C., Boyle, J.F., Graf Pannatier, E. & Martinsen, V. 2016. Long-term P weathering and recent N deposition control contemporary plant-soil C, N, and P. *Global Biogeochemical Cycles*.

Davis, M.R., Alves, B.J.R., Karlen, D.L., Kline, K.L., Galdos, M. & Abulebdeh, D. 2017. Review of soil organic carbon measurement protocols: A US and Brazil comparison and recommendation. *Sustainability (Switzerland)*.

DEFRA. 2011. The British Survey of Fertiliser Practice - Fertiliser use on farm for Crops for Crop Year 2010. *Department for Environment Food and Rural Affairs*.

DEFRA. 2020. National Statistics Organic farming statistics 2019. 19, (At: https://www.gov.uk/government/statistics/organic-farming-statistics-2019.).

Dell'Abate, M.T., Benedetti, A. & Sequi, P. 2000. Thermal methods of organic matter maturation monitoring during a composting process. *Journal of Thermal Analysis and Calorimetry*.

Dell'Abate, M.T., Benedetti, A., Trinchera, A. & Dazzi, C. 2002. Humic substances along the profile of two Typic Haploxerert. *Geoderma*.

Deng, Q., Zhou, G., Liu, J., Liu, S., Duan, H. & Zhang, D. 2010. Responses of soil respiration to elevated carbon dioxide and nitrogen addition in young subtropical forest ecosystems in China. *Biogeosciences*.

Derenne, S. & Quéné, K. 2015. Analytical pyrolysis as a tool to probe soil organic matter. *Journal of Analytical and Applied Pyrolysis*.

Diacono, M. & Montemurro, F. 2010. Long-term effects of organic amendments on soil fertility. A review. *Agronomy for Sustainable Development*, **30**, 401–422.

Dignac, M.F., Derrien, D., Barré, P., Barot, S., Cécillon, L., Chenu, C., Chevallier, T., Freschet, G.T., Garnier, P., Guenet, B., Hedde, M., Klumpp, K., Lashermes, G., Maron, P.A., Nunan, N., Roumet, C. & Basile-Doelsch, I. 2017. Increasing soil carbon storage: mechanisms, effects of agricultural practices and proxies. A review. *Agronomy for Sustainable Development*.

Dixon, R.K., Brown, S., Houghton, R.A., Solomon, A.M., Trexler, M.C. & Wisniewski, J. 1994. Carbon pools and flux of global forest ecosystems. *Science*.

Dominy, C.S. & Haynes, R.J. 2002. Influence of agricultural land management on organic matter content, microbial activity and aggregate stability in the profiles of two Oxisols.

Biology and Fertility of Soils, **36**, 298–305.

Dondini, M., Abdalla, M., Aini, F.K., Albanito, F., Beckert, M.R., Begum, K., Brand, A., Cheng, K., Comeau, L.P., Jones, E.O., Farmer, J.A., Feliciano, D.M.S., Fitton, N., Hastings, A., Henner, D.N., Kuhnert, M., Nayak, D.R., Oyesikublakemore, J., Phillips, L., Richards, M.I.A., Tumwesige, V., Van Dijk, W.F.A., Vetter, S.H., Coleman, K., Smith, J. & Smith, P. 2018. Projecting soil C under future climate and land-use scenarios (modeling). In: *Soil Carbon Storage: Modulators, Mechanisms and Modeling*.

Doran, J.W. 2002. Soil health and global sustainability: Translating science into practice. In: *Agriculture, Ecosystems and Environment*, pp. 119–127.

Doran, J.W. & Parkin, T.B. 1994. Defining and assessing soil quality. *Defining soil quality for a sustainable environment. Proc. symposium, Minneapolis, MN, 1992*.

Dungait, J.A.J., Hopkins, D.W., Gregory, A.S. & Whitmore, A.P. 2012. Soil organic matter turnover is governed by accessibility not recalcitrance. *Global Change Biology*.

EDINA Digimap. 2020a. Historic maps. *Historical Ordnance Survey maps of Great Britain.*

EDINA Digimap. 2020b. Land Cover maps. *Environment Ordnance Survey, Land Cover data for 1990, 2000, 2007 and 2015, all national coverages. Dudley Stamp's maps of the 1930's Land Utilisation Survey of Britain.*

Emsley, J. 2001. Going one better than nature? *Nature*, **410**, 633–634.

Esri. 2018. ArcMap 10.6.1. *ESRI.*

European Commission. 2002. Towards a Thematic Strategy for Soil Protection.

Everingham, Y., Sexton, J., Skocaj, D. & Inman-Bamber, G. 2016. Accurate prediction of sugarcane yield using a random forest algorithm. *Agronomy for Sustainable Development*.

de Faccio Carvalho, P.C., Anghinoni, I., de Moraes, A., de Souza, E.D., Sulc, R.M., Lang, C.R., Flores, J.P.C., Terra Lopes, M.L., da Silva, J.L.S., Conte, O., de Lima Wesp, C., Levien, R., Fontaneli, R.S. & Bayer, C. 2010. Managing grazing animals to achieve nutrient cycling and soil improvement in no-till integrated systems. *Nutrient Cycling in Agroecosystems*, **88**, 259–273.

FAO. 2015. *World Agriculture: Towards 2015/2030 an FAO Perspective*. London, UK.

FAO. 2019. *Measuring and modelling soil carbon stocks and stock changes in livestock production systems: Guidelines for assessment*. Rome, FAO.

Farewell, T.S., Truckell, I.G., Keay, C.A. & Hallett, S.H. 2011. *The derivation and application of Soilscapes: soil and environmental datasets from the National Soil Resources Institute, Cranfield University*.

Feng, W., Shi, Z., Jiang, J., Xia, J., Liang, J., Zhou, J. & Luo, Y. 2016. Methodological uncertainty in estimating carbon turnover times of soil fractions. *Soil Biology and Biochemistry*, **100**, 118–124.

Fernández, J.M., Peltre, C., Craine, J.M. & Plante, A.F. 2012. Improved characterization of soil organic matter by thermal analysis using CO2/H2O evolved gas analysis. *Environmental Science and Technology*.

Fess, T.L. & Benedito, V.A. 2018. Organic versus conventional cropping sustainability: A comparative system analysis. *Sustainability (Switzerland)*.

Fitton, N., Datta, A., Hastings, A., Kuhnert, M., Topp, C.F.E., Cloy, J.M., Rees, R.M., Cardenas, L.M., Williams, J.R., Smith, K., Chadwick, D. & Smith, P. 2014a. The challenge of modelling nitrogen management at the field scale: Simulation and sensitivity analysis of N2O fluxes across nine experimental sites using DailyDayCent. *Environmental Research Letters*.

Fitton, N., Datta, A., Smith, K., Williams, J.R., Hastings, A., Kuhnert, M., Topp, C.F.E. & Smith, P. 2014b. Assessing the sensitivity of modelled estimates of N2O emissions and yield to input uncertainty at a UK cropland experimental site using the DailyDayCent model. *Nutrient Cycling in Agroecosystems*.

Fontaine, S., Bardoux, G., Abbadie, L. & Mariotti, A. 2004. Carbon input to soil may decrease soil carbon content. *Ecology Letters*.

Fontaine, S., Barot, S., Barre, P., Bdioui, N., Mary, B. & Rumpel, C. 2007. Stability of organic carbon in deep soil layers controlled by fresh carbon supply. *Nature*, **450**, 277–280.

Fortune, S., Robinson, J.S., Watson, C.A., Philipps, L., Conway, J.S. & Stockdale, E.A. 2006. Response of organically managed grassland to available phosphorus and potassium in the soil and supplementary fertilization: field trials using grass–clover leys cut for silage. *Soil Use and Management*, **21**, 370–376.

Franzluebbers, A.J., Sawchik, J. & Taboada, M.A. 2014. Agronomic and environmental impacts of pasture-crop rotations in temperate North and South America. *Agriculture, Ecosystems and Environment*.

Franzluebbers, A.J., Stuedemann, J.A., Schomberg, H.H. & Wilkinson, S.R. 2000. Soil organic C and N pools under long-term pasture management in the Southern Piedmont USA. *Soil Biology and Biochemistry*.

García-Palacios, P., Gattinger, A., Bracht-Jørgensen, H., Brussaard, L., Carvalho, F., Castro, H., Clément, J.-C., De Deyn, G., D'Hertefeldt, T., Foulquier, A., Hedlund, K., Lavorel, S., Legay, N., Lori, M., Mäder, P., Martínez-García, L.B., Martins da Silva, P., Muller, A., Nascimento, E., Reis, F., Symanczik, S., Paulo Sousa, J. & Milla, R. 2018. Crop traits drive soil carbon sequestration under organic farming. *Journal of Applied Ecology*, **55**, 2496–2505.

Gattinger, A., Muller, A., Haeni, M., Skinner, C., Fließbach, A., Buchmann, N., Mäder, P., Stolze, M., Smith, P., El-Hage Scialabba, N. & Niggli, U. 2013. Reply to Leifeld et al.: Enhanced top soil carbon stocks under organic farming is not equated with climate change mitigation. *Proceedings of the National Academy of Sciences*, **110**, E985 LP-E985.

Gattinger, A., Muller, A., Haeni, M., Skinner, C., Fliessbach, A., Buchmann, N., Mäder, P., Stolze, M., Smith, P., Scialabba, N.E.-H. & Niggli, U. 2012. Enhanced top soil carbon stocks under organic farming. *Proceedings of the National Academy of Sciences*, **109**, 18226–18231.

Gerzabek, M.H., Haberhauer, G. & Kirchmann, H. 2001. Soil Organic Matter Pools and Carbon-13 Natural Abundances in Particle-Size Fractions of a Long-Term Agricultural Field Experiment Receiving Organic Amendments. *Soil Science Society of America Journal*.

Glendining, M.J., Bailey, N.J., Smith, J.U., Addiscott, T.M. & Smith, P. 1998. *SUNDIAL-FRS user guide, version 1.0.* MAFF, London/IACR-Rothamsted, Harpenden, London, UK.

Godfray, H.C., Beddington, J.R., Crute, I.R., Haddad, L., Lawrence, D., Muir, J.F., Pretty, J., Robinson, S., Thomas, S.M. & Toulmin, C. 2010. Food security: the challenge of feeding 9 billion people. *Science*, **327**, 812–818.

Gomiero, T., Pimentel, D. & Paoletti, M.G. 2011. Environmental Impact of Different Agricultural Management Practices: Conventional vs. Organic Agriculture. *Critical Reviews in Plant Sciences*, **30**, 95–124.

González-Pérez, J.A., Almendros, G., De La Rosa, J.M. & González-Vila, F.J. 2014. Appraisal of polycyclic aromatic hydrocarbons (PAHs) in environmental matrices by analytical pyrolysis (Py-GC/MS). *Journal of Analytical and Applied Pyrolysis*.

González-Pérez, J.A., González-Vila, F.J., Almendros, G. & Knicker, H. 2004. The effect of fire on soil organic matter - A review. *Environment International*.

Goulding, K., Stockdale, E. & Watson, C. 2009. Plant Nutrients in Organic Farming. In: *Organic Crop Production – Ambitions and Limitations*, pp. 73–88. Springer Netherlands, Dordrecht.

Gregory, A.S., Ritz, K., McGrath, S.P., Quinton, J.N., Goulding, K.W.T., Jones, R.J.A., Harris, J.A., Bol, R., Wallace, P., Pilgrim, E.S. & Whitmore, A.P. 2015. A review of the impacts of degradation threats on soil properties in the UK. *Soil Use and Management*, **31**, 1–15.

Del Grosso, S.J., Parton, W.J., Adler, P.R., Davis, S.C., Keough, C. & Marx, E. 2012. Daycent model simulations for estimating soil carbon dynamics and greenhouse gas fluxes from agricultural production systems. In: *Managing Agricultural Greenhouse Gases*.

Del Grosso, S.J., Parton, W.J., Keough, C.A. & Reyes-Fox, M. 2011. Special Features of the DayCent Modeling Package and Additional Procedures for Parameterization, Calibration, Validation, and Applications. *Methods of Introducing System Models into Agricultural Research*, 155–176.

Del Grosso, S.J., Parton, W.J., Mosier, A.R., Hartman, M.D., Brenner, J., Ojima, D.S. & Schimel, D.S. 2001. Simulated interaction of carbon dynamics and nitrogen trace gas fluxes using the DAYCENT model. In: *Modeling carbon and nitrogen dynamics for soil management* (eds. Schaffer, M., Ma, L. & Hansen, S.), pp. 303–332. CRC Press, Boca Raton, FL.

Del Grosso, S.J., Parton, W.J., Mosier, A.R., Walsh, M.K., Ojima, D.S. & Thornton, P.E. 2006. DAYCENT national-scale simulations of nitrous oxide emissions from cropped soils in the United States. *Journal of environmental quality*.

Grunwald, S. 2009. Multi-criteria characterization of recent digital soil mapping and modeling approaches. *Geoderma*, **152**, 195–207.

Guimarães, R.M.L., Ball, B.C. & Tormena, C.A. 2011. Improvements in the visual evaluation of soil structure. *Soil Use and Management*.

Gulde, S., Chung, H., Amelung, W., Chang, C. & Six, J. 2008. Soil Carbon Saturation Controls Labile and Stable Carbon Pool Dynamics. *Soil Science Society of America Journal*.

Guo, L.B. & Gifford, R.M. 2002. Soil carbon stocks and land use change: a meta analysis. *Global Change Biology*, **8**, 345–360.

Gura, I. & Mnkeni, P.N.S. 2019. Crop rotation and residue management effects under no till on the soil quality of a Haplic Cambisol in Alice, Eastern Cape, South Africa. *Geoderma*.

Halvorson, J.J., Smith, J.L. & Papendick, R.I. 1997. Issues of scale for evaluating soil quality. *Journal of Soil and Water Conservation*, **52**, 26 LP – 30.

Hamilton, E.W. & Frank, D.A. 2001. Can plants stimulate soil microbes and their own nutrient supply? *Ecology*, **82**, 2397–2402.

Hamza, M.A. & Anderson, W.K. 2005. Soil compaction in cropping systems: A review of the nature, causes and possible solutions. *Soil and Tillage Research*, **82**, 121–145.

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

Haynes, R.J. & Naidu, R. 1998. Influence of lime, fertilizer and manure applications on soil organic matter content and soil physical conditions: A review. *Nutrient Cycling in Agroecosystems*.

Haynes, R.J. & Williams, P.H. 1993. Nutrient Cycling and Soil Fertility in the Grazed Pasture Ecosystem. *Advances in Agronomy*, **49**, 119–199.

Herrick, J.E. 2000. Soil quality: an indicator of sustainable land management? *Applied Soil Ecology*, **15**, 75–83.

Heyburn, J., McKenzie, P., Crawley, M.J. & Fornara, D.A. 2017. Effects of grassland management on plant C:N:P stoichiometry: implications for soil element cycling and storage. *Ecosphere*, **8**, e01963.

Hillier, J., Abdalla, M., Bellarby, J., Albanito, F., Datta, A., Dondini, M., Fitton, N., Hallett, P., Hastings, A., Jones, E., Kuhnert, M., Nayak, D., Pogson, M., Richards, M., Smith, J., Vetter, S., Yeluripati, J. & Smith, P. 2015. Mathematical Modeling of Greenhouse Gas Emissions from Agriculture for Different End Users.

Hothorn, T., Bretz, F. & Westfall, P. 2008. Simultaneous Inference in General Parametric Models. **50**, 346–363.

Houborg, R. & McCabe, M.F. 2018. A hybrid training approach for leaf area index estimation via Cubist and random forests machine-learning. *ISPRS Journal of Photogrammetry and Remote Sensing*.

Houghton, R.A. 2003. Revised estimates of the annual net flux of carbon to the atmosphere from changes in land use and land management 1850-2000. *Tellus, Series B: Chemical and Physical Meteorology*.

Huang, C.L. & Wang, C.J. 2006. A GA-based feature selection and parameters optimizationfor support vector machines. *Expert Systems with Applications*.

IFOAM. 2012. *The IFOAM Norms for Organic Production and Processing* (B (International Federation of Organic Agriculture Movements (IFOAM) and 2012) Germany, Eds.).

Intergovernmental Panel on Climate Change. 2014. *Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*.

IPCC. 2000. *the Intergovernmental Panel on Climate Change: Land Use, Land-Use Change, and Forestry*.

IPCC. 2003. *Good Practice Guidance for Land Use, Land-Use Change and Forestry* (J Penman, M Gytarsky, T Hiraishi, T Krug, D Kruger, R Pipatti, L Buendia, K Miwa, T Ngara, K Tanabe, and F Wagner, Eds.). Hayama, Japan.

IPCC. 2006. *IPCC Guidelines for National Greenhouse Gas Inventories: Prepared by the National Greenhouse Gas Inventories Programme* (HS Eggleston, L Buendia, K Miwa, T Ngara, and K Tanabe, Eds.). Institute for Global Environmental Strategies, Japan.

IPCC. 2014. *Summary for Policy makers. In: Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (CB Field, VR Barros, DJ Dokken, KJ Mach, MD Mastrandrea, TE Bilir, M Chatterjee, KL Ebi, YO Estrada, RC Genova, B Girma, ES Kissel, AN Levy, S MacCracken, PR Mastrandrea, and LL White, Eds.). Intergovernmental Panel on Climate Change , Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC. 2019. *Summary for Policymakers. In: 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* (PR Shukla, J Skea, E Calvo Buendia, V Masson-Delmotte, H-O Pörtner, DC Roberts, P Zhai, R Slade, S Connors, R van Diemen, M Ferrat, E Haughey, S Luz, S Neogi, M Pathak, J Petzold, J Portugal Pereira, P Vyas, E Huntley, K Kissick, and J Malley, Eds.).

Jabro, J.D., Sainju, U., Stevens, W.B. & Evans, R.G. 2008. Carbon dioxide flux as affected by tillage and irrigation in soil converted from perennial forages to annual crops. *J Environ*

Manage, **88**, 1478–1484.

Jackson, R.D., Isidore, B. & Cates, R.L. 2019. Are plant-soil dynamics different in pastures under organic management? A review. *Agriculture, Ecosystems and Environment*, **279**, 53–57.

Janzen, H.H. 2006. The soil carbon dilemma: Shall we hoard it or use it? *Soil Biology and Biochemistry*.

Jarvis, N., Forkman, J., Koestel, J., Kätterer, T., Larsbo, M. & Taylor, A. 2017. Long-term effects of grass-clover leys on the structure of a silt loam soil in a cold climate. *Agriculture, Ecosystems & Environment*, **247**, 319–328.

Jastrow, J.D., Amonette, J.E. & Bailey, V.L. 2007. Mechanisms controlling soil carbon turnover and their potential application for enhancing carbon sequestration. *Climatic Change*, **80**, 5–23.

Jenkinson, D.S., Poulton, P.R. & Bryant, C. 2008. The turnover of organic carbon in subsoils. Part 1. Natural and bomb radiocarbon in soil profiles from the Rothamsted long-term field experiments. *European Journal of Soil Science*, **59**, 391–399.

Jensen, J.L., Schjønning, P., Watts, C.W., Christensen, B.T., Peltre, C. & Munkholm, L.J. 2019. Relating soil C and organic matter fractions to soil structural stability. *Geoderma*, **337**, 834–843.

Jian, J., Du, X., Reiter, M.S. & Stewart, R.D. 2020. A meta-analysis of global cropland soil carbon changes due to cover cropping. *Soil Biology and Biochemistry*.

JMP. 2019. JMP® Pro 13, Version 13.0.0. SAS Institute Inc., Cary, NC, 1989-2019.

Jobbágy, E.G. & Jackson, R.B. 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications*, **10**, 423–436.

Johnston, A.E., Poulton, P.R., Coleman, K., Macdonald, A.J. & White, R.P. 2017. Changes in soil organic matter over 70 years in continuous arable and ley-arable rotations on a sandy loam soil in England. *European Journal of Soil Science*, **68**, 305–316.

Kaal, E. & Janssen, H.G. 2008. Extending the molecular application range of gas chromatography. *Journal of Chromatography A*.

Kaal, J., Martínez-Cortizas, A., Nierop, K.G.J. & Buurman, P. 2008. A detailed pyrolysis-GC/MS analysis of a black carbon-rich acidic colluvial soil (Atlantic ranker) from NW

Spain. *Applied Geochemistry*.

Karlen, D.L., Andrews, S.S. & Doran, J.W. 2001. Soil quality: Current concepts and applications. *Advances in Agronomy*.

Karlen, D.L., Andrews, S.S., Wienhold, B.J. & Zobeck, T.M. 2008. Soil Quality Assessment: Past, Present and Future . *Journal of Integrative Biosciences* , **6**, 3–14.

Karlen, D.L., Ditzler, C.A. & Andrews, S.S. 2003. Soil quality: Why and how? *Geoderma*.

Karlen, D.L., Mausbach, J.W., Doran, R.G., Cline, R.G., Harris, R.F. & Schuman, G.E. 1997. Soil Quality: A Concept, Definition, and Framework for Evaluation. *Soil Science Society of America Journal*, **61**, 4–10.

Karlen, D.L. & Stott, D.E. 1994. A framework for evaluating physical and chemical indicators of soil quality. *Defining soil quality for a sustainable environment. Proc. symposium, Minneapolis, MN, 1992*.

Kätterer, T. & Andrén, O. 2009. Predicting daily soil temperature profiles in arable soils in cold temperate regions from air temperature and leaf area index. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science*, **59**, 77–86.

Keil, R.G. & Mayer, L.M. 2013. Mineral Matrices and Organic Matter. In: *Treatise on Geochemistry: Second Edition*.

Key, G., Whitfield, M.G., Cooper, J., De Vries, F.T., Collison, M., Dedousis, T., Heathcote, R., Roth, B., Mohammed, S., Molyneux, A., Van der Putten, W.H., Dicks, L. V, Sutherland, W.J. & Bardgett, R.D. 2016. Knowledge needs, available practices, and future challenges in agricultural soils. *SOIL*, **2**, 511–521.

Kirchmann, H., Kätterer, T., Bergström, L., Börjesson, G. & Bolinder, M.A. 2016. Flaws and criteria for design and evaluation of comparative organic and conventional cropping systems. *Field Crops Research*, **186**, 99–106.

Kirkby, C.A., Richardson, A.E., Wade, L.J., Passioura, J.B., Batten, G.D., Blanchard, C. & Kirkegaard, J.A. 2014. Nutrient availability limits carbon sequestration in arable soils. *Soil Biology and Biochemistry*, **68**, 402–409.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R. & Nico, P.S. 2015. Mineral-Organic Associations: Formation, Properties, and Relevance in Soil Environments. *Advances in Agronomy*, **130**, 1–140.

Kleber, M., Nico, P.S., Plante, A., Filley, T., Kramer, M., Swanston, C. & Sollins, P. 2011. Old and stable soil organic matter is not necessarily chemically recalcitrant: Implications for modeling concepts and temperature sensitivity. *Global Change Biology*.

Klotzbücher, T., Kaiser, K., Guggenberger, G., Gatzek, C. & Kalbitz, K. 2011. A new conceptual model for the fate of lignin in decomposing plant litter. *Ecology*.

Klumpp, K., Fontaine, S., Attard, E., Le Roux, X., Gleixner, G. & Soussana, J.F. 2009. Grazing triggers soil carbon loss by altering plant roots and their control on soil microbial community. *Journal of Ecology*.

Kratz, S., Schick, J. & Øgaard, A.F. 2016. P Solubility of Inorganic and Organic P Sources. In: *Phosphorus in Agriculture: 100 % Zero* (eds. Schnug, E. & De Kok, L.J.), pp. 127–154. Springer Netherlands, Dordrecht.

Krull, E.S., Baldock, J.A. & Skjemstad, J.O. 2003. Importance of mechanisms and processes of the stabilisation of soil organic matter for modelling carbon turnover. *Functional Plant Biology*.

Kutsch, W.L., Bahn, M. & Heinemeyer, A. 2010. *Soil carbon dynamics: An integrated methodology*.

Kuzyakov, Y. 2010. Priming effects: Interactions between living and dead organic matter. *Soil Biology and Biochemistry*.

Kuzyakov, Y., Friedel, J.K. & Stahr, K. 2000. Review of mechanisms and quantification of priming effects. *Soil Biology and Biochemistry*.

Kyoto Protocol. 1997. Kyoto Protocol to the United Nations Framework Convention on Climate Change. Dec. 10, 1997. FCCC/CP/1997/7/Add.1. reprinted in (1998) 37 ILM. 22. UN.

De la Rosa, J.M., González-Pérez, J.A., González-Vázquez, R., Knicker, H., López-Capel, E., Manning, D.A.C. & González-Vila, F.J. 2008. Use of pyrolysis/GC–MS combined with thermal analysis to monitor C and N changes in soil organic matter from a Mediterranean fire affected forest. *CATENA*, **74**, 296–303.

Lagacherie, P. & McBratney, A.B. 2006. Chapter 1 Spatial Soil Information Systems and Spatial Soil Inference Systems: Perspectives for Digital Soil Mapping. In: *Digital Soil Mapping* (eds. Lagacherie, P., McBratney, A.B. & Voltz, M.B.T.-D. in S.S.), pp. 3–22. Elsevier.

Lal, R. 2004a. Soil carbon sequestration impacts on global climate change and food security. *Science*, **304**, 1623–1627.

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

Lal, R. 2007. Carbon Management in Agricultural Soils. *Mitigation and Adaptation Strategies for Global Change*, **12**, 303–322.

Lal, R. 2010. Managing soils and ecosystems for mitigating anthropogenic carbon emissions and advancing global food security. *BioScience*.

Lal, R., Negassa, W. & Lorenz, K. 2015. Carbon sequestration in soil. *Current Opinion in Environmental Sustainability*.

Lamy, T., Liss, K.N., Gonzalez, A. & Bennett, E.M. 2016. Landscape structure affects the provision of multiple ecosystem services. *Environmental Research Letters*.

Langier-Kuźniarowa, A. 2002. Thermal analysis of organo-clay complexes. In: *Organo-Clay Complexes and Interactions* (eds. Yariv, S. & Cross, H.), pp. 273–344. Marcel-Dekker, New York.

Lavallee, J.M., Soong, J.L. & Cotrufo, M.F. 2019. Conceptualizing soil organic matter into particulate and mineral-associated forms to address global change in the 21st century. *Global Change Biology*, **0**.

Lawson, D.A. & Tabor, J.H. 2001. Stopping distances: An excellent example of empirical modelling. *Teaching Mathematics and its Applications*.

Lee, J., Necpálová, M. & Six, J. 2020. Biophysical potential of organic cropping practices as a sustainable alternative in Switzerland. *Agricultural Systems*.

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

Leifeld, J., Angers, D.A., Chenu, C., Fuhrer, J., Kätterer, T. & Powlson, D.S. 2013. Organic farming gives no climate change benefit through soil carbon sequestration. *Proceedings of the National Academy of Sciences of the United States of America*, **110**, E984.

Leifeld, J., Bassin, S. & Fuhrer, J. 2005. Carbon stocks in Swiss agricultural soils predicted by land-use, soil characteristics, and altitude. *Agriculture, Ecosystems and Environment*.

Leifeld, J. & Fuhrer, J. 2010. Organic farming and soil carbon sequestration: what do we really know about the benefits? *Ambio*, **39**, 585–99.

Leinweber, P. & Schulten, H.R. 1992. Differential thermal analysis, thermogravimetry and in-source pyrolysis-mass spectrometry studies on the formation of soil organic matter. *Thermochimica Acta*.

Leinweber, P. & Schulten, H.-R. 1993. Dynamics of soil organic matter studied by pyrolysis—field ionization mass spectrometry. *Journal of Analytical and Applied Pyrolysis*, **25**, 123–136.

Lemaire, G., Gastal, F., Franzluebbers, A. & Chabbi, A. 2015. Grassland-Cropping Rotations: An Avenue for Agricultural Diversification to Reconcile High Production with Environmental Quality. *Environ Manage*, **56**, 1065–1077.

Lemaire, G., Da Silva, S.C., Agnusdei, M., Wade, M. & Hodgson, J. 2009. Interactions between leaf lifespan and defoliation frequency in temperate and tropical pastures: a review. *Grass and Forage Science*, **64**, 341–353.

Li, C., Frolking, S. & Frolking, T.A. 1992. A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. *Journal of Geophysical Research*.

Li, J., Wen, Y., Li, X., Li, Y., Yang, X., Lin, Z., Song, Z., Cooper, J.M. & Zhao, B. 2018. Soil labile organic carbon fractions and soil organic carbon stocks as affected by long-term organic and mineral fertilization regimes in the North China Plain. *Soil and Tillage Research*, **175**, 281–290.

Ließ, M., Schmidt, J. & Glaser, B. 2016. Improving the spatial prediction of soil organic carbon stocks in a complex tropical mountain landscape by methodological specifications in machine learning approaches. *PLoS ONE*, **11**.

Loaiza Puerta, V., Pujol Pereira, E.I., Wittwer, R., van der Heijden, M. & Six, J. 2018. Improvement of soil structure through organic crop management, conservation tillage and grass-clover ley. *Soil and Tillage Research*, **180**, 1–9.

Løes, A.-K. & Ebbesvik, M. 2017. Phosphorus deficits by long-term organic dairy farming? In: *Innovative research for Organic Agriculutre 3.0. Proceeedings of the Scientific Track, Organic World Congress, ISOFAR, TIPI and NCOF*, pp. 531–534. India.

Lopez-Capel, E., Abbott, G.D., Thomas, K.M. & Manning, D.A.C. 2006. Coupling of thermal analysis with quadrupole mass spectrometry and isotope ratio mass spectrometry for simultaneous determination of evolved gases and their carbon isotopic composition. *Journal of Analytical and Applied Pyrolysis*, **75**, 82–89.

Lopez-Capel, E., Sohi, S.P., Gaunt, J.L. & Manning, D.A.C. 2005. Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions. *Soil Science Society of America Journal*, **69**, 136–140.

Lorenz, K. & Lal, R.B.T.-A. in A. 2005. The Depth Distribution of Soil Organic Carbon in Relation to Land Use and Management and the Potential of Carbon Sequestration in Subsoil Horizons. pp. 35–66. Academic Press.

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*.

Lori, M., Symnaczik, S., Mäder, P., De Deyn, G. & Gattinger, A. 2017. Organic farming enhances soil microbial abundance and activity—A meta-analysis and meta-regression. *PLOS ONE*, **12**, e0180442.

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. *European Journal of Soil Science*.

von Lützow, M., Kögel-Knabner, I., Ekschmitt, K., Flessa, H., Guggenberger, G., Matzner, E. & Marschner, B. 2007. SOM fractionation methods: Relevance to functional pools and to stabilization mechanisms. *Soil Biology and Biochemistry*, **39**, 2183–2207.

von Lützow, M., Kögel-Knabner, I., Ludwig, B., Matzner, E., Flessa, H., Ekschmitt, K., Guggenberger, G., Marschner, B. & Kalbitz, K. 2008. Stabilization mechanisms of organic matter in four temperate soils: Development and application of a conceptual model. *Journal of Plant Nutrition and Soil Science*, **171**, 111–124.

Maeder, P., Fliessbach, A., Dubois, D., Gunst, L., Fried, P. & Niggli, U. 2002. Soil Fertility and Biodiversity in Organic Farming. *Science*, **296**, 1694–1697.

Maillard, É., McConkey, B.G. & Angers, D.A. 2017. Increased uncertainty in soil carbon stock measurement with spatial scale and sampling profile depth in world grasslands: A systematic analysis. *Agriculture, Ecosystems and Environment*.

Manning, D.A.C., Lopez-Capel, E. & Barker, S. 2005. Seeing soil carbon: use of thermal analysis in the characterization of soil C reservoirs of differing stability. *Mineralogical Magazine*.

Marks, H.F. 1989. *A hundred years of British food & farming: a statistical survey* (DK Britton, Ed.). Taylor & Francis.

Marriott, E.E. & Wander, M.M. 2006. Total and labile soil organic matter in organic and conventional farming systems. *Soil Science Society of America Journal*, **70**, 950–959.

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? *Journal of Plant Nutrition and Soil Science*.

Martens, D.A. 2000. Plant residue biochemistry regulates soil carbon cycling and carbon sequestration. *Soil Biology and Biochemistry*.

Mason, S.L., Filley, T.R. & Abbott, G.D. 2012. A comparative study of the molecular composition of a grassland soil with adjacent unforested and afforested moorland ecosystems. *Organic Geochemistry*.

Mazzetto, J.M.L., Melo, V.F., Bonfleur, E.J., Vidal-Torrado, P. & Dieckow, J. 2019. Potential of soil organic matter molecular chemistry determined by pyrolysis-gas chromatography/mass spectrometry for forensic investigations. *Science and Justice*.

Mazzoncini, M., Sapkota, T.B., Bàrberi, P., Antichi, D. & Risaliti, R. 2011. Long-term effect of tillage, nitrogen fertilization and cover crops on soil organic carbon and total nitrogen content. *Soil and Tillage Research*.

Mc Lean, E.O. 1982. Soil pH and lime requirement. In: *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*.

McBratney, A.B., Mendonça Santos, M.L. & Minasny, B. 2003. On digital soil mapping. *Geoderma*, **117**, 3–52.

McSherry, M.E. & Ritchie, M.E. 2013. Effects of grazing on grassland soil carbon: a global review. *Global Change Biology*, **19**, 1347–1357.

Medina-Roldán, E., Arredondo, J.T., Huber-Sannwald, E., Chapa-Vargas, L. & Olalde-Portugal, V. 2008. Grazing effects on fungal root symbionts and carbon and nitrogen storage in a shortgrass steppe in Central Mexico. *Journal of Arid Environments*, **72**, 546–556.

Meier, D. & Faix, O. 1992. Pyrolysis-Gas Chromatography-Mass Spectrometry BT - Methods in Lignin Chemistry. In: (eds. Lin, S.Y. & Dence, C.W.), pp. 177–199. Springer Berlin Heidelberg, Berlin, Heidelberg.

Meier, M.S., Stoessel, F., Jungbluth, N., Juraske, R., Schader, C. & Stolze, M. 2015. Environmental impacts of organic and conventional agricultural products – Are the differences captured by life cycle assessment? *Journal of Environmental Management*, **149**, 193–208.

Miller, B.A., Koszinski, S., Wehrhan, M. & Sommer, M. 2015. Impact of multi-scale predictor selection for modeling soil properties. *Geoderma*, **239**, 97–106.

Minasny, B., McBratney, A.B., Malone, B.P. & Wheeler, I. 2013. Chapter One - Digital Mapping of Soil Carbon. In: *Advances in Agronomy* (ed. Sparks, D.L.B.T.-A. in A.), pp. 1–47. Academic Press.

Minasny, B., McBratney, A.B., Mendonça-Santos, M.L., Odeh, I.O.A. & Guyon, B. 2006. Prediction and digital mapping of soil carbon storage in the Lower Namoi Valley. *Soil Research*, **44**, 233–244.

Minasny, B., McBratney, A.B. & Whelan, B.M. 2005. VESPER version 1.62. Australian Centre for Precision Agriculture, McMillan Building A05, The University of Sydney, NSW 2006.

Möller, K., Oberson, A., Bünemann, E.K., Cooper, J., Friedel, J.K., Glæsner, N., Hörtenhuber, S., Løes, A.K., Mäder, P., Meyer, G., Müller, T., Symanczik, S., Weissengruber, L., Wollmann, I. & Magid, J. 2018. Improved Phosphorus Recycling in Organic Farming: Navigating Between Constraints. In: *Advances in Agronomy*, pp. 159–237.

Mondelaers, K., Aertsens, J. & Van Huylenbroeck, G. 2009. A meta-analysis of the differences in environmental impacts between organic and conventional farming. *British Food Journal*, **111**, 1098–1119.

Montanarella, L. & Alva, I.L. 2015. Putting soils on the agenda: The three Rio Conventions and the post-2015 development agenda. *Current Opinion in Environmental Sustainability*.

Moore, I.D., Gessler, P.E., Nielsen, G.A. & Peterson, G.A. 1993. Soil attribute prediction using terrain analysis. *Soil Science Society of America Journal*, **57**, 443–452.

Muhammed, S.E., Coleman, K., Wu, L., Bell, V.A., Davies, J.A.C., Quinton, J.N., Carnell, E.J., Tomlinson, S.J., Dore, A.J., Dragosits, U., Naden, P.S., Glendining, M.J., Tipping, E. & Whitmore, A.P. 2018. Impact of two centuries of intensive agriculture on soil carbon, nitrogen and phosphorus cycling in the UK. *Science of the Total Environment*.

Mukherjee, A. & Lal, R. 2014. Comparison of soil quality index using three methods. *PLoS ONE*.

Murty, D., Kirschbaum, M.U.F., Mcmurtrie, R.E. & Mcgilvray, H. 2002. Does conversion of forest to agricultural land change soil carbon and nitrogen? A review of the literature. *Global Change Biology*.

Naden, P., Bell, V., Carnell, E., Tomlinson, S., Dragosits, U., Chaplow, J., May, L. & Tipping, E. 2016. Nutrient fluxes from domestic wastewater: A national-scale historical perspective for the UK 1800–2010. *Science of the Total Environment*.

Nardi, S., Morari, F., Berti, A., Tosoni, M. & Giardini, L. 2004. Soil organic matter properties after 40 years of different use of organic and mineral fertilisers. *European Journal of Agronomy*.

Nash, D.M., Haygarth, P.M., Turner, B.L., Condron, L.M., McDowell, R.W., Richardson, A.E., Watkins, M. & Heaven, M.W. 2014. Using organic phosphorus to sustain pasture productivity: A perspective. *Geoderma*, **221–222**, 11–19.

Necpalova, M., Lee, J., Skinner, C., Büchi, L., Wittwer, R., Gattinger, A., van der Heijden, M., Mäder, P., Charles, R., Berner, A., Mayer, J. & Six, J. 2018. Potentials to mitigate greenhouse gas emissions from Swiss agriculture. *Agriculture, Ecosystems and Environment*.

Nelson, D.W. & Sommers, L.E. 1996. Total carbon, organic carbon, and organic matter. In: *Methods of soil analysis. Part 2. 2.* (eds. Page, A.L., Miller, R.H. & Keeney, D.R.), pp. 961–1010. Madison: ASA.

Nemo, Klumpp, K., Coleman, K., Dondini, M., Goulding, K., Hastings, A., Jones, M.B., Leifeld, J., Osborne, B., Saunders, M., Scott, T., Teh, Y.A. & Smith, P. 2017. Soil Organic Carbon (SOC) Equilibrium and Model Initialisation Methods: an Application to the Rothamsted Carbon (RothC) Model. *Environmental Modeling and Assessment*.

Nierop, K.G.J., Pulleman, M.M. & Marinissen, J.C.Y. 2001. Management induced organic matter differentiation in grassland and arable soil: A study using pyrolysis techniques. *Soil Biology and Biochemistry*.

Nyfeler, D., Huguenin-Elie, O., Suter, M., Frossard, E. & Lüscher, A. 2011. Grass–legume mixtures can yield more nitrogen than legume pure stands due to mutual stimulation of nitrogen uptake from symbiotic and non-symbiotic sources. *Agriculture, Ecosystems & Environment*, **140**, 155–163.

O'Dea, J.K., Miller, P.R. & Jones, C.A. 2013. Greening summer fallow with legume green manures: On-farm assessment in north-central Montana. *Journal of Soil and Water Conservation*.

Oades, J.M. 1989. An Introduction to Organic Matter in Mineral Soils. *Minerals in Soil Environments*, 89–159.

Oberholzer, H.R., Leifeld, J. & Mayer, J. 2014. Changes in soil carbon and crop yield over 60 years in the Zurich Organic Fertilization Experiment, following land-use change from grassland to cropland. *Journal of Plant Nutrition and Soil Science*.

Oliveira, D.M. da S., Schellekens, J. & Cerri, C.E.P. 2016. Molecular characterization of soil organic matter from native vegetation-pasture-sugarcane transitions in Brazil. *Science of the Total Environment*.

Oliveira, D.M.S., Williams, S., Cerri, C.E.P. & Paustian, K. 2017. Predicting soil C changes over sugarcane expansion in Brazil using the DayCent model. *GCB Bioenergy*.

Olsen, S.R. & Sommers, L.E. 1982. *Phosphorus. In: Page AL, Miller RH, Keeney DR (eds) Methods of soil analysis part 2. American Society of Agronomy, Madison, pp 403–430*.

Ordnance Survey (GB). 2019. OS Terrain 5 DTM. *EDINA Digimap Ordnance Survey Service*, **ASC geospa**, Tiles: Nafferton Farm.

Panettieri, M., Rumpel, C., Dignac, M.F. & Chabbi, A. 2017. Does grassland introduction into cropping cycles affect carbon dynamics through changes of allocation of soil organic matter within aggregate fractions? *Sci Total Environ*, **576**, 251–263.

Paradis, E., Claude, J. & Strimmer, K. 2004. APE: analyses of phylogenetics and evolution in R language. Bioinformatics 20: 289-290. R package version 5.0.

Parton, W.J., Hartman, M., Ojima, D. & Schimel, D. 1998. DAYCENT and its land surface submodel: Description and testing. *Global and Planetary Change*, 35–48.

Parton, W.J., Holland, E.A., Del Grosso, S.J., Hartman, M.D., Martin, R.E., Mosier, A.R., Ojima, D.S. & Schimel, D.S. 2001. Generalized model for NOx and N2O emissions from soils. *Journal of Geophysical Research Atmospheres*.

Parton, W.J., Schimel, D.S., Cole, C. V & Ojima, D.S. 1987. Analysis of Factors Controlling Soil Organic Matter Levels in Great Plains Grasslands1. *Soil Science Society of America Journal*, **51**, 1173–1179.

Parton, W.J., Scurlock, J.M.O., Ojima, D.S., Gilmanov, T.G., Scholes, R.J., Schimel, D.S., Kirchner, T., Menaut, J. -C, Seastedt, T., Garcia Moya, E., Kamnalrut, A. & Kinyamario, J.I. 1993. Observations and modeling of biomass and soil organic matter dynamics for the grassland biome worldwide. *Global Biogeochemical Cycles*.

Parton, W.J., Stewart, J.W.B. & Cole, C. V. 1988. Dynamics of C, N, P and S in grassland soils: a model. *Biogeochemistry*, **5**, 109–131.

Paterson, K.C., Cloy, J.M., Rees, R.M., Baggs, E.M., Martineau, H., Fornara, D., Macdonald, A.J. & Buckingham, S. 2020. Estimating maximum mineral associated organic carbon in UK grasslands. *Biogeosciences Discuss.*, **2020**, 1–28.

Paustian, K., Collins, H.P. & Paul, E.A. 1997. Management controls on soil carbon. In: *Soil organic matter in temperate Agroecosystems - Long-term experiments in North America* (eds. Paul, E.A., Paustian, K., Elliott, E.T., Cole, C. V, Paustian, K., Elliott, E.T. & Cole, C. V), pp. 15–49.

Paustian, K., Lehmann, J., Ogle, S., Reay, D., Robertson, G.P. & Smith, P. 2016. Climate-smart soils. *Nature*, **532**, 49–57.

Paustian, K., Parton, W.J. & Persson, J. 1992. Modeling Soil Organic Matter in Organic-Amended and Nitrogen-Fertilized Long-Term Plots. *Soil Science Society of America Journal*.

Pavlů, V., Hejcman, M., Pavlů, L. & Gaisler, J. 2007. Restoration of grazing management and its effect on vegetation in an upland grassland. *Applied Vegetation Science*, **10**, 375–382.

Persson, T., Bergkvist, G. & Kätterer, T. 2008. Long-term effects of crop rotations with and without perennial leys on soil carbon stocks and grain yields of winter wheat. *Nutrient Cycling in Agroecosystems*.

Piccolo, A. 2002. The supramolecular structure of humic substances: A novel understanding of humus chemistry and implications in soil science. *Advances in Agronomy*.

Pickett, J.A. 2013. Food security: intensification of agriculture is essential, for which current tools must be defended and new sustainable technologies invented. *Food and Energy Security*, **2**, 167–173.

Pineiro, G., Paruelo, J.M., Oesterheld, M. & Jobbágy, E.G. 2010. Pathways of grazing effects on soil organic carbon and nitrogen. *Rangeland Ecology and Management*, **63**, 109–119.

Pinheiro., J., Bates., D., DebRoy., S., Sarkar., D. & Team, R.C. 2018. nlme: Linear and

Nonlinear Mixed Effects Models. R package version 3.1-131.1.

Plante, A.F., Fernández, J.M. & Leifeld, J. 2009. Application of thermal analysis techniques in soil science. *Geoderma*, **153**, 1–10.

Plante, A.F., Pernes, M. & Chenu, C. 2005. Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses. *Geoderma*.

Poeplau, C. & Don, A. 2015. Carbon sequestration in agricultural soils via cultivation of cover crops - A meta-analysis. *Agriculture, Ecosystems and Environment*.

Poeplau, C., Don, A., Six, J., Kaiser, M., Benbi, D., Chenu, C., Cotrufo, M.F., Derrien, D., Gioacchini, P., Grand, S., Gregorich, E., Griepentrog, M., Gunina, A., Haddix, M., Kuzyakov, Y., Kühnel, A., Macdonald, L.M., Soong, J., Trigalet, S., Vermeire, M.-L., Rovira, P., van Wesemael, B., Wiesmeier, M., Yeasmin, S., Yevdokimov, I. & Nieder, R. 2018. Isolating organic carbon fractions with varying turnover rates in temperate agricultural soils – A comprehensive method comparison. *Soil Biology and Biochemistry*, **125**, 10–26.

Poeplau, C., Don, A., Vesterdal, L., Leifeld, J., Van Wesemael, B., Schumacher, J. & Gensior, A. 2011. Temporal dynamics of soil organic carbon after land-use change in the temperate zone - carbon response functions as a model approach. *Global Change Biology*.

Ponisio, L.C., M'gonigle, L.K., Mace, K.C., Palomino, J., Valpine, P. De & Kremen, C. 2015. Diversification practices reduce organic to conventional yield gap. *Proceedings of the Royal Society B: Biological Sciences*.

Post, W.M., Izaurralde, R.C., Mann, L.K. & Bliss, N. 2001. Monitoring and Verifying Changes of Organic Carbon in Soil. *Climatic Change*, **51**, 73–99.

Powlson, D.S. 1996. Why evaluate soil organic matter models? In: *Evaluation of soil organic matter models using existing long-term datasets NATO ASI Series I: global environmental change, vol 38.* (eds. Powlson, D.S., Smith, P. & Smith, J.U.), pp. 3–11. Springer, Berlin.

Powlson, D.S., Glendining, M.J., Coleman, K. & Whitmore, A.P. 2011a. Implications for soil properties of removing cereal straw: Results from long-term studies. *Agronomy Journal*, **103:**, 279–287.

Powlson, D.S., Gregory, P.J., Whalley, W.R., Quinton, J.N., Hopkins, D.W., Whitmore, A.P., Hirsch, P.R. & Goulding, K.W.T. 2011b. Soil management in relation to sustainable agriculture and ecosystem services. *Food Policy*, **36**, S72–S87.

Pretty, J.N., Ball, A.S., Lang, T. & Morison, J.I.L. 2005. Farm costs and food miles: An assessment of the full cost of the UK weekly food basket. *Food Policy*, **30**, 1–19.

Probst, P., Wright, M.N. & Boulesteix, A.L. 2019. Hyperparameters and tuning strategies for random forest. *Wiley Interdisciplinary Reviews: Data Mining and Knowledge Discovery*, **9**.

Pullan, S. 2011. Land use change in Northumberland from 1800's to today– lessons from agricultural history. *Aspects of Applied Biology*, **108**, 145–152.

Quemada, M., Lassaletta, L., Leip, A., Jones, A. & Lugato, E. 2020. Integrated management for sustainable cropping systems: Looking beyond the greenhouse balance at the field scale. *Global Change Biology*.

Le Quéré, C., Andrew, R.M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A.C., Korsbakken, J.I., Peters, G.P., Canadell, J.G., Jackson, R.B., Boden, T.A., Tans, P.P., Andrews, O.D., Arora, V.K., Bakker, D.C.E., Barbero, L., Becker, M., Betts, R.A., Bopp, L., Chevallier, F., Chini, L.P., Ciais, P., Cosca, C.E., Cross, J., Currie, K., Gasser, T., Harris, I., Hauck, J., Haverd, V., Houghton, R.A., Hunt, C.W., Hurtt, G., Ilyina, T., Jain, A.K., Kato, E., Kautz, M., Keeling, R.F., Klein Goldewijk, K., Körtzinger, A., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Lima, I., Lombardozzi, D., Metzl, N., Millero, F., Monteiro, P.M.S., Munro, D.R., Nabel, J.E.M.S., Nakaoka, S.-I., Nojiri, Y., Padin, X.A., Peregon, A., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Reimer, J., Rödenbeck, C., Schwinger, J., Séférian, R., Skjelvan, I., Stocker, B.D., Tian, H., Tilbrook, B., Tubiello, F.N., van der Laan-Luijkx, I.T., van der Werf, G.R., van Heuven, S., Viovy, N., Vuichard, N., Walker, A.P., Watson, A.J., Wiltshire, A.J., Zaehle, S. & Zhu, D. 2018. Global Carbon Budget 2017. *Earth Syst. Sci. Data*, **10**, 405–448.

R Development Core Team. 2019. R: A language and environment to statistical computing. R Foundation for Statistical Computing. (At: http://www.r-project.org.).

Ralph, J. & Hatfield, R.D. 1991. Pyrolysis-Gc-Ms Characterization of Forage Materials. *Journal of Agricultural and Food Chemistry*.

Ranalli, G., Bottura, G., Taddei, P., Garavani, M., Marchetti, R. & Sorlini, C. 2001. Composting of solid and sludge residues from agricultural and food industries. Bioindicators of monitoring and compost maturity. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*.

Reay, D.S., Davidson, E.A., Smith, K.A., Smith, P., Melillo, J.M., Dentener, F. & Crutzen, P.J.

2012a. Global agriculture and nitrous oxide emissions. *Nature Climate Change*, **2**, 410–416.

Reay, D.S., Davidson, E.A., Smith, K.A., Smith, P., Melillo, J.M., Dentener, F. & Crutzen, P.J. 2012b. Global agriculture and nitrous oxide emissions. *Nature Climate Change*, **2**, 410.

Red Tractor Assurance. 2015. Red Tractor Assurance Standards. *www.Redtractor.Org.Uk*.

Reganold, J.P. & Wachter, J.M. 2016. Organic agriculture in the twenty-first century. *Nature Plants 2*, **2**, 15221.

Research Rothamsted. 2006. *Guide to the Classical and other long-term experiments, datasets and sample archive. Lawes Agricultural Trust Co. Ltd, Harpenden, UK.*

Robertson, A.D., Davies, C.A., Smith, P., Dondini, M. & Mcnamara, N.P. 2015. Modelling the carbon cycle of Miscanthus plantations: Existing models and the potential for their improvement. *GCB Bioenergy*.

Romig, D.E., Garlynd, M.J. & Harris, R.F. 2015. Farmer-Based Assessment of Soil Quality: A Soil Health Scorecard.

Ross, C.W., Grunwald, S. & Myers, D.B. 2013. Spatiotemporal modeling of soil organic carbon stocks across a subtropical region. *Science of the Total Environment*, **461**–**462**, 149–157.

Rumpel, C., Crème, A., Ngo, P.T., Velásquez, G., Mora, M.L. & Chabbi, A. 2015. The impact of grassland management on biogeochemical cycles involving carbon, nitrogen and phosphorus. *Journal of Soil Science and Plant Nutrition*.

Rumpel, C. & Kögel-Knabner, I. 2010. Deep soil organic matter—a key but poorly understood component of terrestrial C cycle. *Plant and Soil*, **338**, 143–158.

Sainju, U.M., Singh, B.P., Whitehead, W.F. & Wang, S. 2006. Carbon Supply and Storage in Tilled and Nontilled Soils as Influenced by Cover Crops and Nitrogen Fertilization. *Journal of Environmental Quality*.

Sandén, T., Spiegel, H., Stüger, H.P., Schlatter, N., Haslmayr, H.P., Zavattaro, L., Grignani, C., Bechini, L., D′Hose, T., Molendijk, L., Pecio, A., Jarosz, Z., Guzmán, G., Vanderlinden, K., Giráldez, J. V., Mallast, J. & ten Berge, H. 2018. European long-term field experiments: knowledge gained about alternative management practices. *Soil Use and Management*.

Sanderman, J., Hengl, T. & Fiske, G.J. 2017. Soil carbon debt of 12,000 years of human land use. *Proceedings of the National Academy of Sciences of the United States of America*.

Sansoulet, J., Pattey, E., Kröbel, R., Grant, B., Smith, W., Jégo, G., Desjardins, R.L., Tremblay, N. & Tremblay, G. 2014. Comparing the performance of the STICS, DNDC, and DayCent models for predicting N uptake and biomass of spring wheat in Eastern Canada. *Field Crops Research*.

Saxton, K.E. & Rawls, W.J. 2006. Soil Water Characteristic Estimates by Texture and Organic Matter for Hydrologic Solutions. *Soil Science Society of America Journal*.

Schellekens, J., Barberá, G.G., Buurman, P., Pérez-Jordà, G. & Martínez-Cortizas, A. 2013. Soil organic matter dynamics in Mediterranean A-horizons - The use of analytical pyrolysis to ascertain land-use history. *Journal of Analytical and Applied Pyrolysis*.

Schiedung, M., Don, A., Wordell-Dietrich, P., Alcántara, V., Kuner, P. & Guggenberger, G. 2017. Thermal oxidation does not fractionate soil organic carbon with differing biological stabilities. *J. Plant Nutr. Soil Sci.*, **180**, 18–26.

Schimel, D.S. 1995. Terrestrial ecosystems and the carbon cycle. *Global Change Biology*, **1**, 77–91.

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

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.

Scialabba, N.E.H. & Müller-Lindenlauf, M. 2010. Organic agriculture and climate change. *Renewable Agriculture and Food Systems*, **25**, 158–169.

Senapati, N., Chabbi, A., Giostri, A.F., Yeluripati, J.B. & Smith, P. 2016. Modelling nitrous oxide emissions from mown-grass and grain-cropping systems: Testing and sensitivity analysis of DailyDayCent using high frequency measurements. *Science of the Total Environment*.

Seufert, V. & Ramankutty, N. 2017. Many shades of gray—The context-dependent performance of organic agriculture. *Science Advances*, **3**.

Seufert, V., Ramankutty, N. & Foley, J.A. 2012. Comparing the yields of organic and conventional agriculture. *Nature*, **485**, 229.

Singh, K. & Whelan, B. 2020. Soil carbon change across ten New South Wales farms under different farm management regimes in Australia. *Soil Use and Management*, **n/a**.

Six, J., Callewaert, P., Lenders, S., De Gryze, S., Morris, S.J., Gregorich, E.G., Paul, E.A. & Paustian, K. 2010. Measuring and Understanding Carbon Storage in Afforested Soils by Physical Fractionation. *Soil Science Society of America Journal*, **66**, 1981.

Six, J., Conant, R.T., Paul, E.A. & Paustian, K. 2002a. Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. *Plant and Soil*, **241**, 155–176, (At: https://doi.org/10.1023/A:1016125726789.).

Six, J., Elliott, E.T. & Paustian, K. 1999. Aggregate and Soil Organic Matter Dynamics under Conventional and No-Tillage Systems. *Soil Science Society of America Journal*, **63**, 1350–1358.

Six, J., Elliott, E.T., Paustian, K. & Doran, J.W. 1998. Aggregation and Soil Organic Matter Accumulation in Cultivated and Native Grassland Soils. *Soil Science Society of America Journal*, **62**, 1367.

Six, J., Feller, C., Denef, K., Ogle, S.M., de Moraes, J.C. & Albrecht, A. 2002b. Soil organic matter, biota and aggregation in temperate and tropical soils - Effects of no-tillage. *Agronomie*, **22**, 755–775.

Six, J., Ogle, S.M., Breidt, F.J., Conant, R.T., Mosiers, A.R. & Paustian, K. 2004. The potential to mitigate global warming with no-tillage management is only realized when practised in the long term. *Global Change Biology*.

Skinner, C., Gattinger, A., Muller, A., Mader, P., Fliebach, A., Stolze, M., Ruser, R. & Niggli, U. 2014. Greenhouse gas fluxes from agricultural soils under organic and non-organic management - A global meta-analysis. *Science of the Total Environment*.

Smith, P. 2008. Land use change and soil organic carbon dynamics. *Nutrient Cycling in Agroecosystems*, **81**, 169–178.

Smith, P., Davies, C.A., Ogle, S., Zanchi, G., Bellarby, J., Bird, N., Boddey, R.M., McNamara, N.P., Powlson, D., Cowie, A., Noordwijk, M., Davis, S.C., Richter, D.D.E.B., Kryzanowski, L., Wijk, M.T., Stuart, J., Kirton, A., Eggar, D., Newton-Cross, G., Adhya, T.K. & Braimoh, A.K. 2012a. Towards an integrated global framework to assess the impacts of land use and management change on soil carbon: current capability and future vision. *Global Change Biology*, **18**, 2089–2101.

Smith, J., Gottschalk, P., Bellarby, J., Chapman, S., Lilly, A., Towers, W., Bell, J., Coleman, K., Nayak, D., Richards, M., Hillier, J., Flynn, H., Wattenbach, M., Aitkenhead, M., Yeluripati, J., Farmer, J., Milne, R., Thomson, A., Evans, C., Whitmore, A., Falloon, P. & Smith, P. 2010. Estimating changes in Scottish soil carbon stocks using ecosse. I. Model description and uncertainties. *Climate Research*.

Smith, W.N., Grant, B.B., Campbell, C.A., McConkey, B.G., Desjardins, R.L., Kröbel, R. & Malhi, S.S. 2012b. Crop residue removal effects on soil carbon: Measured and inter-model comparisons. *Agriculture, Ecosystems and Environment*.

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. *Global Change Biology*, **22**, 1008–1028.

Smith, L.G., Kirk, G.J.D., Jones, P.J. & Williams, A.G. 2019. The greenhouse gas impacts of converting food production in England and Wales to organic methods. *Nature Communications*.

Smith, P., Martino, D., Cai, Z., Gwary, D., Janzen, H., Kumar, P., McCarl, B., Ogle, S., O'Mara, F., Rice, C., Scholes, B. & Sirotenko, O. 2007. *Agriculture. In Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [B. Metz, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds)]*. Cambridge, United Kingdom and New York, NY, USA.

Smith, P., Martino, D., Cai, Z., Gwary, D., Janzen, H., Kumar, P., McCarl, B., Ogle, S., O'Mara, F., Rice, C., Scholes, B., Sirotenko, O., Howden, M., McAllister, T., Pan, G., Romanenkov, V., Schneider, U., Towprayoon, S., Wattenbach, M. & Smith, J. 2008. Greenhouse gas mitigation in agriculture. *Philosophical Transactions of the Royal Society B: Biological Sciences*, **363**, 789–813.

Smith, J. & Smith, P. 2007. *Environmental Modelling. An Introduction.* Oxford University Press, New York, USA.

Smith, P., Smith, J.U., Powlson, D.S., Mcgill, W.B., Arah, J.R.M., Chertvoc, O.G., Coleman, K., Franko, U., Frolking, S., Jenkinson, D.S., Jensen, L.S., Kelly, R.H., Klein-Gunnewiek, H., Komarov, A.S., Li, C., Molina, J.A.E., Mueller, T., Parton, W.J., Thornley, J.H.M. &

Whitmore, A.P. 1997. A comparison of the performance of nine soil organic matter models using datasets from seven long-term experiments. *Geoderma*, **81**, 153–225.

Smith, P., Soussana, J.F., Angers, D., Schipper, L., Chenu, C., Rasse, D.P., Batjes, N.H., van Egmond, F., McNeill, S., Kuhnert, M., Arias-Navarro, C., Olesen, J.E., Chirinda, N., Fornara, D., Wollenberg, E., Álvaro-Fuentes, J., Sanz-Cobena, A. & Klumpp, K. 2020. How to measure, report and verify soil carbon change to realize the potential of soil carbon sequestration for atmospheric greenhouse gas removal. *Global Change Biology*.

Soil Association. 2019. *Soil Association Standards Farming and Growing*.

Sollins, P., Homann, P. & Caldwell, B.A. 1996. Stabilization and destabilization of soil organic matter: Mechanisms and controls. *Geoderma*.

Sposito, G., Skipper, N.T., Sutton, R., Park, S., Soper, A.K. & Greathouse, J.A. 1999. Surface geochemistry of the clay minerals. *Proceedings of the National Academy of Sciences*, **96**, 3358 LP – 3364.

Stavi, I. & Lal, R. 2012. Agriculture and greenhouse gases, a common tragedy. A review. *Agronomy for Sustainable Development*, **33**, 275–289.

Stoate, C., Boatman, N.D., Borralho, R.J., Carvalho, C.R., De Snoo, G.R. & Eden, P. 2001. Ecological impacts of arable intensification in Europe. *Journal of Environmental Management*, **63**, 337–365.

Stockdale, E.A., Shepherd, M.A., Fortune, S. & Cuttle, S.P. 2006. Soil fertility in organic farming systems - fundamentally different? *Soil Use and Management*, **18**, 301–308.

Stolbovoy, V., Montanarella, L., Filippi, N., Jones, A., Gallego, J. & Grassi, G. 2007. *Soil sampling protocol to certify the changes of organic carbon stock in mineral soil of the European Union.* Version 2. Office for Official Publications of the European Communities, Luxembourg.

Stott, D.E., Karlen, D.L., Cambardella, C.A. & Harmel, R.D. 2013. A Soil Quality and Metabolic Activity Assessment after Fifty-Seven Years of Agricultural Management. *Soil Science Society of America Journal*.

Strezov, V., Moghtaderi, B. & Lucas, J.A. 2004. Computational calorimetric investigation of the reactions during thermal conversion of wood biomass. *Biomass and Bioenergy*.

Suter, M., Connolly, J., Finn, J.A., Loges, R., Kirwan, L., Sebastià, M.-T. & Lüscher, A. 2015. Nitrogen yield advantage from grass–legume mixtures is robust over a wide range of legume proportions and environmental conditions. *Global Change Biology*, **21**, 2424–2438.

Sykes, A.J., Macleod, M., Eory, V., Rees, R.M., Payen, F., Myrgiotis, V., Williams, M., Sohi, S., Hillier, J., Moran, D., Manning, D.A.C., Goglio, P., Seghetta, M., Williams, A., Harris, J., Dondini, M., Walton, J., House, J. & Smith, P. 2020. Characterising the biophysical, economic and social impacts of soil carbon sequestration as a greenhouse gas removal technology. *Global Change Biology*.

Syswerda, S.P., Corbin, A.T., Mokma, D.L., Kravchenko, A.N. & Robertson, G.P. 2011. Agricultural Management and Soil Carbon Storage in Surface vs. Deep Layers. *Soil Science Society of America Journal*, **75**, 92–101.

Taghizadeh-Mehrjardi, R., Nabiollahi, K. & Kerry, R. 2016. Digital mapping of soil organic carbon at multiple depths using different data mining techniques in Baneh region, Iran. *Geoderma*.

Takata, Y., Funakawa, S., Akshalov, K., Ishida, N. & Kosaki, T. 2007. Spatial prediction of soil organic matter in northern Kazakhstan based on topographic and vegetation information. *Soil Science and Plant Nutrition*.

Tautges, N.E., Chiartas, J.L., Gaudin, A.C.M., O'Geen, A.T., Herrera, I. & Scow, K.M. 2019. Deep soil inventories reveal that impacts of cover crops and compost on soil carbon sequestration differ in surface and subsurface soils. *Global Change Biology*.

Taylor, J.A., McBratney, A.B. & Whelan, B.M. 2007. Establishing Management Classes for Broadacre Agricultural Production. *Agronomy Journal*, **99**, 1366–1376.

Tegelaar, E.W., Hollman, G., Van Der Vegt, P., De Leeuw, J.W. & Holloway, P.J. 1995. Chemical characterization of the periderm tissue of some angiosperm species: recognition of an insoluble, non-hydrolyzable, aliphatic biomacromolecule (Suberan). *Organic Geochemistry*.

Thompson, J.A., Pena-Yewtukhiw, E.M. & Grove, J.H. 2006. Soil–landscape modeling across a physiographic region: Topographic patterns and model transportability. *Geoderma*, **133**, 57–70.

Tian, G., Kang, B.T. & Brussaard, L. 1992. Biological effects of plant residues with contrasting chemical compositions under humid tropical conditions-Decomposition and nutrient release. *Soil Biology and Biochemistry*.

Tilman, D. 1999. Global environmental impacts of agricultural expansion: The need for sustainable and efficient practices. *Proceedings of the National Academy of Sciences of the United States of America*.

Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R. & Polasky, S. 2002. Agricultural sustainability and intensive production practices. *Nature*.

Tipping, E., Davies, J.A.C., Henrys, P.A., Kirk, G.J.D., Lilly, A., Dragosits, U., Carnell, E.J., Dore, A.J., Sutton, M.A. & Tomlinson, S.J. 2017. Long-term increases in soil carbon due to ecosystem fertilization by atmospheric nitrogen deposition demonstrated by regional-scale modelling and observations. *Scientific Reports*.

Tipping, E., Rowe, E.C., Evans, C.D., Mills, R.T.E., Emmett, B.A., Chaplow, J.S. & Hall, J.R. 2012. N14C: A plant–soil nitrogen and carbon cycling model to simulate terrestrial ecosystem responses to atmospheric nitrogen deposition. *Ecological Modelling*, **247**, 11–26.

Tisdall, J.M. & Oades, J.M. 1982. Organic matter and water-stable aggregates in soils. *Journal of Soil Science*, **33**, 141–163.

Tokarski, D., Šimečková, J., Kučerík, J., Kalbitz, K., Demyan, M.S., Merbach, I., Barkusky, D., Ruehlmann, J. & Siewert, C. 2019. Detectability of degradable organic matter in agricultural soils by thermogravimetry. *Journal of Plant Nutrition and Soil Science*.

Tracy, B.F. & Zhang, Y. 2008. Soil Compaction, Corn Yield Response, and Soil Nutrient Pool Dynamics within an Integrated Crop-Livestock System in Illinois. *Crop Science*, **48**, 1211–1218.

Trewavas, A. 2001. Urban myths of organic farming. *Nature*, **410**, 409–410.

Triberti, L., Nastri, A. & Baldoni, G. 2016. Long-term effects of crop rotation, manure and mineral fertilisation on carbon sequestration and soil fertility. *European Journal of Agronomy*, **74**, 47–55.

Trumbore, S.E. 1997. Potential responses of soil organic carbon to global environmental change. *Proceedings of the National Academy of Sciences of the United States of America*.

Trumbore, S. 2006. Carbon respired by terrestrial ecosystems - Recent progress and challenges. *Global Change Biology*.

Trumper, K., Bertzky, M., Dickson, B., van der Heijden, G., Jenkins, M. & Manning, P. 2009. *The Natural Fix? The Role of Ecosystems in Climate Mitigation*.

Tsiafouli, M.A., Thébault, E., Sgardelis, S.P., de Ruiter, P.C., van der Putten, W.H., Birkhofer, K., Hemerik, L., de Vries, F.T., Bardgett, R.D., Brady, M.V., Bjornlund, L., Jørgensen, H.B., Christensen, S., Hertefeldt, T.D., Hotes, S., Gera Hol, W.H., Frouz, J., Liiri, M., Mortimer, S.R., Setälä, H., Tzanopoulos, J., Uteseny, K., Pižl, V., Stary, J., Wolters, V. & Hedlund, K. 2015. Intensive agriculture reduces soil biodiversity across Europe. *Global Change Biology*, **21**, 973–985.

Tuomisto, H.L., Hodge, I.D., Riordan, P. & Macdonald, D.W. 2012. Does organic farming reduce environmental impacts?--a meta-analysis of European research. *J Environ Manage*, **112**, 309–320.

Vane, C.H., Martin, S.C., Snape, C.E. & Abbott, G.D. 2001. Degradation of lignin in wheat straw during growth of the oyster mushroom (Pleurotus ostreatus) using off-line thermochemolysis with tetramethylammonium hydroxide and solid-state 13C NMR. *Journal of Agricultural and Food Chemistry*.

Vasques, G.M., Grunwald, S., Comerford, N.B. & Sickman, J.O. 2010. Regional modelling of soil carbon at multiple depths within a subtropical watershed. *Geoderma*, **156**, 326–336.

Wander, M.M. & Drinkwater, L.E. 2000. Fostering soil stewardship through soil quality assessment. *Applied Soil Ecology*, **15**, 61–73.

Wang, B., Waters, C., Orgill, S., Cowie, A., Clark, A., Li Liu, D., Simpson, M., McGowen, I. & Sides, T. 2018. Estimating soil organic carbon stocks using different modelling techniques in the semi-arid rangelands of eastern Australia. *Ecological Indicators*, **88**, 425–438.

Watts, C.W., Whalley, W.R., Longstaff, D.J., White, R.P., Brook, P.C. & Whitmore, A.P. 2006. Aggregation of a soil with different cropping histories following the addition of organic materials. *Soil Use and Management*.

Wendt, J.W. & Hauser, S. 2013. An equivalent soil mass procedure for monitoring soil organic carbon in multiple soil layers. *European Journal of Soil Science*, **64**, 58–65.

Were, K., Bui, D.T., Dick, Ø.B. & Singh, B.R. 2015. A comparative assessment of support vector regression, artificial neural networks, and random forests for predicting and mapping soil organic carbon stocks across an Afromontane landscape. *Ecological Indicators*, **52**, 394–403.

West, A.W. & Sparling, G.P. 1986. Modifications to the substrate-induced respiration method to permit measurement of microbial biomass in soils of differing water contents. *Journal* *of Microbiological Methods*, **5**, 177–189.

Whalen, J.K. & Chang, C. 2002. Macroaggregate Characteristics in Cultivated Soils after 25 Annual Manure Applications. *Soil Science Society of America Journal*.

Whitehead, D., Baisden, T., Beare, M., Campbell, D., Curtin, D., Davis, M., Hedley, C., Hedley, M., Jones, H., Kelliher, F., Saggar, S. & Shipper, L. 2012. Review of soil carbon measurement methodologies and technologies, including nature and intensity of sampling, their uncertainties and costs. *Ministry for Primary Industries, Technical Paper by Landcare Research No. 2012/36. ISBN No: 978-0- 478-40450-0 (online)*.

Wickham, H. 2009. ggplot2: Elegant Graphics for Data Analysis. *Springer-Verlag New York. R package version 2.2.1*.

Wickham, H. 2011. The Split-Apply-Combine Strategy for Data Analysis. *Journal of Statistical Software, 40(1), 1-29.*

Wieder, W.R., Bonan, G.B. & Allison, S.D. 2013. Global soil carbon projections are improved by modelling microbial processes. *Nature Climate Change*.

Wienhold, B.J., Karlen, D.L., Andrews, S.S. & Stott, D.E. 2009. Protocol for indicator scoring in the soil management assessment framework (SMAF). *Renewable Agriculture and Food Systems*, **24**, 260–266.

Willer, H., Schlatter, B., Trávníček, J., Kemper, L. & Lernoud, J. 2020. *The World of Organic Agriculture. Statistics and Emerging Trends 2020*.

WRB. 2015. *World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Rome*.

Yang, R.M., Zhang, G.L., Liu, F., Lu, Y.Y., Yang, F., Yang, F., Yang, M., Zhao, Y.G. & Li, D.C. 2016. Comparison of boosted regression tree and random forest models for mapping topsoil organic carbon concentration in an alpine ecosystem. *Ecological Indicators*, **60**, 870–878.

Yue, Q., Cheng, K., Ogle, S., Hillier, J., Smith, P., Abdalla, M., Ledo, A., Sun, J. & Pan, G. 2019. Evaluation of four modelling approaches to estimate nitrous oxide emissions in China's cropland. *Science of the Total Environment*.

Zak, D.R., Pregitzer, K.S., King, J.S. & Holmes, W.E. 2000. Elevated atmospheric CO2, fine roots and the response of soil microorganisms: A review and hypothesis. *New Phytologist*.

Zani, C.F., Barneze, A.S., Robertson, A.D., Keith, A.M., Cerri, C.E.P., McNamara, N.P. & Cerri, C.C. 2018. Vinasse application and cessation of burning in sugarcane management can have positive impact on soil carbon stocks. *PeerJ*, **6**, e5398.

Zani, C.F., Gowing, J., Abbott, G.D., Taylor, J.A., Lopez-Capel, E. & Cooper, J. 2020. Grazed temporary grass-clover leys in crop rotations can have a positive impact on soil quality under both conventional and organic agricultural systems. *European Journal of Soil Science*, 1–17.

Zhang, G., Liu, F. & Song, X. 2017. Recent progress and future prospect of digital soil mapping: A review. *Journal of Integrative Agriculture*, **16**, 2871–2885.

Zhou, G., Xu, S., Ciais, P., Manzoni, S., Fang, J., Yu, G., Tang, X., Zhou, P., Wang, W., Yan, J., Wang, G., Ma, K., Li, S., Du, S., Han, S., Ma, Y., Zhang, D., Liu, J., Liu, S., Chu, G., Zhang, Q., Li, Y., Huang, W., Ren, H., Lu, X. & Chen, X. 2019. Climate and litter C/N ratio constrain soil organic carbon accumulation. *National Science Review*, **6**, 746–757.

Zimmermann, M., Leifeld, J., Schmidt, M.W.I., Smith, P. & Fuhrer, J. 2007. Measured soil organic matter fractions can be related to pools in the RothC model. *European Journal of Soil Science*.

Zornoza, R., Acosta, J.A., Bastida, F., Domínguez, S.G., Toledo, D.M. & Faz, A. 2015. Identification of sensitive indicators to assess the interrelationship between soil quality, management practices and human health. *SOIL*.

Appendix 1

Table A1.1. Soil textural properties for each sampled point across Nafferton farm at 0-0.15, 0-15-0.30 and 0.30-0.60 m soil depth intervals.

Coordinates	0-0.15 m			0.15-0.30 m			0.30-0.60 m		
	Clay	Silt	Sand	Clay	Silt	Sand	Clay	Silt	Sand
WGS 84 datum	%								
54°59'23.5"N 1°55'00.1"W	12.64	49.37	37.99	14.17	48.68	37.15	19.98	34.97	45.05
54°59'21.7"N 1°55'06.9"W	14.01	49.62	36.37	11.63	45.27	43.1	19.05	47.2	33.75
54°59'20.3"N 1°55'10.6"W	11.02	46.37	42.61	14.42	46.6	38.98	20.6	33.01	46.39
54°59'21.3"N 1°55'13.4"W	14.85	48.96	36.19	20.34	41.39	38.27	22.78	44.46	32.76
54°59'18.9"N 1°54'56.9"W	9.16	43.66	47.18	9.67	41.96	48.37	20.47	41.42	38.11
54°59'22.1"N 1°54'57.3"W	19.45	50.77	29.78	23.01	53.12	23.87	25.87	44.3	29.83
54°59'22.9"N 1°54'50.3"W	12.7	47.35	39.95	19.36	46.22	34.42	20.93	31.66	47.41
54°59'23.4"N 1°54'53.4"W	18.89	51.64	29.47	19.15	49.49	31.36	24.5	43.53	31.97
54°59'19.3"N 1°55'07.0"W	10.78	45.21	44.01	11.63	46.3	42.07	14.4	37.2	48.4
54°59'18.3"N 1°55'06.7"W	13.05	45.95	41	12.46	37.43	50.11	17.27	28.2	54.53
54°59'16.1"N 1°55'09.0"W	9.54	43.44	47.02	9.76	40.98	49.26	17.91	36.74	45.35
54°59'19.3"N 1°55'01.1"W	13	47.76	39.24	14.05	46.57	39.38	19.48	34.95	45.57
54°59'15.9"N 1°54'55.6"W	1.97	15.46	82.57	5.98	30.63	63.39	11.44	42.26	46.3
54°59'14.8"N 1°55'02.4"W	1.5	12.65	85.85	6.4	30.14	63.46	9.57	34.38	56.05
54°59'13.8"N 1°55'05.3"W	3.42	23.18	73.4	4.88	29.09	66.03	7.24	31.25	61.51
54°59'23.5"N 1°54'15.5"W	14.62	48.68	36.7	15.03	46.9	38.07	19.37	43.99	36.64
54°59'27.8"N 1°54'21.7"W	16.89	52.84	30.27	16.3	50.49	33.21	16.83	41.34	41.83
54°59'37.4"N 1°54'13.3"W	13.82	51.73	34.45	16.31	52.01	31.68	18.67	38.63	42.7
54°59'25.6"N 1°54'13.3"W	15.02	47.79	37.19	17.01	41.68	41.31	27.76	42.7	29.54
54°59'25.7"N 1°54'19.0"W	15.66	48.89	35.45	19.3	50.26	30.44	22.09	41.02	36.89
54°59'29.8"N 1°54'14.9"W	14.31	48.46	37.23	13.98	44.49	41.53	23.29	43.17	33.54
54°59'26.1"N 1°54'23.0"W	16.58	52.17	31.25	15.15	48.58	36.27	22.76	42.01	35.23
54°59'24.9"N 1°54'10.6"W	19.09	50.22	30.69	17.85	45.62	36.53	20.55	33.66	45.79
54°59'30.2"N 1°54'19.7"W	12.62	46.62	40.76	13.44	42.07	44.49	20.83	39.37	39.8
54°59'36.8"N 1°54'18.4"W	15.4	54.01	30.59	14.31	43.08	42.61	18.51	34.98	46.51
54°59'34.9"N 1°54'24.4"W	12.4	48.41	39.19	18.64	47.16	34.2	20.53	33.59	45.88
54°59'33.3"N 1°54'18.5"W	18.3	50.43	31.27	19.08	51.23	29.69	25.73	40.5	33.77
54°59'29.6"N 1°54'09.6"W	9.27	43.11	47.62	11.17	40.04	48.79	9.03	31.83	59.14
54°59'26.9"N 1°54'09.1"W	14.82	49.11	36.07	16.7	49.39	33.91	24.42	40.29	35.29
54°59'31.2"N 1°54'08.4"W	8.47	38.3	53.23	12.06	42.94	45	18.18	29.52	52.3
54°59'17.5"N 1°54'07.1"W	11.14	40.49	48.37	10.84	41.37	47.79	21.16	42.09	36.75
54°59'18.0"N 1°54'09.1"W	10.96	41.09	47.95	13.9	41.79	44.31	19.02	34.38	46.6
54°59'16.1"N 1°54'13.9"W	12	40.95	47.05	17.51	47.38	35.11	22.86	41.9	35.24
54°59'14.2"N 1°54'19.3"W	11.82	41.57	46.61	15.5	50.22	34.28	19.92	38.04	42.04
54°59'17.3"N 1°54'18.4"W	13.58	43.47	42.95	11.49	41.92	46.59	18.56	40.9	40.54
54°59'19.0"N 1°54'27.3"W	5.8	30.39	63.81	9.76	38.55	51.69	9.18	32.6	58.22
54°59'21.9"N 1°54'08.9"W	14.21	43.33	42.46	15.07	45.59	39.34	19.7	39.68	40.62
54°59'13.1"N 1°54'23.8"W	8.9	35.41	55.69	10.19	37.64	52.17	14.27	39.37	46.36
54°59'19.9"N 1°54'21.9"W	8.2	32.59	59.21	13.08	39.84	47.08	13.89	32.6	53.51
54°59'20.0"N 1°54'12.7"W	10.92	38.58	50.5	15.36	40.48	44.16	21.26	40.91	37.83
54°59'16.9"N 1°54'25.4"W	12.01	40.81	47.18	16.01	45.3	38.69	24.23	47.51	28.26
54°59'14.4"N 1°54'26.6"W	8.85	34.8	56.35	10.89	39.52	49.59	17.89	41.98	40.13
54°59'09.9"N 1°54'25.6"W	12.5	43.99	43.51	13.62	40.04	46.34	16.21	31.04	52.75

54°59'10.9"N 1°54'17.7"W	9.63	37.8	52.57	14.7	47.5	37.8	21.7	40.62	37.68
54°59'09.7"N 1°54'20.0"W	12.44	46.7	40.86	17	49.58	33.42	22.3	41.66	36.04
54°59'09.3"N 1°54'15.2"W	12.14	44.46	43.4	22.37	73.2	4.43	19.86	43.35	36.79
54°59'09.8"N 1°54'12.1"W	10.1	45.94	43.96	12.7	44.2	43.1	21.42	43.1	35.48
54°59'08.7"N 1°54'24.5"W	17.12	52.02	30.86	16.86	43.27	39.87	19.89	42.95	37.16
54°59'11.6"N 1°54'14.9"W	13.05	44.39	42.56	15.93	38.01	46.06	18.88	42.02	39.1
54°59'07.4"N 1°54'19.5"W	14.85	48.21	36.94	16.41	44.19	39.4	23.06	44.33	32.61
54°59'04.0"N 1°54'24.4"W	12.28	40.76	46.96	21.12	57.3	21.58	13.56	35.52	50.92
54°59'04.0"N 1°54'26.9"W	11.1	38.34	50.56	13.57	43.72	42.71	18.52	44.28	37.2
54°59'02.8"N 1°54'29.1"W	10.69	38.94	50.37	12.46	41.65	45.89	16.51	43.53	39.96
54°59'02.0"N 1°54'26.1"W	10.48	37.79	51.73	12.9	42.63	44.47	15.49	39.84	44.67
54°58'56.8"N 1°54'23.7"W	8.91	35.06	56.03	13.16	42.07	44.77	17.01	37.53	45.46
54°58'54.6"N 1°54'22.1"W	12.57	45.36	42.07	20.54	51.42	28.04	20.1	44.92	34.98
54°58'55.7"N 1°54'18.1"W	11.16	40.1	48.74	13.2	42.55	44.25	16.69	38.81	44.5
54°58'56.4"N 1°54'15.0"W	8.85	36.69	54.46	13.37	42.96	43.67	21.74	42.61	35.65
54°59'00.3"N 1°54'26.7"W	10.8	38.61	50.59	15.59	43.46	40.95	20.73	39.9	39.37
54°58'58.8"N 1°54'18.6"W	8.28	34.42	57.3	15.3	46.8	37.9	20.94	43.37	35.69
54°59'03.4"N 1°54'06.4"W	8.91	36.55	54.54	10.31	37.75	51.94	16.62	39.83	43.55
54°59'00.5"N 1°54'01.7"W	8.42	36.67	54.91	13.12	40.25	46.63	15.22	46.84	37.94
54°58'59.8"N 1°54'05.0"W	11.64	41.5	46.86	13.96	44.44	41.6	16.01	40.04	43.95
54°58'58.2"N 1°54'07.8"W	7.75	31.38	60.87	13.63	36.68	49.69	23.28	42.93	33.79
54°59'01.3"N 1°54'11.5"W	11.41	41.89	46.7	13.4	39.89	46.71	20.71	43.34	35.95
54°59'01.8"N 1°54'07.2"W	8.04	36.67	55.29	12.68	46.6	40.72	21.62	42.66	35.72
54°59'01.9"N 1°54'14.0"W	11.12	42.02	46.86	12.29	41.3	46.41	18.09	35.55	46.36
54°59'04.1"N 1°54'13.7"W	10.93	43.56	45.51	18.76	48.04	33.2	25.43	44.79	29.78
54°59'03.8"N 1°54'15.9"W	12.42	43.65	43.93	13.23	40.47	46.3	22.21	42.87	34.92
54°59'05.4"N 1°54'12.8"W	10.33	38.43	51.24	12.98	45.57	41.45	22.79	42.12	35.09
54°58'57.9"N 1°53'45.1"W	17.19	49.17	33.64	19.17	50.31	30.52	20.62	34.53	44.85
54°59'00.5"N 1°53'31.8"W	11.69	49.36	38.95	13.06	47.44	39.5	25.66	41.07	33.27
54°59'03.3"N 1°53'22.2"W	11.75	47.81	40.44	14.54	48.25	37.21	21.81	40.11	38.08
54°59'11.3"N 1°53'49.0"W	12.35	42.67	44.98	14.32	42.96	42.72	20.61	39.36	40.03
54°59'13.2"N 1°53'38.8"W	8.3	37.33	54.37	14.83	43.16	42.01	22.16	42.06	35.78
54°59'06.8"N 1°53'51.6"W	12.12	43.01	44.87	13.91	48.8	37.29	16.76	35.16	48.08
54°59'10.5"N 1°53'41.7"W	11.46	42.75	45.79	13.66	50.22	36.12	22.13	43.27	34.6
54°59'08.6"N 1°53'48.5"W	7.91	29.67	62.42	13.84	43.53	42.63	22.7	41.87	35.43
54°59'12.0"N 1°53'52.1"W	5.8	25.04	69.16	13.74	45.61	40.65	20.19	38.3	41.51
54°59'08.6"N 1°53'37.5"W	12.47	40.38	47.15	13.04	43.89	43.07	22.4	44.89	32.71
54°59'06.1"N 1°53'45.8"W	11.92	43.51	44.57	16.23	51.36	32.41	17.25	33.03	49.72
54°59'09.4"N 1°53'46.0"W	12.53	43.48	43.99	16.55	45.13	38.32	21.17	44.57	34.26
54°59'13.6"N 1°53'44.4"W	9.46	37.8	52.74	13.84	37.85	48.31	19.46	41.58	38.96
54°59'09.9"N 1°53'51.3"W	11.24	42.72	46.04	10.95	38.29	50.76	21.8	44.3	33.9
54°59'10.6"N 1°53'54.9"W	8.97	35.94	55.09	15.32	51.14	33.54	19.03	43.24	37.73
54°59'07.0"N 1°53'39.0"W	13.54	41.93	44.53	15.82	46.93	37.25	21.32	43.02	35.66
54°59'02.6"N 1°53'47.5"W	13.38	44.54	42.08	16.44	49.1	34.46	20.64	44.6	34.76
54°59'04.3"N 1°53'41.9"W	15.54	46.18	38.28	14.41	47.57	38.02	21.96	42.15	35.89
54°59'14.6"N 1°53'29.4"W	11.24	41.93	46.83	13.71	45.66	40.63	19.12	42.2	38.68
54°59'06.3"N 1°53'25.5"W	13.03	43.63	43.34	10.73	39.82	49.45	18.08	42.68	39.24
54°59'13.9"N 1°53'27.2"W	13.43	39.8	46.77	15.17	42.54	42.29	24.77	37.54	37.69
54°59'09.3"N 1°53'26.2"W	11.18	40.09	48.73	10.68	38.83	50.49	17.77	36.54	45.69
54°59'10.7"N 1°53'29.0"W	11.96	40.78	47.26	11.52	35.53	52.95	17.84	37	45.16
54°59'07.5"N 1°53'24.9"W	11.83	42.09	46.08	11.65	41.84	46.51	19.42	46.98	33.6
54°59'07.9"N 1°53'23.5"W	11.44	41.9	46.66	14.34	46.66	39	15.71	46.05	38.24
54°59'10.6"N 1°53'27.1"W	12.56	42.74	44.7	11.59	42.95	45.46	17.45	39.08	43.47
54°59'12.5"N 1°53'21.7"W	11.28	37.5	51.22	11.8	40.54	47.66	16.17	36	47.83
54°59'13.3"N 1°53'19.1"W	12.26	40.14	47.6	13.36	38.68	47.96	24.9	40.04	35.06
54°59'13.5"N 1°53'24.7"W	6.76	30.47	62.77	11.19	36.66	52.15	14.98	34.83	50.19
54°59'11.6"N 1°53'20.6"W	10.35	34.67	54.98	10.59	38.1	51.31	15.97	38.75	45.28

54°59'14.3"N 1°53'23.6"W	9.48	37.74	52.78	13.44	44.62	41.94	14.75	31.59	53.66
54°59'10.1"N 1°53'19.2"W	14.36	45.49	40.15	12.93	43.07	44	23.06	44.58	32.36
54°59'10.6"N 1°53'22.6"W	9.24	36.14	54.62	13.56	42.94	43.5	17.47	38.3	44.23
54°59'08.0"N 1°53'20.7"W	15.65	48.83	35.52	15.6	46.92	37.48	16.91	43.79	39.3
54°59'34.3"N 1°53'30.9"W	15.32	48.91	35.77	17.33	51.14	31.53	16.23	39.46	44.31
54°59'25.7"N 1°53'26.9"W	16.89	46.81	36.3	13.49	42.1	44.41	19.63	35.56	44.81
54°59'27.9"N 1°53'24.3"W	15.11	46.86	38.03	19.07	46.39	34.54	21.32	40.66	38.02
54°59'37.4"N 1°53'29.7"W	14.99	45.78	39.23	14.88	47.42	37.7	22.46	43.14	34.4
54°59'23.2"N 1°53'22.5"W	12.13	43.98	43.89	13.92	46.36	39.72	18.18	36.84	44.98
54°59'31.7"N 1°53'28.4"W	17.09	48.62	34.29	15.6	47.77	36.63	20.94	35.69	43.37
54°59'36.3"N 1°53'32.8"W	12.97	45.85	41.18	16.1	37.99	45.91	24.56	43.26	32.18
54°59'29.9"N 1°53'27.4"W	14.22	45.88	39.9	16.09	43.14	40.77	19.49	34.66	45.85
54°59'39.5"N 1°53'33.9"W	10.55	41.69	47.76	13.02	34.47	52.51	15.76	28.77	55.47
54°59'35.1"N 1°53'25.8"W	19.59	47.58	32.83	14.32	49.15	36.53	18.38	40.97	40.65
54°59'28.4"N 1°53'40.6"W	18.02	50.5	31.48	15.84	43.59	40.57	18.5	43.08	38.42
54°59'32.1"N 1°53'42.2"W	19.38	50.53	30.09	16.12	51.75	32.13	22.45	38.06	39.49
54°59'36.5"N 1°53'42.7"W	11.16	46.88	41.96	13.01	48.87	38.12	21.52	41.93	36.55
54°59'34.7"N 1°53'38.6"W	14.12	44.82	41.06	13.88	42.9	43.22	21.08	33.3	45.62
54°59'26.3"N 1°53'37.3"W	11.96	44.96	43.08	12.46	45.83	41.71	17.45	38.84	43.71
54°59'25.2"N 1°53'32.0"W	15	43.75	41.25	12.61	36.05	51.34	18.58	37.28	44.14
54°59'28.8"N 1°53'35.3"W	12.03	42.36	45.61	15.48	49.73	34.79	18.16	38.14	43.7
54°59'37.0"N 1°53'39.0"W	12.37	43.09	44.54	9.85	40.66	49.49	15.88	37.05	47.07
54°59'40.1"N 1°53'44.3"W	11.32	47.29	41.39	13.75	47.91	38.34	15.43	33.51	51.06
54°59'32.6"N 1°53'38.3"W	16.41	46.16	37.43	12.69	43.9	43.41	21.09	39.3	39.61
54°59'19.4"N 1°54'01.4"W	9.44	43.77	46.79	12.23	46.72	41.05	19.03	37.92	43.05
54°59'20.0"N 1°53'56.9"W	12.25	47.66	40.09	14.1	40.39	45.51	22.08	37.56	40.36
54°59'22.6"N 1°53'55.4"W	10.01	42.9	47.09	14.08	48.71	37.21	24.63	43.08	32.29
54°59'23.1"N 1°53'47.5"W	11.94	43.64	44.42	11.89	41.73	46.38	18.92	44.58	36.5
54°59'24.2"N 1°53'42.4"W	8.76	38.14	53.1	11.62	44.6	43.78	21.38	39.25	39.37
54°59'22.3"N 1°53'25.6"W	12.37	44.7	42.93	12.96	44.56	42.48	23.79	47.71	28.5
54°59'20.5"N 1°53'21.4"W	7.1	29.99	62.91	10.24	35.92	53.84	12.89	32.3	54.81
54°59'19.3"N 1°53'16.7"W	12.32	41.63	46.05	17.98	46.99	35.03	26.44	41.29	32.27
54°59'13.2"N 1°53'58.5"W	11.9	49.56	38.54	15.45	48.08	36.47	20.73	35.32	43.95
54°59'14.2"N 1°54'01.3"W	12.93	49.83	37.24	17.57	39.33	43.1	23.05	42.34	34.61
54°59'15.2"N 1°54'01.3"W	10.11	44.96	44.93	13.12	44.16	42.72	18.48	37.3	44.22

Table A1.2. Crop grown history of the 12 study fields at Nafferton Farm over 10 years (2008-2017) indicating agricultural system (S) (conventional-CONV and organic-ORG), grazing regime (G) (non-grazed-NG and grazed-GG), and further details on tillage event proportion (TEP).

Field nº	S	G	TEP*	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
1	CONV	NG	80	W. Wheat	W. Wheat	W. Barley	W. Barley	W. OSR	W. Wheat	W. Wheat	W. Barley	W. Barley	W. OSR
2	CONV	NG	50	Ley	W. Barley	W. OSR	W. Wheat	W. Wheat	S. Barley	W. Barley	W. OSR	W. Wheat	W. Wheat
3	CONV	GG	30	W. Wheat	W. Wheat	W. Barley	Ley	Ley	Ley	Ley	Ley	Ley	Ley
4	CONV	GG	40	W. Barley	Ley	Ley	Ley	Ley	Ley	S. Barley	W. Wheat	S. Barley	S. Barley
5	CONV	GG	0	Ley	Ley	Ley	Ley	Ley	Ley	Ley	Ley	Ley	Ley
6	CONV	GG	30	Ley	Ley	Ley	W. Wheat	W. Wheat	W. Barley	Ley	Ley	Ley	Ley
7	ORG	GG	20	Ley	S. Wheat	S. Barley	Ley	Ley	Ley	Ley	Ley	Ley	Ley
8	ORG	GG	40	S. Beans	Ley	Ley	S. Wheat	Beans Dried	S. Barley	Ley	Ley	Ley	Ley
9	ORG	GG	30	S. Barley	Potatoes	Ley	Ley	Ley	Beans Dried	S. Barley	Ley	Ley	Ley
10	ORG	NG	70	S. Wheat	S. Barley	Ley	Ley	Ley	S. Wheat	Beans Dried	S. Barley	Beans Dried	Beans Dried
11	ORG	NG	50	S. Barley	Ley	Ley	Ley	S. Wheat	Beans Dried	S. Wheat	Beans Dried	S. Barley	S. Barley
12	ORG	GG	30	Ley	Ley	Ley	Ley	Ley	Ley	S. Barley	Beans Dried	S. Barley	Ley

* TEP is shown as % of years in which the field had activities that turned the soil over for at least 0.15 m depth prior sampling. Since conversion from conventional to the organic system across 50% of the farm area (i.e. from 2001 onwards), tillage practice was conducted using ploughing and disking practices to a maximum depth of 0.15 m at both sides of the farm.

Appendix 2

Table A2.1. Soil carbon (C) concentration of the individual fractions (particulate organic matter-POM > 53; heavy fraction-HF > 53 µm; silt and clay fraction-SC < 53 µm) and their recovery soil masses after physical fractionation analysis by each sample analysed and considering agricultural system (S) (conventional-CONV and organic-ORG), grazing regime (G) (non-grazed-NG and grazed-GG) and soil depth intervals, 0-0.15, 0.15-0.30 and 0.30-0.60 m.

Sample nº in the LAB	S	G	Depth m	Fraction	C %	Recovery soil mass in 20 g g
5	CONV	NG	0-0.15	POM (> 53 µm)	8.67	0.41
5	CONV	NG	0-0.15	HF (> 53 µm)	1.20	12.51
5	CONV	NG	0-0.15	SC (< 53 µm)	4.14	6.81
21	CONV	NG	0-0.15	POM (> 53 µm)	11.52	0.22
21	CONV	NG	0-0.15	HF (> 53 µm)	0.90	10.87
21	CONV	NG	0-0.15	SC (< 53 µm)	3.92	8.60
25	CONV	NG	0-0.15	POM (> 53 µm)	9.83	0.56
25	CONV	NG	0-0.15	HF (> 53 µm)	1.13	12.50
25	CONV	NG	0-0.15	SC (< 53 µm)	5.08	6.91
85	CONV	NG	0-0.15	POM (> 53 µm)	14.02	0.21
85	CONV	NG	0-0.15	HF (> 53 µm)	0.52	10.71
85	CONV	NG	0-0.15	SC (< 53 µm)	3.91	8.71
89	CONV	NG	0-0.15	POM (> 53 µm)	16.77	0.23
89	CONV	NG	0-0.15	HF (> 53 µm)	0.67	11.08
89	CONV	NG	0-0.15	SC (< 53 µm)	4.24	8.52
113	CONV	NG	0-0.15	POM (> 53 µm)	11.66	0.28
113	CONV	NG	0-0.15	HF (> 53 µm)	1.13	13.31
113	CONV	NG	0-0.15	SC (< 53 µm)	4.15	6.29
121	CONV	GG	0-0.15	POM (> 53 µm)	16.33	0.51
121	CONV	GG	0-0.15	HF (> 53 µm)	1.60	13.65
121	CONV	GG	0-0.15	SC (< 53 µm)	5.78	5.08
129	CONV	GG	0-0.15	POM (> 53 µm)	14.39	0.53
129	CONV	GG	0-0.15	HF (> 53 µm)	1.90	14.11
129	CONV	GG	0-0.15	SC (< 53 µm)	5.17	5.22

161	CONV	GG	0-0.15	POM (> 53 μm)	11.25	0.55
161	CONV	GG	0-0.15	HF (> 53 μm)	1.60	13.64
161	CONV	GG	0-0.15	SC (< 53 μm)	4.86	5.80
177	CONV	GG	0-0.15	POM (> 53 μm)	13.19	0.32
177	CONV	GG	0-0.15	HF (> 53 μm)	1.28	12.40
177	CONV	GG	0-0.15	SC (< 53 μm)	4.65	6.85
185	CONV	GG	0-0.15	POM (> 53 μm)	12.90	0.61
185	CONV	GG	0-0.15	HF (> 53 μm)	1.63	13.70
185	CONV	GG	0-0.15	SC (< 53 μm)	5.01	5.59
193	CONV	GG	0-0.15	POM (> 53 μm)	15.47	0.27
193	CONV	GG	0-0.15	HF (> 53 μm)	1.43	10.88
193	CONV	GG	0-0.15	SC (< 53 μm)	4.79	8.21
217	CONV	GG	0-0.15	POM (> 53 μm)	18.44	0.26
217	CONV	GG	0-0.15	HF (> 53 μm)	2.60	14.51
217	CONV	GG	0-0.15	SC (< 53 μm)	5.42	5.04
221	CONV	GG	0-0.15	POM (> 53 μm)	13.78	0.71
221	CONV	GG	0-0.15	HF (> 53 μm)	2.70	11.18
221	CONV	GG	0-0.15	SC (< 53 μm)	4.70	7.91
225	CONV	GG	0-0.15	POM (> 53 μm)	12.74	0.54
225	CONV	GG	0-0.15	HF (> 53 μm)	1.55	13.61
225	CONV	GG	0-0.15	SC (< 53 μm)	4.92	5.90
245	CONV	GG	0-0.15	POM (> 53 μm)	12.60	0.52
245	CONV	GG	0-0.15	HF (> 53 μm)	1.60	12.96
245	CONV	GG	0-0.15	SC (< 53 μm)	4.94	6.22
261	CONV	GG	0-0.15	POM (> 53 μm)	12.23	0.53
261	CONV	GG	0-0.15	HF (> 53 μm)	1.74	13.41
261	CONV	GG	0-0.15	SC (< 53 μm)	4.86	5.95
273	CONV	GG	0-0.15	POM (> 53 μm)	14.61	0.71
273	CONV	GG	0-0.15	HF (> 53 μm)	1.72	13.28
273	CONV	GG	0-0.15	SC (< 53 μm)	4.88	5.94
325	ORG	GG	0-0.15	POM (> 53 μm)	13.02	0.81
325	ORG	GG	0-0.15	HF (> 53 μm)	1.59	13.51
325	ORG	GG	0-0.15	SC (< 53 μm)	5.15	5.56
333	ORG	GG	0-0.15	POM (> 53 μm)	10.95	0.81
333	ORG	GG	0-0.15	HF (> 53 μm)	1.69	13.22

333	ORG	GG	0-0.15	SC (< 53 µm)	4.79	5.68
349	ORG	GG	0-0.15	POM (> 53 µm)	13.74	0.62
349	ORG	GG	0-0.15	HF (> 53 µm)	1.49	13.15
349	ORG	GG	0-0.15	SC (< 53 µm)	4.86	6.05
357	ORG	GG	0-0.15	POM (> 53 µm)	9.85	0.46
357	ORG	GG	0-0.15	HF (> 53 µm)	1.56	14.80
357	ORG	GG	0-0.15	SC (< 53 µm)	4.59	4.55
365	ORG	GG	0-0.15	POM (> 53 µm)	13.51	0.39
365	ORG	GG	0-0.15	HF (> 53 µm)	1.22	13.84
365	ORG	GG	0-0.15	SC (< 53 µm)	4.64	5.56
381	ORG	GG	0-0.15	POM (> 53 µm)	10.44	0.55
381	ORG	GG	0-0.15	HF (> 53 µm)	1.22	14.33
381	ORG	GG	0-0.15	SC (< 53 µm)	4.93	4.74
397	ORG	GG	0-0.15	POM (> 53 µm)	12.60	0.61
397	ORG	GG	0-0.15	HF (> 53 µm)	1.33	13.94
397	ORG	GG	0-0.15	SC (< 53 µm)	4.95	5.25
405	ORG	GG	0-0.15	POM (> 53 µm)	9.09	0.57
405	ORG	GG	0-0.15	HF (> 53 µm)	1.90	14.20
405	ORG	GG	0-0.15	SC (< 53 µm)	4.37	5.08
413	ORG	GG	0-0.15	POM (> 53 µm)	11.06	0.61
413	ORG	GG	0-0.15	HF (> 53 µm)	1.94	12.78
413	ORG	GG	0-0.15	SC (< 53 µm)	4.54	6.61
417	ORG	NG	0-0.15	POM (> 53 µm)	12.15	0.70
417	ORG	NG	0-0.15	HF (> 53 µm)	1.13	12.95
417	ORG	NG	0-0.15	SC (< 53 µm)	4.06	6.08
437	ORG	NG	0-0.15	POM (> 53 µm)	13.36	0.49
437	ORG	NG	0-0.15	HF (> 53 µm)	1.53	12.81
437	ORG	NG	0-0.15	SC (< 53 µm)	4.55	6.44
441	ORG	NG	0-0.15	POM (> 53 µm)	12.57	0.90
441	ORG	NG	0-0.15	HF (> 53 µm)	1.03	12.73
441	ORG	NG	0-0.15	SC (< 53 µm)	4.59	6.15
457	ORG	NG	0-0.15	POM (> 53 µm)	10.26	0.61
457	ORG	NG	0-0.15	HF (> 53 µm)	1.60	12.33
457	ORG	NG	0-0.15	SC (< 53 µm)	4.06	6.88
461	ORG	NG	0-0.15	POM (> 53 µm)	14.46	0.38

461	ORG	NG	0-0.15	HF (> 53 µm)	1.06	12.51
461	ORG	NG	0-0.15	SC (< 53 µm)	4.34	6.82
465	ORG	NG	0-0.15	POM (> 53 µm)	9.95	0.60
465	ORG	NG	0-0.15	HF (> 53 µm)	1.12	14.50
465	ORG	NG	0-0.15	SC (< 53 µm)	4.86	4.78
501	ORG	GG	0-0.15	POM (> 53 µm)	16.34	0.45
501	ORG	GG	0-0.15	HF (> 53 µm)	1.56	13.25
501	ORG	GG	0-0.15	SC (< 53 µm)	5.20	6.22
505	ORG	GG	0-0.15	POM (> 53 µm)	19.02	0.38
505	ORG	GG	0-0.15	HF (> 53 µm)	0.59	11.46
505	ORG	GG	0-0.15	SC (< 53 µm)	5.08	8.10
525	ORG	GG	0-0.15	POM (> 53 µm)	12.28	0.70
525	ORG	GG	0-0.15	HF (> 53 µm)	1.74	14.00
525	ORG	GG	0-0.15	SC (< 53 µm)	5.45	5.25
6	CONV	NG	0.15-0.30	POM (> 53 µm)	6.72	0.31
6	CONV	NG	0.15-0.30	HF (> 53 µm)	1.53	13.97
6	CONV	NG	0.15-0.30	SC (< 53 µm)	4.30	4.98
22	CONV	NG	0.15-0.30	POM (> 53 µm)	9.51	0.27
22	CONV	NG	0.15-0.30	HF (> 53 µm)	0.89	11.56
22	CONV	NG	0.15-0.30	SC (< 53 µm)	2.62	7.90
26	CONV	NG	0.15-0.30	POM (> 53 µm)	7.42	0.33
26	CONV	NG	0.15-0.30	HF (> 53 µm)	0.71	12.68
26	CONV	NG	0.15-0.30	SC (< 53 µm)	1.77	6.91
86	CONV	NG	0.15-0.30	POM (> 53 µm)	12.40	0.40
86	CONV	NG	0.15-0.30	HF (> 53 µm)	1.93	14.11
86	CONV	NG	0.15-0.30	SC (< 53 µm)	3.69	5.33
90	CONV	NG	0.15-0.30	POM (> 53 µm)	9.34	0.35
90	CONV	NG	0.15-0.30	HF (> 53 µm)	0.90	11.58
90	CONV	NG	0.15-0.30	SC (< 53 µm)	2.51	7.80
114	CONV	NG	0.15-0.30	POM (> 53 µm)	7.89	0.42
114	CONV	NG	0.15-0.30	HF (> 53 µm)	1.11	14.00
114	CONV	NG	0.15-0.30	SC (< 53 µm)	3.30	5.39
122	CONV	GG	0.15-0.30	POM (> 53 µm)	9.12	0.80
122	CONV	GG	0.15-0.30	HF (> 53 µm)	2.09	14.71
122	CONV	GG	0.15-0.30	SC (< 53 µm)	4.66	3.88

130	CONV	GG	0.15-0.30	POM (> 53 μm)	6.81	0.48
130	CONV	GG	0.15-0.30	HF (> 53 μm)	1.44	13.95
130	CONV	GG	0.15-0.30	SC (< 53 μm)	4.22	5.42
162	CONV	GG	0.15-0.30	POM (> 53 μm)	11.57	0.39
162	CONV	GG	0.15-0.30	HF (> 53 μm)	1.67	13.56
162	CONV	GG	0.15-0.30	SC (< 53 μm)	2.64	5.70
178	CONV	GG	0.15-0.30	POM (> 53 μm)	11.02	0.21
178	CONV	GG	0.15-0.30	HF (> 53 μm)	1.30	13.55
178	CONV	GG	0.15-0.30	SC (< 53 μm)	3.28	5.81
186	CONV	GG	0.15-0.30	POM (> 53 μm)	9.91	0.30
186	CONV	GG	0.15-0.30	HF (> 53 μm)	1.58	15.30
186	CONV	GG	0.15-0.30	SC (< 53 μm)	3.63	4.26
194	CONV	GG	0.15-0.30	POM (> 53 μm)	10.80	0.28
194	CONV	GG	0.15-0.30	HF (> 53 μm)	1.26	14.33
194	CONV	GG	0.15-0.30	SC (< 53 μm)	2.39	5.01
218	CONV	GG	0.15-0.30	POM (> 53 μm)	12.91	0.30
218	CONV	GG	0.15-0.30	HF (> 53 μm)	1.20	14.35
218	CONV	GG	0.15-0.30	SC (< 53 μm)	3.17	5.25
222	CONV	GG	0.15-0.30	POM (> 53 μm)	18.04	0.41
222	CONV	GG	0.15-0.30	HF (> 53 μm)	3.00	13.15
222	CONV	GG	0.15-0.30	SC (< 53 μm)	3.39	6.33
226	CONV	GG	0.15-0.30	POM (> 53 μm)	12.76	0.33
226	CONV	GG	0.15-0.30	HF (> 53 μm)	1.56	15.00
226	CONV	GG	0.15-0.30	SC (< 53 μm)	3.21	4.55
246	CONV	GG	0.15-0.30	POM (> 53 μm)	10.25	0.31
246	CONV	GG	0.15-0.30	HF (> 53 μm)	1.44	14.46
246	CONV	GG	0.15-0.30	SC (< 53 μm)	3.63	5.12
262	CONV	GG	0.15-0.30	POM (> 53 μm)	10.10	0.52
262	CONV	GG	0.15-0.30	HF (> 53 μm)	1.59	14.56
262	CONV	GG	0.15-0.30	SC (< 53 μm)	3.39	4.82
274	CONV	GG	0.15-0.30	POM (> 53 μm)	12.88	0.38
274	CONV	GG	0.15-0.30	HF (> 53 μm)	1.43	14.44
274	CONV	GG	0.15-0.30	SC (< 53 μm)	3.05	5.08
326	ORG	GG	0.15-0.30	POM (> 53 μm)	8.57	0.36
326	ORG	GG	0.15-0.30	HF (> 53 μm)	0.71	12.99

326	ORG	GG	0.15-0.30	SC (< 53 µm)	3.63	6.51
334	ORG	GG	0.15-0.30	POM (> 53 µm)	9.69	0.28
334	ORG	GG	0.15-0.30	HF (> 53 µm)	1.37	14.02
334	ORG	GG	0.15-0.30	SC (< 53 µm)	3.47	5.58
350	ORG	GG	0.15-0.30	POM (> 53 µm)	8.86	0.34
350	ORG	GG	0.15-0.30	HF (> 53 µm)	1.50	15.10
350	ORG	GG	0.15-0.30	SC (< 53 µm)	3.59	4.26
358	ORG	GG	0.15-0.30	POM (> 53 µm)	10.12	0.21
358	ORG	GG	0.15-0.30	HF (> 53 µm)	1.41	15.11
358	ORG	GG	0.15-0.30	SC (< 53 µm)	3.84	4.35
366	ORG	GG	0.15-0.30	POM (> 53 µm)	9.45	0.30
366	ORG	GG	0.15-0.30	HF (> 53 µm)	1.50	15.83
366	ORG	GG	0.15-0.30	SC (< 53 µm)	3.85	3.68
382	ORG	GG	0.15-0.30	POM (> 53 µm)	9.53	0.22
382	ORG	GG	0.15-0.30	HF (> 53 µm)	1.37	15.41
382	ORG	GG	0.15-0.30	SC (< 53 µm)	3.96	4.01
398	ORG	GG	0.15-0.30	POM (> 53 µm)	9.85	0.21
398	ORG	GG	0.15-0.30	HF (> 53 µm)	1.23	15.33
398	ORG	GG	0.15-0.30	SC (< 53 µm)	3.78	4.20
406	ORG	GG	0.15-0.30	POM (> 53 µm)	10.93	0.20
406	ORG	GG	0.15-0.30	HF (> 53 µm)	1.59	15.64
406	ORG	GG	0.15-0.30	SC (< 53 µm)	3.63	3.94
414	ORG	GG	0.15-0.30	POM (> 53 µm)	8.70	0.20
414	ORG	GG	0.15-0.30	HF (> 53 µm)	1.41	14.87
414	ORG	GG	0.15-0.30	SC (< 53 µm)	3.58	4.80
418	ORG	NG	0.15-0.30	POM (> 53 µm)	13.69	0.31
418	ORG	NG	0.15-0.30	HF (> 53 µm)	0.93	14.08
418	ORG	NG	0.15-0.30	SC (< 53 µm)	3.65	5.56
438	ORG	NG	0.15-0.30	POM (> 53 µm)	9.50	0.34
438	ORG	NG	0.15-0.30	HF (> 53 µm)	1.13	15.03
438	ORG	NG	0.15-0.30	SC (< 53 µm)	3.30	4.55
442	ORG	NG	0.15-0.30	POM (> 53 µm)	11.13	0.34
442	ORG	NG	0.15-0.30	HF (> 53 µm)	0.81	13.88
442	ORG	NG	0.15-0.30	SC (< 53 µm)	3.22	5.53
458	ORG	NG	0.15-0.30	POM (> 53 µm)	18.84	0.25

458	ORG	NG	0.15-0.30	HF (> 53 μm)	1.39	14.15
458	ORG	NG	0.15-0.30	SC (< 53 μm)	3.87	5.45
462	ORG	NG	0.15-0.30	POM (> 53 μm)	14.21	0.24
462	ORG	NG	0.15-0.30	HF (> 53 μm)	1.10	13.84
462	ORG	NG	0.15-0.30	SC (< 53 μm)	3.61	5.82
466	ORG	NG	0.15-0.30	POM (> 53 μm)	10.83	0.31
466	ORG	NG	0.15-0.30	HF (> 53 μm)	1.13	14.71
466	ORG	NG	0.15-0.30	SC (< 53 μm)	4.28	4.67
502	ORG	GG	0.15-0.30	POM (> 53 μm)	11.57	0.25
502	ORG	GG	0.15-0.30	HF (> 53 μm)	0.89	14.25
502	ORG	GG	0.15-0.30	SC (< 53 μm)	2.60	5.36
506	ORG	GG	0.15-0.30	POM (> 53 μm)	10.13	0.31
506	ORG	GG	0.15-0.30	HF (> 53 μm)	1.39	14.88
506	ORG	GG	0.15-0.30	SC (< 53 μm)	4.16	4.80
526	ORG	GG	0.15-0.30	POM (> 53 μm)	10.37	0.26
526	ORG	GG	0.15-0.30	HF (> 53 μm)	1.26	13.45
526	ORG	GG	0.15-0.30	SC (< 53 μm)	2.67	6.01
7	CONV	NG	0.30-0.60	POM (> 53 μm)	8.09	0.13
7	CONV	NG	0.30-0.60	HF (> 53 μm)	1.11	14.05
7	CONV	NG	0.30-0.60	SC (< 53 μm)	2.21	5.78
23	CONV	NG	0.30-0.60	POM (> 53 μm)	11.25	0.11
23	CONV	NG	0.30-0.60	HF (> 53 μm)	0.63	9.28
23	CONV	NG	0.30-0.60	SC (< 53 μm)	1.87	10.35
27	CONV	NG	0.30-0.60	POM (> 53 μm)	7.44	0.11
27	CONV	NG	0.30-0.60	HF (> 53 μm)	0.36	10.30
27	CONV	NG	0.30-0.60	SC (< 53 μm)	1.40	9.14
87	CONV	NG	0.30-0.60	POM (> 53 μm)	10.17	0.08
87	CONV	NG	0.30-0.60	HF (> 53 μm)	0.71	11.41
87	CONV	NG	0.30-0.60	SC (< 53 μm)	1.52	8.45
91	CONV	NG	0.30-0.60	POM (> 53 μm)	17.28	0.07
91	CONV	NG	0.30-0.60	HF (> 53 μm)	0.50	10.10
91	CONV	NG	0.30-0.60	SC (< 53 μm)	1.51	9.90
115	CONV	NG	0.30-0.60	POM (> 53 μm)	10.75	0.08
115	CONV	NG	0.30-0.60	HF (> 53 μm)	0.48	11.13
115	CONV	NG	0.30-0.60	SC (< 53 μm)	1.65	8.65

123	CONV	GG	0.30-0.60	POM (> 53 µm)	9.39	0.12
123	CONV	GG	0.30-0.60	HF (> 53 µm)	0.83	11.60
123	CONV	GG	0.30-0.60	SC (< 53 µm)	1.62	7.39
131	CONV	GG	0.30-0.60	POM (> 53 µm)	11.26	0.09
131	CONV	GG	0.30-0.60	HF (> 53 µm)	0.39	10.45
131	CONV	GG	0.30-0.60	SC (< 53 µm)	1.34	9.22
163	CONV	GG	0.30-0.60	POM (> 53 µm)	12.86	0.12
163	CONV	GG	0.30-0.60	HF (> 53 µm)	0.57	10.17
163	CONV	GG	0.30-0.60	SC (< 53 µm)	1.53	9.35
179	CONV	GG	0.30-0.60	POM (> 53 µm)	13.63	0.14
179	CONV	GG	0.30-0.60	HF (> 53 µm)	0.51	10.95
179	CONV	GG	0.30-0.60	SC (< 53 µm)	1.55	8.85
187	CONV	GG	0.30-0.60	POM (> 53 µm)	12.33	0.11
187	CONV	GG	0.30-0.60	HF (> 53 µm)	0.64	12.71
187	CONV	GG	0.30-0.60	SC (< 53 µm)	1.78	7.07
195	CONV	GG	0.30-0.60	POM (> 53 µm)	11.82	0.07
195	CONV	GG	0.30-0.60	HF (> 53 µm)	0.31	11.56
195	CONV	GG	0.30-0.60	SC (< 53 µm)	1.68	8.26
219	CONV	GG	0.30-0.60	POM (> 53 µm)	7.07	0.14
219	CONV	GG	0.30-0.60	HF (> 53 µm)	0.51	14.00
219	CONV	GG	0.30-0.60	SC (< 53 µm)	1.42	5.78
223	CONV	GG	0.30-0.60	POM (> 53 µm)	19.20	0.18
223	CONV	GG	0.30-0.60	HF (> 53 µm)	0.78	12.35
223	CONV	GG	0.30-0.60	SC (< 53 µm)	1.94	7.21
227	CONV	GG	0.30-0.60	POM (> 53 µm)	9.45	0.21
227	CONV	GG	0.30-0.60	HF (> 53 µm)	0.63	11.80
227	CONV	GG	0.30-0.60	SC (< 53 µm)	1.64	7.39
247	CONV	GG	0.30-0.60	POM (> 53 µm)	8.04	0.09
247	CONV	GG	0.30-0.60	HF (> 53 µm)	0.79	14.52
247	CONV	GG	0.30-0.60	SC (< 53 µm)	2.17	5.25
263	CONV	GG	0.30-0.60	POM (> 53 µm)	11.79	0.11
263	CONV	GG	0.30-0.60	HF (> 53 µm)	0.59	12.20
263	CONV	GG	0.30-0.60	SC (< 53 µm)	1.76	7.22
275	CONV	GG	0.30-0.60	POM (> 53 µm)	10.43	0.12
275	CONV	GG	0.30-0.60	HF (> 53 µm)	0.69	11.55

275	CONV	GG	0.30-0.60	SC (< 53 µm)	1.40	8.21
327	ORG	GG	0.30-0.60	POM (> 53 µm)	12.85	0.09
327	ORG	GG	0.30-0.60	HF (> 53 µm)	0.39	10.38
327	ORG	GG	0.30-0.60	SC (< 53 µm)	1.25	8.71
335	ORG	GG	0.30-0.60	POM (> 53 µm)	14.56	0.12
335	ORG	GG	0.30-0.60	HF (> 53 µm)	0.58	10.88
335	ORG	GG	0.30-0.60	SC (< 53 µm)	1.38	8.75
351	ORG	GG	0.30-0.60	POM (> 53 µm)	9.04	0.12
351	ORG	GG	0.30-0.60	HF (> 53 µm)	0.48	9.50
351	ORG	GG	0.30-0.60	SC (< 53 µm)	1.51	9.90
359	ORG	GG	0.30-0.60	POM (> 53 µm)	10.88	0.10
359	ORG	GG	0.30-0.60	HF (> 53 µm)	0.46	12.90
359	ORG	GG	0.30-0.60	SC (< 53 µm)	1.84	6.74
367	ORG	GG	0.30-0.60	POM (> 53 µm)	9.37	0.13
367	ORG	GG	0.30-0.60	HF (> 53 µm)	0.21	12.42
367	ORG	GG	0.30-0.60	SC (< 53 µm)	1.80	7.25
383	ORG	GG	0.30-0.60	POM (> 53 µm)	9.23	0.17
383	ORG	GG	0.30-0.60	HF (> 53 µm)	0.19	11.72
383	ORG	GG	0.30-0.60	SC (< 53 µm)	1.87	7.83
399	ORG	GG	0.30-0.60	POM (> 53 µm)	7.26	0.17
399	ORG	GG	0.30-0.60	HF (> 53 µm)	0.17	11.97
399	ORG	GG	0.30-0.60	SC (< 53 µm)	2.09	7.66
407	ORG	GG	0.30-0.60	POM (> 53 µm)	12.62	0.11
407	ORG	GG	0.30-0.60	HF (> 53 µm)	0.37	9.28
407	ORG	GG	0.30-0.60	SC (< 53 µm)	1.61	10.40
415	ORG	GG	0.30-0.60	POM (> 53 µm)	5.31	0.13
415	ORG	GG	0.30-0.60	HF (> 53 µm)	0.66	13.65
415	ORG	GG	0.30-0.60	SC (< 53 µm)	2.11	6.18
419	ORG	NG	0.30-0.60	POM (> 53 µm)	9.97	0.08
419	ORG	NG	0.30-0.60	HF (> 53 µm)	0.69	12.90
419	ORG	NG	0.30-0.60	SC (< 53 µm)	1.65	6.97
439	ORG	NG	0.30-0.60	POM (> 53 µm)	3.47	0.35
439	ORG	NG	0.30-0.60	HF (> 53 µm)	0.30	11.72
439	ORG	NG	0.30-0.60	SC (< 53 µm)	1.72	7.62
443	ORG	NG	0.30-0.60	POM (> 53 µm)	8.27	0.08

443	ORG	NG	0.30-0.60	HF (> 53 µm)	0.47	10.36
443	ORG	NG	0.30-0.60	SC (< 53 µm)	1.39	9.32
459	ORG	NG	0.30-0.60	POM (> 53 µm)	14.04	0.08
459	ORG	NG	0.30-0.60	HF (> 53 µm)	0.31	9.88
459	ORG	NG	0.30-0.60	SC (< 53 µm)	1.95	9.81
463	ORG	NG	0.30-0.60	POM (> 53 µm)	13.46	0.10
463	ORG	NG	0.30-0.60	HF (> 53 µm)	0.18	10.44
463	ORG	NG	0.30-0.60	SC (< 53 µm)	1.74	9.36
467	ORG	NG	0.30-0.60	POM (> 53 µm)	14.10	0.06
467	ORG	NG	0.30-0.60	HF (> 53 µm)	0.19	10.10
467	ORG	NG	0.30-0.60	SC (< 53 µm)	1.55	9.64
503	ORG	GG	0.30-0.60	POM (> 53 µm)	8.87	0.08
503	ORG	GG	0.30-0.60	HF (> 53 µm)	0.38	10.91
503	ORG	GG	0.30-0.60	SC (< 53 µm)	1.43	8.82
507	ORG	GG	0.30-0.60	POM (> 53 µm)	14.45	0.09
507	ORG	GG	0.30-0.60	HF (> 53 µm)	0.44	10.22
507	ORG	GG	0.30-0.60	SC (< 53 µm)	1.43	9.55
527	ORG	GG	0.30-0.60	POM (> 53 µm)	10.36	0.10
527	ORG	GG	0.30-0.60	HF (> 53 µm)	0.45	9.32
527	ORG	GG	0.30-0.60	SC (< 53 µm)	1.65	10.23

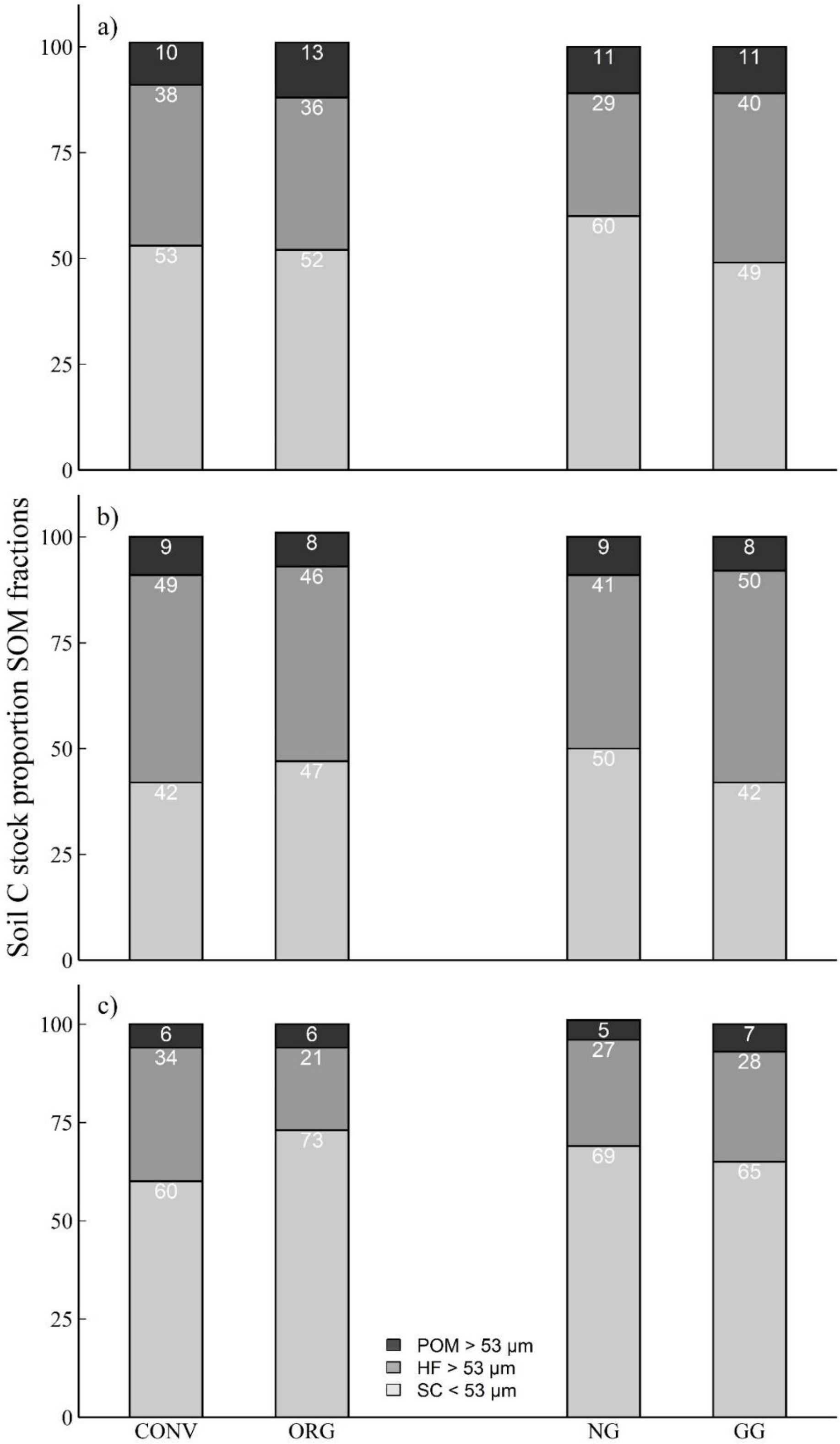

Figure A2.2. Proportion of soil carbon stocks in soil organic matter fractions at 0-0.15 m (a), 0.15-0.30 m (b) and 0.30-0.60 m (c) soil depth intervals. CONV=Conventional; ORG=Organic; POM=Particulate organic matter; HF=heavy fraction; and SC=silt clay fraction.

Appendix 3

Table A3.1. Summary of soil mineralogy composition by X-Ray Diffraction (XRD) analysis for each sample analysed across Nafferton farm, Stocksfield, Northumberland, north-east of England, UK. Feldspar refers to all the feldspars.

Sample_ID	Dominant clay mineral ≥ 20% score by soil depth interval		
	0-0.15m	0.15-0.30 m	0.30-0.60 m
NAF_002	Quartz	Quartz	Quartz
NAF_013	Quartz	Quartz	Quartz
NAF_019	Quartz	Quartz, Nacaphite	Quartz, Illite, Nacaphite
NAF_027	Quartz	Quartz	Quartz, Kaolinite, Illite, Feldspar
NAF_031	Quartz	Quartz, Kaolinite, Feldspar	Quartz, Kaolinite, Illite
NAF_041	Quartz	Quartz	Quartz, Kaolinite, Illite, Feldspar
NAF_047	Quartz	Quartz, Kaolinite, Illite, Feldspar	Quartz, Kaolinite, Feldspar, Illite
NAF_065	Quartz	Quartz	Quartz
NAF_072	Quartz	Quartz	Quartz
NAF_087	Quartz	Quartz	Quartz, Kaolinite, Illite
NAF_103	Quartz	Quartz	Quartz
NAF_112	Quartz	Quartz	Quartz
NAF_123	Quartz	Quartz	Quartz, Kaolinite, Feldspar
NAF_129	Quartz	Quartz	Quartz
NAF_131	Quartz	Quartz	Quartz

Table A3.2. Soil carbon (C) concentration of the individual fractions (particulate organic matter-POM > 53; heavy fraction-HF > 53 µm; silt and clay fraction-SC < 53 µm) and their recovery soil masses after physical fractionation analysis by each sample analysed and considering crop rotation scheme (RS) (conventional-CONV-RT *vs.* organic-ORG-RT), fertility source (FS) (mineral-MINE *vs.* compost-COMP), year of sampling (YR) (2011 and 2018) and soil depth intervals, 0-0.15, 0.15-0.30 and 0.30-0.60 m.

Sample nº in the LAB	RS	FS	YR	Depth	Fraction	C	Recovery soil mass in 20 g
				m		%	g
25	ORG-RT	MINE	2018	0-0.15	HF (> 53 µm)	0.23	14.49
25	ORG-RT	MINE	2018	0-0.15	POM (> 53 µm)	17.01	0.38
25	ORG-RT	MINE	2018	0-0.15	SC (< 53 µm)	5.35	4.98
26	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 µm)	0.82	15.08
26	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 µm)	14.32	0.12
26	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 µm)	4.48	4.53
27	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	1.05	13.61
27	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	16.48	0.05
27	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.53	6.01
28	ORG-RT	MINE	2011	0-0.30	HF (> 53 µm)	2.24	14.93
28	ORG-RT	MINE	2011	0-0.30	POM (> 53 µm)	19.75	0.22
28	ORG-RT	MINE	2011	0-0.30	SC (< 53 µm)	4.95	4.26
29	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 µm)	1.42	12.30
29	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 µm)	10.25	0.05
29	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 µm)	1.53	7.06
30	ORG-RT	MINE	2018	0-0.15	HF (> 53 µm)	0.97	14.72
30	ORG-RT	MINE	2018	0-0.15	POM (> 53 µm)	12.83	0.22
30	ORG-RT	MINE	2018	0-0.15	SC (< 53 µm)	4.89	4.77
31	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 µm)	0.74	14.08
31	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 µm)	10.97	0.10
31	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 µm)	4.09	5.44
32	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	0.35	11.78
32	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	13.57	0.10
32	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.89	8.03
33	ORG-RT	MINE	2011	0-0.30	HF (> 53 µm)	2.38	14.16
33	ORG-RT	MINE	2011	0-0.30	POM (> 53 µm)	15.71	0.18
33	ORG-RT	MINE	2011	0-0.30	SC (< 53 µm)	4.19	5.02
34	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 µm)	0.33	11.14
34	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 µm)	10.25	0.08
34	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 µm)	1.76	8.37
35	CONV-RT	MINE	2018	0-0.15	HF (> 53 µm)	0.68	14.11
35	CONV-RT	MINE	2018	0-0.15	POM (> 53 µm)	9.03	0.44
35	CONV-RT	MINE	2018	0-0.15	SC (< 53 µm)	5.30	5.21
36	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 µm)	1.10	13.79
36	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 µm)	13.52	0.12
36	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 µm)	3.76	5.54
37	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	0.41	12.15
37	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	9.21	0.11
37	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.86	7.50
38	CONV-RT	MINE	2011	0-0.30	HF (> 53 µm)	0.81	13.91
38	CONV-RT	MINE	2011	0-0.30	POM (> 53 µm)	11.84	0.19
38	CONV-RT	MINE	2011	0-0.30	SC (< 53 µm)	4.94	5.20

39	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	2.93	12.16
39	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	10.46	0.09
39	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.96	7.27
40	CONV-RT	MINE	2018	0-0.15	HF (> 53 μm)	1.12	15.03
40	CONV-RT	MINE	2018	0-0.15	POM (> 53 μm)	14.14	0.19
40	CONV-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.30	4.44
41	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	0.44	14.85
41	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	10.61	0.22
41	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	3.09	4.69
42	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	0.61	12.24
42	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	9.67	0.09
42	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	1.67	7.42
43	CONV-RT	MINE	2011	0-0.30	HF (> 53 μm)	0.59	14.73
43	CONV-RT	MINE	2011	0-0.30	POM (> 53 μm)	13.60	0.21
43	CONV-RT	MINE	2011	0-0.30	SC (< 53 μm)	4.59	4.63
44	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	1.28	11.87
44	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	9.25	0.04
44	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.68	7.61
45	ORG-RT	COMP	2018	0-0.15	HF (> 53 μm)	2.11	14.42
45	ORG-RT	COMP	2018	0-0.15	POM (> 53 μm)	12.84	0.30
45	ORG-RT	COMP	2018	0-0.15	SC (< 53 μm)	3.96	4.88
46	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	1.66	14.87
46	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	9.29	0.27
46	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	3.92	4.54
47	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.24	11.61
47	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	15.37	0.08
47	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.96	7.82
48	ORG-RT	COMP	2011	0-0.30	HF (> 53 μm)	0.66	13.60
48	ORG-RT	COMP	2011	0-0.30	POM (> 53 μm)	17.45	0.23
48	ORG-RT	COMP	2011	0-0.30	SC (< 53 μm)	3.36	5.59
49	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	0.29	12.72
49	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	14.02	0.09
49	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	1.85	6.92
50	ORG-RT	COMP	2018	0-0.15	HF (> 53 μm)	0.70	14.80
50	ORG-RT	COMP	2018	0-0.15	POM (> 53 μm)	14.24	0.27
50	ORG-RT	COMP	2018	0-0.15	SC (< 53 μm)	4.83	4.45
51	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	0.36	13.17
51	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	13.33	0.07
51	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	3.20	6.48
52	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.28	11.09
52	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	9.84	0.12
52	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.66	8.66
53	ORG-RT	COMP	2011	0-0.30	HF (> 53 μm)	0.16	14.55
53	ORG-RT	COMP	2011	0-0.30	POM (> 53 μm)	17.18	0.27
53	ORG-RT	COMP	2011	0-0.30	SC (< 53 μm)	3.79	4.80
54	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	1.41	11.42
54	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	14.11	0.04
54	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	1.63	8.22
55	CONV-RT	COMP	2018	0-0.15	HF (> 53 μm)	0.40	13.99
55	CONV-RT	COMP	2018	0-0.15	POM (> 53 μm)	13.90	0.15
55	CONV-RT	COMP	2018	0-0.15	SC (< 53 μm)	5.00	5.49
56	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	0.94	13.90
56	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	9.73	0.21
56	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	4.14	5.53
57	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.39	11.59
57	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	8.25	0.09
57	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.64	7.81

58	CONV-RT	COMP	2011	0-0.30	HF (> 53 µm)	0.98	14.85
58	CONV-RT	COMP	2011	0-0.30	POM (> 53 µm)	13.78	0.23
58	CONV-RT	COMP	2011	0-0.30	SC (< 53 µm)	4.49	4.40
59	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 µm)	0.49	10.39
59	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 µm)	16.82	0.09
59	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 µm)	1.68	9.00
60	CONV-RT	COMP	2018	0-0.15	HF (> 53 µm)	0.81	14.95
60	CONV-RT	COMP	2018	0-0.15	POM (> 53 µm)	13.10	0.29
60	CONV-RT	COMP	2018	0-0.15	SC (< 53 µm)	4.05	4.50
61	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 µm)	0.68	14.92
61	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 µm)	9.91	0.09
61	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 µm)	3.30	4.93
62	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 µm)	0.73	11.84
62	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 µm)	8.59	0.08
62	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 µm)	1.68	7.78
63	CONV-RT	COMP	2011	0-0.30	HF (> 53 µm)	0.28	14.36
63	CONV-RT	COMP	2011	0-0.30	POM (> 53 µm)	15.47	0.39
63	CONV-RT	COMP	2011	0-0.30	SC (< 53 µm)	4.04	4.72
64	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 µm)	0.29	12.49
64	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 µm)	9.52	0.06
64	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 µm)	1.32	7.08
65	ORG-RT	COMP	2018	0-0.15	HF (> 53 µm)	1.63	14.42
65	ORG-RT	COMP	2018	0-0.15	POM (> 53 µm)	11.63	0.19
65	ORG-RT	COMP	2018	0-0.15	SC (< 53 µm)	4.23	5.13
66	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 µm)	0.16	14.35
66	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 µm)	15.53	0.13
66	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 µm)	4.65	5.35
67	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 µm)	0.72	14.17
67	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 µm)	8.09	0.08
67	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 µm)	1.92	4.50
68	ORG-RT	COMP	2011	0-0.30	HF (> 53 µm)	0.30	14.12
68	ORG-RT	COMP	2011	0-0.30	POM (> 53 µm)	12.82	0.12
68	ORG-RT	COMP	2011	0-0.30	SC (< 53 µm)	2.26	5.70
69	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 µm)	0.93	11.63
69	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 µm)	14.11	0.07
69	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 µm)	1.20	8.15
70	ORG-RT	COMP	2018	0-0.15	HF (> 53 µm)	0.66	14.65
70	ORG-RT	COMP	2018	0-0.15	POM (> 53 µm)	12.67	0.32
70	ORG-RT	COMP	2018	0-0.15	SC (< 53 µm)	3.90	4.91
71	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 µm)	1.04	13.75
71	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 µm)	19.13	0.11
71	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 µm)	3.86	6.05
72	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 µm)	0.53	12.81
72	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 µm)	7.88	0.08
72	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 µm)	1.52	6.88
73	ORG-RT	COMP	2011	0-0.30	HF (> 53 µm)	0.39	15.16
73	ORG-RT	COMP	2011	0-0.30	POM (> 53 µm)	13.13	0.20
73	ORG-RT	COMP	2011	0-0.30	SC (< 53 µm)	5.19	4.39
74	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 µm)	0.30	14.05
74	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 µm)	13.67	0.11
74	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 µm)	2.01	5.40
75	CONV-RT	COMP	2018	0-0.15	HF (> 53 µm)	0.46	14.96
75	CONV-RT	COMP	2018	0-0.15	POM (> 53 µm)	13.06	0.22
75	CONV-RT	COMP	2018	0-0.15	SC (< 53 µm)	4.00	4.56
76	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 µm)	0.92	15.44
76	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 µm)	10.55	0.20
76	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 µm)	3.48	4.27

77	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.17	11.51
77	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	8.17	0.09
77	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.43	8.00
78	CONV-RT	COMP	2011	0-0.30	HF (> 53 μm)	1.99	15.77
78	CONV-RT	COMP	2011	0-0.30	POM (> 53 μm)	11.82	0.35
78	CONV-RT	COMP	2011	0-0.30	SC (< 53 μm)	4.38	3.59
79	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	0.29	13.54
79	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	9.52	0.07
79	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	1.67	5.96
80	CONV-RT	COMP	2018	0-0.15	HF (> 53 μm)	0.19	15.76
80	CONV-RT	COMP	2018	0-0.15	POM (> 53 μm)	13.27	0.32
80	CONV-RT	COMP	2018	0-0.15	SC (< 53 μm)	4.50	3.82
81	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	0.20	15.06
81	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	9.91	0.12
81	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	3.02	4.64
82	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.63	13.86
82	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	6.85	0.08
82	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.24	5.73
83	CONV-RT	COMP	2011	0-0.30	HF (> 53 μm)	0.89	15.89
83	CONV-RT	COMP	2011	0-0.30	POM (> 53 μm)	15.91	0.13
83	CONV-RT	COMP	2011	0-0.30	SC (< 53 μm)	3.01	3.56
84	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	0.68	13.56
84	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	19.12	0.08
84	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	1.44	6.19
85	ORG-RT	MINE	2018	0-0.15	HF (> 53 μm)	0.34	15.22
85	ORG-RT	MINE	2018	0-0.15	POM (> 53 μm)	13.12	0.34
85	ORG-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.08	4.24
86	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	1.27	13.80
86	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	14.40	0.09
86	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	3.81	4.73
87	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	0.72	13.40
87	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	12.81	0.05
87	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	2.17	6.24
88	ORG-RT	MINE	2011	0-0.30	HF (> 53 μm)	0.83	15.90
88	ORG-RT	MINE	2011	0-0.30	POM (> 53 μm)	12.63	0.17
88	ORG-RT	MINE	2011	0-0.30	SC (< 53 μm)	3.34	3.56
89	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	0.18	15.57
89	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	13.20	0.08
89	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.90	4.28
90	ORG-RT	MINE	2018	0-0.15	HF (> 53 μm)	0.47	15.94
90	ORG-RT	MINE	2018	0-0.15	POM (> 53 μm)	11.61	0.23
90	ORG-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.07	3.80
91	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	0.27	13.27
91	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	8.96	0.14
91	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	1.95	6.45
92	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	1.79	12.37
92	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	10.27	0.05
92	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	1.31	7.21
93	ORG-RT	MINE	2011	0-0.30	HF (> 53 μm)	0.71	16.52
93	ORG-RT	MINE	2011	0-0.30	POM (> 53 μm)	12.53	0.30
93	ORG-RT	MINE	2011	0-0.30	SC (< 53 μm)	4.35	3.06
94	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	0.17	12.98
94	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	11.06	0.06
94	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.60	6.67
95	CONV-RT	MINE	2018	0-0.15	HF (> 53 μm)	0.55	14.64
95	CONV-RT	MINE	2018	0-0.15	POM (> 53 μm)	14.07	0.17
95	CONV-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.14	5.02

96	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 µm)	0.52	14.74
96	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 µm)	11.91	0.15
96	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 µm)	3.30	4.94
97	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	1.14	11.92
97	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	14.19	0.08
97	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.50	7.73
98	CONV-RT	MINE	2011	0-0.30	HF (> 53 µm)	1.74	15.69
98	CONV-RT	MINE	2011	0-0.30	POM (> 53 µm)	11.52	0.21
98	CONV-RT	MINE	2011	0-0.30	SC (< 53 µm)	4.68	3.91
99	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 µm)	0.65	15.46
99	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 µm)	14.82	0.07
99	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 µm)	2.23	4.18
100	CONV-RT	MINE	2018	0-0.15	HF (> 53 µm)	0.38	14.20
100	CONV-RT	MINE	2018	0-0.15	POM (> 53 µm)	15.36	0.19
100	CONV-RT	MINE	2018	0-0.15	SC (< 53 µm)	5.56	5.30
101	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 µm)	0.82	14.39
101	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 µm)	10.10	0.15
101	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 µm)	3.04	5.05
102	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	0.97	12.11
102	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	9.21	0.05
102	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.34	7.75
103	CONV-RT	MINE	2011	0-0.30	HF (> 53 µm)	0.44	14.71
103	CONV-RT	MINE	2011	0-0.30	POM (> 53 µm)	20.60	0.16
103	CONV-RT	MINE	2011	0-0.30	SC (< 53 µm)	3.54	4.74
104	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 µm)	0.63	11.21
104	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 µm)	9.52	0.07
104	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 µm)	1.62	8.39
129	ORG-RT	COMP	2018	0-0.15	HF (> 53 µm)	0.28	14.15
129	ORG-RT	COMP	2018	0-0.15	POM (> 53 µm)	13.43	0.18
129	ORG-RT	COMP	2018	0-0.15	SC (< 53 µm)	4.58	5.39
130	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 µm)	1.53	14.66
130	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 µm)	15.19	0.06
130	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 µm)	2.98	5.04
131	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 µm)	0.65	13.25
131	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 µm)	10.12	0.03
131	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 µm)	1.58	6.39
132	ORG-RT	COMP	2011	0-0.30	HF (> 53 µm)	0.42	14.90
132	ORG-RT	COMP	2011	0-0.30	POM (> 53 µm)	9.53	0.24
132	ORG-RT	COMP	2011	0-0.30	SC (< 53 µm)	3.19	4.43
133	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 µm)	2.17	12.76
133	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 µm)	9.82	0.11
133	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 µm)	1.75	6.86
134	ORG-RT	COMP	2018	0-0.15	HF (> 53 µm)	0.47	15.13
134	ORG-RT	COMP	2018	0-0.15	POM (> 53 µm)	12.78	0.21
134	ORG-RT	COMP	2018	0-0.15	SC (< 53 µm)	3.88	4.16
135	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 µm)	0.88	14.14
135	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 µm)	11.20	0.17
135	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 µm)	4.28	5.26
136	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 µm)	0.47	13.20
136	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 µm)	14.77	0.05
136	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 µm)	1.63	6.40
137	ORG-RT	COMP	2011	0-0.30	HF (> 53 µm)	0.76	13.71
137	ORG-RT	COMP	2011	0-0.30	POM (> 53 µm)	13.11	0.14
137	ORG-RT	COMP	2011	0-0.30	SC (< 53 µm)	2.62	5.76
138	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 µm)	0.27	12.16
138	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 µm)	16.44	0.03
138	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 µm)	1.58	7.29

139	CONV-RT	COMP	2018	0-0.15	HF (> 53 μm)	2.42	15.10
139	CONV-RT	COMP	2018	0-0.15	POM (> 53 μm)	10.19	0.27
139	CONV-RT	COMP	2018	0-0.15	SC (< 53 μm)	3.81	4.21
140	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	0.20	13.08
140	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	13.07	0.13
140	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	3.14	6.49
141	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.25	12.73
141	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	10.80	0.13
141	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.59	6.87
142	CONV-RT	COMP	2011	0-0.30	HF (> 53 μm)	0.33	15.50
142	CONV-RT	COMP	2011	0-0.30	POM (> 53 μm)	11.98	0.25
142	CONV-RT	COMP	2011	0-0.30	SC (< 53 μm)	3.82	4.08
143	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	0.55	13.33
143	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	5.12	0.11
143	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	2.19	6.13
144	CONV-RT	COMP	2018	0-0.15	HF (> 53 μm)	0.69	14.94
144	CONV-RT	COMP	2018	0-0.15	POM (> 53 μm)	12.42	0.23
144	CONV-RT	COMP	2018	0-0.15	SC (< 53 μm)	3.39	4.40
145	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	1.19	14.81
145	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	9.99	0.14
145	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	3.02	4.56
146	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.36	13.08
146	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	8.38	0.03
146	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.53	6.47
147	CONV-RT	COMP	2011	0-0.30	HF (> 53 μm)	1.24	14.47
147	CONV-RT	COMP	2011	0-0.30	POM (> 53 μm)	17.07	0.29
147	CONV-RT	COMP	2011	0-0.30	SC (< 53 μm)	4.42	4.75
148	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	0.39	11.03
148	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	11.59	0.06
148	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	1.39	8.58
149	ORG-RT	MINE	2018	0-0.15	HF (> 53 μm)	2.68	15.87
149	ORG-RT	MINE	2018	0-0.15	POM (> 53 μm)	8.36	0.32
149	ORG-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.39	3.59
150	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	0.90	13.77
150	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	9.46	0.15
150	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	2.34	5.28
151	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	1.02	11.22
151	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	8.23	0.09
151	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	1.62	8.38
152	ORG-RT	MINE	2011	0-0.30	HF (> 53 μm)	0.64	14.72
152	ORG-RT	MINE	2011	0-0.30	POM (> 53 μm)	7.36	0.10
152	ORG-RT	MINE	2011	0-0.30	SC (< 53 μm)	2.28	4.78
153	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	0.36	12.31
153	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	4.65	0.13
153	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.42	7.29
154	ORG-RT	MINE	2018	0-0.15	HF (> 53 μm)	1.39	15.39
154	ORG-RT	MINE	2018	0-0.15	POM (> 53 μm)	10.16	0.33
154	ORG-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.11	4.00
155	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	0.64	14.32
155	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	8.76	0.19
155	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	4.38	5.15
156	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	0.69	13.41
156	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	8.20	0.09
156	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	1.51	6.15
157	ORG-RT	MINE	2011	0-0.30	HF (> 53 μm)	0.60	15.18
157	ORG-RT	MINE	2011	0-0.30	POM (> 53 μm)	11.88	0.24
157	ORG-RT	MINE	2011	0-0.30	SC (< 53 μm)	3.87	4.10

158	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	0.66	13.67
158	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	12.16	0.05
158	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.66	6.05
159	CONV-RT	MINE	2018	0-0.15	HF (> 53 μm)	1.77	14.59
159	CONV-RT	MINE	2018	0-0.15	POM (> 53 μm)	11.15	0.19
159	CONV-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.05	4.80
160	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	2.43	15.11
160	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	12.02	0.22
160	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	3.53	4.08
161	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	0.78	12.70
161	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	9.89	0.10
161	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	2.01	6.86
162	CONV-RT	MINE	2011	0-0.30	HF (> 53 μm)	0.35	15.07
162	CONV-RT	MINE	2011	0-0.30	POM (> 53 μm)	9.13	0.25
162	CONV-RT	MINE	2011	0-0.30	SC (< 53 μm)	3.12	4.30
163	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	1.39	13.05
163	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	10.46	0.05
163	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.56	6.43
164	CONV-RT	MINE	2018	0-0.15	HF (> 53 μm)	2.23	14.69
164	CONV-RT	MINE	2018	0-0.15	POM (> 53 μm)	11.86	0.36
164	CONV-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.56	4.30
165	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	1.31	14.76
165	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	9.19	0.21
165	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	3.73	4.68
166	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	0.47	12.14
166	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	10.16	0.06
166	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	1.71	7.43
167	CONV-RT	MINE	2011	0-0.30	HF (> 53 μm)	0.41	14.99
167	CONV-RT	MINE	2011	0-0.30	POM (> 53 μm)	14.60	0.18
167	CONV-RT	MINE	2011	0-0.30	SC (< 53 μm)	3.35	4.41
168	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	0.47	11.95
168	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	9.25	0.06
168	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.89	7.78
193	ORG-RT	COMP	2018	0-0.15	HF (> 53 μm)	0.59	14.49
193	ORG-RT	COMP	2018	0-0.15	POM (> 53 μm)	13.47	0.28
193	ORG-RT	COMP	2018	0-0.15	SC (< 53 μm)	4.71	4.91
194	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	0.19	15.34
194	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	7.51	0.23
194	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	3.41	4.29
195	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.29	12.64
195	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	6.09	0.17
195	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.71	6.90
196	ORG-RT	COMP	2011	0-0.30	HF (> 53 μm)	0.33	13.74
196	ORG-RT	COMP	2011	0-0.30	POM (> 53 μm)	11.89	0.27
196	ORG-RT	COMP	2011	0-0.30	SC (< 53 μm)	3.98	4.30
197	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	1.02	13.32
197	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	20.95	0.04
197	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	1.40	6.46
198	ORG-RT	COMP	2018	0-0.15	HF (> 53 μm)	0.69	14.43
198	ORG-RT	COMP	2018	0-0.15	POM (> 53 μm)	11.07	0.25
198	ORG-RT	COMP	2018	0-0.15	SC (< 53 μm)	4.44	4.15
199	ORG-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	0.73	12.80
199	ORG-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	7.93	0.22
199	ORG-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	2.56	6.37
200	ORG-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.64	11.41
200	ORG-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	8.78	0.18
200	ORG-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.56	7.65

201	ORG-RT	COMP	2011	0-0.30	HF (> 53 μm)	1.13	13.97
201	ORG-RT	COMP	2011	0-0.30	POM (> 53 μm)	9.93	0.15
201	ORG-RT	COMP	2011	0-0.30	SC (< 53 μm)	2.63	5.43
202	ORG-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	0.22	12.57
202	ORG-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	9.24	0.13
202	ORG-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	1.71	7.03
203	CONV-RT	COMP	2018	0-0.15	HF (> 53 μm)	1.48	13.79
203	CONV-RT	COMP	2018	0-0.15	POM (> 53 μm)	14.54	0.19
203	CONV-RT	COMP	2018	0-0.15	SC (< 53 μm)	3.84	5.37
204	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	1.10	13.74
204	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	11.92	0.18
204	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	3.45	5.67
205	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	0.53	11.60
205	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	19.26	0.21
205	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.68	7.71
206	CONV-RT	COMP	2011	0-0.30	HF (> 53 μm)	0.91	14.74
206	CONV-RT	COMP	2011	0-0.30	POM (> 53 μm)	7.40	0.28
206	CONV-RT	COMP	2011	0-0.30	SC (< 53 μm)	3.88	4.51
207	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	1.16	12.62
207	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	19.79	0.07
207	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	2.10	6.95
208	CONV-RT	COMP	2018	0-0.15	HF (> 53 μm)	0.89	14.55
208	CONV-RT	COMP	2018	0-0.15	POM (> 53 μm)	13.65	0.25
208	CONV-RT	COMP	2018	0-0.15	SC (< 53 μm)	4.77	4.70
209	CONV-RT	COMP	2018	0.15-0.30	HF (> 53 μm)	0.38	13.21
209	CONV-RT	COMP	2018	0.15-0.30	POM (> 53 μm)	8.61	0.16
209	CONV-RT	COMP	2018	0.15-0.30	SC (< 53 μm)	2.79	6.24
210	CONV-RT	COMP	2018	0.30-0.60	HF (> 53 μm)	1.22	12.03
210	CONV-RT	COMP	2018	0.30-0.60	POM (> 53 μm)	8.38	0.03
210	CONV-RT	COMP	2018	0.30-0.60	SC (< 53 μm)	1.48	7.57
211	CONV-RT	COMP	2011	0-0.30	HF (> 53 μm)	1.80	14.81
211	CONV-RT	COMP	2011	0-0.30	POM (> 53 μm)	9.55	0.34
211	CONV-RT	COMP	2011	0-0.30	SC (< 53 μm)	3.73	4.36
212	CONV-RT	COMP	2011	0.30-0.60	HF (> 53 μm)	0.67	12.86
212	CONV-RT	COMP	2011	0.30-0.60	POM (> 53 μm)	7.44	0.09
212	CONV-RT	COMP	2011	0.30-0.60	SC (< 53 μm)	3.80	6.47
213	ORG-RT	MINE	2018	0-0.15	HF (> 53 μm)	1.67	14.18
213	ORG-RT	MINE	2018	0-0.15	POM (> 53 μm)	12.30	0.32
213	ORG-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.13	5.00
214	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	2.21	14.62
214	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	10.94	0.13
214	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	4.43	4.87
215	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 μm)	0.65	12.41
215	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 μm)	3.65	0.19
215	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 μm)	1.71	7.04
216	ORG-RT	MINE	2011	0-0.30	HF (> 53 μm)	1.34	14.79
216	ORG-RT	MINE	2011	0-0.30	POM (> 53 μm)	12.14	0.40
216	ORG-RT	MINE	2011	0-0.30	SC (< 53 μm)	4.73	4.41
217	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 μm)	0.94	11.62
217	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 μm)	13.90	0.06
217	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 μm)	1.36	8.16
218	ORG-RT	MINE	2018	0-0.15	HF (> 53 μm)	1.18	16.07
218	ORG-RT	MINE	2018	0-0.15	POM (> 53 μm)	10.62	0.20
218	ORG-RT	MINE	2018	0-0.15	SC (< 53 μm)	4.27	3.45
219	ORG-RT	MINE	2018	0.15-0.30	HF (> 53 μm)	0.72	14.73
219	ORG-RT	MINE	2018	0.15-0.30	POM (> 53 μm)	11.69	0.12
219	ORG-RT	MINE	2018	0.15-0.30	SC (< 53 μm)	3.77	4.74

220	ORG-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	0.28	12.41
220	ORG-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	8.97	0.14
220	ORG-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.95	7.17
221	ORG-RT	MINE	2011	0-0.30	HF (> 53 µm)	0.94	14.98
221	ORG-RT	MINE	2011	0-0.30	POM (> 53 µm)	10.75	0.11
221	ORG-RT	MINE	2011	0-0.30	SC (< 53 µm)	4.10	3.71
222	ORG-RT	MINE	2011	0.30-0.60	HF (> 53 µm)	0.19	13.14
222	ORG-RT	MINE	2011	0.30-0.60	POM (> 53 µm)	6.53	0.13
222	ORG-RT	MINE	2011	0.30-0.60	SC (< 53 µm)	1.63	6.03
223	CONV-RT	MINE	2018	0-0.15	HF (> 53 µm)	0.38	15.00
223	CONV-RT	MINE	2018	0-0.15	POM (> 53 µm)	9.67	0.25
223	CONV-RT	MINE	2018	0-0.15	SC (< 53 µm)	4.21	4.25
224	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 µm)	1.41	15.56
224	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 µm)	9.46	0.22
224	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 µm)	4.15	3.93
225	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	0.66	12.94
225	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	11.04	0.13
225	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.70	6.56
226	CONV-RT	MINE	2011	0-0.30	HF (> 53 µm)	0.23	14.47
226	CONV-RT	MINE	2011	0-0.30	POM (> 53 µm)	9.03	0.27
226	CONV-RT	MINE	2011	0-0.30	SC (< 53 µm)	5.06	4.68
227	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 µm)	0.83	12.42
227	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 µm)	6.09	0.09
227	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 µm)	1.59	7.35
228	CONV-RT	MINE	2018	0-0.15	HF (> 53 µm)	0.91	14.57
228	CONV-RT	MINE	2018	0-0.15	POM (> 53 µm)	11.19	0.30
228	CONV-RT	MINE	2018	0-0.15	SC (< 53 µm)	3.82	4.46
229	CONV-RT	MINE	2018	0.15-0.30	HF (> 53 µm)	1.23	14.24
229	CONV-RT	MINE	2018	0.15-0.30	POM (> 53 µm)	9.29	0.13
229	CONV-RT	MINE	2018	0.15-0.30	SC (< 53 µm)	2.83	5.22
230	CONV-RT	MINE	2018	0.30-0.60	HF (> 53 µm)	0.55	12.30
230	CONV-RT	MINE	2018	0.30-0.60	POM (> 53 µm)	9.49	0.14
230	CONV-RT	MINE	2018	0.30-0.60	SC (< 53 µm)	1.43	7.07
231	CONV-RT	MINE	2011	0-0.30	HF (> 53 µm)	0.53	15.64
231	CONV-RT	MINE	2011	0-0.30	POM (> 53 µm)	9.08	0.29
231	CONV-RT	MINE	2011	0-0.30	SC (< 53 µm)	3.14	3.36
232	CONV-RT	MINE	2011	0.30-0.60	HF (> 53 µm)	0.22	11.93
232	CONV-RT	MINE	2011	0.30-0.60	POM (> 53 µm)	8.97	0.14
232	CONV-RT	MINE	2011	0.30-0.60	SC (< 53 µm)	1.95	7.79

Table A3.3. All pyrolysed product compounds released after Py-GC-MS-TMAH analytical procedures and used for identification and quantification from the extracted solid residue at 0-0.30 and 0.30-0.60 m soil depth intervals. Assignments based on Abbott *et al.* 2013 and Schellekens *et al.* 2015a,b.

Name	RT (min)	Layer (m) 0-0.30	0.30-0.60	CODE	Name	RT (min)	Layer (m) 0-0.30	0.30-0.60	CODE
Alkanes					**Lignin Phenols**				
Cyclododecane	23.19	x		AKA1	1,2,3-Trimethoxybenzene	27.57	x	x	LP1
Cycloeicosane	52.27	x		AKA2	1,2,4-Trimethoxybenzene	29.54	x	x	LP2
Cyclohexane, 1-(1,5-dimethylhexyl)-4-(4-methylpentyl)-	46.93	x		AKA3	1,3-Cyclopentadiene, 5-(1-methylethylidene)-	12.24		x	LP3
Cyclohexanone, 2-butyl-	46.54	x		AKA4	2-Propenoic acid, 3-(3,4-dimethoxyphenyl)-, methyl ester	44.41	x	x	LP4
Cyclopentadecane	49.26	x		AKA5	2-Propenoic acid, 3-(4-methoxyphenyl)-, methyl ester	38.98	x		LP5
Cyclopentadecanone, 2-hydroxy-	49.90	x		AKA6	2-Propenoic acid, 3-phenyl-, methyl ester	30.13	x		LP6
Cyclopropane, 1,2-dibutyl-	19.45	x		AKA7	3',5'-Dimethoxyacetophenone	39.93	x		LP7
Cyclopropane, 1-pentyl-2-propyl-	19.46	x		AKA8	Acetophenone, 4'-methoxy-	29.18	x		LP8
Cyclotetradecane	52.26	x		AKA9	Benzaldehyde, 2,4,5-trimethoxy-	36.86		x	LP9
Alkenes					Benzaldehyde, 3,4,5-trimethoxy-	36.86	x		LP10
1,3,12-Nonadecatriene	50.27	x		AKE1	Benzaldehyde, 3,4-dimethoxy-	33.14	x		LP11
1,3,5,7-Cyclooctatetraene	12.13	x	x	AKE2	Benzaldehyde, 3-methoxy-	23.74	x	x	LP12
1,3,5-tris(cyclohexyl)pent-1-ene	46.91	x		AKE3	Benzaldehyde, 4-methoxy-	25.79	x		LP13
13-Methyl-*Z*-14-nonacosene	55.72	x		AKE4	Benzene, 1,2,3-trimethoxy-5-(2-propenyl)-	38.15	x		LP14
1-Eicosene	51.50	x		AKE5	Benzene, 1,2-dimethoxy-	21.58	x	x	LP15
1-Heptadecene	41.86	x		AKE6	Benzene, 1,2-dimethyl-	12.23	x		LP16
1-Octadecene	41.86	x		AKE7	Benzene, 1,3,5-trimethoxy-	30.88	x		LP17
1-Undecene	19.46	x		AKE8	Benzene, 1,3-dimethoxy-	22.48	x		LP18
3-Heptadecene, (*Z*)-	40.54	x		AKE9	Benzene, 1,3-dimethyl-	11.38	x	x	LP19
5-Eicosene, (*E*)-	52.27	x		AKE10	Benzene, 1,4-dimethoxy-	22.31	x	x	LP20
9-Hexacosene	63.87	x		AKE11	Benzene, 1,4-dimethoxy-2-methyl-	25.42	x		LP21
9-Tricosene, (*Z*)-	56.43	x		AKE12	Benzene, 1-ethenyl-4-methoxy-	21.96	x		LP22
Methyl *Z*-11-tetradecenoate	46.54	x		AKE13	Benzene, 1-methoxy-2-methyl-	16.49	x	x	LP23
Z,*Z*-3,13-Octadecadien-1-ol acetate	50.20	x		AKE14	Benzene, 1-methoxy-4-methyl-	16.90	x	x	LP24
Z-7-Pentadecenol	49.27	x		AKE15	Benzene, 4-ethenyl-1,2-dimethoxy-	29.40	x		LP25
Aromatics					Benzene, methoxy-	13.04	x	x	LP26

1,1'-Biphenyl, 4-methyl-	33.50		x	AR1	Benzoic acid, 3,4,5-trimethoxy-, methyl ester	40.15	x	x	LP27
2,2',5,5'-Tetramethoxydiphenyl	50.99	x		AR2	Benzoic acid, 3,4-dimethoxy-, methyl ester	36.46	x	x	LP28
2,5-Dimethoxybenzoic acid	36.98	x		AR3	Benzoic acid, 3-methoxy-, methyl ester	28.61	x	x	LP29
2-Methylseleno-3-benzo[B]thiophenecarboxaldehyde	32.56	x		AR4	Benzoic acid, 4-methoxy-, methyl ester	29.84	x	x	LP30
Acetophenone	18.78		x	AR5	Ethanone, 1-(3,4,5-trimethoxyphenyl)-	39.08	x	x	LP31
Asarone	38.89	x		AR6	Ethanone, 1-(3,4-dimethoxyphenyl)-	35.72	x		LP32
Benzene	6.18		x	AR7	**N compounds**				
Benzene, 2-propenyl-	17.17	x		AR8	1-(2-Hydroxyethyl)-3,6-diazahomoadamantane	36.16	x		N1
Ethylbenzene	11.11	x	x	AR9	1,3,5-Triazine-2,4,6(1*H*,3*H*,5*H*)-trione, 1,3,5-trimethyl-	30.07	x	x	N2
Indene	17.99	x	x	AR10	1*H*-Indole, 1,2,3-trimethyl-	34.99		x	N3
Methyl p-methoxycinnamate, cis	38.98	x	x	AR11	1*H*-Indole, 1,3-dimethyl-	29.70	x	x	N4
p-Xylene	11.34	x	x	AR12	1*H*-Indole, 1-methyl-	26.41	x	x	N5
Styrene	12.13	x	x	AR13	1*H*-Indole, 5-methoxy-2-methyl-	32.26	x		N6
Toluene	8.31	x	x	AR14	1*H*-Isoindole-1,3(2*H*)-dione, 2-methyl-	31.54	x		N7
Benzofurans					1*H*-Pyrrole, 1-methyl-	7.61	x		N8
Benz[e]azulene-3,8-dione, 5-[(acetyloxy)methyl]-3a,4,6a,7,9,10,10a,10b-octahydro-3a,10a-dihydroxy-2,10-dimethyl-, (3a.alpha.,6a.alpha.,10.beta.,10a.beta.,10b.beta.)-(+)-	75.63	x	x	BZ1	1*H*-Pyrrole, 2,3,4,5-tetramethyl-	19.61		x	N9
Benzofuran	16.12	x	x	BZ2	1*H*-Pyrrole, 2,3,5-trimethyl-	15.02		x	N10
Benzofuran, 2-methyl-	20.39	x	x	BZ3	1*H*-Pyrrole, 2,5-dimethyl-	10.20	x	x	N11
Dibenzofuran	34.65	x	x	BZ4	1*H*-Pyrrole-2-carboxaldehyde, 1-methyl-	16.37	x	x	N12
Carbohydrates					2,3,7-Trimethylindole	34.99		x	N13
1*H*,3*H*-Pyrano[3,4-c]pyran-5-carboxaldehyde, 4,4a,5,6-tetrahydro-6-methyl-1-oxo-, [4as-(4a.alpha.,5.alpha.,6.beta.)]-	41.42	x		CB1	2,5-Pyrrolidinedione, 1-methyl-	19.70	x		N14
1*H*-Inden-1-one, 2,3-dihydro-3-methyl-	27.65	x		CB2	2*H*-1,4-Benzothiazin-3(4*H*)-one, 4-hydroxy-2-methyl-, 1,1-dioxide	45.35	x		N15
1*H*-Indene, 1,1-dimethyl-	25.95		x	CB3	2-Propenenitrile, 3-phenyl-, (*E*)-	27.11	x		N16
1*H*-Indene, 1-methyl-	21.98		x	CB4	4-Amino-4'-hydroxystilbene	44.15	x		N17
1*H*-Indene, 1-methylene-	23.35	x		CB5	4-Nitrocatechol	35.51	x	x	N18
1*H*-Indene, 3-methyl-	21.98		x	CB6	4-Pyridinamine, N-cyclohexyl-3-nitro-	45.67	x		N19

1*H*-Indene-1,3(2H)-dione, 2-hydroxy-2-(9-methoxy-9*H*-fluoren-9-yl)-	41.51	x		CB7	9H-Purin-6-amine, N,N,9-trimethyl-	40.35	x	x	N20
2-Cyclopenten-1-one, 2-methyl-	12.68	x	x	CB8	Aziridine, 1-(O-chlorobenzoyl)-2-methyl-	41.24	x		N21
2-Furancarboxaldehyde, 5-methyl-	14.74	x		CB9	Benzyl nitrile	21.46	x	x	N22
2-Methylindene	22.17		x	CB10	Butalbital	44.71	x		N23
Furan, 2,5-dimethyl-	6.77	x		CB11	Cyclopropanecarboxaldehyde, 1-methyl-2,2-diphenyl-	50.11	x		N24
Fatty Acids					p-Methoxybenzamide	34.72	x		N25
10,13-Octadecadienoic acid, methyl ester	54.45	x		FA1	Propane-1,3-diol 2-nitro-4-carboxy-benzeneboronate	55.83	x		N26
10-Nonadecenoic acid, methyl ester	52.02	x		FA2	Pyridine, 2-methyl-	9.98	x		N27
11,14-Octadecadienoic acid, methyl ester	54.45	x		FA3	Pyridine, 3-methyl-	11.47		x	N28
11-Hexadecenoic acid, 15-methyl-, methyl ester	47.41	x		FA4	**Phenols**				
11-Hexadecenoic acid, methyl ester	50.67	x		FA5	Phenol	15.56	x	x	PH1
11-Octadecenoic acid, methyl ester	49.50	x		FA6	Phenol, 2,4-dimethyl-	21.79	x	x	PH2
11-Octadecenoic acid, methyl ester, (*Z*)-	49.61	x		FA7	Phenol, 2,5-dimethyl-	21.82	x		PH3
15-Octadecenoic acid, methyl ester	50.67	x		FA8	Phenol, 2,6-dimethoxy-	29.01	x		PH4
7,10-Octadecadienoic acid, methyl ester	50.27	x		FA9	Phenol, 2-methyl-	18.25	x	x	PH5
7-Octadecenoic acid, methyl ester	49.48	x		FA10	Phenol, 3-methyl-	19.05	x	x	PH6
8,11-Octadecadienoic acid, methyl ester	51.36	x		FA11	Phenol, 4-ethyl-3-methyl-	20.49	x		PH7
8-Octadecenoic acid, methyl ester	49.49	x		FA12	Phenol, 4-methyl-	19.08	x	x	PH8
9,12-Octadecadienoic acid (*Z,Z*)-, methyl ester	54.45	x		FA13	**Polyaromatics**				
9,12-Octadecadienoic acid, methyl ester	54.45	x		FA14	11H-Benzo[b]fluorene	52.83	x		PA1
9,12-Octadecadienoic acid, methyl ester, (*E,E*)-	51.41	x		FA15	2(1*H*)-Naphthalenone, octahydro-4a-methyl-7-(1-methylethyl)-, (4a.alpha.,7.beta.,8a.beta.)-	44.22	x		PA2
9,15-Octadecadienoic acid, methyl ester, (*Z,Z*)-	51.34	x		FA16	9*H*-Fluoren-9-one	41.15	x		PA3
9-Hexadecenoic acid, methyl ester, (*Z*)-	44.80	x		FA17	9*H*-Fluorene, 2-methyl-	39.92		x	PA4
9-Octadecenoic acid (*Z*)-, methyl ester	49.60	x	x	FA18	9*H*-Fluorene, 9-methylene-	42.32	x		PA5
9-Octadecenoic acid, methyl ester	49.61	x		FA19	Anthracene	42.32		x	PA6
9-Octadecenoic acid, methyl ester, (*E*)-	49.48	x		FA20	Benzocycloheptatriene	27.93	x	x	PA7
9-Octadecynoic acid, methyl ester	50.27	x		FA21	Biphenyl	30.13		x	PA8

Cyclopropaneoctanoic acid, 2-[[2-[(2-ethylcyclopropyl)methyl]cyclopropyl]methyl]-, methyl ester	50.27	x		FA22	Fluorene	36.67	x	x	PA9
Cyclopropaneoctanoic acid, 2-hexyl-, methyl ester	46.28	x		FA23	Naphthalene	23.35	x	x	PA10
Cyclopropaneoctanoic acid, 2-octyl-, methyl ester	52.03	x		FA24	Naphthalene, 1,4-dimethyl-	32.69		x	PA11
Cyclopropaneoctanoic acid, 2-octyl-, methyl ester, trans-	52.03	x		FA25	Naphthalene, 1-methyl-	27.31		x	PA12
Docosanoic acid, methyl ester	58.39	x		FA26	Naphthalene, 2,6-dimethyl-	31.01		x	PA13
Eicosanoic acid, methyl ester	54.37	x		FA27	Naphthalene, 2,7-dimethyl-	31.51		x	PA14
Heptadecanoic acid, 10-methyl-, methyl ester	47.80	x		FA28	Naphthalene, 2-ethenyl-	30.12		x	PA15
Hexacosanoic acid, methyl ester	65.58	x		FA29	Naphthalene, 2-methyl-	27.91	x	x	PA16
Hexadecanoic acid, 14-methyl-, methyl ester	46.34	x		FA30	Phenanthrene	42.32	x	x	PA17
Hexadecanoic acid, 9-methyl-, methyl ester	46.35	x		FA31					
Hexadecanoic acid, methyl ester	45.27	x		FA32					
Methyl 9-methyltetradecanoate	34.27	x		FA33					
Methyl tetradecanoate	40.05	x	x	FA34					
Nonanedioic acid, dimethyl ester	34.99	x		FA35					
Octadecanoic acid, 10-methyl-, methyl ester	50.90	x		FA36					
Octadecanoic acid, methyl ester	50.01	x		FA37					
Octanedioic acid, dimethyl ester	31.87	x	x	FA38					
Pentadecanoic acid, 14-methyl-, methyl ester	45.28	x	x	FA39					
Pentadecanoic acid, methyl ester	41.75	x	x	FA40					
Tetracosanoic acid, methyl ester	62.11	x		FA41					
Tetradecanoic acid, 12-methyl-, methyl ester	41.98	x		FA42					
Tricosanoic acid, methyl ester	60.29	x		FA43					
Tridecanoic acid, 12-methyl-, methyl ester	40.06	x		FA44					

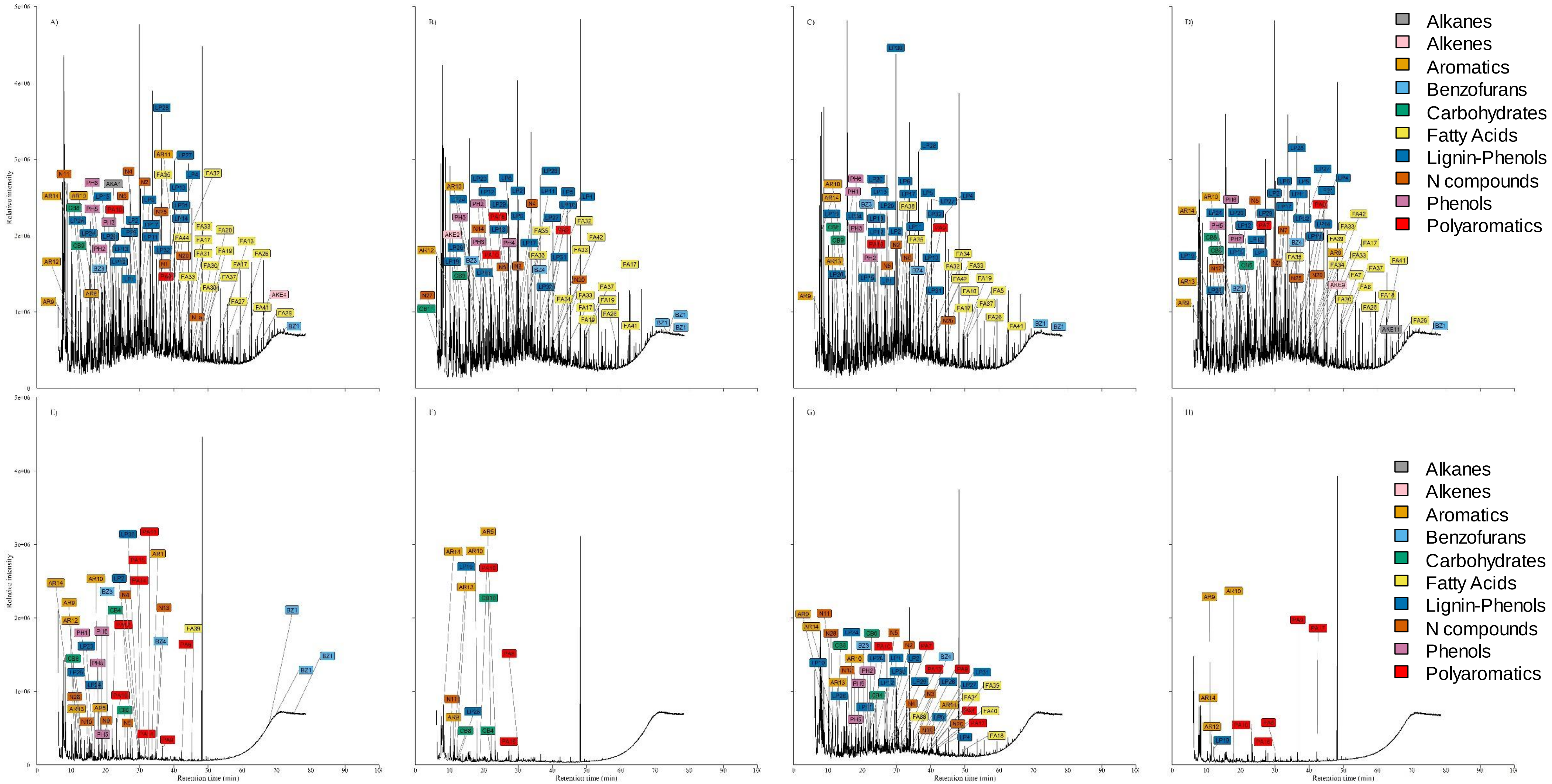

Figure A3.4. Py-GC-MS-TMAH examples of representative chromatograms from the extracted solid residue of the conventional rotation (A and E), organic rotation (B and F), mineral fertiliser (C and G) and compost fertiliser (D and H) at 0-0.30 (A, B, C, D) and 0.30-0.60 m (E, F, G, H) soil depth intervals. See Table A3.3 for codes.

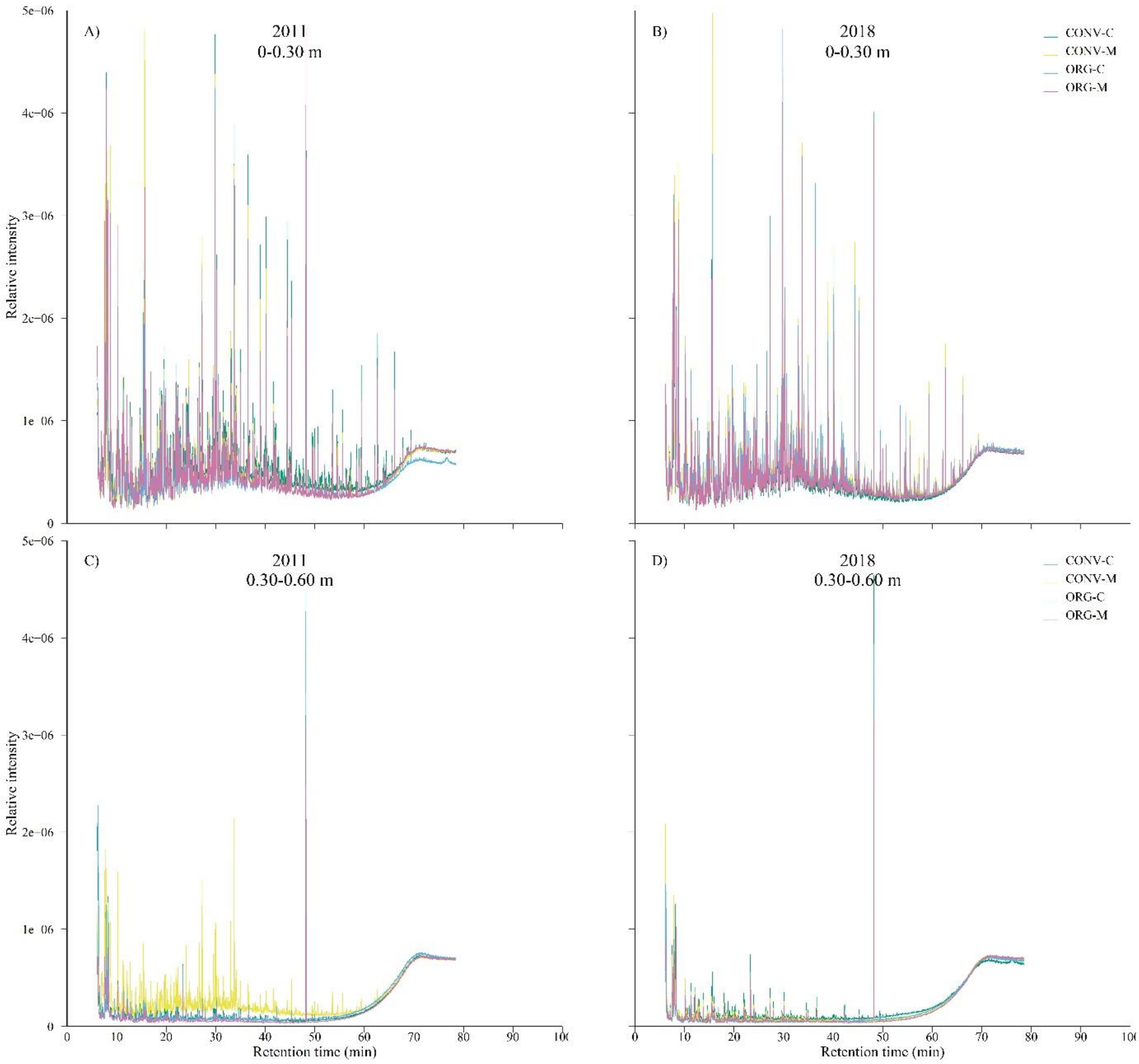

Figure A3.5. Py-GC-MS-TMAH chromatograms from the extracted solid residue of the combined treatment factors: conventional rotation with mineral fertilisation (CONV-M), conventional rotation with compost fertilisation (CONV-C), organic rotation with mineral fertilisation (ORG-M) and organic rotation with compost fertilisation (ORG-C) at 0-0.30 (A and B) and 0.30-0.60 m (C and D) soil depth intervals and different years of sampling 2011 (A and C) and 2018 (B and D).