The importance of inorganic carbon in soil carbon databases and stock estimates: a case study from England.

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Abstract

Many national and regional databases of soil properties and associated estimates of soil carbon stock consider the organic, but not the inorganic carbon (IC) fraction. Any future change in soil carbon stock resulting from the formation of pedogenic carbonates will be difficult to set in context because historical measurements or estimates of IC concentration and stock may not be available. In their paper describing a database of soil carbon for the United Kingdom published in this journal, Bradley et al. (2005) only considered data for organic carbon (OC), despite the occurrence of IC-bearing calcareous soils across a substantial part of southern England. Robust techniques are required for establishing IC concentrations and stocks based on available data. We present linear regression models (R^2) between 0.8 and 0.88) to estimate IC in topsoil based on total Ca and Al concentrations for soils over two groups of primary, carbonate-bearing parent materials across parts of southern and eastern England. By applying the regression models to geochemical survey data across the entire area (18 165 km^2) we estimated IC concentrations on a regular 500-metre grid by ordinary kriging. Using bulk density data from across the region, we estimated the total IC stock of soil (0-30 cm depth) in this area to be 186 MtC. This represents 15.5% and 5.5% of the estimated total soil carbon stock (OC plus IC) across England and the UK, respectively, based on the data presented by Bradley et al. Soil geochemical data could useful for estimating primary IC stocks in other parts of the world.

Keywords: soil organic carbon; carbon stock; linear regression, ordinary kriging

Introduction

The global soil resource represents a larger dynamic carbon reservoir than the atmosphere (Prentice, 2001). In the context of climate change, the soil is therefore of great importance

because carbon dioxide released from it can have a substantial impact on atmospheric carbon dioxide concentrations, which in terms of emissions is the most significant of the anthropogenic greenhouse gases in terms of global warming potential (Ehhalt & Prather, 2001). Substantial efforts have been made to quantify terrestrial soil carbon stocks at both national and global scales. In his assessment of global soil carbon (C) stocks, estimates made by Batjes (1996) for the upper 1m of soil (excluding litter) were 2293 Pg (1 Pg = 10^{15} g) total C, of which two thirds (1548 Pg) was organic carbon (OC) and one third (748 Pg) was inorganic carbon (IC).

This IC comprises both primary carbonate inherited from the parent material or deposited as dusts, and secondary carbonate which forms by precipitation of carbonate ions derived from root and microbial respiration and calcium and magnesium ions from weathering (Lal & Kimble, 2000). There is a strong correlation between the depth in the soil profile at which substantial quantities of secondary carbonate-mineral phases occur and mean annual rainfall (Jenny, 1980) and land cover type (Na *et al.*, 2008). For example, at sites with mean annual rainfall of around 50 cm per year, carbonate tends to occur at about 50 cm depth in the soil profile; smaller quantities of annual rainfall prevent the rapid removal of carbonate and base cations through leaching.

A global map (1:5 million scale) of soil IC shows that in general much larger densities (kg m⁻²) occur at lower latitudes in the northern hemisphere compared to those at higher latitudes, whilst densities of OC increase at higher northern latitudes (NRCS, 2000). The pattern of soil IC in part reflects drier climates at lower latitudes, where evaporation rates are typically greater, and mean annual rainfall is smaller. National and regional databases of soil properties have tended to focus on reporting OC concentrations and stocks, and rarely

provide the same figures for IC. In Europe for example, no IC concentrations were measured in the FOREGS survey (Salminen *et al.*, 2005), nor are they included in the Soil Profile Analytical Database of Europe (SPADE-2) described by Hannam et al. (2009). In some cases, national-scale soil carbon databases and the estimation of soil carbon stocks made from them have only considered OC; this was the case for the estimates of soil carbon stocks across the United Kingdom undertaken by Bradley et al. (Bradley *et al.*, 2005). Given the potential for the enhanced sequestration of atmospheric carbon dioxide as pedogenic carbonate in soil through both natural and artificial means (Manning, 2008), it is important that baseline values of soil IC stocks are available so the magnitude of any changes can be set in context.

Bradley et al. may have omitted soil IC from their database because they considered there was insufficient data to make a robust estimate of its stock, or that the total quantity was insignificant to not be worthy of consideration. Soil IC concentrations are generally relatively small (<1%) across most of Northern Ireland, Wales, Scotland and parts of northern England because of the carbonate-poor parent material types and elevated mean annual rainfall (>600 mm year). This is also shown in values of soil IC measurements published by the Soil Survey of England and Wales; see Soil Survey (1984) for a full list of soil these regional publications. However, in common with much of Europe (Durr & Meybeck, 2005) large areas of southern and eastern England are underlain by sedimentary carbonate could make a substantial contribution to the soil carbon stock of England. This is particularly the case because some soils over carbonate bedrock tend to be thin, and ploughing brings fresh, carbonate-rich material to the surface of the soil profile.

To overcome the lack of available data with which to estimate IC concentrations in soil robustly, we considered that it may be possible to obtain accurate model-based estimates of IC from geochemical predictors available in the form of geochemical survey data. Recent work has shown how such data can be used to accurately estimate properties such as topsoil texture (Rawlins *et al.*, 2009).

In this paper we present regression models for estimation of IC concentrations in soil (0-30 cm depth) over two carbonate-rich parent materials which cover large parts of southern and eastern England based on geochemical predictors. We use these regression models to estimate topsoil IC concentrations using geochemical data from soil samples collected across the entire area, and then use ordinary kriging on a point support to make local estimates of soil IC concentrations. Using values for soil bulk density we estimate the fine-earth fraction soil IC stock across the selected parts of southern and eastern England and compare this to the total carbon stock (OC plus IC).

Methods

Study region geology and soils

We considered that the IC stock of soil across England is likely to be dominated by the large quantities of primary carbonate mineral phases derived from two dominant lithologies in southern and eastern England; soils developed from outcrops of the Jurassic Limestone and the Cretaceous Chalk, plus soil developed in Quaternary deposits derived from the latter (see Figure 1). Polygons delineating these two main groups of parent material type were selected in a GIS based on the 1:50 000 scale soil parent material map of the British Isles (Lawley, 2009); their distributions are shown in Figure 1 covering 14% (18 165 km²) of the total land area of England. The complex superficial geology across part of northern East Anglia is

currently being re-surveyed, and because there is greater uncertainty concerning the distribution of soil parent materials in this region we excluded from our study the soils developed from these superficial deposits.

Soil geochemical survey datasets

The geochemical data comprised analyses of topsoil samples collected from two surveys. First, the National Soil Inventory (NSI) the sampling for which was undertaken between 1978 and 1983 and consists of topsoil samples collected on a 5-km grid across England and Wales. The original analysis for 17 major and trace elements was based on an *aqua regia* digest followed by ICP-AES analyses (McGrath & Loveland, 1992). Excess material from these samples was recently re-analysed using X-ray fluorescence spectrometry (XRF-S) to determine the total concentration of 55 major and trace elements including calcium (Ca) and aluminium (Al). These are the data used in the current study. This second geochemical dataset were XRF-S analyses of topsoil samples collected under the Geochemical Baseline Survey of the Environment (G-BASE) project (Johnson *et al.*, 2005). The G-BASE soil sample locations over the selected parent materials are shown in Figures 2a and 2b; they are at a higher spatial resolution (1 sample per 2 square kilometres) than the NSI samples. The G-BASE samples used here were collected between 1986 and 2006.

Although the locations of the NSI samples span the entire region, the differences in sampling density can be seen most easily in the lower section of Figure 2a where there are to date no sampling locations from the G-BASE survey, only NSI sampling locations. Although soil samples from the two surveys were collected across a period spanning 20 years, the primary carbonate content is likely to change relatively slowly with time and we do not consider any difference is likely to be substantial in relation to the total stock of IC. The sampling support

(the 20 m square from which individual soil cores were combined to form a composite sample) and sampling depths (0–15 cm depth after removal of surface litter) were consistent for the two surveys. In the case of the NSI, a composite sample from each site was created from twenty-five individual soil cores across the square, whereas in the G-BASE survey five samples were collected from the corners and centre of the square to form a composite sample. In each case, the analyses are based on the less than 2 mm fraction of the soil. Throughout the XRF-S analyses a combination of internal reference materials and certified reference materials were analysed to ensure the analytical determinations were consistent across all analyses.

Procedure for sample selection for inorganic carbon measurements

The primary IC components of both the Cretaceous Chalk and the Quaternary material derived from it are the same so we considered that a regression model between soil geochemistry and IC for samples over the Cretaceous Chalk would suffice for both groups. We extracted data for the concentrations of Ca and Al for archived soil samples at sites over the Cretaceous Chalk and Jurassic Limestone and Quaternary deposits derived from the former. Excess, archived sample material was not available from the NSI sites for this study, so our selection was restricted to the G-BASE samples (see Figures 2a and 2b) which do not currently extend to the south coast of England. To establish effective regression models to estimate IC from soil geochemistry, we wanted to ensure the analyses encompassed a large range of IC concentrations. We considered that Ca was likely to have a strong positive correlation with soil IC content because calcium carbonate is the dominant carbonate mineral in the selected Chalk and limestone bedrock types. We also considered that Al would have a negative correlation with IC content because it is a major component of alumino-silicate minerals which dilutes the amount of carbonate. We produced scatterplots of total soil Ca

versus total soil Al from the G-BASE samples for Cretaceous Chalk (n=4537) and Jurassic Limestone (n=1241) bedrock types. We used the scatterplots to select subsets of archived sample material to be analysed for their IC concentration, and which encompassed the greatest variation in both elements. We selected 45 samples over the Cretaceous Chalk and Quaternary Chalk and 55 over the Jurassic limestone; their locations are shown in Figures 2a and 2b.

Inorganic carbon analyses

A subsample of mass 0.2 g was weighed into a crucible and total carbon concentration (TC; %) estimated using an ELTRA CS800 (ELTRA GmBH, Germany) combustion instrument. Another identical analysis was undertaken using another subsample but each was pre-treated with 10% hydrochloric acid (to remove inorganic carbon), by dropwise addition to each crucible until no further reaction occurred. These samples were also analysed by the same instrument to estimate total organic carbon (TOC) and the difference (TC minus TOC) provides an estimate of total inorganic carbon concentration (TIC; %). Eight subsamples of an internal reference material (IRM) were also included with the samples for IC analyses. An accurate value for the IC concentration of the IRM had been established by multiple contemporaneous analyses with three certified reference materials under a Wageningen Evaluating program for Analytical Laboratories (WEPAL) inter-laboratory comparison exercise. The mean of the eight IRM analyses (IC=1.42%) was very similar to the established mean (IC=1.34 %; n=131) from repeat analyses. The coefficient of variation was small (CV= 3.8%) and so we considered the IC estimates from analyses of the selected soil samples were sufficiently accurate and precise for the purpose of our study.

Building and applying the regression models

We formed scatter plots between potential predictors (total Ca and Al) and total IC to determine the strength of the linear relationships between them and we calculated coefficients to test whether the data were skewed. We formed regression models from the predictor variables (Ca and Al) using ordinary least squares with IC as the predictand. We chose to include an intercept term in the model because we know there may be small quantities of IC which may be unrelated to our predictors (Ca and Al). We retained only those predictors which were significant at the 5% confidence level (P < 0.05).

Estimating spatial distribution of soil IC concentrations by ordinary kriging

In each case the regression models explained large proportions of the variance in IC so we proceeded to estimate IC concentrations at all soil locations across the two groups of parent material; 4492 locations over the Cretaceous Chalk related parent materials and 1186 locations over the Jurassic Limestone. We then tested the IC values across the two types of parent material for spatial auto-correlation by estimating semi-variances using method of moments (Webster & Oliver, 2001). This was carried out using the geoR package ((Ribeiro Jr. & Diggle, 2001) in the R Environment (R Development Core Team, 2006). We calculated skewness coefficients for the two soil IC variates; the Jurassic Limestone soil IC was strongly skewed (Table 1) and so we transformed these data by taking natural logarithms prior to further geostatistical analysis. We computed semi-variance estimates in four directions (0, 45, 90, 135 degrees from north). There was no significant directional variation at lags shorter than 10 kilometres and the trend functions did not account for a significant amount of the variance so we proceeded to compute isotropic variograms up to a maximum distance of 30 kilometres for both datasets. To these we fitted both exponential and spherical functions (Webster & Oliver, 2001) and examined the goodness of fit using ordinary least squares. A single exponential model provided the best fit in both cases. We used the variogram model

from the Cretaceous chalk and associated Quaternary deposits to estimate IC concentrations across this parent material by ordinary kriging. In the case of the Jurassic Limestone, we applied lognormal ordinary kriging in which the kriged estimates were backtransformed (Webster & Oliver, 2001). The locations for estimating soil IC concentrations were selected first by generating grid coordinates at a spacing of 500 metres on a regular grid across the study region and then selecting only those coordinates which occur within polygons of the two main parent material types. This grid spacing was chosen as a balance between our wish to maximise the resolution of the estimates but also to limit the time required to compute the kriged values. We produced a map of the distribution of soil IC by plotting their concentrations on the 500-metre grid across the study region.

Estimates of bulk density

Data from the Countryside Survey (CS; Emmett et al. 2009) were used to estimate bulk density in soil on different parent material types. Bulk densities were taken from CS locations occurring within the polygons of Jurassic Limestone and Cretaceous Chalk defined from the parent material map (Lawley, 2009). This led to Cretaceous chalk and Jurassic limestone parent materials being represented by 70 and 20 CS plot locations, respectively. The CS habitat classification accounts for 64% of the variability in bulk density values; so average bulk density for each parent material type is strongly related to habitat composition. Using CS habitat classifications from each of the plot locations, the bulk density estimates were therefore weighted by proportions of broad habitats covering each parent material derived from Land Cover Map 2000 (Fuller *et al.*, 2002). This provided an average bulk density sensitive to habitat. These estimates, however, may be a biased representation of bulk density for 0-30cm depth of topsoil because CS only samples from 0 to 15cm depth. Estimates were

therefore extended to cover the 0–30cm depth range using land-use specific bulk density depth curves from Kiely et al. (2009).

Estimating inorganic carbon stock

To estimate IC stock over the two parent materials we multiplied the IC concentrations in each 500 by 500 metre grid cell by the respective bulk density values to a depth of 30 cm. In agriculturally dominated areas of England much of the soil is mixed to plough depths of between 20 and 30 cm. We therefore thought it reasonable to assume that the IC concentration in the top 15cm of the soil profile provides an unbiased estimate of that in the full depth range between 0 and 30 cm of the soil profile.

Results

Linear regression models

Summary statistics for geochemical data of the selected samples and those for all samples across the three parent material types are shown in Table 1. The range of IC concentrations in the selected archived soil samples over the Cretaceous Chalk span an order of magnitude (0.7 - 7%) whilst those over the Jurassic Limestone span a slightly smaller range (1 - 6%). The linear regression model for estimation of IC concentrations in topsoil over the Cretaceous Chalk accounted for 80% of the variance based on two predictors, Al and Ca (see Table 2). It is noteworthy that Al has a negative regression coefficient; presumably because it occurs principally in alumina-silicate minerals which dilutes the carbonate content. By contrast, Ca has a positive coefficient because it is present in calcium carbonate minerals. The linear regression model for IC in topsoil over the Jurassic Limestone is based on Ca alone and accounts for 89% of the variance (Table 2). Scatterplots of measured and predicted values of IC based on the two models are presented in Figures 3a (Cretaceous Chalk) and 3b (Jurassic Limestone). Summary statistics of soil geochemistry for the other geochemical survey samples used to estimate IC concentrations across the study region are shown in Table 1. In both cases the median Ca concentrations in the survey datasets are substantially smaller than in the selected sample subsets. In both cases, Ca is positively related to soil IC, so the median IC concentrations in soil over the two parent materials across the entire study region will be smaller than in the selected subsets.

Variogram models and ordinary kriging

Parameters of the isotropic variogram models used to undertake ordinary kriging of soil IC for the two groups of soil parent material are shown in Table 3. The nugget variances account for 25% and 49% of the variance for Cretaceous Chalk and Jurassic Limestone parent materials respectively indicating that those locations where the sampling density is greatest capture a considerable proportion of spatially correlated variance of soil IC from the regression estimates. In both cases the distance parameter of the variograms models – the distance over which values of a soil property can usefully provide data for estimation of a soil property around a site of interest – are greater than the largest sampling interval (5 km) in our dataset.

Summary statistics for estimates of IC concentration at soil sampling locations and grid locations (Table 4) demonstrate that the interpolation results in smoothing of the former in relation to the latter; in both cases the standard deviation of the interpolated values are smaller. The spatial distribution of soil IC (Figure 4) highlights some notable features. The largest soil IC concentrations (between 5 and 6%) are generally associated with soil developed directly over the Cretaceous Chalk (grid references around 550km Easting, 250 km Northing; Figure 4). The majority of the soil IC concentrations across the Jurassic Limestone are generally between 1 and 2 %, although there are areas where the values are between 2 and 3%. There is a clear difference between soil IC estimates in soils developed from Quaternary deposits (see Figures 1 and 4) which contain carbonate derived from the Cretaceous Chalk. Those deposits to the north-east generally have soil IC concentrations between 3 and 4 % whilst those further south and west generally have concentrations between 2 and 3%; this pattern highlights differences in the soil properties inherited from the soil parent materials in this region.

The bulk density values in soils developed over the two main groups of parent material were 1.049 g cm^3 for Cretaceous chalk and 1.08 g cm^3 for Jurassic Limestone. The difference between the two values is caused by the different habitat composition of the two parent material areas. The more arable-dominated Jurassic Limestone soils have greater bulk density than those over the Cretaceous Chalk.

Inorganic carbon stock

Using the spatial estimates of soil IC and the bulk density values, we estimate a total IC stock for soil developed over the Cretaceous Chalk and associated Quaternary deposits to 30 cm depth of 166 Tg IC (or MtC); the equivalent stock over the Jurassic Limestone is 20.5 Tg (10^{12} g) IC. So there is a total of 186.5 Tg IC (or MtC) in soil (0 to 30 cm depth) across the area of these two parent materials presented in this study. If we add this IC stock to that for organic carbon across England (0-30 cm; 1015 MtC) estimated by Bradley et al. (2005), the IC accounts for 15.5% of the total carbon stock (IC plus OC).

Discussion

In contrast to soil OC, a substantial component of IC is likely to occur in the coarser soil fraction (>2mm) in the form of limestone and chalk fragments. We could not account for the magnitude of this component in our study because we did not have sufficient data on the size distribution and IC concentration in coarse material across the study region. Our estimate for IC stock is likely to be conservative. It is the finer soil carbonate fraction which is likely to be more rapidly altered by soil pH reduction resulting from any increase in the use of nitrogen fertilisers or introduction of perennial crops under changing land use. The overwhelming majority of the carbonate in the soil across our study region is primary (i.e. derived from bedrock); this has been demonstrated by the dominance of geogenic coccoliths in soil developed over the Cretaceous Chalk using scanning electron microscopy (Kerry et al., 2009), but we do not have observations of the form of carbonate in soils over the Jurassic Limestone. By continent, Europe has twice as much carbonate bedrock as the global average (Durr & Meybeck, 2005) so the soil IC stock associated with primary carbonate in many countries across Europe is likely to be larger than the global average. Although changes to the quantities of primary carbonate occur over vastly greater (geological) timescales compared to the shorter turnover times of SOC, recent research has highlighted that soil biota may play an important role in the generation of secondary carbonates (Lee et al., 2008) highlighting potentially rapid changes to soil IC concentrations at local scales.

We have shown that an estimate of soil IC stock across 14% of the land area of England represents a substantial proportion (15.5%) of the total C stock across all of England, as estimated by Bradley et al. However, there are other areas of England, most notably the Magnesian Limestone of Yorkshire and the Carboniferous Limestone of Derbyshire (not shown) where parent material may lead to soil IC concentrations >1%, but we do not have

sufficient data to make IC stock estimates. Consequently, soil IC will contribute an even greater proportion to total C stock across the whole of England.

We demonstrated that linear regression could be used to estimate soil IC and the concentrations of Ca and Al from soil geochemical survey data across large areas. These data were of sufficient density to be interpolated using ordinary kriging to make optimal estimates of soil IC at regular grid locations. We consider that this approach may have value in other regions where scientists wish to estimate soil IC concentration and stock based on available geochemical and other survey data. These regression models would need to be tested in other landscapes with different soil parent material types; for example, we might expect soil magnesium (Mg) concentration to be a significant predictor of IC in areas with Mg-bearing, dolomitic limestone parent material.

There are three main sources of error in our estimate of IC stock. First, that associated with analysis and sub-sampling associated with measurement of IC concentrations in the two subsets of selected samples. Second, the error associated with our estimates of IC at all soil sampling locations based on linear regression. Third, that from the interpolation (ordinary kriging) of these estimates onto the 500 metre grid across the soils developed over the selected parent materials. We considered that quantifying the magnitude of this uncertainty was beyond the scope of our study.

Projections for climate change across southern England by 2080 (UK Climate Projections, 2010) suggest that although there may be significant differences in the seasonality of rainfall, total annual rainfall based on a (medium emission scenario) may be the same or increase slightly (10%). The size of precipitation events, their frequency and seasonality could play a

role in the formation of secondary carbonates. However, evaporation is not likely to increase markedly which would have a strong impact on development and maintenance of secondary soil carbonate. We believe that without substantial intervention, the formation of pedogenic carbonates is unlikely to greatly increase the IC stock. The addition of fine (reactive) magnesium silicates to soil has been suggested as a mechanism for enhancing carbon sequestration in soil (Schuiling & Krijgsman, 2006) leading to the precipitation of carbonate, or enhanced leaching of bicarbonate ions (HCO_3^-). Our estimate of naturally occurring soil IC provides a baseline stock against which any attempts to enhance IC sequestration in the soil – in the form of carbonate – can be compared.

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Figure captions

Figure 1 Distribution of carbonate-rich soil parent materials across southern and eastern England

Figure 2 Soil sampling locations over carbonate-rich parent materials across: a) northern England, and b) southern England.

Figure 3 Scatterplots of measured versus predicted values of soil IC (%) based on linear regression models (see Table 2) over two parent material types: a) Jurassic Limestone (n=55), and b) Cretaceous Chalk and associated Quaternary deposits (n=45).

Figure 4 The distribution of soil inorganic carbon concentrations (%) across the study region. Coordinates are kilometres on the British National Grid.

Table 1 Summary statistics for geochemical analysis and IC concentrations measured for i) selected archive soil samples and ii) other survey samples across two parent material types. All values in mg kg⁻¹ unless otherwise stated.

| | Crategoous Challe Queternery | | | | Iurogaia Limogtona | | | |
|----------|--------------------------------|--------|--------|-----------------|--------------------|------------------|--------|-----------------|
| | Cretaceous Chalk + Quaternary | | | | Jurassic Limestone | | | |
| | Selection (n=45) | | | Survey (n=4492) | | Selection (n=55) | | Survey (n=1186) |
| | IC (%) | Al | Ca | Al | Ca | IC (%) | Ca | Ca |
| Minimum | 0.74 | 1058 | 4717 | 1046 | 214 | 1.05 | 28370 | 1072 |
| Mean | 4.44 | 38300 | 166000 | 43005 | 32330 | 3.61 | 173900 | 40150 |
| Median | 4.72 | 30680 | 155500 | 44436 | 9220 | 3.7 | 199500 | 22041 |
| Maximum | 7.06 | 112700 | 343500 | 96807 | 351700 | 6.08 | 357800 | 279519 |
| St. Dev | 1.89 | 32668 | 89357 | 19343 | 53121 | 1.41 | 89306 | 42874 |
| Skewness | -0.57 | 0.71 | 0.005 | -0.19 | 2.74 | -0.17 | 0.05 | 1.54 |

 Table 2 Regression Coefficients for two models for estimating IC (%) in soils over: a) Cretaceous Chalk and associated Quaternary deposits,

 and b) Jurassic Limestone. Concentration units of Ca and Al are mg kg⁻¹

| | Estimate | ± Std. Error | <i>t</i> -value | <i>P</i> -value | $adj R^2$ |
|-----------|-----------------------------|------------------------------|-----------------|-----------------------------|-----------|
| a) | | | | | 0.80 |
| Intercept | 4.65 | 0.434 | 10.7 | 2.57×10^{-13} | |
| Al | $-3.33 	imes 10^{-05}$ | $4.40\times10^{\text{-}05}$ | -7.56 | 3.11×10^{-09} | |
| Ca | $7.11\times10^{\text{-}06}$ | $1.73\times10^{\text{-}06}$ | 4.12 | $1.86 	imes 10^{-04}$ | |
| b) | | | | | |
| Intercept | 0.949 | 0.152 | 6.25 | $1.23\times10^{\text{-}07}$ | 0.89 |
| Ca | 1.57×10^{-05} | $8.05\times 10^{\text{-}07}$ | 19.5 | $< 2 \times 10^{-16}$ | |

Table 3 Parameters of exponential variogram models fitted to semi-variances of IC in topsoil at soil survey locations for: a) Cretaceous Chalk

and associated Quaternary deposits, and b) Jurassic Limestone.

| | Variances | | ^b Range (m) |
|---------------------------------|-----------|-------|------------------------|
| | Nugget | Sill | |
| Cretaceous Chalk and Quaternary | 0.132 | 0.406 | 18518 |
| ^a Jurassic Limestone | 0.064 | 0.067 | 4560 |

^a models fitted to log transformed values

^b the effective ranges are $3 \times$ the stated range values

Table 4 Summary statistics for estimates of soil IC concentrations based on linear regression models at soil survey locations (SS) and at kriged

| | Cretaceous C | halk + Quaternary | Jurassic Limestone | | |
|----------------------------|--------------|-------------------|--------------------|-----------------|--|
| | SS | GL | SS | ^a GL | |
| | (n=4492) | (n=57639) | (n=1186) | (n=15022) | |
| Minimum | 1.7 | 2.28 | 0.97 | 1.07 | |
| Mean | 3.47 | 3.66 | 1.58 | 1.69 | |
| Median | 3.32 | 3.59 | 1.3 | 1.64 | |
| Maximum | 6.7 | 6.03 | 5.34 | 3 | |
| St. Dev | 0.81 | 0.66 | 0.67 | 0.31 | |
| Skewness | 0.92 | 0.32 | 1.54 | 0.75 | |
| Log _e transform | med | | | | |
| Skewness | | | 0.85 | | |

grid locations (GL: 500 metre grid) across the study region for the two groups of parent material types.

^a estimates backtransformed after log-normal kriging





Figure 2a



Figure 3



Figure 4

