



# Potential of near-infrared reflectance spectroscopy and chemometrics to predict soil organic carbon fractions

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## Abstract

The potential of near-infrared reflectance spectroscopy (NIRS) to predict soil organic C in different particle-size fractions was evaluated. Soil samples ( $n = 180$ ) from various crop rotations in Uruguay were analysed by standard chemical and NIRS methods. Partial least squares (PLS) regression with cross validation was used to develop calibrations between reference data and NIRS spectra ( $n = 87$ ) and validated using an independent set of samples ( $n = 87$ ). Coefficients of determination in calibration ( $R^2_{\text{CAL}}$ ) and standard errors in cross validation (SECV) were 0.90 and 0.6 for coarse-sand C, 0.92 and 0.4 for fine-sand C, and 0.96 and 2.1 for clay + silt C, respectively. Calibrations were poor for C/N ratio ( $R^2_{\text{CAL}} < 0.65$ ). Although NIRS demonstrated great potential to predict soil organic C in different particle-size fractions, the nature of sampling and number of samples analysed should be considered in future developments.

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## 1. Introduction

Soil organic matter (SOM) is an important source of nutrients for plant production in natural and managed ecosystems, and is itself influenced in kind and amount by land use, soil type, climate and vegetation (Loveland and Webb, 2003). It is also an important factor affecting soil quality, long-term

sustainability of agriculture, soil aggregate stability and crop yield (Freixo et al., 2002; Loveland and Webb, 2003). Unfortunately, modern agricultural practices can lead to soil degradation and consequently a decrease in productivity (Lal, 2000). Until the 1950s, continuous cropping with disking and ploughing was the predominant crop production system in Uruguay (South America). Lack of techniques to control soil erosion and fertiliser application led to soil degradation resulting in negative carbon (C) and nitrogen (N) balances as well as deleterious effects on soil physical, chemical

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and biological properties. In Uruguay, the negative effect of continuous cropping with conventional tillage was reversed with the adoption of crop and pasture rotations and with the use of fertilisers (Morón and Sawchik, 2002). Quantification and evaluation of changes in SOM together with soil textural analysis are key factors to assess soil quality under different agricultural practices (Jenkinson and Rayner, 1977; Freixo et al., 2002). Grassland soils are characterised by their high levels of SOM and high structural stability, however these properties decrease upon cultivation (Elliott, 1986; Cambardella and Elliott, 1992; Paul, 1984; Loveland and Webb, 2003).

Quantitative assessment of SOM fractions is important for understanding SOM dynamics in intensively managed systems as we move towards adoption of sustainable agricultural practices (Elliott, 1986). Among the factors that control SOM under agricultural production, crop rotation and tillage are two important variables under the control of a manager. Often it takes years before changes in agricultural management lead to detectable changes in the quantity and quality of SOM (Hassink et al., 1997; Freixo et al., 2002). In this context, there has been an increasing interest to define soil quality indicators suitable for evaluating sustainable soil management.

In the early 1980s, a model describing particulate organic matter (POM) enhanced our understanding of SOM associations with different soil physical units (sand, clay and silt) (Cambardella and Elliott, 1992; Kettler et al., 2001). Particulate organic matter has been used to characterise soil organic C and N in soils under different crop systems in different countries (Cambardella and Elliott, 1992; Angers et al., 1993; Carter, 1992, 1996; Carter et al., 1994; Morón and Sawchik, 2002; Freixo et al., 2002). However, most of the actual methods used to determine SOM and POM are costly, time consuming (1–3 weeks to deliver the results), and requiring specialised equipment, that is not widely available for routine soil analysis by commercial or research laboratories (Cambardella and Elliott, 1992).

Near-infrared reflectance spectroscopy (NIRS) utilizes electromagnetic spectra between the visible and infrared regions (700–2500 nm). Near-infrared reflectance spectroscopy is based on the absorption of C–H, N–H and O–H groups found in organic constituents. These absorptions are the overtones

and combination bonds of much stronger absorption found in the mid infrared spectral region (Murray, 1993; Batten, 1998; Deville and Flinn, 2000; Reeves, 2000). Multiple regression techniques are used to relate NIRS data at selected wavelengths to reference values for calibration (Deville and Flinn, 2000).

Near-infrared reflectance spectroscopy represents a radical departure from conventional analytical methods, because a single sample is characterised in terms of its absorption properties, rather than separate batches being treated with various chemicals to isolate specific components (Murray, 1993; Deville and Flinn, 2000; Reeves, 2000). This technique has been used to determine organic C and total N in arable soils (Dalal and Henry, 1986; Morra et al., 1991; Ben-Dor and Banin, 1995; Reeves et al., 2001; Morón and Cozzolino, 2002), to predict micronutrients and macrominerals in soil (Malley et al., 1999; Chang et al., 2001; Dunn et al., 2002; Cozzolino and Morón, 2003), to estimate various soil physical properties (Chang et al., 2001; Dunn et al., 2002) and to predict potentially mineralizable nitrogen (Fystro, 2002). However, no reports were found in the literature using NIRS to predict soil organic C in soil size fractions.

In this study we evaluated the potential of NIRS to predict soil organic C, N and C/N ratio in different particle-size fractions of soils under different crop rotation systems in Uruguay.

## 2. Materials and methods

### 2.1. Soils and sampling

Uruguay (34°S, 57°W) is located entirely within the temperate zone with average high and low temperatures in summer (January) of 28 and 17 °C and in winter (July) of 14 and 6 °C, respectively. Rainfall is fairly evenly distributed throughout the year with mean annual precipitation of 950 mm. A total of 160 soil samples (0–15 cm depth) were collected from 10 commercial farms during May and September 1998. Farms were located in the regions of Soriano, Paysandu, Rio Negro and Tacuarembó (Uruguay Regional Division). Soil varied in physical and chemical characteristics from Hapludalfs (sand content > 500 g kg<sup>-1</sup>) to Argiudolls (clay con-

tent  $> 600 \text{ g kg}^{-1}$ ) (Ministerio de Agricultura-Pesca, 1979). Additionally, 24 soil samples from four treatments in one field were collected in July 1999 at depths of 0–7.5 and 7.5–15 cm from a long-term experiment established in 1963 in La Estanzuela Agricultural Experimental Research Station. This experiment was located on an Argiudoll, silty clay loam soil (organic C of  $15\text{--}22 \text{ g kg}^{-1}$ , total N of  $1.3\text{--}2 \text{ g kg}^{-1}$ , pH of 5–6.8) (Ministerio de Agricultura-Pesca, 1979). Treatments were: (a) cropping system 1 (CS-1) continuous cropping of wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), sunflower (*Helianthus annuus* L.), sorghum (*Sorghum bicolor* L.) without application of fertilisers (two crops per year); (b) (CS-2) same crop sequence as CS-1 with N and P fertilisers; (c) (CS-5) a 6-year sequence fertilised with N and P, with 3 years under the same crops as CS-1 and 3 years under a grass–legume pasture; (d) (CS-7) a 3-year sequence fertilised with N and P with 2 years under crops and 1 year under red clover (*Trifolium pratense* L.). Tillage was with conventional ploughing and disking. Pastures were cut by hand with no grazing. Treatments were arranged in a randomised complete block design with three replicates in plots  $25 \text{ m} \times 200 \text{ m}$ .

Soil cores were randomly collected with a steel-coring bit without removing surface residues along the length of each plot in both commercial and experimental farms. Soil cores were broken apart by hand in the laboratory and passed through 2 mm sieve while still moist. Sieved soil was dried overnight at  $65^\circ \text{C}$  after which the soil cores taken from each plot at different depths were combined and stored at  $4^\circ \text{C}$  before analysis.

## 2.2. Soil analyses

Soil organic C was determined by wet digestion using an acid solution of potassium dichromate under external heat and reflux condensers, followed by titration of excess potassium dichromate using a solution of ferrous ammonium sulphate following modifications of Cambardella and Elliott (1992). Particulate organic C was measured in two sand fractions:  $53\text{--}212 \mu\text{m}$  (fine-sand C) and  $212\text{--}2000 \mu\text{m}$  (coarse-sand C) after soil dispersion and sieving (Cambardella and Elliott, 1992). Soil was dispersed by shaking 3.33 or 6.66 g dry soil with 10 mL sodium

hexamethaphosphate (5%) on a reciprocal shaker for 16 h, and then passed through 212 and  $53 \mu\text{m}$  to remove the particulate organic matter fractions. The material collected on each sieve was retained and dried at  $80^\circ \text{C}$  (Fabrizzi et al., 2003). The C fraction  $< 53 \mu\text{m}$  (clay + silt C) was calculated by difference of two sand fractions from whole soil organic C. Total N was determined on the different soil fractions by micro Kjeldhal method (Bremner and Mulvaney, 1982) and used to calculate the C/N ratio in different particle-size fractions.

The statistical analysis and interpretation of data in relation to soil organic C fractions were published elsewhere and are not discussed in this paper (Morón and Sawchik, 2002).

Dried and sieved (2 mm) soil samples ( $n = 180$ ) were scanned with a NIRSystems<sup>TM</sup> 6500 monochromator instrument (NIRSystems, Silver Spring, MD, USA). The visible (VIS) and near-infrared (NIR) region were analysed (400–2500 nm) at 2 nm interval, to produce a total of 1050 datapoints. Samples (approx. 10 g) were placed in small circular capsules (5 cm diameter) and sealed at the back with paper. Spectra were stored in the form of reciprocal of reflectance ( $\log 1/R$ ) ( $R$  = reflectance). Spectral collection and data manipulation were performed using ISI 3.01 software (Infrasoft International [ISI], Port Matilda, USA) (NIRS 2, 1995). Spectral data were exported from the ISI software for chemometric analysis to *The Unscrambler* software (Version 7.5, CAMO ASA, Norway). Sample spectra were pre-processed using the second derivative to reduce baseline variation and enhance spectral features (Hruschka, 1992) using Savitzky–Golay derivation and smoothing (20 point and second order filtering operation). Principal Component Analysis (PCA) was performed before partial least squares (PLS) regression models were developed between chemical and NIRS data. The PCA was used to select samples for allocation in either the calibration or validation set, as well as to detect outliers. The PCA is a mathematical procedure for separating data into orthogonal components whose linear combinations approximate the original data to a selected degree of accuracy (Naes et al., 2002). The PCA was used to derive the first 20 principal components, which were examined for relevant and interpretable structure. Two outlier detection methods provided by the ISI software were

applied:  $t$  and  $H$ . The outlier samples identified by the  $t$  statistics having residuals from the reference analysis greater than 2.5 times the standard error of calibration (SEC) were samples whose reference analysis was in doubt. These outliers would be recommended for re-analysis by the reference method. The  $H$  statistic (Mahalanobis distance) identified outliers from samples whose spectra were atypical of all the others that made up the calibration set. These samples would not belong in the population. No outlier samples were observed, thus no samples were deleted from the calibration set. The optimum number of terms in the PLS calibration models were determined by cross validation (Naes et al., 2002) and defined by the PRESS function in order to avoid overfitting of the models. Cross validation estimated the prediction error by splitting the calibration samples into groups (four in this case). One group was reserved for validation and the remaining groups were used for calibration. The process was repeated until all groups had been used for validation once. Calibration statistics included the SEC, coefficient of determination in calibration ( $R_{\text{CAL}}^2$ ), standard error of cross validation (SECV) and the coefficient of determination in cross validation ( $R_{\text{VAL}}^2$ ). Calibration between chemical analyses and NIRS was evaluated based on  $R_{\text{CAL}}^2$  and SECV. The ratio of standard deviation and

standard error in cross validation (RPD) was used to test the accuracy of the calibration models (Williams, 2001; Fearn, 2002). An RPD > 3 is considered adequate for analytical purposes in most NIRS applications for agricultural products (Williams, 2001; Fearn, 2002). However, some reports state that for soil analysis an acceptable RPD could be >2 (Chang et al., 2001). A validation set ( $n = 87$ ) was used to test the NIRS calibration models developed. Consequently, the coefficient of simple correlation (RSQ), the standard error of prediction (SEP), the slope and bias were calculated.

### 3. Results and discussion

Table 1 shows NIRS calibration statistics for C in the various soil fractions against both absorbance and after applying the second derivative. Excellent NIRS calibrations were obtained for C in different soil fractions, accounting for >85% of the variation ( $R_{\text{CAL}}^2 = 0.85\text{--}0.96$ ) using either absorbance or the second derivative. The best NIRS calibrations were obtained for clay + silt C ( $R_{\text{CAL}}^2 > 0.94$ ). Poor calibrations were found for C/N ratio for whole soil and soil fractions ( $R_{\text{CAL}}^2 = 0.13\text{--}0.64$ ). Although the  $R_{\text{CAL}}^2$  were higher for absorbance than the second

Table 1  
Near-infrared calibration and cross-validation statistics for C/N and C in various soil fractions (g kg<sup>-1</sup>)

	Concentration	SEC	$R_{\text{CAL}}^2$	SECV	$R_{\text{VAL}}^2$	$T$	RPD
Raw spectra							
C/N	6.5–13.7	0.75	0.60	0.98	0.30	10	1.2
C/N (coarse-sand)	7.5–18.0	4.5	0.30	4.90	0.28	10	1.0
C/N (fine-sand)	6.2–12.7	0.72	0.64	0.99	0.41	10	1.2
C/N (clay + silt)	6.1–12.0	0.99	0.30	1.04	0.30	10	1.2
Coarse-sand C							
Fine-sand C	0.2–11.0	0.6	0.90	1.0	0.80	8	2.2
Clay + silt C	0.1–9.1	0.4	0.92	0.6	0.85	8	2.3
Clay + silt C							
Second derivative							
C/N	6.5–13.7	0.85	0.45	0.90	0.35	10	1.3
C/N (coarse-sand)	7.5–18.0	5.1	0.13	5.2	0.10	10	1.0
C/N (fine-sand)	6.2–12.7	0.81	0.56	1.0	0.32	10	1.2
C/N (clay + silt)	6.1–12.0	0.87	0.50	1.01	0.31	10	1.2
Coarse-sand C							
Fine-sand C	0.2–11.0	0.8	0.85	1.0	0.80	6	2.2
Clay + silt C	0.1–9.1	0.4	0.89	0.7	0.85	6	2.0
Clay + silt C							
Clay + silt C							
Clay + silt C							

SEC: standard error in calibration; SECV: standard error in cross validation;  $R_{\text{CAL}}^2$ : coefficient of determination in calibration;  $R_{\text{VAL}}^2$ : coefficient of determination in cross validation;  $T$ : number of PLS terms used to develop the NIR calibration models; RPD: SD/SECV;  $n = 87$ .

Table 2  
Near-infrared reflectance prediction statistics for C/N and C in various soil fractions

	<i>r</i>	SEP	Linear relationship between chemical method and NIRS method	Bias
Absorbance				
C/N	0.65	0.97	$y = 5.12 + 0.52x$	0.10
Coarse-sand C	0.88	0.9	$y = 0.05 + 0.83x$	0.02
Fine-sand C	0.70	0.9	$y = 0.07 + 0.61x$	0.01
Clay + silt C	0.96	2.5	$y = -0.02 + 1.01x$	0.02
Second derivative				
C/N	0.49	1.12	$y = 10.3 + 0.32x$	0.34
Coarse-sand C	0.83	1.1	$y = 0.05 + 0.77x$	0.01
Fine-sand C	0.70	1.0	$y = 0.06 + 0.62x$	-0.001
Clay + silt C	0.94	3.1	$y = -0.001 + 0.98x$	-0.03

SEP: standard error of prediction; *r*: coefficient of regression; *y*: reference value; *x*: NIRS predicted value; validation set, *n* = 87.

derivative of C/N ratios, no major differences were observed in SECV. The NIRS calibrations for C/N ratios in whole soil and soil fractions were considered unsatisfactory. The narrow range for C/N ratio (6.5–13.7) among samples could explain the poor calibrations.

The RPD in NIRS calibrations was >2 for all soil fractions indicating good performance. The RPD for C/N ratio of soil fractions was <2. The highest RPD (>3) was for clay + silt C. It is well known that SECV must be at least three times smaller than SD of the reference to produce a reliable calibration for analytical purposes. However, interpretation of the

RPD depends on the context and purpose for which the measurement is to be used (Fearn, 2002). Values of RPD > 2 were considered excellent, and non reliable when <1.4 (Chang et al., 2001; Dunn et al., 2002). Table 2 shows the prediction statistics for C in the different soil fractions. No attempts were made to predict C/N in the soil fractions due to poor calibrations (Table 1). Standard error of prediction (SEP) was lowest for the fine-sand C and coarse-sand C.

Fig. 1 shows the wavelengths with highest influence in the PLS models for predicting C in different soil fractions. The visible (VIS) part of the

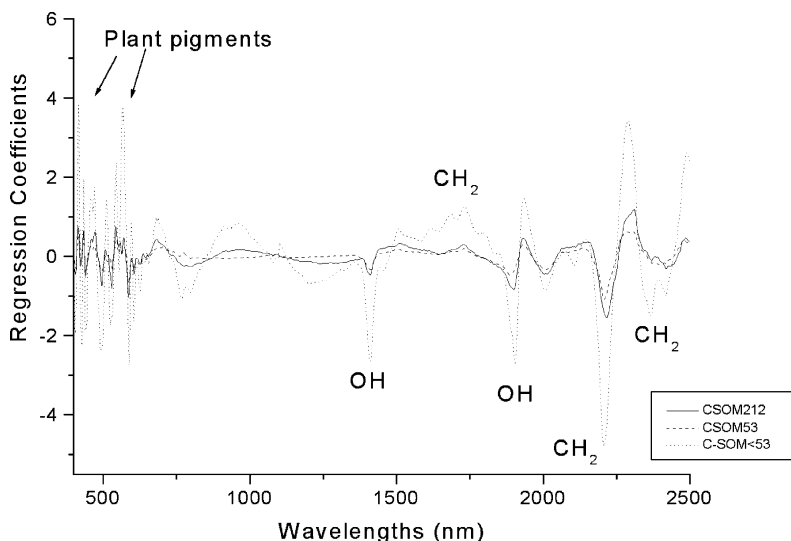


Fig. 1. Partial least squares regression coefficients for the VIS–NIR spectra from the calibration models for soil organic carbon in different soil fractions (PLS terms = 10).

spectrum between 400 and 700 nm had a large influence on calibrations. Regions around 690–700 and 788 nm had particular influence on calibrations of clay + silt C. These wavelengths are associated with absorption from crop and plant residues, as well as from some minerals in the soil matrix (Dalal and Henry, 1986; Morra et al., 1991; Salgó et al., 1998; Daughtry, 2001). The region between 700 and 800 nm is thought to be associated with humic compounds in arable soils and with pigments derived from chlorophyll and phenolic compounds, during decomposition of SOM and plant residues (Daughtry, 2001; Fidencio et al., 2002). Wavelengths around 1400 nm (OH second overtone, related with water) (Murray, 1986), 1700 nm (CH<sub>2</sub> overtones), 1900 nm OH third overtones related with water and at 2200 and 2300 nm (aliphatic C–H and OH phenolic compounds) had large influences on predicting C in soil fractions.

The wavelength at 2218 nm was previously correlated with C in different particle size fractions (Dalal and Henry, 1986; Murray, 1986; Morra et al., 1991). Wavelengths at 1770 and 2020 nm were correlated with C in whole soil (Morra et al., 1991). Although clay was not measured directly in this study, some reports indicated that wavelengths associated with OH overtones (water) could be associated with the presence of montmorillonitic clay, which was abundant in the soils we collected.

The region around 2200 nm was correlated with absorption from clay minerals (Daughtry, 2001; Madejova, 2003). Fig. 2 shows the VIS and NIR spectra of soil samples analysed indicating different groups of samples.

Particle size can have an important effect on diffuse reflectance spectra. Dahm and Dahm (2001) suggested that increased accuracy from NIRS predictions of matrix properties might result from decreased variability in particle size. High simple correlations were found between whole soil C and clay + silt C (Pearson  $r = 0.97$ ), which could explain the excellent calibrations for NIRS and clay + silt C. Another possible explanation could be that small particles absorb much less energy than large particles. Poorer correlations were found between whole soil C and coarse-sand C (Pearson  $r = -0.40$ ) and between whole soil C and fine-sand C (Pearson  $r = -0.50$ ).

Although our results are promising, NIRS has a continual need for calibration and quality control, which can be a major disadvantage. More samples with different characteristics (e.g. soil types, crop rotations) should be incorporated to expand prediction domain and increase prediction accuracy. NIRS spectra gave a global signature of chemical composition and could be useful in understanding interactions of soil organic C in different soil fractions and different agricultural systems.

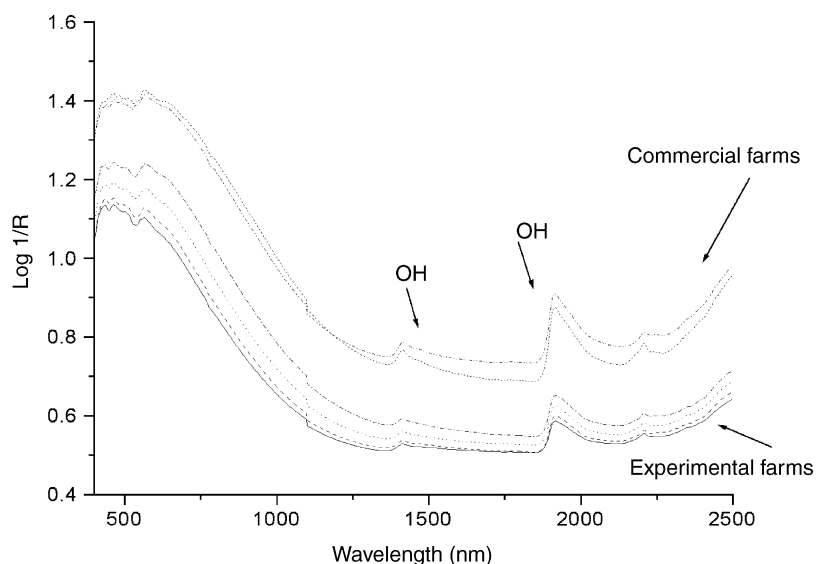


Fig. 2. Visible and near-infrared spectra of soil samples sourced from commercial and experimental farms.

#### 4. Conclusions

Near-infrared reflectance spectroscopy (NIRS) has great potential to predict soil organic C in different particle-size fractions. Despite these encouraging results, caution should be taken regarding the nature of sampling and number of samples analysed for developing prediction equations. The accuracy of NIRS prediction of C/N ratios was not considered good enough to replace routine lab analysis methods. Further work is needed to evaluate different soil types, soil characteristics and agronomic conditions in order to expand the utilization of NIRS for soil C and N predictions in particle-size fractions.

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