

Reflectance spectroscopy: a tool for predicting soil properties related to the incidence of Fe chlorosis

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Abstract

Chlorosis due to iron (Fe) deficiency (internervial yellowing) is the most important nutritional problem a susceptible plant can have in calcareous soils. Fe chlorosis is related with calcium carbonate equivalent (CCE), clay content and Fe extracted with oxalate (Fe_o). Reflectance spectroscopy (RS) is a rapid, non-destructive, less expensive alternative tool that can be used to enhance or replace conventional methods of soil analysis. The aim of this work was to assess the usefulness of RS for the determination of some properties of Mediterranean soils including clay content, CCE, Fe_o , cation exchange capacity (CEC), organic matter (OM) and pH in water (pH_w), with emphasis on those with a specially marked influence on the risk of Fe chlorosis. To this end, we used partial least-squares regression (PLS) to construct calibration models, leave-one-out cross-validation and an independent validation set. Our results testify to the usefulness of qualitative soil interpretations based on the variable importance for projection (VIP) as derived by PLS decomposition. The accuracy of predictions in each of the Vis-NIR, MIR and combined spectral regions differed considerably between properties. The R^2_{adj} and root mean square error (RMSE) for the external validation predictions were as follows: 0.83 and 37 mg kg⁻¹ for clay content in the Vis-NIR-MIR range; 0.99 and 25 mg kg⁻¹ for CCE, 0.80 and 0.1 mg kg⁻¹ for Fe_o in the MIR range; 0.93 and 3 cmol_c kg⁻¹ for CEC in the Vis-NIR range; 0.87 and 2 mg kg⁻¹ for OM in the Vis-NIR-MIR range, 0.61 and 0.2 for pH_w in the MIR range. These results testify to the potential of RS in the Vis, NIR and MIR ranges for efficient soil analysis, the acquisition of soil information and the assessment of the risk of Fe chlorosis in soils.

Additional key words: iron chlorosis; MIR; NIR; partial least squares regression; reflectance spectroscopy.

Resumen

Espectroscopía de reflectancia: una herramienta para predecir las propiedades del suelo relacionadas con la clorosis férrica

La clorosis debida a una deficiencia de hierro (Fe) (amarilleamiento internervial) es el problema nutricional más importante que una planta susceptible puede sufrir en suelos calcáreos. La clorosis férrica está relacionada con el contenido en carbonato cálcico equivalente (CCE), contenido de arcilla y Fe extraído con oxalato (Fe_o). La espectroscopía de reflectancia (RS) es una herramienta rápida, menos cara, no destructiva y proporciona una buena alternativa a los métodos convencionales de análisis. El objetivo de este trabajo fue estudiar la utilidad de la RS en la determinación de algunas propiedades (contenido de arcilla; CCE; Fe_o ; capacidad de intercambio catiónico, CEC; materia orgánica, OM; y pH_w) de los suelos de la región mediterránea, con énfasis en aquellas propiedades que más influyen en la clorosis férrica. Se utilizaron regresiones de mínimos cuadrados parciales (PLS), validación cruzada y validación externa para obtener los modelos de calibración. Nuestros resultados demuestran la validez en la interpretación cualitativa de los suelos de la variable de importancia para la proyección (VIP) descomponiendo los PLS. La precisión de

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Abbreviations used: AIC (Akaike information criterion); CCE (calcium carbonate equivalent); CEC (cation exchange capacity); Fe_o (Fe extracted with Acid NH₄-oxalate); MIR (medium infrared); NIR (near infrared); OM (organic matter content); PCA (principal components analysis); pH_w (potentiometric measurement in a 1:2 soil:water suspension); PLS (partial least squares regression); RMSE (root mean squared error); RPD (ratio performance deviation); RS (reflectance spectroscopy); VIP (variable importance for projection); Vis (visible).

las predicciones para cada región espectral Vis-NIR, MIR y combinaciones varió considerablemente entre las propiedades. Los valores de R^2_{adj} y RMSE obtenidos tras la validación externa fueron: contenido de arcilla = 0,83 y 37 mg kg⁻¹ para el intervalo Vis-NIR-MIR; CCE = 0,99 y 25 mg kg⁻¹, Fe_o = 0,80 y 0,1 mg kg⁻¹ para la región MIR; CEC = 0,93 y 3 cmol_c kg⁻¹ para Vis-NIR; OM = 0,87 y 2 mg kg⁻¹ para el intervalo Vis-NIR-MIR; y pH_w = 0,61 y 0,2 para la región MIR, respectivamente. Este trabajo demostró el potencial de la RS usando las regiones del Vis, NIR y MIR para un análisis eficiente de las propiedades, adquirir información y detectar el riesgo de clorosis férrica en los suelos.

Palabras clave adicionales: clorosis férrica; espectroscopia de reflectancia; MIR; NIR; regresión de mínimos cuadrados parciales.

Introduction

Iron (Fe) deficiency chlorosis is one of the most important nutritional disorders in susceptible plants grown on calcareous soils (Morris *et al.*, 1990). The most characteristic symptom of this plant disease is internervial yellowing in the youngest leaves. Furthermore, plants can suffer latent Fe deficiency and exhibit reduced vegetative growth before the typical symptoms of Fe chlorosis become apparent (Fernández-Escobar *et al.*, 1993).

Calcareous soils occupy large areas in Southern Spain, where agriculture plays an important economic role. Fe chlorosis symptoms have been observed in different crops grown in the region including olive (*Olea europaea* L.), orange (*Citrus sinensis* L.) and lemon (*Citrus limon* L.) trees, grapevine (*Vitis vinifera* L.), sunflower (*Helianthus annuus* L.) and tomato (*Solanum lycopersicum* L.). Before a new plantation is established, we must know the chlorosant power of the soil in order to choose the most appropriate variety to prevent or correct the problem.

The fact that Fe chlorosis is often observed in calcareous soils, has promoted a number of studies on the influence of calcium carbonate on this deficiency (Drouineau, 1942; Inskip & Bloom, 1987; Loepfert *et al.*, 1988). Del Campillo & Torrent (1992) found that chlorophyll content was negatively correlated with the calcium carbonate equivalent (CCE) in chickpea and sunflower. Schinas & Rowell (1977) reported a lack of correlation between the yield of various chlorosis-sensitive crops and the carbonate content at levels below 200 g CCE kg⁻¹ soil. In Spain, soils containing more than 10% of active lime, which is the most reactive fraction calcium carbonate, are assumed to induce Fe chlorosis (Yaalon, 1957; González, 1990).

The contents in silicate clays and poorly crystalline Fe oxides are properties related to the occurrence of Fe chlorosis in various plant species (Yangüas *et al.*, 1997). Clay may stabilize poorly crystalline Fe oxides in forms

where Fe is more available to plants; also, some structural Fe (especially in smectites) may serve as a source of Fe (Loepfert and Hallmark, 1985). Thus, a soil with less than 300 g clay kg⁻¹ may induce Fe chlorosis in olive trees (Benítez *et al.*, 2002). Acid NH₄-oxalate extracts poorly crystalline Fe oxides (Fe_o), which have larger specific surface areas and higher solubility than the crystalline forms (*e.g.* goethite and hematite) (Schwertmann, 1964). Therefore, this extractant provides an estimate of the most easily mobilizable Fe sources in the rhizosphere. According to Díaz *et al.* (2010), leaf chlorophyll concentrations in grapevine are positively correlated with the soil content in poorly crystalline Fe oxides, with a clear-cut critical level of 0.35 g kg⁻¹.

Reflectance spectroscopy (RS) measurements have been widely adopted for soil studies and used for the simultaneous prediction of a variety of primary and secondary soil attributes (Janik *et al.*, 1998; Malley *et al.*, 2004; Viscarra-Rossel *et al.*, 2006). The RS technique has some advantages over conventional methods of soil analysis including expeditiousness and economy, which make it more efficient when large numbers of analyses on samples are required (McCarty & Reeves, 2006; Nanni & Dematte, 2006). RS has been used in conjunction with chemometric analysis to relate soil spectra to soil attributes such as carbonate concentration (Ben-Dor & Banin, 1990, 1995), clay (Brown *et al.*, 2006; Madari *et al.*, 2006) and iron oxides (Selitto *et al.*, 2009; Cañasveras *et al.*, 2010).

Light absorption in the visible (400 to 750 nm) (Vis), near infrared (750 to 2,500 nm) (NIR) and mid infrared (2,500 to 25,000 nm) (MIR) regions involves electronic transitions of atoms, and vibrational stretching and bending of molecules and crystals, all of which are frequency dependent. This dependence allows one to obtain information about the chemistry of some minerals (Viscarra-Rossel *et al.*, 2006). Thus, strong peaks for fundamental vibration bands of Si-O, Al-O, Fe-O, H-O, H-C and H-N bonds in the MIR region have been related to the presence of silicates, Fe and Al oxides,

calcium carbonate and organic matter (Nguyen *et al.*, 1991), whereas weak overtones and combinations of the previous H-bands in the NIR region indicate the presence of water, clays and organic components (Bend-Dor & Banin, 1995) and overlapping weak bands in the Vis region reflect the presence of iron oxides (Sherman & Waite, 1985; Scheinost *et al.*, 1998).

The objective of this work was to study the usefulness of RS for the determination of some properties of Mediterranean soils, with emphasis on those related with the risk of Fe chlorosis such as carbonate, clay and iron oxides concentration.

Material and methods

Soil sampling and analysis

A total of 331 surface soil samples were collected from different areas in Andalusia, southern Spain. The crops grown on the studied soils (olive trees, grapevine and cereals) had shown Fe chlorosis to a variable extent, from no symptoms to a strong internervial yellowing in the youngest leaves. The soils, mostly Lithic and Petrocalcic Calcixerepts and Calcic Haploxerepts, had developed on marls, calcareous marls and limestones of the Mesozoic and Tertiary, and were slightly to severely eroded.

The samples were collected from the surface horizon (0-50 cm), air-dried, ground to pass through a 2-mm sieve and analysed for particle size distribution (pipette method), organic matter content (OM) (dichromate oxidation), pH_w (potentiometric measurement in a 1:2 soil:water suspension), cation exchange capacity (CEC) (Soil Survey Staff, 1992), CCE (van Wesemael, 1955) and Fe_o (Schwertmann, 1964) in the laboratory.

Spectral measurements

Visible, NIR and MIR spectra were recorded by using three different instruments and spectral ranges, namely:

— (1) A Cary 5000 UV-Vis-NIR spectrophotometer (Varian Inc., Palo Alto, CA, USA) equipped with an integrating sphere accommodating a photomultiplier/PbS detector. Reflectance values were acquired at 1 nm intervals over the 400-2,500 nm range.

— (2) An ASD Labspec® Vis-NIR spectrometer (Analytical Spectral Devices, Boulder, Colorado, USA) spanning the range 350-2,500 nm. Spectra were ac-

quired at a sampling resolution of 1 nm, so each spectrum comprised 2,151 wavelengths.

— (3) A Tensor 27 MIR spectrophotometer from Bruker Optics. Spectra were recorded from 4,000 to 600 cm^{-1} (2,500 to 16,666 nm) at 8 cm^{-1} resolution and 64 scans s^{-1} .

Measurements on samples ground to < 0.2 mm in an agate mortar were made with instruments (1) and (3) on fine earth (< 2 mm) with (2). Vis-NIR spectra were recorded by using Halon (PTFE) powder as white standard. Finally, MIR measurements were made with ground pre-dried potassium bromide as reference.

Chemometric analysis

Summary statistics and correlation analysis were performed by using the software package ParLeS (Viscarra Rossel, 2008).

Chemometric calibration was done on mean centre absorbance measurements [$\text{Log}_{10}(1/\text{Reflectance})$] using a calibration set (276 random samples). Other data transformations such as the Kubelka-Munk function [$(1 - \text{Reflectance})^2/(2 \times \text{Reflectance})$], scatter and smoothing corrections, or derivative pretreatments, were also tested, but the results were not significantly better. Spectral data were compressed by using principal components analysis (PCA) and the scores of the first 15 principal components (PCs) were analysed. Scatter-plots of such components were used to visualise the structure of the multivariate data and to check for possible outliers. A partial least squares regression (PLS) algorithm and leave-one-out cross-validation were used to model of single y-variables. An independent validation set (55 random samples) was tested. ParLeS facilitates the implementation of bootstrap aggregation with partial least squares regression (or bagging-PLSR). The bagging-PLSR technique has some advantages including improved predictions, robust models that are less sensitive to overfitting and the provision of a measure of uncertainty in the predictions (Viscarra Rossel, 2007). In this work, the bagging-PLSR results were similar to PLS results.

Normally, the model with the lowest root mean squared error (RMSE) is selected; however, we chose to use the Akaike Information Criterion (AIC) (Akaike, 1973) here to preserve parsimony in the models. Thus, we selected the model with lowest AIC value. $AIC = \ln(RMSE) + 2p$, where n is the number of observations and p is the number of PLSR factor used. The calibration accuracy was evaluated via the

determination coefficient, R^2_{adj} , and the ratio performance deviation (RPD), calculated as the standard deviation (SD) of the validation set divided by the RMSE. Chang *et al.* (2001) divided prediction results into three classes with (i) good predictions as $RPD > 2$, (ii) predictions with potential as RPD around 1.4-2 and (iii) unreliable predictions as $RPD < 1.4$.

Specific Vis-NIR and MIR frequencies potentially useful for PLS predictions were identified by using the variable importance for projection (VIP) (Wold *et al.*, 2001).

Results and discussion

Soil properties

Soil samples varied widely in particle size distribution from, sandy to clayey ($50\text{-}720\text{ g kg}^{-1}$). CCE also

varied widely (almost carbonate-free to strongly calcareous), as expected from the differences in the parent materials. Thus, pH_w ranged from 7.2 to 8.7 (alkaline), Fe_o from 0.02 to 1.7 g kg^{-1} and CEC from 7 to $82\text{ cmol}_c\text{ kg}^{-1}$ (Table 1). Most of the soils had low OM contents ($1.5\text{-}33.8\text{ g kg}^{-1}$).

Soil spectra

The peaks in the MIR range were much stronger than those in the Vis-NIR range (Fig. 1). Differences in optical density [$\text{Log}(1/\text{Reflectance})$] in the visible range can be ascribed to differences in the types of iron oxides and their contents. The absorption bands in the NIR region were overtones or combinations of fundamental stretching bands occurring in the MIR region. Fig. 1 shows the absorption bands at near 1,400, 1,900 and 2,200 nm, which may be due to vi-

Table 1. Selected properties of the studied soils

Properties	Clay (g kg^{-1})	CCE (g kg^{-1})	Fe_o (g kg^{-1})	CEC ($\text{cmol}_c\text{ kg}^{-1}$)	OM (g kg^{-1})	pH_w
Mean	275	559	0.33	23	14.7	8.1
SD	97	207	0.22	11	5.7	0.3
Median	262	560	0.29	21	14.6	8.2
Maximum	720	969	1.7	82	33.8	8.7
Minimum	50	20	0.02	7	1.5	7.2

CCE = calcium carbonate equivalent; Fe_o = oxalate-extractable Fe; CEC = cation exchange capacity; OM = organic matter content. SD = standard deviation.

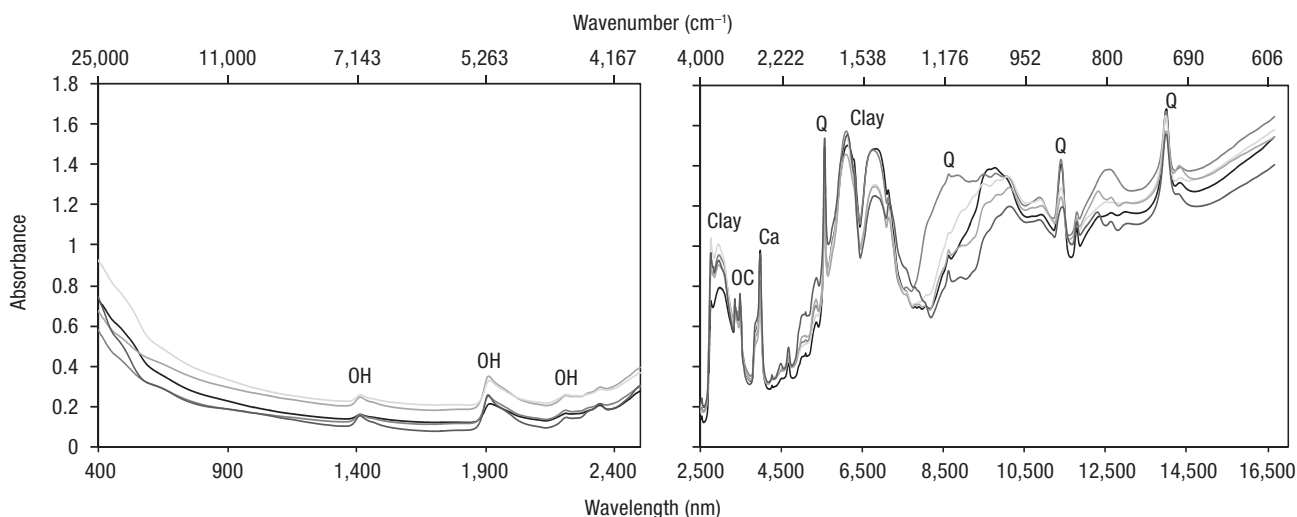


Figure 1. Selected soil spectra obtained in the Vis-NIR-MIR range. The spectrum is annotated with some dominant soil components and absorption peaks such as those for quartz, organic compounds, calcite, clay minerals and the OH features of free water. Q = quartz; OC = organic compounds; Ca = calcite.

bration combinations and overtones of molecular water contained in various locations in the mineral (Hunt, 1977). A higher optical density and more absorption peaks were observed in the MIR region reflecting the type of clay mineral, quartz, calcite and organic compounds. The absorption bands in the regions between 2,600-2,800 nm and 6,000-6,700 nm can be assigned to clay minerals such as kaolinite, smectite and illite. The bands at 3,400-3,500 nm are particularly useful for the detecting OM in soils. These soils contained carbonates as shown by the absorption band at 3,950 nm, which can be assigned to calcite. Quartz exhibited several characteristic absorption bands at 5,550, 8,580, 11,350 and 13,900 nm (Nguyen *et al.*, 1991).

PCA analysis

The first five principal components (PC) explained over 99% of the variance in the Vis-NIR spectrum and over 95% in the MIR spectrum. No outliers were detected. Scores plots revealing the overall structure of the data are shown in Fig. 2.

PLS analysis

Table 2 shows the statistics for the cross validation and external validation of soil attributes by applying PLS to the spectroscopic systems and the combined wavelength ranges. The best correlations are in bold-face in this table and their VIPs are shown in Fig. 3; these correlations are represented in Fig. 4.

The clay content was better predicted by using the MIR range than the Vis-NIR range, but the best result was obtained with the Vis-NIR-MIR combination ($R^2_{adj} = 0.83$) using the ASD instrument to record the Vis-NIR spectrum. Fig. 3 shows the highest VIP values obtained over the range 6,000-6,700 nm which contains the absorption bands for different types of clay. CCE was well predicted by all spectral regions ($R^2_{adj} > 0.92$). The best correlation was obtained with the MIR range ($R^2_{adj} = 0.99$). There were many spectral bands with $VIP > 2$ (especially that associated with calcite at 3,950 nm). Despite the differences in absorbance in the visible range ascribed to differences in the types of iron oxides, the best Fe_o correlation was obtained in the MIR range ($R^2_{adj} = 0.80$). The highest VIP values

were those for the 6,000-6,700 nm range which is normal since poorly crystalline Fe oxides are associated with clay minerals. This region is also important for OM prediction. Although the range for OM is very short, good predictions were obtained with the Vis-NIR-MIR ($R^2_{adj} = 0.87$) using the Cary instrument to record the Vis-NIR spectrum. Provided the Vis-NIR spectrum acquired with Cary, R^2_{adj} value of the prediction of CEC was 0.93. The most salient features of the VIP graph were the absorption peaks associated with bending and stretching of O-H

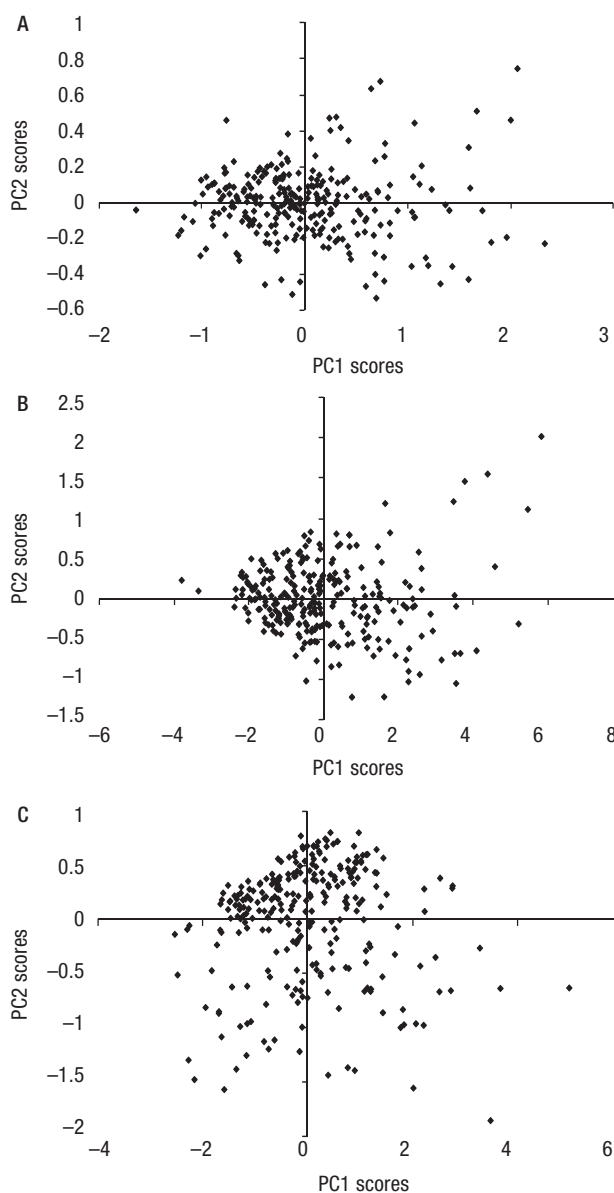


Figure 2. PC2 vs PC1 scores plot showing the overall structure of the data. (A) Vis-NIR Cary; (B) Vis-NIR ASD; (C) MIR.

Table 2. Statistics for the cross-validation and external validation of various soil attributes by applying partial least squares regression (PLSR) to the three spectroscopic systems and their combined ranges. The best correlations are in boldface

	N° PLS	Cross-validation			External validation			
		R^2_{adj}	RMSE	RPD	R^2_{adj}	RMSE	RPD	
Cary Vis-NIR	Clay (g kg ⁻¹)	12	0.78	43.9	2.2	0.77	43.8	2.1
	CCE (g kg ⁻¹)	12	0.84	79.8	2.5	0.94	53.9	4.0
	Fe _o (g kg ⁻¹)	10	0.61	0.13	1.6	0.73	0.10	1.9
	CEC (cmol_c kg⁻¹)	9	0.70	5.6	1.8	0.93	3.4	3.4
	OM (g kg ⁻¹)	13	0.68	3.2	1.8	0.72	3.3	1.8
	pH _w	11	0.59	0.2	1.6	0.47	0.2	1.4
ASD Vis-NIR	Clay (g kg ⁻¹)	11	0.77	47.4	2.1	0.80	40.7	2.2
	CCE (g kg ⁻¹)	13	0.86	76.7	2.7	0.93	60.1	3.5
	Fe _o (g kg ⁻¹)	8	0.58	0.15	1.5	0.70	0.11	1.8
	CEC (cmol _c kg ⁻¹)	8	0.69	5.9	1.8	0.88	3.9	2.9
	OM (g kg ⁻¹)	14	0.65	3.3	1.7	0.77	3.1	1.9
	pH _w	13	0.43	0.2	1.3	0.48	0.2	1.4
MIR	Clay (g kg ⁻¹)	16	0.82	41.6	2.4	0.82	37.9	2.4
	CCE (g kg⁻¹)	9	0.96	39.2	5.3	0.99	24.9	8.5
	Fe_o (g kg⁻¹)	16	0.67	0.13	1.7	0.80	0.09	2.3
	CEC (cmol _c kg ⁻¹)	8	0.74	5.5	2.0	0.91	3.5	3.2
	OM (g kg ⁻¹)	14	0.75	2.6	2.0	0.84	2.4	2.5
	pH_w	13	0.55	0.2	1.5	0.61	0.2	1.6
Cary Vis-NIR + MIR	Clay (g kg ⁻¹)	13	0.72	50.2	1.9	0.79	40.5	2.2
	CCE (g kg ⁻¹)	9	0.90	65.0	3.1	0.97	34.3	6.2
	Fe _o (g kg ⁻¹)	16	0.67	0.12	1.8	0.62	0.12	1.6
	CEC (cmol _c kg ⁻¹)	10	0.68	5.8	1.8	0.93	3.3	3.4
	OM (g kg⁻¹)	14	0.63	3.4	1.6	0.87	2.4	2.5
	pH _w	11	0.51	0.2	1.4	0.58	0.2	1.6
ASD Vis-NIR + MIR	Clay (g kg⁻¹)	11	0.83	40.2	2.4	0.83	37.0	2.4
	CCE (g kg ⁻¹)	10	0.96	39.9	5.2	0.99	25.5	8.3
	Fe _o (g kg ⁻¹)	10	0.67	0.13	1.8	0.76	0.10	2.0
	CEC (cmol _c kg ⁻¹)	7	0.75	5.3	2.0	0.92	3.3	3.4
	OM (g kg ⁻¹)	16	0.76	2.7	2.0	0.86	2.3	2.6
	pH _w	12	0.51	0.2	1.4	0.60	0.2	1.6

bonds in free water at around 1,400, 1,950 and 2,200 nm; pH_w was poorly predicted because the data spanned a short range (7.2-8.7).

The predictions of clay content, CCE, Fe_o and OM provided RMSE values of 37, 25, 0.1 and 2 g kg⁻¹ respectively; those of CEC RMSE = 3 cmol_c kg⁻¹ and those of pH_w RMSE = 0.2.

Very good (external validation) calibrations (RPD > 2) were obtained, in decreasing order, for CCE, CEC, OM, clay content and Fe_o, highlighting CCE with RPD = 8.53 (Table 2). Modest calibration (1.4 > RPD > 2) was obtained for pH_w, however these results are similar to those obtained in previous spectroscopic studies (e.g. Janik *et al.*, 1998; Viscarra-Rossel *et al.*, 2006).

Our results show that RS in the Vis-NIR, MIR and Vis-NIR-MIR ranges can be useful for the simultaneous assessment of various soil properties (particularly carbonate, clay and iron oxides) which are the most influential on the risk of Fe chlorosis. The specific spectral region to be used depends on the amount of sample preparation required, the accuracy of the predictions and the cost of the technology. For example, the gain in prediction accuracy from using an MIR instead of a Vis-NIR spectrometer may not justify the greater cost of MIR technology and the need for more extensive sample preparation. These results are interesting with a view of performing methods based on the use of portable Vis-NIR fibre optic spectrometers in the fast identification in field of soils

with a high risk of inducing Fe chlorosis. The direct application to the field may present different problems due to the samples are not sieved so that should be checked in next studies.

As conclusions, reflectance spectroscopy in the Vis, NIR, MIR and Vis-NIR-MIR was effective acquiring

information from soil. Accurate estimation of the content of different soil components by PLS was achieved. The following R^2_{adj} and RMS were obtained for external validated predictions: 0.83 and 37 g kg⁻¹ for clay content in the Vis-NIR-MIR range, 0.99 and 25 g kg⁻¹ for CCE in the MIR range, 0.80 and 0.1 g kg⁻¹ for Fe_o in the MIR

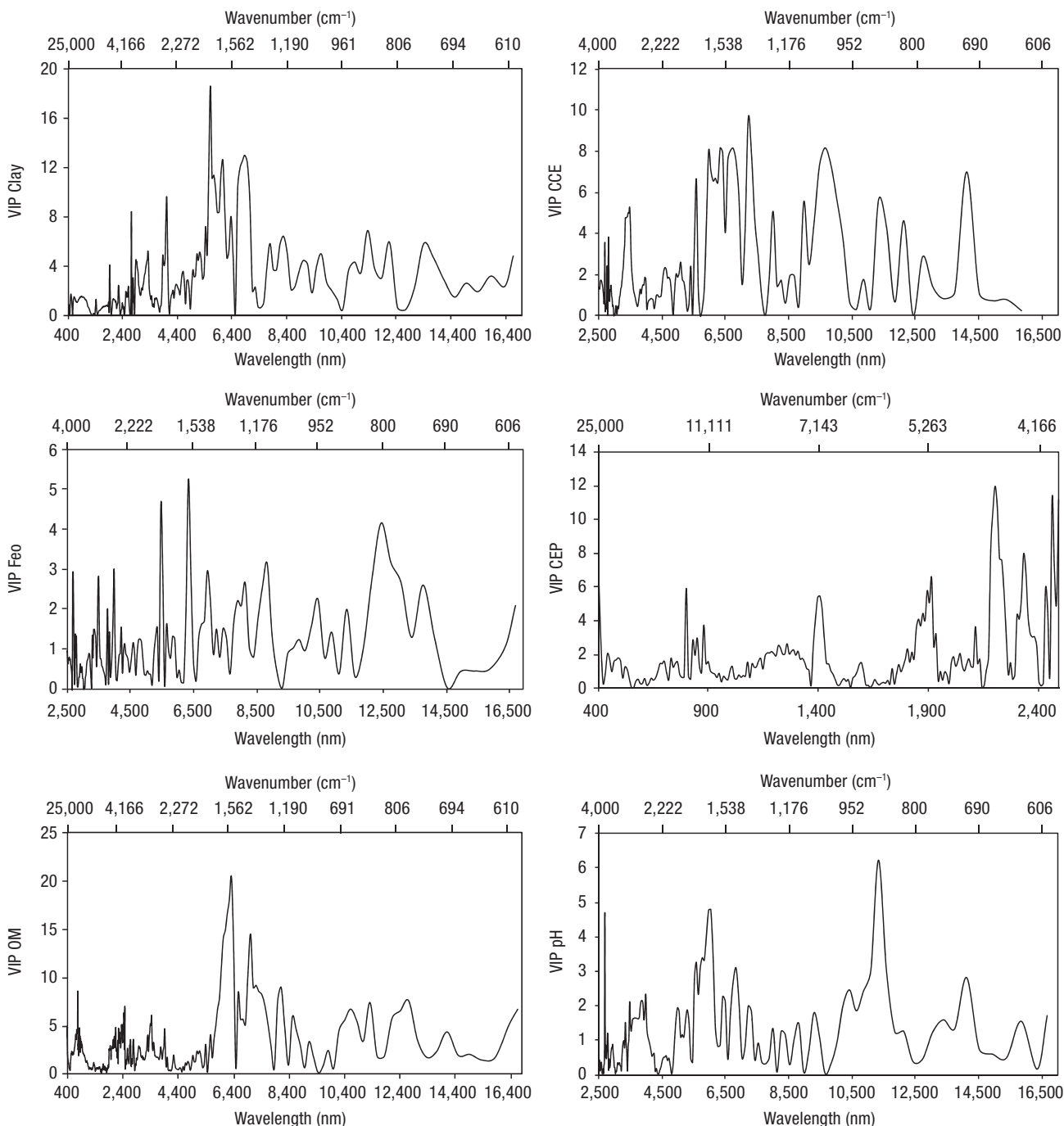


Figure 3. Variable importance for projection (VIP) for the best correlations of (A) clay content, (B) calcium carbonate equivalent (CCE), (C) oxalate-extractable Fe (Fe_o), (D) cation-exchange capacity (CEC), (E) organic matter content (OM) and (F) pHw.

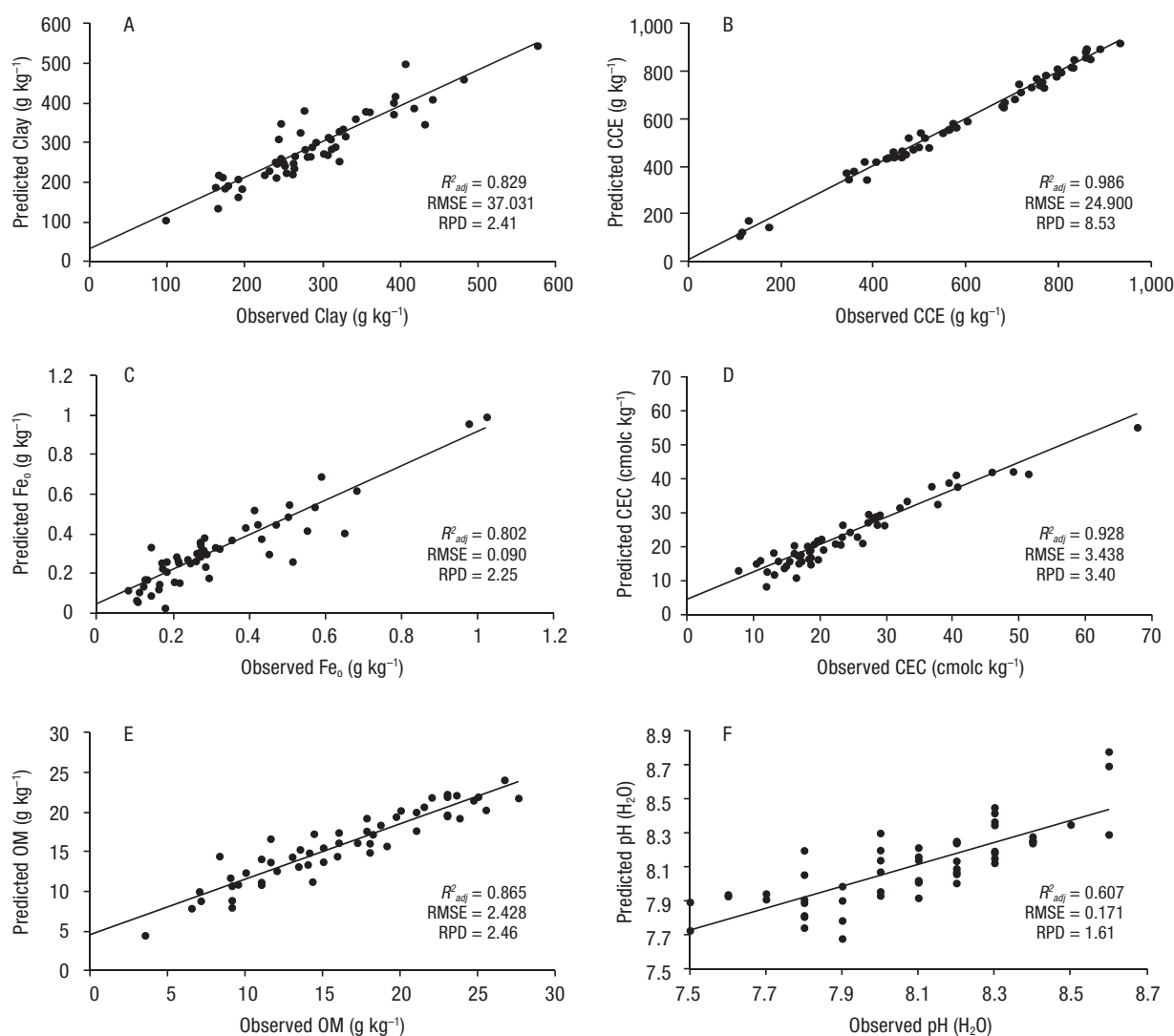


Figure 4. Predicted vs. observed (external validation) values of (A) clay content, (B) calcium carbonate equivalent (CCE), (C) oxalate-extractable Fe (Fe_o), (D) cation-exchange capacity (CEC), (E) organic matter content (OM) and (F) pHw.

range, 0.93 and 3 cmol_c kg⁻¹ for CEC in the Vis-NIR range, and 0.87 and 2 g kg⁻¹ for OM in the Vis-NIR-MIR range. Very good calibration (RPD > 2) was obtained in all instances. Thus, these spectroscopic analyses combined with PLS regression can provide a very useful information for environmental monitoring, modeling and precision agriculture, and specifically, for identify the risk of iron chlorosis in soils

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