



Mapping soil organic carbon content using spectroscopic and environmental data: A case study in acidic soils from NW Spain



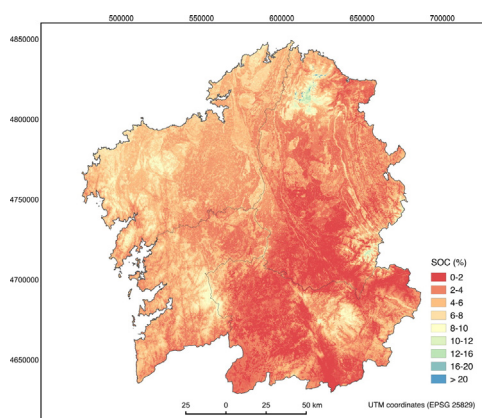
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HIGHLIGHTS

- We used FTIR–ATR data to model the distribution of SOC in topsoils from NW Spain.
- SOC predictions using FTIR–ATR are similar to those obtained by wet chemistry data.
- Climate is the main parameter influencing the accumulation of SOC in the study area.
- This method is suitable to quickly map SOC in acidic soils under similar conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 April 2015

Received in revised form 15 July 2015

Accepted 16 August 2015

Available online xxxx

Editor: Simon Pollard

Keywords:

Spatial statistics

FTIR–ATR

Random Forest

Partial Least Squares Regression

ABSTRACT

In this study we present a methodology to estimate and map the content of soil organic carbon (SOC) in topsoils using spectroscopic (FTIR–ATR) and environmental raster data. We determined the SOC content in 221 topsoil samples in Galicia (NW Spain) using the Walkley–Black method. FTIR–ATR spectroscopic data was measured upon the same set of samples. The Random Forest (RF) technique was used to link the measured SOC concentrations to the FTIR–ATR measurements in order to identify the relevant absorbance bands explaining most of the variability in SOC. We then used linear regression (MLR) to predict SOC concentrations from the selected FTIR–ATR bands as independent proxy. This model showed a good predictive performance (r -squared = 0.88; RSME = 2.14; ME = 0.05; RPD = 3.14), indicating that SOC can be effectively estimated from the identified spectral bands. Finally, we used Partial Least Squares (PLS) to model the spatial distribution of the predictor bands using a number of environmental raster maps (climate, land use and geology) as covariates. This new raster was used within the MLR model previously created to generalize the predictions of SOC in the whole study area. This approach shows that FTIR data can be used to map SOC while minimizing analytical costs and time efforts.

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1. Introduction

Soil organic carbon (SOC) stock constitutes the largest pool of terrestrial organic carbon, acting as an important long-term sink for carbon released to the atmosphere by human activities (Bellon-Maurel and McBratney, 2011; Grinand et al., 2012; Lal, 2004; Madari et al., 2006; Pedersen et al., 2011). The evaluation of SOC stocks is important for a proper evaluation of the effect of the emission of greenhouse gases to the atmosphere under different climate-change scenarios (Abd-Elmabod et al., 2014; Lal, 2004; Page et al., 2013).

Climate, land use and the nature of the soil mineral fraction are environmental variables closely related to the amount of SOC stored in soils. At a global scale, climate has a clear effect on the amount of organic carbon stored in soils, being low temperatures and high precipitation the most favourable conditions for enhanced accumulation (Barford et al., 2001; Batjes, 1996; Melillo et al., 2002; Trumbore et al., 1996). Anthropogenic practices such as deforestation, drainage and forest fires are converting large areas into globally significant sources of carbon dioxide to the atmosphere (Lal, 2004; Monastersky, 2014; Moore et al., 2013). Soil mineralogy also has an effect on both the quantity and turnover of SOC in soils. Torn et al. (1997) showed a positive relationship between the presence of non-crystalline minerals and the SOC content, and it has been observed that amorphous phases of iron and aluminium oxy-hydroxides in soils derived from metamorphic and igneous basic rocks can form stable organo-mineral complexes with organic compounds, which promotes the accumulation of SOC (Álvarez et al., 1992; Carballas et al., 1979; García-Rodeja et al., 1987; Verde et al., 2004). Additionally, stable micro-aggregates, which protect organic compounds against microbial degradation, have been observed in soils with high clay contents (Jobbágy and Jackson, 2000; Lal, 2004; Torn et al., 1997).

Over the past few decades, Digital Soil Mapping has been used to predict and describe the spatial distribution of soil properties (Behrens et al., 2005; McBratney et al., 2003; Scull et al., 2003; Vaysse and Lagacherie, 2015). Digital Soil Mapping makes use of statistical algorithms to relate soil parameters, measured on field samples, to environmental auxiliary data and make predictions on a spatial basis. The approaches most commonly used to estimate SOC include multiple linear regression, ordinary kriging, co-kriging, regression-kriging and geographically weighted regression (Chaplot et al., 2001; Chen et al., 2000; Dobos et al., 2006; Grimm et al., 2008; Kumar and Lal, 2011; Kumar et al., 2012; Martin et al., 2014; Mishra et al., 2009; Phachomphon et al., 2010; Simbahan et al., 2006). Recent studies obtained good SOC predictions using Random Forest and Partial Least Squares Regression algorithms (Grimm et al., 2008; Rodríguez-Lado and Martínez-Cortizas, 2015; Were et al., 2015).

The development of methods for mapping SOC contents along extensive areas while minimizing sampling and laboratory analyses is still a challenge. Wet chemistry techniques to measure SOC concentrations, such as the Walkley–Black method, are time consuming and relatively expensive. During the last years, infrared spectroscopy has been proposed as a robust, rapid and effective alternative technique to

evaluate soil compounds and properties such as organic carbon, total carbon, total nitrogen, potassium, phosphorus, organic matter and clay contents, CEC, pH or water potential by using statistical models (Ge et al., 2014; Linker, 2011; Soriano-Disla et al., 2014; Viscarra Rossel et al., 2006). Models using spectroscopic measurements to evaluate SOC concentrations mostly involve data either in the mid-infrared (MIR, Table 1) or near-infrared (NIR) regions, or a combination of data in the near-infrared and visible (VisNIR) regions (Nocita et al., 2014; Shi et al., 2015; Stenberg et al., 2010). Accurate models should present small standard errors, high R-squared values and high ratios of standard deviation (RPD) (Bellon-Maurel et al. 2012).

MIR (4000 to 400 cm^{-1}) is a prominent region that clearly discriminates molecular functional groups, easily identifiable through spectral libraries (Reeves, 2010). Since bands in MIR can be affected by distortion or total absorption phenomena, the dilution of the samples before the measurement is often required (Linker, 2011; McCarty et al., 2002). MIR spectroscopy coupled to Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR) is a powerful technique for quantitative and qualitative analyses which avoids the dilution of the samples required by MIR analysis and thus decreases the time required for each measurement (Ge et al., 2014). FTIR-ATR has been widely used to quantify different soil properties and processes such as nitrate concentrations and the kinetics of its transformation (Borenstein et al., 2006; Janh et al., 2006; Kira et al., 2014; Linker et al., 2004, 2005, 2006; Shaviv et al., 2003), the speciation and amount of organic and inorganic carbon and the sand and clay contents (Ge et al., 2014; Solomon et al., 2005), the adsorption mechanisms of phosphate and arsenate (Arai and Sparks, 2001; Sun and Doner, 1996), and it has been even used to perform agro-environmental classifications of soils (Aranda et al., 2014; Du et al., 2008).

Multivariate statistics constitute a highly suitable mean to analyse complex data such as data from spectroscopy (Linker, 2011). Algorithms such as Multiple Linear Regression (MLR), Principal Component Regression (PCR), Partial Least Squares regression (PLS), Artificial Neural Networks (ANN), Multivariate Adaptive Regression Splines (MARS) or Random Forest (RF) make use of spectroscopic data to predict specific soil properties (Bellon-Maurel and McBratney, 2011; Knox et al., 2015; Stenberg et al., 2010). MLR, PLS and PCR are mostly used for this purpose, while ANN, MARS and RF constitute more elaborated algorithms mainly used when the former methods fail to ascertain relationships between soil properties and the spectroscopic signal (Næs and Mevik, 2001; Viscarra Rossel et al., 2006). The identification of specific spectroscopic bands, within the whole spectroscopic signal, explaining a high proportion of variability of the soil property under investigation, is of special interest since it can provide information on the dominant constituents or processes influencing such property. Recent studies showed that non-linear methods, such as regression trees, can be used to identify specific spectroscopic bands that improve the performance of the obtained models. Knox et al. (2015) modelled soil carbon fractions using Random Forest and concluded that the most influential bands to explain SOC were those allocated around 2200 and 1700 cm^{-1} . Peaks around 2000 cm^{-1} have been identified as Si–O vibration from quartz. These peaks are usually intense in mineral soils with poor organic matter content (Du and Zhou, 2009; Reeves and Smith, 2009; Soriano-Disla et al., 2014). Peaks around 1700 cm^{-1} were attributed to stretching of C=O bonds from aldehydes, ketones and carboxylic acids associated to hydrophobic and hydrophilic compounds of soil organic matter (Ellerbrock and Kaiser, 2005; Pedersen et al., 2011; Simkovic et al., 2008; Viscarra Rossel and Behrens, 2010; Vohland et al., 2014).

Despite the good model performance obtained in these studies, the results can only be used to quantify the amount of SOC from spectroscopic data at sample scale. However studies showing how to translate the statistical relationships between SOC and spectroscopic data to a predictive model depicting SOC variability in space are lacking. In this study we present an approach to map SOC content in soil epipedons

Table 1

Summary of the goodness of fit of models developed to predict SOC from MIR data in bibliography.

Location	Samples	R ² _{validation}	RPD	Reference
Texas, USA	270	0.77	2.1	Ge et al. (2014)
France	2084	0.90	3.0	Grinand et al. (2012)
Australia	298	0.92	–	Janik and Skjemstad (1995)
Australia	116	0.77	–	McBratney et al. (2006)
Central USA	273	0.94	4.1	McCarty et al. (2002)
Central USA	237	0.94	–	Reeves (2010)
Australia	118	0.73	1.7	Viscarra Rossel et al. (2006)
Germany	60	0.78	2.1	Vohland et al. (2014)
Switzerland	111	0.94	4.1	Zimmermann et al. (2006)

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