Contents lists available at ScienceDirect

# Geoderma

journal homepage: www.elsevier.com/locate/geoderma

# National calibration of soil organic carbon concentration using diffuse infrared reflectance spectroscopy



**GEODERM** 

Michaël Clairotte <sup>a,1</sup>, Clovis Grinand <sup>b,c</sup>, Ernest Kouakoua <sup>b</sup>, Aurélie Thébault <sup>b,2</sup>, Nicolas P.A. Saby <sup>d</sup>, Martial Bernoux <sup>b</sup>, Bernard G. Barthès <sup>b,\*</sup>

<sup>a</sup> INRA, UMR Eco&Sols, 2 place Viala, 34060 Montpellier, France

<sup>b</sup> IRD, UMR Eco&Sols, 2 place Viala, 34060 Montpellier, France

<sup>c</sup> EtcTerra, 127 rue d'Avron, 75020 Paris, France

<sup>d</sup> INRA, Unité Infosol, BP 20619, 45166 Olivet, France

#### ARTICLE INFO

Article history: Received 24 September 2015 Received in revised form 11 March 2016 Accepted 23 April 2016 Available online 14 May 2016

Keywords: Soil organic carbon Near infrared reflectance spectroscopy (NIRS) Mid infrared reflectance spectroscopy (MIRS) Global regression Local regression

#### ABSTRACT

This study presents the potential of infrared diffuse reflectance spectroscopy (DRS) to predict soil organic carbon (SOC) content. A large national soil library was used, including about 3800 samples collected at two soil depths (0–30 and 30–50 cm) using a 16 × 16 km plot grid over the French metropolitan territory (552,000 km<sup>2</sup>). Reflectance spectra were collected in the laboratory using visible and near infrared (VNIR), near infrared (NIR) and mid infrared (MIR) spectrophotometers. The soil data library was broken down into calibration and validation sets through sample selection at random or based on spectral representativeness. The calibration intensity was investigated in order to assess the optimum number of calibration samples required to obtain accurate models. Predictions were achieved using global or local partial least square regression (PLSR) built using VNIR, NIR and MIR spectra separately or in combination. Local PLSR uses only calibration samples that are spectral neighbors of each validation set based on the standard error of prediction (SEP), the ratio of performance to deviation (RPD<sub>v</sub>). Using all calibration samples, the global PLSR model provided the most precise predictions of SOC content with

Using an calibration samples, the global PLSR induce provided the flost precise predictions of soc content with the MIR spectra, then with the NIR spectra, and less accurate predictions with the VNIR spectra (SEP = 2.6, 4.4 and 4.8 g kg<sup>-1</sup>, RPD<sub>v</sub> = 2.7, 2.3 and 1.5, and RPIQ<sub>v</sub> = 3.3, 2.2 and 1.9, respectively). The combination of spectral libraries did not improve model performance noticeably. Local PLSR provided better models than global PLSR, allowing accurate predictions with only 30% of the calibration set, whatever the spectral library (RPD<sub>v</sub> and RPIQ<sub>v</sub> > 2.0). Optimum calibration intensity was estimated at about 60% for MIR spectra with both global and local PLSR, 30–40% for VNIR and NIR spectra with global PLSR, but 50% for VNIR spectra and 70% for NIR spectra with local PLSR. The most accurate models, which were obtained using the MIR spectra and local PLSR with calibration intensity higher than 50%, allowed very good SOC determination for the most frequent French soils (SEP < 2 g kg<sup>-1</sup>). This highlights the potential of infrared DRS for national SOC monitoring, provided that calibration database is strengthened with samples from less frequent soil types.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Organic carbon is a key component in soil, where it plays a central role in essential functions. Soil organic carbon (SOC) quantification enables to assess soil quality through its structural stability, water retention, as well as chemical and biological fertility (Vaughan and Malcolm, 1985; Reeves, 1997). In addition, as the greatest terrestrial carbon pool, SOC is involved in global carbon cycling, thus in global warming (Batjes, 1996; Lal, 2004), with, for instance, an estimated amount of about 75 Mt SOC in the EU-27 (Schils et al., 2008). However, SOC declines across Europe to such an extent that it has become a dramatic threat (Lugato et al., 2014; De Brogniez et al., 2015).

With its ease to use, fast implementation and low cost, infrared diffuse reflectance spectroscopy (DRS) has become increasingly popular these last decades to estimate SOC (Gholizadeh et al., 2013; Soriano-Disla et al., 2014). In comparison with the traditional laboratory methods, infrared DRS does not require chemical reagents and tedious sample preparation, therefore, it can be quickly implemented in both laboratory and field conditions (Gras et al., 2014). The first studies demonstrating the capability of infrared DRS to determine SOC were based



<sup>\*</sup> Corresponding author.

E-mail address: bernard.barthes@ird.fr (B.G. Barthès).

<sup>&</sup>lt;sup>1</sup> Present address: European Commission Joint Research Centre Ispra, Institute for Energy and Transport, Sustainable Transport Unit, Ispra 21027, VA, Italy.

<sup>&</sup>lt;sup>2</sup> Present address: ITK, Cap Alpha, avenue de l'Europe, 34830 Clapiers, France.

on visible and near infrared (VNIR), or only near infrared (NIR) spectral ranges (Ben-Dor and Banin, 1995; Shepherd and Walsh, 2002; Brown et al., 2005). Infrared DRS based on the mid infrared (MIR) spectral range has also demonstrated its ability to quantify SOC (Janik and Skjemstad, 1995; Grinand et al., 2012). Regarding information related to the chemical structure, the visible range is dominated by electronics transitions, the NIR range by the weak overtones and combinations of fundamental vibrations bands, and the MIR range by the fundamental vibrational bands for H—C, N—H and O—H bonds (Reeves, 2010).

Infrared DRS is generally based on calibrations, which require samples that have been characterized both conventionally (in the laboratory) and spectrally. Calibration models valid for large regions require large soil data libraries, and such libraries require demanding and expensive sampling and analysis campaigns (Nocita et al., 2015). Hence, calibration of soil properties has often been built from the scan of archived soil libraries (e.g., Genot et al., 2011; Viscarra Rossel and Webster, 2012; Shi et al., 2015). At the global scale, the ICRAF-ISRIC soil spectral library is composed of 4438 samples originating from Africa, Asia, Europe and America (van Reeuwijk, 1992). At the continental scale, there are several large soil spectral libraries, regarding Australia (21,500 spectra from samples collected during a lot of surveys; Viscarra Rossel and Webster, 2012), the United States (144,833 spectra from samples collected under the Rapid Carbon Assessment project; USDA, 2013), and Europe (20,000 spectra from samples collected under the Land Use/Cover Area Frame Statistical Survey - so-called LUCAS; Stevens et al., 2013). These large global- and continental-scale soil libraries were scanned in the VNIR range. There is also a French national-scale soil library, which has been scanned in both the VNIR (Gogé et al., 2012) and MIR (Grinand et al., 2012). Several studies have addressed the question of the spectral range most appropriate for predicting SOC concentration, considering VNIR, NIR and/or MIR (Viscarra Rossel et al., 2006; Brunet et al., 2008; Rabenarivo et al., 2013). However, the spectral libraries used in these comparisons included rather limited numbers of samples, and had local or regional application domains. Thus comparative studies based on large national soil libraries are scarce.

The scope of the present study was to assess the performances of SOC predictions made with a national soil spectral library, using VNIR, NIR and MIR spectra acquired with different spectrophotometers, individually or in combination. These instruments differed in terms of spectral range but also in terms of conception (e.g. more or less sophisticated dispersive elements); thus performances and comparisons did not refer strictly to spectral ranges, but rather, to spectral ranges and technologies. Moreover, different calibration strategies were tested:

- the proportion of calibration samples was varied for optimization purposes;

- calibration samples were either selected at random or according to their spectral representativeness;

- and calibration was either global (one unique model was built using all calibration samples) or local (one individual model was built for each validation sample, using calibration samples that were its spectral neighbors).

#### 2. Materials and methods

## 2.1. The soil library

The studied soil samples belong to a large national soil library provided by the French national soil quality monitoring network (RMQS, Réseau de mesures de la qualité des sols). The RMQS aims at providing a national overview of soil quality, identifying gradients, monitoring the evolution of soil quality over time (with a frequency of a decade), and building a bank of soil samples (Arrouays et al., 2002). This soil library was built over a 10-year sampling campaign over the 552,000 km<sup>2</sup> of the French metropolitan territory. The sample design is based upon a square grid with spacing of 16 km (Fig. 1). At the center of each square, 25 individual core samples were taken at 0–30 and 30–50 cm depth



Fig. 1. The RMQS sampling grid.

using an unaligned sampling design within a  $20 \times 20$  m area, and were then bulked to obtain composite samples (Arrouays et al., 2002). In total, the RMQS national soil library is composed by >2200 sites and 3800 samples covering numerous soil types: Cambisols, Calcosols, Luvisols, Leptosols, Andosols, Albeluvisols, etc. (FAO, 2014).

#### 2.2. Reference analyses

Reference determinations were achieved in a single ISO/CEI 17025:2005 accredited laboratory (INRA soil analysis laboratory, Arras, France), according to the standard French procedure NF ISO 10694 (ISO, 1995a). In brief, the method consists in a dry combustion of the air dried, 2-mm sieved then finely ground (<0.25 mm) sample at circa 1200 °C in an oxygen-rich atmosphere. Thus, carbon is converted into carbon dioxide, and quantified using a thermal conductivity detector (TCD). This was done using a CHN elemental analyzer (Flash 2000, Thermo Scientific, Bremen, Germany). This analysis leads to the determination of total carbon content (g  $kg^{-1}$ ), which was then corrected for inorganic carbon possibly present in the sample as carbonates. This was done according to the French procedure NF ISO 10693 (ISO, 1995b), which consists of measuring the volume of carbon dioxide produced after the addition of chlorhydric acid (Pansu and Gautheyrou, 2006). In order to not unduly influence the prediction models, samples with SOC content higher than the mean plus 10 times the standard deviation were considered outliers and removed from the studied sample population. This led to the removal from the soil library of three samples with SOC > 200 g kg<sup>-1</sup>. The SOC content of the library then ranged from 0.6 to 177 g kg<sup>-1</sup>, averaged 18.9 g kg<sup>-1</sup>, and had a skewness value close to 3 (Fig. 2).

# 2.3. Spectral analysis

The soils were air dried, 2-mm sieved then finely ground (<0.2 mm), and oven dried overnight at 40 °C before spectral analysis. Three spectrophotometers were used in this study. Reflectance spectra in the VNIR region were acquired between 350 and 2500 nm (ca. 28,500 and 4000 cm<sup>-1</sup>, respectively) at 1 nm interval using a portable system LabSpec 2500 (Analytical Spectral Devices, Boulder, CO, USA). This spectrophotometer is equipped with a halogen lamp source, a fixed

Download English Version:

https://daneshyari.com/en/article/4572930

Download Persian Version:

https://daneshyari.com/article/4572930

Daneshyari.com