

The performance of portable mid-infrared spectroscopy for the prediction of soil carbon

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Abstract

This study sets out to test the performance of portable mid-infrared (MIR) spectroscopy for the prediction of soil C and its related soil attributes across a range of soils. One objective of this study was to assess the influence of conventional laboratory SOC analysis error in the prediction performance from MIR multivariate modeling. A further objective was to evaluate the accuracy of the infrared predictions using a selection of different multivariate MIR models

For this assessment, 458 soils from Australia were scanned with a portable MIR spectrometer and partial least squares regressions (PLSR) applied for the prediction of total carbon (TC) and SOC using measured and calculated data. Three modeling approaches (PLSR, LOCAL and Neural Network) were developed and compared for their prediction performance of three soil attributes (cation exchange capacity, pH and clay content) which are related to SOC. Our results supported the hypothesis that the MIR regression method represents a viable alternative for the prediction of soil C and related parameters. Our results also demonstrate the importance of having highly reliable analytical data for the success of MIR regressions. In terms of model optimization, the LOCAL method resulted in the most successful approach. This method might be better suited than global PLSR for routine predictions of soil properties in large and diverse spectra libraries using infrared spectroscopy.

Keywords: chemometrics, mid-infrared, organic carbon, soil, spectroscopy

Introduction

Soils play a vital role to life on earth and soil organic carbon (SOC) is one of the most important components responsible for a number of their ecosystem services (FAO, 2015; FAO and ITPS, 2015). Soil organic carbon in soil is characterized by its large variability, spatially and down the profile. This, linked to the existence of different crop types and highly variable seasonal conditions, implies that management responses need to be targeted to each particular situation. Such management strategies require a high spatial density of soil analytical data (Nocita et al., 2015) that traditional laboratory approaches (e.g. wet chemistry analyses) are unable to provide cheaply and quickly

Mid-infrared (MIR) soil spectroscopy is an attractive alternative. It is rapid, cheap and accurate and portable versions can be used directly in the field (Soriano-Disla et al., 2014; Nocita et al., 2015). The technique relies on the interaction of infrared light with soil compositional components, and the characteristics of the resulting soil spectrum which is unique to each soil and provides information about its composition (Nguyen et al., 1991). The technique is well suited to the study of SOC and other related key soil attributes, such as particle size, cation exchange (CEC) and pH, using multivariate regression (Janik et al., 1998).

Despite these advances, there are still very few studies which evaluate the performance of portable MIR instruments for the prediction of SOC. In order to derive the best possible regression models, there is a need

to choose high quality analytical data produced by a trusted laboratory by consistent analytical methods. The precision and accuracy of the reference method is crucial, since the error of the predictive multivariate models depends heavily on the reference data from conventional laboratory analysis. It is also important to test different chemometric approaches.

The main objective of this study was to test the performance of a portable MIR instrument for the prediction of soil C and to evaluate the influence of reference analytical error on the accuracy of the predicted SOC values. It was also an objective of the article to test the influence of different multivariate models on the accuracy of the predictions of related key soil attributes.

Methodology

Soil samples and analysis

The samples used in this study were obtained from the Australian CSIRO National Soil Archive (CNSA, <http://www.clw.csiro.au/aclep/archive/>). The final selection comprised 80 soil profiles (n = 458 samples) from South Australia (66 %) and New South Wales (34 %). Soil samples were dried at 40°C and sieved < 2 mm. Samples were sourced from variable depths, most of the samples (n = 315) represented the first 100 cm, the rest (n = 143) representing depths from 100 to 180 cm.

The following properties were determined by the methodology described in Rayment and Lyons (2011): cation exchange capacity, 1M ammonium chloride; pH, 1:5 soil/water suspension; soil organic carbon, Walkley and Black (SOC_{W&B}); particle size distribution (only clay presented as being representative); total carbon, Leco dry combustion (TC).

Descriptive statistics for the properties analysed were: CEC (N = 458, mean±SD = 22±10 cmol⁺/kg, range = 1-48 cmol⁺/kg), pH (N = 439, mean±SD = 7.9±1.3, range = 4.4-10.3), SOC (N = 308, mean±SD = 0.45±0.58 %, range = 0.02-4.90 %), clay (N = 451, mean±SD = 40.5 ±15.7 %, range = 2.0-80.2 %), TC (N = 457, mean±SD = 1.63±1.64 %, range = 0.04-9.18 %).

There were concerns about the validity of the reference SOC_{W&B} data. A substantial number were only estimated, leaving only about 300 samples for this analyte with real analytical data. For this reason, it was necessary to have a more reliable determination of SOC calculated (SOC_{calc}) as follows:

- Spectra scanned with a benchtop Fourier-Transform (FT-IR) instrument (Frontier, Perkin Elmer) were used for the assessment of inorganic carbon (IC) from the prediction of CaCO₃. A previously developed model using archival data (0-50 % CaCO₃ and two spectral ranges specific for carbonate response around 2500 cm⁻¹ and 1800 cm⁻¹) were used for predictions.
- Negative predictions of IC were reported to be zero.
- The IC values were then subtracted from TC to calculate the SOC. Negative values of SOC were considered to be zero.
- The calculated SOC values (SOC_{calc}) were used to derive PLSR regressions from the MIR spectra and compared with those previously developed by using SOC_{W&B} as the reference data.

Mid-infrared scanning and chemometrics

Samples were scanned with a Fourier-Transform infrared (FTIR) portable spectrometer (ExoScan 4100, Agilent, USA) in the frequency range 6000–650 cm⁻¹. For each sample, four replicate scans were recorded using a diffuse reflectance (DRIFT) accessory with a resolution of 8 cm⁻¹, and scanning time of 15 s. A coarse-grained silicon carbide (SiC) reference disc (assumed to have a reflectance $R_0 = 1$) was used as the background.

Only the MIR range (4000-750 cm⁻¹) was considered because the energy of the instrument is optimised for that region. Partial least square regressions (PLSR) were developed following de-trending correction in the selected spectral range. For model development, 25 % of the samples were randomly selected and set aside (prediction set). The remaining 75 % were used for model calibration by leave-one-out cross-validation and selection of the optimum number of factors. These models were then tested on the prediction set. The performances of the models were evaluated in terms of the root means square error of the prediction

(RMSEP), coefficient of determination (R^2), and the ratio of the standard deviation of the reference values to the RMSEP of the prediction (RPD) (Williams, 1987). In general, models with high values of R^2 and RPD are preferred and indicative of good prediction performance (conversely, models with RPD and R^2 values below 1.5 and 0.5 considered poor or unreliable; Sudduth & Hummel 1996).

All the transformations and model development were carried out by Unscrambler X 10.3 (Camo, Norway). We also tested the influence of different multivariate models on the accuracy of the predictions of related key soil attributes. We first tested if PLSR model performances were affected by using different software packages. Partial least squares regressions performed with Unscrambler were compared with those provided by WinISI (Foss, Denmark). The WinISI algorithms M-PLSR and LOCAL were also tested. This latter method is able to adapt to unknown sample variability by searching in the spectral library for the most similar samples. Model development and validation were performed following the approach explained above. Models were tested for the prediction of key properties which are related to SOC such as CEC, clay or pH. In addition, the Neural Networks (NN) algorithm (WinISI) was also tested for such properties. The specific NN method does not have the option to predict unknowns so only cross-validation is presented.

Results and Discussion

Performance of portable mid-infrared spectroscopy for the prediction of soil carbon and influence of the accuracy of reference data

A high predictive performance was obtained for TC (RMSEP = 0.30 %, $R^2 = 0.94$, RPD = 4.1) but lower accuracy for SOC (RMSEP = 0.31 %, $R^2 = 0.67$, RPD = 1.8). Reasons for a less successful performance for SOC seem related to a) inaccuracies of the reference analytical data, and to b) the very limited concentration range, which made the model more influenced by analytical error.

Following the concerns raised by the $SOC_{W\&B}$ data, we decided to “calculate” SOC using infrared spectroscopy. The calculated SOC values (mean = 0.5 %, median = 0.4 %, range = 0-3.9 %) were similar to those provided by the W&B method. The spectroscopic model using OC_{calc} from the subtraction of TC and predicted IC was considerably better than the one produced by using reference W&B data (see Figure 1), which confirmed the concerns about the W&B determination. This was despite issues with the prediction of samples with $SOC_{W\&B}$ values near zero, which were randomly predicted positively or negatively. This seems to be related to uncertainties in the TC determination used for the calculation of SOC.

Thus, and with this infrared application, we were able to confirm the issues regarding the W&B determination, and to have new SOC data for all samples (W&B only available for around 300 samples).

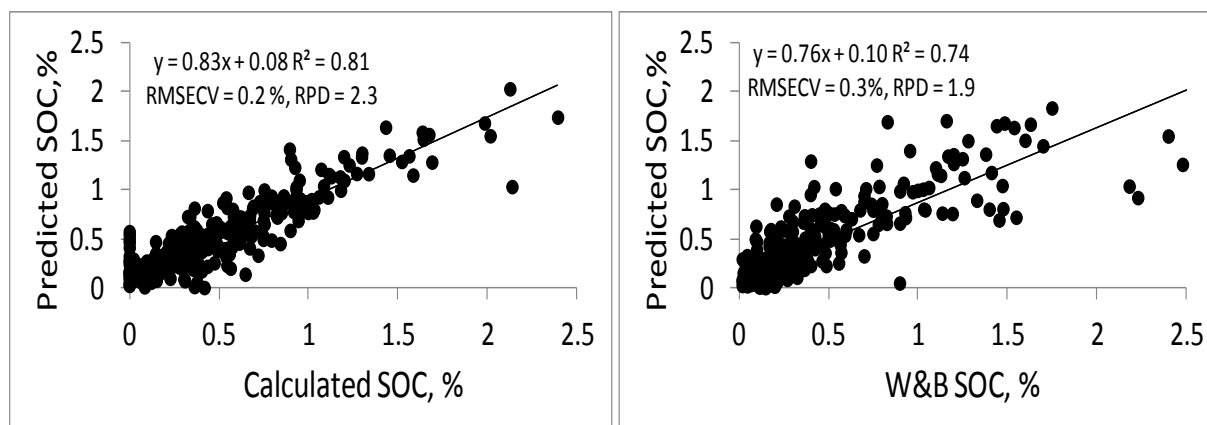


Figure 1. Reference vs. partial least squares regression predicted soil organic carbon using calculated (left) and Walkley & Black (right) data. Results shown for models developed by cross-validation (N = 308).

Assessment of different multivariate models for the prediction of soil properties

A summary of the regression statistics is presented in Table 1. Among the PLSR models, those developed by the Unscrambler software were the most successful, possibly due to the use of different modeling settings. Cross-validation and prediction performances were generally similar. M-PLSR only improved cross-validation performance but not predictions.

The intended application of the MIR technique is to predict “any” unknown soil sample. To make this possible, we need to make sure that the variability of these unknown samples are well represented within the calibration set. In a scenario of predicting samples which are highly variable, both spatially and temporally, global PLSR may not be the best option. In global PLSR methods (the most widely used multivariate algorithm), a single set of soil spectra and corresponding data are used to derive a calibration model. Such models need to be occasionally updated with new uncharacteristic or outlier samples, a non-trivial task. In these cases we may need “adaptive” methods, such as the so-called, “LOCAL”, a local calibration PLSR method. This technique is well suited for that purpose, attributed to: 1) no requirement for updating calibrations when new soils are incorporated in the calibration method; and 2) the fact that this method only uses samples that are spectrally similar to unknowns being predicted, expected to result in more accurate predictions and more efficient routine analyses.

Preliminary results for the prediction of CEC, clay and pH using LOCAL, with spectra scanned by Exoscan, showed similar or better results compared to global PLSR. This represents an important advance, especially when using a larger number of samples and in a scenario of large spatial and temporal variability. Neural Networks were not better than PLSR or LOCAL approaches.

Table 1. Summary statistics¹ for different multivariate modeling using Exoscan spectra

Method	Analyte	Conc. Range	R ²	RMSECV
Unsc PLSR CV	pH (1:5 w)	4.4-10.3	0.80	0.6
WinISI PLSR CV	pH (1:5 w)	4.4-10.3	0.84	0.5
WinISI MPLSR CV	pH (1:5 w)	4.4-10.3	0.89	0.4
WinISI LOCAL CV	pH (1:5 w)	4.4-10.3	0.83	0.5
WinISI NN CV	pH (1:5 w)	4.4-10.3	0.79	0.6
Unsc PLSR CV	CEC (cmol ⁺ /kg)	1-48	0.83	4.3
WinISI PLSR CV	CEC (cmol ⁺ /kg)	1-48	0.85	4.0
WinISI MPLSR CV	CEC (cmol ⁺ /kg)	1-48	0.88	3.7
WinISI LOCAL CV	CEC (cmol ⁺ /kg)	1-48	0.84	4.1
WinISI NN CV	CEC (cmol ⁺ /kg)	1-48	0.85	4.0
Unsc PLSR CV	Clay (%)	2.0-80.2	0.72	8.3
WinISI PLSR CV	Clay (%)	2.0-80.2	0.75	7.9
WinISI MPLSR CV	Clay (%)	2.0-80.2	0.88	3.7
WinISI LOCAL CV	Clay (%)	2.0-80.2	0.75	8.0
WinISI NN CV	Clay (%)	2.0-80.2	0.74	8.1
Method	Analyte	Conc. Range	R ²	RMSEP
Unsc PLSR Pred	pH (1:5 w)	4.5-10.0	0.82	0.6
WinISI PLSR Pred	pH (1:5 w)	4.5-10.0	0.80	0.6
WinISI MPLSR Pred	pH (1:5 w)	4.5-10.0	0.82	0.6
WinISI LOCAL Pred	pH (1:5 w)	4.5-10.0	0.84	0.5
Unsc PLSR Pred	CEC (cmol ⁺ /kg)	1-46	0.84	4.4
WinISI PLSR Pred	CEC (cmol ⁺ /kg)	1-46	0.83	4.6
WinISI MPLSR Pred	CEC (cmol ⁺ /kg)	1-46	0.83	4.5
WinISI LOCAL Pred	CEC (cmol ⁺ /kg)	1-46	0.83	4.4
Unsc PLSR Pred	Clay (%)	5.0-69.3	0.77	7.5
WinISI PLSR Pred	Clay (%)	5.0-69.3	0.75	7.9
WinISI MPLS Pred	Clay (%)	5.0-69.3	0.75	8.0
WinISI LOCAL Pred	Clay (%)	5.0-69.3	0.79	7.2

¹Summary statistics: Coefficient of determination (R²), root mean square error of the cross-validation (RMSECV), root mean square error of the prediction (RMSEP)

Conclusions

This study has showed that MIR portable spectroscopy represents a viable and practical alternative to traditional techniques for the determination of soil carbon and related soil properties. In terms of prediction accuracy, aspects related to the reference analyte accuracy play a very important role. Calculation of SOC from reference TC and predicted IC values yields better infrared predictive models than those using reference SOC_{W&B} data.

The optimization tests have proved that, for being successful in the development of infrared model development for prediction purposes, it is crucial to select samples for calibration which adequately represent the variability of the expected unknowns. In this regard, sample specific method, which select samples based on their spectral characteristics, are the best suited. This is, for example, the case of adaptative methods such as LOCAL. In terms of model optimisation, LOCAL resulted in the most successful approach. This method might be better suited, than traditional PLSR, for future routine predictions of soil properties in large spectra libraries using infrared spectroscopy.

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