CRANFIELD UNIVERSITY

Jonah Matthew Prout

A Soil Organic Carbon Indexing and Measurement System

School of Water, Energy & Environment
PhD Environment and Agrifood

PhD
Academic Year: 2017 - 2021

Supervisor: Professor Guy JD Kirk
Associate Supervisor: Dr Stephan M Haefele
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This thesis is submitted in partial fulfilment of the requirements for the degree of PhD

ABSTRACT

Soil organic carbon (SOC) is an important component of soils for the various goods and services that soils perform. But SOC stocks have declined significantly in soils around the world over many years due to poor land management. To enable land managers and policy makers to manage SOC better, simple guideline values and measures of SOC concentration are needed. An index based on the SOC to clay concentration ratio as related to soil structural conditions was tested for soils across England and Wales using data from the National Soil Inventory (NSI). Threshold values of SOC/clay equal to 1/8, 1/10 and 1/13 indicated Very Good, Good, Moderate and Degraded levels of SOC. Land use was a driver of SOC/clay ratio, with 38% of arable soils classed as Degraded compared with < 7% of permanent grass or woodland soils. To examine how SOC/clay ratios have been changing over time, I analysed data from resampled sites in the NSI (mean interval of 15 years). The Very Good class was particularly vulnerable to losses compared with other classes. This finding agrees with SOC protection being limited by soil clay concentration. Long-term experiments on soils of contrasting clay concentration showed that the index was sensitive to management activities. In further work I explored the use of dry soil spectral analysis to measure SOC and clay concentrations. I compared dry spectral and conventional wet laboratory analyses of soils in the NSI and in the US National Soil Survey Center-Kellogg Soil Survey Laboratory spectral library (NSSC-KSSL). The NSSC-KSSL results, and to a lesser extent the NSI results (which used older, less-accurate wet laboratory analyses), showed that the technique is suitable for assigning soils to Very Good, Degraded, or Good/Moderate ranges. The index provides quantitative guideline concentrations for SOC with a functional basis and scope for rapid assessment.

Keywords:
Land use, clay concentration, soil structure, soil organic matter, long-term experiments, national soil inventory, soil monitoring, MIR spectral library.

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LIST OF ABBREVIATIONS

D	Degraded (index class)
G	Good (index class)
M	Moderate (index class)
MIRS	Mid-infrared spectroscopy
NCC	Non-complexed clay
NSI	National Soil Inventory of England and Wales
NSSC-KSSL	National Soil Survey Center – Kellog Soil Survey Laboratory
PLSR	Partial least squares regression
SOC	Soil organic carbon
VG	Very Good (index class)
vis-NIRS	Visible-near infrared spectroscopy

1 Introduction

1.1 Soil Organic Carbon

Soil organic carbon (SOC) is one of the key components of a soil and underpins many important soil properties and functions. On a global scale, soils are estimated to hold more than twice the amount of carbon as in the atmosphere and terrestrial vegetation combined. Soil carbon can be in the form of inorganic as well as organic matter, and the organic portion can be further sub-divided into overlapping particulate, biological, mineral-associated and dissolved portions. As soils are dynamic biological systems, SOC moves between and within these different "pools" at varying rates depending on biotic and abiotic variables. These include the nature and activities of biological communities, the quantity and quality of carbon inputs, and the soil air and water contents, temperature, pH, and texture. Millenia of human activity have led to an estimated loss of 116 Pg C from soils (Sanderman, Hengl and Fiske, 2017, 2018), and soils in many parts of the world continue to lose carbon as a result of poor management (Lal, 2018). There is an urgent need to address such losses and if possible, to increase SOC stocks globally to contribute to climate change mitigation, food security, and to protect soils for future generations.

In response to this need, initiatives such as the 4 per 1000 (Minasny et al., 2017; Soussana et al., 2019) have been proposed, which seeks to increase SOC stocks globally by 0.4% per year (based on a 2m depth calculation) to offset man-made emissions of CO_2 and other greenhouse gases. Such initiatives give admirable goals, but face criticism from various angles, including the availability of organic matter (Poulton et al., 2018), nitrogen limitations (Van Groenigen et al., 2017), the finite capacity of soils under given land uses to accumulate SOC (Smith, 2014), and the rapid reversibility of changes in SOC stocks (Smith, 2005). Effective soil carbon sequestration from the atmosphere requires a net, long-term removal of carbon globally to be stored in soil in organic or inorganic forms or both (Haque, Santos and Chiang, 2020; Monger et al., 2015; Olson et al., 2014; Powlson, Whitmore and Goulding, 2011). Accumulation of SOC, even if not net long-term sequestration, could improve soils to better perform functions other than removing atmospheric CO_2, such as water storage for reducing risk of flooding or drought, nutrient cycling, supporting biological diversity, and providing food, fibre and fuel. Agricultural soils with above-average SOC concentrations tend to be lighter, more resistant to compaction, and have better pore structure for water infiltration, storage and, as habitats for micro- and meso-fauna.

However, because soil systems are dynamic, it is important for SOC levels to be monitored to avoid losses and best direct organic resources. Long-term experiments provide benchmark sites that are a rich source of information for this, in that they allow repeated measurements over time giving insights into the long-term effects of management practices and the feasibility of soil initiatives and frameworks (e.g. the 4 per 1000; (Poulton et al., 2018; Smith et al., 2020)). At a larger scale, national soil surveys can provide an accounting of the state of soils at the time of sampling and, with repeated samplings, they can be used to assess large-scale changes and trends. But, the diversity of soils and their uses can make it difficult to assign critical threshold SOC concentrations against which to monitor changes (as reviewed by Loveland and Webb, 2003). Indices of SOC concentration are needed based on variables that can be determined with sufficient accuracy and resolution in time and space in national surveys to detect changes. Policies for soil management need to be set at regional to national scales but enacted at local scales. Therefore, both scales need to be considered. In this thesis I use data from the National Soil Inventory of England and Wales (NSI) and from long-term experiments on soil management run by Rothamsted Research to develop a simple index for monitoring SOC at local and national scales and I assess practical methods for measuring the index.

1.2 The National Soil Inventory of England and Wales

The National Soil Inventory of England and Wales (NSI) was carried out to provide grid-based information in support of the landscape-based Soil Survey of England and Wales (Soil Survey Staff, 1983). It was originally sampled between 1978 to 1983 on a 5 km grid across the whole of England and Wales, excluding water bodies and urban areas. The soil was sampled to a fixed-depth of 0–15 cm and analysed for a range of chemical elements. The full results are available via the LandIS soil information system (Proctor et al., 1998) and the Advanced Soil Geochemical Atlas of England and Wales (Rawlins et al., 2012). The dataset includes SOC concentrations, soil particle size fractions and pH, as well as site characteristics such as land use, aspect, slope and soil subgroup. The original sampling was made at 5686 sites. Approximately 40% of the sites were resampled after 11–25 years, depending on land use. The results have been used to investigate national scale changes in SOC over time (Bellamy et al., 2005) and also changes in soil pH (Kirk, Bellamy and Lark, 2010). Bellamy et al. (2005) found widespread losses of carbon from soils across a range of soil types and land uses between the two NSI samplings (1978–2003). The SOC concentrations of soils which originally had low values (< 20 g kg^{-1}) tended to increase. But, with higher SOC concentrations, losses tended to increase, and overall there was a large net loss. The widespread distribution of the losses across land uses suggested a possible link to climate change and accelerated turnover of SOC with increased temperature. But, modelling results showed that changes in land management activities were a stronger driver of the changes than climate change (Kirk and Bellamy, 2010; Smith et al., 2007). The Countryside Survey of Great Britain which was carried out over a similar timeframe (Emmett et al., 2010) did not detect the same degree of carbon losses as the NSI, only finding a consistent decrease for soils under arable and horticultural land use. However, the Countryside Survey used a different sampling design, and there were changes in sampling methods between the surveys at different times (Kirk et al., 2011). A subsequent sampling of the Countryside Survey did reveal net SOC losses over the period 1998–2007 (Reynolds et al., 2013).

1.3 SOC Guidelines

Guidelines for SOC need to be quantitative measures which can be assessed and monitored to support soil managers and policy makers, for example through payment schemes, assessing resource allocations, and/or ensuring that soils are productive and resilient for the future. Policy tends to rely on more-qualitative measures, such as supporting practices which are expected to mitigate SOC losses, but these do not call for direct soil measurements nor account for the various factors which might impact SOC (e.g. soil type, texture, climate). Land managers (e.g. farmers) will often send soils for testing to manage fertiliser use and liming requirements, so SOC guidelines could be used in a similar manner to these. For England and Wales the current rule-of-thumb for a “good” SOC concentration is 1–2% for agricultural soils, based on the effects of SOC on aggregate stability (Greenland, Rimmer and Payne, 1975). The review of Loveland and Webb (2003), however, found little quantitative evidence to support the use of this threshold. More recent work utilised the NSI to identify typical ranges of SOC for arable and ley-arable soils based on clay concentration and precipitation classes

(Verheijen et al., 2005). This work tested the influence of a range of variables which might impact SOC, finding that clay concentration, annual precipitation and depth of topsoil explained 25.5% of the variation in SOC concentration. Statistically robust ranges of SOC concentration were applied to combinations of precipitation class (dry < 650, intermediate 650–800, wet 800–1100 mm yr^{-1}) and clay ranges of 10%, with the implication that these might define achievable limits for similar soils. The ranges suggested that SOC concentration should be higher with increasing clay concentration and/or wetter precipitation class. Whilst not necessarily generated as an assessment metric these ranges were based on relatively routine soil measurements (SOC and texture) and readily available weather data.

In preliminary works for this thesis, I used the RothC soil organic matter model (Coleman and Jenkinson, 1996) to assess how to take this concept further. RothC is a semi-empirical pool-based model with first-order decomposition kinetics, developed at Rothamsted Research using data from long-term experiments. The input variables are SOC concentration, soil bulk density (or an estimate provided by a pedotransfer function) and soil clay concentration, together with information on climate, carbon inputs from plants and farmyard manure, and crop management, including soil preparation and crop cover. I attempted to use this model with the NSI data to provide modelled ranges for various land use scenarios, with the distance from the theoretical steady-state SOC concentration providing a metric for SOC assessment. The results were not successful, in part due to the broad land use categories of the NSI, and I have not included them in the thesis. However, this work did give insights useful for the eventual route of the work.

The standard version of RothC calculates steady-state SOC stocks without a saturation limit. Whilst SOC stocks of soils might in principle increase indefinitely, as in the case of peats where great depths may accumulate, under most land use and climate conditions, soils do not become peats but reach some saturation point. This may be because of an inherent constraint, for example because the protecting capacity of soil clays is exceeded, or because of an imposed management or climatic restraint. The SOC saturation concept has been proposed based on soil texture (Hassink, 1996, 1997) and a whole-soil SOC saturation was conceptualized by Six et al. (2002) which was investigated mathematically by Stewart et al. (2007). An attempt to apply the mathematical saturation equation to RothC directly was not very successful in accounting for observed data (Heitkamp et al., 2012). However, if a soil could become saturated in SOC, at least in some SOC pool, this could form a measurable metric. Another modelling study successfully used clay concentration and fine-silt to define SOC pool limits, on the basis that SOC stabilisation by mineral association is limited by particle surface areas (Hassink and Whitmore, 1997).

1.4 Clay and SOC

Clay-sized particles (<2 µm diameter) are part of the mineral component of soils and generally consist of layer silicates (such as kaolinite, smectite, and illite), chain silicates, and sesquioxides. Clay mineralogy depends on parent material and weathering characteristics of a soil, and affects properties such as shrink-swell behaviour, cation exchange capacity and surface sorption processes. Charge properties of clay surfaces affect the physical characteristics of soils, including interactions of clay particles with themselves, water and organic matter. For the most part, mineralogy is not considered in soil assessment and modelling, because it is difficult and expensive to measure reliably. As mentioned previously, SOC concentration is expected to have a positive relationship with clay concentration due to interactions between clay and organic matter resulting in SOC protection from microbial decomposition. Conventional theory of SOC persistence in soil focused on the chemical recalcitrance of organic compounds. This of course plays some part, but there is now a greater emphasis on physical protection of SOC by association with mineral matter (Dungait et al., 2012). Association with clay particles can protect SOC against mineralisation via occlusion in macro- and microaggregates, and adsorption of SOC to clay particles. Soil mineralogy may affect this protection and therefore clay concentration as such is not always the best measure of SOC protection (Rasmussen et al., 2018). Nonetheless, research has shown consistent relationships between SOC/clay ratios and soil physical properties and structure (Czyz et al., 2017; Dexter et al., 2008; Getahun, Munkholm and Schjønning, 2016; Johannes et al., 2017; De Jonge, Moldrup and Schjonning, 2009; Schjønning et al., 2012). This gives scope for using clay concentration to define whether a soil is deficient in SOC for functions reliant on soil structure as well as to give a gauge of minimum C storage potential.

Dexter et al. (2008) explored the interaction between organic matter and clay particles in relation to soil physical properties (bulk density, matrix porosity, clay dispersibility) in Polish and French soil databases, and found an approximate capacity for the interaction of SOC and clay particles to be at a clay/SOC ratio of 10. They did not suggest this as a limit for SOC accumulation. But, based on the effects of soil physical properties, they suggested a possible limit to an SOC-mineral interaction which in theory would relate to protection capacities. Readily dispersible clay increased with "non-complexed" clay concentration (i.e. a fraction of clay not associated with organic matter). This is consistent with organic matter acting as a glue for clay particles and aggregate formation. Subsequent research has tested these concepts. In a long-term experiment site in Denmark, non-complexed clay (NCC, defined as NCC = clay – 10×SOC) was shown to be more related to the tensile strength and related parameters of natural aggregates than total clay and SOC (though this was not the case for remoulded aggregates) (Getahun, Munkholm and Schjønning, 2016). Correlations of dispersed clay against total clay and NCC also supported Dexter et al. (2008), showing a positive relationship in both cases but the R^2 was greater using NCC and varying the ratio to define NCC agreed with clay/SOC = 10 as a general threshold (Schjønning et al., 2012).

The clay/SOC ratio was also studied in the context of soil structure, showing contrasting structures of soils depending on having clay/SOC greater than or less than 10 (De Jonge, Moldrup and Schjonning, 2009). They linked greater NCC to cementation effects resulting in instability under wet conditions and hard, strong aggregates under dry conditions. Their investigation of pore architecture suggested that a pipe-like pore structure may be the result for a low C soil with NCC compared with a sponge-like structure for a high C soil without NCC. Such relationships between relative amounts of SOC and clay with structure were tested by (Johannes et al., 2017). This study was conducted on a regional dataset from western Switzerland with an aim of accounting for structural quality and soil type. The soils selected for sampling were of a single soil classification, developed on the same parent material and sampled at 5-10 cm depth, including soils under pasture, ploughed or no-till practices. Visual evaluation of soil structure on core samples suggested that four classes could be defined: SOC/clay > 1/8, 1/8–1/10, 1/10–1/13, and < 1/13, indicating very good, good, improvement suggested and bad structural quality. The use of SOC/clay is a logical inversion of the clay/SOC (1/10 in the former equals 10 in the latter) from a management perspective since SOC is the property which is actively managed and changes over shorter timescales than soil texture.

These studies suggested that the relative amounts of SOC and clay might be a solid foundation for a metric for SOC assessment and monitoring with implications for soil structure, as well as providing a measure of a capacity for protection of SOC.

1.5 Measuring and Monitoring SOC

To monitor, assess and inform management of SOC soil testing needs to be readily accessible at multiple scales from individual field mapping to national assessments. Current methods of SOC measurement are costly and time consuming, particularly the most accurate methods involving dry combustion analysis. Likewise, conventional methods for measuring soil clay concentration are expensive and laborious. Spectral techniques provide a potential solution to this, requiring minimal sample processing (typically drying and grinding) and having high throughput capabilities, short scan times, lower running costs and the capability to determine a range of properties simultaneously. The latter depends on developing calibration models relating spectra to reference data. Infrared spectroscopy has been tested quite extensively for soil analyses (Janik, Merry and Skjemstad, 1998; McCarty et al., 2002; Nocita et al., 2015; Reeves, 2010, 2012; Shepherd and Walsh, 2007). Commonly, visible-near-infrared spectroscopy (vis-NIRS) has been used due to affordability of instruments and scope for in-field testing. However, mid-infrared spectroscopy (MIRS) has been shown to give better predictive performance for SOC and clay concentrations (Reeves, 2010). For MIRS to be cost effective, spectral libraries need to be developed covering large sampling areas to capture variation in soil properties. There are examples at national scale for France (Clairotte et al., 2016; Grinand et al., 2012), and the USA (Dangal et al., 2019; Sanderman, Savage and Dangal, 2020). Considering the use of spectroscopy for assessing SOC/clay ratios, Hermansen et al. (2016) found very good predictions could be achieved for clay/SOC ratios in a regional scale study of Danish and Greenlandic soils considering a clay/SOC = 10 threshold. It will be of interest to see how well SOC/clay ratios can be predicted using national-scale data.

1.6 Aims and Objectives

1.6.1 Aim

The overall aims are to develop a simple index for assessing the organic carbon status of soils across England and Wales, suitable for application at local and national scales, and to explore the use of dry spectral methods to quantify the components of the index. Towards these ends there are four main objectives as follows.

1.6.2 Objective 1

To investigate the use of an index of soil organic carbon (SOC) status based on SOC/clay concentration ratios for soils under contrasting land uses using data in the National Soil Inventory (NSI) of England and Wales. (Chapter 2)

1.6.3 Objective 2

To investigate the use of the SOC index based on SOC/clay concentration ratios to monitor changes in SOC over time using data in the NSI and long-term experiments on organic management. (Chapter 3)

1.6.4 Objective 3

To investigate the sensitivity of thresholds in the SOC/clay index to agricultural management activities. (Chapters 2 and 3)

1.6.5 Objective 4

To investigate how well SOC concentration, clay concentration and SOC/clay concentration ratio can be predicted using a mid-infrared (MIR) spectra for soils in the National Soil Inventory and an established spectral library for US soils. (Chapter 4)

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2 AN INDEX BASED ON ORGANIC CARBON TO CLAY RATIO*

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2.1 Abstract

Simple measures of appropriate levels of soil organic matter are needed for soil evaluation, management, and monitoring, based on readily-measurable soil properties. We test an index of soil organic matter based on the soil organic carbon (SOC) to clay ratio, defined by thresholds of SOC/clay ratio for specified levels of soil structural quality. The thresholds were originally delineated for a small number of Swiss soils. We assess the index using data from the initial sampling (1978–83) of the National Soil Inventory of England and Wales, covering 3809 sites under arable land, grassland and woodland. Land use, soil type, annual precipitation and soil pH together explained 21% of the variance in SOC/clay ratio in the dataset, with land use the most important variable. Thresholds of SOC/clay ratio of 1/8, 1/10 and 1/13 were supported by structural assessments and indicated the boundaries between ‘Very Good’, ‘Good’, ‘Moderate’ and ‘Degraded’ levels of SOC. On this scale, 38.2, 6.6, and 5.6% of arable, grassland and woodland sites, respectively, were Degraded. The index gives a method to assess and monitor soil organic matter at national, regional or sub-regional scales based on two routinely measured soil properties. Given the wide range of soils and land uses across England and Wales in the dataset used to test the index, we suggest it should apply to other European soils in similar climate zones.

2.2 Highlights

- We assess the use of SOC/clay ratios as guidelines for soil management in England and Wales.
- We use data from 3809 sites to assess thresholds based on work for Polish, French and Swiss soils.
- SOC/clay threshold values can indicate degraded and good soil structural condition.
- The thresholds show the effect of land use and provide an index for use in England and Wales.

2.3 Introduction

What is a good level of soil organic matter? Maintaining and if possible increasing the level of soil organic matter is generally a good thing for most functions expected of soils, including carbon sequestration, and increased levels improve soil structure. Farmers, food producers and governments need to know their soil status in relation to a critical value of soil organic matter. However, as soil organic matter varies with land use, soil type, location, and other variables, an index for gauging the level of soil organic matter under given conditions needs to account for these variables.

Verheijen *et al.* (2005) derived indicative ranges of soil organic carbon (SOC) concentration for arable soils of England and Wales that are potentially attained under different types of management and environmental conditions. They found that clay concentration, precipitation and depth of topsoil could explain 25% of the variation in SOC concentration. Clay soils under wetter conditions had higher values than more-sandy soils, and grassland soils had higher values than arable soils with similar clay concentration. Clay concentration is a key factor because of its effects on SOC protection including adsorption on mineral surfaces and occlusion within soil aggregates (Dungait *et al*., 2012; Six *et al.*, 2002). Under constant land management and organic matter inputs, soils tend towards a steady-state SOC concentration, with a capacity for stabilising SOC modelled as a function of clay concentration (Hassink, 1997; Hassink & Whitmore, 1997; Six *et al.*, 2002; Stewart et al., 2007).

Dexter *et al*. (2008) found that soil physical properties (bulk density, water retention characteristics and clay dispersibility) could be better explained by the relative amounts of SOC and clay to each other than by their total concentrations. In their analysis of data on French and Polish arable and grassland soils, maxima of correlations between the mass of clay per unit mass of SOC and soil physical properties corresponded to SOC/clay = 1/10, the SOC/clay concentration ratio was a good indicator of soil physical conditions, and this ratio gave a general separation between the different land uses. These findings were subsequently supported by others (de Jonge *et al*., 2009; Jensen *et al*., 2019; Schjønning *et al*., 2012). Johannes *et al*. (2017) developed the approach further, and, in an analysis of Swiss soils, defined SOC/clay thresholds of 1/8, 1/10 and 1/13 as indicating the boundaries between 'Very Good', 'Good', 'Suggest Improvement' and 'Poor' levels of structural condition.

In this paper, we assess the three SOC/clay thresholds of Johannes *et al*. (2017) for soils across different land uses and climates in England and Wales. We use data from the original sampling of the National Soil Inventory (NSI) which contains information on soils at 5662 sites under agricultural and non-agricultural land uses across the two countries (Bellamy *et al*., 2005). This is a far larger dataset with greater variation in soils, environments, and land use than the datasets used by Dexter *et al*. (2008) and Johannes *et al*. (2017), and so provides a more comprehensive test of the SOC/clay ratio. We have three objectives. First, to assess the variation in SOC/clay ratio and its drivers across the NSI dataset. Second, to test its ability to delineate soils of different structural quality. Third, to illustrate the use of the SOC/clay index for mapping soil carbon across England and Wales, and for gauging changes in a long-term experiment with contrasting organic and inorganic fertiliser treatments.

2.4 Materials and Methods

2.4.1 National-Scale Data

The NSI was first sampled between 1978 and 1983. Topsoil (0–15 cm depth) samples were collected at the intersections of an orthogonal 5 km grid over the entire area. A full description of the survey methods, analytical methods and available data is given in the LandIS database (www.landis.org.uk; Proctor *et al*., 1998). We considered only arable, ley grassland, permanent grassland and woodland sites, and excluded sites without measurements of soil clay concentration, pH or depth of topsoil, or that were classified as 'peat'. To reduce the impact of sites with very high SOC concentration relative to clay concentration, we excluded 290 outliers with SOC/clay > third quartile + 1.5 ×

interquartile range (SOC/clay > 0.36125). This gave 3809 sites. Figure 2-1 shows the distribution of the sites across the two countries and Table 2-1 gives summary statistics for SOC and clay concentrations.

Soils at each site were classified by major soil group (Avery, 1980). Data on soil carbonate content were obtained from field observations of fizzing on addition of HCl to samples on a five-point scale from non-calcareous to very calcareous.

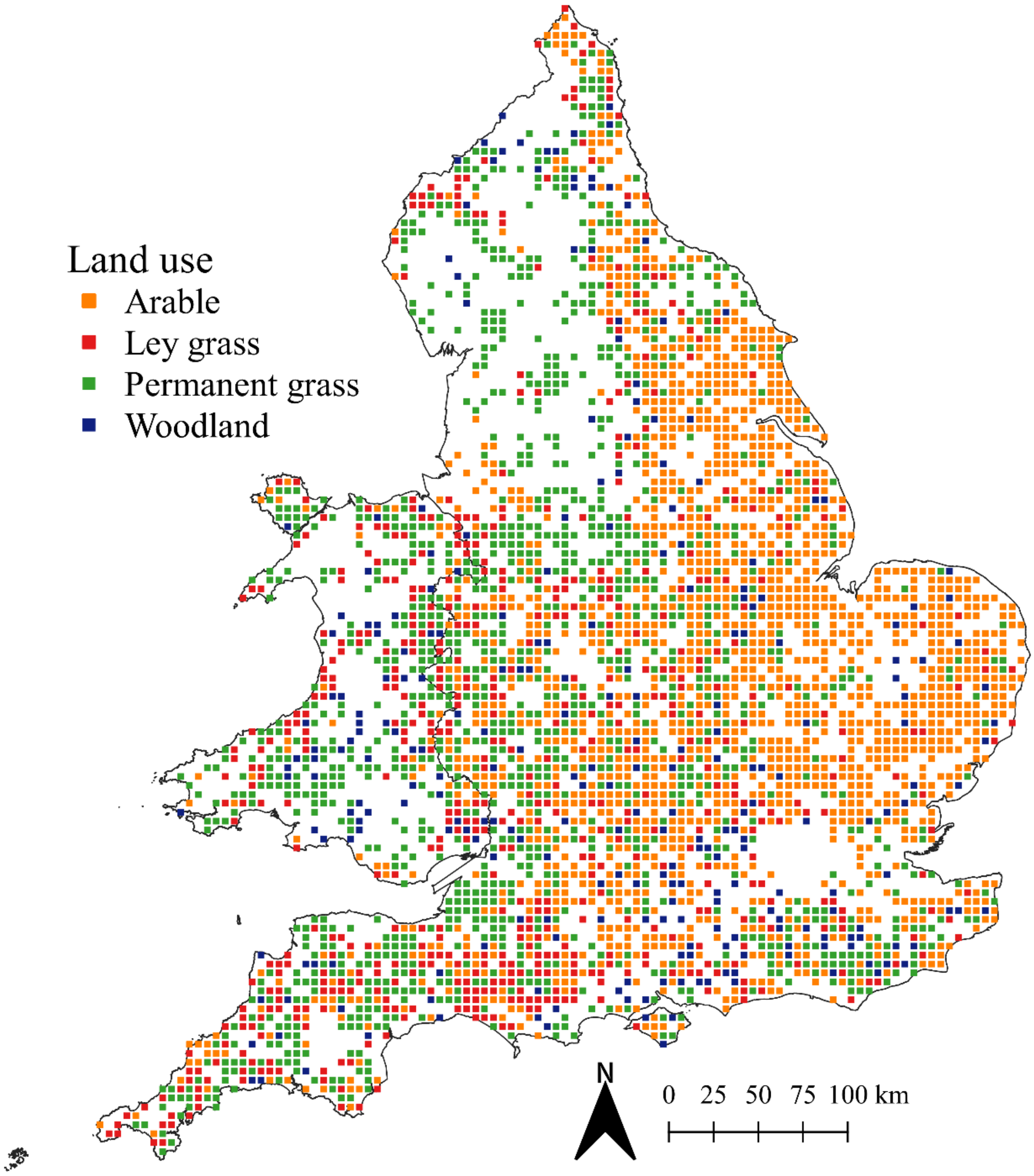

Figure 2-1 Map of arable, ley grass, permanent grass and woodland sites in the National Soil Inventory sampled between 1978 and 1983 (*n* = 3809).

Table 2-1 Soil organic carbon (SOC) and clay concentrations by land use class in the National Soil Inventory.

		SOC concentration (g kg^{-1})				Clay concentration (g kg^{-1})			
	n	Mean	Median	Min.	Max.	Mean	Median	Min.	Max.
Arable	1661	25	22	4	126	262	247	26	879
Ley grass	602	34	31	7	109	267	257	60	756
Permanent grass	1277	42	39	6	138	281	260	47	795
Woodland	269	40	37	1	158	251	242	10	606
All land uses	3809	34	30	1	158	268	252	10	879

Soil structural quality was characterised using the Agricultural Land Classification of England and Wales (MAFF, 1988), which gave scores of good, moderate or poor structural quality according to the texture and shape, size and development of aggregates, and friability of subsoil. The NSI contains values for each of these except friability, therefore we estimated based on the shape and size criteria (and where possible development of aggregates was taken into account) (Table A-1).

Monthly average precipitation was obtained from the UKCP09 dataset (Met Office, 2017). Mean accumulated annual precipitation was calculated for the years 1910–1983, and values at each NSI site were intersected using ArcGIS version 10.4. (ESRI, 2015). Ranges for precipitation classes were taken from Verheijen et al. (2005): < 650, 650–800 and 800–1100 mm $year^{-1}$ with the addition of "Very Wet" for annual precipitation > 1100 mm $year^{-1}$.

2.4.2 Data Analysis

Statistical analyses were performed in R version 3.5.0 (R Core Team, 2017). Random Forest analysis (package: randomForest; Liaw & Wiener, 2002) was used to analyse the variance of SOC/clay with land use, average annual precipitation, major soil group, pH, lower depth of topsoil, calcareous score and risk of flooding. A square-root transformation was applied to SOC/clay to reduce the skewness of the data. Three-quarters of the data (*n* = 2857) was used as a training set, and the RMSE and R^2 values of predictions of the remaining set (*n* = 952) were calculated. Training and sample sets were randomly selected. Spatial or other correlations across training and validation sets were unlikely because only topsoil samples were used and the minimum distance between sites was 5 km.

Chi-square tests were used to compare numbers of sites within SOC/clay ranges under different land uses and precipitation classes and to test the relationship between the SOC/clay thresholds and soil structure. We used the results of statistically significant chi-square tests to interpret interactions between variables, with contributions by specific combinations of variables to the chi-square statistic inferred from the differences between observed frequency and that expected if there was no interaction between the variables.

We tested SOC/clay thresholds of 1/8, 1/10 and 1/13 as indicating the boundaries between 'Very Good', 'Good', 'Moderate' and 'Degraded' levels of structural condition, following Johannes *et al*. (2017).

Figures were produced using R package ggplot2 (Wickham, 2016) and maps were produced using QGIS 3.0.1-Girona (QGIS Development Team, 2020).

2.4.3 Field-Scale Data

We assessed the effects of field-scale soil management on SOC/clay ratios relative to the threshold values using data from a long-term organic manuring experiment at Woburn, Bedfordshire, UK (Mattingly, 1974). The experiment had eight treatments with four replicates: (1) peat for 6 yr then ley, (2) farmyard manure (FYM), (3) grass ley plus nitrogen, (4) grass-clover ley, (5) green manure (GM) for 6 yr then ley, (6) straw, and (7) and (8) two inorganic fertiliser treatments (details in Mattingly, 1974). Treatments were applied in two cycles (1965 to 1972 and 1979 to 1987), and second cycle treatment was denoted by 'then' above if different from first. We calculated SOC/clay ratios for each plot and then averaged the values for each treatment. The plot-level soil clay concentration ranged from 78 to 131 g kg^{-1} and the initial SOC concentration ranged from 5.7 to 8.6 g kg^{-1} (Table A-2).

2.5 Results

2.5.1 Variation in SOC and clay concentrations and SOC/clay ratio

Mean SOC concentrations increased in the order arable << ley grass < permanent grass ≈ woodland soils (Table 2-1). Mean clay concentrations and their ranges were similar across land uses, except those of woodland soils were smaller. The dominant soil types in all land uses were brown soils and surface-water gleys; the proportions of other soil groups varied (Table A-3). Arable sites tended to have smaller average annual precipitation than the other land uses (Table A-4 and Table A-5).

The proportions of sites above and below the three SOC/clay thresholds differed between land uses, particularly for the SOC/clay = 1/13 threshold (Figure 2-2 and Table 2-2). A greater proportion of arable sites had SOC/clay < 1/13 (i.e. depleted in SOC for their clay concentration) and a greater proportion of permanent grassland and woodland sites had SOC/clay > 1/8 (i.e. enriched in SOC for their clay concentration; $X^2(9) = 681.3$, $p < 0.001$).

Analysis of the influence of land use, soil and other variables on SOC/clay ratio by random forest analysis showed that 21.0% of the variance was explained by the variables examined (Table 3). Land use, average annual precipitation, major soil group and pH were more important than carbonate score, flood risk and depth of topsoil. When the model was run with just the top four variables, the variance explained did not change, however the importance of land use increased relative to the other variables.

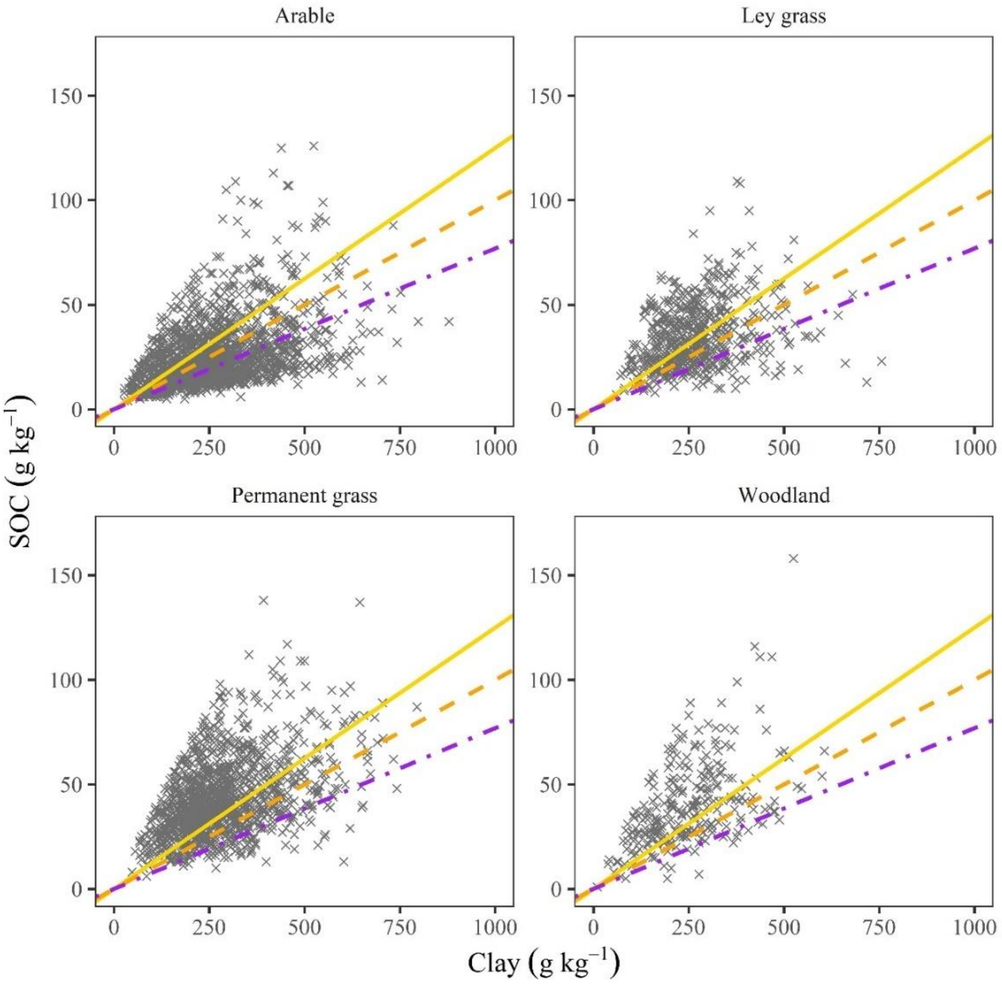

Figure 2-2 Soil organic carbon concentration as a function of clay concentration for different land uses. Lines are SOC/clay thresholds: solid = 1/8, dashed = 1/10, dot-dash = 1/13.

Table 2-2 Percentages of sites above, below and between SOC/clay thresholds of 1/8, 1/10 and 1/13 for each land use.

		Percentage of sites with indicated SOC/clay ratio			
	n	≥ 1/8	<1/8 ≥1/10	<1/10 ≥1/13	<1/13
Arable	1661	28.8	14.0	19.0	38.2
Ley grass	602	50.2	20.3	14.6	15.0
Permanent grass	1277	66.9	15.4	11.1	6.6
Woodland	269	67.7	16.0	10.8	5.6

Table 2-3 Contributions of indicated variables to variance in SOC/clay ratio analysed using random forests. Training data was a random selection of 75% of the data (n = 2857). With all seven explanatory variables, root mean square error (RMSE) for training data = 0.06, $R^2 = 0.21$; RMSE for remaining data = 0.07; $R^2 = 0.21$. With only top four variables, RMSE for training data = 0.06, $R^2 = 0.21$; RMSE for remaining data = 0.06; $R^2 = 0.22$.

	Increase of mean square error (%)	
Land use	32.7	39.8
Annual precipitation	28.0	26.0
Major soil group	26.4	20.3
pH	22.5	20.3
Depth of topsoil	10.4	
Carbonate score	10.0	
Risk of flooding	5.2	

2.5.2 Effects of land use and precipitation

The effect of land use was clear with lower SOC/clay ratios observed for arable and predominantly higher SOC/clay ratios for grassland and woodland (Table 2-2). As there was some geographical relationship between the distributions of land use and precipitation, the effects of each on numbers of sites relative to the SOC/clay thresholds were considered. Verheijen *et al.* (2005) suggested that dry sandy soils were more at risk of lower SOC concentration than wetter clayey soils and that grassland soils would have higher SOC concentration than (ley-) arable soils. Comparing SOC/clay threshold ranges, land uses, and precipitation classes (< 650, 650 to 800, 800 to 1100 and > 1100 mm yr^{-1}; Table S6), two questions were asked: 1) were arable soils in the Dry precipitation class (< 650 mm yr^{-1}) more likely to have SOC/clay < 1/13 than arable soils under wetter conditions, and 2) for soils in the Dry precipitation class, were arable soils more likely to have SOC/clay < 1/13 than other land uses?

In answer to the first question, chi-squared analysis showed that precipitation class was not independent of SOC/clay ratio for arable soils ($X^2(9) = 78.9$, $p < 0.001$). Comparing the contributions of each combination to the chi-square statistic allows us to see which combinations have more or fewer counts than expected if there was no relationship between the precipitation class and SOC/clay ratio. This showed that a larger number of soils receiving less than 650 mm yr^{-1}, and smaller numbers of soils receiving more than 650 mm yr^{-1}, had SOC/clay < 1/13 than if there was no relationship. Also, a smaller number of dry soils and larger number of soils with greater than 800 mm yr^{-1} had SOC/clay > 1/8. This suggests that lower precipitation conditions were related to SOC/clay < 1/13 for arable soils.

Chi-squared analysis to answer the second question showed that land use was not independent of SOC/clay ratio for soils in the Dry precipitation class ($X^2(9) = 94.0$, $p < 0.001$). A larger number of arable soils and smaller number of grassland and woodland soils than expected had SOC/clay < 1/13 than if the land use was independent of SOC/clay ratio range for soils receiving < 650 mm yr^{-1} annual precipitation. For soils with SOC/clay > 1/8, the reverse was true (i.e. arable < grassland or woodland). This suggests that land use was affecting the number of Dry precipitation class soils with SOC/clay < 1/13.

The relative effects of land use, precipitation and soil type were evident from the distribution of the 820 sites with SOC/clay ratio < 1/13 across England and Wales (Figure A-1). These sites were predominantly arable, and their distribution across eastern and central England confirmed the lesser statistical effect of precipitation and major soil group observed. Northwest England and Wales had notably few degraded sites though soils sampled there were mostly under non-arable land uses.

2.5.3 Effects of soil type and pH

The statistical effect of major soil group appeared to be driven by two of the soil groups and some of this might already have been accounted for by land use (Figure 2-3). Podzolic soils tended to have SOC/clay > 1/8 and were mostly not arable, whereas clay-rich pelosols were more likely to have SOC/clay < 1/13 and a higher proportion were arable. The lower importance of soil group might be linked to the smaller sample sizes of the podzolic and pelosol soils compared with brown and gley soils for which SOC/clay ratios showed similar variation.

As pH decreased below pH = 5, the SOC/clay ratio tended to increase (Figure A-2). Above pH = 5 there was less of a trend when considering permanent grass and woodland soils, however, arable and ley grass soils showed decreasing minimum

SOC/clay ratio particularly above pH = 7, though sites with SOC/clay > 1/8 were still observed.

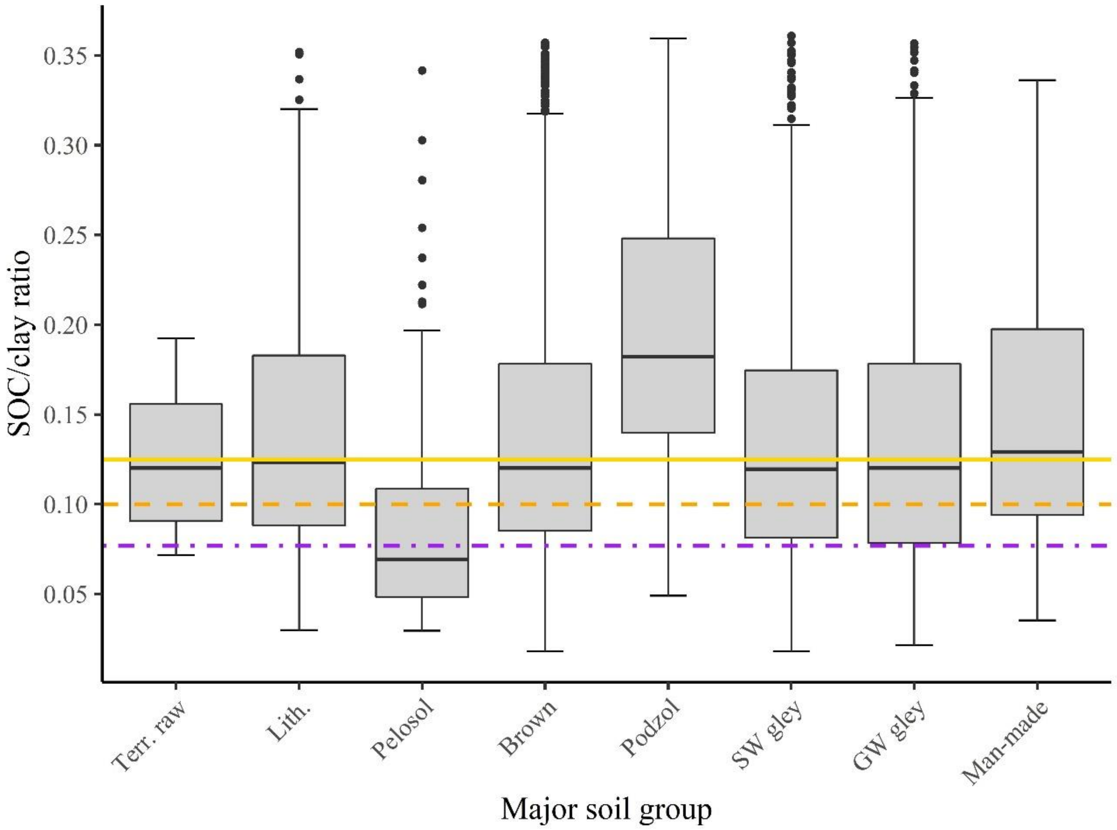

Figure 2-3 Box plots of SOC/clay ratio for each major soil group. Horizontal lines are SOC/clay thresholds: solid = 1/8, dashed = 1/10, dotted = 1/13. Abbreviated major soil groups: Terr. raw = terrestrial raw, Lith. = lithomorphic, SW gley = surface-water gley, GW gley = ground-water gley.

2.5.4 Relation between structural quality and SOC/clay ratio

Structural quality – classified as Good, Moderate, Moderate-Degraded and Degraded – tended to improve with increasing SOC/clay ratio as shown by the box plots in Figure 2-4 and the chi-squared test result for the relation between SOC/clay range between the thresholds and structural quality ($X^2(9) = 129.3$, $p < 0.001$). Most (82%) of the relationship between SOC/clay and structural quality was explained by (a) a larger than expected frequency of sites with SOC/clay < 1/13 and Moderate-Degraded or Degraded structure; (b) a smaller than expected frequency of sites with SOC/clay > 1/8 and Degraded structure; and (c) smaller than expected frequency of sites with SOC/clay < 1/13 and Good structure.

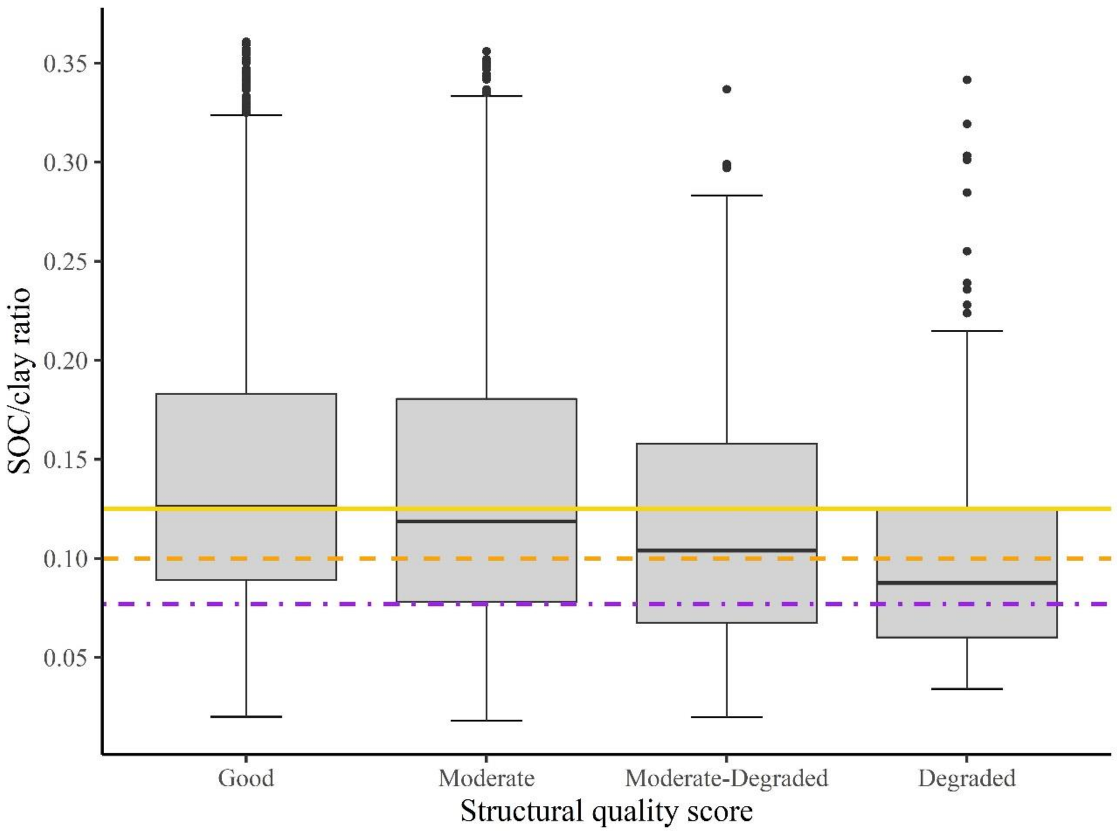

Figure 2-4 Box plots of SOC/clay ratio for each structural quality score. Horizontal lines are SOC/clay thresholds: solid = 1/8, dashed = 1/10, dotted = 1/13. Numbers of samples in each group were *n* = 2250, 1111, 229 and 208 for Good, Moderate, Moderate-Degraded and Degraded, respectively.

2.5.5 Variation in SOC/clay ratio across England and Wales

Mapping the index across the two countries (Figure 2-5) showed the effect of land use and geography at the time of survey. For any land use, Degraded sites were not limited to a particular region. But, as previously mentioned, there were fewer Degraded sites towards the Northwest and in Wales. Calculating summary values of SOC/clay by land use (Table 2-4) showed, though not tested statistically, that the minimum value increased slightly in the order: arable = ley grass < permanent grass < woodland. The median results showed a stronger difference between arable sites and the other land uses, with arable in the moderate category and the other land uses equal to or above the Very Good threshold. The different land uses had similar upper SOC/clay values as a result of excluding outliers.

Table 2-4 Summary of SOC/clay ratio decimal values calculated for each land use in the NSI subset.

	SOC/clay ratio			
	Mean	Median	Min.	Max.
Arable	0.109	0.090	0.018	0.357
Ley grass	0.139	0.125	0.018	0.359
Permanent grass	0.165	0.154	0.022	0.360
Woodland	0.174	0.160	0.025	0.355

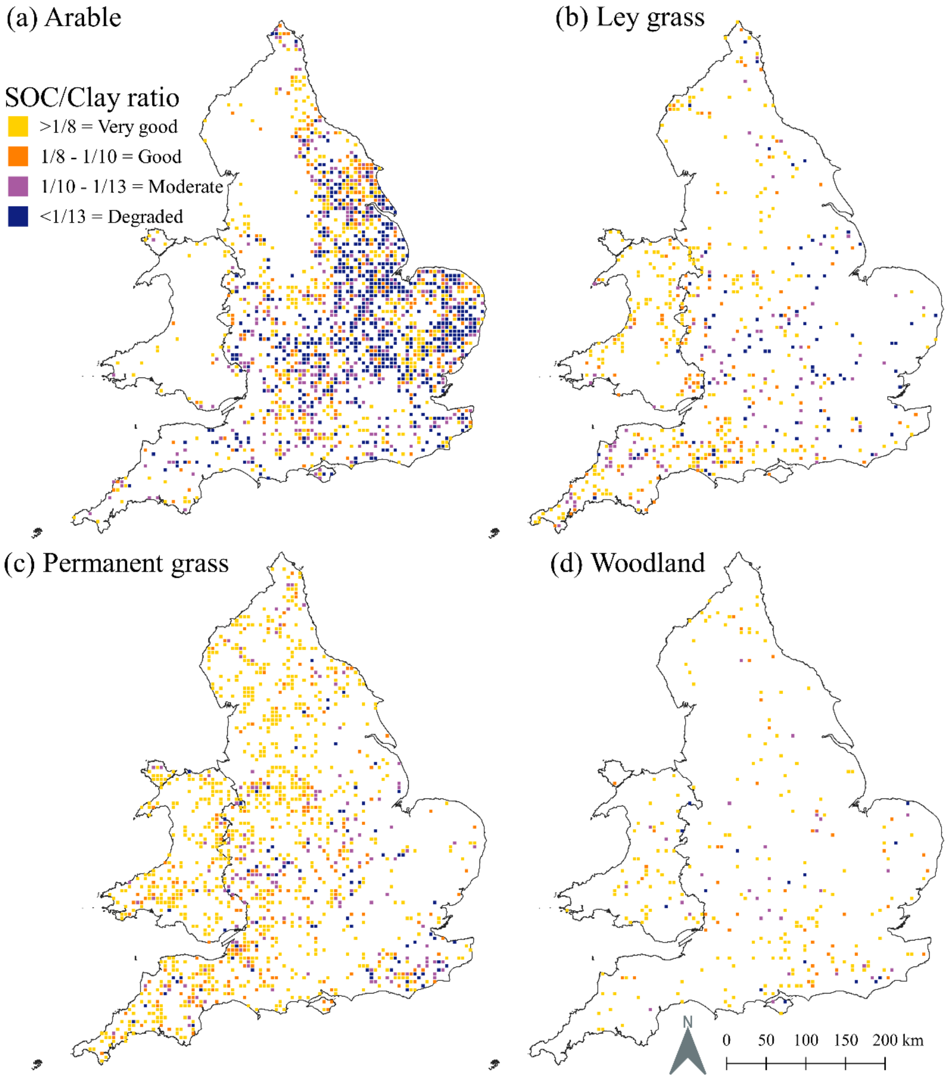

Figure 2-5 Maps of SOC/clay ratio across England and Wales under (a) arable, (b) ley grass, (c) permanent grass, and (d) woodland coloured by SOC/clay index.

2.5.6 Changes in SOC/clay ratio with field management

Figure 2-6 shows changes in SOC/clay ratios over 30 years of the Woburn organic manuring experiment. Leys and treatments with organic matter application (straw, manures) showed similar trends of increasing SOC/clay ratio during the application period and decreasing ratio after the treatment was stopped, but with differing magnitudes. Peat and farmyard manure gave the largest increases, followed by the ley treatments and then straw. Inorganic fertiliser only treatments showed a general trend of decreasing SOC/clay ratio, and consistently remained in the Degraded class.

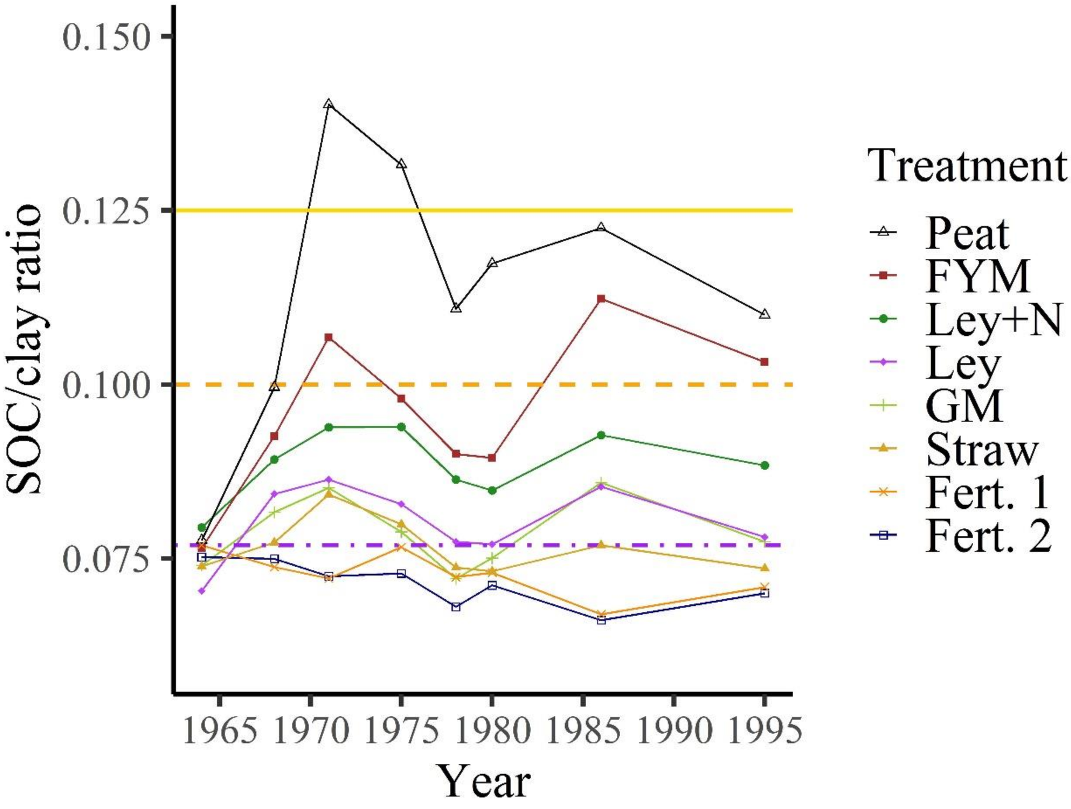

Figure 2-6 Changes over time in SOC/clay ratio in the Woburn long-term manuring experiment. Points are treatment means. Horizontal lines are thresholds separating Degraded (SOC/clay < 1/13), Moderate (SOC/clay = 1/13–1/10), Good (SOC/clay = 1/10–1/8) and Very Good (SOC/clay > 1/8) soil conditions. Treatments were applied in two cycles (1965 to 1972 and 1979 to 1987); peat and green manure (GM) treatments were replaced by grass ley for the second cycle. Fert. 1 = (PKMg) ≡ Straw plus P, Fert. 2 = (PKMg) ≡ FYM.

2.6 Discussion

2.6.1 Variation in SOC/clay ratio with land use and soil type

In agreement with Dexter *et al.* (2008) and Johannes *et al.* (2017), arable soils had a larger proportion of sites with SOC/clay ratios below 1/10, and permanent grassland soils had a larger proportion above 1/10. Dexter *et al*. (2008) did not consider soil group or structural condition of the soils in their study, and Johannes *et al*. (2017) chose only one soil type. Based on the agreement of their results with previous studies on the importance of the SOC/clay = 1/10, Johannes *et al.* (2017) suggested it should apply to a range of soils. Our finding that few grassland and woodland sites had SOC/clay < 1/13 supports the use of SOC/clay = 1/13 as an indicative threshold for degradation, as grassland and woodland soils are not generally subject to major disturbance and are close to semi-natural systems. Our analysis shows that many arable soils were depleted in SOC compared with the more natural systems. Ley grassland soils were intermediate between arable and permanent grassland soils. The NSI survey did not include information on the length of leys nor the time under ley at sampling, but typically this is between 3 and 8 years. Some proportion of arable sites will have been part of ley rotations at the time of sampling.

The large variation of SOC/clay ratio within each land use and soil group demonstrates that clay concentration is not the only determinant of SOC dynamics, especially considering land use history before the sampling will have big effects too. As discussed above, despite the scatter, the thresholds show differences between soils under different land management.

The variance of the SOC/clay ratio explained by random forest analysis was similar to the variance of SOC concentration explained by Verheijen *et al.* (2005) with step-wise general regression modelling, using similarly-derived precipitation data, and the same soil dataset (though a different subset). We would expect the variance explained to increase with more specific measures of land management within land use classes (crop type, residue treatment, land-use history and, for grassland systems, grazing management). Interpolated precipitation data is another estimation which could be improved, however this is what is generally available at this scale.

The effect of major soil group on SOC/clay ratio suggests some consideration should be given to soil type, as highlighted by Johannes *et al.* (2017). Comparing the variation in SOC/clay ratio between major soil groups, similar variation and medians were found for lithomorphic, brown, gley and man-made soils. The tendency for higher SOC/clay ratio of podzolic soils might be attributed to concentrated organic horizons in the topsoil. The tendency for lower SOC/clay ratios of pelosols might be attributed to higher clay concentrations combined with a higher proportion (62%) being arable than most major soil groups. Whilst acidic soils had a tendency for higher SOC/clay ratios, there appeared to be little relationship between pH and SOC/clay ratio in agriculturally productive pH ranges (circa. pH = 5.5 to 7).

A wide range of soil clay concentrations were sampled in the NSI for each of the land uses (Table 2-1) and the variation in SOC by land use across this range suggested that the index was still applicable at the extremes of clay concentrations (Figure 2-2). Logically, there might be a clay concentration below which the SOC-clay interaction mechanisms and effects on soil physical properties are less relevant than other effects of SOC however, the long-term experiment on a sandy loam soil with clay concentration ≤ 131 g kg^{-1}, showed the index to be sensitive to different treatments, despite small SOC concentrations.

2.6.2 Significance of the threshold values

The fact that the empirical threshold values found by Johannes *et al.* (2017) for Swiss soils also hold for the wide range of soils and land uses across England and Wales in our study, suggests they have some fundamental basis, and that they may apply in soils in similar climate zones across Europe. An association of soil structural quality with the SOC/clay = 1/10 ratio was expected from physico-chemical considerations (de Jonge *et al.*, 2009; Jensen *et al.*, 2019). Intuitively there will be some minimum range of SOC/clay ratio below which soil structure is impaired, and some maximum range above which the capacity of soil clays of given mineralogy to bind SOC is exceeded. However, there are no obvious reasons why the precise threshold values indicated by our and the Swiss study should be absolute.

The observed decrease in soil structural quality with decreasing SOC/clay ratio was statistically significant, though there was overlap between the boxplots of SOC/clay ratio between structure classes. Our analysis was limited by the quality of the available data on structure. This was based on the scheme defined for the Agricultural Land Classification of England and Wales, which includes a measure of friability. Since friability was not recorded in the NSI, we had to estimate structural quality without it, introducing error. Other management factors affecting soil quality will not have been captured in the SOC/clay ratio also. Despite this, the structural quality analysis provided a way to validate the SOC/clay thresholds independent of the distribution of SOC/clay alone.

The basis of the index on literature that supported the concept of a saturable capacity of SOC-to-clay interaction at SOC/clay = 1/10 suggested that the class names of Very Good, Good, Moderate, and Degraded better reflected the SOC status. As defining guideline values for SOC was the aim of this study, rather than the SOC/clay ratio as a specific proxy measure for soil structure, this divergence from the Agricultural Land Classification structural quality scores did not seem inappropriate. The Very Good class (SOC/Clay $\geq$ 1/8) represents a low risk of degraded structure whilst also recognising that these soils are likely to have SOC in excess of a clay-interaction-capacity (SOC/clay between 1/8 and 1/11; Dexter *et al.*, 2008). The Good class (SOC/clay <1/8, ≥1/10) represents some risk of moderate to degraded structural quality but with SOC/clay close to or achieving the clay-interaction capacity. The Moderate class (SOC/clay <1/10, ≥1/13) represents a higher risk of lower structural quality and low probability of achieving the clay-interaction capacity. The Degraded class then represents a higher risk of degraded structure and with SOC/clay further from the clay-interaction capacity, also coinciding with a low rate of occurring under sampled woodland or permanent grass.

The mechanistic link between structural quality and SOC/clay ratio should reduce errors due to cross correlation with spatial and temporal variations in the data. We found, as did Verheijen *et al.* (2005), that SOC concentration tended to decrease with decreasing precipitation across England and Wales, partly in interaction with land use. However, low SOC/clay ratios were not limited to particular combinations of land use and precipitation; therefore, we would not consider precipitation to limit SOC/clay ratio in this data set and geographical range. Land management was shown to affect proportions of Very Good and Degraded soils under dry (< 650 mm year^{-1}) conditions. So, SOC/clay ratios of at least 1/10 should be attainable in such soils.

2.6.3 Practical usefulness of the index

The SOC/clay index is a simple measure to evaluate the SOC status of any given soil in England and Wales, independent of the land use. It will therefore be meaningful for experts and non-experts and has consequences for many soil functions beyond agricultural uses. The index provides guideline values for SOC across soil types which can be of use to policy makers in relation to potential payments for soil management. On top of this, the index allows for more meaningful interpretation of SOC measurements across managed land to help inform management activities (whether self-motivated or in-line with policy).

The index does not cover peatlands or other highly organic soils for which carbon dynamics are different to mineral soils and other assessments, such as changes in peat depth, are more appropriate.

Application of the index to data from the long-term Woburn experiment showed its behaviour was consistent with expectations, with an improving index in treatments favouring organic matter accumulation, and a deteriorating index in soil-degrading treatments. This illustrates the magnitude and time taken for the various contrasting managements to change SOC and the index. The soil in the Woburn experiment is a sandy loam; the results showed that the index can be used for soils with low clay concentration, despite the narrowing of the SOC/clay thresholds with decreasing clay concentration, and the relatively small changes in SOC concentration between the treatments. It should be noted that, to be useful for monitoring purposes, measurements of SOC and clay over time and between sites need to be consistent.

Similarly, sampling depth should be consistent. The NSI used a sampling depth of 0–15 cm and the long-term experiment used 0–23 cm. The results of the long-term experiment did not look to be compromised by this and we suggest that the index can be applied to topsoils at least to 23 cm depth. As multiple depth samples are sometimes taken for topsoils (e.g. 0–10 cm and 10–30 cm), it would be suggested to combine these for assessment in this case.

Whilst the development and validation of the index thresholds was based on structural assessments, in practice soil structure assessments should be carried out since management activities can affect this separate to the mechanisms of soil organic matter.

It would be interesting to look at other longer-term studies to explore a wider range of clay concentrations, treatments and time periods. Saturation concepts suggest that a soil closer to steady state or saturation limit should accumulate carbon more slowly than one further from saturation (Six *et al.,* 2002; Stewart *et al.*, 2007). Hence, whether sites with lower index values (higher degradation) improve more quickly could be tested.

2.7 Conclusions

An index of soil organic matter with threshold SOC/clay ratios of 1/8, 1/10 and 1/13 separated the mineral topsoils of England and Wales into Very Good, Good, Moderate and Degraded classes of SOC concentration. In agreement with previous publications, grassland and woodland soils mostly had SOC/clay ratio > 1/10, indicating that their SOC concentrations were close to or above the capacity for protection of SOC by interaction with clay particles. That these more natural systems tended to have SOC/clay ratio > 1/10 supports this as a suitable threshold for good SOC status. The SOC/clay index's relationship to soil structure was supported with the caveat that there is likely unaccounted for variation in this large dataset.

Arable soils and soils receiving less annual rainfall were most likely to have SOC/clay in the Degraded class, though rainfall was a less important factor determining SOC/clay ratio. Very Good status soils (SOC/clay > 1/8) occurred in low rainfall areas, even under arable management, suggesting that low rainfall does not fundamentally limit SOC concentration in this climate.

The index is applicable across major soil groups of England and Wales as SOC/clay ratios showed similar distributions between groups, except in the case of pelosols which are particularly high in clay or podzols which have organic surface horizons. The index should still apply to these soil groups understanding the reasons for their differences.

. The index gives a ready metric for communication to experts and non-experts, enabling users to adjust their practices and decision makers to develop adequate policies. SOC/clay ratios greater than 1/10 should be achievable for all mineral topsoils of different textures. Many arable soils in England and Wales evidently have a substantial SOC deficit, suggesting a significant opportunity to increase SOC storage to both improve soil conditions and sequester carbon.

Being based on two routinely measured soil properties, the index provides a suitable means of monitoring SOC at national, regional or sub-regional scales. Given the wide range of soils and land uses across England and Wales in the dataset used to test the index and agreement with literature using French, Polish and Swiss soils, it should apply to other European soils in similar climate zones.

2.8 Authorship

Study concept and design: all. Analysis and interpretation of data: JMP, KDS, SMH. Drafting of the manuscript: JMP. Critical revision of the manuscript for important intellectual content: GK, SPM, SMH, KDS. Statistical analysis: JMP and KDS.

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3 CHANGES IN ORGANIC CARBON TO CLAY RATIO OVER TIME AT MULTIPLE SCALES*

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3.1 Abstract

Easily measured indices of soil organic carbon (SOC) status are needed for quantifying the potential for SOC sequestration in different soils and land uses, and for monitoring progress against targets. We assess an index based on the SOC to clay concentration ratio and classes supported by soil structural condition. We use data from (a) the National Soil Inventory of England and Wales sampled twice between 1978 and 2003, and (b) two long-term experiments under ley arable rotations on contrasting soils in the East of England. In the inventory, soils with high SOC/clay ratios (> 1/8, Very Good) had the biggest rates of loss of carbon over time, whereas soils that already had SOC/clay ratio < 1/13 (Degraded) could not lose much more carbon or even gained carbon. Between the first and the second sampling, arable soils showed a negative trend in index class with the proportion of Degraded class soils increasing from 43% to 47%. Permanent grass soils lost some Very Good class soils but still retained a high proportion. Woodlands showed a majority of increases in SOC/clay and had a higher proportion in the Very Good class. In the two long-term experiments, arable treatments

showed similar SOC/clay ratios even though SOC concentrations were different between sites (ranges: 8-9 vs 16-18 g kg^{-1}). The SOC/clay index is a useful metric for comparing the effects of land management on the SOC concentration of soils even between sites with different clay concentrations. The index holds promise for monitoring soils over time and informing management decisions. By providing a guideline on SOC concentrations in topsoils, the SOC/clay index can also help to inform carbon sequestration potentials for agricultural soils. We propose SOC/clay target levels for good management and realistic carbon storage potentials for different land uses. Since the index was developed on a range of soils in Europe, it is expected to be applicable across temperate regions.

3.2 Highlights

- SOC/clay analysed on national scale over 11-23 years, and two long-term experiments.
- SOC/clay useful for assessing SOC changes and sequestration potential.
- SOC/clay targets for arable, ley-arable, and grassland soils: 1/13, 1/10, and 1/8.

3.3 Introduction

There is much interest in the potential for increasing soil organic carbon (SOC) stocks to offset anthropogenic greenhouse gas emissions; indicated for example by the 4 per mille initiative which seeks to increase SOC stocks in the top 2 m of soils globally by 4 ‰ per year (Minasny et al., 2017). How realistic this is has been debated, given the required large-scale changes in land management, the finite scope for SOC accumulation in any given soil, and the reversibility of changes (van Groenigen et al., 2017; Anderson et al., 2019; Smith et al., 2020). Over millennial time scales, cultivation has caused losses of soil carbon of 116 Pg C globally (Sanderman, Hengl and Fiske, 2017, 2018), and soils are currently losing carbon in many parts of the world. For example, in an analysis of data in the National Soil Inventory (NSI) of England and Wales, Bellamy et al. (2005) found widespread losses of carbon from soils across both countries during the 1980s and 90s, mostly due to past changes in land management but possibly also linked to warming during that period (Smith et al., 2007; Kirk & Bellamy, 2010). On the other hand, soils in some regions show gains in carbon under both managed and natural vegetation (Minasny et al., 2011; Kurganova et al., 2012; Jonard et al., 2017; Qubaja et al., 2020). Gauging the potential for SOC sequestration at local to national scales, and monitoring progress against targets, requires practicable indices which allow for governing factors and are based on readily measurable soil properties (Smith et al., 2020).

Soil clay concentration is a key factor because of its effects on SOC protection, including adsorption on mineral surfaces and occlusion within soil aggregates (Six et al., 2002; Dungait et al., 2012). In an earlier paper (Prout et al., 2020) we assessed an index of soil carbon based on the SOC/clay ratio using data in the NSI of England and Wales. We showed the index could separate soils with good and degraded structural condition under different land uses. The threshold SOC/clay ratios for different levels of structural condition were based on earlier work with French, Polish and Swiss soils, which found SOC/clay thresholds of 1/8, 1/10 and 1/13 marked boundaries between 'very good', 'good', 'moderate' and 'degraded' levels of structural condition (Dexter et al., 2008; Johannes et al., 2017). Given the importance of soil clay for carbon protection, these thresholds are promising components of a soil carbon index with widespread applicability.

In this paper we look at changes in the SOC/clay index over the interval between the two samplings of the NSI to test whether the SOC/clay index is a useful framework for monitoring changes in SOC in response to land use and management, and for assessing the soil carbon sequestration potential. Long-term experiments are used to indicate the realistic rate of change on different soils and under different management options. We discuss implications for the potential of carbon sequestration in soils at regional to national scales in similar climatic zones.

3.4 Materials and Methods

3.4.1 National Soil Inventory

The NSI was first sampled between 1978 and 1983. Topsoil (0-15 cm depth) samples were collected at intersections of an orthogonal 5 km grid over the entire area of England and Wales, excluding urban areas and water bodies (www.landis.org.uk; Proctor et al., 1998). Sufficient subsets of the sites (approximately 40% of the original sites) were resampled at intervals from 12 to 25 yr after the original sampling to be able to detect changes in SOC concentration ≥ 2 g kg^{-1} with 95% confidence (Bellamy et al., 2005). This was done in three phases: in 1994–95 for arable and ley grass sites (853 of the original 2,578 sites), in 1995–96 for managed permanent grassland sites (771 of the original 1,579), and in 2003 for non-agricultural sites (including deciduous and coniferous woodland; 555 of the original 1,505). Soil from both samplings was analysed using the standard methods of the Soil Survey of England Wales (Avery & Bascomb, 1973): organic carbon by the Walkley-Black method, clay by the pipette method and pH in water at 1:2.5 soil:solution ratio. To check for differences in analytical precision between the samplings, stored samples from 10% of the original sites were reanalysed for SOC, and good agreement (± 1 g kg^{-1}) with the original values was found across the full range of values (Bellamy et al., 2005). How accurately the sites could be relocated was assessed by revisiting 10 sites following the original site descriptions and recording positions with a global positioning system; accuracy was better than 20 m on enclosed land and better than 50 m on open land (Bellamy et al., 2005).

For the analyses presented here, we only considered arable, ley grass, permanent grass and woodland sites. We excluded sites (a) classified as peat (i.e, SOC concentration > 120 g kg^{-1} if no clay in the mineral faction, or > 180 g kg^{-1} if clay concentration ≥ 600 g kg^{-1}; Avery & Bascomb, 1973), (b) without measurements of clay concentration or pH, (c) with SOC/clay ratio > 0.361 to agree with Prout et al. (2020), and (d) if the recorded land use differed between the samplings. We calculated annual rates of change in SOC/clay ratio from the change between the samplings divided by the time interval, i.e. we assumed the rate of change was constant. Since clay concentration was only measured on soils from the original sampling, we also assumed clay concentration was constant. We excluded sites for which changes in SOC/clay per yr were greater than 0.02. This gave 1,418 sites, whose distributions across England and Wales are shown in Figure 3-1.

We divided sites according to SOC/clay thresholds of 1/8, 1/10 and 1/13 as the boundaries between very good, good, moderate and degraded levels of SOC, respectively, following Johannes et al. (2017). In our earlier paper (Prout et al, 2021) we showed that the SOC/clay ratios of soils from the first NSI sampling that differed in structural condition, as assessed using the Agricultural Land Classification of England and Wales (MAFF, 1988), supported these thresholds.

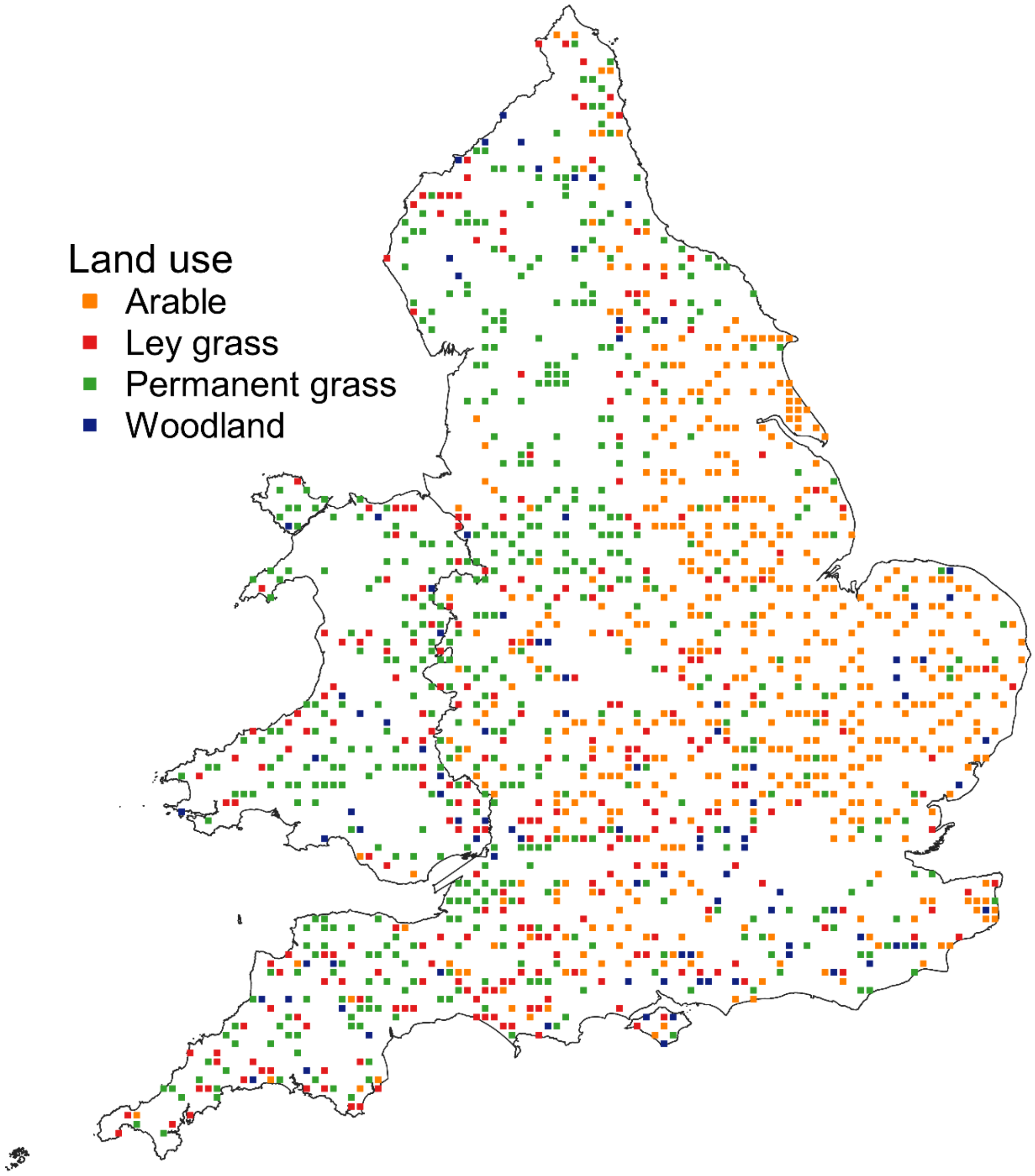

Figure 3-1 Distribution of National Soil Inventory sites selected for analyses (*n* = 1,418). The map was produced using QGIS 3.0.1-Girona (QGIS Development Team, 2020).

3.4.2 Long-term experiments

Detailed land management practices were not recorded in the NSI. We therefore used data from two long-term experiments to explore the effects of organic matter management practices on SOC/clay ratios and index classes over time under arable, ley grass and permanent grass. The two experiments have run over similar time periods, overlapping the years of the NSI samplings. One is on a sandy loam soil (Woburn) and the other on a silty clay loam (Harpenden).

3.4.2.1 Woburn ley-arable experiment

The Woburn experiment was established at Woburn Experimental Station, Woburn, Bedfordshire in 1938–42. Details and treatments are in Table 3-1. We considered six treatments: arable (with or without fallows), lucerne (or sainfoin) converted to 3-yr grass-clover ley, grazed ley converted to 3-yr grass ley with inorganic nitrogen (N) additions, and alternating cycles of arable, lucerne, and grazed ley converted to 8-yr leys (either grass-clover or with inorganic N). Farmyard manure (FYM) additions (fresh weight of 38 Mg ha^{-1} yr^{-1}) were applied to the first test-crop on one of the two paired-rotation plots in each experimental block until the mid-1960s; the SOC measurements of with- and without FYM plots were averaged for each treatment. Soils were sampled every fifth year. The SOC values used here are averages of five experimental blocks for each treatment. Only the first of the two 8-yr ley treatment cycles was used for this analysis. Clay concentration was taken as 138 g kg^{-1} for all plots, the mean of the measurements taken by Catt et al. (1980).

3.4.2.2 Highfield ley-arable experiment

The Highfield experiment was established at Rothamsted Research (formerly Rothamsted Experimental Station), Harpenden, Hertfordshire in 1948. Details and treatments are in Table 3-1. We considered the following treatments: arable, ley grass, reseeded grass, old grass, and bare fallow. From 1961, FYM additions (fresh weight of 30 Mg ha^{-1} yr^{-1}) to sub-plots of potato crops were made to whole plots instead, then discontinued in 1970. The experiment was designed with four blocks and for each treatment the SOC/clay ratio was averaged across blocks. Incomplete sampling between years meant that the number of SOC measurements averaged was not always four. The bare fallow treatment comprised 4 plots, for which the SOC measurements per sampling year are averaged here. Where clay concentration was not measured directly in a plot, we used the clay concentration of the closest plot.

3.4.2.3 Changes in SOC stocks

Estimates of SOC stocks (Mg C ha^{-1} to 25 cm) were calculated for each SOC/clay threshold using the mean clay concentration of each long-term dataset (138 g kg^{-1} for Woburn, and 263 g kg^{-1} for Highfield), and the difference between each SOC/clay threshold (including a value of SOC/clay = 0.065, which emerged as a common ratio for long-term arable management at the two sites; see Section 3.2.2). For Woburn, a topsoil weight of 3770 t ha^{-1} was used as calculated by Johnston et al. (2017) for continuous arable soils. The bulk density of Highfield soil was estimated to be 1.12 g cm^{-3} (topsoil weight = 2880 Mg ha^{-1}) at the start of the experiment using starting SOC, texture measurements of Jensen et al. (2017), and a pedotransfer function from Hollis et al. (2012; All other mineral horizons) which gave good agreement with the bulk density back-calculated from the soil weight for the arable soil of Woburn. Our calculations were on the basis of equivalent soil mass, so just considered the magnitude of changes in carbon stock relative to changes in the SOC/clay ratio. The standard deviations of SOC/clay values for each of the long-term experiments are in Appendix B.

3.4.3 Statistical analysis

R version 4.0.2 (R Core Team, 2020) was used to process the data and produce figures (package: ggplot2; Wickham, 2016). Regression analysis was used to test how much of the variance in rate of change of SOC/clay could be explained by land use, average annual precipitation, major soil group, and mean pH between samplings. These variables were derived in the same way as Prout et al. (2021), except that average annual precipitation was averaged over 1910-2003 (extended to include the second sampling period). Empirical cumulative distribution functions, with pointwise bootstrapped 95% confidence intervals, were used to assess the difference in rate of change of SOC or SOC/clay by index class and land use. A chi-squared goodness of fit test was used to determine the representativeness of the smaller subset (n = 1418) compared to that of Prout et al. (2021) (n = 3809). Genstat (version 19; VSN International, 2018) was used to compare counts of index classes between the two time points of the subset (n=1418) using a chi-squared test.

Table 3-1 Summary of treatments in the long-term experiments.

	Woburn		Highfield	
Location	52°1'12"N, 0°37'12"W		51°80'N, 00°36'W	
Establishment	1938–42		1948 (1959 for bare fallow)	
Previous history	> 62 yr of arable		> 100 yr of permanent grass	
Soil	Sandy loam, 114–164 g clay kg^{-1} (Catt et al., 1980)		Flinty silty clay loam, 233–335 g clay kg^{-1} (Jensen et al., 2017)	
Structure	Three yr of treatment crops followed by 2 yr of test crops		Three yr of treatment crops followed by 3 yr of test crops	
Treatments	Arable (no fallows)	Arable crop rotations with 1-yr hay in rotation until 1975	Arable	Arable crop rotations
	Arable (with fallows)	Arable crop rotations with 1-yr root crop until 1975 and 1-yr fallow until 1995	Bare fallow	Routinely ploughed and kept free of vegetation
	Lucerne / LC3	Changed from Lucerne or sainfoin to 3-yr grass-clover ley (LC3) from 1975	Grazed ley / LC3	Changed from grazed ley to grass-clover ley (no inorganic nitrogen) from 1962
	Grazed ley / LN3	Changed from Grazed ley to 3-yr grass with inorganic N (LN3) from 1975	Cut grass / LN3	Changed from cut-grass ley to grass-ley with inorganic N additions from 1962
	Alternating / LC8	Alternating cycles (arable, lucerne, or grazed ley) until 1975 after which a 10-yr structure of either 8-yr grass-clover ley (LC8) or 8-yr grass with inorganic N (LN8)	Old grass	Old grass was undisturbed pasture and reseeded grass was broken up and re-sown to long-term grass; 3-yr cycles (2 yr sheep grazing, 1 yr hay with aftermath grazing); grazing was discontinued in 1962 (old grass) and 1963 (reseeded grass)

3.5 Results

3.5.1 National Soil Inventory

3.5.1.1 Rates of change in SOC and SOC/clay

The rates of change in SOC (Figure 3-2a) and SOC/clay (Figure 3-2b) were explored for each land use when grouped by index class of the first sampling. The rates of change for both variables have the same cumulative frequencies of positive and negative rates for each index class (as clay did not change) and therefore the following applies to both. The Very Good class (SOC/clay > 1/8) had higher proportions of negative rates than other index classes for all land uses, though woodland had a lower proportion than the other land uses. The other index classes had more similar curves to each other compared to the Very Good class. This was seen to varying degrees in the other land uses. In general, the proportion of negative rates followed the order of Very Good > Good > Moderate > Degraded. The proportion of the Very Good class with negative rates was similar for arable, ley grass and permanent grass (75, 73, and 73% respectively), however lower proportions of negative rates were observed for all other index classes of ley and permanent grass compared with those of arable. Woodland soils had a majority of positive rates of change, but negative rates were greatest and more frequent for the Very Good class.

The difference between Figure 3-2a and Figure 3-2b was the distribution of the rates of change along the x-axis; one shows the change in SOC and the other SOC relative to clay concentration. The general trends between index classes for each land use were similar with the Very Good index class tending to have a greater range of negative rates than the other index classes. The difference between the two rates of change was most evident for the separation of the Very Good and Good curves, particularly those of ley grass. For the rate of change in SOC, the two means and respective confidence intervals overlapped, however for SOC/clay, the separation of the curves indicates a difference between classes. Considering the change in rate variable: the very high positive rate of change in SOC for the Degraded class of the ley grass data (8.0 g kg^{-1} yr^{-1}) was brought into line with the rest of the data when clay concentration was accounted for. The next highest rate of increase in SOC for Degraded ley grass soils was 2.7 g kg^{-1} yr^{-1}, in line with the highest rates for Very Good and Moderate ley grass soils.

Regression analysis was used to assess several factors, other than land use, which might affect changes in SOC/clay. However, this showed that less than 1% of the variation in rate of change of SOC/clay could be explained by average annual precipitation, mean pH, major soil group and carbonate score. Because such a small amount of the variation was explained by these factors, this result was not considered further.

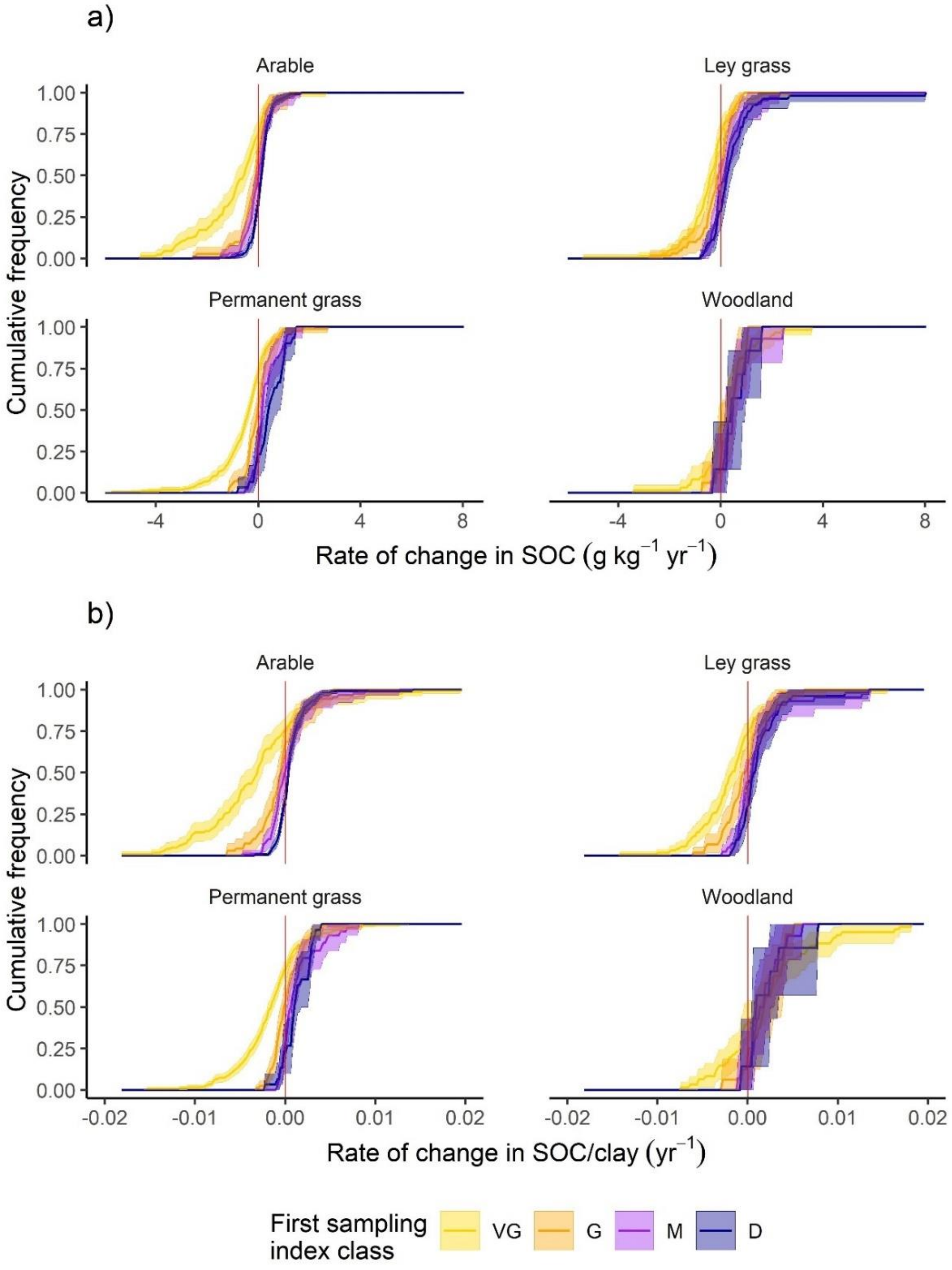

Figure 3-2 Empirical cumulative frequency distributions of change per year of a) SOC, and b) SOC/clay ratio in the two samplings of the National Soil Inventory, 1978–2003. Line colours of (a) and (b) indicate the first sampling index class: Very Good (VG; SOC/clay ≥1/8), Good (G; SOC/clay 1/10-1/8), Moderate (M; SOC/clay 1/13-1/10) and Degraded (D; SOC/clay <1/13). Shaded areas represent bootstrapped 95% confidence intervals. The vertical line indicates rate of change equal to zero.

3.5.1.2 Changes in index class between samplings

The subset of the NSI used in this analysis (n = 1418) was found to have slightly different distributions to that of Prout et al. (2021) (n = 3809) (X^2(9) = 17.61, p = .04). The changes which contributed most to the difference were a decrease in the proportion of permanent grass soils in the Moderate class, an increase in the proportion of arable and ley grass soils in the Degraded class, and a lower proportion of arable and ley grass soils in the Very Good class. Despite these, the general trends were the same, with arable having fewer Very Good sites than Degraded sites contrasting with permanent grass and woodland, and ley grass having intermediate proportions (Table 3-2).

Table 3-2 Percentages of sites with a given index class under each land use in each sampling

		Percentage of sites with indicated SOC/clay index class							
		First sampling				Second sampling			
Land use	n	Very Good	Good	Moderate	Degraded	Very Good	Good	Moderate	Degraded
Arable	504	25.6	13.9	17.9	42.7	20.7	12.5	20.0	46.8
Ley grass	284	45.1	21.1	15.1	18.7	41.2	17.6	21.1	20.1
Permanent grass	532	70.5	15.6	8.3	5.6	60.9	18.8	15.2	5.1
Woodland	98	62.2	16.3	14.3	7.1	77.6	12.2	5.1	5.1

The distribution of index scores by land use changed between the NSI samplings (X^2(15) = 32.24, p < .001). From the first to the second sampling, the proportion soils in the Very Good class decreased under arable and ley grass by close to 5%, and permanent grass by almost to 10%. The increased proportion of the Moderate class under ley and permanent grass also contributed to the statistic. Arable soils in the Degraded class increased from 43% to 47%. Woodlands showed an increase in the proportion of the Very Good class and a decrease in the other index classes.

The proportion of Very Good soils that changed index score followed the trend: arable > ley grass > permanent grass > woodland; the inverse was evident for Degraded soils (Table 3-2). Despite having similar numbers of Very Good soils, 18% fewer of the ley grass changed class compared to arable.

Table 3-3 Changes in index class between the two NSI samplings by land use and first sampling index score. Note very good soils could only move to a lower class and degraded soil to a higher class, but good and moderate soils could move both up and down.

Land use		Index class at first sampling			
		Very good	Good	Moderate	Degraded
Arable	Number at first sampling	129	70	90	215
	Number that changed class	61	50	57	55
	% that changed class	47	71	63	26
Ley grass	Number at first sampling	128	60	43	53
	Number that changed class	37	40	25	24
	% that changed class	29	67	58	45
Permanent grass	Number at first sampling	375	83	44	30
	Number that changed class	86	51	25	18
	% that changed class	23	61	57	60
Woodland	Number at first sampling	61	16	14	7
	Number that changed class	2	13	11	4
	% that changed class	3	81	79	57

The extent of decreases from Very Good, increases from Degraded, and changes in either direction for Good or Moderate classes could also be seen for each land use (Figure 3-3). More arable soils became Degraded than grassland soils, irrespective of initial class. A higher number of Very Good soils changed to a lower class under permanent grass, but the changes tended to be to Good or Moderate scores, and permanent grass had a higher proportion remain Very Good than arable or ley grass. A larger number of Good soils moved down index classes than moved up under arable or ley, though under permanent grass the split was even. A larger proportion of Moderate soils were likely to become Degraded under arable than grassland. The number of Degraded sites increasing to another index class showed a similar trend for each of these three land uses, with few Degraded soils achieving Good status, and very few becoming Very Good. Though arable soils had the largest number of sites improving from Degraded to Moderate it also had the largest number of Degraded sites and the largest proportion remaining Degraded.

Fewer woodland soils changed class and most of the changes were to a better class than when first sampled. As the woodland sites tended to be Very Good already, had a smaller sample size, and changes in index class tended to be upward, the smaller numbers changing class is to be expected.

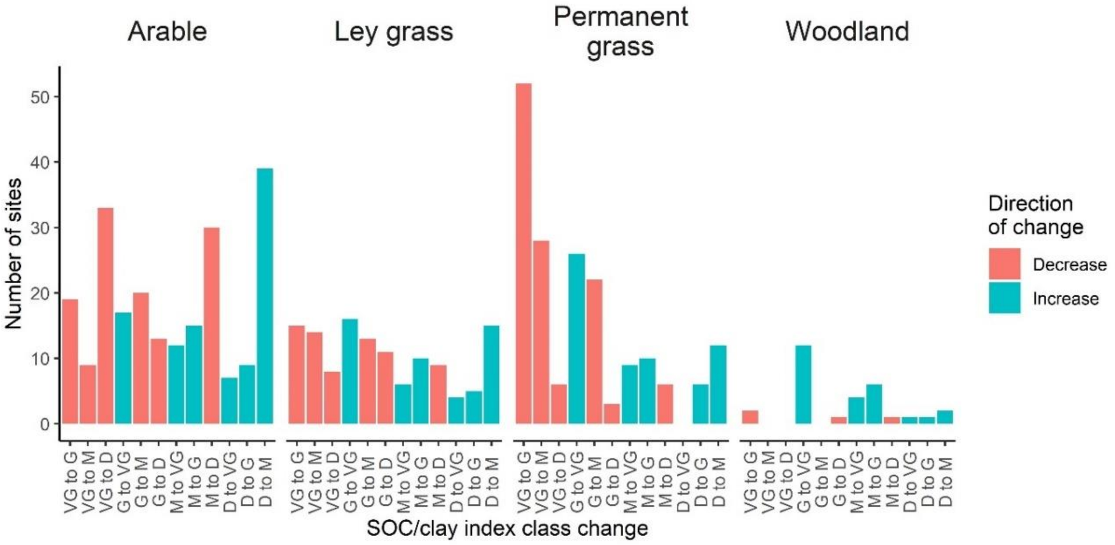

Figure 3-3 Numbers of sites that changed SOC/clay index class between the NSI samplings. Numbers of sites in each land use: arable, 223; ley grass, 126; permanent grass, 180; woodland, 30. VG, G, M and D indicate Very Good (SOC/clay ≥1/8), Good (SOC/clay 1/10-1/8), Moderate (SOC/clay 1/13-1/10) and Degraded (SOC/clay <1/13) classes.

3.5.2 Long-term experiments

The land use information for the national scale data did not record specific land management practices. So, long-term experiment data was used to try to understand how some management practices affect the SOC/clay ratio and index class over time of soils under arable, ley grass and permanent grass. The two experiments were running over similar time periods (including the years of the NSI samplings), however they differ from each other by approximately a factor of two in soil clay concentration, and their management history.

3.5.2.1 Woburn

Despite a history of arable management, the arable treatments in the Woburn experiment showed a general decrease over 70 years, remaining Degraded for the most part (Figure 3-4a). The treatment without fallows started each treatment cycle with one-year hay crop, which seems to have been sufficient to maintain a higher SOC/clay than the other arable treatment. After the hay rotation was stopped in 1975, the SOC/clay decreased to approximately where the other arable treatment was before fallows were introduced to its rotations (at this time), which then caused the SOC/clay to decrease further.

Apart from the three-year grazed-ley (Grazed ley / LN3), which increased SOC/clay from Degraded to a high Moderate score, the other treatments were relatively similar to the arable treatment with one-year hay for approximately the first 35 years. The two eight-year ley treatments were under an alternating rotation which included the grazed grass ley but did not stabilise much SOC possibly due to the other treatments between grazed rotations. After the mid-1970s, however, the 3-year ley with clover (previously lucerne) and the eight-year leys showed similar, but more substantial increases. The peaks and troughs of the eight-year leys after 1970 correspond with samplings in the 8th and 3rd year under ley respectively. The replacement of grazing with inorganic N fertilizer resulted in a decline in SOC/clay for the grazed-ley treatment but it remained higher than the other ley treatments for approximately 15 years until they caught up. There was little difference between the shorter and longer leys from the 1990s onwards, though the shorter leys had lower SOC/clay in the 2000s, and relatively little difference between the nitrogen-fertilized or clover leys of the longer rotations both achieving or close to SOC/clay 1/10 after the second phase of eight-years under ley grass. It is notable that in each case the eight-year leys decrease to a similar SOC/clay as the three-year ley rotation soils.

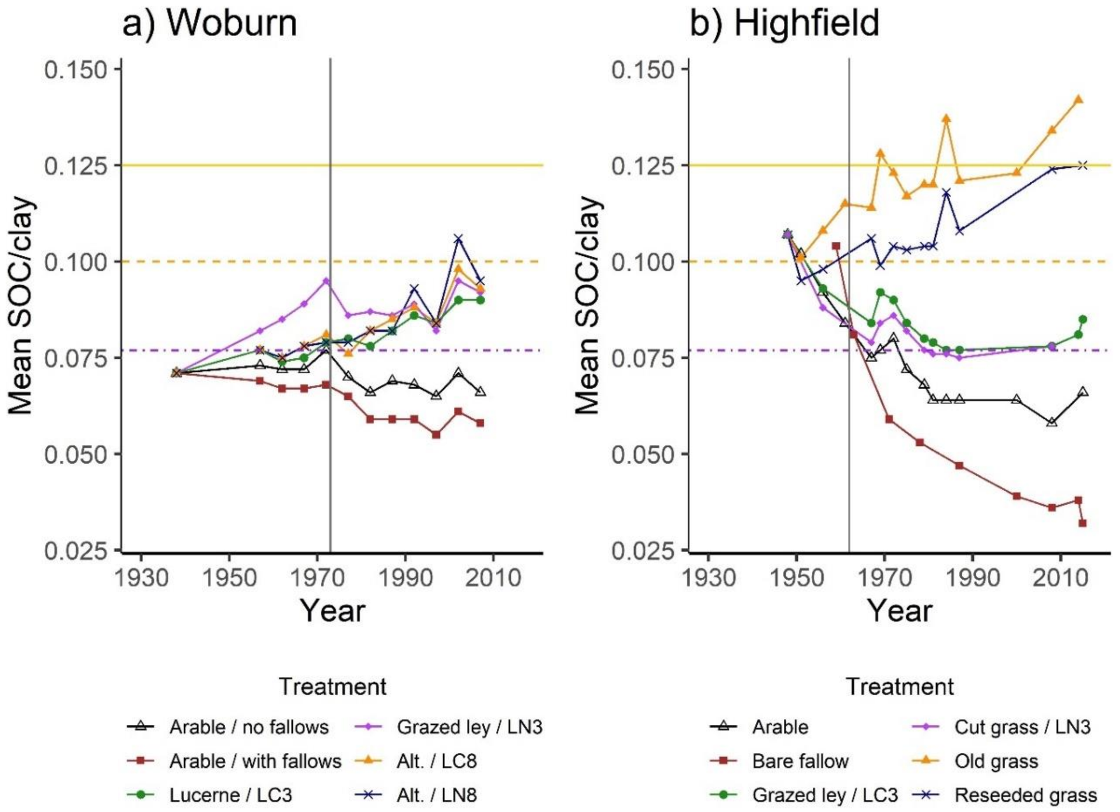

Figure 3-4 Mean SOC/clay ratios over time in the long-term ley-arable rotation experiments at (a) Woburn (sandy loam) and (b) Highfield (silty clay loam). For standard deviations of each treatment at each timepoint see Appendix A. Horizontal lines represent SOC/clay index thresholds equal to 1/8 (solid), 1/10 (dashed), and 1/13 (dot-dash). The vertical line marks a change in treatments as indicated by the "/" in the legend entry. Alt. = Alternating treatment of 3-yr arable, 3-yr Lucerne, and 3-yr grazed ley; LC3 = 3-yr ley + clover; LN3 = 3-yr ley + nitrogen; LC8 = 8-yr ley + clover; LN8 = 8-yr ley + nitrogen.

3.5.2.2 Highfield

Starting from long-term grass management and therefore higher index scores (Good, rather than Degraded), the arable, ley grass, and bare fallow treatments resulted in decreased SOC/clay ratios, whereas grassland treatments (retained old grass or reseeded grass) resulted in an eventual increase over 67 years (Figure 3-4b). During the first 20 years, the arable plots had decreased from a Good index score to the Moderate-degraded threshold, then decreased further over the next 15 years before reaching something of a plateau at approximately SOC/clay = 0.064. The Woburn arable treatments also plateaued at approximately SOC/clay = 0.058 and 0.068 (with or without fallows, respectively) despite Highfield having 110-160 g kg^{-1} higher clay concentrations. The ley treatments decreased over the same time periods as arable but maintained a Moderate index score until approximately 1980. Between 1987 and 2008 there were no measurements on these treatment plots, but they had maintained SOC/clay close to the Moderate-Degraded threshold over that period, after which ley with clover increased and ley with inorganic N decreased. The continuous bare fallow treatment started ten years after the other treatments, however within four years the SOC/clay had decreased from Good to the level that arable and ley treatments took nearly 20 years to reach, and the soil was lower in the Degraded class within 10 years. The SOC/clay continued to decline over the following 45 years. The SOC concentration associated with the last samplings presented for bare fallow was approximately 10 g kg^{-1}. This was comparable to, though slightly higher than, the arable treatments of Woburn which plateaued at 8-9 g kg^{-1}.

After initial ploughing and reseeding, the SOC/clay index of reseeded grass decreased across the Moderate-Good threshold in the first three years followed by a general increase after this point, approaching Very Good status after 2000. The SOC/clay of the old grass treatment showed an increasing trend over the course of the experiment, from a Good index score up to Very Good over 60 years. Both treatments were grazed until 1962-63, which might explain some of the increase up to this point and subsequent plateau.

3.5.3 Carbon storage potential

Using the clay concentrations of the long-term experiments as examples, the carbon stock at each SOC/clay threshold and the difference that would result from a change in SOC/clay class (threshold to threshold) was calculated (Table 3-3). SOC/clay = 0.065 was included as a possible arable scenario.

Table 3-4 Carbon stock differences between SOC/clay thresholds for Woburn and Highfield soils. Carbon stock calculated to 25 cm depth.

			Difference in carbon stock between SOC/clay ratios (Mg C ha^{-1})		
			SOC/clay[a]		
Site	SOC/clay	Carbon stock at SOC/clay (t C ha^{-1})	1/8	1/10	1/13
Woburn	1/8	65.0	-	-	-
	1/10	52.0	13.0	-	-
	1/13	40.0	25.0	12.0	-
	0.065[b]	33.8	31.2	18.2	6.2
Highfield	1/8	92.1	-	-	-
	1/10	73.6	18.4	-	-
	1/13	56.6	35.4	17.0	-
	0.065[b]	47.9	44.2	25.8	8.8

[a] Dashes indicate not applicable.

[b] Typical of arable management in the two experiments.

Changes in SOC/clay equivalent to SOC/clay = 1/10 to 1/13 (or vice versa) were observed in each experiment for various treatments over time. At Woburn, most ley treatments achieved close to this SOC/clay increase over 30-35 years, though at different times (0.40-0.34 t C ha^{-1} yr^{-1}). At Highfield, the SOC/clay of the bare fallow treatment decreased this much in four years, a rate of 4.93 t C ha^{-1} yr^{-1}, compared with arable which took approximately 20 years, a rate of 0.985 t C ha^{-1} yr^{-1}. If we consider the increase in SOC/clay for the Highfield "Old grass" treatment from SOC/clay = 1/10 to 1/8 between years 1951-2008 (58 years), the rate was 0.317 t ha^{-1} yr^{-1} (overall).

3.6 Discussion

3.6.1 National Soil Inventory

Kirk & Bellamy (2010) found that the rates of change in SOC between the NSI samplings were well-described with a simple single-pool model for each land use, equating the rate of change with C inputs minus outputs in proportion to the current SOC content. In spite of the diversity of soils and managements in each land use, the model showed soils with small SOC contents tended to gain C whereas those with larger values increasingly lost it, and there was a characteristic steady-state SOC content for each land use at which C was neither gained nor lost. The steady-state values increased in the order arable < ley grass ≈ permanent grass < other (mainly woodland), and the rate of gain or loss increased with the degree of departure from the steady-state SOC content.

Consistent with these findings, we have found that soils with Very Good SOC/clay indices tended to lose C between the NSI samplings in the order arable > ley grass > permanent grass > woodland (Figure 3-2a and Figure 3-2b), which is the order of greatest departure from the respective steady-state SOC contents shown by Kirk & Bellamy (2010). Since clay concentration is a major determinant of SOC protection and stability, the SOC/clay ratio gives a more definitive separation between different managements, climates and other factors within a land use category than SOC concentration alone, and so a clearer separation between index values (Figure 3-2b).

Soils with higher SOC showing more negative rates compared with positive rates for those with lower SOC might suggest regression towards the mean effects. However, Lark et al. (2006) showed that this was having little effect on the rate of change in SOC against baseline SOC (which relates to first survey index score) in the NSI data. The rates of change of Very Good soils compared to those of the other classes suggested that a mechanistic effect was in play rather than random effects. Very Good soils were more prone to quicker declines in SOC suggesting that this threshold can indicate where protective measures should be directed. This is of particular importance for arable land where higher rates and frequencies of decline were observed, but also for ley and grassland systems which tended to decline less but still require attention. That Degraded soils increased at similar rates and frequencies to the other index classes could also highlight that rate of accumulation of SOC has some limitations relative to clay for agricultural soils compared with woodland. Woodland soils showed more prospects for increasing SOC accumulation even in very good soils than the other land uses and incorporation of trees where possible and practical could help to support carbon storage efforts on other land use sites. All of this supports the use of the index as a measure of sequestration potential and for monitoring changes in SOC.

3.6.2 Long-term experiments and implications for management

The long-term experiments illustrate that changes in SOC following changes in management last over decadal time scales, that in general SOC losses happen faster than gains, and that the amounts of SOC potentially stored in or lost from clayey soils, such as those at Highfield, are greater than for sandy soils, such as those at Woburn. However, despite the differences in clay concentration (approximately 125 g kg^{-1}), the arable treatments on both soil types levelled off at a similar SOC/clay ratio of 0.06-0.07. Another way in which the SOC/clay ratio reflected protection of SOC by clay was shown in that the bare fallow treatment had an equivalent SOC concentration to the arable soils on Woburn (approximately 10 g kg^{-1}) but a much lower SOC/clay ratio. Based on SOC alone these situations might be treated similarly, however it can be seen that there is a greater potential for C storage for the bare fallow soil. The index also suggested it to be in a worse structural state due to the lower SOC/clay ratio (Prout et al, 2021).

The SOC/clay ratios of the ley treatments in the two experiments did not match as well as the arable treatments, however a Moderate index score seems achievable for ley soils. The eight-year ley soils did not stabilise more SOC than the three-year ley soils as evident through the decrease in SOC/clay to equivalent levels 3-years after arable test crops. The value of grazing to help achieve SOC targets might be evident however through the retained SOC in the grazed-ley treatment after grazing was stopped. The Woburn organic manuring experiment used in Prout et al. (2021) showed agreement with these index classes across treatments, though the arable and ley treatments differ in some practical respects. This is not to suggest that the SOC/clay ratio can or should be used to "diagnose" land management precisely, but that the index can be a useful tool to help inform future management and understand the effects of previous management with more uniformity across soil types than SOC alone.

Whilst climate is an important factor for SOC cycling, it is not expected to affect the threshold values but might change how land is treated to achieve the same SOC/clay at different sites or the "effective saturation limit". Based on the analysis of Prout et al. (2021), we would not expect a soil to be limited to a Degraded status in temperate regions due to climate. Climate change may affect this, with rising temperatures and more frequent extreme weather events. However, we would suggest that improving the

SOC status of the soil will help it to be more resilient for future food production and other soil functions which benefit the wider environment (e.g. water and flood management). Future work might study the effects of management on SOC/clay ratio at sites with a wider range of climatic variables, as both long-term experiments presented here were in Southeast England.

The key step for soil management is soil testing to identify if a soil is Degraded (or better) and then monitoring to keep track of how management decisions are impacting the soil. Soil clay concentration is not expected to change, except with extreme erosion or management, so this requires less frequent monitoring and once mapped, SOC can be monitored periodically to compare to the index. An implication of not thoroughly mapping clay concentration might be evident in the variability of SOC/clay which was evident in the standard deviations of the Woburn data (Table B-1). We expect that with more precise clay concentration data, as for Highfield, the mean SOC/clay results would be similar but with variability better accounted for.

3.6.3 Implications for carbon storage

Our results show that it is unlikely all land uses can achieve the same index values. We summarise in Figure 3-5 a realistic set of targets for each land use. For arable soils, a realistic long-term SOC/clay ratio in topsoil is 1/13, whereas for ley-arable systems it is 1/10, for permanent grassland it is 1/8 and for woodland soils it is > 1/8. Timescales for achieving these targets depend on land use history, the availability of organic matter amendments, the length of ley rotations, and practices such as the use of cover crops and reduced tillage. To the extent that many arable and grassland soils nationally have SOC/clay ratios below these targets, the increases to carbon storage across England and Wales is considerable.

It might be desirable for all soils to have SOC/clay > 1/8 in the interest carbon storage but, crop types (including if a site is grassland or forest) and management practices will impose limitations to how much carbon is added and how much of this remains in the system. Using SOC/clay provides both a normalisation for SOC across soil types and another way to assess whether a predicted increase might be feasible with planned activities, or if a land manager should aim to store more carbon than was previously planned for.

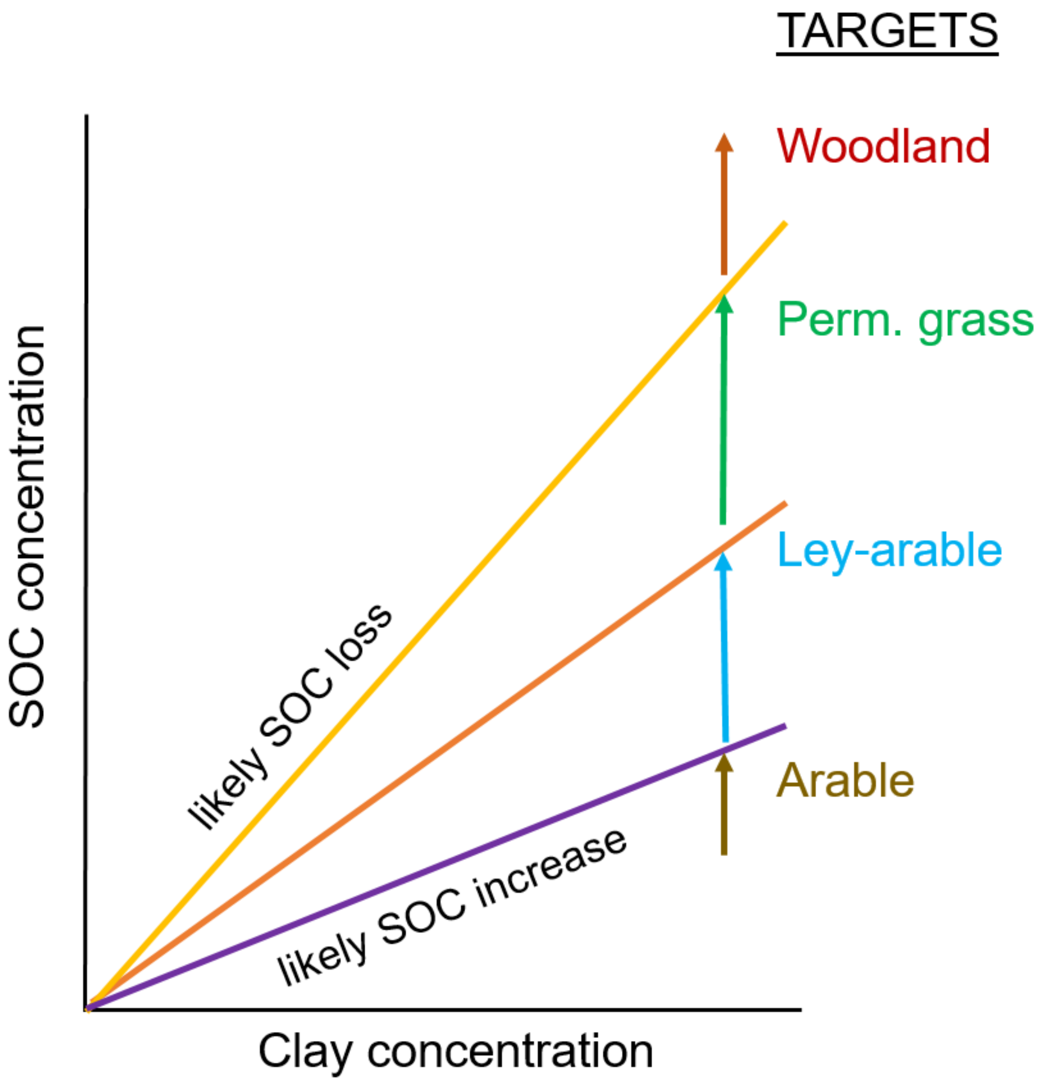

Figure 3-5 Feasible trajectories for SOC sequestration under different land uses.

The agreement between SOC/clay ratio of different soils under similar management, demonstrates the theory of an "effective C saturation limit" (Stewart et al., 2007), at a lower level than the theoretical maximum due to factors such as tillage or organic matter supply. Management is one of the key drivers. When organic inputs are increased or SOC protecting and building practices such as ley rotations are employed, the soil moves towards a higher effective C capacity. The arable soils of the experiments presented maintained a SOC/clay ratio of approximately 0.065 (SOC/clay ≈ 1/15), while a soil with ley rotations could get close to SOC/clay of 1/10 (from previous arable management). On these soils, improving the arable soils to SOC/clay =

1/13 could result in 6-9 t C ha^{-1} being stored. If this were to go up to SOC/clay = 1/10 that is 18-26 t C ha^{-1}, which we have shown could be achievable with frequent or well managed ley rotations in approximately 40 years. Dexter et al. (2008) proposed that SOC/clay = 1/10 was an approximate saturation capacity for SOC-clay interaction, however it is not a limit to SOC accumulation as evidenced by the high numbers of Very Good soils under permanent grass and woodland. This ratio has been shown to relate to physical and structural properties in other studies also (De Jonge et al., 2009; Jensen et al., 2017; Johannes et al., 2017; Prout et al., 2021). All arable soils should aim to at least have SOC/clay = 1/13 to be at lower risk of degraded structural quality. If already achieving this, then the index can be used to monitor ongoing management to maintain SOC and improve further where possible. Grasslands should have SOC/clay > 1/10 and aim for 1/8. Soils with SOC/clay > 1/8 (except woodlands for the most part) might be vulnerable to losing SOC, depending on previous and current land management. Monitoring changes in SOC/clay might help to understand these losses better and allow mitigation of such losses through interventions.

3.7 Conclusions

The SOC/clay ratio index provides a simple method to monitor changes in SOC and inform soil management to maximise carbon storage in given soils and land uses. The NSI results showed that most soils under arable, ley grass and permanent grass declined in quality as defined by the SOC/clay index over the period of the NSI samplings. The proportion of degraded soils under arable management, which was already high compared with other land uses, increased from 43 to 47%. The results of the long-term experiments showed that SOC/clay tracked differences in SOC between management practices over more frequent samplings. Similar management practices resulted in a similar SOC/clay ratio on the two soils with contrasting clay concentration, despite SOC concentrations that differed by a factor of two. A suitable target SOC/clay ratio for arable soils is 1/13, which increases to 1/10 where leys are employed; permanent grassland soils should have SOC/clay > 1/10 and a suitable target is 1/8. Soils with SOC/clay > 1/8 should be monitored to ensure management does not cause losses of SOC. Woodland soils are not expected to be at risk of low SOC/clay ratio, often having SOC/clay > 1/8 and generally improving between the NSI samplings. The SOC/clay ratio index seems appropriate as a simple metric for monitoring SOC over time across land managements and temperate soils and helping to identify those which are low or high in SOC for effective restoration or protection.

3.8 Authorship

All authors: Conceptualization, writing – review & editing. JMP: Methodology, Software, Formal analysis, Investigation, Data curation, Writing – Original draft, Visualisation, Project administration. KDS: Methodology, Supervision. SPM: Supervision, Funding acquisition. GJDK: Supervision. KLH: Methodology, Software, Formal analysis. SMH: Supervision, Project administration, Funding acquisition.

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4 USE OF SOIL SPECTRA TO MEASURE SOIL ORGANIC CARBON TO CLAY RATIOS[*]

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4.1 Abstract

In earlier work we showed that an index based on the soil organic carbon to clay concentration (SOC/clay) ratio is an effective tool for assessing the soil organic matter status of mineral soils and for monitoring changes over time. Conventional analyses of SOC and clay concentrations are expensive and time-consuming. Mid-infrared spectroscopy (MIRS) potentially provides a cost-effective alternative for simultaneous measurement of SOC and clay. But whether this is sufficiently accurate for quantifying the SOC/clay index needs investigation. In this study, a national spectral library was built from archived soil samples from the National Soil Inventory of England and Wales (NSI; n = 3622) for SOC, clay, and SOC/clay. This was compared with a library built from a subset of the US National Soil Survey Center-Kellogg Soil Survey Laboratory spectral library (NSSC-KSSL; n = 7680). Predictions of both SOC and clay concentration were better using the NSSC-KSSL (RMSE = 2.2 and 23 g kg^{-1}, R^2 = 0.98 and 0.95, respectively) than the NSI (RMSE = 9.2 and 49 g kg^{-1}, R^2 = 0.73 and 0.78, respectively). Direct prediction of SOC/clay ratio gave a similar RMSE (~ 0.05) for both libraries. This error was large compared with the ranges of two of the four index classes (~0.02). Our results suggest that the NSSC-KSSL predictions of SOC/clay could

be practically applied for screening three index classes: Very Good, Good/Moderate, and Degraded.

4.2 Introduction

Monitoring and assessment of soils is important for managing land and achieving environmental goals. We have shown the value of an index of soil organic matter status based on the soil organic carbon to clay concentration (SOC/clay) ratio for soils across England and Wales (Prout et al., 2021). This SOC/clay index has three thresholds separating four classes (Table 4-1). Despite its simplicity, the costs and speed of measuring SOC and clay concentrations using conventional sampling and wet analytical methods may be prohibitive for most applications. However, mid-infrared spectroscopy (MIRS) has been shown to be a practical method for determining these soil properties with benefits such as reduced requirements for sample preparation and labour, high-throughput capabilities, and the prospect of determining several other useful soil properties simultaneously (Nocita et al., 2015).

Table 4-1 Summary of the SOC/clay ratio index (after Prout et al., 2021)

	SOC/clay ratio		
Index class	Fraction	Decimal	Description
Very Good	≥ 1/8	≥ 0.125	Good structure likely, > SOC-mineral interaction capacity
Good	≥ 1/10, < 1/8	0.10 - < 0.125	Low risk of poor structure, ≥ SOC-mineral interaction capacity
Moderate	≥ 1/13, < 1/10	0.0769 - < 0.10	Moderate risk of poor structure, potential for SOC storage
Degraded	< 1/13	< 0.0769	High risk of poor structure, higher potential for SOC storage

The accuracy and precision of MIRS depends on calibrating MIR spectra with results of conventional analyses of relevant samples. This can be done at a site-specific scale. But to avoid the time and effort needed for pre-testing and calibration, spectral libraries developed from a wide range of relevant soils can be used instead or to supplement local calibration data. Such spectral libraries have been developed globally, mostly with visible-near infrared spectroscopy (vis-NIRS) (Brown et al., 2006; Stevens et al., 2013; Viscarra Rossel et al., 2016) but also MIRS (Clairotte et al., 2016; Dangal et al., 2019; Grinand et al., 2012; Sanderman, Savage and Dangal, 2020) for a range of soil properties. The predictive performance of calibrating MIRS to SOC and clay concentrations has been shown to agree well with conventional lab methods (i.e. SOC derived from dry combustion and inorganic C determination, and clay measured by pipette method). MIR generally shows higher predictive capabilities than vis-NIR for SOC and clay (McCarty et al., 2002; Reeves, 2010). In terms of measuring the combined metric of SOC and clay, a study using vis-NIRS on a regional-scale in Denmark and Greenland found high prediction accuracy accounting for one ratio of clay/SOC (Hermansen et al., 2016) however they only considered a single threshold (Dexter et al., 2008).

The purpose of the work reported here was to test whether SOC, clay and SOC/clay could be predicted accurately enough using MIRS for application of the SOC/clay index at the national scale of England and Wales, using samples from the National Soil Inventory. A large spectral library from the USA was used alongside the English and Welsh data as a benchmark since we expected the former to have very good predictions for SOC and clay (Dangal et al., 2019; Sanderman, Savage and Dangal, 2020).

4.3 Materials and Methods

4.3.1 Soil Samples and data

4.3.1.1 USDA NSSC-KSSL soil spectral library

The National Soil Survey Center – Kellogg Soil Survey Laboratory (NSSC-KSSL) MIR spectral library and associated soil characterization database was provided by the Kellogg Soil Spectroscopy Laboratory (Lincoln, Nebraska) containing > 80,000 spectra with some associated laboratory data. SOC was derived from total carbon (dry combustion method) and inorganic carbon (determined by manometer). Laboratory methods for these properties and clay concentration are detailed in the Kellogg Soil Survey Laboratory Methods Manual (Soil Survey Staff, 2014).

A limit on SOC was applied to exclude organic soils using the definition from FAO World Reference Base (2006) of SOC > 120-180 g kg^{-1} for clay concentrations 0-60%, and >0.2 g kg^{-1} limit of detection. Soils were sampled and analysed by horizon. A depth of 0-<24 cm was selected to represent topsoil horizons. As a final data cleaning step for the analysis, a partial least squares regression (PLSR) model was run with 10-fold cross-validation, and a number of sites, equal to 1% of the total, were removed which had the highest absolute residuals in SOC/clay. A similar step was carried out by Dangal et al. (2019) and Sanderman, Savage and Dangal (2020) to account for the chance of inaccuracies in the lab or spectral data measurements. The resultant sample count was 7680. Table 4-2 has a summary of SOC, clay and SOC/clay.

4.3.1.2 National Soil Inventory of England and Wales soil spectral library

The soil samples and data for creating the library were from the National Soil Inventory of England and Wales (NSI). Samples were taken between years 1978-1983 on a 5-km grid of England and Wales (McGrath and Loveland, 1992). Clay concentration (mineral particles < 2 μm) was measured using the sieve-pipette method on < 2 mm (peroxide-treated) soil samples (Avery and Bascomb, 1974).

Data were filtered to remove cases of missing data in SOC or texture values and removing soils which had major soil group recorded as Terrestrial Raw, Raw Gley, Man-Made soil, Peat, or if no group was recorded. Soils were removed if they had peat in their texture description. A limit on SOC was applied to exclude organic soils using the definition from FAO World Reference Base (2006) of SOC > 120 -180 g kg^{-1} based on clay concentration 0-60%. The laboratory methods for SOC were modified-Walkley-Black (Kalembasa and Jenkinson, 1973). Land uses were limited to arable, ley grass, and permanent grass as these were the most relevant to application of the SOC/clay index. The same procedure to remove the 1% of samples with highest residuals for SOC/clay as for the NSSC-KSSL data was carried out. The number of samples remaining was 3622 out of a total 5541. Table 4-2 has a summary of SOC, clay and SOC/clay.

Table 4-2 Summary of soil properties in the spectral libraries

Dataset	Property[a]	Unit	Mean	Med.	Min.	Max.	25% quantile	75% quantile
NSSC-KSSL (n = 7680)								
	SOC	g kg^{-1}	31	22	0.2	171	14	40
	Clay	g kg^{-1}	216	196	0.4	859	115	287
	SOC/clay[b]		0.207	0.124	0.002	2.610	0.076	0.257
NSI (n = 3622)								
	SOC	g kg^{-1}	34	30	4	138	20	44
	Clay	g kg^{-1}	265	248	22	879	179	329
	SOC/clay[b]		0.149	0.122	0.018	0.948	0.081	0.184

[a] Summary statistics for all properties were calculated before transforming as described in 4.3.2.3

[b] Summary statistics for SOC/clay were calculated using individual SOC/clay data not from summary statistics of SOC divided by summary statistics of clay.

4.3.2 Spectroscopy

4.3.2.1 NSSC-KSSL

Soil samples were air-dried and ground (to pass an 80-mesh sieve, < 180 μm), and quadruplicate samples were filled into standardized 96-well microplates (with 4 blank wells for reference). A Bruker Vertex 70 FTIR spectrometer with an HTS-XT high throughput accessory was used to acquire spectra, with 32 co-added scans were collected at 4 cm^{-1} resolution. Details as in (Dangal et al., 2019).

4.3.2.2 NSI

Soil samples, ground to < 100 μm for wet chemistry analysis (McGrath and Loveland, 1992), were obtained from Rothamsted Research Sample Archive. Prior to plate-filling, sample bottles (with lids removed) were placed in an oven at 40 °C for at least 8 hr. Samples were filled in duplicate to 96-well plates (the first six wells of each plate were: gold-reference cap, blank, and duplicates of two internal reference soils). A Bruker Tensor II spectrometer (Bruker scientific, Berlin, Germany) with an HTS-XT high throughput accessory was used to acquire the spectra. The instrument has a spectral range of 8000-340 cm^{-1}, a KBr broadband beam-splitter and window, and an MCT (mercury cadmium telluride) mid-band detector cooled by liquid nitrogen. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were collected with a diffuse reflectance accessory. Spectral resolution was 4 cm^{-1} and scan time was 32 s per sample. Absorbance data in the 4000-600 cm^{-1} range were obtained. The same instrument was used to record each sample's mid-infrared (MIR).

4.3.2.3 Pre-processing of soil data and spectral data

For both spectral libraries, the SOC, clay and SOC/clay data were square-root-transformed to improve the skewness of the data. For the NSSC-KSSL library: four replicates of spectra corresponding to each soil sample were averaged, spectra were resampled over 4000-600 cm^{-1}, and regions showing atmospheric CO_2 features (2389-2268 cm^{-1}; Dangal et al., 2019) were removed to create a complete dataset. For the NSI library: two replicates were averaged, spectra were resampled to 4000-600 cm^{-1} and the CO_2-region 2930-2330 cm^{-1} was removed. A 1st-derivative Savitzky-Golay filter (window size = 21, polynomial = 3) was applied to the spectra (performing better than the baseline-offset transformation used by Dangal et al. (2019)). All processing was carried out in R computing language (R Core Team, 2021), using packages simplerspec and prospectr.

4.3.2.4 Spectral modelling

PLSR is a widely used technique for building spectral calibrations. Whilst other methods such as random forests, Cubist, and memory-based learning (Ramirez-Lopez et al., 2013; Sanderman, Savage and Dangal, 2020) can produce better models, for the NSI data random forests and Cubist models performed similarly to PLSR and computing capabilities for memory-based learning were not available. A Kennard Stone algorithm was used to split the data (for each dataset) into calibration and validation sets (75:25 split, respectively). For the NSSC-KSSL data, the "Pedon" variable within the soil data was used as a grouping argument within the kenStone function (prospectr package in R) since some samples had the same Pedon ID. This avoids samples from the same pedon being present in both calibration and validation sets. The minimum number of principal components which explained 80% of the variance in the spectra was selected for each dataset for Kennard Stone splitting. The number of components each PLSR model was run with was selected using the one-sigma approach from a total of 15. This resulted in all NSSC-KSSL models using 14 components and the NSI models using 9 for SOC, 8 for clay, and 7 for SOCclay. The predicted SOC, clay, and SOC/clay were back-transformed prior to statistical comparison with the back-transformed reference data. The performance of models was assessed using the root mean squared error (RMSE), R-squared (R^2), bias, Lin's concordance correlation coefficient (CCC) ((Lin, 1989, 2000); epiR package in R), and the ratio of performance to interquartile distance (RPIQ). R^2 is included as it is often used in this area, however the CCC relates more directly to the 1:1 line.

Index class determination was assessed by the proportion of observations predicted to fall in the corresponding index class range using chi-square tests and standardised residuals (chisq.test function in stats package R).

4.4 Results

4.4.1 SOC and clay

The two datasets had similar distributions of SOC and clay concentration (although the maximum SOC value for the NSSC-KSSL data was higher) (Table 4-2). SOC and clay were predicted very well using the topsoil subset of the NSSC-KSSL data (RMSEs = 2.2 and 23, and CCC = 0.99 and 0.97 g kg^{-1} for SOC and clay respectively) and better than using the NSI subset (RMSEs = 9.2 and 49 g kg^{-1}, and CCC = 0.83 and 0.87 for SOC and clay respectively) (Figure 4-1). Whilst the NSI predictions were not as good as the NSSC-KSSL predictions, they were close to what might be considered very good models ($R^2 > 0.75$) and their CCC exceeded the R^2. The RMSE of SOC for the NSI data might be higher than desirable given that concentrations of SOC ca. 10-20 g kg^{-1} can be observed on arable farms. SOC concentration in the NSI data tended to be underestimated at concentrations higher than 50 g kg^{-1}. Clay concentration predictions behaved similarly at concentrations higher than 250-300 g kg^{-1}. This affected more observations for clay as evidenced by the larger magnitude bias.

4.4.2 SOC/clay

SOC/clay was directly predicted with similar RMSEs in both datasets, however the NSSC-KSSL library had higher R^2, CCC, and RPIQ (Figure 4-2). The RMSE of 0.05-0.06 was relatively large compared with the scale of the SOC/clay index, for which the SOC/clay ranges for the Good and Moderate classes are 0.025 and 0.023 respectively. Recalculating the statistics for the subset of the predictions with SOC/clay ≤ 0.125

(below the upper threshold of the index), the R^2, CCC, and RPIQ were lower however the RMSE decreased to more reasonable values. Calculating SOC/clay using separate predictions of SOC and clay ($SOC_{Pred}/clay_{Pred}$) showed worse performance for the full validation set of the NSSC-KSSL data but an improvement in the subset with SOC/clay ≤ 0.125 (Table 4-3). For the NSI data there was little difference between the $SOC_{Pred}/clay_{Pred}$ (Table 4-3) and the direct calibration (Figure 4-2) for the full calibration set but the SOC/clay ≤ 0.125 set was marginally better. Calculating SOC_{Pred}/measured clay ($clay_{Meas}$), did give some improvements to RMSE for each dataset as well as better agreement (CCC and R^2) than using direct prediction or $SOC_{Pred}/clay_{Pred}$. This was to be expected given that error in predicting clay concentration was removed.

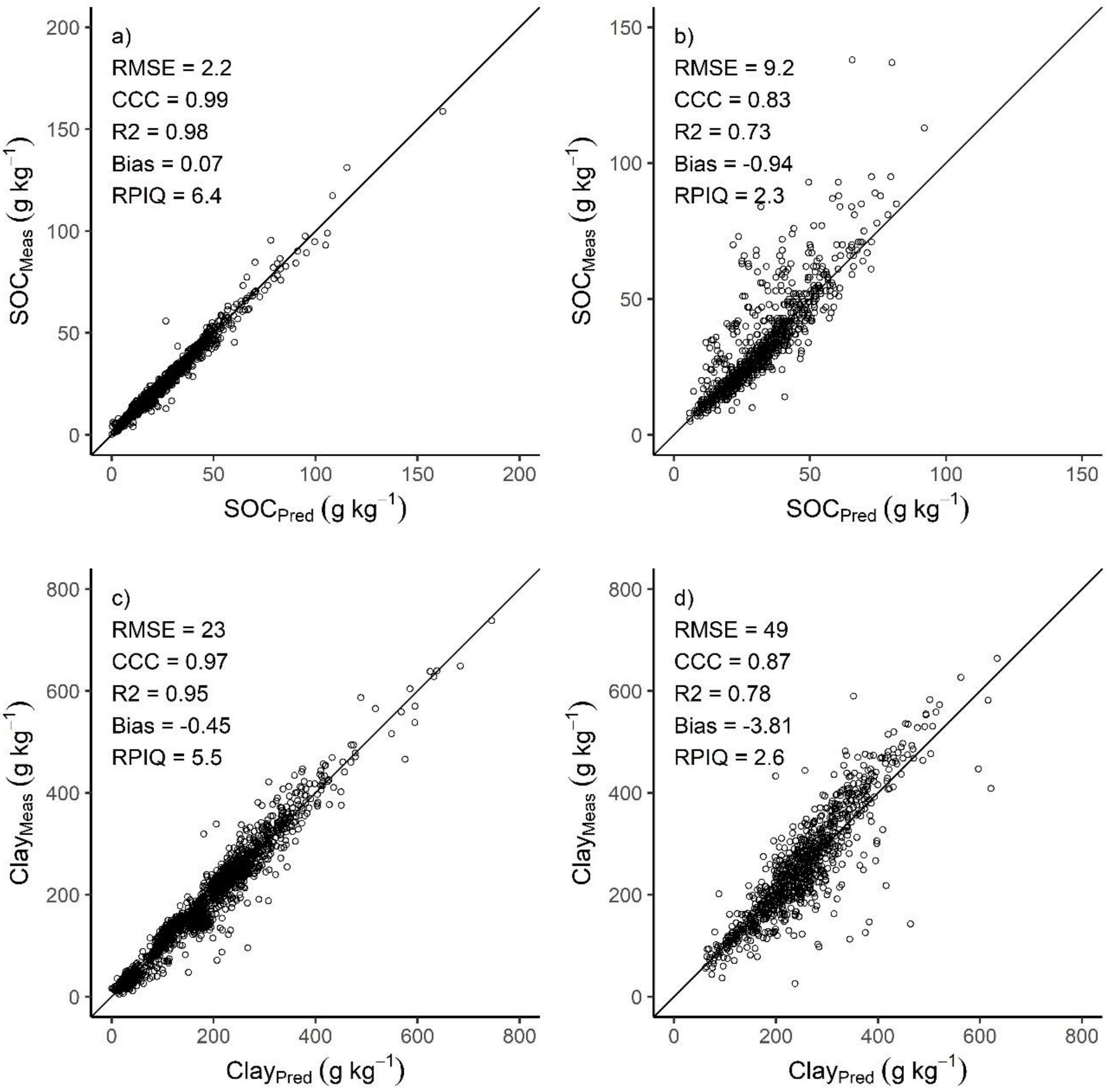


Figure 4-1 Predictions of soil organic carbon (SOC) and clay concentrations using partial least squares regression (PLSR) on the validation holdout set: a), c) the NSSC-KSSL spectral library (n = 1919), and b), d) the NSI spectral library (n = 905).

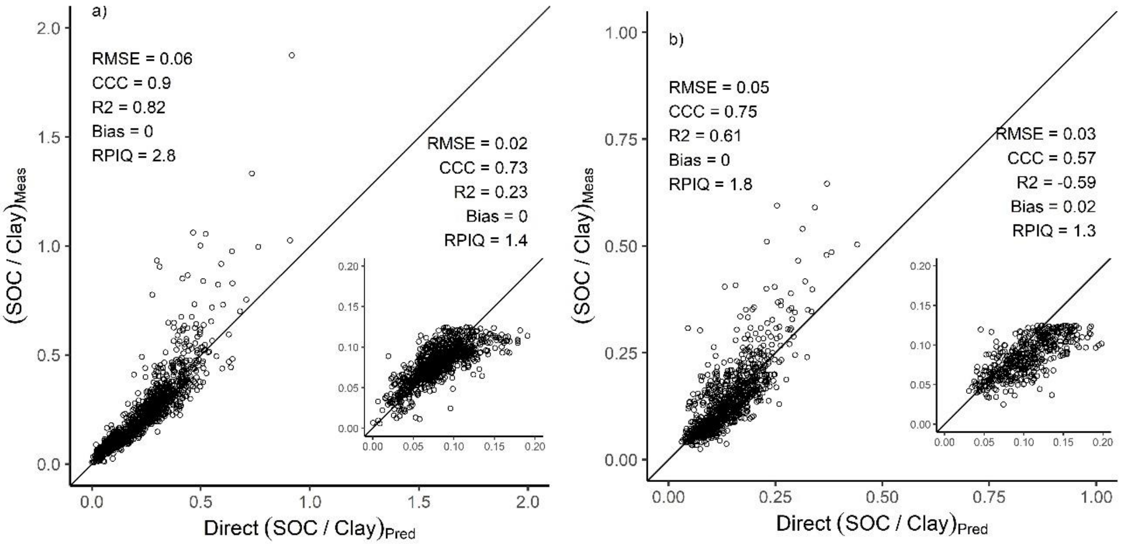


Figure 4-2 Predictions of SOC/clay using partial least squares regression (PLSR) on a validation holdout set of a) the NSSC-KSSL spectral library (n = 1919) and b) the NSI spectral library (n = 905). Insets show predictions for a subset with measured SOC/clay ≤ 0.125 (n = 1079 and 468 respectively for a) and b)) with recalculated statistics. RMSE = root mean square error, CCC = concordance correlation coefficient, R2 = R squared, RPIQ = ratio of performance to interquartile distance.

Table 4-3 Prediction statistics for SOC/clay calculated from separate predictions of SOC and clay for the validation set and the subset of this set with SOC/clay ≤ 0.125.

Dataset	Calculation of SOC/clay[a]	Validation set subset	n	RMSE	CCC	R^2	Bias	RPIQ
NSSC-KSSL	$SOC_{Pred}/clay_{Pred}$	Full	1919	0.10	0.81	0.60	0	1.8
	$SOC_{Pred}/clay_{Pred}$	≤ 0.125	1079	0.01	0.86	0.68	0	2.2
	$SOC_{Pred}/clay_{Meas}$	Full	1919	0.03	0.98	0.96	0	5.6
	$SOC_{Pred}/clay_{Meas}$	≤ 0.125	1079	0.01	0.94	0.87	0	3.5
NSI	$SOC_{Pred}/clay_{Pred}$	Full	905	0.05	0.74	0.61	-0.01	1.8
	$SOC_{Pred}/clay_{Pred}$	≤ 0.125	468	0.02	0.63	-0.07	0.01	1.6
	$SOC_{Pred}/clay_{Meas}$	Full	905	0.04	0.87	0.76	0	2.2
	$SOC_{Pred}/clay_{Meas}$	≤ 0.125	468	0.02	0.79	0.49	0.01	2.3

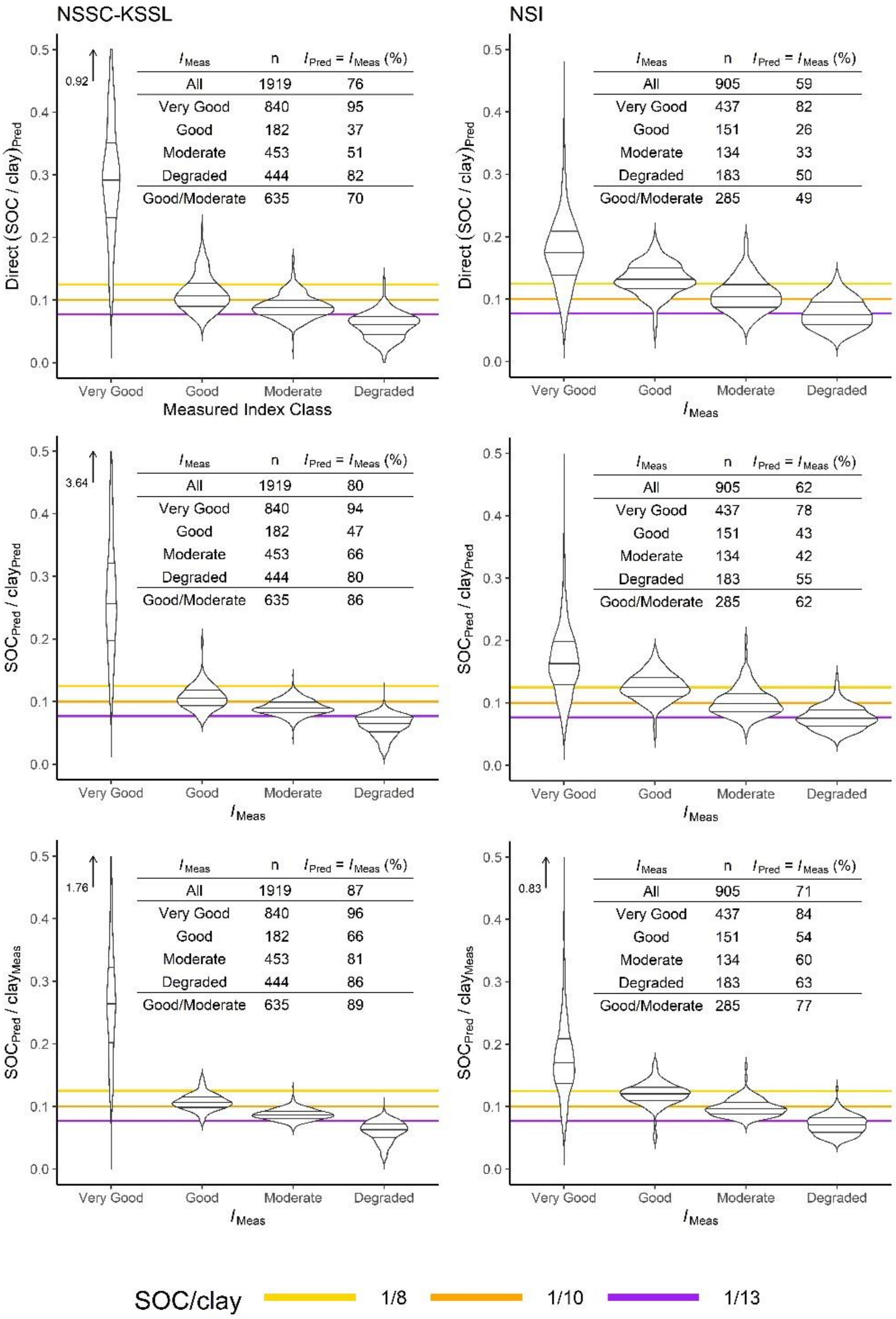
[a] Subscripts correspond to MIRS-predicted (SOC_{Pred} and $clay_{Pred}$) and conventionally measured ($clay_{Meas}$) variables.

4.4.3 Index class determination

Besides determining the precise SOC/clay ratio, the agreement between a predicted observation falling in an index class (I_{Pred}) and its reference value (I_{Meas}) was also assessed. For both datasets the agreement was best for the Very Good class, followed by Degraded, Moderate, and Good classes (Figure 4-3). The poorer agreement for Good and Moderate classes were likely due to their smaller ranges. A combined Good/Moderate class was created which gave better results than either individually.

For both datasets, there was a general trend of increasing agreement between I_{Pred} and I_{Meas} when predicting SOC/clay in the order: direct < $\text{SOC}_{\text{Pred}}/\text{clay}_{\text{Pred}}$ < $\text{SOC}_{\text{Pred}}/\text{clay}_{\text{Meas}}$. This was most evident for the Good and Moderate classes. Despite some variation for Very Good and Degraded class using the NSSC-KSSL, both remained at ~95% and 80-86% respectively. Using the NSI data, the Very Good class could be predicted with ~80% agreement (depending on prediction calculation), but the Moderate and Degraded classes were predicted less well than when using the NSSC-KSSL data. The Good index class was predicted similarly poorly between the two datasets. The Good/Moderate class for both datasets improved markedly upon the separate class predictions of Good and Moderate. In both cases where SOC/clay was calculated from predictions ($\text{SOC}_{\text{Pred}}/\text{clay}_{\text{Pred}}$ or $\text{SOC}_{\text{Pred}}/\text{clay}_{\text{Meas}}$), the combined class outperformed the degraded class.

Figure 4-4 shows the results, for both datasets using a combined Good/Moderate class, of chi-square tests and the standardised residuals of these which showed how well the predicted and measured classes agreed. The results for the analysis with separate Good and Moderate classes are included in Appendix C.



I_{Meas}	n	$I_{Pred} = I_{Meas}$ (%)
All	1919	76
Very Good	840	95
Good	182	37
Moderate	453	51
Degraded	444	82
Good/Moderate	635	70

I_{Meas}	n	$I_{Pred} = I_{Meas}$ (%)
All	905	59
Very Good	437	82
Good	151	26
Moderate	134	33
Degraded	183	50
Good/Moderate	285	49

I_{Meas}	n	$I_{Pred} = I_{Meas}$ (%)
All	1919	80
Very Good	840	94
Good	182	47
Moderate	453	66
Degraded	444	80
Good/Moderate	635	86

I_{Meas}	n	$I_{Pred} = I_{Meas}$ (%)
All	905	62
Very Good	437	78
Good	151	43
Moderate	134	42
Degraded	183	55
Good/Moderate	285	62

I_{Meas}	n	$I_{Pred} = I_{Meas}$ (%)
All	1919	87
Very Good	840	96
Good	182	66
Moderate	453	81
Degraded	444	86
Good/Moderate	635	89

I_{Meas}	n	$I_{Pred} = I_{Meas}$ (%)
All	905	71
Very Good	437	84
Good	151	54
Moderate	134	60
Degraded	183	63
Good/Moderate	285	77

Figure 4-3 Predictions of SOC/clay grouped by measured index class for the NSSC-KSSL (left) and NSI (right) spectral library validation sets. Rows of plots show different ways of predicting SOC/clay. Inset tables show the percentage of each measured index class predicted to fall in the same index class, indicated by the horizontal lines defined in the legend. Horizontal lines on each violin plot indicate the 25th, 50th and 75th quantiles; the widths of the violin indicate the distribution. Where predicted SOC/clay was greater than 0.5 (only applicable for Very Good), the value next to the arrow indicates the maximum value.

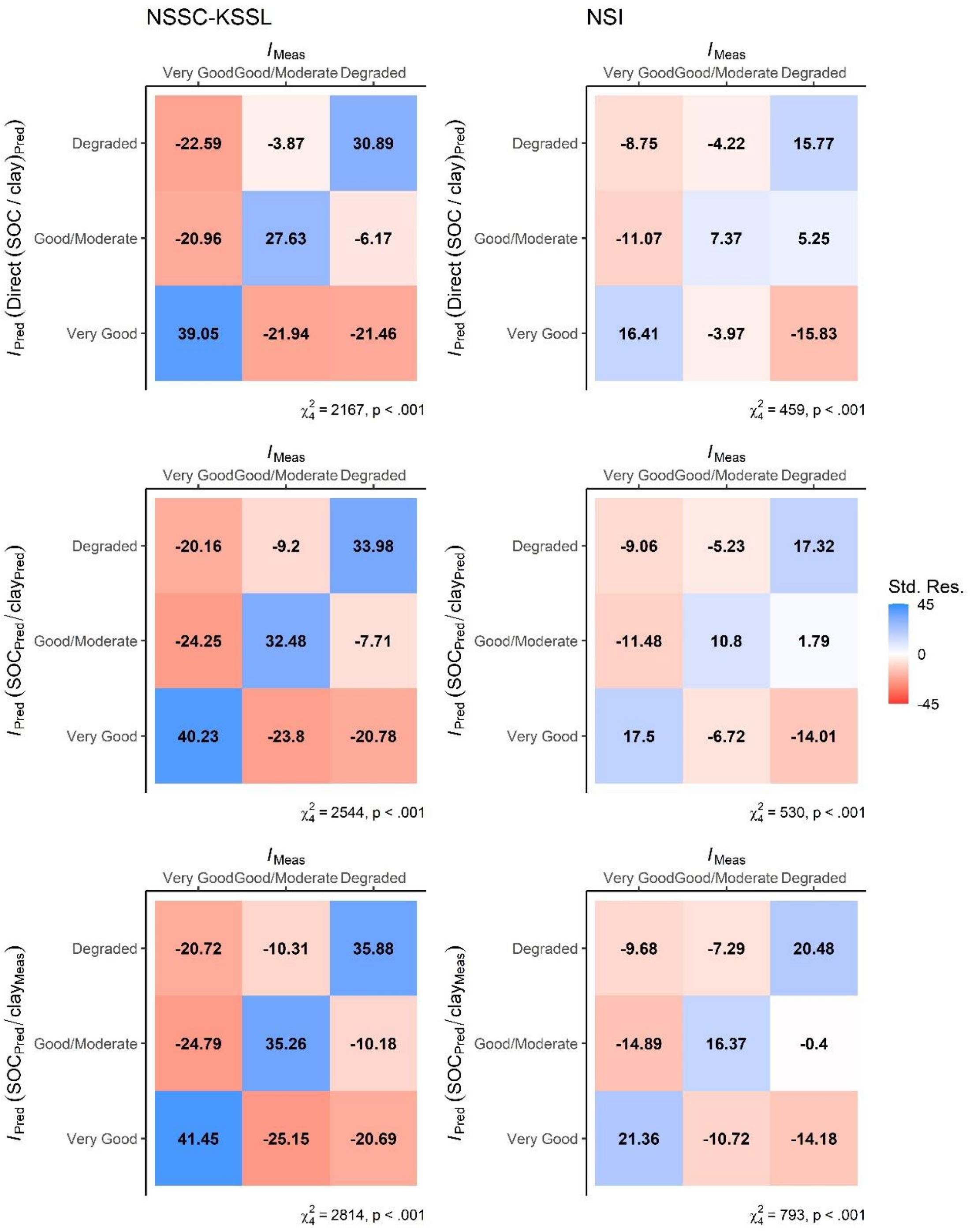


Figure 4-4 Standardised residuals of chi-square tests for the NSSC-KSSL (left) and NSI (right) validation sets between measured index class (I_{Meas}) and predicted index class (I_{Pred}) for each of the SOC/clay calculation methods (top, middle, bottom) and with Good and Moderate class combined. Positive values suggest association for that combination of I_{Pred} and I_{Meas} classes, negative values suggest a lack of association.

The chi-square results strongly suggested associations between I_{Pred} and I_{Meas}, though to a higher degree using the NSSC-KSSL. The sign and magnitude of the standardised residuals for each combination of I_{Pred} and I_{Meas} suggested that Very Good class was predicted well and was unlikely to be misclassified. This was similar for Degraded class, but more sites were misclassified. Residuals tended to be or become negative (and have larger magnitude) for index classes further apart from each other i.e. misclassifications were more likely with adjacent classes. Using either dataset, the best specificity for these classes was achieved with $\mathrm{SOC}_{\mathrm{Pred}}/\mathrm{clay}_{\mathrm{Meas}}$, however, using the NSSC-KSSL the $\mathrm{SOC}_{\mathrm{Pred}}/\mathrm{clay}_{\mathrm{Pred}}$ predictions performed similarly. Using the NSI, lower rates of agreement were evident in lower magnitude residuals than for the NSSC-KSSL. The Very Good and Degraded class predictions showed some specificity to their corresponding class and association decreased the further from each, however in general there was higher association (i.e., less negative and in some cases positive) in mismatched index classes than using the NSSC-KSSL.

4.5 Discussion

4.5.1 Spectral library comparison

The predictions of SOC and clay were better for the NSSC-KSSL library than expected from the PLSR results of Dangal et al. (2019) and Sanderman, Savage and Dangal (2020), which could be due to the selection of mineral topsoil horizons for this study. The NSI library developed here showed worse performance for both characteristics with $R^2 < 0.8$, CCC < 0.9, and larger biases (particularly for clay concentration but with similar RMSE to the PLSR models of Sanderman, Savage and Dangal (2020). Whilst other modelling approaches (random forests or Cubist; not presented) did not improve performance for the NSI validation set, memory-based learning approaches (Ramirez-Lopez et al., 2013; Sanderman, Savage and Dangal, 2020) may improve predictions. Memory-based learning matches a new spectrum to a small number of spectrally similar samples from the library and then builds a new model (e.g. PLSR) from these. The SOC results of the NSSC-KSSL were similar to those of national calibrations of SOC for France which used the dry combustion method (minus inorganic carbon) to determine SOC and PLSR for the calibrations (Clairotte et al., 2016; Grinand et al., 2012). This highlights a potential reason for the lower performance of the NSI data relating to the analytical techniques used for sample analysis. The NSI used a modified-Walkley-Black wet oxidation technique (Bellamy et al., 2005 as detailed in Kalembasa and Jenkinson, 1973) for SOC analysis which can have variable and incomplete recovery of SOC (Conyers et al., 2011; Kalembasa and Jenkinson, 1973) and involved manual titrations, whereas the NSSC-KSSL used a modern dry combustion method to determine total C which is more automated and suited to high throughput and then subtracted inorganic C determined manometrically. If this was the case, and to minimise analytical costs, a subset of the NSI samples could be selected for re-analysis and models built to predict these properties for the remainder of the samples using the MIRS data. For both datasets, the clay concentration was measured by the pipette method, therefore the lower performance of the NSI may be due to the process of measuring such a large sample set at the time compared with more recently or perhaps due to the data selection and soils represented within since the RMSE was similar to those achieved previously using a different subset of the NSSC-KSSL (Dangal et al., 2019; Sanderman, Savage and Dangal, 2020) but with stronger bias.

4.5.2 Predicting SOC/clay

The RMSEs of SOC/clay ratio (Figure 4-2) were more similar between the two libraries than might be suggested based on the predictions of SOC and clay. In both cases however, the RMSEs were larger than ideal given the narrow ranges in the SOC/clay index (Good and Moderate ranges of SOC/clay are small: 0.025 and 0.023), though the NSSC-KSSL gave higher model performance statistics. In both cases there was a tendency for bias at higher SOC/clay (>0.5 for NSSC-KSSL, and > 0.25 for NSI). It might be advised to use MIRS-predicted SOC with either predicted or conventionally measured clay concentration rather than direct prediction of SOC/clay ratio. Removing the variation in clay concentration was particularly good for the NSSC-KSSL data and might be achieved either through conventional measurements or through predicting at a single time point (or creating an average for a site) as clay concentration is unlikely to change unless there is extreme soil disturbance. This route to using clay concentration was shown to be applicable for using the index in our previous work applying the index to long-term experiments which) showed that clay measurements need not have high spatial-resolution or be measured at a close timepoint to SOC to show expected effects of management on SOC/clay ratio and monitor these changes over time (Prout et al., 2021 and Chapter 3).

The analysis of Hermansen et al. (2016) had similar aims to spectrally predict the ratio of clay and SOC in line with the clay/SOC ratio (based on (Dexter et al., 2008)). They used vis-NIRS and a regional scale (eight agricultural fields with 24-95 samples per site) and showed excellent results for SOC and clay similar to those of the NSSC-KSSL. They achieved an RMSE for direct predictions of clay/SOC of 0.64 which seems very good and would be useful for use with the analogous index thresholds (clay/SOC = 8, 10, and 13). The RMSEs of the reciprocal variables (clay/SOC and SOC/clay) cannot be compared or transformed directly between the two works but we expect that the errors of clay/SOC for the libraries used here would give similar results to SOC/clay (i.e. relatively large compared with the index class ranges). We do not expect this to be due to the difference of using vis-NIRS or MIRS but rather the difference in scale. This could suggest that smaller scale calibrations or those with local samples "spiked" into a larger library might give better utility of the index. Spiking a library involves using a relatively small number of samples from a site with reference data to increase the representativeness of a particular area and has shown improvements for use of large spectral libraries at smaller scales (Brown, 2007; Guerrero et al., 2010; Viscarra Rossel et al., 2009; Wetterlind and Stenberg, 2010). Smaller subsets of national spectral libraries could also be an option and spiking has been shown to improve these if they are also insufficient (Seidel et al., 2019). Often vis-NIRS has been studied for this, however the same concepts have been shown to apply for MIRS of soil inorganic carbon (Barthès et al., 2020). This was not tested here but could present a cost-effective route to allow for increased testing without sacrificing accuracy if predictions using the NSI cannot be improved.

Despite the relatively large errors associated with SOC/clay (considering index ranges), the predictions of index class showed good results for an applied assessment of soils. From the violin plots (Figure 4-3) and the chi-square results (Figure 4-4), the lower accuracy when using the NSI library was able, using $SOC_{Pred}/clay_{Meas}$ to achieve few misclassifications between Very Good and Degraded class soils, however a library with the performance of the NSSC-KSSL would be preferable. Using the NSSC-KSSL library 84-91% of the validation set could be correctly assigned when Good and Moderate classes were grouped (depending on how SOC/clay prediction was calculated). Very Good sites were predicted with ~95% accuracy irrespective of whether prediction was direct or calculated from SOC_{Pred} and $clay_{Pred}$ or $clay_{Meas}$. We anticipate that the four index classes could be used with improvements to data selection and/or more advanced modelling techniques but in the current state we would suggest a three-index-class assessment comprising Very Good, Degraded, or in-between (Good/Moderate) to be supported by MIRS. This would highlight soils in need of improvement (Degraded) or protection (Very Good), and land management history or current management might indicate the risk of SOC losses for any of the index classes.

The index can also be used to monitor soils over time to help inform management decisions. Whilst we have not tested the use of these libraries for predicting samples on the same site over time, Sanderman et al. (2021) showed that the NSSC-KSSL spectral library with a memory-based learning approach could be used to achieve monitoring of SOC comparative to conventional lab techniques for several long-term experiments in the USA. Prediction error of clay concentration is an additional factor to consider for monitoring SOC/clay but this might be mitigated by accepting a single time point of clay concentration for future samplings or applying an average of clay concentration for an area. Clay concentration is unlikely to change, unless there are extreme soil disturbances, however site heterogeneity would need to be assessed.

Another benefit of using spectroscopy is that a sample's spectrum acts as a digital record of that sample. If the data is stored (as highlighted by Nocita et al. (2015)), improved calibrations (or calibrations for other properties than originally called for) can be used to provide more detailed information with minimal effort and allow for time series to be reassessed.

4.6 Conclusions

Using two national spectral libraries, and PLSR models, we could reliably distinguish three SOC/clay index classes: Very Good (SOC/clay $\geq 1/8$), Good/Moderate (SOC/clay $<1/8$ and $\geq 1/13$), and Degraded ($<1/13$). The library built from the NSI data did not seem adequate for immediate application in England and Wales. But the NSSC-KSSL library for soils in the USA suggested that in principle national MIRS spectral libraries can produce predictions accurate enough for cost-effective and quick assessment of the SOC/clay index. The better performance of the NSSC-KSSL library could be due to use of better, modern SOC measurement methods, and the greater size of the dataset. The three-index-class assessment framework would give an efficient, and cost-effective way to identify soils in need of improvement or protection. The NSI represents a large dataset of diverse soils, which might be improved to the level of the NSSC-KSSL through remeasurement of SOC using standard modern methods.

4.7 Authorship

JMP, KDS, SPM, GJDK, SMH: Conceptualization, writing – review & editing. JMP: Methodology, Software, Formal analysis, Investigation, Data curation, Writing – Original draft, Visualisation, Project administration. KDS: Methodology, Supervision. GA: Investigation, Resources. FH: Investigation. SPM: Supervision, Funding acquisition. GJDK: Supervision. TSB: Methodology, Software. SMH: Supervision, Project administration, Funding acquisition.

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5 DISCUSSION

5.1 How much SOC should a soil have?

From the perspectives of land managers and policy makers, how much SOC a soil should hold depends on the specific function required of the soil. An index for SOC using soil structural condition as a way to define and validate thresholds has merit as good soil structure underpins many important soil functions – such as water retention, providing a biological habitat, and food and fibre production (Rabot et al., 2018) – and soil structure is involved in the physical protection of SOC (Dungait et al., 2012). Previously the "rule of thumb" of 20 g SOC kg^{-1} soil (Greenland, Rimmer and Payne, 1975) was thought to be a useful threshold to indicate whether a soil might be degraded or not. But, the review of literature carried out by Loveland and Webb (2003) determined there was little quantitative evidence that such a threshold was widely valid. The paper by Dexter et al. (2008) and publications that built on it, including this thesis, suggest that taking into account clay concentration is a key step in defining widely valid thresholds. The SOC/clay index makes explicit the common observation that soils with higher clay concentration tend to have more SOC, and that this relationship gives insight into the role of organic matter in affecting physical properties.

The index can be used to monitor and assess soils to help land managers achieve and maintain sufficient SOC to reduce the risk of structural degradation, across soil types, and better understand carbon storage capabilities.. The SOC/clay = 1/13 threshold defines a minimum SOC that soils should have, and the higher thresholds of 1/10 and 1/8 in the index are expected to increasingly lower the risk of structural degradation. The range of minimum target SOC concentrations (corresponding to SOC/clay = 1/13) is 7.7–38.5 g kg^{-1} for the clay concentration range of 100-500 g kg^{-1} (that accounted for 90% of soil in the NSI). Soils with less SOC than this should be prioritised for improvement.

The structural analysis in this work helped to justify that the SOC/clay thresholds had value beyond the distribution of SOC/clay in soils from the different land uses. It was based on descriptions of the soils at the time of sampling, so has some inherent subjectivity, alongside the adaptation of the Agricultural Land Classification method for the level of detail in the NSI and the soil depth of interest. In spite of this and with the wider variation in SOC/clay ratio for each structural class than the analysis of Johannes et al. (2017), my analysis could support that the highest and lowest thresholds of SOC/clay showed some differences in the distribution of structural quality score and that the thresholds were in a relevant range for assessment and monitoring of soils. Future work might look to develop on this to further understand the relationship between the structure and SOC/clay. Studies of the effects of the relative proportions of SOC and clay on soil physical properties support mechanisms for improved properties and structure with higher SOC/clay (De Jonge et al., 2009; Dexter et al., 2008; Johannes et al., 2017), however, there could be a correlative effect with lower SOC/clay and worse structure (and the inverse) due to management effects (e.g. frequency and magnitude of soil disturbance).

The SOC/clay = 1/10 threshold corresponds to the approximate capacity for SOC protection by mineral interaction (there is likely a continuum range between 1/8 and 1/11 but 1/10 is supported as reasonable value; Dexter et al., 2008; De Jonge, Moldrup and Schjonning, 2009; Schjønning et al., 2012). All soils should aim to have SOC/clay of at least 1/10, and those with greater SOC/clay can still accumulate SOC. However, considering how many arable soils across England and Wales are below the SOC/clay = 1/13 threshold, and the feasibility of management interventions to increase SOC/clay ratios, this lower threshold is a realistic minimum target value. Management is not the only factor to be considered, given that climate and soil type will also affect SOC/clay ratio (Chapter 2). But, management can be adjusted to increase SOC/clay ratios either through protective strategies for soils with high SOC relative to clay or strategies to improve soils deficient in SOC.

5.2 Implications for land use and management

Once calculated, the current index class and SOC/clay ratio can be used to assess future potential based on land use and available resources, and management history to date. Whilst this will be on a site-basis, considering the local management history and circumstances, national datasets and long-term experiments give insight into trends and examples of management effects (Chapters 2 and 3). Nationally, SOC/clay ratios increased in the order: arable < ley grass < permanent grass ≈ woodland. The long-term experiments showed a similar trend – though they did not include woodland – since conventional arable systems with low organic matter additions had SOC/clay ratios in the Degraded range (< 1/13), ley systems were in the Moderate range (1/13–1/10) and grassland systems were in the Good to Very Good ranges (1/10–1/8, >1/8, respectively).

As previously mentioned, SOC/clay ≥ 1/10 would be optimal, but the results from the large- and small-scale datasets analysed in Chapter 3 suggest that arable soils are only likely to achieve SOC/clay 1/13–1/10. This puts the broad land use category at higher risk of degraded soil structure but, without sufficient organic matter inputs and low disturbance management activities this might be the achievable states for many soils. Ley systems are at lower risk, and it would be desirable to expand the area under ley rotations to improve degraded sites, where possible. However, a consequence would be that the national area under crops at any time would be decreased, with implications for national food production and requiring expansion of production overseas (Searchinger et al., 2018; Smith et al., 2019). The same argument applies for conversion of arable land to long-term grass.

The time taken to realise sequestration potentials should also be appreciated. The long-term experiments showed that improvements are on a decadal time-scale, though depending on starting SOC/clay and intervention types, positive changes can be seen within 10-years. Increases can be quite dramatic if sufficient organic matter is available, for example with FYM additions on low clay concentration soils. However, the availability of organic amendments, application rates and relevant restrictions (Poulton et al., 2018) have implications for the environmental and economical sustainability of such interventions.

The observations and trends at national and local scale suggested that an achievable SOC/clay ratio for each broad land use considered was 1/13 for arable, 1/10 for ley grass, and 1/8 (or above) for permanent grass and woodland. The national data showed that each land use could have greater SOC concentrations than suggested by these ratios (Figure 2-2), but they might then be at risk of SOC losses (particularly if SOC/clay > 1/8; Figure 3-2). Woodland soil management is somewhat less invasive than that on agricultural land, and woodland soils are expected to fall in the Very Good index class. The index should be valid for other forms of agricultural land use in England and Wales not considered here, such as rough grazing and heathland. But this work focused on land uses for which soil management is more direct.

Each land use showed a wide range of SOC/clay values, and explanations for this might be provided by the specific management and history, time since management or land use change and site characteristics. This is not to say that arable soils with greater SOC concentration are destined to have SOC/clay $\leq 1/13$ but that conventional arable systems with limited access to or application of organic matter may struggle to exceed this value.

The index gives a clearer picture of where to prioritise interventions. The arable treatments of the three long-term experiments had relatively similar SOC/clay ratios (ca. 0.065; Figure 2-6 and Figure 3-4) despite differences in clay concentration, but the bare fallow treatment in the Highfield experiment (Figure 3-4) had a markedly lower SOC/clay ratio. Based on SOC alone and that 10–20 g SOC kg^{-1} soil might have been considered acceptable for arable soils (Loveland and Webb, 2003), all the soils might have been considered a bit low to on par for arable but the index shows all to be classed as Degraded with the bare fallow particularly in need of attention.

Soils managed under different climatic conditions – for example, the wetter West of England and Wales and the drier East of England – may respond differently to management interventions to increase SOC/clay ratios (results in Chapter 2). However, the same thresholds should be applied

5.3 Soil testing

Appropriate and reliable soil testing is needed to assess whether management needs to be improved and to what degree (Smith et al., 2020). SOC and clay concentrations are among the most informative measurements for managing soils and are routinely tested. Conventional analysis of clay concentration can be expensive and laborious. However, there are simple surrogate measures that may be adequate. The broad texture class might be insufficient due to sometimes large ranges in clay concentration (100 g kg^{-1} to 600 g kg^{-1}), but testing a subset of samples for clay can provide an effective measure of the heterogeneity at a site and allow for appropriate averaging of clay concentration. This can then be used for future samplings also. Spectral analyses, supplemented by conventional wet analyses on a subset of samples, can allow assessments at high spatial resolution with reduced costs, labour and time (Nocita et al., 2015). Whilst spectral predictions for SOC and clay could not be modelled accurately with the NSI data in its current state (using PLSR) the results with the large spectral library of US soils indicated that spectral methods can be used for index class determination (Figure 4-3). Predictions are also expected to be better when more advanced models such as memory-based learning (Ramirez-Lopez et al., 2013) can be employed. Sample preparation for MIRS analysis (oven-drying and grinding to <100 μm) is similar to that for other analyses but with the scope for simultaneous measurement of a range of properties, including SOC, if calibrations are developed. After sample preparation, SOC/clay ratio can be determined rapidly. The digital spectral record of a sample is also valuable for predicting new variables in old samples or updating predictions if better calibrations are created (Nocita et al., 2015). These advantages need to be set against technical limitations, such as instrument-to-instrument variation – which can be mitigated (Dangal and Sanderman, 2020) – and limitations related to data ownership and storage.

5.4 Assessment and monitoring

The index provides a uniform framework based on readily measurable variables to assess soil SOC status and potential across different soil textures and land uses for topsoils of England and Wales. This is of interest to policy for the provision of guideline values but also to land managers directly who regularly test their soils to assess fertilizer requirements or adjustments to pH. In a similar way, the index can be monitored to help determine if and in what way management changes are required. The key index classes at a national scale might be the Very Good class and the Degraded class, respectively indicating soils which should be protected as they have high carbon concentrations or soils which are deficient in SOC and are more likely to be affected by poor structural quality and have higher carbon storage potential. These interpretations are consistent across agricultural and woodland land uses. The protection of already realised carbon stores is just as important as restoring soils which have lost carbon over years of management, and the identification of both scenarios is vital to achieve sustainability goals. As the index considers fundamental soil properties (SOC, clay, soil structure), there is a high suitability for it to be used to quantify assessment criteria in monitoring schemes. The Sustainable Farming Incentive for land in England (DEFRA, 2021) is one such example.

Currently in the pilot stage and due to rollout in 2022, the Sustainable Farming Incentive (DEFRA and Rural Payments Agency, 2021) sets out soil standards for arable and horticultural (including temporary grassland), and improved grasslands. These are practice-based and have a payment scale per hectare related to increasing soil improvement activities in aid of wider landscape benefits. The first action of the first level for both sets of soil standards is to carry out a soil assessment including lab analysis of soil texture and soil organic matter. Clay concentration is specified to be measured alongside soil organic matter due to its effect on organic matter storage and participants are advised to “use your results to identify fields with below average soil organic matter” but there are no quantitative values for guidance. From the analyses in this thesis, many arable soils will be degraded and therefore the average soil organic matter is a poor metric to use. Without specifying how to use clay concentration to compare different values of organic matter, prioritising of soils might not be optimal but, SOC/clay is easily calculated. The index would be a suitable metric for incorporation into such incentives. The organic matter action of the arable and horticultural scheme is to add organic matter to an increasing minimum area for each payment level (from 10–20% of the land entered into the standard). This might be improved by additionally utilising index thresholds, for example, specifying that arable soils should have SOC/clay $\geq 1/13$. This could be added at the highest payment level or as an additional payment at any level it is achieved. Improving and maintaining organic matter is part of the ethos behind the actions and the soil assessments allow for this to be tracked but planning management activities and the resultant effects are likely to be less effective without quantitative guidelines. On a positive note however, the advice provided for minimum inputs of organic matter, has the potential to achieve target SOC/clay ratios for soils under these land uses (SOC/clay $\geq 1/13$ for arable, and $\geq 1/8$ for improved grassland) based on the long-term experiment results presented in this thesis and this could be monitored without strict definition within policy standards.

5.5 Future work

The SOC/clay index makes more explicit the limits of a soil to hold organic carbon which can be used to help predict carbon stock potentials as shown in Section 3.5.3. It was not within the scope of this work to assess how the index might affect various predictions for carbon stocks at large scales. But this might be analysed in future work. The index is also focused on topsoils and whether such relationships can or should be considered in subsoils, which hold a substantial stock of carbon, might warrant investigation.

Given a soil’s SOC/clay ratio, understanding how to improve its organic matter status in a sustainable, economical way is a separate but no less important issue for land managers. Long-term experiments give model examples of how, for a certain soil type, specific management conditions resulted in changes in recorded soil properties. They can be a readily accessible source for deriving management guidelines for particular soil types and management scenarios. It would be of interest to test SOC/clay ratios across a wide range of farms and management regimes, to assess and develop management strategies to effectively improve SOC/clay ratio, whilst also taking into account other dependencies. The SOC/clay index could also be a valuable tool in assessing the impact of regenerative farming practices involving reduced/no-till, cover crops and novel crop-rotations, which are becoming more commonplace. The work reported here, suggests that SOC/clay would be a more useful metric for understanding the effects of these managements than SOC concentration alone.

Given that it is over 20 years since most of the NSI sites were last sampled, a third sampling is overdue and would be highly useful to further the research discussed in this thesis. One specific analysis could be to explore the relationship between land use, climate and SOC/clay ratio to highlight where interventions might be most needed. By calculating ranges of SOC/clay for each land use and rainfall class, similar to the analysis of Verheijen et al. (2005), the scale of required interventions for each combination could be gauged. This was considered for index class categorically in the first sampling of the NSI (Table A-6), but more up-to-date soil information and “robust ranges” of measured SOC/clay would give more information for policy and advisory groups. The intention being to actively help direct resources for improvement or protection efforts rather than observe such SOC/clay ranges as expected based on land use and rainfall class. The direction of resources could be to provide subsidies for soil testing to land managers in certain areas to better map SOC and clay on their land.

With the development of the NSI spectral library, and scope to improve its calibrations, analysis of a future NSI sample set using modern analytical methods could provide a template for streamlining national soil monitoring programmes. The NSI spectral library might be improved through more complex modelling, such as involving memory-based learning (Ramirez-Lopez et al., 2013), and by reanalysis of SOC in archived samples using modern analytical techniques.

The index currently does not take account of differences in clay mineralogy. In practice, the differences in the chemistry of clay minerals will affect applicability of SOC/clay ratio thresholds. This is likely to be particularly true of highly weathered soils of the humid tropics, in which clay mineralogies are dominated by sesquioxides (Feller and Beare, 1997; Rasmussen et al., 2018). These interact with SOC in very different ways to the constant charge minerals that dominate temperate soils. Future work is needed to develop an index appropriate for such soils.

5.6 References

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6 CONCLUSIONS

In this thesis I have shown that an index based on the ratio of SOC to clay concentrations is an effective tool for assessing the SOC status of mineral topsoils across England and Wales under different land uses. The variety of soils included in the analyses, and results from other countries in Europe, suggest that the index might be applied in other locations with temperate climates. The index is sensitive to agricultural management at local scales and is a better metric for assessing and monitoring SOC management than SOC concentration alone.

The index can be used across soils under different land uses. The results suggest realistic target SOC/clay ratios for different land uses are: 1/13 for arable, 1/10 for ley-grass, 1/8 for permanent grass, and > 1/8 for woodland. Close to 40% of arable soils sampled in England and Wales were Degraded at time of sampling compared with < 7% of permanent grass and woodland soils. Over an average sampling interval of 15 years, decreases in SOC/clay index class occurred for arable and grassland soils and these were most pronounced in the Very Good class (SOC/clay ≥ 1/8). These soils have high SOC relative to clay concentration and should be managed protectively. Increasing SOC/clay to greater than 1/13 is proposed to reduce the risk of degraded structural conditions. The expected targets for SOC/clay ratio, under the land uses covered here, can be used alongside measures of carbon stock to help gauge whether predicted increases are feasible, taking account of soil texture and land use.

Regular testing of soils helps to inform management, and mid-infrared spectroscopy can determine SOC/clay ratio accurately enough to help reduce costs and labour. At a national scale, soils could be reliably assigned to Very Good, Good/Moderate, or Degraded index classes using a US soil spectral library. The soil spectral library for England and Wales did not perform as well but there is scope to improve this in the future. Overall, the index provides a quantitative approach for SOC assessment with a functional basis and sensitivity to soil management, such that policy makers can set more definitive and effective policy and schemes, and land managers can work better with these to improve and protect soils for carbon storage, food production and wider ecosystem services.

APPENDICES

Appendix A Supplementary Materials for Chapter 2

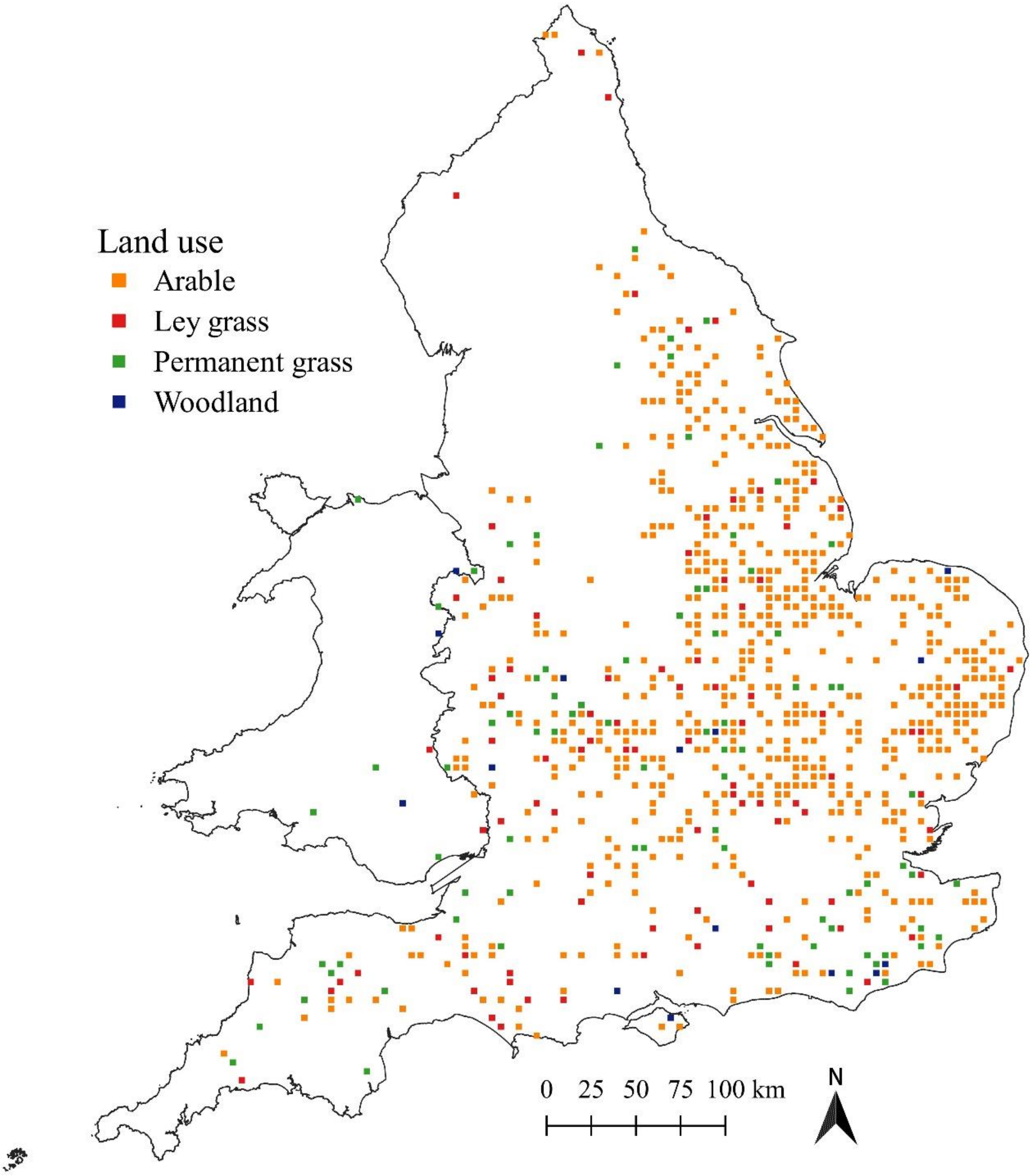


Figure A-1 Map of arable, ley grassland, permanent grassland and forest sites sampled between 1978 and 1983 with SOC/clay < 1/13 (*n* = 820).

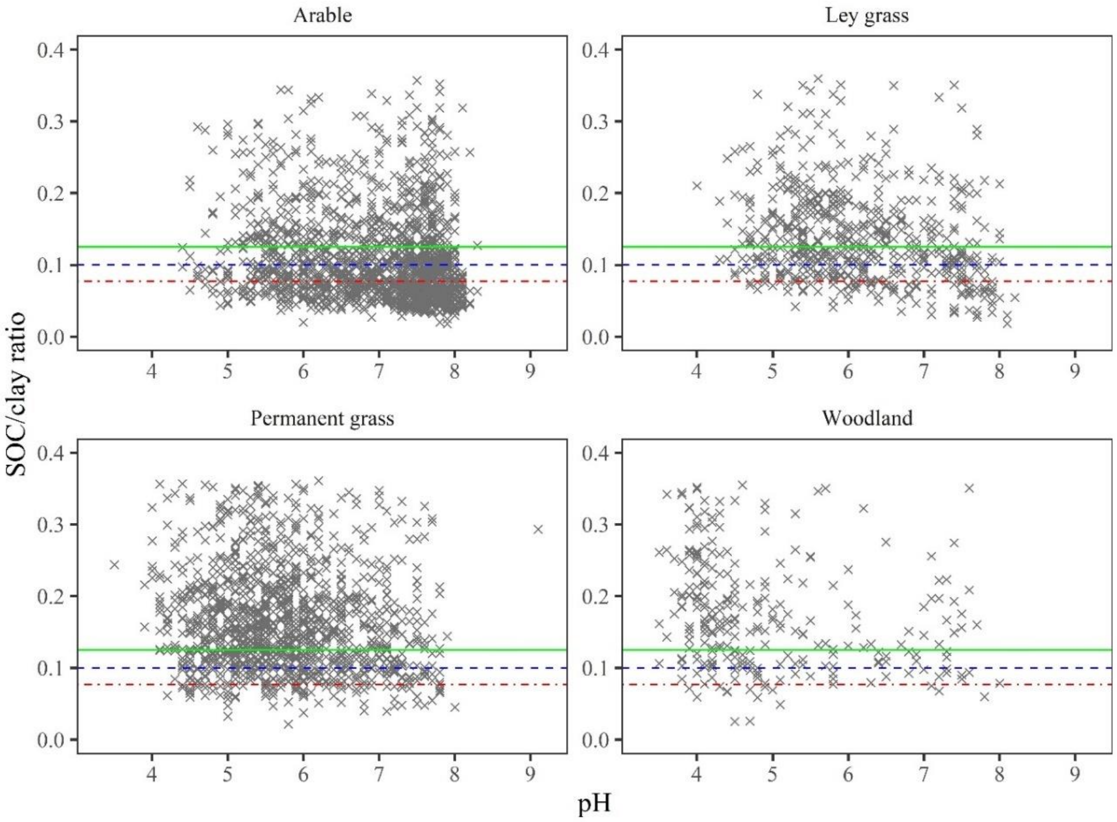


Figure A-2 SOC/clay ratio as a function of soil pH. Horizontal lines are SOC/clay thresholds: solid = 1/8, dashed = 1/10, dot-dash = 1/13.

Table A-1 Structural quality scores (by colour) for combinations of texture, shape, size and development of aggregates, adapted from the Agricultural Land Classification of England and Wales (MAFF, 1988).

		Texture group 1	Texture group 2	Texture group 3
Single grain		🟥	🟧	🟧
Massive		🟡	🟧	🟥
Granular	fine	🟨 *	🟨	🟨
	medium	🟨	🟨	🟨 *
	coarse	🟨	🟨	🟨 *
	very coarse	🟨	🟨	🟨 *
Subangular blocky	fine	🟨	🟨 *	🟨 *
	medium	🟨	🟨	🟨 *
	coarse	🟨	🟡	🟡
	very coarse	🟡	🟡	🟧
Angular blocky	fine	🟡	🟡	🟡
	medium	🟡	🟡	🟧
	coarse	🟡	🟧	🟥
	very coarse	🟡	🟥	🟥
Prismatic	fine	🟡	🟧	🟧
	medium	🟧	🟧	🟥
	coarse	🟧	🟥	🟥
	very coarse	🟥	🟥	🟥
Platy	fine	🟡	🟧	🟥
	medium	🟧	🟥	🟥
	coarse	🟥	🟥	🟥
	very coarse	🟥	🟥	🟥

Structural quality score (colour; example combination) = Good (yellow; Texture group 1, granular, fine), Moderate (dark yellow; Texture group 2, subangular blocky, coarse), Moderate-Degraded (orange; Texture group 3, subangular blocky, very coarse), Degraded (red; Texture group 1, single grain). * = (Very) Weak development of aggregates would be considered moderate structure. Texture group 1 = Sand, loamy sand. Texture group 2 = Sandy loam, sandy silt loam, silt loam. Texture group 3 = Sandy clay loam, clay loam, silty clay loam, sandy clay, silty clay, clay.

Table A-2 Mean clay concentration and mean soil organic carbon concentration for each treatment of the Woburn Organic Manuring experiment (mean of four blocks).

Treatment[a]	Clay (g kg^{-1})	Soil organic carbon from indicated years (g kg^{-1})							
		1964	1968	1971	1975-6	1978-9	1980-1	1986-7	1995
GmLc	10.40	0.76	0.84	0.89	0.81	0.74	0.77	0.88	0.80
LnLC	10.28	0.81	0.91	0.96	0.96	0.88	0.87	0.95	0.90
PtLc	9.68	0.75	0.96	1.35	1.26	1.06	1.13	1.18	1.06
Dg	9.65	0.73	0.88	1.03	0.94	0.86	0.86	1.07	0.99
Fd	9.98	0.74	0.74	0.72	0.72	0.68	0.70	0.66	0.70
Fs	9.83	0.76	0.73	0.71	0.75	0.71	0.72	0.66	0.70
Lc	10.88	0.77	0.92	0.94	0.90	0.84	0.84	0.93	0.85
St	11.28	0.83	0.87	0.95	0.89	0.83	0.82	0.86	0.83

[a] Treatment cycles were from 1965 to 1972 (1st cycle) and 1979 to 1987 (2nd cycle): GmLc = 1st cycle: green manuring, 2nd cycle: grass/clover ley; LnLc = 1st cycle: grass ley + nitrogen, 2nd cycle: grass/clover ley; PtLc = 1st cycle: peat, 2nd cycle: grass/clover ley; Dg = dung (farmyard manure); Fd = inorganic fertiliser (PKMg) equivalent to manuring; Fs = inorganic fertiliser (PKMg) equivalent to straw plus supplementary P; Lc = grass/clover ley; St = straw. (Full details of experiment: Mattingly, 1974).

Table A-3 Counts of major soil group under each land use from the selection of National Soil Inventory sites (3809 sites).

Major soil group	***n***	**Land use**			
		Arable	Ley Grass	Permanent Grass	Woodland
Terrestrial raw	4	0	0	3	1
Lithomorphic	230	133	39	50	8
Pelosol	219	137	29	42	11
Brown	1661	767	270	508	116
Podzolic	192	20	45	93	34
Surface-water gley	1015	364	169	403	79
Ground-water gley	420	219	41	149	11
Man-made	68	21	9	29	9

Table A-4 Summary of mean accumulated annual precipitation (years 1910–1983) for sites under each land use.

		Mean accumulated annual precipitation / mm yr^{-1}			
	n	Mean	Median	Min.	Max.
All land uses	3809	829	745	514	2473
Arable	1661	703	660	514	1651
Ley grass	602	916	844	540	2145
Permanent grass	1277	927	845	523	2473
Woodland	269	940	820	543	2438

Table A-5 Percentages of sites in each annual precipitation class (defined by Verheijen *et al*. (2005)) under each land use.

		Percentage of sites in land use			
Precipitation class[a]	***n***	Arable	Ley Grass	Permanent Grass	Woodland
Dry	1006	75.0	6.6	15.0	3.5
Intermediate	1240	49.7	13.8	29.5	7.0
Wet	1024	24.5	22.5	44.1	8.9
Very wet	539	7.4	25.0	57.1	10.4

[a] Precipitation class: Dry: < 650 mm year^{-1}, Intermediate: 650 to 800 mm year^{-1}, Wet: 800 to 1100 mm year^{-1} and Very wet: > 1100 mm year^{-1}.

Table A-6 Percentages of sites above and below SOC/clay thresholds of 1/8, 1/10 and 1/13 for each land use and land use precipitation class (defined by Verheijen *et al.* (2005)) combination.

Land use	Precipitation class[a]	*n*	Percentages of sites (*N*) with indicated SOC/clay ratio			
			≥ 1/8	< 1/8, ≥ 1/10	< 1/10, ≥ 1/13	< 1/13
Arable	All	1661	28.8	14.0	19.0	38.2
	Dry	754	24.0	11.7	15.6	48.7
	Int.	616	29.5	15.7	21.9	32.8
	Wet	251	37.8	16.7	21.5	23.9
	V. Wet	40	50.0	12.5	22.5	15.0
Ley Grass	All	602	50.2	20.3	14.6	15.0
	Dry	66	30.3	12.1	16.7	40.9
	Int.	171	41.5	16.4	21.6	20.5
	Wet	230	52.2	28.3	9.1	10.4
	V. Wet	135	67.4	15.6	14.1	3.0
Permanent Grass	All	1277	66.9	15.4	11.1	6.6
	Dry	151	51.7	16.6	15.9	15.9
	Int.	366	58.7	15.8	15.8	9.6
	Wet	452	65.9	18.6	11.1	4.4
	V. Wet	308	85.4	9.7	3.2	1.6
Woodland	All	269	67.7	16.0	10.8	5.6
	Dry	35	62.9	17.1	17.1	2.9
	Int.	87	59.8	20.7	11.5	8.0
	Wet	91	64.8	17.6	11.0	6.6
	V. Wet	56	87.5	5.4	5.4	1.8

[a] Precipitation class: Dry: < 650 mm year^{-1}, Int. (Intermediate): 650 to 800 mm year^{-1}, Wet: 800 to 1100 mm year^{-1} and V. Wet (Very Wet): >1100 mm year^{-1}.

Appendix B Supplementary Material for Chapter 3

Table B-1 Summary data of SOC/clay for the treatments of Woburn long-term experiment used to plot Figure 5 of the main paper. Mean and standard deviation (SD) represent five blocks each with two plots (one treated with farmyard manure for part of the experiment). The farmyard manure effect was not considered here.

	SOC/clay																	
	Arable (without fallows)			Arable (with fallows)			Lucerne / LC3			Grazed ley / LN3			Alternating / LC8[b]			Alternating / LN8[b]		
Year[a]	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
1938	10	0.071	0.006	10	0.071	0.006	10	0.071	0.006	10	0.071	0.006	10	0.071	0.006	10	0.071	0.006
1957	10	0.073	0.013	10	0.069	0.010	10	0.077	0.014	10	0.082	0.010	10	0.077	0.010	10	0.077	0.013
1962	10	0.072	0.011	10	0.067	0.011	10	0.074	0.013	10	0.085	0.012	10	0.075	0.009	10	0.075	0.012
1967	10	0.072	0.010	10	0.067	0.012	10	0.075	0.014	10	0.089	0.010	10	0.078	0.011	10	0.078	0.008
1972	10	0.077	0.011	10	0.068	0.009	10	0.079	0.014	10	0.095	0.011	10	0.081	0.012	10	0.079	0.009
1977	10	0.070	0.012	10	0.065	0.012	10	0.080	0.013	10	0.086	0.009	10	0.076	0.011	10	0.079	0.011
1982	10	0.066	0.012	10	0.059	0.012	10	0.078	0.009	10	0.087	0.013	10	0.082	0.009	10	0.082	0.011
1987	10	0.069	0.013	10	0.059	0.012	10	0.082	0.012	10	0.086	0.013	10	0.085	0.008	10	0.082	0.009
1992	10	0.068	0.011	10	0.059	0.012	10	0.086	0.013	10	0.089	0.014	10	0.088	0.006	10	0.093	0.014
1997	10	0.065	0.010	10	0.055	0.010	10	0.084	0.010	10	0.082	0.010	10	0.084	0.011	10	0.084	0.013
2002	10	0.071	0.013	10	0.061	0.012	10	0.090	0.013	10	0.095	0.013	10	0.098	0.010	10	0.106	0.016
2007	10	0.066	0.014	10	0.058	0.012	10	0.090	0.014	10	0.092	0.015	10	0.093	0.018	10	0.095	0.016

[a]After 1938, year is the midpoint of 5-year

[b]Values used are from the first cycle of this treatment. The second cycle started the second part of the treatment (LC8 or LN8) five years after the first cycle, but was not used in this analysis as it was not appropriate to merge the data and made the plot difficult to read if both were presented.

Table B-2 Summary data of SOC/clay for the treatments of Highfield long-term experiment used to plot Figure 5 of the main paper. Mean and standard deviation (SD) represent four blocks each with a single plot (or two subplots, treated as one plot together here, for old grass and reseeded grass) per treatment.

	SOC/clay[a]														
	Arable			Old grass			Reseeded grass			Grazed ley / LC3			Cut grass / LN3		
Year	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
1948	4	0.107	0.004	4	0.107	0.004	4	0.107	0.004	4	0.107	0.004	4	0.107	0.004
1951	2	0.102	0.003	2	0.101	0.011	2	0.095	0.002	-	-	-	-	-	-
1956	2	0.092	0.005	2	0.108	0.006	2	0.098	0.002	2	0.093	0.004	2	0.088	< 0.001
1961	2	0.084	0.001	2	0.115	0.009	-	-	-	-	-	-	-	-	-
1967	2	0.075	0.002	2	0.114	0.009	2	0.106	0.003	2	0.084	0.001	2	0.079	0.001
1969	1	0.077	-	1	0.128	-	1	0.099	-	1	0.092	-	1	0.084	-
1972	4	0.080	0.009	4	0.123	0.010	4	0.104	0.007	4	0.090	0.003	4	0.086	0.004
1975	4	0.072	0.008	4	0.117	0.011	4	0.103	0.008	4	0.084	0.005	4	0.082	0.006
1979	4	0.068	0.008	4	0.120	0.007	4	0.104	0.007	4	0.080	0.005	4	0.077	0.005
1981	4	0.064	0.007	4	0.120	0.009	4	0.104	0.007	4	0.079	0.005	4	0.076	0.005
1984	4	0.064	0.008	4	0.137	0.012	4	0.118	0.010	4	0.077	0.003	4	0.076	0.003

[a] Dashes (-) represent no data recorded (or not applicable in the standard deviation of year 1969 for which there was just one plot sampled).

[b] Each of the four plots (one per block per treatment) had three subsamples collected and measured in 2015. The mean and standard deviation were calculated at the plot-level (after taking the mean of the subsamples per plot).

Table B-2 (Continued)

	SOC/clay[a]														
	Arable			Old grass			Reseeded grass			Grazed ley / LC3			Cut grass / LN3		
Year	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD	n	Mean	SD
1987	4	0.064	0.006	4	0.121	0.010	4	0.108	0.009	4	0.077	0.005	4	0.075	0.006
2000	4	0.064	0.007	3	0.123	0.019	-	-	-	-	-	-	-	-	-
2008	4	0.058	0.005	4	0.134	0.013	4	0.124	0.006	4	0.078	0.004	4	0.078	0.005
2014	-	-	-	4	0.142	0.011	-	-	-	4	0.081	0.005	-	-	-
2015[b]	4	0.066	0.005	-	-	-	4	0.125	0.009	4	0.085	0.004	-	-	-

[a] Dashes (-) represent no data recorded (or not applicable in the standard deviation of year 1969 for which there was just one plot sampled).

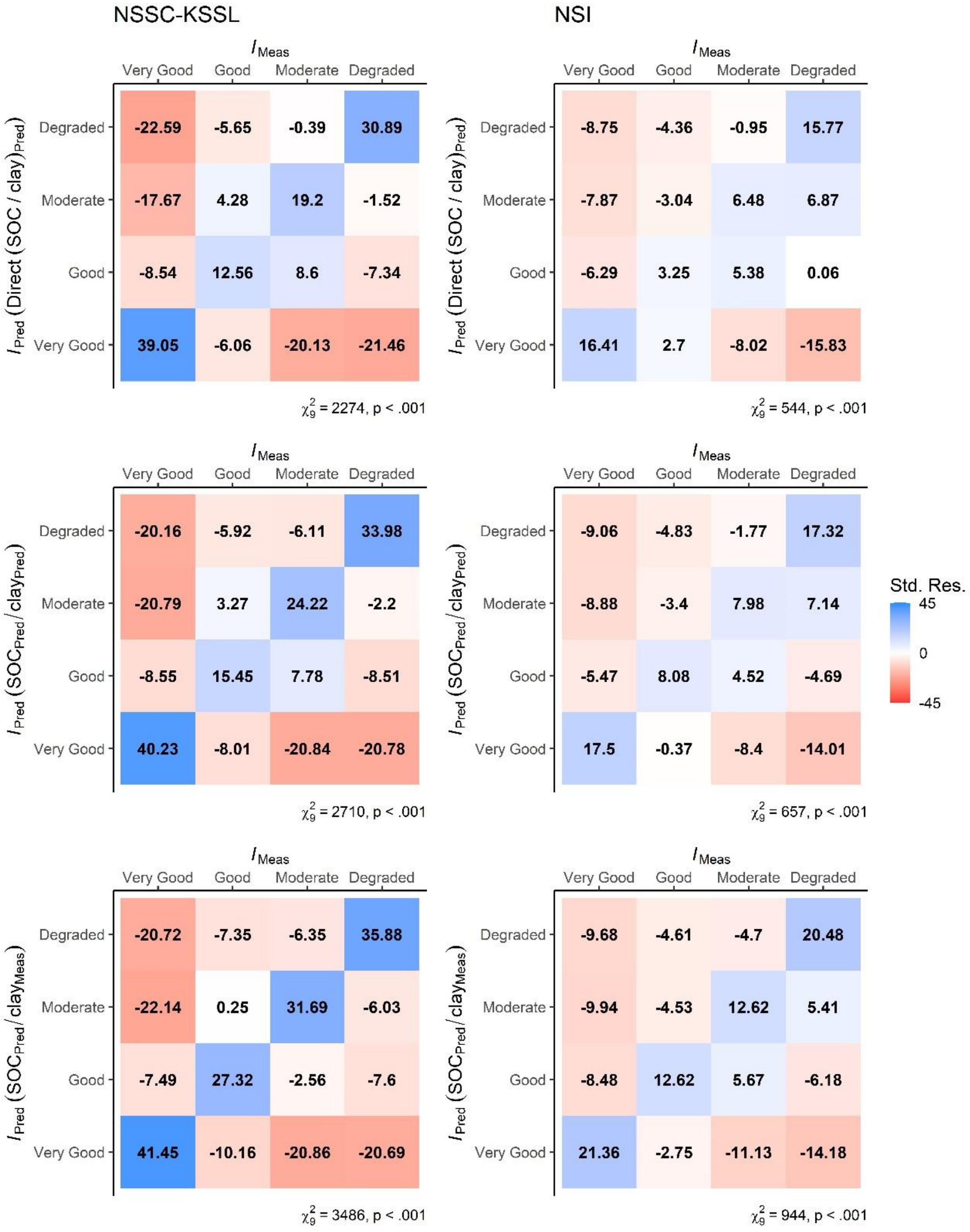
[b] Each of the four plots (one per block per treatment) had three subsamples collected and measured in 2015. The mean and standard deviation were calculated at the plot-level (after taking the mean of the subsamples per plot).

Table B-3 Summary data of SOC/clay for the bare fallow treatment of Highfield long-term experiment used to plot Figure 5 of the main paper. Mean and standard deviation represent four subplots within the bare fallow area.

	SOC/clay		
	Bare fallow		
Year	n	Mean	SD
1959	4	0.104	0.003
1963	4	0.081	0.002
1971	4	0.059	0.002
1978	4	0.053	0.003
1987	4	0.047	0.006
2000	4	0.039	0.004
2008	4	0.036	0.004
2014	4	0.038	0.004
2015[a]	1	0.032	-

[a] Mean was calculated from three samples of one subplot.

Appendix C Supplementary material for Chapter 4



	Very Good	Good	Moderate	Degraded
Degraded	-22.59	-5.65	-0.39	30.89
Moderate	-17.67	4.28	19.2	-1.52
Good	-8.54	12.56	8.6	-7.34
Very Good	39.05	-6.06	-20.13	-21.46

$\chi^2_9 = 2274$, $p < .001$

	Very Good	Good	Moderate	Degraded
Degraded	-8.75	-4.36	-0.95	15.77
Moderate	-7.87	-3.04	6.48	6.87
Good	-6.29	3.25	5.38	0.06
Very Good	16.41	2.7	-8.02	-15.83

$\chi^2_9 = 544$, $p < .001$

	Very Good	Good	Moderate	Degraded
Degraded	-20.16	-5.92	-6.11	33.98
Moderate	-20.79	3.27	24.22	-2.2
Good	-8.55	15.45	7.78	-8.51
Very Good	40.23	-8.01	-20.84	-20.78

$\chi^2_9 = 2710$, $p < .001$

	Very Good	Good	Moderate	Degraded
Degraded	-9.06	-4.83	-1.77	17.32
Moderate	-8.88	-3.4	7.98	7.14
Good	-5.47	8.08	4.52	-4.69
Very Good	17.5	-0.37	-8.4	-14.01

$\chi^2_9 = 657$, $p < .001$

	Very Good	Good	Moderate	Degraded
Degraded	-20.72	-7.35	-6.35	35.88
Moderate	-22.14	0.25	31.69	-6.03
Good	-7.49	27.32	-2.56	-7.6
Very Good	41.45	-10.16	-20.86	-20.69

$\chi^2_9 = 3486$, $p < .001$

	Very Good	Good	Moderate	Degraded
Degraded	-9.68	-4.61	-4.7	20.48
Moderate	-9.94	-4.53	12.62	5.41
Good	-8.48	12.62	5.67	-6.18
Very Good	21.36	-2.75	-11.13	-14.18

$\chi^2_9 = 944$, $p < .001$

Figure C-1 Standardised residuals of chi-square tests for the NSSC-KSSL (left) and NSI (right) validation sets between measured index class (I_{Meas}) and predicted index class (I_{Pred}) for each of the SOC/clay calculation methods (top, middle, bottom). Positive values suggest association for that combination of I_{Pred} and I_{Meas} classes, negative values suggest a lack of association.