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Determination of potentially mineralizable nitrogen and nitrogen in particulate organic matter fractions in soil by visible and near-infrared reflectance spectroscopy

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SUMMARY

Visible (VIS) and near-infrared reflectance spectroscopy (NIRS) combined with multivariate data analysis was used to predict potentially mineralizable nitrogen (PMN) and nitrogen in particulate organic matter fractions (PSOM-N). Soil samples from a long-term experiment ($n=24$) as well as soils under commercial management ($n=160$) in Uruguay (South America) were analysed. Samples were scanned in a NIRS 6500 monochromator instrument by reflectance (400–2500 nm). Modified partial least square regression (MPLS) and cross validation were used to develop the calibration models between NIRS data and reference values. NIRS calibration models gave a coefficient of determination for the calibration (R^2_{CAL}) > 0·80 and the standard deviation of reference data to standard error in cross validation (RPD) ratio ranging from 2 to 5·5 for the variables evaluated. The results obtained in the study showed that NIRS could have the potential to determine PMN and PSOM-N fractions in soils under different agronomic conditions. However, the relatively limited number of samples led us to be cautious in terms of conclusions and to extend the results of this work to similar conditions.

INTRODUCTION

Soil organic matter (SOM) is composed partly of organic carbon (OC) and total nitrogen (TN) and affects the physical, biological and chemical properties of the soil. The mineral N in soil, which is immediately available to plants, can be easily quantified. However, the release of N from organic forms is dependent on mineralization rates. This in turn depends on various factors including the quantity or quality of the organic material, agricultural practices, environmental and soil variables (i.e. pH, aeration, soil structure and texture) (Jarvis *et al.* 1996; Trindade *et al.* 2001; Benbi & Richter 2002).

The quantification of SOM-N mineralization from crop residues on intensively managed agricultural systems is an important step towards improved N use efficiency and reduced losses to the environment (Bundy & Meiseinger 1994; Trindade *et al.* 2001). In addition, soil texture affects soil water retention, plant nutrient storage, organic matter dynamics and carbon sequestration capability (Elliott 1986; Cambardella & Elliott 1992). Therefore the determination of SOM together with soil textural analysis is a key component of any minimum data set to be used for assessing soil quality to elucidate SOM dynamics in soils under different agricultural practices (Cambardella & Elliott 1992). Grassland soils are characterized by their high levels of SOM and high structural stability, however, these properties decrease upon cultivation (Elliott 1986). Soil structure protects SOM turnover and soil fertility as well as avoiding losses in both OC and N (Paul 1984). The ability to estimate quantitatively particulate SOM (PSOM) fractions are especially important to understanding SOM dynamics in intensively managed systems where total SOM changes slowly. Different soil PSOM fractions are related to physical units (sand, clay and silt) which matches the effect of cultivation upon losses of SOM and isolates the PSOM fractions which

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matches the decomposable, the stabilized or SOM pool used in simulation models (Elliott 1986). In general, most of the actual wet chemistry and combustion methods used to determine SOM, OC, TN and PSOM fractions are costly, time-consuming, require specialized equipment and are not widely available for routine soil analysis by commercial or research laboratories in many countries.

Near-infrared reflectance spectroscopy (NIRS) has been used for the quality evaluation of foods and forages since the early 1970s (Murray 1993; Batten 1998). Molecular bonds which dominate the near-infrared (NIR) region containing H attached to atoms such as N, O and C, provide information about the relative proportions of C-H, N-H and O-H bands which are constituents of the organic matrix (Murray 1993; Batten 1998). NIRS calibration is a mathematical process, which uses multivariate regression techniques relating NIR optical measurements (absorbance values) at selected wavelengths (1100–2500 nm) to reference values measured by conventional chemical or physical methods (Deaville & Flinn 2000). The advantages of the NIRS are the speed of the analysis, simplicity in sample preparation, multiplicity of analysis, and that there is no requirement for the use of chemical reagents (Deaville & Flinn 2000). A number of studies have applied NIRS to determine OC and TN in arable soils (Dalal & Henry 1986; Morra *et al.* 1991; Ben-Dor & Banin 1995; Salgó *et al.* 1998; Reeves *et al.* 2001; Morón & Cozzolino 2002), to predict minerals (Malley *et al.* 1999; Chang *et al.* 2001; Dunn *et al.* 2002) and to estimate physical properties (Chang *et al.* 2001; Dunn *et al.* 2002). Recently, NIRS has been used as a tool to determine potentially mineralizable nitrogen (PMN) in organic potting mixes (Smith *et al.* 2001), in heterogeneous soil samples (Fystro 2002) and PMN in Australian soils to predict the optimum rate of N to apply in rice (Russell *et al.* 2002).

The objective of the present work was to explore the potential of NIRS to predict both potentially mineralizable nitrogen (PMN) and N in various PSOM fractions in soils under different experimental and commercial agriculture managed systems in Uruguay (South America).

MATERIALS AND METHODS

Soil samples

The majority of soil samples ($n = 160$) were collected from soils under commercial agricultural production from May to September 1998. The samples were taken from 10 different farms, where different agronomic and soil management were applied. Typical practices included crop-pasture rotations, where the crops occupy 20% of the land area, rotated with seeded grass and legume pastures, as well as tillage and non-tillage. Beef, wool and dairy are the main commodities (García-Prechac *et al.* 2004). Samples came from the Departments of Soriano (South West), Paysandu and Rio Negro (North West) and Tacuarembó (North East) (Uruguay regional divisions). The soil characteristics varied from Hapludalfs (high sand content) to Argiudoll (high content of clay).

Additionally, 24 samples came from four treatments (one field) selected from a long-term experiment established in 1963 in La Estanzuela Agricultural Experimental Research Station, INIA La Estanzuela – Uruguay (34°S, 57°W) (South West). Uruguay is located entirely within the temperate zone where average high and low temperatures in summer (January) are 28 and 17 °C, and in winter (July) are 14 and 6 °C, respectively. Rainfall is relatively evenly distributed throughout the year with mean annual precipitation of 950 mm. The experiment was located in an Argiudoll, silty clay loam soil (C range 15–22 g/kg, N range 1·3–2 g/kg, pH range 5–6·8 in water). The samples selected for calibration came from the following treatments from a long-term experiment: (a) cropping system 1 (CS–1) consisting of continuous crops (wheat, barley, sunflower, sorghum) without application of fertilizers (two crops per year); (b) continuous crops (CS–2) (same crop sequence as CS–1) with N and P fertilizers; (c) (CS–5) a 6-year sequence fertilized with N and P, with 50% of the time under the same crops as CS–1 and CS–2 and the 50% under a grass-legume pasture; (d) (CS–7) a 3-year sequence fertilized with N and P with 67% of the time under crops and 33% under red clover. Conventional tillage was used throughout all the treatments (conventional plough, disc harrow, experimental harvester was used). Pastures were cut, no grazing treatments were applied. Treatments CS–2 and CS–7 had 40 kg P_2O_5/ha/year and between 30–40 kg N/ha/year. Treatment CS–5 received similar P quantities but less N (15 and 25 kg N/ha/year). Treatments were arranged in a randomized complete block design with three replications, with a plot size of 25 × 200 m. In July 1999 soil samples were collected from each experimental unit at two depths (0–7·5 and 7·5–15 cm). Soil cores were taken with a steel coring bit without removing surface residues and collected randomly along the length of each plot. Soil cores were broken apart by hand in the laboratory and passed through a 2 mm sieve while still moist. The sieved soil was dried overnight at 65 °C after which the soil cores taken from each plot and different depths were combined and stored at 4 °C before analysis.

Laboratory analysis and procedures

Total nitrogen (TN) in particulate soil organic matter (PSOM) was measured in 53 to 212 μm (PSOM-N 53) and in 212 to 2000 μm (PSOM-N 212) fractions after soil dispersion and sieving (Cambardella & Elliott 1992) where the N fraction smaller than 53 microns (PSOM-N $<$ 53), was calculated as the difference between TN and the sum of PSOM-N 212 and PSOM-N 53. TN was determined on the different soil fractions by the micro Kjeldhal method and used to calculate the N in the different PSOM fractions (Bremner & Mulvaney 1982). Total organic carbon (OC) in each fraction was determined by wet digestion with an acid solution of potassium dichromate with external heat and reflux condensers, followed by a titration of the excess dichromate using a solution of sulphate of ferrous ammonium (Cambardella & Elliott 1992). Potentially mineralizable nitrogen (PMN) was determined by incubation under waterlogged conditions at 40 °C during 7 days on wet sieved soil samples following the methodology recommended by Bundy & Meisinger (1994). An equivalent of 5 g of oven dry soil was placed in 25 ml glass tubes with 12·5 ml of distilled water. The glass tubes were then sealed and incubated at 40 °C for 7 days. At the end of the incubation period the solution was transferred to 125 ml plastic flasks and then 12·5 ml of 4 M KCl was added. The supernatant was then filtered through Whatman No. 1 filter paper and ammonium was determined using colorimetric analysis with sodium salicillate. PMN was calculated as the difference between the ammonium at the end of the incubation and the initial ammonium value.

Table 1. *Statistics for NIRS calibration and cross validation using all samples and after outlier deleted* (n = *174*)

	R^2_{CAL}	SEC	1-VR	SECV	RPD
Organic carbon	0·94	2·6	0·91	3·1	3·6
Total Nitrogen	0·95	0·2	0·92	0·2	4·5
PSOM-N212	0·83	0·04	0·74	0·05	2·1
PSOM-N53	0·87	0·038	0·82	0·046	2·3
PSOM-N $<$ 53	0·94	0·03	0·90	0·038	5·5
PMN	0·81	13	0·72	16	2·2

R^2_{CAL}, coefficient of determination in calibration; SEC, standard error in calibration; 1-VR, coefficient of determination in validation; SECV, standard error in cross validation; RPD, SD/SECV; PSOM-N212, particulate organic matter nitrogen in 212 fractions; PSOM-N53, particulate organic matter nitrogen in 53 fractions; PSOM-N $<$ 53, particulate organic matter nitrogen in fractions lower than 53.

Spectroscopic procedures and calibration

Dried soil samples were scanned for reflectance in a NIRSystems 6500 monochromator instrument (NIRSystems, Silver Spring, MD, USA). Soil samples (*c*. 10 g) were placed in small circular capsules (55 mm diameter) (Part number NIRSystems IH-0307, USA) and sealed with paper. The visible (VIS) and NIR region were collected (400–2500 nm) at 2 nm intervals, to produce a total of 1050 datapoints. The spectra were the average of 32 successive scans and stored as the logarithm of the reciprocal of reflectance (log $1/R$). Samples were not rotated while spectra were collected. Spectral collection, data manipulation and calibrations were performed using Infrasoft International software (ISI, version 3.01, Infrasoft International, NIRSystems, Silver Spring, MD, USA). The mathematical treatment used in the transformation of the spectra was 1, 4, 4, 1 (ISI, NIRS 2 1995), where the first number indicates the order of derivative (one is first derivative of log $1/R$), the second number is the gap in nm over which the derivative is calculated; the third number is the number of nm used in the first smoothing and the fourth number refers to the number of nm over which the second smoothing is applied (1 = no smoothing) (Shenk & Westerhaus 1993). The regression method used to build the calibration equations was a modified partial least squares regression (MPLS), with cross validation used to estimate the optimal number of terms in the calibration to avoid overfitting (Shenk & Westerhaus 1993). Cross validation estimates the prediction error by splitting the calibration samples into groups (four in this study). The process is repeated until all groups have been used for validation once for calibration purposes (Shenk & Westerhaus 1993). The optimal number of MPLS terms (factors) to be included in the calibration models was determined as having the lowest standard error in cross validation (SECV). The maximum number of MPLS terms used to develop the calibration equation was six in all cases. In spectroscopy, scatter correction can be used to correct the whole spectrum for particle size variation. In the present study standard normal-variate (SNV) and detrending was used as scatter correction (Barnes *et al.* 1989). The resulting calibration equations between the chemical analyses and the NIRS were evaluated based on the coefficient of determination in calibration (R^2_{CAL}) and the SECV (Shenk & Westerhaus 1993). A preliminary calibration was developed using the entire set of samples ($n = 184$) in order to visualize the ability of NIRS to predict these variables in soil (Table 1). Then, a new calibration set was built by selecting randomly two thirds of the samples ($n = 124$), where the remaining one third ($n = 60$) was used as an independent set to test the performance of the calibration set. The standard error of prediction (SEP), bias, slope and simple correlation coefficient (RSQ) were calculated (Shenk & Westerhaus 1993). The CENTER algorithm (ISI, NIRS 2 1995) was used for the calculation of Mahalanobis distance (H) to identify collected spectra of each sample corresponding to each treatment. Samples with standardized H $>$ 3 were identified as outliers and were removed during calibration development.

Table 2. *Composition of soils used to perform NIRS calibrations*

	Units	Mean	s.d.	Min.	Max.	1st quartile	Median	3rd quartile
Organic carbon	g/kg	26·8	11·4	6·4	64·8	34·0	26·1	17·6
Total Nitrogen	g/kg	5·8	12·3	0·1	9·0	3·0	2·1	1·7
PSOM-N212	g/kg	0·12	0·12	0·012	0·66	0·19	0·07	0·04
PSOM-N53	g/kg	0·14	0·11	0·03	0·49	0·20	0·11	0·06
PSOM-N < 53	g/kg	0·08	0·21	0·01	0·90	0·30	0·02	0·06
PMN	mg/kg	44·6	36·3	6	189	54·7	33·5	19·5

s.d., standard deviation; Min., minimum; Max., maximum; PMN, potentially mineralizable nitrogen; PSOM, particulate organic matter fractions; PSOM-N212, particulate organic matter nitrogen in 212 fractions; PSOM-N53, particulate organic matter nitrogen in 53 fractions; PSOM-N < 53, particulate organic matter nitrogen in fractions lower than 53.

As well as H distance, t statistics were also used as selection criteria for outlier samples. Samples with $t > 2·5$ were not considered during calibration development. In all the calibrations less than 10% of outliers were detected. The ratio of standard deviation and SECV (RPD) were used to test the accuracy of the calibration models (Williams 2001; Fearn 2002). An RPD value greater than three was considered acceptable for analytical purposes in most of NIRS applications for agricultural products (Williams 2001; Fearn 2002). However, some reports state that for soil analysis an acceptable RPD value would be 2 or higher (Chang *et al.* 2001).

RESULTS

The mean, standard deviation and range of soil properties analysed are shown in Table 2. A wide range of both PMN and PSOM-N fractions were observed due to different agronomic practices, fertilization levels and crop management under both commercial and the experimental conditions. The various agronomic situations represented by sampled areas are the most common in Uruguay. High positive correlation (Pearson linear correlation, $P < 0·05$) were found among OC and PMN (0·73); OC and PSOM-N 212 (0·70); OC and PSOM-N 53 (0·75); TN and PSOM-N < 53 (0·70); PMN and PSOM-N 212 (0·88); PMN and PSOM-N 53 (0·83). The intercorrelations indicate strong relationships between SOM and PMN as well as PSOM-N fractions, as we would expect due to the nature of the variables evaluated.

Characterization of spectra

Figure 1 shows the spectra in the VIS and NIR region indicating a soil sample with the highest and lowest PMN, respectively. In the VIS region, absorptions around 470 nm and 570 nm are associated with the presence of iron and iron oxides (Kemper & Sommer 2002) and with the absorption of humic and fulvic acid (Kumada 1987), components of the SOM. The spectra of the soil samples showed absorption bands in the near-infrared region at 1414 nm (O-H second overtone), at 1914 nm (O-H bonds) associated with water content and at 2208 nm (C-H overtone) associated with both SOM (Salgó *et al.* 1998; Fidencio *et al.* 2002) and with protein and cellulose from roots and vegetable residues (Chang *et al.* 2001; Daughtry 2001). The second derivative of the spectra (Fig. 2) had a peak corresponding to each major absorption band in the original spectra (Hruschka 1992). The second derivative of the VIS region showed a band of chlorophyll (660 nm, vibration band) indicating the accumulation of SOM due to the different treatments (roots, crop residues and weeds). Two new bands were also observed in the second derivative of the VIS region, around 750 nm related with O-H third overtone (soil moisture) and around 820 nm associated with N-H third overtone, respectively (Murray 1986; Daughtry 2001).

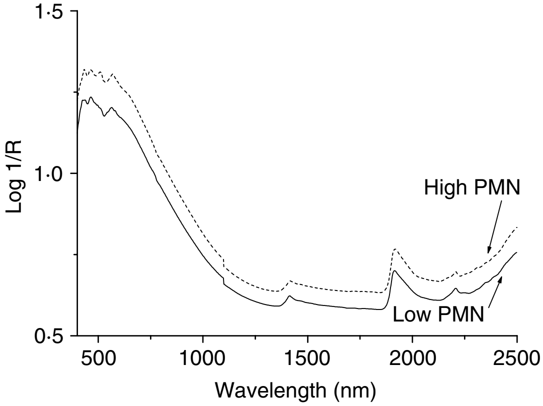

Fig. 1. Visible and near-infrared spectra of soil samples showing the maximum (dotted line) and minimum (line) in potentially mineralizable nitrogen (PMN).

Table 3. *Statistics for prediction using two thirds as a calibration set* (n = *116*) *and one third as validation set* (n = *58*) *and after outlier deletion*

	RSQ	SEP	Bias	Slope	RPD
Organic carbon	0·88	3·9	0·04	1·09	3·0
Total Nitrogen	0·90	0·3	0·03	1·06	4·0
PSOM-N212	0·71	0·06	0·66	1·15	2·0
PSOM-N53	0·85	0·05	0·47	1·19	2·2
PSOM-N<53	0·88	0·03	0·03	1·02	7·0
PMN	0·71	15·6	1·6	0·87	2·3

RSQ, coefficient of regression; SEP, standard error of prediction; RPD, SD/SEP; PSOM-N212, particulate organic matter nitrogen in 212 fractions; PSOM-N53, particulate organic matter nitrogen in 53 fractions; PSOM-N<53, particulate organic matter nitrogen in fractions lower than 53.

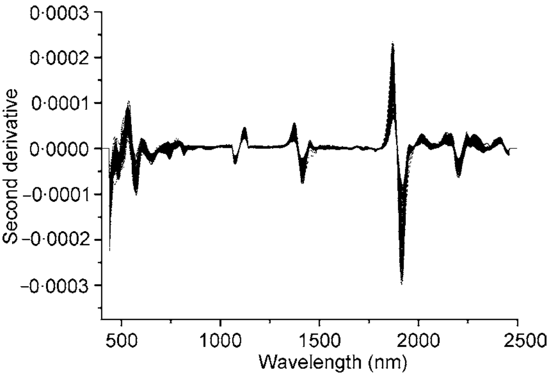

Fig. 2. Second derivative of visible and near-infrared spectra of soil samples.

Near-infrared calibration

The coefficients of determination in calibration (R^2_{CAL}) and the SECV for the soil constituents measured are listed in Table 1. Table 3 shows the prediction statistics using an independent validation set. Good predictions were obtained for PSOM-N53 and PSOM-N<53, where the poorest were for PMN and PSOM-N212. Figure 3 (*a–d*) shows the actual *v.* predicted results for PMN, PSOM-N212, PSOM-N53 and PSOM-N<53 in calibration, respectively. The PLS loadings used to develop the calibration for PMN showed strong negative influence of wavelengths around O-H tones (900, 1400 and 1900 nm) related mainly to water and close to 2200 nm related to SOM (Fig. 4) (Salgó *et al.* 1998; Fidencio *et al.* 2002). Positive correlation was found near 1500 nm (N-H overtones), 2100 and 2370 nm (C-H and C-H_2 combinations) associated with both vegetable residues and SOM (Murray 1986; Daughtry 2001). The loadings used to develop the PMN and PSOM-N calibrations showed the same shape as those used to develop the TN and OC calibrations. The loadings observed in the VIS region were similar to those described above.

DISCUSSION

The spectra of the soil samples showed absorption bands in the near-infrared region assigned to water, SOM and vegetable residues (Salgó *et al.* 1998; Fidencio *et al.* 2002). It has also been reported by other authors that the presence of strong molecular water bands at 1400 and 1900 nm appear to indicate the presence of montmorillonitic clay (Krishnan *et al.* 1980; Madejova 2003). Although clay was not measured directly in the present study, some reports indicated that wavelengths associated with O-H overtones (water) could be associated with the presence of montmorillonitic clay, which is abundant in the soils analysed. The second derivative of the spectra showed absorption bands around 2100 nm related with absorption of the N-H and $CONH_2$ groups, principally associated with structures containing N such as proteins (Murray 1986) (Fig. 2). Both absorptions at 2260 nm (O-H stretch and C=O stretch combination tones) and at 2344 nm (CH and CH_2 overtones) are associated with lignin and cellulose (Murray 1986). These features are associated with SOM and crop residues (Daughtry 2001). In the present study, very good correlations ($R^2_{\text{CAL}} > 0{\cdot}80$) between NIR spectral data and reference values were obtained for both PMN and N in different PSOM fractions. Both PSOM-N212 and PMN showed the lowest calibration statistics in cross validation. The R^2_{CAL} and SECV obtained for PMN were similar in magnitude to those obtained by Fystro (2002), and better than those obtained by other authors (Chang *et al.* 2001; Reeves *et al.* 2001). As reported by Fystro (2002), soil texture and structure is considered to have an important effect on mineralization, therefore the correlation between collected spectra and particle size or clay content may have had an important influence during the NIR calibrations. The former could indicate that low particle size fractions associated with different components of the SOM would have a better signal in the NIR region. The results show that good predictions were obtained for both PSOM-N<53 and PSOM-N53, respectively. The accuracy of the

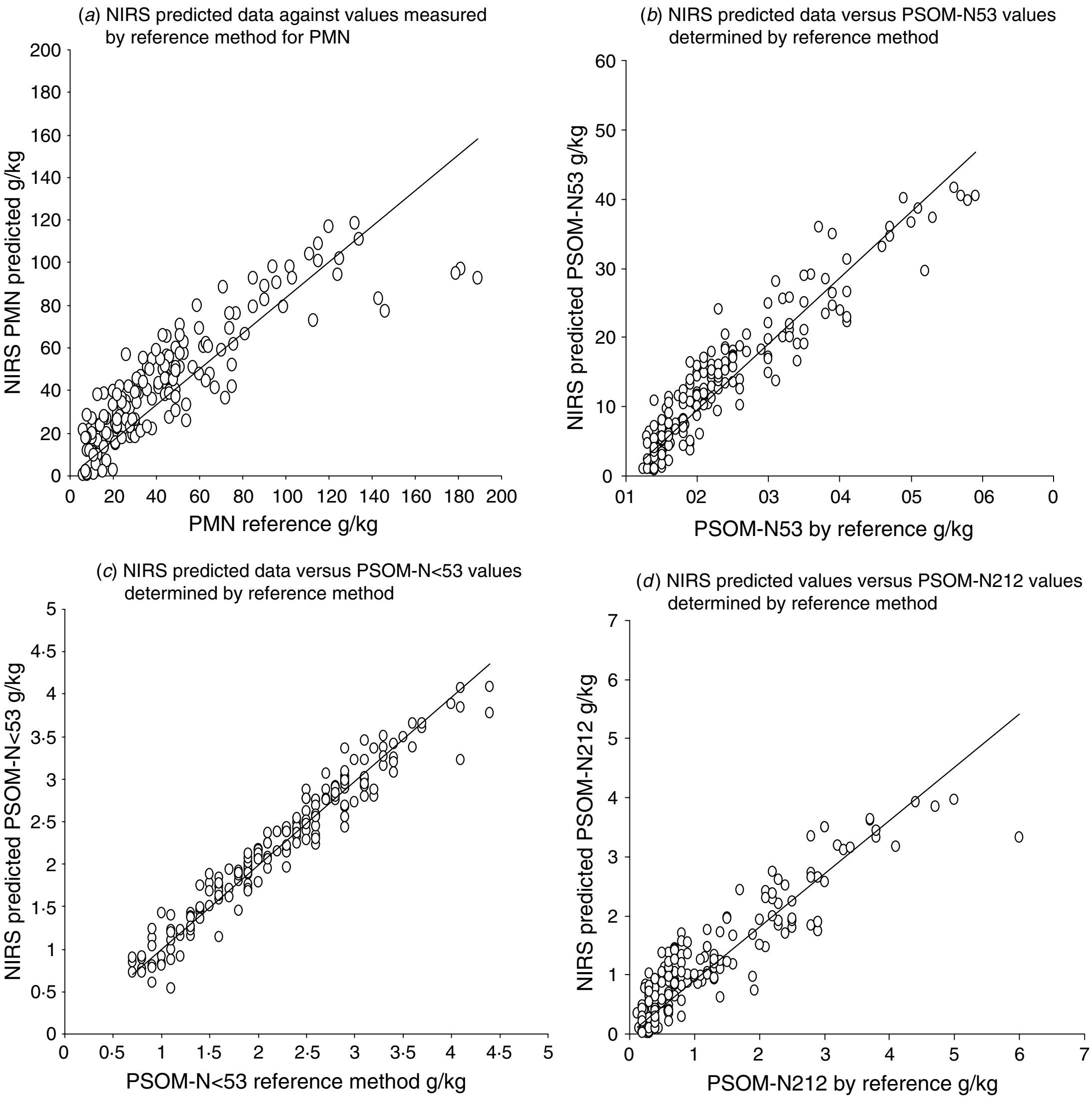

Fig. 3. NIRS predicted data *v*. chemical reference data in soil samples for (*a*) PMN, (b) PSOM-N53, (*c*) PSOM-N < 53 and (*d*) PSOM-N212.

calibrations was also tested using the RPD ratio defined previously by other authors (Williams 2001; Fearn 2002). The interpretation of the RPD depends very much on the context and the purpose for which the measurement is to be used (Chang *et al.* 2001). In the present study the PSOM-N < 53 fraction gave the highest RPD (RPD = 7) considered excellent for analytical purposes. The other three parameters gave intermediate values in terms of their value as an analytical tool (RPD < 3). However, these results showed that NIR could be used to predict these soil quality parameters as an indicator variable of the quality of SOM to be used in routine analysis (i.e. high, low or medium). It was observed that 2% of the samples in either calibration or validation were considered as outliers, although these samples did not show any relevant or particular spectral feature or soil property. It is well known that when using a small set of samples or those with small variation, the risk of overfitting the NIR calibration models is high. However, in the present study the validation results confirmed that the prediction of these soil parameters were possible combining the VIS-NIR region. Some non-linearity effects were also observed (Fig. 3*a*, *d*). However, it

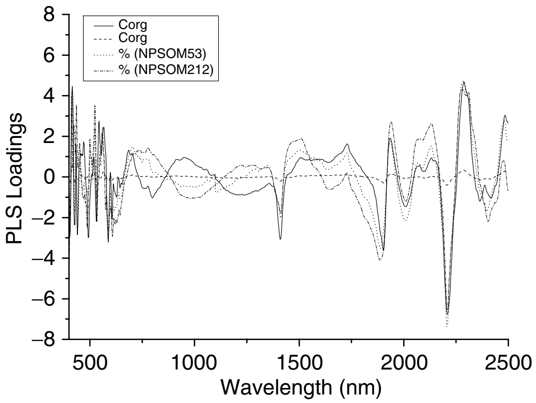

Fig. 4. Partial least squares loading for VIS-NIR calibrations on soil samples. PSOM, particulate organic matter fractions; PSOM-N212, particulate organic matter nitrogen in 212 fractions; PSOM-N53, particulate organic matter nitrogen in 53 fractions; PSOM-N<53, particulate organic matter nitrogen in fractions lower than 53.

was difficult to know exactly the causes for this effect. One possible cause will be related with detector saturation at high analyte concentration observed for PMN and PSOM-N212. Similar effects were reported in agricultural products by other authors (Martens & Naes 2001). Unlike other soil chemical or physical analysis, PMN is related to a biochemical process, and does not have unique features in the VIS-NIR region due to variations on the amount of SOM, the nature of the SOM or other soil properties (Reeves *et al.* 2001). SOM contains large amounts of N as readily decomposable proteins and will have higher PMN than soils with large amounts of N due to other sources. Experimental treatments, as well as commercial farms that included pastures in the system showed the highest values in PMN, resulted from organic matter accumulation as well as TN content. Tillage also produces bio-degradation of plant residues and led to increases in SOM (effect not evaluated in the present study). The presence of different forms of N in the soil matrix, the SOM and the different residues due to tillage, agricultural practices and agronomic conditions may explain the correlations between NIR spectra and reference values for PMN. As reported by other authors, the composition of the soil varied greatly due to factors such as tillage, depth, location and vegetation (Cambardella & Elliot 1992; Dunn *et al.* 2002; Fystro 2002). These combined factors result in a very diverse sample population set in which biological, chemical and physical characteristics of the soil vary across the data, although not addressed in the present study. NIRS calibration models will only be accurate for unknown samples when the samples used to generate the calibration reflect the spectral variability of the unknowns. In the present study, the samples used in the validation set were selected randomly from the original set of samples, with the aim of representing the variability of the population. It is important to take into account that when calibrations are developed, the models have to deal not only with quantitative differences (amount of OC, TN) but also with qualitative differences (tillage *v.* non-tillage, different crops). In order to understand the relationship between spectra and reference values, the complexity of the calibrations is also increased when parameters constructed or derived from theoretical models or artificial measures such as those analysed in this study are incorporated into the calibration models. A single soil property is often related to complex and inter-related underlying soil chemistry which spectroscopy and multivariate analysis might help to resolve (Janik *et al.* 1998). Because some variables may not have any particular feature in the VIS-NIR spectrum, in terms of overall spectral variation as well as correlation between variables (i.e. co-correlation between clay or SOM with PMN). This implies that in order to extend the results of the present study to other soils or agronomic situations, the spectral and data variation accounted by each new, different, soil analysed will need to be incorporated, if the objective is to develop a robust calibration for analytical purposes (i.e. regional or universal calibration). NIRS shows the potential to predict PMN and N in PSOM fractions in the soil samples analysed. Taking into account the nature of the parameters analysed, the accuracy of the NIRS calibrations were considered to be excellent. Although these results are promising, NIRS still requires the need for further calibration and quality control. Calibrations with greater sample variation (region, management) could be used to improve both prediction robustness and accuracy of the NIRS models then developed.

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