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A pilot study to assess soil spectroscopic methods for mapping key topsoil properties in the Blackwater sub-catchments (Wensum DTC).

Climate Change Programme

Open Report OR/11/053



BRITISH GEOLOGICAL SURVEY

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A pilot study to assess soil spectroscopic methods for mapping key topsoil properties in the Blackwater sub-catchments (Wensum DTC).

B G Rawlins

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Foreword

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Summary

This report describes findings from sampling and analyses of soils across the Blackwater drain catchments, part of the Wensum demonstration test catchment (DTC) project funded by Defra. Recent studies have shown how spectroscopic techniques can be used to estimate soil properties and airborne spectroscopy could be an effective means to aid continuous mapping of soil properties across the landscape. Before an airborne survey is undertaken it is important to assess whether the relationships between infra red (IR) spectra and soil properties are sufficiently strong for the cost of the airborne survey to be justified. A secondary objective was to determine the concentrations of soil organic carbon (SOC) in soils across the cultivated parts of the catchment to determine whether there is any evidence that low SOC concentrations might indicate that the topsoil may exhibit poor structural stability contributing to enhanced sediment in stream and drainage channels.

In general, statistical models based on both near and mid infra red spectroscopy were not effective in predicting soil properties across the Blackwater drain catchments. However, dithionite extractable iron was well estimated by mid infra red spectroscopy. The most likely reasons for failure of the IR spectroscopic techniques are that there is general little variation in the properties across the catchments. In the case of soil particle size, it appears this is determined in these catchments largely by quartz content which is poorly detected by IR spectroscopy. These results suggest that an airborne spectral survey of the Blackwater drain catchments is unlikely to provide data which could be used to map soil properties at fine spatial scales.

Soil organic carbon (SOC) concentrations in cultivated fields of the Blackwater drain catchments are generally small (median=1.4%). By contrast, median topsoil SOC for the East Anglia region is 2.24 % based on analyses of 2858 topsoil survey samples collected between 2002 and 2005 (unpublished data, British Geological Survey). Previous research has suggested that topsoil in the Blackwater drain catchments are below the threshold at which scientists consider soil structural stability may be impaired and may lead to mobilisation of sediment to watercourses. Effective measures to mitigate sediment losses to watercourse in the Blackwater drain catchments may involve those which can halt the decline in SOC concentrations (e.g. changing tillage practices) or even raise SOC concentrations in topsoil through careful application of organic matter.

The total organic carbon stock for the upper 30cm of soil across the four Blackwater drain sub-catchments - an area of 16.1 km² - is 0.119 MtC (Megatonnes carbon) or 119000 tC (tonnes carbon). This estimate is based on sampling and analysis of topsoil only from cultivated land. Incorporation of data for other land use types – which are likely to have different topsoil carbon concentrations – would improve this estimate. The benchmark data on SOC concentrations, bulk density and stock from 50 sites could aid the assessment of on-farm measures aimed at stabilising or increasing soil organic carbon concentrations in soils across the Blackwater drain catchments.

1 Introduction

In 2010, Defra established three Demonstration Test Catchments across England to test the hypothesis that it is possible to cost-effectively reduce the impact of agricultural diffuse water pollution on ecological function while maintaining sustainable food production through the implementation of multiple on-farm mitigation measures. One of the three DTCs selected for study was the Wensum in Norfolk, within which a smaller set of subcatchments – known as Blackwater drain – were selected for detailed study and instrumentation.

Streams across the Blackwater drain subcatchments were identified as having some problems associated with large sediment loads which suggest that soil and sediment erosive losses of fine material to the stream channels may be substantial. Only low-resolution information is currently available on topsoil properties in the Blackwater drain sub-catchments. The spatial variation of soil properties such as texture (%sand, silt and clay), organic carbon content and bulk density have a substantial impact on the hydrological response of catchments, controlling how runoff water and suspended sediment are delivered to stream channels. In addition, soil phosphorus is dominantly associated with oxides and hydroxides of iron and aluminium {Hartikainen, 2010 #2642}. Traditional analyses to determine these soil properties are time consuming and expensive. Spectroscopic techniques – specifically near and mid infra red diffuse reflectance spectroscopy – are increasingly being used to determine soil properties both *in situ* and remotely from aeroplanes and satellites (Selige *et al.*, 2006; Lagacherie *et al.*, 2008). For accurate quantification of soil properties, statistical models need to be developed between primary measurements on field samples and their infra red spectra - based on lab measurements - before the models can be used to estimate concentrations of these properties in a larger number of samples, or from remote sensing. Before airborne remote sensing can be deployed, baseline data needs to be collected on the ground and the approach tested using laboratory-based methods. Although spectroscopic approaches have been demonstrated to be effective at regional scales (>50 km; see Rawlins *et al.*, (2011) they may be less effective at finer spatial scales where there may be less variation in soil mineralogy, particularly if the soils are derived from the same parent material type.

As part of the wider studies into the Blackwater drain catchments, funding was made available to investigate whether airborne spectroscopy might be an effective approach to mapping soil properties at fine (2m pixel) spatial scales. The first objective of the proposed soil sampling and analysis is to provide baseline data which can be used to assess the potential for applying spectroscopic techniques for cost-effective mapping of these soil properties. These data could provide the basis for ground-calibration of a subsequent (Feb 2012) application to the NERC airborne survey facility (www.arsf.nerc.ac.uk/). The second objective of the soil baseline data is to provide some indication of the current quantity of soil organic carbon (SOC) in topsoil of the Blackwater drain catchments which it has been suggested may determine soil structural stability (Loveland & Webb, 2003) and erosion (Malinda, 1995). For example, in Australian conditions, Malinda (1995) found that soil loss from 10-year plots under wheat, was strongly controlled by SOC content, with a steep increase in amounts of soil loss at SOC contents <1.6%.

The collection of both total organic carbon and soil bulk density across the cultivated areas of the catchment make it possible to calculate an unbiased carbon stock for this area of land. This may be of use by comparison with estimates of particulate carbon losses from suspended sediments calculated from analyses of sediments from the catchment outflows. Although particulate carbon is not currently determined routinely as part of the catchment monitoring, analyses could be undertaken cost-effectively using infra-red spectroscopic techniques using sediments collected on filter papers.

2 Methods

2.1 SOIL SAMPLING

Fifty sampling sites were selected across the catchments to maximise variation in soil properties based on current knowledge of the distribution of parent material types using expert knowledge of local deposits. Twenty-five soil sampling sites were randomly assigned within each of the two dominant parent materials; glacial till and sands and gravels (Figure 1). The soil sample locations were recorded with a kinematic differential GPS (2cm accuracy) and aggregate samples were collected across a 2 metre support which would be consistent with any subsequent airborne survey. At each site a Dutch auger was used to collect topsoil (0-15cm depth from the soil surface) at the corners and centre of a square of side length 2 metres. The soil material was placed in plastic bags prior to transport to the laboratory. Within each of the sampling squares, two small soil cores were also collected in bespoke 'Kubiena style' tins (45 mm diameter) for the determination of bulk density.

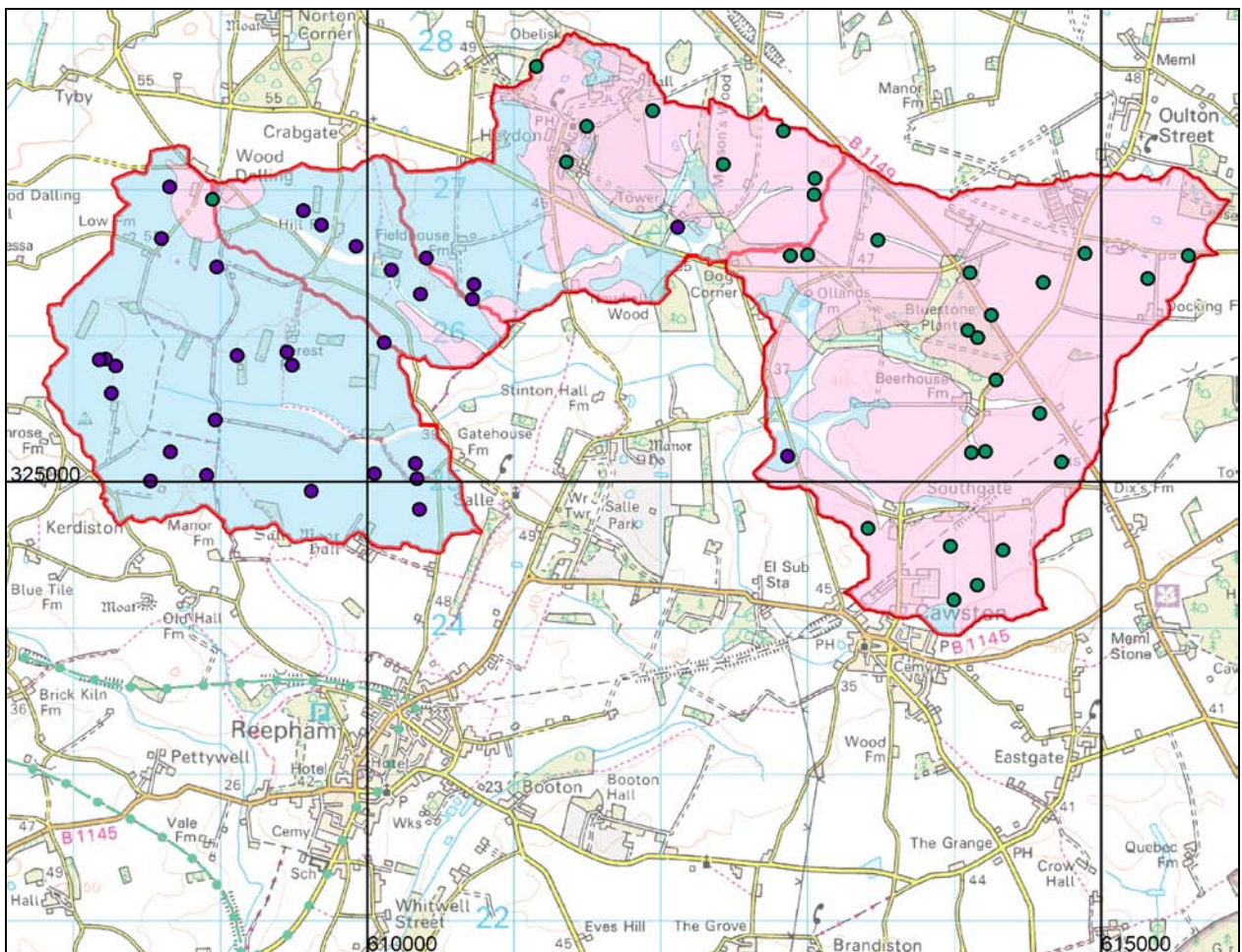


Figure 1 - Location (discs) of fifty soil sampling locations across the Blackwater drain catchments over the two dominant parent materials (blue represents dominantly glacial till, pink represents dominantly sands and gravel). Grid lines provide coordinates in metres of the British National Grid.

2.1 SAMPLE PREPARATION

2.1.1 Composite samples

The following protocol was applied for preparation of the 50 composite soil samples. Each was air-dried at room temperature prior to disaggregation and then sieved to pass 2 mm. The samples were then coned and quartered to retrieve 50 g sub-sample and this material was ball milled. The other < 2mm component was retained. Aliquots of the ball milled material and the <2 mm fraction were used for a range of soil analyses.

2.1.2 Kubierna tin samples

The soils were removed from their tins and oven dried at 105° C overnight. They were then disaggregated and sieved to pass a 2mm aperture sieve. The mass of the <2mm and > 2mm fraction (stones) were then weighed and the masses recorded. The volume of the stones in each sample was measured by adding them to a known volume of water in a volumetric cylinder and recording the increase in volume. The bulk density (BD; g cm⁻³) of the fine earth fraction (< 2mm) of each core section will be calculated as:

$$BD = \frac{\text{dry mass soil} - \text{mass stones}}{\text{volume of core} - \text{volume of stones}}$$

where the masses are measured in grammes, and the volumes in cubic centimetres.

2.2 COMPOSITE SOIL SAMPLE ANALYSES

A total set of six soil properties were determined on each of the 50 soil samples: total organic carbon, particle size distribution (% clay, silt and sand), dithionite extractable iron, dithionite extractable aluminium, oxalate extractable iron and oxalate extractable aluminium. The sampling locations were identified using a differential GPS system. The position of the centre of the square - from which the five composite samples were collected - was recorded in metres on the British National Grid.

2.2.1 Total Organic Carbon (TOC)

A mass of 0.2g of each sample was weighed out and placed in a crucible. Cold 10% hydrochloric acid (HCl) was then added dropwise to each sample until it was wet, and a vacuum bath on which the crucibles were standing was turned on. More 10 % HCl was added until the mixture ceased to react. This process was then repeated using 10 % HCl at 95°C, followed by concentrated HCl at 85°C. Each aliquot of HCl was allowed to drain through the crucible prior to addition of the next aliquot. The purpose of this was to remove all inorganic carbon from the sample in order to obtain the TOC content.

Each sample was then washed using hot (95°C) distilled water and placed in an oven at 105°C for at least two hours to dry. The samples were then cooled in a dessicator for at least thirty minutes, followed by combustion analysis using an ELTRA CS800 analyser. An internal reference material with a known quantity of organic carbon was also analysed five times throughout the analyses to assess accuracy and precision.

2.2.2 Particle size distribution

A 3g aliquot of the <2mm soil was also taken for the analysis of particle size distribution (psd) after removal of organic matter with hydrogen peroxide. A Coulter Beckman laser granulometer

was used for the determination of psd assuming an 8 micron threshold between the clay and silt size fractions (Konert & Vandenberghe, 1997).

2.2.3 Dithionite and oxalate extractable iron and aluminium

To determine the concentration of dithionite extractable iron and aluminium in a soil sample, 1g of ground soil was weighed into a 30 ml centrifuge tube and add 20 ml of 25% (w/v) sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$). Add a further 5 ml of 10 % (w/v) sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and shake overnight. Centrifuge the sample at 1370 g for 4 minutes. A 10 ml aliquot was then taken and the concentrations of Fe and Al determined by ICP-AES. The dithionite extractant isolates the magnitude of the crystalline oxyhydroxides whilst the oxalate extractant isolates the amorphous mineral phases.

To determine the concentration of oxalate extractable iron and aluminium in a soil sample, weigh 1.5g of ground soil into a centrifuge tube and add 25 ml ammonium oxalate ($28.4 \text{ g l}^{-1} = 0.2\text{M}$) and oxalic acid (15.76 g l^{-1}). Shake the sample in darkness for 2 hours, then filter the supernatant through a 0.45 micron filter membrane. Then measure the concentrations of Fe and Al by ICP-AES.

2.2.4 Visible and near infra red diffuse reflectance spectroscopy

Sub-samples of each soil were scanned in the visible-near infrared region (350--2500~nm) using an ASD (Analytical Spectral Devices, Boulder, CO) Agri-Spec NIR Spectrometer. A 20-g subsample from each original (<2mm sieved) soil sample was placed in a quartz vial and placed on a holder with a quartz window for scanning. Soils were illuminated and scanned from below using the spectrometer connected to an ASD muglight with an internal tungsten--quartz--halogen light source and a 12 mm spot size. Data were collected every 1 nm and every spectrum was an average of 25 readings.

Each sample was scanned twice; the second scan was made after rotating the sample in its holder through 90° whilst placed on the muglight. During scanning, a Spectralon reflectance panel was used to optimize and white-reference the spectrometer after scanning every set of ten samples. We checked that both sides of the Spectralon panel gave consistent baselines. Before further statistical analysis, we obtained an average of two spectra for each sample.

2.2.5 Mid infra red diffuse reflectance spectroscopy

A Biorad Excalibur series (GS3000MX) fourier transform infra red spectrometer was used for measuring the diffuse reflectance of each sediment sample. Background spectra were collected using a powdered KBr sample (Pike Technologies, Madison, WI). Each sample was scanned 40 times at a resolution of 4 cm^{-1} in the range 400-4000 cm^{-1} .

3 Statistical models based on infra red spectroscopy

The objective was to assess the predictive power of the two types of reflectance spectra (VNIR and MIR) for estimating each of the six soil properties. The airborne survey can only capture reflectance spectra in the VNIR range but we also assessed the MIR range because field portable instruments could be deployed to capture these spectra if they were shown to be effective.

The approach to forming statistical models between each of the six soil properties and their reflectance spectra was similar for each, but in the case of soil texture the proportions of the three size fractions (clay, silt and sand) were first transformed by taking additive log ratios

(Rawlins *et al.*, 2009) before models were formed to avoid the problems associated with compositional data analysis. All statistical models were created using the *pls* package in the R environment.

4 Results and their interpretation

4.1 TOPSOIL PROPERTIES

Summary statistics for the various soil properties are shown in Table 1 below.

Table 1 – Summary statistics for a range of topsoil properties for the 50 samples collected across the Blackwater drain catchments.

	Min	25%ile	Median	Mean	75%ile	Max	n
SOC (%)	0.49	1.2	1.4	1.7	1.6	13	50
Dithionite extractable Al (mg/kg)	1143	1320	1614	1604	1780	2340	50
Dithionite extractable Fe (mg/kg)	3854	5405	6232	6700	8184	10569	50
Oxalate extractable Al (mg/kg)	910	1250	1435	1470	1675	2293	50
Oxalate extractable Fe (mg/kg)	1229	1982	2321	2326	2617	3900	50
Clay (<2 microns) %	16.6	30.9	38.9	40.5	49.1	66	50
Silt (2-63 microns) %	13.6	27.5	30.2	30.4	34.2	42.9	50
Sand (63-2000 microns) %	0.2	13.9	27.2	27.8	38.3	65.3	50
*Bulk density (g cm ⁻³)	1.13	1.32	1.40	1.42	1.51	1.79	100

*summary of analyses of a pair of samples from each site

4.1.1 Soil organic carbon

The SOC values are relatively low (median 1.4 %) when compared to a median for the East Anglia region in general (2.24 %) based on analyses of 2858 soils from a survey of topsoils between 2002 and 2005 (unpublished data, British Geological Survey). In their paper Loveland and Webb (2003) cite 2 % as a threshold below which many soil scientists believe potentially serious decline in soil quality may have occurred. Based on the analyses from the Wensum catchment, 88% of the soils have SOC values below 2 %, indicating that the vast majority of soils are below this 2% threshold.

4.1.2 Extractable iron and aluminium

The range (maximum to minimum) of the extractable Fe and Al concentrations by oxalate and dithionite were generally small; in most cases the variation was only two or three-fold. There are few published analyses of extractable Al across the region, but median values (5000 mg/kg Fe_d) reported for a range of soil series across Eastern England (Soil Survey, 1984) are similar to those reported in Table 1 for soils across the Blackwater drain catchments.

4.1.3 Particle size distribution

The particle size distribution as percent sand, silt and clay for the fifty topsoil samples are shown in Figure 2 for the two groups of soil parent material, plus the mean compositions of each group. The greatest variations occur in the clay and sand fractions, with very little variation in the

proportion of silt sized material. The samples over the two types of mapped soil parent material cover much the same space on the ternary diagram (Figure 2) and the mean composition for the two groups are quite similar. This suggests that based on topsoil texture analyses the maps of soil parent material are not effective in separating the sand and gravel dominated deposits from the more clay-rich glacial tills. This may simply reflect either the local complexity of the deposits where short range variations in particle fractions cannot be accounted for, or possibly that topsoil deposits include a component of aeolian derived sand-sized material which is not included on maps of parent material.

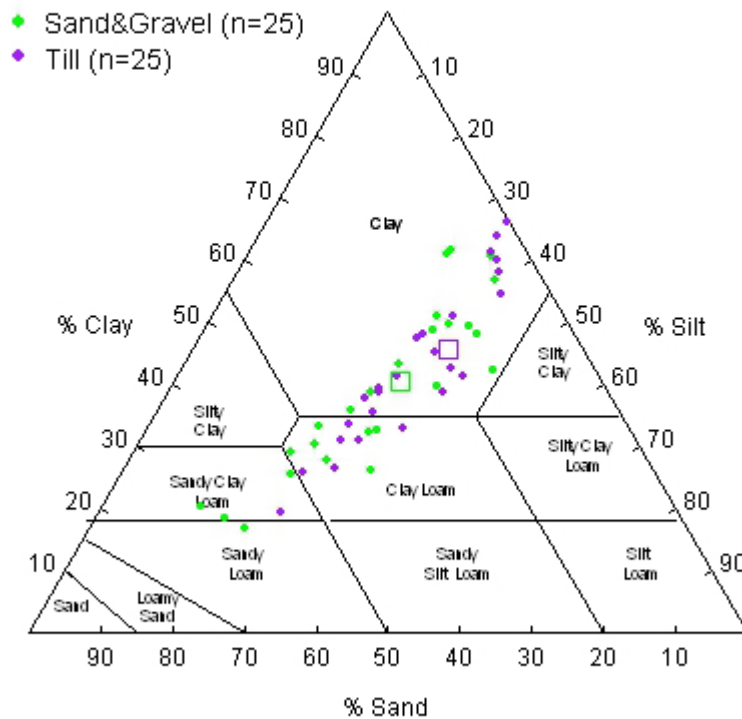


Figure 2 – Particle size distribution of topsoil samples grouped by parent materials. Mean composition of each group shown as square symbol.

4.1.4 Bulk density

Although soil bulk density varies seasonally, snapshot measurements provide an indication of the status of soil structure. There is a broad range of BD values for topsoil across the catchments (min=1.13; max=1.79) which are within the typical range of values observed for topsoils in England and Wales (Hall *et al.*, 1977). There is a positive linear correlation between the paired samples (Pearson correlation: $r=0.6$); the differences shown in the scatterplot highlight the variations in bulk density at short (< 1m) spatial scales.

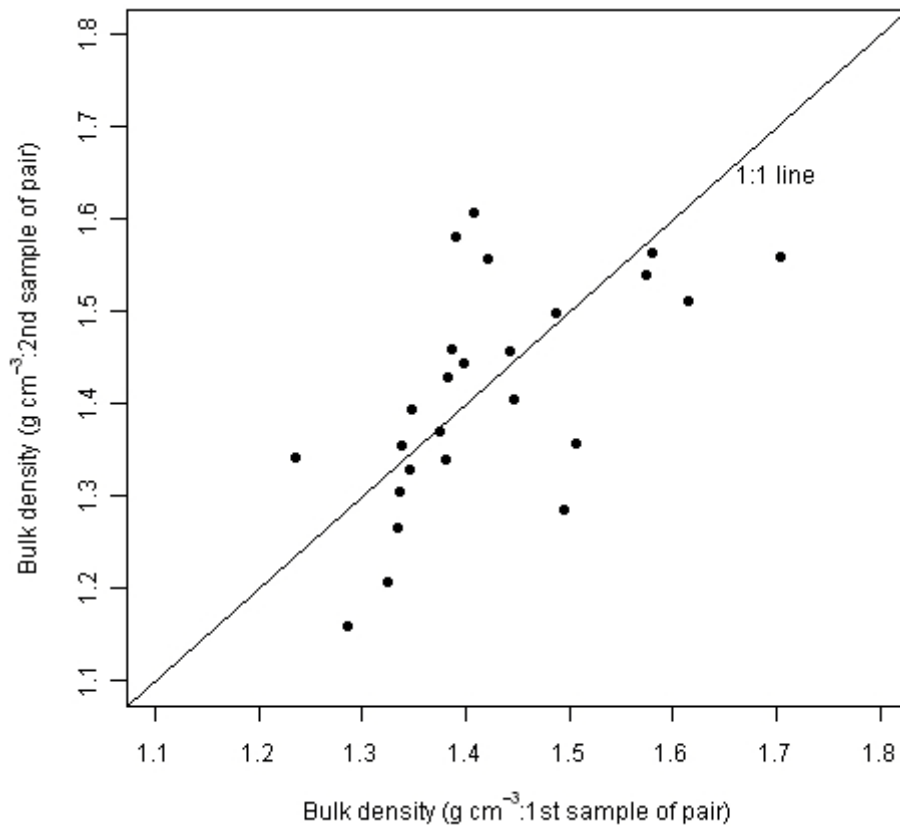


Figure 3 - Paired bulk density values of topsoil samples at 50 sites across the Blackwater drain catchments

4.2 SPATIAL VARIATION IN SOIL PROPERTIES

The spatial variation (auto-correlation) of the various soil properties were investigated using REML based estimation of variograms. Although using data from only 52 sites is sub-optimal for confidently identifying whether soil properties exhibit spatial autocorrelation, they can provide some indication of the likely scales below which spatial structure may be observed.

Models estimated using REML for a range of soil properties did not demonstrate evidence for autocorrelation even at short scales; the models were almost entirely nugget variance. However, in the case of bulk density there was some evidence for autocorrelation at scales less than 500 metres (Figure 4). In this figure the semivariance estimates at shorter lag intervals are generally smaller than those at larger scales and the exponential model based on REML also suggests this. In contrast to some of the other soil properties, continuous maps of bulk density across the catchments based on interpolation are likely to be more warranted on the scale of sampling undertaken in this pilot study.

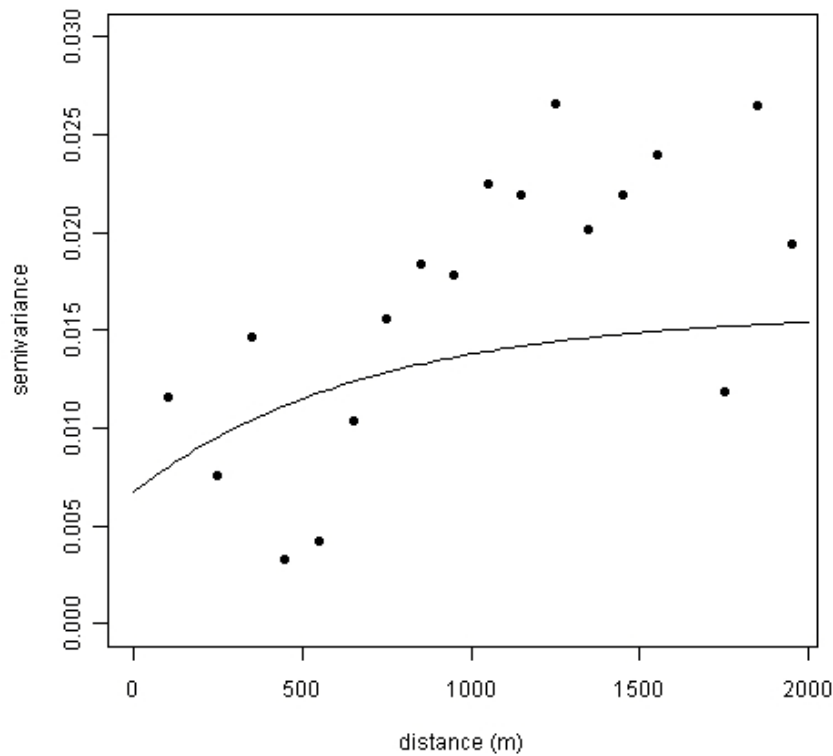


Figure 4 – Semivariance estimates for mean bulk density calculated from pairs of samples from 50 sites (discs) across the Blackwater drain catchments and an exponential variograms model based on REML estimation (line).

4.3 PERFORMANCE OF STATISTICAL MODELS BETWEEN INFRA RED SPECTRA AND TOPSOIL PROPERTIES

The images below show individual spectra in the mid (2.5-25 μm) and near (0.35-2.5 μm) infra red ranges for each of the 50 samples across the catchments.

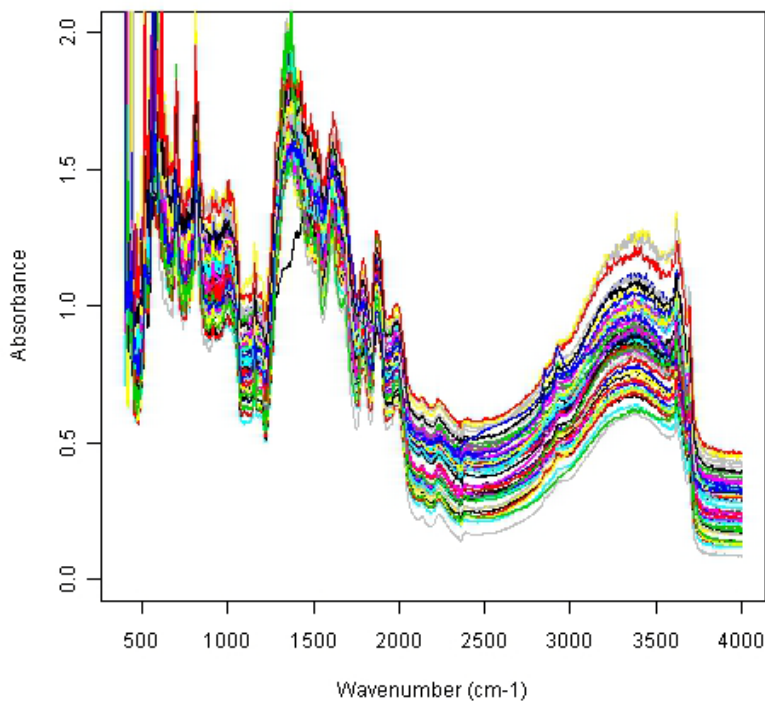


Figure 5 – Mid infra red spectra for topsoil samples from the Blackwater drain catchment (n=50) – untransformed data

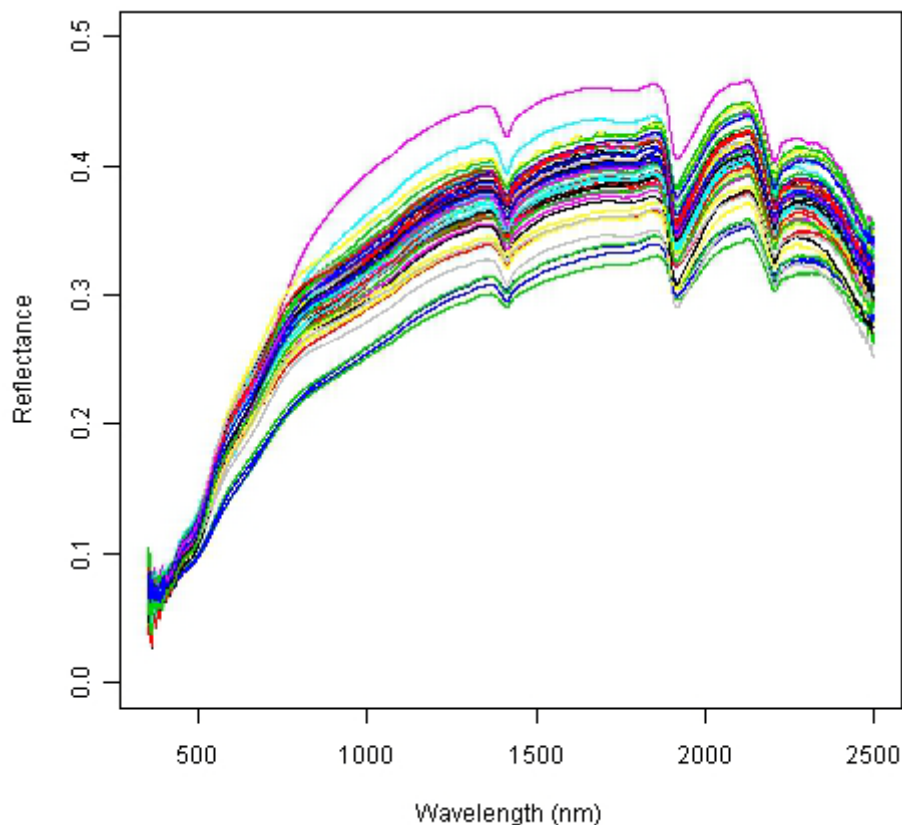


Figure 6 – Near infra red spectra for topsoil samples from the Blackwater drain catchment (n=50) – untransformed data

Previous research has shown that diffuse reflectance near infra red spectroscopy can be used to estimate soil particle size fractions using statistical models between the spectra and size fractions at regional scales (Rawlins et al., 2011). Both near and mid infra spectroscopy have been shown to be effective for estimating a variety of soil properties (Viscarra Rossel *et al.*, 2006). Statistical models were developed between both types of spectra and each of the soil properties. The performance of these models is summarised below (Table 2) showing the proportion of variance the optimum model accounted for (adjusted R^2) and the number of model components used in each model.

The only property which could be estimated adequately based on a statistical model was dithionite extractable Fe (Fe_d) from mid infra red spectra of which 78% of the variance was accounted for. A scatter plot showing both measured and predicted values based on the optimum statistical model is shown in Figure 7. The generally poor performance of the statistical models can be attributed to a number of reasons. First, the range of variation in most of the soil properties measured is limited; for example the inter quartile range of SOC is only between 1.2 and 1.6% and spectroscopic-based data will struggle to differentiate between such small differences. In the case of soil texture, there is little variation in silt content which suggests that much of the variation is related to differences in the clay and sand fractions. The latter is dominated by quartz which is poorly detected by MIR and has no features in NIR spectra. If variations in quartz content is the dominant control on soil particle size distribution then spectroscopic approaches will not be effective in estimating the three size fractions. In the case of the oxalate extractable components, the limited range of variation observed for the soils makes the performance of spectroscopic approaches very poor. On the basis of this pilot study there is little point in undertaking an airborne spectroscopic survey.

Table 2 – Summary of statistical model performance for estimating various soil properties using near and mid infra red diffuse reflectance spectroscopy

Soil property	NIR spectra		MIR spectra	
	R^2	* n components	R^2	* n components
alr clay:silt	<0.01	NA	<0.01	NA
alr silt:sand	<0.01	NA	<0.01	NA
SOC	<0.01	NA	<0.01	NA
Fe _d	0.19	3	0.78	3
Fe _o	0.01	2	0.19	4
Al _d	0.03	7	0.29	3
Al _o	0.03	7	0.27	3

*number of PLSR components in optimal model

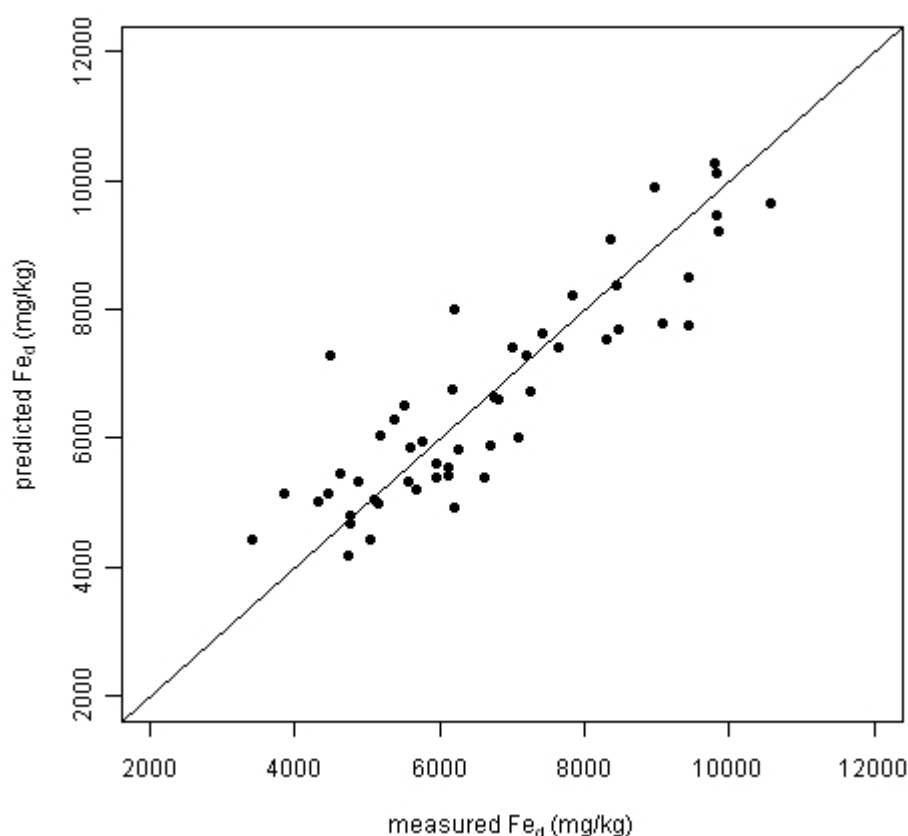


Figure 7 – Cross-validation plot showing predictions of dithionite extractable iron (Fe_d) concentrations in the soil using a statistical model based on mid infra red spectra. The partial least square regression model accounts for 78% of the variance in (Fe_d)

4.4 ESTIMATE OF SOIL ORGANIC CARBON STOCK (CULTIVATED LAND)

To estimate the total soil organic carbon stock for the upper 30 cm of the soil across the four Blackwater mini catchments (see Figure 1), the data on soil bulk density and SOC concentration

for 50 soil sampling locations were used. Although soil sampling extended from 0 to 15 cm depth, regular cultivation mixes soil to around 30cm depth and so it is reasonable to assume SOC concentrations are reasonably constant to 30cm. The areal proportions of the two dominant parent material types and the total catchment area (16.1 km²) were used in the calculations. To provide an unbiased estimate of SOC stock, it was necessary to account for the different sampling selection probabilities (de Gruijter *et al.*, 2006) due to the differences in areas of the two parent material types. In addition, the carbon densities (carbon concentration multiplied by bulk density) for each soil sampling location were calculated before estimation of the weighted mean to take account of any correlation between the SOC concentration and soil bulk density in the data. Only soil from cultivated land was sampled, so the stock estimate cannot account for other land use types in the catchments; the stock estimate therefore assumes all soil in the catchments is cultivated. Using the available data the total carbon stock for the top 30cm of soil across the four Blackwater drain sub-catchments is 0.119 MtC (Megatonnes carbon) or 119000 tC (tonnes of C). If reduced soil structural stability due to diminishing OC concentrations in part account for higher sediment loads in streams draining the Blackwater catchments, then estimating the total quantities of organic carbon lost in suspended sediment may help to understand the organic carbon budget of the catchments. It may be beneficial in future work to focus on suspended sediment OC fluxes from the catchments.

5 Conclusions

- Soil organic carbon (SOC) concentrations in cultivated fields of the Blackwater drain catchments are generally small (median=1.4%). Previous research suggests that these soils are below the threshold at which scientists consider the soil structural stability may be impaired and may lead to mobilisation of sediment to watercourses. Effective measures to mitigate sediment losses to watercourse in the Blackwater drain catchments may involve those which can halt the decline in SOC concentrations (e.g. changing tillage practices) or even to raise SOC in topsoil through careful application of organic matter.
- In general, statistical models based on both near and mid infra red spectroscopy were not effective in predicting soil properties across the Blackwater drain catchments. However, dithionite extractable iron was well estimated by mid infra red spectroscopy. The most likely reasons for failure of the spectroscopic techniques are that there is general little variation in the properties across the catchments, and in the case of soil particle size, this is determined here largely by quartz content which is poorly detected by IR spectroscopy. These results suggest that an airborne spectral survey of the Blackwater drain catchments is unlikely to provide data which could be used to map soil properties at fine spatial scales.
- The total carbon stock for the upper 30cm of soil across the four Blackwater drain sub-catchments - an area of 16.1 km² - is 0.119 MtC (Megatonnes carbon) or 119000 tC (tonnes carbon). This estimate is based on sampling and analysis of topsoil only from cultivated land. Incorporation of data for other land use types - which are likely to have different topsoil carbon concentrations - would improve this estimate. The benchmark data on soil organic carbon concentrations, bulk density and stock from 50 sites could aid the assessment of on-farm measures aimed at stabilising or increasing soil organic carbon concentrations in soils across the Blackwater drain catchments. The positions of each sampling location were recorded with low (<10cm) positional error differential kinematic GPS. It is therefore possible to resample these sites with a low positional error would could be beneficial for soil monitoring purposes.

6 References

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