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CHEMICAL CHARACTERIZATION OF VOLCANIC SOILS USING NEAR INFRARED SPECTROSCOPY (NIRS)

CARACTERIZACIÓN QUIMICA DE SUELOS VOLCANICOS UTILIZANDO ESPECTROSCOPIA DE INFRARROJO CERCANO (NIRS)

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RESUMEN

La cuantificación de la concentración de nutrientes en los suelos es importante para la implementación de estrategias de fertilización adecuadas y mejorar la productividad agrícola. En las últimas décadas se han desarrollado nuevos métodos instrumentales, tales como el uso de la espectroscopía de infrarrojo cercano (NIRS). Aunque su potencial ha sido reconocido por los científicos del suelo durante algunas décadas, el uso de NIRS para el análisis de rutina del suelo, según nuestro conocimiento, está poco desarrollado en Chile. Los modelos de calibración se desarrollaron utilizando la regresión de mínimos cuadrados parciales (PLSR). El objetivo de este estudio fue evaluar el uso de NIRS para la determinación de la concentración de calcio, magnesio, fósforo, potasio, pH (agua), materia orgánica, sodio, aluminio intercambiable, amonio y nitrato en suelos volcánicos del sur de Chile. El coeficiente de determinación en la calibración obtenida fluctuó entre 0,79-0,95 y 0,79-0,89, en Andisoles y Ultisoles, respectivamente; los valores de la desviación de predicción residual (RPD) variaron entre 2,1-4,4 y 2,2-3,1, en Andisoles y Ultisoles, respectivamente; y no fue posible generar modelos de calibración robustos para Al Exch, Na y NH_4^+ en Andisoles y Al Exch, Mg, NO_3^- y Na en Ultisoles. Aunque algunos de los modelos desarrollados presentaron elevados R^2, esta metodología requiere una validación adicional que incluya un mayor número de muestras, una distribución espacial más amplia que cubra una variedad de condiciones climáticas y agrícolas.

Palabras clave: suelos volcánicos, modelo de calibración, FT-NIRS, composición mineral.

ABSTRACT

The quantification of nutrient concentration in soils is important for the implementation of adequate fertilization strategies, and also to improve agricultural productivity. In recent decades, new instrumental methods have been developed, including the use of near infrared spectroscopy (NIRS). Although its potential has been recognized by soil scientists for a few decades, the use of NIRS for routine soil analysis has been, to the best of our knowledge, poorly developed in Chile. Calibration models were developed by partial least squares regression (PLSR). The objective of this study was to assess the use of NIRS for the determination of concentrations of Calcium, Magnesium,

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Phosphorus, Potassium, pH (water), organic matter, Sodium, exchangeable aluminum, ammonium and nitrate in volcanic soils of southern Chile. The coefficient of determination in the calibration obtained ranged from 0.79 to 0.95 and 0.79 to 0.89 in Andisols and Ultisols, respectively. The residual prediction deviation (RPD) values varied between 2.1 and 4.4 in Andisols, and between 2.2 and 3.1 in Ultisols. It was not possible to generate robust calibration models for Al Exch, Na and NH_4^+ in Andisols and Al Exch, Mg, NO_3^- and Na in Ultisols. Although some of the models developed presented high R^2, this methodology requires further validation, including a greater number of samples from a wider spatial distribution, covering a variety of climatic and agricultural conditions.

Key words: volcanic soil, calibration model, FT-NIRS, mineral composition.

INTRODUCTION

Currently, the main challenge for agriculture is to produce more food with the same (or less) amount of agricultural supplies, including fertilizer application. Thus, quantifying nutrients concentration in soil is particularly important for the implementation of adequate fertilization strategies to improve agricultural productivity. Soil analysis has become a routine practice for the evaluation of soil fertility. However, standard laboratory techniques for chemical soil analysis require pretreatments, such as, density fractionation, ultrasonic, acidic, alkaline or oxidizing treatments, electrostatic separation and sequential extraction, among others (Blaesing and Amelung, 2018). Furthermore, traditional analysis also uses chemical products, which may be harmful to the environment, because some of the consumables used are corrosive, toxic, or flammable (Bonett et al., 2015; Mouazen and Kuang, 2016). Moreover, chemical processes are usually time-consuming and expensive (Ge et al., 2011).

In this sense, new instrumental methods have been developed to estimate soil physical and chemical properties, such as near-infrared spectroscopy (NIRS) (Viscarra-Rossel and Webster, 2012; Jaconi et al., 2017). This technique obtains the reflectance spectrum of a sample in the range of the NIR region (780-2500 nm). Briefly, when a sample is scanned, the radiant energy is absorbed selectively according to the specific vibration frequency of the molecules present, which produces an overtone in the spectrum. Reflectance signals result from vibrations in C–H, O–H, N–H chemical bonds, and provide information about the proportion of each element in the analyzed sample. NIRS in combination with chemometric methods is a powerful tool for classification tasks or quantitative analyses.

Soil scientists have preferred to use NIRS because of its ease of use, portability, and lesser demand for sample preparation (Bellon-Maurel et al., 2010). Moreover, due to the low absorption coefficients of the higher overtones compared to fundamental vibrations, NIR can penetrate deeper than IR and thus handle larger sample volumes. In fact, the advantages of NIRS over MIR and other spectroscopic techniques (Rodríguez et al., 2016) rely on these capacities, and also on a much lower sensitivity to water and the possibility to work with quartz materials for fibers and optical elements (Paul et al., 2019).

The partial least square regression (PLSR) is a common chemometric method used for estimating regression models from spectral information and reference analytical data (Lucà et al., 2017). Different soil chemical and physical properties have been successfully predicted by PLSR modelling of spectroscopic data. Therefore, spectroscopy in the near-infrared region of the electromagnetic spectrum, combined with chemometric treatments, has been suggested as a cost and time saving procedure to characterize soil chemical properties (Conforti et al., 2018).

This analytical tecnique has been used in agricultural sciences to quantify soil nutrients such as Ca, Mg, Fe, Mn and K; heavy elements such as Co, Cu, Ni, Pb, Zn and Mn or possible contaminants in urban soils (Hong et al., 2018; Ramaroson et al., 2018; Dematte et al., 2019; Hong et al., 2019; Recena et al., 2019). Although its potential has been recognized by soil scientists, the use of NIRS for routine soil analysis remains, to the best of our knowledge, poorly developed in Chile. In this sense, it is worth highlighting the importance of this study since it is the first publication regarding the use of this technique in southern Chilean soils.

The objective of this study was to assess the use of NIRS for the determination of Ca, Mg, P, K, pH (water), organic matter (OM), Na, exchangeable aluminum (Al Exch), ammonium (NH_4^+) and nitrate (NO_3^-) concentrations in two volcanic ash soils in southern Chile.

MATERIALS AND METHODS

Soil sample collection and preparation

Volcanic ash soil samples (0-10 cm) were used to determine the concentration of the selected nutrients: Ca, Mg, P, K, pH (water), organic matter (OM), Na, exchangeable aluminum (Al Exch), ammonium (NH_4^+) and nitrate (NO_3^-). For each site, individual soil samples were randomly collected between 2012 and 2016 from farms located in southern Chile (39° to 42° S), representing the natural variability in local livestock farm production systems. A total of 164 samples were collected from Andisols (Typic Hapludands) and 147 samples from Ultisols (Typic Hapludults) (Soil Survey Staff, 2014).

Soil samples were collected and homogenized, dried at ambient temperature (18-20°C) and sieved through a 2 mm sieve. The resulting material was divided into two fractions, one was used for the traditional wet chemistry analyses and one for NIRS determinations.

Chemical soil analyses

All chemical analyses were performed according to the methodology compiled by Sadzawka et al. (2006) at the Soil Laboratory of Instituto de Investigaciones Agropecuarias (INIA), Chillán, Chile. Briefly, soil pH was potentiometrically measured in water by soil suspension at a 1:2.5 soil:solution ratio. Organic matter was estimated by wet digestion through a modified Walkley-Black method. Ammonium and nitrate were determined by automated colorimetry (autoanalyzer SA 4000, Skalar Analytical B.V., Breda, The Netherlands). Exchangeable cations (Ca^{+2}, Mg^{+2}, K^+, and Na^+) and exchangeable Al^{+3} was extracted with 1 M NH_4Ac at pH 7.0 and 1 M KCl, respectively, and analyzed by atomic absorption spectrophotometry (AAS 969, UNICAM, Cambridge, UK). Olsen P was extracted with 0.5 M $NaHCO_3$ at pH 8.5 and analyzed by the Murphy and Riley method and turbidimetry.

NIRS and chemometric analysis

For spectral analysis, dried and grounded soil samples were scanned using NIR spectroscopy (MPA-FT NIR, Bruker Optik GmbH, Ettlingen, Germany). Spectral data were transformed to absorbance (A) according to the equation: A = log10 (1/R), where R is the reflectance obtained at each wavenumber from 12.000 to 4.000 cm^{-1} (NIR region) with 16 cm^{-1} resolution and 64 scans. Partial least-squares regression (PLSR) with leave-one-out (LOO) cross-validation was performed to fit predictive models using chemometrical software OPUS version 6.5 (Bruker Optik GmbH, Melvyn Becerra Cia. Ltda).

The OPUS software was used to apply different preprocessing to spectra: vector normalization (VN), multiplicative scatter correction (MSC), straight line subtraction (SLS), first derivative (FD), and second derivative (SED). Outliers were identified and removed during the calibration process as they could affect model performance and diminish precision for most samples. A maximum of two outlier elimination passes (T and H) were performed before completing the final calibration. T outliers corresponded to samples with significant differences between their laboratory and predicted values, whereas H outliers were samples whose spectra were too distant (H > 3) from the spectral centre of the calibration set (Conzen, 2006).

Another important factor in a chemometric model is the number of PLS factors. The selection of PLS factors is of major importance for the quality of the analysis, for example: i) Choosing too few factors will lead to an insufficient explanation of the changes in the spectral and concentration data (underfitting), ii). On the contrary, if too many factors are chosen, the model tries to account for even the smallest changes in the data set, such as spectral noise (overfitting). Thus, every PLS model has the optimum number of factors to obtain the smallest possible error of analysis. The maximum number of PLS factors was restricted to 10 (Conzen, 2006).

There are numerous hints that lead to the optimum number of factors for a certain model: The value of the mean error of predicction go through a minimum for the optimal PLS factors. In contrast, the value of the R^2 possesses a maximum. Thus, the optimum number of PLS factors for a certain calibration model can be found easily: First, the R^2 values and the mean error of prediction are computed. Then, these values are plotted as function of the PLS factors. The number of PLS factors is to be regarded as optimal, when the characteristics mentioned go through an optimum value, and/or do not change significantly for higher factor numbers. If several numbers of factors lead to comparably good results, it is recommended to select the model with the smallest number of PLS factors.

Criteria for model selection

The criteria used to choose the best prediction model consider: i) low root mean square error of cross validation (RMSECV); ii) high coefficients of determination in cross-validation (R2cv); iii) root mean square error of estimation (RMSEE); iv) residual predictive deviation (RPD: ratio between the standard deviation -SD- of the reference values and the error of prediction); and v) number of factors.

The RPD value could be an important criterion, but Bellon-Maurel et al (2010) pointed out that soil physical properties and chemical contents, both exhibit a biased normal distribution; therefore, the ratio of performance to IQ (RPIQ) value is more objective than RPD (Bellon-Maurel et al., 2010). RPIQ is based on quartiles, which better represent the spread of the population. The quartiles are milestones in the population range: Q1 is the value below which we can find 25% of the samples; Q3 is the value below which we find 75% of the samples; and Q2, commonly called the median, is the value under which 50% of samples are found. RPIQ is the ratio of IQ to RMSE, where IQ is the difference between the third quartile Q3 and the first quartile Q1. A larger RPIQ value indicates improved model performance. A similar classification can be used for RPIQ and RPD (Jin et al., 2020).

In this study, the selection criteria were the lowest RMSECV, the lowest number of PLS factors and the highest RPD. The smaller the error of cross-validation (compared to the variance of the reference values), the larger the RPD value and thus the better the model.

RESULTS AND DISCUSSION

Chemical soil characterization

The variation coefficient in both soil types was low, while soil nutrient concentration varied among samples as a reflection of variations in agricultural management, climatic factors, and soil type, which is in agreement with Vohland and Emmerling (2011) (Table 1).

Phosphorus concentration in Andisols was lower than that registered in Ultisols, in agreement with Cardenas et al. (2013), who found Olsen P concentrations five and ten-times lower in Andisols than in Ultisols, respectively, in southern Chile. The concentrations of OM found for each soil type in this study coincide with the values reported by other authors (Vistoso et al., 2012; Lobos et al., 2016). Volcanic soils have a high OM concentration, and it is common to find 14% to 20% of OM within the first 15 cm of soil in Andisols (Carvajal et al., 2016), whereas it is slightly smaller in Ultisols (Clunes et al., 2014). The concentrations of Ca found in this study were lower than those found by Cardenas et al. (2013) in three different soil series (including Andisols and Ultisols) in southern Chile. Mg concentration was similar in both soil types but lower than the values reported by Debaene et al. (2010), Jarquín-Sánchez et al. (2012), and Cardenas et al. (2013) for Polish, Mexican, and volcanic Chilean ash soils, respectively. This difference is probably explained by the fact that the data of the present study correspond to fertilized and non-fertilized soils, while the studies mentioned before included Mg fertilizer application. Potassium concentration found in Ultisols was 1.9 times greater than that of Andisols and coincide with the levels reported by other authors (Vistoso et al., 2012; Lobos et al., 2016). The average values of pH (water), Sodium concentration and exchangeable Al were similar to those reported by Cardenas et al. (2013), Carbajal et al., (2016) and Lobos et al. (2016) for similar soil types. Finally, the concentration of ammonium and nitrate was similar to that found by Dixon et al. (2011) in volcanic ash soils in southern Chile.

Chemometric analysis

The best calibration was deemed to be one with the lowest RMSECV, the lowest standard deviation, and the highest R^2 and RPD (Table 2). The coefficient of determination in the calibration sets fluctuated between 79% and 95%, and between 79% and 89%, in Andisols and Ultisols, respectively. The RPD values varied between 2.1 and 4.4 in Andisols, and between 2.2 and 3.1 in Ultisols. RPIQ values ranged from 0.8 to 4.5 and 1.3 to 3.7, in Andisols and Ultisols, respectively.

Table 1. Soil chemical characterization of two Chilean volcanic ash soil types (0-10 cm depth).

	Andisols (n = 164)			Ultisols (n = 147)		
Parameters	**Range**	**Mean ± SEM**	**CV**	**Range**	**Mean ± SEM**	**CV**
P, mg kg^{-1}	2.69-36.00	14.27 ± 0.74	0.52	2.29-143.25	20.86 ± 1.55	0.94
pH water	5.13-6.11	5.62 ± 0.02	0.04	5.01-5.91	5.60 ± 0.02	0.03
OM, %	8.92-31.60	21.50 ± 0.38	0.21	7.44-31.00	15.70 ± 0.38	0.29
Ca, cmol (+) kg^{-1}	0.68-18.57	5.30 ± 0.26	0.65	1.65-18.37	7.15 ± 0.21	0.35
Mg, cmol (+) kg^{-1}	0.28-2.05	1.00 ± 0.03	0.42	0.53-2.44	1.38 ± 0.04	0.33
K, cmol (+) kg^{-1}	0.15-1.38	0.47 ± 0.03	0.62	0.15-5.44	0.87 ± 0.05	0.74
Na, cmol (+) kg^{-1}	0.02-0.60	0.16 ± 0.01	0.79	0.03-1.21	0.14 ± 0.01	0.79
Al, cmol (+) kg^{-1}	0.02-2.50	0.23 ± 0.02	1.18	0.00-8.73	0.34 ± 0.07	2.50
N-NH_4, mg L^{-1}	2.34-19.37	7.26 ± 0.42	0.66	0.50-122.92	18.50 ± 2.13	1.30
N-NO_3, mg L^{-1}	1.40-573.56	73.01 ± 12.35	1.20	0.01-182.46	38.86 ± 3.35	0.98
Available N, mg kg^{-1}	1.45-579.22	53.47 ± 7.59	1.37	2.71-190.83	57.43 ± 4.10	0.81

SEM: standard error of mean; CV: Coefficient of variation

Table 2. Statistical descriptors for the partial least-squares regression (PLSR) predictions for each type of soil.

Parameters	Andisols						Ultisols					
	Calibration group			Validation group			Calibration group			Validation group		
	R^2	RMSEE	RPD	R^2	RMSECV	RPD	RPIQ	R^2	RMSEE	RPD	R^2	RMSECV	RPD	RPIQ
P, mg kg^{-1}	0.95	1.70	4.4	0.89	2.50	3.0	3.9	0.82	5.30	2.3	0.76	5.8	2.1	2.7
pH, water	0.81	0.10	2.3	0.75	0.11	2.0	1.6	0.81	0.08	2.2	0.71	0.1	1.8	1.9
OM, %	0.91	1.40	3.3	0.88	1.56	2.9	4.5	0.88	1.40	2.8	0.86	1.5	2.6	3.2
Ca, cmol (+) kg^{-1}	0.80	1.10	2.2	0.77	1.21	2.1	4.0	0.89	0.70	3.1	0.84	0.8	2.4	3.7
Mg, cmol (+) kg^{-1}	0.79	0.10	2.2	0.70	0.22	1.8	2.5	0.72	0.20	1.9	0.52	0.3	1.4	1.9
K, cmol (+) kg^{-1}	0.79	0.10	2.1	0.74	0.14	2.0	2.5	0.84	0.20	2.4	0.80	0.2	2.2	2.6
Na, cmol (+) kg^{-1}	0.74	0.05	1.9	0.57	0.06	1.5	1.1	0.21	0.05	1.1	0.11	0.05	1.1	1.4
Al exch, cmol (+) kg^{-1}	0.32	0.06	1.2	0.25	0.07	1.2	0.8	0.21	0.07	1.1	0.16	0.07	1.2	1.3
NH_4+, mg L^{-1}	0.69	1.70	1.8	0.62	1.88	1.6	2.0	0.79	4.70	2.2	0.76	4.9	2.0	1.8
NO_3-, mg L^{-1}	0.82	16.70	2.3	0.62	23.00	1.6	1.4	0.22	25.80	1.1	0.16	26.6	1.1	1.8

R^2: Coefficient of determination; RMSEE: root mean square error of estimation; RPD: residual prediction deviation; RPIQ: ratio of performance to interquartile range; RMSECV: root mean square error of cross validation.

It was not possible to generate robust calibration models for Al Exch, Na and NH_4^+ in Andisols and Al Exch, Mg, NO_3^- and Na in Ultisols. The relation between NIRS prediction and composition obtained by reference methods for all parameters are shown in Fig. 1a, b.

In both soil types, predicted values of P, OM and Ca have a strong relation with the reference values. However, the predictive quality was moderate for pH and K in both soils type, and Mg in Ultisols, but extremely low for Al Exch, Na, NH_4^+ and NO_3^- in both soils (Fig. 1a, b).

These results could be associated with the low variability in the sample sets for some of the parameters studied, being this a potential limiting factor in the prediction of soils properties from NIR spectra. The generation of a successful statistical model requires wider data sets, this is, data sets covering a wide range of concentrations. When random samples are used for the calibration purpose, as was the case in this study, the performance may be constrained by narrow data sets. This may be the case of the poor models obtained for Al Exch, Na and Mg (Fig. 1 a, b). Calibration models could improve by enlarging the number of samples and paying attention to increase the concentration range of the analysed elements.

In this study, the optimal number of PLS factors is determined by a leave-one-out cross-validation (CV) based on the minimum RMSECV and a maximum PLS factor of 10. All pre-preprocessing used were different depending on the soil type (Table 3). The decision of when to stop extracting components depends on when there is only very little variability left.

The results show number of PLS factors with values between 3 and 10 in Andisols, and between 1 and 10 in Ultisols. Figure 2 shows the mean prediction errors for PLS regression in two contrasting cases such as Al and P in both soil types. It can be observed that each PLS model has an optimum number of with the minimum error.

In general, pre-preprocessing strategies are used to remove or reduce unwanted signal noises, accentuate the spectral features of interest, and optimize the extraction of useful spectral information. Some studies have demonstrated that spectral preprocessing is an important component of multivariate modelling analysis and that this would improve predictive performance (Gao et al., 2014; Nawar et al., 2016; Vašát et al., 2017). Spectrum pre-treatment may improve the quality of NIRS calibration when a powerful software is used, but the accuracy of the reference data and the quality of the spectra (i.e., reduced interference) are the key elements of reliable calibration models.

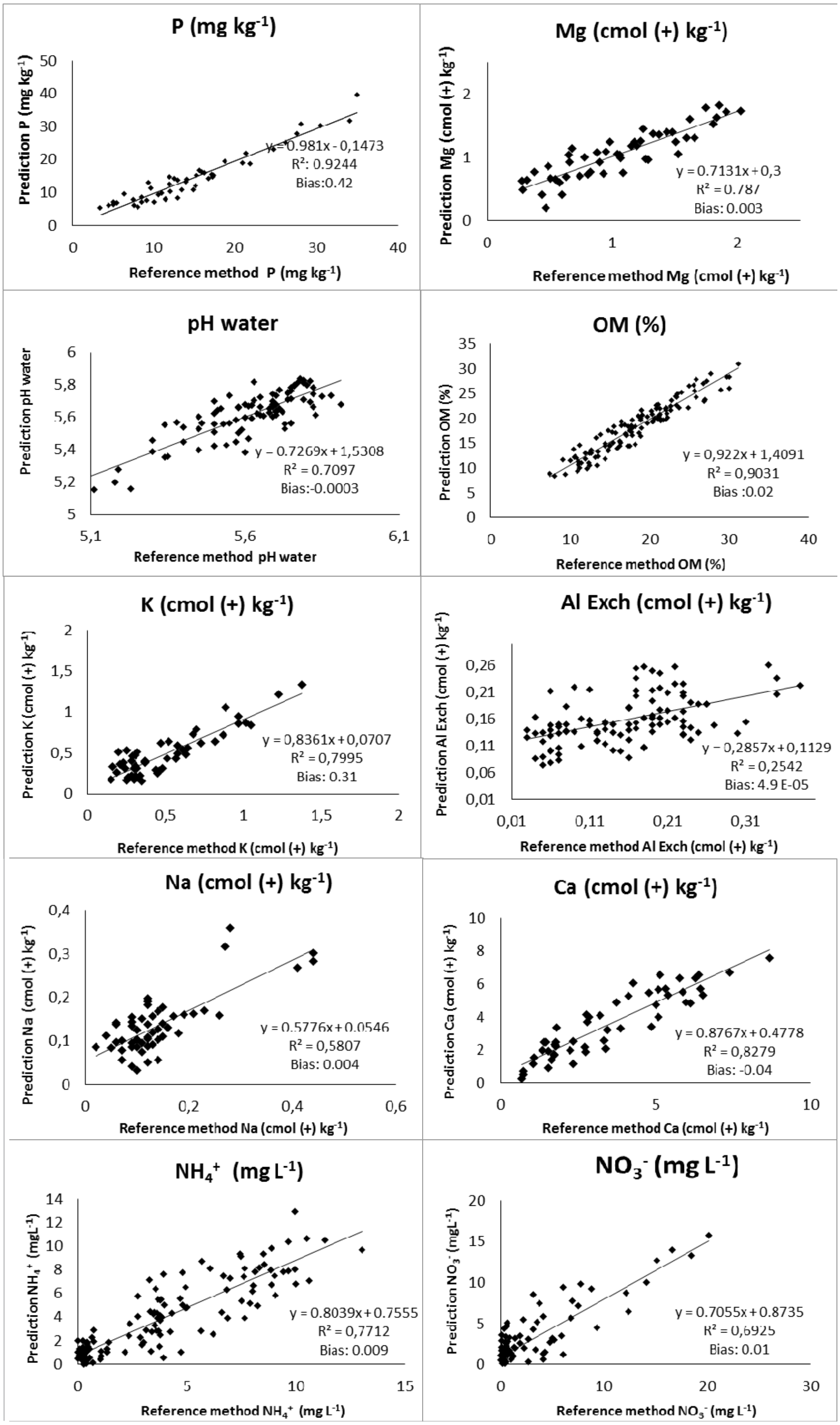

Fig. 1a. Model performance for the correlation of values obtained in the laboratory with respect to those predicted by NIRS for a) P (mg kg^{-1}), b) Mg (cmol(+) kg^{-1}), c) pH water, d) OM (%), e) K (cmol(+) kg^{-1}), f) Al exch (cmol(+) kg^{-1}), g) Na (cmol(+) kg^{-1}), h) Ca (cmol(+) kg^{-1}), i) N-NH$_4$ (mg L^{-1}) and j) N-NO$_3$ (mg L^{-1}) in Andisols.

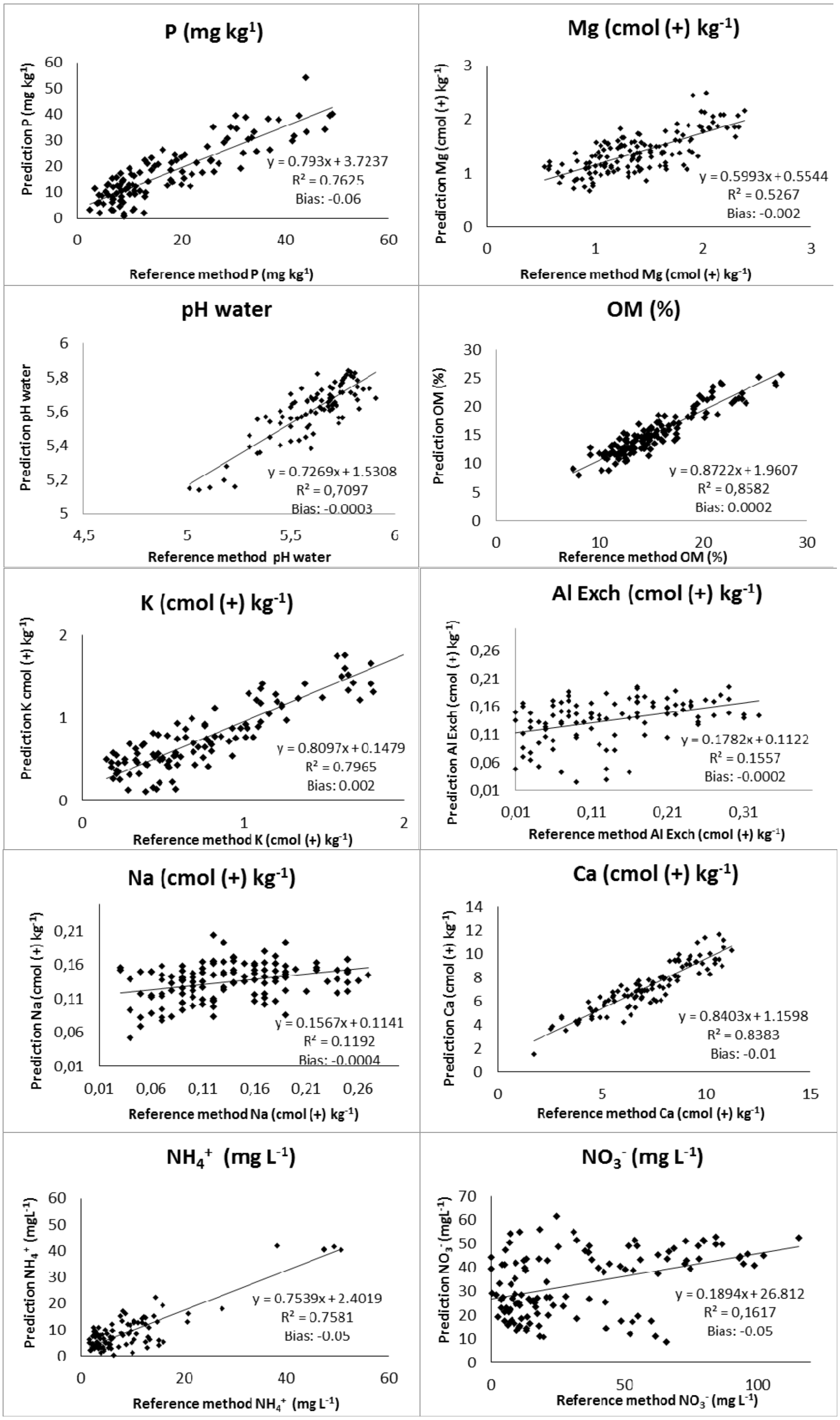

Fig. 1b. Model performance for the correlation of values obtained in the laboratory with respect to those predicted by NIRS for a) P (mg kg^{-1}), b) Mg (cmol(+) kg^{-1}), c) pH water, d) OM (%), e) K (cmol(+) kg^{-1}), f) Al exch (cmol(+) kg^{-1}), g) Na (cmol(+) kg^{-1}), h) Ca (cmol(+) kg^{-1}), i) N-NH$_4$ (mg L^{-1}) and j) N-NO$_3$ (mg L^{-1}) in Ultisol.

Table 3. Partial least-squares (PLS)-based predictions from NIR data after applying different methods of spectra pre-processing.

Parameters	Andisols		Ultisols	
	Treatment	PLS factors	Treatment	PLS factors
P, mg kg^{-1}	Second derivate	7	First derivate	10
pH, water	Second derivate	8	Straight line sustration	7
OM, %	Second derivate	7	Constant offset elimination	7
Ca, cmol (+) kg^{-1}	First derivate	4	Vector normalization	9
Mg, cmol (+) kg^{-1}	Straight line sustration	9	Multiplicative scattering correction	9
K, cmol (+) kg^{-1}	First derivate	3	Straight line sustration	7
Na, cmol (+) kg^{-1}	First derivate + Vector normalization	9	First derivate	3
Al exch, cmol (+) kg^{-1}	Second derivate	3	Min- MaxNormalization	1
N-NH$_4$, mg L^{-1}	Straight line sustration	4	First derivate + Vector normalization	3
N-NO$_3$, mg L^{-1}	Vector normalization	9	First derivate + Vector normalization	2

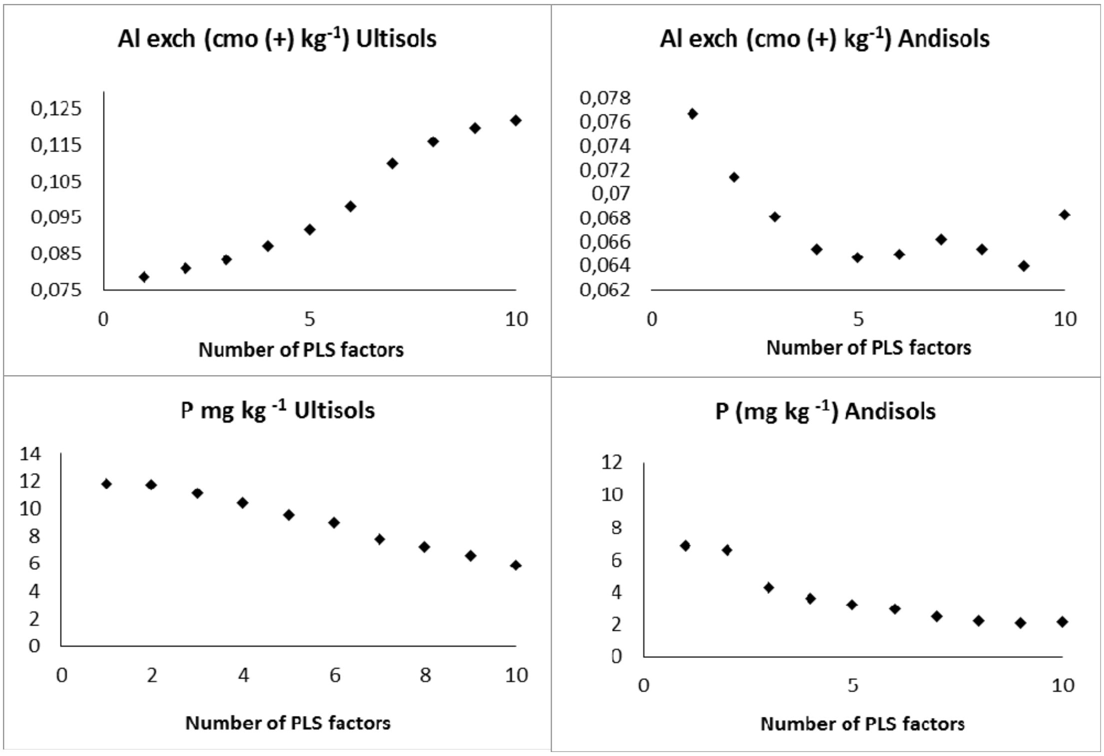

Fig 2. Mean Errors of Prediction for Al exch and P plotted against the number of PLS factors in Andisols and Ultisols.

Our calibration models were similar to those reported by Bonett et al. (2015) and Recena et al. (2019) for Ca, Mg, pH and K. Debaene et al. (2010) obtained very poor models for pH, Mg, K and P in Polish soils with R^2 in the range of 0.01-0.69 for a Podzoluvisol in Wielkopolska, Poland. Dematte et al. (2019) reported similar models for OM, P, K, Ca, Mg, and better models for Al in soil samples of Brazil. Our results for OM were more robust than those reported by Hong et al. (2018, 2019). There are few studies using NIRS to quantify NH_4^+ and NO_3^-. Freschet et al. (2011) reported R^2 varying between 0.81 and 0.95 for NH_3-N, but these values were obtained using a low number of samples (n = 56), with high variability (mean and standard deviation of reference data was 32.08 ± 30.25). These differences can be explained by the different reference methods used for determining soil properties .

Different reference methods may produce different reference values, affecting the precision of NIRS calibrations. Thus, the identification of reliable reference methods that are best correlated with NIRS spectra would be valuable for standardization of NIRS in soil analysis. On the other hand, the lack of standardized methodology in relation to: (i) sample preparation, (ii) spectrum acquisition, (iii) spectrum pre-treatment, (iv) soil texture, (v) geological heterogeneity, (vi) reference method, and (vii) calibration method are factors that need to be taken care of to get more accurate results using the NIRs technique. In addition, the identification of soil properties that require spectrum pre-processing and those for which the visible-near-infrared or the near-infrared region should be used during calibration requires more investigation. This would make NIRS more user-friendly and would allow comparisons between different studies.

However, in practice, many factors may affect soil spectra, and the acquired NIR spectra may contain environmental information and noise, which would influence the model performance (Stenberg et al., 2010; Shi et al., 2014; Viscarra Rossel et al., 2016). Moreover, the correlations between spectral signatures and the specific wavelengths may be masked given the complexity of the interaction between light and the presence of overlapping wavebands in NIR spectra, which result from the different chemical components of soils (Hong et al., 2019). Our results may have varied because of high heterogeneity in the samples (different places, soil types, management, among others), suggesting a high variability on NIRS reliability depending on soil sampling and processing, as well as intrinsic soil characteristics. This represents a limitation in the use of this method as it implies the development of specific calibration methods representing this variability.

NIR spectroscopy can be used for determining mineral concentrations due to the association between minerals and organic functional groups in the organic matrix. The near-infrared radiation is absorbed by various chemical bonds (e.g., C-H, O-H, N-H, CO, S-H, CH2, and C-C) causing the bonds to be bent, twisted, stretched, or scissored. However, near-infrared reflectance spectra of soil samples do not contain distinct or sharp peaks that can be directly associated with specific constituents, particularly for dry samples.

CONCLUSIONS

The coefficient of determination in the calibration model obtained ranged from 0.76 to 0.95, and 0.79 to 0.89, in Andisols and Ultisols, respectively. The RPD values varied between 2.1 and 4.4 in Andisols, and between 2.2 and 3.1 in Ultisols. It was not possible to generate robust calibration models for Al Exch, Na and NH_4^+ in Andisols, and Al Exch, Mg, NO_3^- and Na in Ultisols.

The results showed that although some of the models developed have high coefficients of determination (R^2) for the soil complex matrix, more research is required to generate universal models that could be applied to a wide range of soil types and characteristics. As starting point, this methodology would benefit from a greater number of samples from a wider spatial distribution, covering a variety of climatic and agricultural conditions to further improve the validation models obtained.

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LITERATURE CITED

Bellon-Maurel, V., E. Fernandez-Ahumada, B. Palagos, J-M. Roger, and A. McBratney. 2010. Critical review of chemometric indicators commonly used for assessing the quality of the prediction of soil attributes by NIR spectroscopy. Trends in Analytical Chemistry 29(9):1073-1081. https://doi:10.1016/j.trac.2010.05.006

Blaesing, M., and W. Amelung. 2018. Plastics in soil: analytical methods and possible sources. Sci. Total. Environ. 612:422–435. https://doi.org/10.1016/j.scitotenv.2017.08.086

Bonett, J., J. Camacho-Tamayo, and L. Ramírez-López. 2015. Mid-infrared spectroscopy for the estimation of some soil properties. Agron. Colomb. 33:99-106. http://dx.doi.org/10.15446/agron.colomb.v33n1.49245

Cardenas, L., D. Hatch, D. Scholefield, D. Jhurreea, I. Clark, P. Hirsch, et al. 2013. Potential mineralization and nitrification in volcanic grassland soils in Chile. J. Soil Sci. Plant Nutr. 59(3):1-12. https://doi.org/10.1080/00380768.2013.789395

Carvajal, A., R. Vargas, and M. Alfaro. 2016. Abundance of denitrifying genes and microbial community structure in volcanic soils. J. Soil Sci. Plant Nutr. 16(3):677-688. http://dx.doi.org/10.4067/S0718-95162016005000049

Clunes, J., J. Navarro, and D. Pinochet. 2014. Variación temporal del contenido de materia orgánica en dos suelos volcánicos bajo diferentes manejos agrícolas. Agro Sur 42(3):1-14. DOI:10.4206/agrosur.2014.v42n3-01

Conforti, M., G. Matteucci, and G. Buttafuoco. 2018. Using laboratory Vis-NIR spectroscopy for monitoring some forest soil properties. J. Soils Sediments 18:1-11. https://doi.org/10.1007/s11368-017-1766-5

Conzen, P. 2006. Multivariate calibration a practical guide for developing methods in the quantitative analytical chemistry BrukerOptik GmbH. Ettlingen, Germany.

Debaene, G., J. Niedzwiecki, and A. Pecio. 2010. Visible and near-infrared spectrophotometer for soil analysis: preliminary results. Pol. J. Agron. 3:3-9.

Dematte, J., A. Dotto, L. Bedin, V. Sayao, and A. Souza. 2019. Soil analytical quality control by traditional and spectroscopy techniques: Constructing the future of a hybrid laboratory for low environmental impact. Geoderma 337:111-121. DOI: 10.1016/j.geoderma.2018.09.010

Dixon, E., L. Cardenas, M. Alfaro, F. Salazar, and D. Hatch. 2011. High rates of nitrogen cycling in volcanic soils from Chilean grasslands. Rapid Communications in Mass Spectrometry 25:1521-1526. https://doi.org/10.1002/rcm.4969

Freschet, G., B. Barthes, D. Brunet, E. Hien, and D. Masse. 2011. Use of near infrared reflectance spectroscopy (NIRS) for predicting soil fertility and historical management. Comm. Soil Sci. Plant. 42(14):1692-1705. DOI: 10.1080/00103624.2011.584597

Gao, Y., L. Cui, B. Lei, Y. Zhai, T. Shi, J. Wang, et al. 2014. Estimating soil organic carbon content with visible- near- infrared (Vis-NIR) spectroscopy. Appl. Spectrosc. 68:712-722. https://doi.org/10.1366/13-07031

Ge, I., C. Morgan, S. Grunwald, D. Brown, and D. Sarkhot. 2011. Comparison of soil reflectance spectra and calibration models obtained using multiple spectrometers. Geoderma 161:202-211. DOI: 10.1016/j.geoderma.2010.12.020

Hong, Y., S. Chen, Y. Zhang, Y. Chen, L. Yu, Y. Liu, et al. 2018. Rapid identification of soil organic matter level via visible and near-infrared spectroscopy: Effects of two-dimensional correlation coefficient and extreme learning machine. Sci. Total Environ. 644:1232- 1243. https://doi.org/10.1016/j.scitotenv.2018.06.319

Hong, Y., Y. Liu, Y. Chen, Y. Lui, L. Yu, Y. Liu, et al. 2019. Application of fractional-order derivative in the quantitative estimation of soil organic matter content through visible and near-infrared spectroscopy. Geoderma 337:758-769. http://doi.org/10.1016/j.geoderma.2018.10.025

Jaconi, A., A. Don, and A. Freibauer. 2017. Prediction of soil organic carbon at the country scale: stratification strategies for near-infrared data. Eur. J. Soil Sci. 68(6):919-929. https://doi.org/10.1111/ejss.12485

Jarquín-Sánchez, A., S. Salgado-García, D. Palma-López, and W. Camacho-Chiu. 2012. Analysis of soil organic matter in tropical soil with near-infrared spectroscopy (NIRS) and chemometrics. Cien. Investig. Agra. 39(2):387-394. http://dx.doi.org/10.4067/S0718-16202012000200015

Jin, X., S. Li, W. Zhang, J. Zhu, and J. Sun. 2020. Prediction of soil-available potassium content with visible near-infrared ray spectroscopy of different pretreatment transformations by the boosting algorithms. Appl. Sci. 10:1520-1538. http://dx.doi:10.3390/app10041520

Lobos, I., M. Alfaro, and J. Martínez-Lagos. 2016. Soil nitrogen contribution to grasslands yield in southern Chile: its implications for nitrogen use efficiency. J. Soil Sci. Plant Nutr. 16(2):310-322. http://dx.doi.org/10.4067/S0718-95162016005000027

Lucà, F., M. Conforti, A. Castrignanò, G. Matteucci, and G. Buttafuoco. 2017. Effect of calibration set size on prediction at local scale of soil carbon by Vis-NIR spectroscopy. Geoderma 288:175–183. https://doi.org/10.1016/j.geoderma.2016.11.015.

Mouazen, A, and B. Kuang. 2016. On-line visible and near infrared spectroscopy for infield phosphorous management. Soil Till. Res. 155:471–477. https://doi.org/10.1016/j.still.2015.04.003

Nawar, S., H. Buddenbaum, J. Hill, J. Kozak, and A. Mouazen. 2016. Estimating the soil clay content and organic matter by means of different calibration methods of vis-NIR diffuse reflectance spectroscopy. Soil Till. Res. 155:510-522. https://doi.org/10.1016/j.still.2015.07.021

OPUS. 2009. MPA SYSTEM. Version 6.5. Alemania. Melvin Becerra Cia. Ltda, Santiago, Chile.

Paul, A., L. Wander, R. Becker, C. Goedecke, and U. Braun. 2019. High-throughput NIR spectroscopic (NIRS) detection of microplastics in soil. Environ. Sci. Pollut. R. 26:7364- 7374. http://doi.org/10.1007/s11356-018-2180-2

Ramaroson, V., T. Becquer, S. Oliveira, H. Razafimahatratra, J. Delarivier, D. Blavet, et al. 2018. Mineralogical analysis of ferralitic soils in Madagascar using NIR spectroscopy. Catena 168:102-109. https://doi.org/10.1016/j.catena.2017.07.016

Recena, R., V. Fernández, and A. Delgado. 2019. Soil fertility assessment by Vis-NIR spectroscopy: Predicting soil functioning rather than availability índices. Geoderma 337:368-374. https://doi.org/10.1016/j.geoderma.2018.09.049

Rodriguez, W., P. Garcia, and A. Fajardo. 2016. Aplications of spectroscopy techniques for soil análisis. Revista Facultad de Ciencias Básicas 12:228-251. http://dx.doi.org/10.18359/rfcb.2030

Sadzawka, A., M. Carrasco, R. Grez, M. Mora, H. Flores, and A. Neaman. 2006. Métodos de análisis recomendados para los suelos de Chile. Revisión 2006. Serie Actas INIA N° 34. 164 p. Instituto de Investigaciones Agropecuarias (INIA), La Platina, Santiago, Chile.

Shi, T., Y. Chen, Y. Liu, and G. Wu. 2014. Visible and near-infrared reflectance spectroscopy: an alternative for monitoring soil contamination by heavy metals. J. Hazard. Mater. 265:166–176. https://doi.org/10.1016/j.jhazmat.2013.11.059

Stenberg, B., R. Viscarra Rossel, A. Mouazen, and J. Wetterlind. 2010. Visible and near infrared spectroscopy in soil science. In Sparks, D.L. (ed.) Adv. Agron. 107:163–215. https://doi.org/10.1016/S0065-2113(10)07005-7

Soil Survey Staff. 2014. Keys to soil taxonomy. 11th ed. USDA Natural Resources Conservation Service, Washington, D.C., USA.

Vasat, R., R. Kodesova A. Klement, and L. Boruvka. 2017. Simple but efficient signal preprocessing in soil organic carbon spectroscopic estimation. Geoderma 298:46–53. https://doi.org/10.1016/j.geoderma.2017.03.012

Viscarra-Rossel, R, and R. Webster. 2012. Predicting soil properties from the Australian soil visible-near infrared spectroscopic database. Eur. J. Soil Sci. 63:848–860. https://doi.org/10.1111/j.1365-2389.2012.01495.x

Viscarra, R., T. Behrens, E. Ben- Dor, D. Brown, J. Dematte, K. Shepherd, et al. 2016. A global spectral library to characterize the world´s soil. Earth Sci. Rev. 155:198-230. https://doi.org/10.1016/j.earscirev.2016.01.012

Vistoso, E., M. Alfaro, S. Sagga, and F. Salazar. 2012. Effect of nitrogen inhibitors on nitrous oxide emissions and pasture growth following an autumn application in a volcanic soil. Chil. J. Agr. Res. 72:133-139. http://dx.doi.org/10.4067/S0718-58392012000100021

Vohland, M., and C. Emmerling. 2011. Determination of total soil organic C and hot water-extractable C from VIS-NIR soil reflectance with partial least squares regression and spectral feature selection techniques. Eur. J. Soil Sci. 62:598-606. https://doi.org/10.1111/j.1365-2389.2011.01369.x