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Quantification of soil carbon from bulk soil samples to predict the aggregate-carbon fractions within using near- and mid-infrared spectroscopic techniques

M.P.N.K. Henaka Arachchi, D.J. Field *, A.B. McBratney

Department of Environmental Sciences, Faculty of Agriculture and Environment, The University of Sydney, NSW 2006, Australia

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ABSTRACT

There is a persistent general concern with carbon sequestration and modeling of soil carbon change affecting global issues, such as climate change and food security. To address these concerns requires the measurement of carbon everywhere and routinely, but the rate limiting step is the need to physically fraction the soil carbon to establish; where it is stored in soil, to model the formation of soil aggregates that physically protect soil carbon, and in-turn to populate soil carbon models. To remove the need for this fractionation pretreatment, commonly done by wet-sieving, this study scopes the notion of the efficacy of using near- (NIR) and mid- (MIR) infrared derived spectra taken of bulk soil samples to predict carbon in the separated aggregate fractions contained within. Forty five surface soil samples were collected from three bioregions of New South Wales providing for a range of soil types and associated soil carbon. The carbon content was measured of the bulk soil samples and their aggregate fractions of <63 μm, 63–250 μm, and >250 μm subsequently separated by wet-sieving. The bulk soil samples were scanned in the spectral ranges 800–2500 nm (NIR region) and 2500–25,000 nm (MIR region). The Cubist regression tree model was used to predict the carbon content in the aggregate fractions scanned from the bulk soil samples. The cross-validation results reveal that the MIR demonstrated the strongest correlation between measured and predicted carbon of the aggregate fractions demonstrated by high R^2 (0.63–0.85) and ration of performance to inter-quintile distance (RPIQ, 0.53–0.93). The wavelengths selected in the Cubist model coincide with wavelengths identified as characterizing adsorption due to chemistry of soil carbon in some recently published works in this area of research.

1. Introduction

Soil carbon has been a major focus globally in the last 5 to 10 years and this is partly driven by its sequestering potential in soil having a significant and achievable impact on mitigating rises in atmospheric carbon (Bellon-Maurel and McBratney, 2011; Knox et al., 2015). This is because SOC is the largest terrestrial store of carbon making it the second largest to the ocean (Lal, 2009; Stockmann et al., 2013). The singling out of soil carbon as one of the seven unique functions of soil is in the further evidence of wide ranging interest of soil carbon (CEC, 2006; Bouma and Droogers, 2007; McBratney et al., 2014). Also, there remains an on-going need to integrate knowledge of SOC and SOC models into existing models, such as those focusing on hydrology and predicting ecosystem change (Karim Malamoud et al., 2009; Bouma and McBratney, 2013). Finally, the fact that carbon responds quickly to changes in the soil makes it a amenable indictor of soil change, and the fact that the carbon is already recognized by the broader community means it could be easily understood by policy makers and the general public (Schmidt et al., 2011; Koch et al., 2014), makes it a amenable indictor of soil change.

In response to these recent observations there is an urgent need to be able to routinely, efficiently, and cheaply measure carbon everywhere (Grunwald, 2009) so as to effectively monitor its change. This not only includes the assessment of total soil carbon but a rapid assessment of soil fractions that are routinely used in soil carbon models. Equally important is the need to quantify where the carbon is stored within soil aggregate fractions providing for their integrity and in-turn it being physically protecting from immediate degradation. Although there has been progress in expediting the quantification of SOC of bulk soil using spectroscopic techniques, such as near- (NIR) and mid-infrared (MIR) spectroscopy, (Janik et al., 2007; Reeves, 2010; Stenberg et al., 2010; Bellon-Maurel and McBratney, 2011) the rate limiting step of having to physically fraction the soil carbon (Reeves et al., 2006; Zimmermann et al., 2007) to address where it is stored and to populate current carbons models, such as Struc-C and CAST, remains (Karim Malamoud et al., 2009; Stamati et al., 2013).

The natural variation of soil types and the impact of land-use result in variation of soil carbon both spatially and temporarily (Knox et al., 2015). This is because the distribution of carbon is partly determined

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* Corresponding author at: Department of Environmental Sciences, Faculty of Agriculture and Environment, Suite 103, Biomedical Building, C81, Australian Technology Park, NSW 2006, Australia.
E-mail address: damien.field@sydney.edu.au (D.J. Field).

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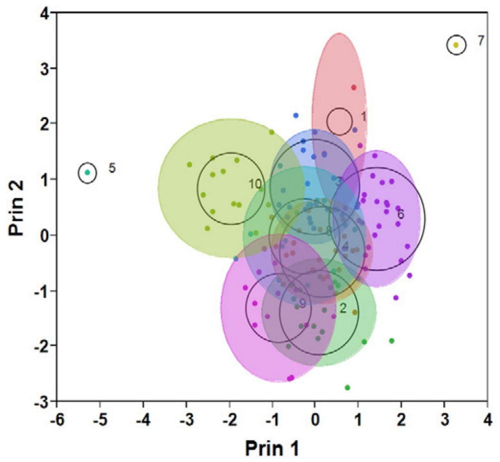

Cluster	Count	No. Of samples selected
1	2	0
2	19	8
3	24	10
4	22	14
5	1	0
6	28	4
7	1	0
8	15	5
9	13	5
10	14	4
Total	150	50

Fig. 1. Sample selection for aggregates fractionation and spectroscopy measurements.

by the potential sources and nature of soil carbon provided by the associated above ground biomass and microbial residues (Gregorich et al., 2006; Clemente et al., 2011). Within soil SOC is distributed throughout soil aggregate fractions and is implicated in their formation and stabilization. The smallest of these aggregates are composed of organo-mineral associations, which are in-turn bound with bacterial and fungal debris to form microaggregates, and the clustering of these into macroaggregates (Emerson, 1959; Edwards and Bremner, 1967; Tisdall and Oades, 1982; Six et al., 2000). Over time the degradation of organic carbon binding agents in macroaggregates results in the release of the more stable microaggregates, and these microaggregates have the potential to form the building blocks for the next cycle of macroaggregate formation (Six et al., 2000). Up to 90% of SOC in surface soils is found to be located within aggregates (Six et al., 2002) and 20–40% of the SOC is intra-microaggregates (Jastrow et al., 1996; Carter, 1996). To obtain these fractions requires separation using pre-treatments of wet sieving and density separation which is expensive, time consuming, and therefore preclude this from being part of most routine soil analysis procedures (Ashman et al., 2003; McBratney et al., 2006; Viscarra Rossel and Hicks, 2015).

It has been shown that spectroscopic methods can be used to measure soil carbon rapidly, inexpensively, and nondestructively (Janik et al., 1998; Viscarra Rossel et al., 2006). A number of databases now exist where the SOC has been determined by mid-infrared spectroscopy (Reeves et al., 2006; Zimmermann et al., 2007; Bornemann et al., 2008; Yang et al., 2012) and recently Viscarra Rossel and Hicks (2015) reported on the use of vis-NIR to predict carbon fractions used to populate soil carbon models associated with the measured SOC. A few studies have also reported on the prediction of soil structural properties, such as soil aggregation, using NIR and MIR spectra (Chang et al., 2001; Madari et al., 2005; Minasny and McBratney, 2008; Sarkhot et al., 2011), but the aggregate associated carbon still has not been predicted without fractionation. This research will investigate the potential to predict soil carbon fractions from bulk soil scanned using NIR and MIR spectroscopy.

Table 1
Basic soil properties of the surface horizon of the soil orders sampled.

Soil order	Number of samples	pH	Clay (%)	Silt (%)	Sand (%)	TOC (g/kg)
Chromosol	4	6.70	26	11	63	11.20
Kandosol	12	7.08	13	12	75	10.60
Kurosol	2	5.54	10	13	77	6.05
Rudosol	2	6.35	7	24	24	6.72
Sodosol	21	7.21	17	13	70	8.62
Vertosol	9	7.09	31	12	56	8.90

2. Material and methods

2.1. Soil sampling

Soil samples were obtained from a soil survey conducted in 2010 (Singh et al., 2012) which focused on developing a soil spectral library for the prediction of soil carbon, primarily to be used to populate soil carbon turnover models. It is known that variation in soil carbon is strongly influenced by soil type and its associated variation with climate and land use (Lou et al., 2010) so to maximize the variation in SOC in the 2010 soil survey of three major bio-regions of New South Wales (NSW), Australia, namely the South Eastern highlands, NSW South Western Slopes and South Brigalow Belt covering an area of 158,000 km^2 (Fig. 2) were sampled. The mean annual rainfall of the area sampled varies from 412 to 987 mm and the land-use types range from cropping, grazing of modified pasture, and natural vegetation. The sample sites were identified using Conditioned Latin Hypercube sampling (Minasny and McBratney, 2006) which enabled effective sampling of the regional soil variation with a minimal number of sampling sites. This resulted in 150 samples collected to a depth of 30 cm and the covariates and sample locations are reported in Singh et al. (2012).

Due to the large number of samples that is generated when separating aggregates to study the size distribution and associated SOC the sample selection for this study was reduced from 150 to 50 samples. To maximize the changes in SOC and the variation in soil aggregation these parameters were used to cluster the 150 soil samples collected in the 2010 survey into 10 clusters from which the 50 samples were randomly selected (Fig. 1), using the influential properties of total organic carbon (TOC%) the quantity of clay, silt and changes in the cation exchange capacity (CEC) (Amézketa, 1999; Six et al., 2002; Bronick and

Table 2
The total organic carbon (TOC), pH, particle size distribution, mass recovery, and carbon recoveries of bulk soil.

Character	Mean	St. dev.	Max.	Min.	Skewness
pH	7.06	0.91	8.66	5.09	−0.31
Clay (%)	19	9.94	43	4	0.50
Silt (%)	12	4.55	24	3	0.98
Sand (%)	68	9.33	89	38	−0.40
Bulk carbon (g/kg)	10.21	6.51	29.80	2.53	1.72
Macroaggregate-C (g/kg)	3.09	2.22	10.90	0.80	2.35
Microaggregate-C (g/kg)	2.456	1.45	7.10		1.23
Organo-mineral-C (g/kg)	4.08	2.27	10.50	1.10	1.10
Mass recovery (%)	96.63	3.27	102.67	90.08	
Carbon recovery (%)	98.25	19.22	128.20	74.84	