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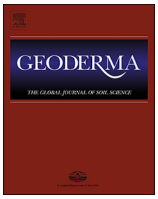

Soil fertility assessment by Vis-NIR spectroscopy: Predicting soil functioning rather than availability indices

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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.

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., 2012; Cordell and Neset,

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Abbreviations: AER-P, anion exchange resin extractable P; CAP, critical available P; CCE, Ca carbonate equivalent; CEC, cation exchange capacity; Fe_{ca}, Fe soluble in citrate–ascorbate; Fe_{cbd}, Fe soluble in citrate–bicarbonate–dithionite; MPLSR, Modified Partial Least Squares Regression; NIRS, near infrared spectroscopy; PBC, P buffer capacity; R^2, coefficient of determination in calibration; r^2, coefficient of determination for cross validation; SD, standard deviation; SECV, standard error of cross-validation; SNV-DT, Standard Variate and De-trending; SOM, soil organic matter; SPT, soil P test; TAP, total available P; Vis–NIR, visible and near infrared; VRA, variable rate application; X_m, maximum P sorption capacity; XRF, X-ray fluorescence

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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, 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 are 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 perform 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 a usual availability index for these nutrients. Olsen P was determined as soil P test according to Olsen (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 (Fe_{ca}) and iron in crystalline oxides as Fe soluble in citrate–bicarbonate–dithionite (Fe_{cbd}) 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 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 Sánchez-Alcalá et al. (2015) and Recena et al. (2017). Fitting sorption data to the Freundlich equation