Determination of chemical and physical properties in arable soils in Uruguay by near infrared reflectance spectroscopy

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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.[1] Organic carbon (C), total nitrogen (N) and pH of the soil are the mayor constituents measured in conventional soil analysis. However, the conventional analytical determinations of chemical and physical characteristics of soils are time consuming, sample destructing and use many chemical reagents. Near infrared reflectance spectroscopy (NIRS) has been in use since the 1970´s for the evaluation of foods and forages.[2] 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.[3] 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.[2] NIRS relies on calibrations, which utilize absorbances at many wavelengths, to predict composition of a sample. [2, 3] Several authors have reported the use of NIRS to determine C and N in arable soils. [4, 5, 6] More recently, some authors have reported the use of NIRS to predict micronutrients in soil samples.[7, 8] 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. The objective of this work was to explore the use of near infrared reflectance spectroscopy to predict soil physical characteristics (sand, lime 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 three hundred and thirty two (n: 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 (1979).[9] 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 0.212-mm sieve (sand fractions). Silt was estimated by difference (sand - clay).[10] The physical fractions were expressed as per cent. The macro and microelements were analysed according to reference methods, using atomic absorption spectroscopy (AAS).[11] Potassium, Ca and Mg were measured in a solution of ammonium acetate, while 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; NIRS2 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.[12] The regression method used to build the equations was modified partial least squares regression (MPLS) with standard normal-variate and detrend (SNV-D).[13] Cross validation estimates the prediction error by splitting the calibration samples into groups (four in this 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. Calibration statistics calculated include the standard error of calibration (SEC), the coefficient of determination in calibration (R^2_{cal}), the standard error of cross validation (SECV) and the coefficient of determination in cross validation (1-VR).[12] 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_{cal}) and the standard error in the cross validation (SECV). Two outlier detection provided by the ISI software were applied: t and H. The t statistics outliers having residuals from the reference analysis of greater than 2.5 times SEC, are samples whose reference analysis is in doubt.[12] These should be re-analysed by the reference method. The H statistics 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 SD/SECV relationship (standard deviation of the population to standard error in cross validation) for the NIRS calibration models for the chemical and physical parameters evaluated, demonstrate how well the calibration models could predict chemical data. This ratio is known as the RPD.[14] If a product shows a narrow range in composition, or if the error in estimation is large compared with the spread (as SD) in composition, then regression finds increasing difficulty in finding stable NIR calibrations. Where the error exceeds one-third of the SD of the population, regression can be misleading.

Results and discussion

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 nm and 1914 nm related with O-H bands (water) and at 2208 nm related with CH absorption and combination bands.[15] 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).[9] The R^2_{cal} for physical characteristics were higher than 0.80 (Table 1). The SECV for

macro elements were 0.10 for K, 2.9 for Ca, and 0.73 for Mg in g/kg and for microelements 0.82 and 25.5 for Cu and Fe in mg/kg respectively (Table 1).
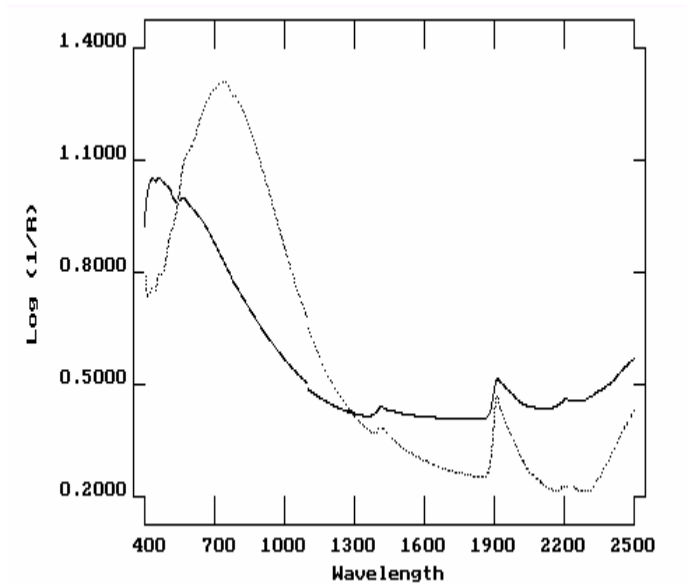

Figure 1. VIS and NIR mean spectrum of soil samples (whole line) and standard deviation (dotted line).

Table 1. Near infrared calibration statistics for chemical and physical characteristics in Uruguayan soils.

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

A poor relationship was observed between chemical reference and NIRS for K. Figures 2, 3, and 4, and illustrate the relationship between NIRS optical data with chemical reference data for Ca, K, and sand in the soil samples analysed. 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 per cent 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 seems to work well in the lower range. The SD/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 moderate acceptable. In the soil matrix, macro and microelements are associated with organic matter fractions or under the form of oxides, hydroxides and other compounds. Soil NIRS calibration statistics for both chemical and physical characteristics agreed with those reported by others.[8] 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. The ability of NIRS to predict levels of minerals in soil may due to the relationship between elements and soil organic matter and between organic matter and particle size.[4, 8] High simple positive correlations (P > 0.05) 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). The correlations between physical properties and chemical parameters could explain the NIRS calibration obtained for macro and micro elements.

Conclusions

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 lime and clay. For rapid field and laboratory measurements, the accuracy obtained by NIRS method is quite sufficient judging by the SD/SECV obtained. The results show the potential of NIRS as a method for the routine determination of both chemical parameters and physical properties in soil 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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