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Comparison between predictions of C and N contents in tropical soils using a Vis-NIR spectrometer including a fibre-optic probe versus a NIR spectrometer including a sample transport module

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Abstract

Increasing attention is being paid to near infrared reflectance (NIR) spectroscopy for the rapid and cost-effective determination of soil carbon (C) and nitrogen (N) contents. The objective of the present paper was to compare the performances of two spectrometers: one covered the visible and NIR ranges (Vis-NIR, 350-2500 nm) and included a fibre-optic probe, the other covered the NIR range only (1100-2500 nm) and included a sample transport module. The comparison was carried out on two sets of clayey ($n = 97$) and sandy ($n = 72$) soil samples from tropical Africa and America.

On the whole, both technologies provided good calibrations ($R^2 > 0.74$) and predictions ($R^2 > 0.62$) of soil C and N contents. The most accurate calibrations were achieved with the NIR spectrometer ($R^2 > 0.86$), which also yielded the most accurate predictions for the sandy soils ($R^2 = 0.90$ and standard error of prediction $< 15\%$ of the mean). For the clayey soils, the best predictions of both spectrometers were similar ($R^2 \geq 0.68$ and standard error of prediction $< 20\%$ of the mean). Using first or second derivatives of spectra did not affect calibration but had an impact on validation.

Keywords: soil, spectroscopy, near infrared, visible, carbon, nitrogen

1. Introduction

Interest in the development of rapid and low-cost methods for measuring carbon (C) allocation in ecosystems has been stimulated by the need to quantify soil C storage precisely. Indeed, there is great concern about the increase in atmospheric C content, which could be limited through soil C sequestration (Cerri *et al.*, 2004). However, due to spatial variability

and non-linear temporal dynamics, accurate soil C estimates require measurements on numerous samples (Soussana *et al.*, 2004).

Two basic approaches are used to quantify organic C in soils, namely, dry combustion and wet oxidation (Bernoux & Cerri, 2005). In both instances, CO₂ released from organic and inorganic C is determined through volumetric, titrimetric, gravimetric, or conductimetric techniques. However, these methods are time-consuming and/or costly. New approaches based on spectroscopy are being developed even to characterize soils *in situ*. One approach, the laser-induced breakdown spectrometry (Cremers *et al.*, 2001), uses a laser focused on a solid sample to form a microplasma that emits light, which is analyzed to determine the elemental composition of the sample. Other approaches are based on the analysis of light reflected by samples in different regions of the electromagnetic spectrum. As regards soil C determination, near infrared reflectance (NIR) spectroscopy has been the most reported in the literature (Dalal & Henry, 1986; Morra *et al.*, 1991; Ludwig *et al.*, 2002; Reeves *et al.*, 2006; Brunet *et al.*, 2007). More recently, the use of visible-NIR (Vis-NIR) spectroscopy has been evaluated, but for relatively homogeneous soil sets from temperate regions only (Stevens *et al.*, 2006; Mouazen *et al.*, 2007).

Thus, the objective of this study was to test a Vis-NIR spectrometer including a fibre-optic probe and compare its performance with those of a NIR spectrometer already validated for the determination of C and nitrogen (N) contents in a set including various tropical soils (Brunet *et al.*, 2007).

2. Materiel and methods

2.1. Soil sampling

A population of 97 clayey and 72 sandy soil samples from tropical Africa and America was studied (Table 1). Total C of clayey soils ranged from 0.86 to 30.45 g kg⁻¹ and N from 0.10 to 2.93 g kg⁻¹. Total C of sandy soils ranged from 1.87 to 16.55g kg⁻¹. Soil N content was not considered in sandy soils, due to the lack of reference values for most samples. All samples were air-dried, crushed and sieved to pass a 2 mm mesh, and again oven-dried at 40°C during 24 h before spectrum acquisitions. Aliquots were finely ground to pass a 0.2 mm mesh and analyzed by dry combustion using an Elemental Analyzer CHN Fisons / Carlo Erba NA 2000 (Milan, Italy) for reference values. In the absence of carbonates, all C was assumed to be organic.

2.2. Spectral instruments

The Vis-NIR spectrometer (LabSpec Pro ASD, Boulder, CO, USA) uses fibre-optic probe with a quartz-halogen source and several detectors: one Si photodiode array in the range 350-1000 nm (sampling interval 1.4 nm) and two Peltier cooled InGaAs detectors in the ranges 1000-1800 nm and 1800-2500 nm (sampling interval 2 nm). For the NIR spectrophotometer (Foss NIRSystems 5000, Silver Spring, MD, USA), the light source is a tungsten-halogen lamp with a lead sulphide (PbS) photodetector. The light at different wavelengths is selected by a monochromator at concave holographic grating.

2.3. Spectrum acquisition and pre-processing

The samples were scanned using a static ring cup containing ~ 5 g of soil, with Vis-NIR spectrometer in the full wavelength range (FWR) 350-2500 nm, in the short wavelength range (SWR₁) 1100-2500 nm, and with NIR spectrometer in the short wavelength range 1100-2500 nm (SWR₂). Spectral data were measured as reflectance, with two replicates per sample (involving independent refilling of the cup). They were recorded as absorbance (A) according to the following equation:

$$A = [\log (1/R)],$$

where R is the reflectance. Absorbance data were averaged every 10 nm. They were processed using the software WinISI III-version 1.50e software (Foss NIRSystems, Infrasoft International, State College, PA, USA). Derivatives were used to reduce baseline variation and enhance spectral features (Reeves *et al.*, 2002). They were calculated over a 2-point gap with 2-point smoothing. Both first derivatives and second derivatives were evaluated in conjunction with a standard normal variate transform (SNV) to reduce the particle size effect, and detrend to remove the linear or curvilinear trend of each spectrum (Barnes *et al.*, 1989).

2.4. Processing methods

A principal component analysis (PCA) was carried out for the calculation of the Mahalanobis distance (H) on the two sets (Mark & Tunnell, 1985). Samples whose spectra were atypical ($H > 3$) were considered outliers and were eliminated from further investigations (Shenk & Westerhaus, 1991a). Then, MPLS regression was used to relate spectral data to conventional values of C and N (Shenk & Westerhaus, 1991b). Each set of spectra was divided into a calibration subset and a remaining validation subset. The calibration subsets were selected by the software to include the 70 and 50 most representative samples of the clayey and sandy sets, respectively. Cross validation was performed on the calibration subsets to determine the

optimal numbers of terms to be included in the prediction model. For this purpose, each calibration subset was split into six groups, five being used for developing the model and one for prediction. The procedure was performed six times to use all groups for both model development and prediction. The residuals of the six predictions were pooled to calculate the standard error of cross validation (SECV) between predicted and measured values. The outliers for calibration (i.e. samples with $t > 2.5$) were removed and another cross validation was performed, the procedure being carried out twice. Then all remaining calibration samples were used to calculate the final model. The number of factors giving the lowest final SECV determined the optimal number of terms to be used for the calibration. The performance of the calibration model was assessed using the coefficient of determination (R^2) and the ratio of performance to deviation (RPD), which is the ratio of standard deviation to SECV (Chang *et al.*, 2001). Finally, the accuracy of the prediction model was evaluated on the validation subset, using the standard error of prediction (SEP), validation R^2 between predicted and reference data, and CV, which is the ratio of SEP to the mean reference value, in % (Morra *et al.*, 1991).

3. Results and discussion

The number of spectral outliers ranged from 0 to 2 for both clayey and sandy sets, representing less than 2% and 3% of the sets, respectively. This number depended on the apparatus, wavelength range (it tended to be higher in FWR), and derivative order; nevertheless spectral outliers were similar for C and N (clayey set). The number of calibration outliers ranged from 2 to 8 in the clayey set (3-11%) and from 3 to 6 in the sandy set (6-12%), and depended on the apparatus, wavelength range, derivative order, and studied variable (C or N).

Whatever the spectrometer and wavelength range, RPD for the clayey set was higher or equal to 2.3 for C and higher than 1.9 for N (Table 2). SECV ranged from 1.63 to 3.31 g kg⁻¹ for C and from 0.16 to 0.30 g kg⁻¹ for N. For C in the sandy set, RPD was higher than 1.9, and SECV ranged from 0.67 to 0.92 g kg⁻¹ (Table 3) The most accurate calibrations were generally achieved in SWR₂ (clayey set: SECV ≤ 1.64 g C kg⁻¹ and ≤ 0.16 g N kg⁻¹, RPD > 4.1, R² > 0.94; sandy set: SECV ≤ 0.72 g C kg⁻¹, RPD > 2.6, R² > 0.86). As regarded validation, SEP ranged from 1.92 to 3.45 g kg⁻¹ for C, and from 0.16 to 0.29 g kg⁻¹ for N for clayey soils, and from 0.62 to 2.08 g C kg⁻¹ for sandy soils. The best C predictions for the clayey set were obtained in SWR₂ with the second derivative and in FWR with the first

derivative (validation $R^2 \geq 0.88$; Figure 1); those for the sandy set were obtained in SWR₂ with both derivatives ($R^2 > 0.90$). The best N prediction for the clayey set was achieved in FWR with the first derivative ($R^2 \geq 0.81$).

Comparing the same Vis-NIR spectrometer in the wavelength range 350-2500 nm (FWR) with another Vis-NIR instrument in a shorter wavelength range (300-1700 nm), Mouazen *et al.* (2006) found better predictions for total C and total N in FWR. With both derivatives, CV was $< 20\%$ for C and N in FWR and SWR₂ for the clayey soils, and for C in SWR₂ for sandy soils. Some authors reported CV ranges from 25 to 35% when predicting C or N for heterogeneous soil sets (Chang *et al.*, 2001; Shepherd & Walsh, 2002; Sørensen & Dalsgaard, 2005). Brunet *et al.* (2007) reported $CV \leq 25\%$ and 20% on clayey and sandy soils, respectively.

Using first or second derivatives did not affect calibration but impacted validation. The first derivatives improved C and N calibrations for clayey soils, and C calibration for sandy soils, except in SWR₁. As regarded validation, second derivatives yielded better results for C in SWR₂ for both sets, and in FWR for the sandy set. First derivatives gave best results for N validation for clayey soils.

Sørensen & Dalsgaard (2005) found that C prediction accuracy was insensitive to the mathematical treatment of spectra, whereas some authors obtained more accurate predictions with first derivatives (Chang *et al.*, 2001; Coûteaux *et al.*, 2003) or second derivatives (Salgó *et al.*, 1998; Fystro, 2002).

4. Conclusion

This study showed the ability of these instruments, involving two distinct technologies, to build good C and N prediction models. The NIR spectrometer yielded the best calibrations. The results for validation were more contrasted and were affected by using first or second derivatives. Comparing SWR₁ and SWR₂, the NIR spectrometer gave better calibrations and validations than the Vis-NIR spectrometer, except for N validation. The ASD Vis-NIR spectrometer is also available in a portable version, allowing field investigations, and has a scanning time < 1 second, whereas it is around 50 seconds for the Foss spectrometer. Finally, it must be noted that the performance of both instruments might certainly be improved using dedicated software and other preprocessing corrections, such as multiplicative scatter correction (Maleki *et al.*, 2007).

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Table 1. Presentation of the studied samples.

Location	Texture and soil type ^a	n ^b	Sample depth (cm)	Clay content (%)	C ^c (g kg ⁻¹)	N ^c (g kg ⁻¹)
Brazil	Clayey Ferralsols	30	0-5 and 5-10	45-50	22.61 ± 2.92	1.71 ± 0.24
Martinique ^d	Clayey Vertisols	67	0-10 to 90-100	51-86	12.31 ± 7.65	1.12 ± 0.70
Senegal	Sandy Lixisols	72	0-10 to 30-40	5-21	4.72 ± 2.58	n.d.

n.d. not determined.

^a World Reference Base for Soil Resources (www.fao.org).

^b number of soil samples.

^c mean ± standard deviation.

^d French West Indies

Table 2. Calibration and validation results for C and N contents in clayey soils, using different wavelength ranges and derivatives.

Wavelength range	Derivatives	Calibration set					Validation set			
		n ₁ ^a	SECV ^b (g kg ⁻¹)	R ²	RPD ^c	Terms ^d	n ₂ ^e	SEP ^f (g kg ⁻¹)	R ²	CV ^g (%)
<i>Carbon</i>										
FWR ^h	First	67	2.62	0.883	2.92	8	25	1.92	0.885	9.3
	Second	68	3.28	0.834	2.47	4	26	2.75	0.808	14.4
SWR ₁ ⁱ	First	66	2.67	0.883	2.94	7	25	3.45	0.765	31.5
	Second	68	3.31	0.810	2.30	4	27	3.40	0.721	35.8
SWR ₂ ^j	First	64	1.64	0.962	5.14	8	27	3.42	0.701	18.3
	Second	64	1.63	0.959	4.94	7	26	1.92	0.913	10.1
<i>Nitrogen</i>										
FWR ^h	First	68	0.23	0.875	2.82	8	25	0.16	0.811	9.6
	Second	66	0.23	0.879	2.87	5	26	0.26	0.626	16.9
SWR ₁ ⁱ	First	68	0.26	0.821	2.37	7	25	0.29	0.782	30.7
	Second	67	0.30	0.745	1.99	5	27	0.29	0.778	34.2
SWR ₂ ^j	First	62	0.16	0.942	4.17	7	27	0.24	0.730	16.0
	Second	62	0.16	0.942	4.17	7	26	0.26	0.688	16.8

^a Number of samples after the elimination of calibration outliers.

^b Standard error of cross validation.

^c Ratio of standard deviation to SECV.

^d Number of terms to build the calibration models.

^e Number of samples in the validation set.

^f Standard error of prediction.

^g Ratio of SEP to the mean reference value.

^h Full wavelength range (350-2500 nm) using the ASD Vis-NIR spectrometer.

ⁱ Short wavelength range (1100-2500 nm) using the ASD Vis-NIR spectrometer.

^j Short wavelength range (1100-2500 nm) using the Foss NIR spectrometer.

Table 3. Calibration and validation results for C content in sandy soils, using different wavelength ranges and derivatives.

Wavelength range	Derivatives	Calibration set					Validation set			
		n_1^a	SECV ^b (g kg ⁻¹)	R ²	RPD ^c	Terms ^d	n_2^e	SEP ^f (g kg ⁻¹)	R ²	CV ^g (%)
<i>Carbon</i>										
FWR ^h	First	44	0.67	0.845	2.44	3	20	1.14	0.852	20.7
	Second	44	0.92	0.802	2.23	3	20	0.80	0.842	16.1
SWR ₁ ⁱ	First	46	0.78	0.754	1.93	5	22	0.77	0.899	14.5
	Second	47	0.73	0.757	2.02	3	22	2.08	0.783	36.7
SWR ₂ ^j	First	46	0.68	0.887	2.91	7	21	0.76	0.906	14.7
	Second	45	0.72	0.866	2.66	5	20	0.62	0.931	12.6

^a Number of samples after the elimination of calibration outliers.

^b Standard error of cross validation.

^c Ratio of standard deviation to SECV.

^d Number of terms to build the calibration models.

^e Number of samples in the validation set.

^f Standard error of prediction.

^g Ratio of SEP to the mean reference value.

^h Full wavelength range (350-2500 nm) using the ASD Vis-NIR spectrometer.

ⁱ Short wavelength range (1100-2500 nm) using the ASD Vis-NIR spectrometer.

^j Short wavelength range (1100-2500 nm) using the Foss NIR spectrometer.

Figure 1. Comparison between best C (g kg⁻¹ soil) predictions for clayey soils achieved using (a) the Vis-NIR spectrometer in FWR (with first derivative) and (b) the NIR spectrometer in SWR₂ (with second derivative).

