Quantification of soil total phosphorus using mid-infrared spectroscopy

Kimberly Y. Epps,[1] James B. Reeves, III,[2] Nicholas B. Comerford[1]
[1]Soil and Water Science Department, University of Florida, Gainesville, FL, USA
[2]Environmental Management and By-Products Laboratory, ANRI-ARS-USDA, Beltsville, MD, USA

Overview

Infrared-spectroscopy, a cost- and time-effective means of chemometric analysis, has been used to successfully assess soil properties as well as to quantify total carbon and nitrogen concentrations in soils and plant residues with little sample preparation or alteration (Ben-Dor and Banin 1995, Cohen et al. 2005, Ludwig et al. 2002). While the near-infrared region spanning 2,500 nm – 25,000 nm is considered instrumental in highlighting organic functional groups, the mid-infrared has been deemed useful in the discrimination of mineral as well as carbon components of soil and plant tissue (McCarty et al. 2002). The aim of this work was to investigate the usefulness of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in the mid-infrared region on the determination of soil total phosphorus.

We asked:

> ***Are local calibrations that account for variations in the soil population due to texture, mineralogy and resident vegetation superior to global calibrations?***

Methods

<u>Study Sites.</u> Samples were drawn from eight paired study plots representing two land-uses (secondary forest and traditional cacao production) in the region of the Brazilian Atlantic Rain Forest of southern Bahia, Brazil (Figure 1). The areas ranged in soil texture from 7%-52% clay; 2%-12% organic matter as estimated by loss-on-ignition and comprised three mineralogies, as judged by visual and textural assessment.

<u>Sampling and Preparation.</u> Each 50m x 50m study site was divided into 25 subplots of 10m x 10m. Soils were sampled three times from the 0-10 cm depth and bulked within each subplot, yielding a total of 200 samples from all eight sites. Soils were air-dried, sieved to pass through a <2mm screen and hand-ground prior to wet chemistry analysis.

Figure 1. Location of study area on satellite image of Brazil.

<u>Chemical Analysis.</u> Total phosphorus was measured with the sulfuric acid/ hydrogen peroxide digestion method. Spectral data were obtained with a Digi-Lab FTS-7000 FTIR instrument and collected as pseudo-absorbance (log reflectance^{-1}) at a resolution of 2cm^{-1} in the mid-infrared region (4000-400 cm^{-1}).

<u>Calibration.</u> The study sites were divided into training sets and test sets such that the two sets held equal representation of the study sites. The calibration equations were calculated using the orthogonal partial least-squares regression (O-PLS) method (Martens and Naes 1986) and leave-n-out cross-validation ($n = 15$ for size of training set, $N \geq 100$; $n = 5$ for $N < 100$) was used to estimate the optimal number of factors in the calibration to avoid overfitting. Calibrations were validated using the test groups and the final model was further validated using bootstrap aggregation which was repeated 25 times. Assessment statistics used were R^2 and the root mean square error of prediction (RMSE). All analyses were conducted using the ParLeS software package of Viscarra-Rossel (2007).

<u>Pretreatments.</u> For each calibration, eight combinations of mathematical treatments were compared. Multiplicative scatter correction (MSC) and standard normal variate (SNV) are used for spectral baseline correction and the reduction of light scatter effects due to particle size; the application a Savitzky-Golay filter (SG) or the use of first or second derivatives can be used for spectral smoothing. Analyte values (TP) were log transformed to improve fits. After comparison of the results of various treatments, the model that gave the best results in terms of the final R^2 and RMSE values was selected. Models were developed from the entire data set and then from subsets corresponding to land use, texture and mineralogy.

Results and Discussion

Principal components analysis (PCA) of raw spectra (subjected to no mathematical treatments) representing all eight sites showed distinct separation of sites, separating the two very sandy sites (Sand =70%-85%) supporting both secondary forest and cacao production (Figure 2). PCA did not result in a separation of sites along land uses or mineralogy, even after the two sandy sites were removed (Data not shown.).

Of the spectral pre-treatments performed, the application of standard normal variate plus the Savitzky-Golay filter provided the best fits. Four mathematical treatments are presented in Figure 3.

Figure 2. Two land uses featured in the study: traditional, low-input cacao production (left) and secondary forest (right). Principal components analysis distinguished the spectra of two of the eight sites, one cacao and the adjacent secondary forest, due to its texture and/or mineralogy.

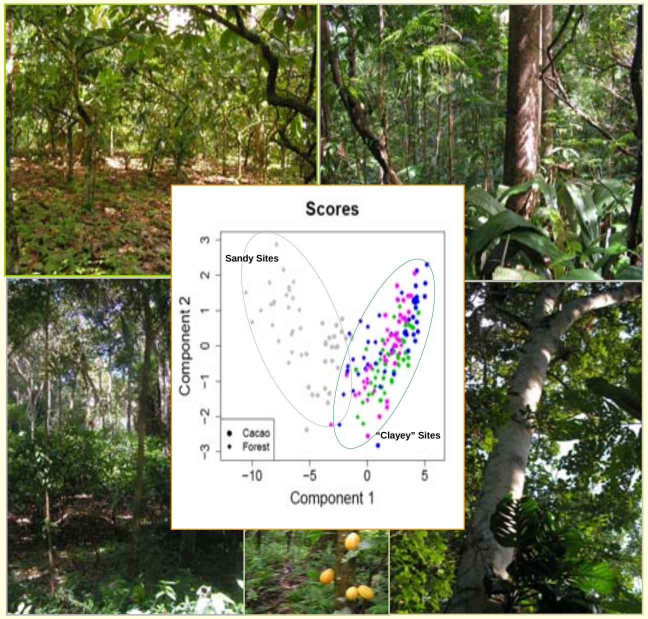


Figure 3. Diffuse reflectance spectra before and after mathematical treatments, where MSC = multiplicative scatter correction, SNV = standard normal variate. Mathematical treatments such as SNV and MSC facilitate the analysis of soil spectra with minimal handling by reducing the effects of particle size.

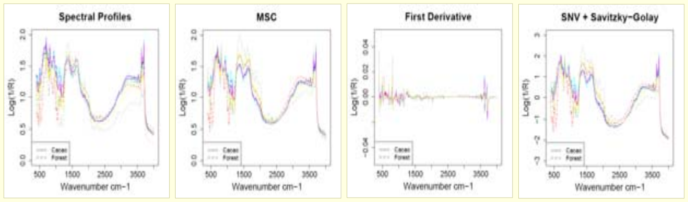
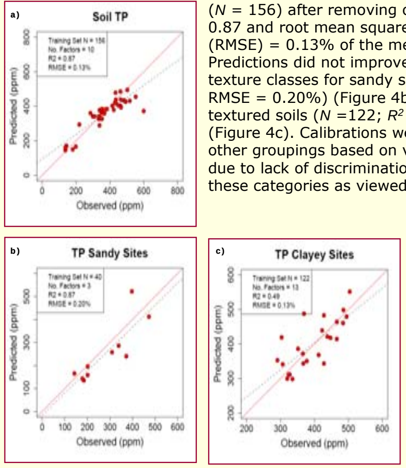


Figure 4. DRIFTS calibration results based on a) all soil textures; b) sandy sites and c) clayey sites.



The final calibration results arising from all sites ($N = 156$) after removing outliers yielded an R^2 of 0.87 and root mean square error of prediction (RMSE) = 0.13% of the mean TP value (Figure 4a). Predictions did not improve by calibration within texture classes for sandy soils ($N = 40$; R^2 of 0.87; RMSE = 0.20%) (Figure 4b), and worsened for finer textured soils ($N = 122$; $R^2 = 0.49$; RMSE = 0.13% (Figure 4c). Calibrations were not performed on other groupings based on vegetation or mineralogy due to lack of discrimination between spectra on these categories as viewed by PCA analysis.

Conclusions

Results show promise for the use of DRIFTS in predicting total soil phosphorus. These same data were used to predict carbon content (loss-on-ignition) with $R^2 = 0.97$ and RMSE = 0.09% in accordance to the success of other calibration studies with mid-range DRIFTS and carbon fractions (Zimmerman et al. 2007). It is suggested that the presence of clays may deter the effective calibration of soil phosphorus in this spectral region.

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