**Soil fertility assessment by Vis-NIR spectroscopy: predicting soil functioning rather than availability indices**

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**Abstract**

Soil fertility is typically assessed by chemical analysis, which is expensive and time-consuming, and hence impractical for site-specific fertilizer management. Visible and near infrared (Vis–NIR) spectroscopy has been used for determining soil properties and chemically extractable plant nutrients. However, the suitability of Vis–NIR for accurate assessment of nutrient availability to plants has not yet been fully explored. In this work, we examined the accuracy of this technique as a new nutrient availability index, and in the case of P as a proxy for plant-available P. To this end, total plant-available P in soil was quantified in a P-depletion experiment with crops, and the availability of Ca, Mg, K, and Fe was assessed by chemical extraction.

Vis–NIR spectroscopy allowed us to accurately estimate plant-available P, which depends not only on soil factors but also on the crop performance to take up P. Vis–NIR spectroscopy proved effective in identifying P, Ca, Mg, K, and Fe responsive sites. Precise estimation of plant-available P was a result of accurately predicting soil properties governing P availability to plants by Vis–NIR spectroscopy. In addition, this technique provided accurate predictions of soil properties influencing the dynamics of applied P and K fertilizer, which can be useful to adapt fertilization practices to soil properties. Vis–NIR spectroscopy can therefore enable a qualitative leap to cost-effective integral assessment of soil fertility by providing accurate predictions of soil functioning rather than mere estimates of availability indices, thereby facilitating more sustainable use of resources in agriculture.

Key words: nutrient availability, phosphorus, potassium, iron, soil functioning, NIRS.

Abbreviations: AER-P, Anion exchange resin extractable P; CAP, Critical available P; CCE, Ca carbonate equivalent; CEC, Cation exchange capacity; Feca, Fe soluble in citrate–ascorbate; Fecbd, Fe soluble in citrate–bicarbonate–dithionite; MPLSR, Modified Partial Least Squares Regression; NIRS, Near infrared spectroscopy; PBC, P buffer capacity; R2, Coefficient of determination in calibration; r2, Coefficient of determination for cross validation; SD. Standard deviation; SECV, Standard error of cross-validation; SNV-DT, Standard normal variate and Detrending; SOM, Soil organic matter; SPT, soil P test; TAP, Total available P; Vis–NIR, Visible and near infrared; VRA, Variable rate application; *Xm*; Maximum P sorption capacity; XRF, X-ray fluorescence;

1. **Introduction**

Feeding a growing population while facing the consequences of agriculture on global change and environmental stress requires efficient resource management of plant nutrients, among other factors (McDonald et al., 2011; Tilman et al., 2011; Amundson et al., 2015). Soil fertility is typically assessed in terms of nutrient availability indices that are usually determined by chemical analysis of soil. This is an expensive, time-consuming process that produces hazardous waste and is completely useless for site-specific fertilizer management under the principles of precision agriculture (Bermudez and Mallarino,2007; Mouazen and Kuang, 2016). In addition, precise mapping for effective large-scale prediction or development of management policies is made difficult in practice by the large number of observations required, and also by the heavy workload and high cost of soil sampling and analyses (Tóth et al., 2014; Ballabio et al., 2016). In-season canopy spectral measurements of N have proved effective for variable rate application (VRA) of N fertilizers (Cilia et al., 2014; Basso et al., 2016) thanks to the close relationship between plant N status and spectral properties of vegetative organs (Knyazikhin et al., 2013). By virtue of the mobility N in the soil profile, fertilization management based on crop spectral measures is feasible with top-dress application. However, P, K, Ca, Mg and most micronutrients are not mobile, so they require broadcast or banded pre-plant application. For these nutrients, soil analysis before sowing is thus the only realistic approach to assessing crop requirements. This limits the potential of VRA for non-mobile nutrients in accordance with the principles of precision agriculture.

Accurate fertilizer management is of particular concern for P, which is a non-renewable strategic resource a future scarcity of which might constrain global food security (Ryan et al., 2013; Cordell and Neset, 2014; Withers et al., 2014). Although the within-field variability of P is usually lower than that of N as result of its lower mobility, it is assumed to be high enough to recommend using VRA fertilizer strategies (Mallarino and Wittry, 2004; Mouazen and Kuang, 2016). Fertilization recommendations are based on P chemical extractions used as “soil P availability indices” (also called “soil P tests” –SPT–), such as the widely used Olsen P (Olsen et al., 1954). These chemical extractions do not provide actual estimates of total available P (TAP) in soil, i.e. P that can be taken up by crops till complete depletion of the available pool of the nutrient, but rather identify sites responding to P fertilization (Recena et al., 2016; Recena et al., 2017). However, these SPTs have been deemed inaccurate for precise fertilization (Jordan-Meille et al., 2012; Recena et al., 2015; Recena et al., 2016). This is the result of the frequently observed poor relationship between SPT values (amounts of P chemically extracted) and P uptake by plants (Recena et al., 2017).

In the last decades, the development of spectral non-destructive techniques augmented significantly in order to increase the speed of analytical response for soil quality and VRA assessment. Visible and near-infrared reflectance spectroscopy (350–2500 nm) has proved to be an interesting alternative to some conventional laboratory analyses (Viscarra Rossel et al., 2006; Stenberg et al., 2010). The basis of this spectroscopic method is the absorption of radiation at specific wavelengths by certain molecular bonds in the NIR region, e.g. O-H, C-H, N-H and C-O groups (Morra et al., 1991), or depending on the colour in the visible region (Torrent and Barrón, 2002). For calibration, the absorption spectra of a set of calibration samples is subjected to chemometric procedures to build a predictive model. This means that spectra traits of the samples (i.e., absorption or transformed data of the absorption at given wavelengths) are related to specific properties of samples determined by reference methods (e.g. chemical analysis) by using appropriate statistical methods for model calibration. After that, validation of the model is performed by other specific statistical methods. Applied to the spectra of unknown samples, the model gives an estimate of the required analytical value. This has obvious advantages: (i) it is a fast analysis technique, since only take minutes to acquire one spectrum on which grounds several sample attributes can be determined; (ii) the potential to analyse different sample types and attributes with the same instrument, reducing the time required for its economic amortization, (iii) it is not usually necessary to use reagents which may be hazardous, placing it as an environmental friendly technique, and (iv) the reduced analytical cost by all these reasons (Viscarra Rossel et al., 2006; Xu et al., 2018). As an evidence of all these benefits in using near infrared spectroscopy (NIRS), the Canadian Grain Commission (CGC) saved, between 1974 and 1993, CAN$ 2.5 million per year in protein analysis using NIRS while the purchase price of NIR instrument was CAN$ 96,000; this avoided the generation of 47 t of caustic waste (Stark, 1996). Other official organisms like the US Food and Grain Inspection Service (FGIS) also performs protein determinations by NIRS since 1994 (Pierce et al., 1996).

Near infrared spectroscopy (NIRS) has proved effective in determining some soil properties such as soil organic matter (SOM), clay content, water, and pH (Stenberg et al., 2010; Viscarra Rossel, 2011; Stevens et al, 2013). However, assessments of available nutrient status by correlating spectral measurements with the concentrations of chemically extracted nutrients (availability indices) not always provide consistent results; for example, the variance explained for soil P tests typically ranges from 49 to 80 % and is usually lower than that for exchangeable cations (He et al., 2007; Terhoeven-Urselmans et al., 2008; Zornoza et al., 2008). In-field NIRS studies have proved effective towards reducing field variability, but not towards accurate assessment of P-responsive sites (Tóth et al., 2014). In addition to the information obtained by NIRS, the visible spectra can provide information about other soil properties influencing the nutrient cycle in soil (e.g., mineralogy, Fe oxide contents), which affects the availability and dynamics of P in soil (Torrent and Barrón, 2002; Stenberg et al., 2010). Thus, the integral management and interpretation of visible and near infrared (Vis–NIR) spectra may thus allow the determination of crucial parameters for assessing soil fertility.

Spectral measurements have never been correlated with actual nutrient uptake by crops. Although NIRS has been used to predict the concentrations of chemically extracted nutrients in soil (availability test), the suitability of this method for accurately assessing actual plant-available nutrients and other, more specific soil functioning parameters remains largely unexplored. Also, NIRS is known to allow a number of soil properties influencing nutrient dynamics to be determined. In combination with visible reflectance spectra, NIRS might allow crucial properties influencing the plant availability of many nutrients to be assessed. On these grounds, we hypothesized that Vis–NIR spectral measurements could provide reliable estimates of the amount of available nutrients to plant in soil. This would enable more accurate assessment of soil fertility than with estimates based on chemical extractions, which may be inconclusive as regards fertilizer recommendations. The primary aim of this work was thus to confirm the accuracy of the Vis–NIR technique as a multi-nutrient availability index for soil, establishing threshold value for identifying fertilizer responsive sites, and predicting total plant-available P. The results could enable fast, cost-effective soil fertility assessment with a view to implementing VRA strategies and producing high-density soil fertility maps.

**2. Materials and Methods**

*2.1. Soil collection*

We used a set of 36 soil samples, 18 of them were previously described by Recena et al. (2017), who studied the main physic-chemical properties and some of the P availability parameters described here. The samples were collected from different locations in agricultural lands of Spain and deemed representative of soil types developed under Mediterranean climate. The soils included Mollisols, Entisols, Inceptisols, Alfisols and Vertisols as per Soil Taxonomy (Soil Survey Staff, 2010). These soil orders can be considered between the most typical in temperate agricultural regions (USDA, 2017). Samples were all obtained from the Ap horizon (0–20 cm) at each location. The agricultural use of the land, parent material of the soil, site location and associated climatological data can be found elsewhere (Recena et al., 2017).

*2.2. Soil characterization*

The soils were analysed for particle size distribution, organic matter (SOM), cation exchange capacity (CEC), Ca carbonate equivalent (CCE) and pH according to standard methods described by Recena et al. (2017). Exchangeable cations were determined by emission (K) or absorption (Ca and Mg) spectrometry after neutral acetate extraction, which is an usual availability index for these nutrients. Olsen P was determined as soil P test according to Olsen et al. (1954). Anion exchange resin extractable P (AER-P) in bicarbonate form was used as an estimate of total available P in soil (Recena et al., 2017). Total P, total inorganic P and organic P were determined according to Saavedra et al. (2007). Iron in poorly crystalline Fe oxides was determined as Fe soluble in citrate–ascorbate (Feca) and iron in crystalline oxides as Fe soluble in citrate–bicarbonate–dithionite (Fecbd) after citrate–ascorbate extraction (de Santiago and Delgado, 2006).

After plant harvest, rhizospheric soil was sampled. To this end, all roots were separated from bulk soil by hand and after that by gentle shaking during 1 min. Fine roots and soil were gently shaken for another 1 min in a plastic container to separate the the rhizospheric soil from roots (Gobran and Clegg, 1996). Phosphatase activity in rhizospheric soil was determined as the average of four crops as described by Recena et al. (2017).

The soil properties governing P dynamics were examined from sorption curves run at 6 d according to Sanchez Alcalá et al. (2015) and Recena et al. (2017). Fitting sorption data to the Freundlich equation allowed the amount of P sorbed at a unit P concentration in solution (*A*), and the affinity factor of P for sorbent surfaces (*b*), to be estimated. The value of P buffer capacity (PBC), which describes the capability of the soil to replenish P in solution, was calculated as the slope of the sorption curve at 1 mg L−1. The maximum P sorption capacity of the soils (*Xm*) was estimated with the Langmuir model. An example of estimation of all these parameters is given in Figure S1.

All data for the studied soils are given in Table S1 (Supporting Information).

*2.3. Plant-available phosphorus*

The total available P to plants in soil (TAP) was determined by P depletion with plant cultivation according to Recena et al. (2017), who showed TAP values for 18 of the studied soil samples. This involved alternately growing wheat and sunflower under controlled conditions in pots. After each crop, Olsen P and a proxy for P concentration in the soil solution (molybdate reactive P in 0.01 M CaCl2 extracts; Recena et al., 2017) were determined in the soil. This allows us to describe the relationship between cumulative P uptake (calculated by adding to the P taken up by each crop, the uptake in previous crop steps) and the proxy measure for P concentration in solution. Total available P to plants in soil was estimated as cumulative P uptake by plants as extrapolated to the proxy measure of P in the soil solution at which negligible P absorption by the crops can be expected (an example is described in Figure S2 in supplemental material).

In addition to TAP, we calculated a new index based on the P depletion by successive crops. To this end, the cumulative P uptake of the successive crops was represented as a function of Olsen P after each crop (Figure 1 shows an example). This index was defined as the cumulative P uptake interpolated to the Olsen P threshold value above which no fertilizer response was to be expected. We called this index “critical available P” (CAP) because no fertilizer response can be expected at CAP values higher than zero. We can consider CAP as a P availability index more closely related to the ability of plants to absorb P from a given soil than are the indices based on chemical extraction (e.g., Olsen P).

*2.4. Visible and near-infrared (Vis–NIR) spectra*

The reflectance spectra for the soils were obtained by using a Foss-NIRSystems 6500 SY-II instrument from Foss NIRSystems (Silver Spring, MD) in the visible (400–1098 nm) and near infrared region (1100–2498 nm). The spectral resolution was 2 nm and the bandpass (10 ± 1) nm. Samples were scanned by using a transport module furnished with a ¼ rectangular cup (4.6 × 5.7 cm). Reflectance data were computed as absorbances (log 1/R) and a total of 1050 data points per soil sample acquired. The spectrum for each soil was recorded in duplicate on different subsamples. Each replicate was the result of 32 successive scans (16 reference/32 sample/16 reference). The average spectra for each pair of replicates for each soil (n = 36) were used for calibration. Spectra were acquired and processed, and calibration done, with the software WINISI v. 1.5 (Infrasoft International, State College, PA).

*2.5. Calibration and validation of predictive models based on Vis-NIR*

Spectral scatter was corrected by using the Standard Normal Variate, followed by de-trending mathematical treatments (Barnes et al., 1989). Two spectral derivatives (1,5,5,1 and 2,5,5,1) were also applied, the first digit indicating the derivative order, the second the derivative gap, the third the smoothing segment and the fourth the second smoothing segment (Shenk et al., 1989). Untreated raw spectra were also used for calibration. The calibration for each soil property studied was done over the Vis–NIR spectral range (400–2498 nm). Predictive models for each variable were constructed by using Modified Partial Least Squares Regression (MPLSR) (Shenk and Westerhaus, 1995) with the PLS1 algorithm. Cross-validation was used to determine the optimum number of factors for the regression models and also to avoid overfitting. Because of the small number of samples in the calibration set, the data set was split into six sub-sets for cross-validation, each group then being predicted with a calibration model developed with the other samples. Finally, validation errors were combined to obtain a standard error of cross-validation (SECV).

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 (Shenk and Westerhaus, 1996). The goodness of the MPLSR models was assessed in terms of their calibration statistics, namely: Coefficient of Determination in calibration (R2), Standard Error of Cross-Validation (SECV) and Coefficient of Determination for Cross-Validation (r2). SECV is considered to be the best individual estimate of the predicting ability of an equation; also, it provides accurate, useful information for evaluating models obtained from a small number of samples (Shenk and Westerhaus, 1996). The best calibrations were assumed to be those with the highest r2 and lowest SECV values.

**3. Results**

*3.1. Soil properties*

Soils ranged widely in properties (see Table 1, and Table S1 for details of each soil in supplemental material). Thus, they had clay contents ranging from 48 to 640 g kg–1, soil organic C (SOC) levels below 20 g kg–1, pH ranging from 6.5 to 8.3, and a Fe oxide content < 50 g kg–1 (predominantly in crystalline Fe oxides). Thirty were calcareous. Based on their Olsen P values (4.8–49.1 mg kg–1), the soils spanned a wide range of P available status, with a median value of 15.6 mg kg–1. AER-P ranged from 0.5 to 33.5 mg kg–1. Total available P (TAP) as estimated in depletion tests ranged from 4.3 to 81.7 mg kg–1 (median 21.5 mg kg–1), and critical available P (CAP, no fertilizer response being expected with values above 0) from 0.2 to 73.6 mg kg–1 (median 12 mg kg–1) (Table 1). The estimates of P buffer capacity (PBC) and maximum P sorption capacity (*Xm*) as determined with the Langmuir model, and the affinity factor (*b*) and adsorption at 1 mg P L–1 (*A*) as per the Freundlich model, also varied widely (Table 1). There was also a wide range of values for alkaline phosphatase activity (72–172 mg PNP kg–1 h–1). The availability indices for Ca, Mg, and K also spanned wide ranges (Table 1).

*3.2. Visible and NIR spectral features*

The Vis–NIR spectra for all samples exhibited a typical absorbance band at 426 nm and a shoulder at 620 nm in the visible region (see the average raw spectra for the soils in Figure 2). The most salient peaks in the NIR region were those at 1400, 1900 and 2200 nm. The standard deviation (SD) of the raw spectra was higher for the band at 460 nm and the shoulder at ca. 660 nm (Figure 2). However, calculating the SD spectrum after applying a scatter correction pre-treatment based on the Standard Variate and De-trending (SNV-DT) in combination with the first derivative (1,5,5,1) led to a dramatically different absorption pattern (Figure 2). Thus, new, highly variable bands appeared at 488, 548, 660 and 772 nm in the visible region; and at 1118, 1358, 1380, 1404, 1462, 1720, 1876, 1896, 1944, 2086, 2134, 2182, 2200, 2240, 2266, 2294, 2310, 2336, 2380, 2404 and 2446 nm in the NIR region.

*3.3. Estimating soil properties from Vis–NIR spectra*

Accurate estimates based on Vis–NIR spectra were obtained for a number of soil properties (Table 1). As expected, the NIR region provided good estimates for clay content, pH and cation exchange capacity. Surprisingly, SOC estimates were not so good (r2 = 0.61), and carbonate estimates from spectra in the NIR region were excellent (R2 = 0.99 and r2 = 0.97). Iron in poorly crystalline and crystalline oxides (Feca and Fecbd, respectively) was accurately estimated from the Vis–NIR spectra (r2 > 0.89). A reasonably good estimate of phosphatase activity was also obtained from the spectra, the predictive model explaining 80 % of the variance, albeit with a modest r2 value (0.57). Good estimates of factors involved in the equilibrium of P between the solid and aqueous phase of soil and governing P availability to plants (PBC, *A*, and *b*) were also obtained (Table 1), particularly for PBC (R2 = 0.93; r2 = 0.78). Neither P extraction method used to determine P availability (Olsen P and AER-P) were reasonably predicted, however (see Table 1). Total P, inorganic P and organic P in soil were also poorly predicted (R2 < 0.52); by contrast, TAP and CAP were highly accurately predicted, albeit from NIR spectral data. The variance explained exceeded 90 % and was 96 % for CAP (Figure 3); also, the cross-validation coefficients of determination were all very good (r2 > 0.88). Finally, the availability indices for K, Ca, and Mg were predicted with reasonably good accuracy (particularly that for Mg, with R2 = 0.91; r2 = 0.8; Table 1).

**4. Discussion**

According to their properties, tstudied P dynamics is expected to be controlled by Ca-phosphate precipitation and adsorption onto crystalline Fe oxides (Delgado and Torrent, 2000; Recena et al, 2017). The median value of the Olsen P exceeded the usual threshold of these soils for P fertilizer response (Recena et al., 2016). The median values of Ca, Mg, and K availability indices were also

Spectral measurements in the Visible–NIR region were useful towards estimating many soil properties (Stenberg et al., 2010; Nawar et al., 2016). In any case, the best predictions were those of total plant-available P (TAP) and critical available P (CAP). Therefore, the actual P availability to plants measured by crop extraction can be accurately predicted by Vis–NIR spectroscopy. This means that this technique estimates not only the ability of soil to supply P, but also that of plants to absorb P in specific soils. Therefore, Vis–NIR spectroscopy has for the first time been shown to predict plant response by extracting information about not only soil components but also soil functioning.

In practice, accurately predicting CAP may be very useful towards establishing accurate P fertilization strategies. The threshold value for fertilizer response is 0, negative values implying a response of yield to P fertilization. In contrast to P availability indices based on chemical extraction, CAP estimates represent the actual amounts of P present in soil that can be extracted by crops. Negative CAP values represent no absolute limitation in available P; rather, they suggest a very high probability of a response to P fertilization.

Vis–NIR spectroscopy not only identifies P responsive sites, but also provides useful information about the dynamics of applied P fertilizer. *A* and *b* values predicted with the Freundlich model describe the P sorption curve. This curve relates adsorbed P with the concentration in equilibrium in the soil solution (see Figure S1). Thus, it can be used to predict the P rate required to achieve the P concentration in the soil solution needed for optimum plant growth. This P rate is equivalent to the increment in the adsorbed P required for increasing the P concentration in the solution from the current to the optimal value for P absorption by plants. Although this is only a proxy estimate, it allows P fertilization patterns to be suited to the characteristics of the particular soil. This was never previously accomplished and is thus of great practical significance since the currently used P availability indices (e.g., Olsen P) only identify P responsive sites and are thus useless towards estimating the amount of P fertilizer required to ensure an adequate P level in soil (one above the threshold for a response to P fertilizer).

The availability of a nutrient in soil is not the result of its accumulating in it; in fact, TAP is rarely related to total P in soil (Delgado and Scalenghe, 2008). Rather, nutrient availability depends on the particular nutrient forms in equilibrium with those in the soil solution (the so called quantity factor) and on the ability of soil to replenish nutrients lost from the solution (the capacity or buffer capacity factor). The P buffer capacity (PBC) and the affinity factor for P in soil in the Freundlich model (*b*) were accurately estimated by Vis–NIR spectroscopy (Table 1). Both properties are crucial to explain the equilibrium of P between the solid phase and the soil solution —from which P is absorbed by plants (Recena et al., 2016; Recena et al., 2017). This is the first time that the factors governing P availability to plants have been estimated by Vis–NIR spectroscopy. Possibly, the good estimates of TAP and CAP thus obtained are a result of this technique accurately predicting the soil properties that govern P availability to plants.

PBC, P affinity for sorbent surfaces and TAP are all related to clay, Fe oxide content, mineralogy and carbonate content (Recena et al., 2017). It should be noted that the best estimates among soil components were those of Fe in poorly crystalline and crystalline oxides. This result may account for the accurate prediction of PBC from Vis–NIR spectra. According to Stenberg et al. (2010), the major absorption peaks for soil in the visible region can be ascribed to inorganic constituents such as iron minerals (goethite and hematite) and to SOM-related chromophores. Our average and SD raw spectra exhibited typical peaks at 426 and 460 nm that may be associated to goethite (Sherman and Waite, 1985). Also, the shoulder at 620 nm probably corresponded to hematite. SD for the first-derivative spectra exposed further differences in the peaks at 480 and 660 nm associated to goethite. These results are consistent with previous evidence that visible spectra are useful for characterizing Fe oxide mineralogy (Viscarra Rossel et al., 2010).

Iron determinations with Vis–NIR spectroscopy have traditionally focused on total Fe (Udelhoven et al., 2003) or Fe mineralogy (Viscarra Rossel et al., 2010). In this work, however, we found the Vis–NIR technique to be effective for separating two Fe fractions (Feca and Fecbd) with two very different effects on P adsorption and Fe availability. P has a lower affinity for poorly crystalline Fe oxides (Feca) than for crystalline oxides (Fecbd); also, the Feca/Fecbd ratio is crucial to explain P availability to plants (Recena et al., 2017). Feca has been deemed an accurate Fe availability index for assessing the risk of Fe deficiency chlorosis (de Santiago and Delgado, 2006). Therefore, Vis–NIR spectroscopy provides information not only about the main soil components influencing P adsorption in soil, but also about the risk of a major nutritional disorder for crops growing on alkaline soils.

Vis–NIR spectroscopy allows the accurate prediction not only of Fe fractions, but also of other properties influencing PBC, affinity for sorbent surfaces and availability to plants (e.g., pH, and clay and total carbonate contents). As expected, the NIR region is more useful for this purpose (Stenberg et al., 2010). Thus, the peak at 2200 nm may be associated to clay (Lobell and Asner, 2002), and those at 2336 and 2446 nm to illite (Post and Noble, 1993), the last of which was probably the dominant clay mineral in most of the studied soils. The absorption peaks near 1468 and 1970 nm could be due to adsorbed water in the clay fraction (Stenberg et al., 2010). The bands at ca. 1118, 1720–1748 and 2200–2400 nm in the first-derivative spectrum highlight the variability in soil organic carbon (SOC) and total N (Stenberg, 2010) among soils, and those at 1876 and 2336 nm the variability in carbonate content (Clark et al., 1990).

The TAP predictions provided by the Vis–NIR technique were much more accurate than those based on the usual P availability indices. Overall, Olsen P explained 53 % of the variance in TAP among the studied soils, whereas the best estimates obtained, which was obtained with AER-P, accounted for 81 % (Recena et al., 2017). The usefulness of most P availability indices is limited by the fact that a single measurement cannot encompass all the factors influencing plant performance (e.g., PBC) (Sánchez-Alcalá et al., 2015). Vis–NIR spectroscopy, however, allows simultaneous estimation of most of such factors and hence affords more accurate predictions than traditional P availability indices, obtaining analytical results in less than 3 minutes.

Phosphatase activity was also reasonably accurately estimated (80 % of the variance in the set of samples was explained). This result reveals the potential of this analytical technique for assessing biochemical properties influencing soil quality and functioning (e.g., nutrient cycling) and is consistent with previous predictions of soil enzyme activities with the Vis–NIR technique (Zornoza et al., 2008). Organic P contributes to P uptake by plants and phosphatase activity is crucial with a view to explaining P availability (Recena et al., 2015). As a result, accurately estimating phosphatase activity with Vis–NIR spectroscopy can help explain the good predictions of TAP and CAP obtained.

Vis–NIR spectroscopy proved a good predictor of many soil properties influencing P dynamics and availability in the studied soils. On the other hand, the estimated amounts of chemically extractable P used as P availability indices (e.g., Olsen P, AER-P), and those for P fractions (inorganic, organic, total), were inaccurate. Although plant nutrients are not expected to absorb in Vis–NIR region (Stenberg et al., 2010), according to Maleki et al. (2006) P can be correlated with Vis–NIR spectra through different soil components acting as P sorbent surfaces. In fact, components involved in P geochemistry and soil factors governing P availability (PBC or *b*) were accurately predicted from Vis–NIR spectra, but neither major soil P fractions or P availability indices were. This result may explain why the Vis–NIR technique was accurate in estimating soil performance in terms of P supply to plants but not the concentrations of chemical extractable P in soil.

The accuracy of Ca, Mg and K predictions was comparable with best reported estimates (Zornoza et al., 2008). Extraction with neutral ammonium acetate has been deemed an accurate availability index for these nutrients in many soil types. Precise fertilizer recommendations should consider not only extractable amounts, but also soil texture and cation exchange capacity (CEC) since the threshold levels for response to fertilization increase with increasing clay content and CEC. The latter two properties were also accurately estimated by Vis–NIR spectroscopy. Therefore, this technique provides an accurate tool for predicting Ca, Mg and K responsive sites. The efficiency of K fertilization is limited by interlayer fixation in clay minerals. Vis–NIR estimates of clay content and mineralogy provide useful information for predicting K fertilizer dynamics after application. The content in illite, which is the clay mineral with the strongest effect on interlayer K fixation, can also be accurately predicted from NIR peaks (Post and Noble, 1993).

Unlike most studies on the subject, which used 50 to 400 samples for calibration (Stenberg et al., 2010), we used only two subsamples of each of 36 different soils to record spectra. This relatively small number of samples was imposed by the difficulty of determining actual TAP in soil, which involves long-term P-depletion experiments with successive crops. However small, our number of soils is comparable to those used in many other studies, namely: 52 for examining various nutrients and total Fe (Udelhoven et al., 2003), 60 for exchangeable cations and enzyme activity (Zornoza et al., 2008), and 38 for crop performance (Terhoeven-Urselmans et al., 2008). In addition, the ranges spanned by the target soil properties were similarly wide or even wider than those of some previous studies (Stenberg et al., 2010).

**5. Conclusions**

Vis–NIR proved to be a precise multi-nutrient availability index for soil. It accurately predicted total plant-available P, and P, Ca, Mg, and K responsive sites. The Vis–NIR technique also provides information about the dynamics of applied P and K fertilizers, which can be useful to develop fertilization strategies suited to specific soil types. This use of Vis–NIR spectroscopy constitutes a qualitative leap in the integral assessment of soil fertility as it allows one to predict soil functioning more accurately than with functioning-related chemical indices. Also, it opens up new prospects for developing cost-effective analytical methods for establishing good agricultural practices and affords high-density surveys. Although the suitability of the Vis–NIR technique for field measurements was not demonstrated, the results suggests that it affords fast acquisition of field data for accurate VRA in precision agriculture. This can be especially useful for developing strategies enabling more sustainable use of agricultural resources with very little environmental impact.

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FIGURE CAPTIONS

**Figure 1.** Example of the estimation of the critical available P (CAP) in the soil identified as ID 25 (see Table S1 for other soil properties). The figure represents the cumulative P uptake (calculated by adding to the P taken up by each crop step, the uptake in previous crop steps, according to Recena et al., 2017) as a function of Olsen P in soil (Y = 0.1 X2 – 6.1 X + 91). The vertical line identifies the threshold Olsen P value for response to P fertilizer response (Recena et al., 2016), and the horizontal line identifies the CAP value for this case.

**Figure 2.** Average and standard deviation of the raw and first-derivative spectra for the soil samples.

**Figure 3.** Estimation of critical available P (CAP) from Vis–NIR spectra. Dependent and independent variables were normally distributed as per the Kolmogorov–Smirnov test (*P* < 0.05). *Y* = *X*, *R*2 = 0.97, *P* < 0.001 for the whole dataset. Two influential points detected (5 times the average leverage), exclusion of which had no significant impact on the model (*Y* = 0.97*X*; *R*2 = 0.88; *P* < 0.001).