



Soil pH value, organic matter and macronutrients contents prediction using optical diffuse reflectance spectroscopy



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ABSTRACT

Accurate information about the variability of soil attributes and characteristics is essential for the site-specific management of agricultural inputs, also known as precision agriculture; however, the inability to obtain soil information rapidly, inexpensively and reliably remains one of the biggest challenges. Recently, visible and near infrared (VIS/NIR) diffuse reflectance spectroscopy has emerged as a rapid and low-cost tool for extensive investigation of soil characteristics, such as macronutrients contents, pH value, and organic matter content. In the present work, the potential of VIS/NIR diffuse reflectance spectroscopy to predict the contents of N, P, K and OM and the value of pH in soils was analyzed using two spectrometers: Veris VIS/NIR soil sensor from Veris Technology Inc. and MPA FT-NIR spectrometer from Bruker Optics Inc. Subsequently, different pretreatment methods were adopted to improve the correlation between soil properties and the spectra, and then principal component regression was used, with the optimum numbers of PCs were selected on the basis of PRESS value in the leave-one-out validation. The primary conclusions in our study include: (i) optical reflectance spectroscopy in visible and near-infrared regions combined with appropriate pretreatment was an ideal tool for the estimation of soil pH value and OM content, while presented poor potentials in the prediction of total N, total P and total K; (ii) the models established with spectra after the preprocessing methods include MSC and S–G filter for smooth and first-order derivative together presented preferable results than those after MSC or S–G filter for smooth and first-order derivative individually; and (iii) the prediction results of the two spectrometers with different light-splitting techniques produced similar variation tendencies among the measured soil properties. Consequently, a scanning grating spectrometer in the NIR region proves to be an effective tool to measure certain soil properties, namely OM content, pH value and total N. Moreover, compared with a FR instrument, a scanning grating spectrometer is a preferable choice in the design of an on-the-go soil sensor.

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1. Introduction

Modern technological developments in positioning, sensing, and control systems have opened a new era in which many traditional agricultural practices were left behind (Adamchuk et al., 2004; Wang, 1999; Zhao, 2010). Instead, precision agriculture, also known as site-specific crop management, is a new farming management concept based on observing, measuring and responding to inter and intra-field variability in crops (Lee et al., 2010). Since soils are prone to significant spatial and temporal variability, the potential of managing soils on a site-specific basis has been

recognized gradually (Adamchuk et al., 2004). As an important part of modern precision agriculture, precision fertilization is required to take organic matter, nitrogen, phosphorus, potassium and many growth-promoted elements and organic fertilizer to a scientific formula, and thereby leads to a scientific application of fertilizers according to different soil types, as well as gains and losses of soil nutrients and crop types.

An accurate site-specific perception of soil properties is a prerequisite for precision fertilization; however, the inability to obtain such information rapidly, inexpensively and reliably remains one of the biggest challenges. Traditional laboratory chemical analyses in combination with sampling methods in fields may be cost prohibitive and time-consuming. During the past three decades, optical diffuse reflectance spectroscopy (DRS) has emerged as a rapid and nondestructive analytical method, which correlates the

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diffusely reflected radiation with several chemical and physical properties of soil samples (Chang and Larid, 2001; Hummel et al., 2001; Chaudhary et al., 2012; Gomez et al., 2008; Maleki et al., 2006; Mouazen et al., 2010; Liu and Liu, 2014; Peng et al., 2014). When a sample is illuminated with light, certain bonds within the molecules vibrate with the varying electric field, and the vibration absorbs optical energy and causes less light to be reflected off the sample. As generally reported, most of soil-related DRS studies to date have been focused on the visible (VIS: 400–700 nm) and near-infrared regions (NIR: 700–2500 nm) with both the accuracy of measurements and the cost of instruments taken into considerations. The predominant absorbers in the NIR region are the C–H, N–H and O–H functional groups, making NIR ideal for quantifying forms of carbon, nitrogen and water, respectively (Blanco and Villarroya, 2002; Franklin, 2002; Siesler et al., 2008); while VIS spectra were frequently associated with the estimation of soil OM content, with the recommended wavelengths being 564 nm, 660 nm, 623 nm, etc., and adopted as an assistant in the measurements of soil properties (Krishnan et al., 1980; Shonk et al., 1991).

As described in early studies, the correlations of several soil properties content with both visible and near-infrared spectroscopy were proved. Sudduth and Hummel employed soil NIR reflectance to estimate soil OM, moisture and cation exchange capability (CEC) for both surface and subsurface soils from US Corn Belt (Hummel et al., 2001; Sudduth and Hummel, 1993). Fystro adopted VIS/NIR spectroscopy to predict the content of soil organic matter and total nitrogen (TN), with appreciable results of $r^2 = 0.65$ for OM and $r^2 = 0.87$ for TN, respectively (Fystro, 2002). By comparing the performance of three calibration methods, namely, principal component regression (PCA), partial least squares regression (PLSR) and back propagation neural network (BPNN), the accurate measurements of some soil properties were evaluated, and the results indicated that the BPNN modeling with the optimal number of latent variables (LVs) was recommended (Mouazen et al., 2010). Using a commercially available portable spectrophotometer (Field-Spec Pro FR, ASD Inc., USA), He confirmed the good potential of VIS/NIR spectroscopy to assess soil nitrogen, organic matter and pH content; however, it was a not ideal tool for soil phosphorus and potassium prediction (He et al., 2007). On the basis of favorable relationships between the soil characteristic parameters and VIS/NIR spectra in experiments, Li developed a soil-organic-matter detector and obtained good results in practical applications (Li et al., 2010).

Based on the different light-splitting principles, bench-top NIR instruments can be classified into several types, such as filter, scanning grating, Fourier transform (FT), acousto-optical tunable filter (AOTF) and hadamard transform (HT), in which scanning grating and FT spectrometers were of most wide applications. A scanning grating spectrometer is ideal for quantitative measurements across a broad wavelength range with high signal/noise ratio, particularly in the visible region; while a FT spectrometer can provide preferable spectral resolution and wavelength accuracy within a limited wavelength range. Besides, due to the fact that a FT-NIR spectrometer is based on the principle of Michelson interferometer, it exhibits extremely high sensitivity to vibration and thus may be improper for the on-the-go detection. As stated previously, soil properties sometimes presented a quite complex spatial variability beyond traditional sampling density. While lab-based VIS/NIR produced favorable estimation of several soil properties, on-the-go VIS/NIR DRS was proposed and tentatively developed for intensively mapping soil macronutrients contents, OM contents and pH values. Obviously, scanning grating spectrometers are the preferred choices for on-the-go measurements; however, they exhibit comparatively low spectral resolution and wavelength accuracy, and therefore may produce poor results compared with FT spectrometers (Andersen et al., 2013).

There is always a tradeoff to be made between wavelength range, resolution, signal to noise ratio and other parameters of the instrument. For some specific soil properties, the best sensing range may vary with the adopted analysis method and dataset. For example, Krishnan et al. (1980) reported preferable estimation of OM content with VIS data than those with NIR data. However, Sudden and Hummel suggested that NIR data were more predictive of organic C. Using a commercial three-detector spectrometer (specifically, 350–975 nm, 975–1770 nm and 1770–2500 nm), Lee et al. (2009) conducted an in-depth study on estimating soil physical and chemical properties by means of optical diffuse reflectance spectroscopy. They performed PLS and SMLR to construct the relationship between soil properties and reflectance data, and similar accuracies were obtained by these two methods. Moreover, the third detector range (1770–2500 nm) could provide results comparable to those obtained using the total spectral range. Viscarra Rossel et al. (2006) compared the prediction results of different soil properties using each VIS, NIR and MIR region and the combined VIS–NIR–MIR to determine whether the combined information produces better predictions of soil properties than each of the individual regions, and accordingly deduced which of these regions may be best suited for simultaneous analysis of various soil properties. Quantitatively, the accuracy of PLSR predictions in each of the VIS, NIR, MIR and VIS–NIR–MIR spectral regions varied considerably amongst properties. In most situations, when performing quantitative measurements, the spectral resolution may be of less importance than the other parameters. Armstrong et al. (2006) used a 10-nm grating instrument and a 8 cm^{-1} FT instrument to perform quantitative analysis of several properties in wheat, and the comparison results indicate a comparable performance of two instruments. Similarly, Kolomiets and Siesler (2004) concluded that the high-resolution measurement cannot improve the accuracy in quantitative measurements of a narrow band drug active ingredient.

In the present work, the capability of VIS/NIR diffuse spectroscopy to predict soil total nitrogen content (N), total phosphorus content (P), total potassium content (K), organic matter content (OM), and pH value were studied with the use of two different spectrometers: VIS/NIR soil sensor by Veris Technology Inc. and MPA FT-NIR spectrometer from Bruker Optics Inc., with the specifications listed in Table 1. The experimental results from two spectrometers with different light-splitting principles were analyzed and compared. Different pretreatment methods were adopted to enhance the relativity between the spectra and measurements, and then principal components regression were used, while the optimum numbers of PCs were selected according to PRESS values in the leave-one-out validation. The ultimate goals of the present work include: (i) to analyze the potential of VIS/NIR diffuse reflectance spectroscopy to predict the contents of N, P, K and OM and the value of pH in soils; (ii) to seek the optimal pretreatment and regression methods for each property of soil; and (iii) to make a comparison of predictive capability between two spectrometers, with different light-splitting principles; specifically, to access the effects of wavelength range and spectral resolution on the prediction accuracy.

2. Materials and methods

2.1. Field description and sampling strategy

The soil samples were collected in Longkang Farm, Bengbu City, Anhui Province ($33^{\circ}6'15''\text{N}$ and $118^{\circ}52'33''\text{E}$), where annual average temperature and rainfall were 14.84°C and 789 mm, respectively. With an altitude ranging from 22.7 to 25.9 m, the overall flat fields in Longkang Farm could be classified as the lime concretion black soils. As one type of ancient cultivated soils, lime

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