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# The potential of near-infrared reflectance spectroscopy to analyse soil chemical and physical characteristics

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## SUMMARY

Near-infrared reflectance spectroscopy (NIRS) was used for the analysis of soil samples for silt, sand, clay, calcium (Ca), potassium (K), sodium (Na), magnesium (Mg), copper (Cu) and iron (Fe). A total of 332 samples of different soils from Uruguay (South America) were used. The samples were scanned in a NIRS 6500 (NIRSystems, Silver Spring, MD, USA) in reflectance. Cross validation was applied to avoid overfitting of the models. The coefficient of determination in calibration ($R^2_{cal}$) and the standard errors in cross validation (SECV) were 0·80 (SECV: 6·8), 0·84 (SECV: 6·0), 0·90 (SECV: 3·6) in per cent for sand, silt and clay respectively. For both macro and microelements the $R^2_{cal}$ and SECV were 0·80 (SECV: 0·1), 0·95 (SECV: 2·9), 0·90 (SECV 0·8), for K, Ca, Mg in g/kg respectively, and 0·86 (SECV: 0·82) and 0·92 (SECV: 25·5) for Cu and Fe in mg/kg. It was concluded that NIRS has a great potential as an analytical method for soil routine analysis due to the speed and low cost of analysis.

## INTRODUCTION

Soil chemical and physical characteristics are especially important for understanding organic matter dynamics in intensively managed systems as we move toward adoption of more environmentally friendly and sustainable practices (Cambardella & Elliott 1992). Organic carbon (C), total nitrogen (N) and pH of the soil are the major constituents measured in conventional soil analysis. These are used to characterize the different soil types and to detect the effects of different soil cultivation and management. On the other hand, to obtain a better response from inputs in agriculture, cost-effective soil analysis is needed so these inputs can be applied (Dunn *et al.* 2002). However, the conventional analytical determinations of chemical and physical characteristics of soils are time consuming, tend to destroy samples and use many chemical reagents.

Near-infrared reflectance spectroscopy (NIRS) has been in use since the 1970s for the evaluation of foods and forages (Murray 1993; Batten 1998). The NIR spectral region is dominated by weak overtones and combinations of vibrational bands of atoms that have strong fundamental vibrations in the mid-IR. These chemical bonds contain hydrogen attached to atoms such as nitrogen, oxygen and carbon (Wetzel 1983; Dalal & Henry 1986; Osborne *et al.* 1993). Spectroscopy in the near-infrared region will provide information about the relative proportions of C–H, N–H and O–H bonds that are the primary constituents of the organic molecules (Murray 1993). NIRS relies on calibrations, which utilize absorbances at many wavelengths, to predict composition of a sample (Murray 1988; Batten 1998).

The advantages of NIRS are speed of analysis, simplicity in sample preparation, multiplicity of analysis and that it does not use chemical reagents (Norris *et al.* 1976; Osborne *et al.* 1993; Deaville & Flinn 2000).

Several authors have reported the use of NIRS to determine C and N in arable soils (Dalal & Henry 1986; Morra *et al.* 1991; Ben-Dor & Banin 1995; Salgó *et al.* 1998; Reeves *et al.* 1999; Reeves & Van Kessel 1999). More recently, some authors have reported the use of NIRS to predict micronutrients in soil samples (Malley *et al.* 1999; Chang *et al.* 2001; Dunn *et al.* 2002). According to those authors, the results achieved appeared promising, but importantly many of the investigations involved a limited number of samples, or the samples came from a limited number of sites of similar range of soils. To have widespread commercial

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usefulness, NIR needs to be a reliable analytical technique across a range of soil types where variations in the inorganic and organic components of soils are present (Dunn *et al.* 2002).

The objective of the present work was to explore the use of near-infrared reflectance spectroscopy to predict soil physical characteristics (sand, silt and clay), macro elements (Ca, K, Mg) and microelements (Fe, Cu) in a wide range of soils in Uruguay, South America.

## MATERIALS AND METHODS

A total of 332 soil samples were taken from different locations across Uruguay. At each site 10 to 15 cores, 0–15 cm depth were collected and mixed to make a composite sample.

Soil samples were taken from different regions of Uruguay and in different years (1997–99), having different physical and chemical characteristics due to different soil types and management. Soil samples represent most of the agricultural soils present in Uruguay (about 80%) and approximately 30% of the samples came from either sandy or red soils.

In all cases, the soils were under pasture conditions (alfalfa or white clover), pure or associated with other species. The predominant soil types in the different regions were classified according to the system of classification of soils of the Uruguay Ministry of Agriculture and Fisheries (Ministerio de Agricultura y Pesca 1979): (a) Florida region: Brunosol Eutrico and Vertisol (Units Isla Mala, Tala-Rodriguez and Trinidad); (b) Young region: Brunosol Eutrico (Units Young and San Manuel) and Argisol dìstrico (Units Algorta and Tres bocas); (c) East region: Brunosol Subéutrico and Argisol Subéutrico (Unit Alferez); (d) North region: Litosol Eutrico (Unit Queguay Chico); Brunosol Eutrico (Units Queguay Chico, Itapebì-Tres Arboles); Vertisol (Units Queguay Chico, Itapebi-Tres Arboles, Cuaró); Brunosol Subéutrico (Units Constitution, Cuchilla Palma, Arroyo Hospital); Planosol Eutrico (Unit Cuaró) and Luvisol ócrico (Unit Cuchilla Corrales).

Before soil analysis, samples were dried at 40 °C in a forced-air oven for 24 h, crushed and sieved through a 2-mm Wiley mill (Arthur H. Thomas, PA, USA). For physical characteristics, samples were sieved through a 0·053-mm sieve (silt and clay fractions) and a 0·212-mm sieve (sand fractions). Silt was estimated by difference (sand − clay) (Gee & Bauder 1986). The physical fractions were expressed as per cent.

The macro and microelements were analysed according to reference methods, using atomic absorption spectroscopy (AAS) (Bremner 1965). Potassium, Ca and Mg were measured in a solution of ammonium acetate; Cu in DTPA-EA solution, followed by AAS analysis.

The samples were scanned dry in a NIRS 6500 monochromator (NIRSystems, Silver Spring, USA) in reflectance mode from 400 to 2500 nm at 2 nm intervals. Small circular cups of 55 mm diameter were used (Part number NIRSystems IH-0307, USA). The spectra were stored in the form of logarithm of the reciprocal reflectance (log $1/R$).

The mathematical treatment used in the transformation of the spectra was 1, 4, 4, 1 (ISI, Infrasoft International; NIRS 2 1995). 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 (Shenk & Westerhaus 1993). The regression method used to build the equations was modified partial least squares regression (MPLS) (Shenk & Westerhaus 1993) with standard normal-variate and detrend (SNV-D) (Barnes *et al.* 1989). Cross validation was used to avoid overfitting of the equations. Cross validation estimates the prediction error by splitting the calibration samples into groups (four in the present study). One group is reserved for validation and the remaining groups are used for calibration. The process is repeated until all groups have been used for validation once (Shenk & Westerhaus 1993).

Calibration statistics calculated include the standard error of calibration (SEC), the coefficient of determination in calibration ($R^2_{\text{cal}}$), the standard error of cross validation (SECV) and the coefficient of determination in cross validation (1-VR) (Shenk & Westerhaus 1993).

The resulting calibration equations of the regression between the chemical analyses and the NIRS were evaluated in terms of the coefficient of determination in calibration ($R^2_{\text{cal}}$) and the standard error in the cross validation (SECV) (Shenk & Westerhaus 1993). Two outlier detection methods provided by the ISI software were applied: $t$ and $H$. The $t$ statistic outliers, having residuals from the reference analysis of greater than 2·5 times SEC, are samples whose reference analysis is in doubt. These should be re-analysed by the reference method. The $H$ statistic outliers are samples whose spectra are atypical of all the others that make up the calibration set. They may not belong in the population.

The S.D./SECV ratio (standard deviation of the population to standard error in cross validation) for the NIRS calibration models for the chemical and physical parameters evaluated demonstrates how well the calibration models could predict chemical data. This ratio is known as the RPD statistic. If a product shows a narrow range in composition, or if the error in estimation is large compared with the spread (as S.D.) in composition, then regression finds increasing difficulty in finding stable NIR calibrations. Where the error exceeds one-third of the S.D. of the population, regression can be misleading.

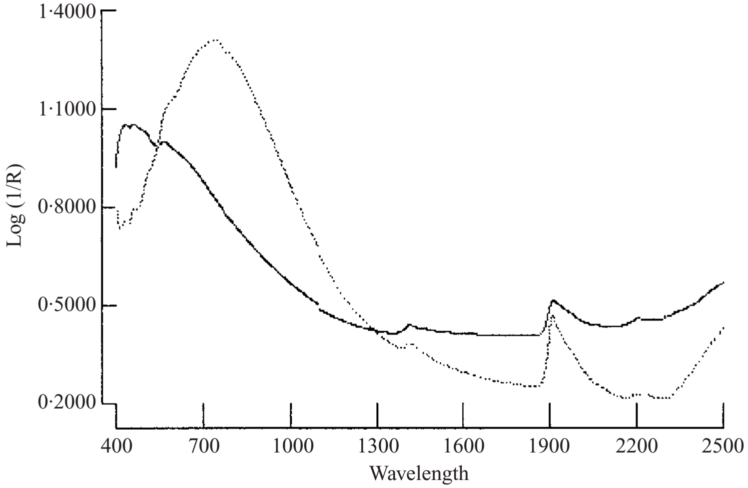

Fig. 1. Visible and near-infrared mean spectra of soil samples and standard deviation (dotted line).

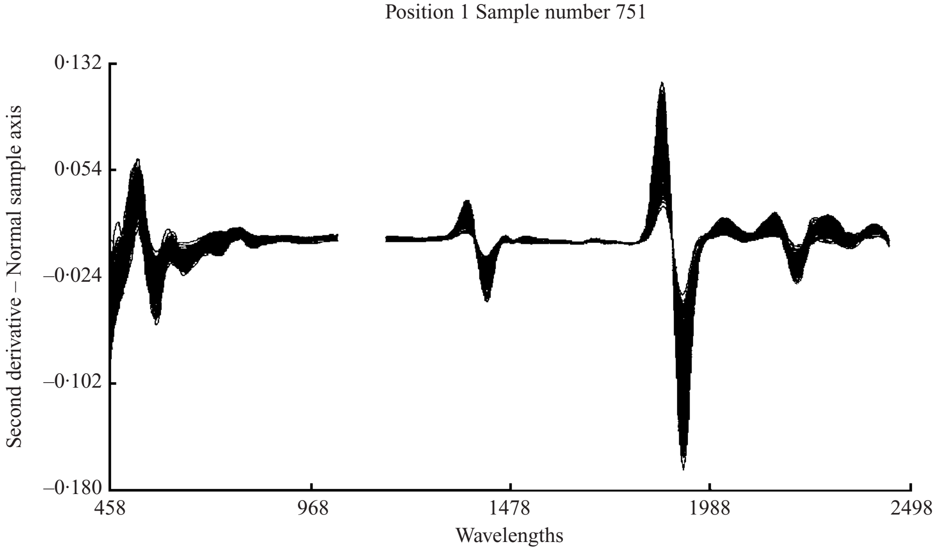

Fig. 2. Second derivative of visible and near-infrared spectra of soil samples.

## RESULTS

Figure 1 shows the mean spectrum and standard deviation of soil samples in the visible and near-infrared region. The mean spectrum showed prominent absorption bands in the near-infrared region at 1414 and 1914 nm related with O–H bands (water) and at 2208 nm related with CH absorption and combination bands. The second derivative of the mean spectrum shows three new absorption bands (Fig. 2).

The absorption band at 2080 nm could be related to absorption of the amine N–H group and $CONH_2$ groups because this region is associated with chemical structures such as protein. Absorption bands at 2260 nm were related with absorption of CH and CH combination tones and at 2344 nm to the absorption of CH and $CH_2$ (cellulose).

Table 1 shows descriptive statistics for the soil analysed. A wide range of physical and chemical characteristics was observed, representing most of the soils present in Uruguay. Most of the samples came from arable soils containing between 30 and 45% clay and 40 to 50% silt (about 80% of the Uruguayan agricultural territory). The $R^2_{cal}$ for physical characteristics were higher than 0·80 (Table 2). The SECV for macro elements were 0·10 for K, 2·9 for Ca and 0·73

Table 1. *Mean, standard deviation* (S.D.) *and range for physical components, macroelements and microelements in soil samples* (*dry weight*)

| | Units | Mean | S.D. | Min | Max |
|---|---|---|---|---|---|
| Sand | % | 24·8 | 12·7 | 2 | 71 |
| Silt | % | 47·6 | 13·1 | 18 | 74 |
| Clay | % | 27·8 | 9·6 | 8 | 53 |
| K | g/kg | 0·48 | 0·2 | 0·13 | 1·4 |
| Ca | g/kg | 18·1 | 9·5 | 2·6 | 43·1 |
| Mg | g/kg | 3·9 | 2·2 | 0·37 | 14·6 |
| Cu | mg/kg | 3·2 | 3·2 | 0·6 | 31·3 |
| Fe | mg/kg | 131 | 84·2 | 8 | 528·1 |

Table 2. *Calibration and cross validation statistics for physical parameters, macroelements and microelements in soil samples* (*dry weight*) (*units as in Table 1*)

| | *n* | $R^2_{\text{cal}}$ | SEC | 1-VR | SECV | SEP |
|---|---|---|---|---|---|---|
| Sand | 319 | 0·80 | 5·7 | 0·70 | 6·8 | 7·2 |
| Silt | 317 | 0·84 | 5·1 | 0·80 | 6·0 | 6·2 |
| Clay | 321 | 0·90 | 3·3 | 0·86 | 3·6 | 3·8 |
| K | 317 | 0·80 | 0·1 | 0·72 | 0·1 | 0·1 |
| Ca | 309 | 0·95 | 2·1 | 0·90 | 2·9 | 4·2 |
| Mg | 315 | 0·90 | 0·6 | 0·90 | 0·8 | 0·9 |
| Cu | 310 | 0·86 | 0·7 | 0·82 | 0·8 | 1·6 |
| Fe | 311 | 0·92 | 21·3 | 0·90 | 25·5 | 32·2 |

$R^2_{\text{cal}}$ coefficient of determination in calibration; SEC, standard error in calibration; 1-VR, coefficient of determination in cross validation; *n*, number of samples used to perform the calibration; SECV, standard error of cross validation; SEP, standard error of prediction.

for Mg in g/kg and for microelements 0·82 and 25·5 for Cu and Fe in mg/kg respectively (Table 2). A poor relationship was observed between chemical reference and NIRS for K.

Figures 3, 4, 5, 6 and 7 illustrate the relationship between NIRS optical data with chemical reference data for Ca, K, Mg, Fe and Cu in soil samples. The more accurate the predictive equation, the more closely all points cluster near the theoretical 1:1 (solid line) correspondence. In the present work less than 10% of outliers were detected. The presence of these outliers could be explained by atypical samples in the population used to perform the calibration equations (some soils with reddish colour from basaltic material). On the other hand, outlier samples were detected on soils with high sand content. For Ca the high values correspond with soils containing high levels of either chalk or limestone. For Mg, Fe and Cu, NIRS calibration models seem to work well in the lower range.

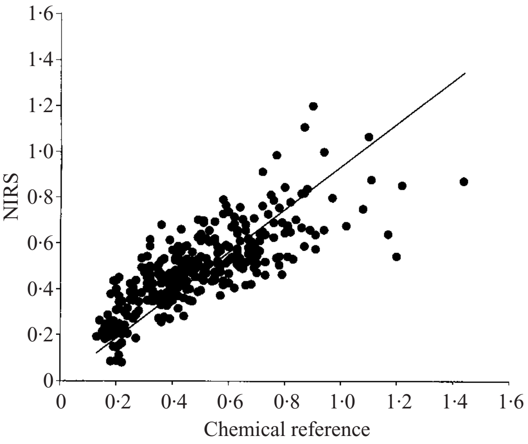

Fig. 3. NIRS predicted data *v*. chemical reference data for K in soil samples (g/kg).

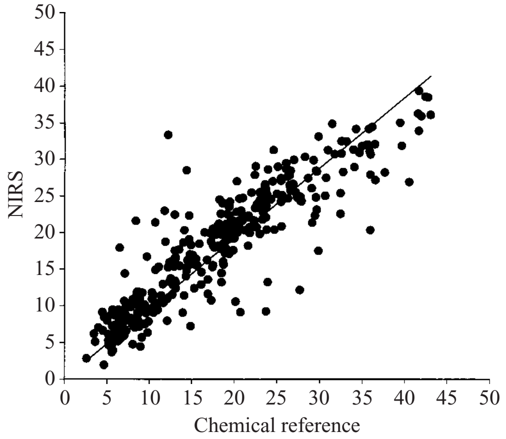

Fig. 4. NIRS predicted data *v*. chemical reference data for Ca in soil samples (g/kg).

The S.D./SECV found in the present study were 1·9 for sand, 2·2 for lime, 2·7 for clay, 2 for K, 3·3 for Ca, 2·8 for Mg, 2 for Cu and 3·3 for Fe, indicating that all the NIRS calibration models were moderately acceptable.

## DISCUSSION

The visible and NIR regions showed absorption of O–H bonds (1914 nm) related with water, O–H second overtone (1414 nm) and with absorption of C–H overtone (2208 nm) related with organic matter, respectively (Murray 1986; Salgó *et al*. 1998). Organic matter has multiple absorption bands between 2100 and 2400 nm (Morra *et al*. 1991; Salgó *et al*. 1998). Soil minerals have distinct spectral fingerprints in the NIR

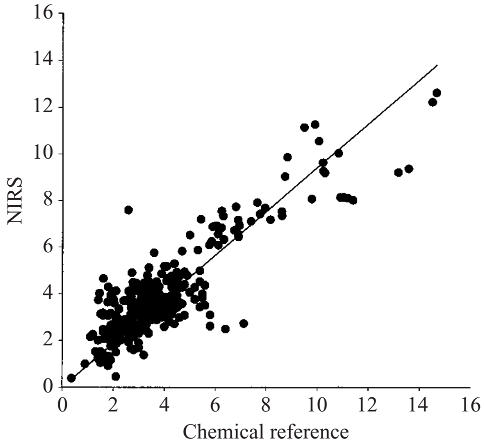

Fig. 5. NIRS predicted data *v*. chemical reference data for Mg in soil samples (g/kg).

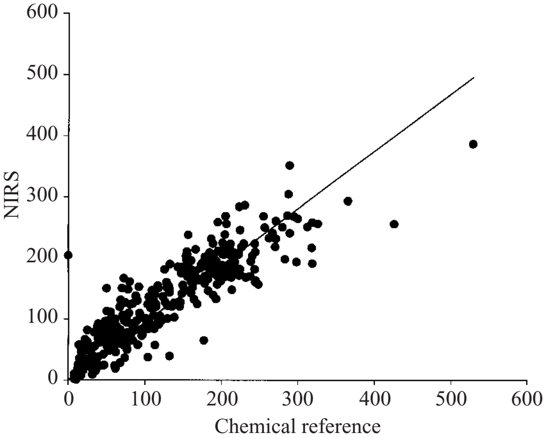

Fig. 6. NIRS predicted data *v*. chemical reference data for Fe (mg/kg).

region because of relatively strong absorption of the overtones and combination modes of the OH, sulphate and carbonate groups (Fidencio *et al.* 2002). However, in the soil matrix, macro and microelements are associated with organic matter fractions or under the form of oxides, hydroxides and other compounds. Chang & Laird (2002) reported that absorption bands around 2340–2500 nm could be related to $CaCO_3$, possibly related with the carbonate ion. Humic acids also have absorption at 2310–2350 nm and around 1700–2150 nm (Chang & Laird 2002). The spectral bands found in this study are consistent with data reported by other authors (Stenberg & Nordkvist 1995; Meyer 1998; Chang *et al.* 2001; Fidencio *et al.* 2002).

Soil NIRS calibration statistics for both chemical and physical characteristics in the present study agreed with those reported by others (Chang *et al.* 2001; Dunn *et al.* 2002). Although physical properties showed lower $R^2_{cal}$ these results suggested that physical fractions could be predicted by NIRS. Macro and microelements had the best $R^2_{cal}$ and gave the lowest SECV.

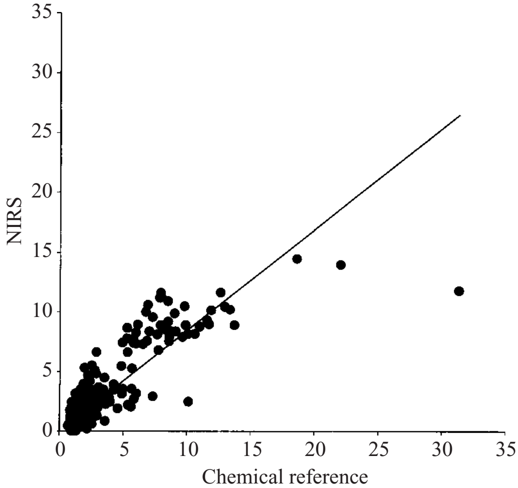

Fig. 7. NIRS predicted data *v*. chemical reference data for Cu in soil samples (mg/kg).

The ability of NIRS to predict levels of minerals in soil may be due to the relationship between elements and soil organic matter (Chang *et al.* 2001) and between organic matter and particle size (Dalal & Henry 1986).

High simple positive correlations ($P > 0{\cdot}05$) were found between Ca and clay (0·80), K and clay (0·60), Mg and clay (0·51), Cu and Mg (0·71) and negative correlation for Mg and sand (−0·63). These high correlations between physical properties and chemical parameters could explain some of the NIRS calibrations obtained.

It is often difficult to compare results from different calibrations using the $R^2_{cal}$ or the standard error of prediction (SEP). Clark *et al.* (1987, 1989) proposed the use of the coefficient of variation (CV) values as a means to facilitate the evaluation of equation performance. While much effort has been applied to the development of calibration for agricultural products, no critical levels of RPD have been set for NIRS analysis of soils (Dunn *et al.* 2002). The RPD was suggested by other authors to evaluate NIRS calibration performance on both soil physical and chemical properties (Dunn *et al.* 2002). When near-infrared spectroscopy is used for agricultural products applications, RPD higher than 3 for NIRS calibrations are considered acceptable, and when RPD is higher than 5 calibrations are considered excellent (Malley *et al.* 1999; Dunn *et al.* 2002).

Reports by other authors (Chang *et al.* 2001) state that NIRS has the ability to predict values of soil properties using the following categories for RPD statistics: $>2$; 1·4–2; $<1{\cdot}4$. These authors suggested that prediction of soil properties in the middle category between 1·4 and 2 could be improved by using different calibration strategies, while properties in the lower category may not be reliably predicted by NIRS.

However, Dunn *et al.* (2002) suggested that when using NIRS for the analysis of soils for site-specific agriculture, suitable limits for RPD may be: $<1{\cdot}6$ poor; 1·6–2·0 acceptable; and $>2{\cdot}0$ excellent. In the present work sand, Cu and K fall in the acceptable range using the above classification while silt, clay, Ca, Mg and Fe fall into the excellent category.

The results suggest that useful prediction of chemical and physical characteristics of soils were obtained by NIRS.

The calibration and cross validation statistics obtained showed the potential of NIRS to predict macro and microelements in soils, particularly for Ca, Mg and Fe, as well as silt and clay. For rapid field and laboratory measurements, the accuracy obtained by the NIRS method is quite sufficient judging by the S.D./SECV obtained. The results show the potential of NIRS as a method for the routine determination of both chemical parameters and physical properties in soils of Uruguay. Further work will be carried out for the determination of other macro and microelements, and for the prediction of soil carbon and nitrogen mineralization.

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