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Estimating the organic carbon stabilisation capacity and saturation deficit of soils: a New Zealand case study

M. H. Beare · S. J. McNeill · D. Curtin ·
R. L. Parfitt · H. S. Jones · M. B. Dodd ·
J. Sharp

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Abstract The capacity of a soil to sequester organic carbon can, in theory, be estimated as the difference between the existing soil organic C (SOC) concentration and the SOC saturation value. The C saturation concept assumes that each soil has a maximum SOC storage capacity, which is primarily determined by the characteristics of the fine mineral fraction (i.e. <20 μm clay + fine silt fraction). Previous studies have focussed on the mass of fine fractions as a predictor of soil C stabilisation capacity. Our objective was to compare single- and multi-variable statistical approaches for estimating the upper limit of C stabilisation based on measureable properties of the fine mineral fraction [e.g. fine fraction mass and surface area (SA), aluminium (Al), iron (Fe), pH] using data from New Zealand's National Soils Database. Total SOC ranged from 0.65 to 138 mg C g^{-1}, median values being 44.4 mg C g^{-1} at 0–15 cm depth and 20.5 mg C g^{-1} at 15–30 cm depth. Results showed that SA of mineral particles was more closely correlated with the SOC content of the fine fraction than was the mass proportion of the fine fraction, indicating that it provided a much better basis for estimating SOC stabilisation capacity. The maximum C loading rate (mg C m^{-2}) for both Allophanic and non-Allophanic soils was best described by a log/log relationship between specific SA and the SOC content of the fine fraction. A multi-variate regression that included extractable Al and soil pH along with SA provided the "best fit" model for predicting SOC stabilisation. The potential to store additional SOC (i.e. saturation deficit) was estimated from this multivariate equation as the difference between the median and 90th percentile SOC content of each soil. There was strong evidence from the predicted saturation deficit values and their associated 95 % confidence limits that nearly all soils had a saturation deficit >0. The median saturation deficit for both Allophanic and non-Allophanic soils was 12 mg C g^{-1} at 0–15 cm depth and 15 mg C g^{-1} at 15–30 cm depths. Improving predictions of the saturation deficit of soils may be important to developing and deploying effective SOC sequestration strategies.

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M. H. Beare (✉) · D. Curtin · J. Sharp
Sustainable Production Portfolio, New Zealand Institute for Plant & Food Research Limited, Private Bag 4704, Christchurch 8140, New Zealand
e-mail: Mike.Beare@plantandfood.co.nz

S. J. McNeill · R. L. Parfitt
Landcare Research, Private Bag 11052, Palmerston North, New Zealand

H. S. Jones
Scion, Private Bag 3020, Rotorua 3046, New Zealand

Present Address:
H. S. Jones
Waikato Regional Council, Private Bag 3038, Hamilton 3240, New Zealand

M. B. Dodd
AgResearch Limited, Grasslands Research Centre, Private Bag 11008, Palmerston North, New Zealand

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Introduction

Developing strategies to sequester organic carbon (C) in soils depend on understanding the key factors that affect soil organic carbon (SOC) stabilisation and the capacity of individual soils to stabilise additional SOC. The sequestration of stable SOC has been attributed to several possible mechanisms including biochemical recalcitrance, physical protection or inaccessibility and the formation of organo-mineral complexes involving fine (clay + silt) soil particles (Sollins et al. 1996; Baldock and Skjemstad 2000; von Lützow et al. 2006; Dungait et al. 2012). The SOC associated with fine soil particles is generally regarded has highly stable, with a relatively long turnover time (Buyanovsky et al. 1994; Balesdent et al. 1998) and slow response to changes in management (Campbell et al. 1991; Chung et al. 2008; Skjemstad et al. 2004). It also represents a large proportion of the total SOC in most soils and, therefore serves as a useful measure of the stable organic C.

Hassink and Whitmore (1997) equated the capacity of a soil to stabilise C with the maximum concentration of SOC found in the clay + fine silt fraction (fine fraction) of whole soil. A number of studies have shown that total SOC content is strongly and positively correlated with the amount of fine mineral particles in soils (Scott and Cole 1996; Bosatta and Agren 1997; Hassink 1997; Homann et al. 2007). This relationship is generally attributed to the role that the fine fraction plays in providing mineral surface for the formation of organo-mineral complexes. Several studies have shown that the amount of SOC in the fine fraction is positively correlated to its proportion of the whole soil mass (Hassink 1997; Six et al. 2002; Liang et al. 2009; Feng et al. 2011). The theoretical maximum concentration of SOC has also been referred to as the upper limit of soil C stabilisation or the soil C "protective" or "saturation" capacity (Baldock and Skjemstad 2000; Chung et al. 2010). The difference between the theoretical saturation capacity and the actual SOC concentration in the fine fraction is often defined as the saturation deficit (Angers et al. 2011; Stewart et al. 2007; Six et al. 2002) and has been taken to represent the potential for SOC sequestration.

Several different approaches have been used to define the upper limit of soil C storage, based on the stabilisation capacity of the fine fraction. Using a meta-analysis of soil C data from temperate and tropical regions around the globe, Hassink (1997) reported that differences in the SOC content of paired grassland and cropland sites were primarily due to losses of C from the >20 μm fine fraction of soils. This result, he argued, was evidence for a limit to the C content of soils that was determined by the amount of fine soil particles (i.e. a SOC saturation capacity). Hassink (1997) proposed that the mass proportion of fine soil particles (clay + silt) in whole soil could be used to predict the saturation capacity based on a least squares regression (LSR) model, $y = 0.37x + 4.07$, where y is the SOC content of fine soil particles (mg C g^{-1} soil) and x is the proportion of fine soil particles in whole soil (g fine particles 100 g^{-1} soil).

Six et al. (2002) applied a similar approach to estimating the stabilisation capacity based on a meta-analysis of published SOC data from additional studies covering soils of different mineralogies and land use histories. They reported different LSR parameters for soils dominated by 1:1 versus 2:1 minerals. For each mineralogy class, the slope of the LSR was assumed to represent the SOC concentration of the fine fraction at the theoretical saturation limit. However, Feng et al. (2011) showed that the values reported by Hassink (1997) and Six et al. (2002) were relatively low compared with published values of SOC in the fine fraction, suggesting that the LSRs underestimated the upper limit of SOC stabilisation in the fine fraction. They proposed two alternative methods for estimating the stabilisation capacity of soils, i.e. a SOC loading method and a boundary line (BL) analysis method.

The SOC loading method is based on the knowledge that different soil minerals have different specific surface areas, SAs (Parfitt et al. 2001) and that there is a positive relationship between specific SA and the SOC concentration of particle size fractions and whole soils (Kahle et al. 2002b; Mayer 1994; Wiseman and Püttmann 2005). The upper limit of soil C stabilisation is then estimated assuming a monolayer-equivalent C loading of ~ 1 mg C m^{-2} of specific SA, based on evidence from marine sediments and mineral soils (Mayer 1994). More recent work has shown that organic matter is not present as a continuously dispersed monolayer (Mayer and Xing 2001; Wagai et al. 2009), but rather as series of discrete irregular bulges that may be associated with mesopores and aluminous clay edges (Mayer 1999). However, SA does appear to serve as a marker for clay domains that are physically associated with organic matter and, broadly speaking, the relationship between specific SA and C content holds for a wide range of mineral soils and sediments.

The BL analysis method was first used by Webb (1972) to define the productivity potential of field crops, but has subsequently been used to predict the upper limits of N_2O emissions in the field in response to different soil conditions (Elliott and Dejong 1993; Schmidt et al. 2000). The method is a statistical approach to define the upper (or lower) limits of a dependent variable where there is evidence for a limiting response to an independent variable(s) along a defined boundary (Schnug et al. 1996; Schmidt et al. 2000; Milne et al. 2006).

Based on their analysis of data from 32 published studies (342 data points), Feng et al. (2011) showed that the BL method produced an estimate of the upper limit of soil C stabilisation that was more than twice that of the LSR method in both 1:1 and 2:1 clay soils. Their application of the organic C loading method produced an estimate of the upper limit of SOC stabilisation in 2:1 clay soils that was very similar to that of BL method, but greatly underestimated a majority of the values in 1:1 clay soils. However, Feng et al. (2011) based their BL analysis on the upper 10 % of fine fraction SOC content values (distributed across the range from <10 to 90 % fine particle content). Quantile regression (QR) analysis (Koenker 2005) offers an alternative approach to examine the upper distribution of SOC in the fine fraction, based on analysis of the entire data set rather than the behaviour of a subset of the data, which may well lead to a different interpretation.

Given the differences observed between 1:1 and 2:1 mineral soils, Feng et al. (2011) concluded that a model based on a mechanistic understanding of the factors that affect soil C stabilisation was preferable to a purely statistical approach for predicting the upper limits of SOC stabilisation. They recommended that future work should focus on the physical and chemical properties of soils that may be useful in predicting the upper limits of soil C stabilisation.

New Zealand has soils and soil databases that are well suited to address this recommendation. The soil taxonomic diversity is relatively high and encompasses a wide range of clay mineral compositions. New Zealand's National Soils Database (NSD) contains data for soils covering a wide range of land uses, climatic zones and soil depths. The NSD includes data on SOC, pH, extractable aluminium (Al) and iron (Fe), texture, bulk density and other potentially important soil properties (Wilde 2003). Furthermore, previous research in New Zealand suggests that the extractable Al is a better predictor of SOC concentrations than the silt or clay content (Percival et al. 2000). This is consistent with the ability of Al to alter the solubility and conformation of SOC molecules (Parfitt 2009). Volcanic soils, that have sufficient rainfall to leach silicon (Si), have Allophanic mineralogy, and allophane has a high specific SA that can react strongly with SOC (Parfitt 2009).

The objectives of this study were to: (1) evaluate the least-square linear regression (LSR), BL and QR methods for estimating the SOC stabilisation capacity of New Zealand soils, (2) compare estimates of SOC stabilisation obtained by these statistical methods with those of an organic C loading method based on an indirect measure of soil specific SA, and (3) investigate the potential to use a multi-factor analysis of soil properties to better describe the upper limits of soil C stabilisation and the saturation deficit of soils based on a case study of New Zealand long-term pasture soils. We hypothesized that a multi-factor model based on the specific SA of mineral particles would provide a more robust estimate of the C stabilisation capacity and saturation deficit of New Zealand soils compared to a model based the mass proportion of fine mineral particles.

Materials and methods

Datasets

The data used in this study were obtained from New Zealand's NSD. The NSD consists of data for soil samples collected from across New Zealand for a range of purposes (Wilde 2003). It contains site description, soil profile morphology and soil classification information, as well as data on the physical, chemical, and mineralogical properties for over 1,500 soil profiles (Wilde 2003). While the NSD is not the

Table 1 Soil records used in this study by soil order in the New Zealand Soil Classification (Hewitt 2010) and corresponding orders in the USDA Soil Taxonomy (Soil Survey Staff 2010)

NZ soil order	USDA equivalent	Number of records
Allophanic	Andisols	31
Brown	Inceptisols, alfisols	47
Gley	Aquic groups	46
Granular	Ultisols	3
Melanic	Mollisols	10
Organic	Histosols	–
Oxidic	Oxisols, ultisols	3
Pallic	Inceptisols, alfisols	31
Podzol	Spodosols	6
Pumice	Andisols (vitric)	22
Raw	Entisols	–
Recent	Entisols, inceptisols	38
Semiarid	Alfisols	10
Ultic	Ultisols	9
Total		256

only soils database in New Zealand, it is unique in that it contains data on soil properties thought to influence the storage of SOC, and represents a wide range of soils and sites across the country.

The NSD data used in this study were restricted to long-term pasture soils/sites that included comprehensive soil description information and where there was a minimum dataset of selected physical and chemical properties. The long-term pasture soils were targeted because they are generally known to have high SOC concentrations compared with soils under other land uses and because this land use is well represented across a wide range of soil classes and climatic zones. The minimum dataset of properties included soil bulk density and pH; SOC, Al, Si, and Fe concentrations; air-dry water content; and sand, silt and clay content. Data for individual sites were excluded where organic, calcareous, or saline horizons, or podzolic pans were identified. A small number of profiles on volcanic mud (i.e. ejected lake-floor sediments) were also excluded, as were profiles where topsoil data were missing. The resulting dataset contained information for 256 soil profiles that reflected a wide range of soil orders in the New Zealand Soil Classification (Hewitt 2010). These soil orders and the corresponding orders in the USDA Soil Taxonomy (Soil Survey Staff 2010) are given in Table 1.

Soil physical and chemical properties

The soil physical and chemical properties included in our analyses were determined by the following methods. Soil pH (10 g air-dry soil in 25 mL in water), pyrophosphate-extractable Al (Al-p), oxalate-extractable Al (Al-o), oxalate-extractable Si (Si-o), and dithionite–citrate-extractable Fe (FED) were measured by the standard methods reported in Blakemore et al. (1987) and Parfitt and Childs (1988). The organic C content of whole soils was measured using a LECO induction furnace (Blakemore et al. 1987). Sand (50–2,000 µm), silt (2–50 µm) and clay (<2 µm) content were measured by sieving and sedimentation using the pipette method (Claydon 1989). Bulk density was measured using the driving hammer method (Parfitt et al. 2013).

As the NSD does not contain data on the SOC content of the clay + fine silt (<20 µm) fraction (fine fraction), these values were estimated based on the results of previous studies. Angers et al. (2011) reported that the SOC stabilised by fine particles represented 85 ± 2.5 % of the total SOC based on an analysis of topsoils in France. This value agrees well with the mean values (84–89 %) reported in other studies (Balesdent 1996; Jolivet et al. 2003), including a meta-analysis of data representing >400 particle size fractions by Gregorich et al. (2006) and our own measurements (81–89 %) for grassland soils representing three common soil orders (Allophanic, Brown and Recent Soils) in New Zealand (Curtin unpublished). For the purposes of this study, we assumed that 85 % of the total SOC was associated with the fine fraction.

The water content of air-dried soils was measured by oven drying (105 °C for 24 h) soils that had first been air-dried at 30 °C for 24 h and allowed to equilibrate at the relative humidity of the laboratory (Blakemore et al. 1987; Parfitt et al. 2001). The specific SA of soil was then estimated from the water content of air-dried soil as described by Parfitt et al. (2001):

$$\text{Surface area}\left(\text{m}^2\,\text{g}^{-1}\right) = 2 \times \text{air} - \text{dry water content}\left(\text{g}\,\text{kg}^{-1}\right).$$

Data preparation

In order to achieve greater consistency with respect to the depth of organic matter deposition, we converted the NSD data, which were derived from samples collected by genetic horizon, to values based on fixed depth intervals. We estimated the soil property values for the 0–15 and 15–30 cm layers of each soil profile by fitting a quadratic mass-preserving spline model (Bishop et al. 1999) where data are provided in the form of mean values within adjacent soil horizons, with the assumption that the underlying soil property varies smoothly with depth. The spline fit is controlled by a parameter λ, which represents a trade-off between the fit and the roughness penalty (Malone et al. 2009). For this study, λ values of 10, 1, 0.1, and 0.01 were evaluated, with the best overall results (lowest RMS error) obtained over a broad range of values; as a result, a value of $\lambda = 0.1$ was adopted. The spline fits to the original horizon measurements for each profile were checked by visual inspection.

Statistical analyses

Building on the original work of Hassink (1997) and other more recent studies (Six et al. 2002; Feng et al. 2011; Zhao et al. 2006), we applied several different methods to estimate the stabilisation capacity of the fine fraction based on statistical analyses of the relationship between the C content of the fine fraction and the mass proportion of fine particles. These methods included LSR modelling, BL analysis, and QR analysis.

Single-factor regression analyses

Hassink (1997) first proposed the use of a LSR model to estimate the stabilisation capacity of the fine fraction in relation to the mass proportion of fine particles. We applied a similar analysis to the New Zealand dataset, using the mass proportion of fine particles (g fraction 100 g^{-1} soil) as the independent variable and the soil C content of the fine fraction (mg C g^{-1} soil) as the dependent variable. The regression parameters and uncertainties from our analyses were compared with those reported in other soil classification- or location-specific studies (Hassink 1997; Liang et al. 2009; Zhao et al. 2006) and to the meta-analyses of Six et al. (2002) and Feng et al. (2011). Like Feng et al. (2011), we carried out a further set of LSR analyses where we forced the y-intercepts to 0 on the assumption that a positive intercept reflects SOC that is not stabilised by the fine fraction.

The BL analysis method described by Feng et al. (2011) was also applied to our data as an alternative to the LSR method for estimating the C stabilisation capacity. The BL method is a statistical approach to define the upper (or lower) limits of a dependent variable where there is evidence for a limiting response to an independent variable(s) along a defined boundary (Schnug et al. 1996; Schmidt et al. 2000; Milne et al. 2006). Briefly, the method involves applying linear regression analysis to the upper-most (e.g. the top 10 %) values of fine fraction C content across a wide range of fine particle masses.

For comparison to the results of Feng et al. (2011), we used the same BL method described in their study to estimate the C stabilisation capacity of the fine fraction. This involved sorting the data set into nine groups based on the mass proportions of fine soil particles, at intervals of 10 g fraction 100 g^{-1} soil, ranging from <10 to >90 g fraction 100 g^{-1} soil. The upper 10 % of soil C values in each group were identified and extracted along with the corresponding mass proportion data. These BL data were subjected to a regression analysis where the y-intercept was forced through 0 based on the assumptions outlined above. We report the results of our analyses, including the slope and P values, along with those of Feng et al. (2011) for comparison.

QR analysis (Koenker 2005) was also applied to the data set as an alternative to the LSR (Hassink 1997) and BL (Feng et al. 2011) methods. QR estimates a specific conditional quantile of the response variable (e.g. the 90th quantile), rather than the conditional mean as in LSR. In this way, QR has the advantage of modelling soil C data based on the entire response distribution. The quantile approach avoids the assumption of the LSR approach that most of the values are at or near the upper range of the response distribution (Feng et al. 2011). It also avoids a reduction in accuracy of the estimated C stabilisation capacity owing to a reduced sample size, which is a risk with the BL method.

Organic C loading method

In this study, we used the water content of individual air-dried soils to estimate the specific SA of the fine fraction based on the method of Parfitt et al. (2001) as described above. The specific SA estimates were then used to calculate the assumed maximum SOC content of the fine fraction in each soil using an organic C loading of ~ 1 mg C m^{-2} (Mayer 1994). A LSR analysis was then applied to derive an estimate of the upper limit of soil C stabilisation from the relationship between the maximum SOC content of the fine fraction (by this organic C loading method) and the mass proportion of fine particles in the soils studied. This was then compared with the organic C loading results derived from the meta-analysis of Feng et al. (2011) and those derived from our study using the LSR, BL and QR analyses. We also investigated the relationship between measured specific SA and the measured SOC content of the fine fraction, to derive an independent estimate of the SOC loading limit of fine particles.

Multi-factor regression analyses

Using the soil property data calculated for standard depths, log-transformations were applied to all the soil properties (except pH), since a paired plot indicated increasing variability in the mean values, and the distributions were strongly right-skewed.

A number of different QR models (Koenker 2005) for different quantiles ($\tau = 0.5, 0.9, 0.95$) of $\log(C)$ were developed in terms of specific SA [the explanatory variable most strongly correlated with $\log(C)$, as discussed below], and for combinations of specific SA and the other potential explanatory variables. The multivariate regressions were developed in order to maximise explanatory ability, measured by way of the minimum residual standard error. Explanatory variables were dropped if their inclusion resulted in coefficients that were not physically plausible, resulting in, for instance, an increase in SOC with a decrease in the physical quantity. This situation occurs where two explanatory variables are strongly correlated with each other [e.g. log(Al-o) and log(Al-p), see Table 5], and one provides strong correlation with SOC; in this case, the inclusion of the second explanatory variable yields a negative coefficient, contrary to the expected physical model.

Results and discussion

The data used in this study were obtained from soils representing a diverse range of soil orders (Table 1). Of the 256 records, 31 were for Allophanic soils. These volcanic soils contain amorphous and poorly crystalline minerals (allophane; oxides of Al and Fe) with a large capacity to adsorb organic matter (Matus et al. 2006, 2008). The other soils, derived from sedimentary parent materials, contain a mixture of 1:1 and 2:1 clay minerals (Officer et al. 2006; Surapaneni et al. 2002). The data also encompassed soils with a wide range of textures and SOC contents (Fig. 1). The fine fraction (<20 μm) content ranged from 1.4 to 98 g 100 g^{-1} soil and followed a normal distribution; the median value at 0–15 cm depth was 55 g 100 g^{-1} and at 15–30 cm depth was 54 g 100 g^{-1}. The SOC content of the fine fraction ranged from 0.55 to 117.5 mg C g^{-1} soil. The SOC distribution was skewed towards low values, the median values being 37.7 mg C g^{-1} soil at 0–15 cm depth and 17.5 mg C g^{-1} soil at 15–30 cm depth. These normal and skewed distributions for fine fraction and SOC contents, respectively, are consistent with those reported in previous studies (Angers et al. 2011).

Relationships between SOC and fine fraction content

LSR analyses

In the first phase of our regression modelling, we applied an unrestricted LSR analysis to the entire 0–15 cm soils dataset (i.e. both Allophanic and non-Allophanic soils) to describe the relationship between the SOC content of the fine fraction (<20 μm clay + fine silt, mg C g^{-1}) and the mass proportion of fine particles (g 100 g^{-1} soil), as in previous studies (e.g. Hassink 1997; Six et al. 2002; Feng et al. 2011; Zhao et al. 2006). The slope (0.09) of this relationship was very low and the overall relationship was not significant ($P = 0.253$). This contrasts strongly with the slope (0.37, $P = 0.001$) reported by Hassink (1997) and the overall slope (0.30, $P < 0.01$) obtained from the meta-analysis of 32 different studies reported by Feng et al. (2011). However, Feng et al. (2011) also reported substantial variation in the slopes (0.08–0.64) derived from their analysis of data obtained from a number of other individual studies (e.g. Amelung et al. 1998; Barthès et al. 2008; Feller and Beare 1997; Zinn et al. 2007). The slope (0.06) of the relationship for the 15–30 cm soils in this study was also non-significant ($P = 0.089$), although there was greater evidence that the C content of the fine fraction increased with increases in the mass proportion of fine soil particles at that depth.

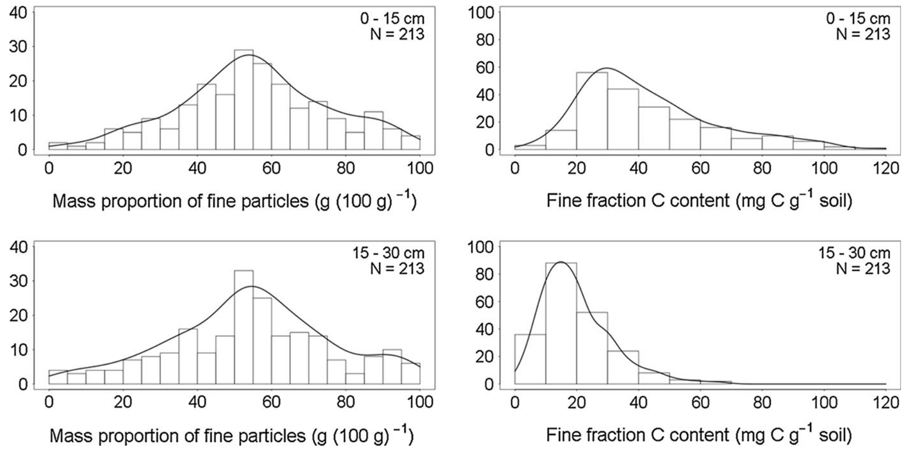

Fig. 1 The distribution of values for the **a** mass proportion of fine soil particles and the **b** soil organic C content of the fine fraction used in this study to estimate the soil C stabilisation capacity of New Zealand soils using a range of methods. The histogram is derived from the measured values, while the *solid line* is a kernel density estimate of the distribution

Efforts to quantify the relationship between the SOC content of the fine fraction and the mass proportion of fine particles are based on the assumption that clay and fine silt particles provide the majority of the mineral surfaces needed to stabilise SOC. Previous studies have shown positive relationships between the SOC content and specific SA of mineral particles in both terrestrial soils and marine sediments (Kahle et al. 2003; Mayer 1994; Zinn et al. 2007) that support this assumption. On this basis, Feng et al. (2011) argued that a restricted LSR model, where the intercept is forced through 0, would provide a more mechanistic understanding of the relationship between the SOC content of the fine fraction and the mass proportion of fine particles. Our application of a restricted LSR to the 0–15 cm data from New Zealand produced regression models that were highly significant ($P < 0.001$), with an overall slope (0.70 ± 0.03 SE) that was about twice that reported by Feng et al. (2011) using the same approach (Table 2). Within this wider dataset, the slope of the relationship for Allophanic soils (1.35 ± 0.09 SE) was substantially greater than the slope for non-Allophanic soils (0.62 ± 0.03 SE). The relationships derived for the 15–30 cm soils using a restricted LSR model were also highly significant; the slopes being about one-half those of the 0–15 cm soils but with similar relative differences between Allophanic and non-Allophanic soils. This difference between soil depths implies that 15–30 cm soils are further from their stabilisation capacity. This is consistent with the expected inputs of C from plant production being much lower at greater soil depth and the idea that the SOC content is input-limited. Feng et al. (2011) also noted differences in the slope of the relationship between the SOC content and the mass proportion of the fine fraction in soils of different mineralogy. Their results showed that the slope of this relationship for soils dominated by 2:1 minerals was significantly greater than that of soils dominated by 1:1 minerals (Table 2), but they did not report estimates for Allophanic soils.

The constraint imposed by the restricted LSR model of Feng et al. (2011), where the intercept is forced through 0, appears to give dubious results when applied to New Zealand soils (Fig. 2). While the restricted LSR model may be favoured from a mechanistic viewpoint, our result suggests that a better model is needed, either one with different covariates, with a curvilinear rather than a simple linear relationship, or using a different regression methodology. In the following sections, several of these alternatives are explored, and then compared.

BL and QR analyses

An important limitation of the LSR approach for estimating the SOC stabilisation capacity is the implicit assumption that the majority of the values used to generate the relationship are at or near the upper SOC limit and that any differences between the LSR predicted and measured values are due to random error (Feng et al. 2011). If this assumption is not met, the LSR approach does not satisfy one of the key criteria needed to predict the soil C stabilisation capacity using this approach. The data used in this study and the previous studies where the LSR approach has been applied (e.g. Hassink 1997; Feng et al. 2011) do not appear to meet this criteria. Consequently, BL and QR modelling were applied to

Table 2 Estimates of the stabilisation capacity of fine soil particles (<20 µm) based on the slope of the least-square linear regression model with a forced 0 intercept

Sources	Depth (cm)	Dataset	Slope[a]	*P*	*n*
New Zealand	0–15	All	0.70 ± 0.03	<0.001	213
	0–15	Non-Allophanic	0.62 ± 0.03	<0.001	184
	0–15	Allophanic	1.35 ± 0.09	<0.001	29
	15–30	All	0.32 ± 0.02	<0.001	213
	15–30	Non-Allophanic	0.28 ± 0.01	<0.001	177
	15–30	Allophanic	0.70 ± 0.04	<0.001	36
Feng et al. (2011)	Variable	All	0.33 ± 0.01	<0.0001	342
	Variable	1:1 Minerals	0.25 ± 0.01	<0.0001	101
	Variable	2:1 Minerals	0.36 ± 0.01	<0.0001	241

[a] Units are mg C g^{-1} fine fraction soil particle ± 1 SE

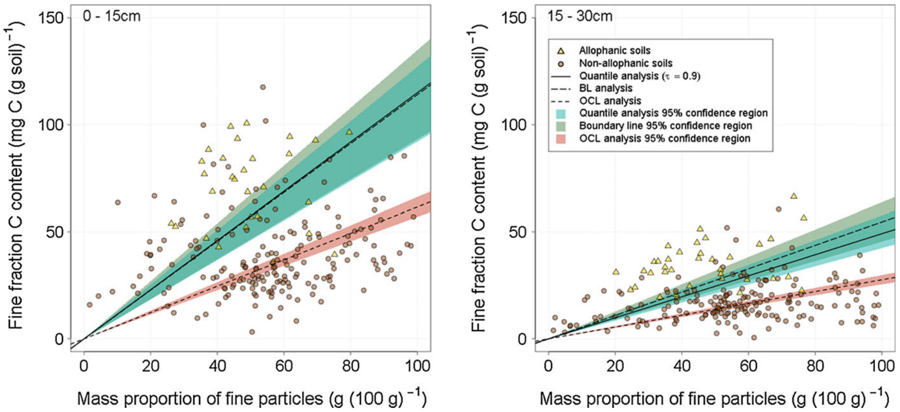

Fig. 2 The C content of the fine fraction in relation to the mass proportion of fine soil particles in Allophanic and non-Allophanic soils from 0–15 to 15–30 cm sample depths. The best-fit lines representing the boundary line (BL), quantile regression (QR), and organic C loading (OCL) methods apply only to non-Allophanic soils. The *shaded regions* represent the 95 % confidence interval for the relationship derived by each estimation method

our data as alternatives to the LSR for estimating the upper limits of SOC stabilisation.

The BL approach used by Feng et al. (2011) estimates the upper limit of SOC stabilisation from the upper 10 % of fine fraction SOC values in soils with different mass proportions of fine soil particles, whereas QR modelling estimates the limit based on analysis of the entire dataset. Our analysis of the New Zealand data using these two methods produced similar estimates of the upper limits of SOC stabilisation in non-Allophanic soils for each of 0–15 and 15–30 cm layers (Fig. 2), as evidenced by the very similar slope and overlapping 95 % confidence intervals (CIs). Overall, these analyses suggest that the stabilisation capacity of Allophanic soils was 33–91 % higher than that of non-Allophanic soils (Table 3). The higher C content of Allophanic soils has been attributed to the stabilisation ability of allophane and the associated reactive Al (Percival et al. 2000; Parfitt et al. 2002; Baisden et al. 2011). The estimates of SOC stabilisation capacity derived from the QRs of the Allophanic soils at both depths (0–15 and 15–30 cm) were significantly higher than those derived using the BL method. As for the LSR results, the slope of the relationship between the SOC content and the mass proportion of the fine fraction for non-Allophanic soils at the 15–30 cm depth was about one-half the slope obtained for 0–15 cm soils using both BL and QR methods (Table 3). This difference is perhaps not surprising, given that surface soils are expected to have higher inputs of C from primary production.

Table 3 Estimates of the stabilisation capacity of fine soil particles (<20 µm) in New Zealand soils based on boundary line (BL) and quantile regression (QR) modelling with forced 0 intercepts and the organic C loading method (OCL) compared with those reported by Feng et al. (2011)

Source/method	Layers (cm)	Datasets	Slope[a]	*P*	*n*
New Zealand					
BL	0–15	Non-Allophanic	1.16 ± 0.11	<0.0001	22
		Allophanic	1.53 ± 0.17	<0.0001	9
	15–30	Non-Allophanic	0.56 ± 0.05	<0.0001	21
		Allophanic	0.86 ± 0.07	<0.0001	7
QR	0–15	Non-Allophanic	1.23 ± 0.09	<0.0001	184
		Allophanic	2.35 ± 0.11	<0.0001	29
	15–30	Non-Allophanic	0.64 ± 0.07	<0.0001	177
		Allophanic	1.14 ± 0.06	<0.0001	36
OCL	0–15	Non-Allophanic	0.62 ± 0.04	<0.0001	207
		Allophanic	1.35 ± 0.09	<0.0001	29
	15–30	Non-Allophanic	0.28 ± 0.01	<0.0001	200
		Allophanic	0.70 ± 0.04	<0.0001	36
Feng et al. (2011)					
BL		1:1 Minerals	0.43 ± 0.04	<0.0001	5
		2:1 Minerals	0.84 ± 0.04	<0.0001	20
OCL		1:1 Minerals	0.15		
		2:1 Minerals	0.80		

[a] Units are mg C g^{-1} fine fraction soil particles ± 1 SE

Mineral SA and organic carbon loading

The result of this study and those of Six et al. (2002) and Feng et al. (2011) showed clear differences in the relationship between SOC and the mass proportion of fine particles in soils of different mineral composition. This indicates that the mass proportion of fine soil particles alone is not sufficient to explain the variability in soil C stabilisation capacity across a wide range of soils and that other properties of the fine fraction may be important in defining the stabilisation capacity. One well established and potentially important difference between soils of different mineral composition is the specific SA (Theng et al. 1999; Hedley et al. 2000). Previous studies have shown that the specific SA of whole soils is positively correlated to the SOC concentration in bulk soil and in particle size fractions (Kahle et al. 2002b, 2003; Kaiser and Guggenberger 2003; Mayer 1994; Wiseman and Püttmann 2005; Zinn et al. 2007). Other studies have reported apparent differences in the organic C stabilisation capacity in soils of contrasting mineralogy (Schulten and Leinweber 2000; Denef et al. 2004). Because many soils are composed of a mixture of clay minerals [e.g. allophane, and 1:1 (kaolinite), and 2:1 clay (mica, smectite, vermiculite)] with different specific SAs (Theng et al. 1999; Hedley et al. 2000; Parfitt et al. 2001), a measure of soil SA could provide a more universal predictor of organic C stabilisation capacity than the mass proportion of fine particles.

Where the specific SA of soil particles is known, the results of previous studies suggest that the upper limit of soil C storage in the fine fraction is approached at a monolayer equivalent C loading of ~1 mg C m^{-2} (Mayer 1994; Keil et al. 1994). Although the assumptions of the mono-layer equivalent loading method have been challenged (Mayer and Xing 2001; Wagai et al. 2009), evidence of SOC loadings >1 mg C m^{-2} are typically associated with coarse mineral fractions with a high proportion of labile (unstable) organic C (Kahle et al. 2002a; Mayer 1994; Wiseman and Püttmann 2005). Those cases where estimated SOC loadings are <1 mg C m^{-2} are typically associated with cropping soils or deep soil horizons, where C inputs are typically lower. Feng et al. (2011) used the organic C loading method to estimate the soil C stabilisation capacity of the fine fraction from their meta-analysis of data from 32 independent studies. To do this, they assumed specific SAs of 15 and 80 $m^2\ g^{-1}$ for soils dominated by 1:1 and 2:1 clay minerals, respectively, based on the average specific SA of selected 1:1 (i.e. kaolinite) and 2:1 (i.e. montmorillonite, vermiculite and illite) minerals obtained from Mitchell and Soga (2005).

In this study, we used measurements of the water content of air-dried soil to estimate SA following the method of Parfitt et al. (2001) as described above. We recognise that some SA arises from organic C itself but inspection of the data with multiple regression indicated that clay content was a more important driver of water content than SOC content, particularly for the Allophanic soils. This is a topic that requires further investigation, but at this stage water content is the best measure of SA that is available. The SA estimates ranged from 5.8 to 227 $m^2\ g^{-1}$ of soil, but were skewed to the low end of the range. The median values were 57 $m^2\ g^{-1}$ for 0–15 cm soil and 45 $m^2\ g^{-1}$ for 15–30 cm soil. We then applied the same organic C loading rate ($\sim$1 mg C m^{-2}) used by Feng et al. (2011) to our estimated SAs to predict the SOC stabilisation capacity of individual soils. The slope of the LSR between this estimate of stabilised SOC and the mass proportion of the fine fraction in 0–15 cm non-Allophanic soils (0.62 ± 0.04) was lower than the slope reported by Feng et al. (2011) (based on an assumed SA) for soils dominated by 2:1 minerals (0.80), but much higher than their estimate for soils dominated by 1:1 minerals (0.15; Table 3). However, the slope of the relationship between the SOC content and mass proportion of fine particles in 0–15 cm Allophanic soils was about 1.7 times the values reported for 2:1 soils by Feng et al. (2011). By comparison, the slope of the relationship for both Allophanic and non-Allophanic soils at 15–30 cm depth was about one-half that reported for 0–15 cm soils.

We also investigated the relationship between the specific SA of soil (estimated from air-dried water content) and the SOC content of the fine fraction for both sample depths. There was a strong positive linear relationship between the log-transformed SA of air-dried soil and the log-transformed SOC content of the fine fraction for both sample depths (Fig. 3). The 95 % CIs showed a clear separation of median ($\tau = 0.5$) and 90th percentile ($\tau = 0.9$) quantile lines. Plots of the untransformed data at both depths emphasize that the uncertainty in this relationship increases with increases in mineral SA, as evidenced by widening 95 % CIs (data not shown). Contrary to the linear organic C loading rate assumed by Feng et al. (2011), our results suggest that the relationship between the SA and SOC content of the fine fraction is best explained by a non-linear relationship of the form:

$$\log(C_\tau) = a_{0,\tau} + a_{1,\tau} \cdot \log(\mathrm{SA}) + \varepsilon,$$

where $\log(C_\tau)$ is the log of SOC (mg C g^{-1}), log(SA) is the log of the surface area ($m^2\ g^{-1}$), a_0 is the intercept for a given quantile τ with residuals ε. The coefficients and 95 % CIs for the median ($\tau = 0.50$) and 90th percentile ($\tau = 0.90$) regressions in 0–15 and 15–30 cm soils are given in Table 4.

The slope of the log–log relationship between the SOC content and specific SA of the fine fraction in this study was <1.0, which is equivalent to the organic C loading rate of 1 mg C m^{-2} used by Feng et al. (2011) (Fig. 3). Our estimate of a maximum (90th percentile) organic C loading rate was very close to 1 mg C m^{-2} in soils with a relatively low to moderate specific SA. However, there was a greater divergence in the estimates of maximum organic C loading at the high end of the specific SA range, particularly in the soils from the 15–30 cm sample depth. This may be due to true under saturation of soils with a high specific SA or it may indicate that some of the mineral SA is inaccessible (or less accessible) for SOC adsorption. Furthermore, the role that Al and Fe oxides play in relation to mineralogy and specific SA are not well understood and may be important to reconciling differences between the organic C loading method and other statistical methods discussed above.

Multivariate QR analyses

Correlation analyses showed that specific SA was the most important soil property among those we assessed to explain variability in the SOC content of the fine fraction (Table 5). Several other variables (extractable Al and Si; soil pH) also exhibited significant relationships with soil C. There was a positive relationship with extractable Al, with Al-p giving a slightly stronger correlation than Al-o. This observation is consistent with the finding of Percival et al. (2000) that Al is an important determinant of the SOC storage

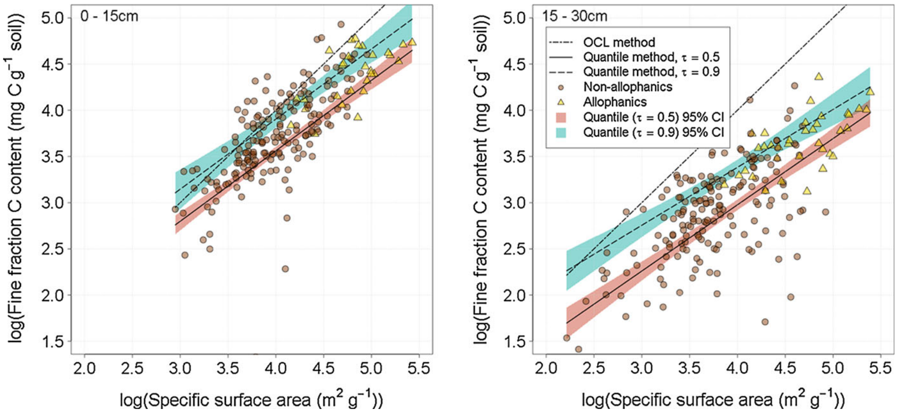

Fig. 3 The quantile relationships between specific surface area (m^2 g^{-1}) and the soil organic C content of the fine fraction (mg C g^{-1}) in both Allophanic and non-Allophanic soils at 0–15 and 15–30 cm depths. The *shaded regions* are the 95 % confidence interval of the quantile estimates

Table 4 Coefficients for the best-fit single-variable quantile regressions for predicting log(C) from estimates of soil specific surface area in 0–15 and 15–30 cm soils

Layers (cm)	Variables	Median $\tau = 0.50$		90th Percentile $\tau = 0.90$	
		Estimates	95 % CI[a]	Estimates	95 % CI
0–15	Intercept	0.51	[0.28, 0.67]	0.87	[0.50, 1.44]
	Log(SA)	0.76	[0.72, 0.81]	0.76	[0.63, 0.86]
15–30	Intercept	0.11	[−0.09, 0.37]	0.88	[0.21, 1.33]
	Log(SA)	0.72	[0.65, 0.77]	0.63	[0.51, 0.80]

[a] 95 % confidence interval (CI)

capacity of New Zealand soils. Concentrations of Al are particularly high in the Allophanic and podzol soils and this might help to explain the relatively high C stocks in these soils. Our analysis indicated that soil C tended to decrease as soil pH increased; however, the effect of pH was relatively weak (Table 5). Previous studies of factors underpinning soil C storage have not identified pH as a significant explanatory variable and the reason why pH might had a negative influence on C in our soils is not clear. Raising pH can result in desorption of some organic matter from Al and Fe surfaces, although the amounts released are probably small in relation to the total stock of soil organic matter. The bacterial decomposition pathway tends to dominate at higher pH, and possibly leads to more mineralisation of SOC.

Based on the results of our correlation analyses, multivariate QR analyses were undertaken to identify the relationship that best explained variability in the SOC content of the fine fraction. In this case, all the explanatory variables in Table 5 were initially included followed by a model selection process to find the best fit for each QR. There are a variety of possible strategies for model selection in the literature for QR (Koenker 2005), but in this case we selected the best model on the basis of minimisation of the Akaike Information Criterion, AIC (Burnham and Anderson 2002), while at the same time ensuring that the coefficients of each model were physically plausible. The AIC provides a measure of the relative quality of one regression model compared to others by incorporating the trade-off between goodness-of-fit and model complexity. When used in this manner, the AIC criterion defined for QR yields a model that may have better predictive ability, but one that is possibly not as parsimonious as the optimal model (Koenker 2005). The best-fit multivariate regression yielded a relationship of the form:

$$\log(C_\tau) = a_{0,\tau} + a_{1,\tau} \cdot \log(\mathrm{SA}) + a_{2,\tau} \cdot [\mathrm{pH}] + a_{3,\tau} \cdot [\mathrm{pH}]^2 + a_{4,\tau} \cdot \log(\mathrm{Al} - \mathrm{p}) + \varepsilon,$$

where log(C) is the log of SOC (mg C g^{-1}) as defined by the specific surface area (SA), pH, and Al-p for a

Table 5 Matrix of the correlation ρ for 0–15 cm soil between response log(C) and the explanatory factors

ρ	Log(C)	pH[a]	Log(Al-p)	Log(Al-o)	Log(Si-o)	Log(SA)	Clay
Log(C)	1.00	−0.37	0.72	0.68	0.40	0.81	0.16
pH		1.00	−0.34	−0.23	−0.04	−0.22	−0.05
Log(Al-p)			1.00	0.90	0.56	0.69	0.03
Log(Al-o)				1.00	0.76	0.77	0.04
Log(Si-o)					1.00	0.57	0.01
Log(SA)						1.00	0.40
Clay							1.00

[a] SA (specific surface area), pH, Al-p, Al-o and Si-o are as defined in the methods

Table 6 Coefficients for the best-fit multivariate quantile regressions for predicting log(C) from selected soil properties in 0–15 and 15–30 cm

Layers (cm)	Variables[a]	Median $\tau = 0.50$		90th Percentile $\tau = 0.90$	
		Estimates	95 % CI[b]	Estimates	95 % CI
0–15	Intercept	6.61	[4.54, 8.35]	6.36	[4.82, 23.5]
	Log(SA)	0.610	[0.580, 0.664]	0.568	[0.451, 0.672]
	pH	−1.69	[−2.30, −0.929]	−1.41	[−9.08, −0.771]
	$(\mathrm{pH})^2$	0.135	[−0.049, −0.178]	0.103	[−0.041, −0.792]
	Log(Al-p)	0.144	[0.117, 0.191]	0.040	[−0.019, 0.082]
15–30	Intercept	2.10	[−3.00, 3.66]	4.80	[2.41, 12.4]
	Log(SA)	0.479	[0.374, 0.538]	0.405	[0.332, 0.627]
	pH	−0.116	[−0.713, 1.78]	−0.744	[−3.64, −0.033]
	$(\mathrm{pH})^2$	−0.001	[−0.172, 0.058]	0.040	[−0.011, 0.335]
	Log(Al-p)	0.189	[0.168, 0.246]	0.167	[0.056, 0.207]

[a] SA (specific surface area), pH and Al-p are as defined in the methods

[b] 95 % confidence interval (CI)

given quantile τ with residuals ε. The coefficients and 95 % CIs for the median ($\tau = 0.50$) and 90th percentile ($\tau = 0.90$) regressions in 0–15 and 15–30 cm soils are given in Table 6.

The best-fit 90th percentile quantile ($\tau = 0.90$) regression models described above were used to predict the SOC content of the fine fraction (0–15 cm soils) from measurements of the mass proportion of fine soil particles, soil SA or SA in combination with Al-p and pH. These predicted results were then plotted against the measured results to show the improvements made in estimating fine fraction SOC content using the multivariate regression compared with the single variable regression models (Fig. 4). The single-variable regression with log-transformed fine-fraction C content as the response variable and log-transformed SA as the predictor is a model that is a subset of the multivariate regression involving SA, pH, and Al-p, so comparison between these models on the basis of the AIC is valid. For 0–15 cm soils, the change in AIC between the single and multiple variable models (−71.2 at $\tau = 0.50$ and −95.5 at $\tau = 0.90$) indicates that the multivariate relationship is significantly better. Results for the 15–30 cm layer (−96.5 at $\tau = 0.50$ and −91.2 at $\tau = 0.90$) also provide strong evidence that the multivariate model is a significant improvement on the single variable model based on SA alone. While it is not possible to use AIC to compare the single or multivariate models based on SA to the single-variable model based on the mass proportion of fine particles, the improvements are clearly visible in Fig. 4. It

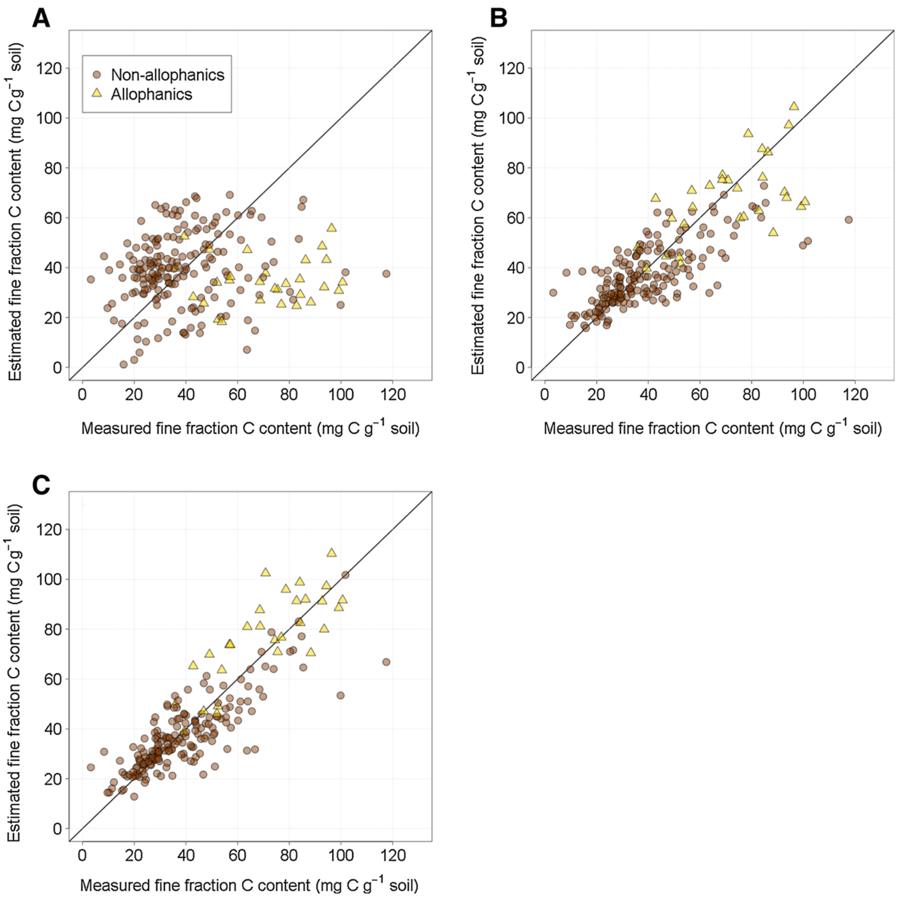

Fig. 4 Measured fine fraction C content (mg C g^{-1}) compared with the fine fraction C content estimated (predicted) from single variable quantile ($\tau = 0.90$) regressions based on **a** the mass proportion of the fine fraction, or **b** the specific water surface area of soils, and **c** a multivariate quantile ($\tau = 0.90$) regression based on specific surface area, pH and pyrophosphate-extractable aluminium (Al-p). The results presented are for both Allophanic and non-Allophanic soils

should be noted that the results of our study did not provide clear and irrefutable evidence of a limiting response of organic C using any of the models we investigated. Formal tests of such a limiting behaviour have been proposed in the literature (Milne et al. 2006) for bivariate data, but it is far from clear how one would test for limiting behaviour with multivariate data. Consequently, we believe that the QR models proposed in this study (i.e., using SA or the multiple factors) should more accurately be described as providing a prediction of the lower bound of the true upper limit of SOC stabilisation.

SOC saturation deficit

In the final phase of our research, we used the multivariate model to predict the SOC saturation deficit for each soil in our dataset. In this case, the saturation deficit was defined as the difference between the fine fraction SOC contents estimated for the upper quantile (90th percentile, $\tau = 0.90$) and median quantile ($\tau = 0.50$) regressions. The CI for this difference was estimated by assuming that the two quantile estimates were uncorrelated, yielding a conservative estimate of the interval. For each point in the analysis dataset, the potential increase in SOC concentration from the median ($\tau = 0.50$) to the upper quantile ($\tau = 0.90$) was calculated, along with the 95 % CI of the concentration increase. This difference was taken to represent the saturation deficit. These values were plotted against both the SOC content and the mass proportion of fraction particles (Fig. 5). The results of these model predictions suggest that the median saturation deficits for 0–15 cm soil was 12 mg C g^{-1} and for 15–30 cm soil was 15 mg C g^{-1}. In the 0–15 cm soils, all the soils with a fine fraction C content <60 mg C g^{-1} had positive saturation deficit values and >93 % of those values had CIs that did not overlap with 0. In those 0–15 cm soils with a fine fraction C content >60 mg C g^{-1}, all but two of the soils had positive

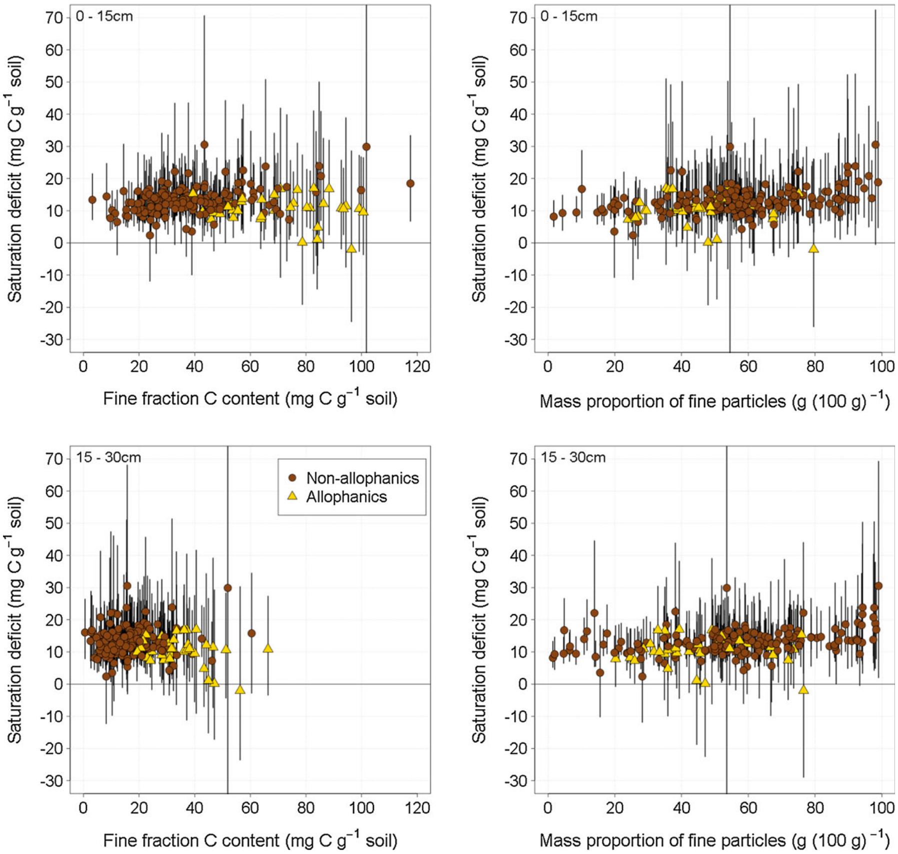

Fig. 5 The saturation deficit of stable soil organic C in relation to **a** the fine fraction C content (mg C g^{-1} soil) and **b** the mass proportion of fine particles of Allophanic and non-Allophanic soils collected as two sample depths (0–15 and 15–30 cm). The *error bars* are the 95 % confidence interval of the saturation deficit estimates

saturation deficit values and >60 % of those values had CIs that did not overlap with 0. Similar differences were noted for the 15–30 cm soils, albeit over a narrower range of fine fraction C contents. Although, on average, the saturation deficit remained relatively constant across a wide range of fine fraction SOC contents, there was some evidence that the saturation deficit increased slightly with increases in the mass proportion of fine soil particles.

These data provide strong evidence, at least empirically, that a positive saturation deficit exists, based on the application of the best-fit multivariate regression model described above, and taking into account the inherent uncertainty in the modelling. Although it is clear that the saturation deficit is no smaller than the values presented here, we are unable to say with certainty how large the deficit is since we were unable to find clear evidence of a limiting response of SOC from the available data. In part, the difficulty lies in the soil sampling approached used to establish the NSD dataset, which imposed some limitations on the interpretation of results from this study. The NSD sample sites were selected to broadly represent specific land use and soil type characteristics, but were not necessarily selected to represent the extremes of these categories in relation to potential SOC storage. Further work is needed to identify those extreme conditions, and the SOC contents associated with them, in order to improve our confidence in the prediction of SOC saturation deficits.

Based on the median values given above and assuming a fixed bulk density of 1.1 g cm^{-3}, we calculated the size of the potential SOC stock increase that could be achieved if the saturation deficit was filled (i.e. if the potential increase was met). At a total SOC content of 25 mg C g^{-1} in the top 15 cm, the median increase would amount to about 19.8 Mg C ha^{-1}, or a 48 % increase on the current stock of 41 Mg C ha^{-1}. At 75 mg C g^{-1} in the top 15 cm, the median increase would be equivalent to a 16 % increase on a current stock of 124 Mg C ha^{-1}. We do not intend to imply by these results that it may be possible to fill any large proportion of the potential saturation deficit in most soils in any meaningful timeframe. However, studies of this form can help us to understand which soils or soil characteristics may be most useful to target in developing SOC sequestration strategies or practices that may help to mitigate any SOC losses that result from land use change or intensification of agriculture. Further research is needed to identify the key soil properties and primary mechanisms that affect SOC stabilisation, as well as any biophysical factors that may limit the rate of SOC stabilisation in soils that have a significant saturation deficit.

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