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Research article

Rapid prediction of particulate, humus and resistant fractions of soil organic carbon in reforested lands using infrared spectroscopy

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ABSTRACT

Reforestation of agricultural lands with mixed-species environmental plantings can effectively sequester C. While accurate and efficient methods for predicting soil organic C content and composition have recently been developed for soils under agricultural land uses, such methods under forested land uses are currently lacking. This study aimed to develop a method using infrared spectroscopy for accurately predicting total organic C (TOC) and its fractions (particulate, POC; humus, HOC; and resistant, ROC organic C) in soils under environmental plantings. Soils were collected from 117 paired agricultural-reforestation sites across Australia. TOC fractions were determined in a subset of 38 reforested soils using physical fractionation by automated wet-sieving and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Mid- and near-infrared spectra (MNIRS, 6000–450 cm^{-1}) were acquired from finely-ground soils from environmental plantings and agricultural land. Satisfactory prediction models based on MNIRS and partial least squares regression (PLSR) were developed for TOC and its fractions. Leave-one-out cross-validations of MNIRS-PLSR models indicated accurate predictions ($R^2 > 0.90$, negligible bias, ratio of performance to deviation > 3) and fraction-specific functional group contributions to beta coefficients in the models. TOC and its fractions were predicted using the cross-validated models and soil spectra for 3109 reforested and agricultural soils. The reliability of predictions determined using *k*-nearest neighbour score distance indicated that >80% of predictions were within the satisfactory inlier limit. The study demonstrated the utility of infrared spectroscopy (MNIRS-PLSR) to rapidly and economically determine TOC and its fractions and thereby accurately describe the effects of land use change such as reforestation on agricultural soils.

1. Introduction

The soil organic carbon (SOC) pool is one of the largest terrestrial stores of carbon (C), containing about 1500 Gt C (Schlesinger,

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1986). Consequently, even small changes in the amounts of soil C in response to land use, management or climate may have large effects on global C cycling and climate change. Reforestation is implemented around the world to sequester C and improve environmental conditions (e.g., water quality and habitat availability, Cunningham et al., 2015b). The total area of world's planted forest in 2010 was estimated to be 264 million ha, making up 6.6% of the world's forest area (FAO, 2010). In Australia, mixed-species environmental plantings are established on previous agricultural land for C sequestration and other environmental outcomes accounting up to 20% of the 1.14 million ha of reforestation between 1990 and 2012 (Paul et al., 2013). Studies have focused on improving measurement and modelling of biomass C following reforestation with environmental plantings (Paul et al., 2015; Perring et al., 2015), and measured associated changes in SOC (Cunningham et al., 2015a).

Conventional measurement of SOC as total organic C (TOC) using chemical oxidation (Walkley and Black, 1934) or dry combustion (Merry and Spouncer, 1988) is inadequate to explain changes in SOC in terms of soil physical, chemical and biological activity. Partitioning TOC into fractions that are related to active, intermediate or slow and passive or inert conceptual pools used in soil C turnover models (e.g., RothC, Jenkinson et al., 1992; CENTURY, Parton et al., 1987), can help elucidate their role in soil processes (Skjemstad et al., 2004). Such fractions may represent labile, humified and inert C with turnover times respectively of the order of annual (<3 year), decadal (20–50 year) and millennial (>1000 year, Jenkinson and Coleman, 1994). Several functional pools are known which are accessible by different fractionation methods. Physical fractions are such as aggregates, particle sizes and density fractions, chemical fractions are usually extracts (DOM, soil microbial biomass, organic matter soluble in alkali and acid, etc.) and also combinations of fractionation methods are used (von Lützow et al., 2007).

Skjemstad et al. (2004) demonstrated that the RothC model could be initialised and changes in soil C stock simulated by replacing the conceptual stocks of resistant plant material (RPM), humus (HUM) and inert organic matter (IOM), respectively, with operationally measured particulate (POC), humus (HOC) and resistant (ROC) organic C. Subsequently, Janik et al. (2007) showed that the concentrations of POC, HOC and ROC in <2 mm sieved soil could be predicted from mid-infrared (MIR) spectra acquired from finely ground samples.

Diffuse reflectance mid-infrared spectroscopy (MIRS) is a rapid, non-destructive and low-cost technique, demonstrated to be suitable for routine analysis of a variety of soil properties (Soriano-Disla et al., 2014). The MIRS technique requires minimal sample preparation (i.e. air drying and fine grinding) and no use of hazardous chemicals. MIR spectra and corresponding analytical data in multivariate analyses such as partial least squares regression (PLSR) can be combined to develop prediction models for soil attributes. The predictive ability of MIRS-PLSR techniques for total, organic and inorganic C of soils has been well investigated and reported (Grinand et al., 2012; Madari et al., 2006; Madhavan et al., 2016). However, the use of MIRS-PLSR to predict the concentrations of fractions of TOC is limited (Bornemann et al., 2010; Janik et al., 2007; Zimmermann et al., 2007). MIRS-PLSR prediction models have been developed for total, organic and inorganic C, and TOC fractions (Baldock et al., 2013a), and these models were applied to predict the content of TOC fractions in subsequent agricultural soil C studies (Karunaratne et al., 2014; Rabbi et al., 2014). However, the applicability of such predictive models to soils under woody vegetation has not been investigated. Further, there is increasing interest in reforestation of agricultural lands to mitigate greenhouse gas emissions through sequestering C in woody biomass (Canadell and Raupach, 2008) and in soil (Lal, 2005). Thus, there is a need to develop accurate and efficient measurement techniques and prediction models applicable to reforested land to understand and predict their potential to sequester C and mitigate greenhouse gas emissions.

An extensive study was conducted to investigate the changes in TOC and its fractions following reforestation with mixed-species environmental plantings at 117 sites from temperate, Mediterranean-type and tropical climatic regions of Australia, for the purpose of calibrating a soil C accounting model (FullCAM, Brack and Richards, 2002) developed from the RothC model (Paul et al., 2015), and to provide measurements and predictions of TOC fractions. Prediction models for TOC fractions have been reported in agricultural soils by Baldock et al., 2013a, but these models are unlikely to be accurate for reforested soils because of the difference in plant inputs, chemistry and decomposition rates between land uses, and thereby changes in TOC fractions (Del Galdo et al., 2003; Berthrong et al., 2012; Cunningham et al., 2015a). This warrants a need to develop infrared spectroscopic prediction models for TOC fractions that are suitable for soils under reforestation. This work presents the first attempt to develop prediction models for TOC fractions in a treed ecosystem whereas previous work has focused on agricultural soils (Baldock et al., 2013a). Our objectives were to measure soil TOC fractions (POC, HOC and ROC) in a representative set of reforested soils; develop robust infrared and PLSR prediction models for TOC and its fractions for reforested soils; and predict TOC and its fractions for both environmental planting and reference agricultural soils (i.e. pastures and cropping).

2. Methods

2.1. Soils

Soils were collected from 117 sites, each comprising a mixed-species environmental planting paired with an adjacent agricultural land use (Fig. 1). Details of site characteristics and sampling methods are detailed in England et al., 2016 and summarised here. The sites were across southern and eastern Australia (latitude 30.9

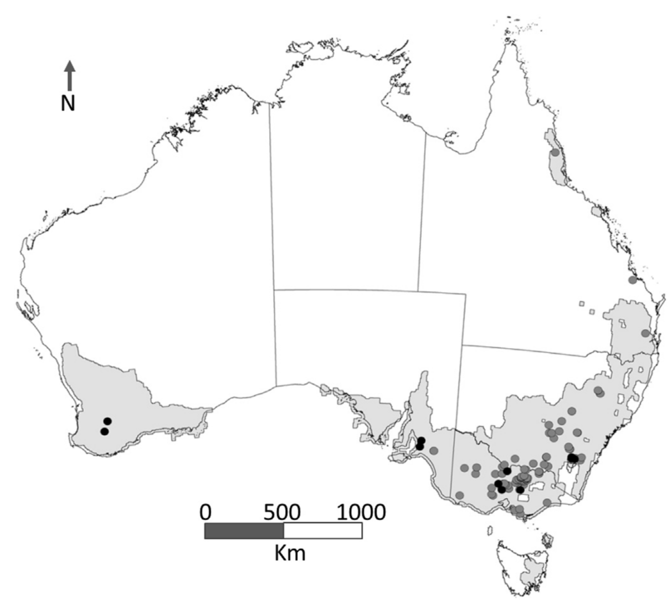

Fig. 1. Distribution of environmental planting sites and adjacent agricultural references sites ($n = 117$, all circles). Soils from a subset of these plantings ($n = 19$, black circles) were physically fractionated. The shaded area represent the geographical regions of application of calibration for the environmental planting study area (after Paul et al., 2015).