Soil Particle Size Effect on Absorbance Spectra of Sandy Soils in UV-VIS-NIR Regions

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Abstract. The reflectance spectra of the soil samples are influenced by soil particle size. Elimination of this effect requires a calibration model to remove the effect of soil particle size. Therefore, this study aimed to investigate the effects of soil particle size on reflectance spectra of sandy soil samples and to produce a particle size calibration model for the spectra of a sandy soil sample. Sandy soils were obtained from Edgar, Putnam County in Florida. Soil was sieved into three fractions. Leaching with de-ionized water and hydrochloric acid (0.1 molar HCl) was conducted in order to remove the current nutrient contents, which may contribute to the reflectance spectra of a soil sample. Reflectance spectra of soil samples were measured in UV, VIS and NIR regions between 200 and 2500 nm with a sampling interval of 1 nm. A particle size calibration model was developed using multiple linear regressions (MLR). The results from this calibration model enhanced the prediction accuracy terrestrial phosphorus (P) sensing in the Lake Okeechobee drainage basins.

Keywords. Reflectance, Sensor, Phosphorus, Lake Okeechobee, UV, VIS, NIR, Spectroscopy, Soil, Particle size.

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Introduction

Reflectance from a soil sample varies with regard to soil particle size in UV-VIS-NIR regions of the electromagnetic spectrum. This photo-physical property of the soil sample is very useful in determining the particle size distribution. However, the same feature is not desirable in sensing P concentration of a soil sample due to the fact that this photo-physical property introduces different variation of reflectance intensity at different wavelengths. Therefore, the effect of particle size on reflectance spectra of a soil sample should be calibrated while determination of chemical properties of the soil sample is conducted. Particle size is not the only contributor of variation to the soil spectra. There are other factors such as moisture content, soil reaction, soil orders, and etc.

Zhang (1992) studied the spectral properties of soils in order to improve the prediction of soil particle size fractions in near infrared band (0.76-0.90 μm). Reflectance of the near infrared band was used as an auxiliary variable in the prediction of soil particle size fractions on a 100 m x 100 m grid in a 2200 m x 1300 m field. It was reported that with cokriging, soil texture was predicted successfully in a 1300 m x 220 m field using reflectance data (NIR) as an auxiliary variable. The mean square error between the actual and estimated values was reduced up to 18 and 33 % for estimations of sand and clay, respectively. Arnold (1991) measured the spectral emittance of different particulate minerals at wavelengths from 5 to 25 μm in order to study the variation of diagnostic features with particle size and packing density. Conclusions were that spectral contrast features in the emittance spectrum of a particulate mineral were controlled by both particle size and packing density. Whereas the particle size was responsible for the type of feature that occurred, the packing density controlled the final contrast. Salisbury and D'Aria (1992) researched on infrared (8-14 μm) remote sensing of soil particle size. Their study suggested that the particle sizes of dry, quartz-dominated soils with low organic matter content and lack of overlying vegetation could be estimated with good accuracy using band ratios. Ristori et al., (1992) investigated the characterization of organic matter in particle size fractions of vertisols. The nature of organic matter of five vertisols was investigated using diffuse reflectance fourier transform infrared spectroscopy. Their results showed that organic matter was concentrated in the silt size aggregates and its nature appeared rather uniform in the five vertisols. Measurements of pristine and disturbed soils to determine spectral contrast differences between field and laboratory data were conducted (Johnson et al., 1998). Merry and Janik (2001) used mid infrared (MIR) spectroscopy for rapid and cheap analysis of soils. They found that after minimal sample preparation, the MIR spectrum of a soil took about two minutes to acquire and analyze. Their study demonstrated that the technology could provide good quality prediction of soil properties, e.g. carbonate and organic carbon, total nitrogen, cation exchange capacity, some exchangeable cations, electrical conductivity, pH, soil texture, and a number of other properties, some of which are expensive to measure by conventional methods and not usually available.

The objective of this research was to investigate the effects of soil particle size on reflectance spectra for pure sandy soil using reflectance spectroscopy in sensing P concentration in ultraviolet (UV), visible (VIS), and near infrared (NIR) regions.

Material and Methods

In order to study the effects of soil particle size on reflectance spectra of soils, pure sandy soil was obtained from Edgar, Putnam County in Florida. Sandy soil was graded into three particle sizes using a sieve shaker (RO-TAP, W. S. TYLER, Inc.). Sandy soil particle sizes were 600, 250, 125 μm for coarse, medium, and fine, respectively. A total of 84 sandy soil samples were
used in this study. Soil samples were leached using 0.1 molar HCl acid solutions and de-ionized water in order to remove existing P. After leaching, pH and P concentration of sandy soils were analyzed. Soil pH was measured using a pH/temperature meter (HI 991000, Hanna Instruments) and soil P was determined using a soil test kit (Luster Leaf Products, Inc.). If P was detected in the soil samples, further leaching was applied. Soil samples were incubated for 7 days with all P rates. P solution was prepared from potassium phosphate monobasic (KH$_2$PO$_4$) (Fisher Scientific). P rates were 0, 12.5, 62.5, 175, 375, 750, and 1000 mg/kg. P solution was added into soil thoroughly and soil samples were wetted to field capacity level (8% wet-basis moisture content for the Okeechobee county soils in Florida).

A spectrophotometer (Cary 500 Scan UV-VIS-NIR, Varian Inc.) equipped with a diffuse reflectance accessory (DRA-CA-5500, Labsphere) was used to collect spectral reflectance data for each soil sample. A 27.5 g of soil sample was placed into a sample holder. A reference material (Spectralon, Labsphere Inc.) was used to collect baseline. Spectral signature for each soil sample was collected using baseline correction mode. Reflectance for each soil sample was measured in 175-2550 nm with an increment of 1 nm. Since spectra of each soil sample had signal noise between 175-225 and 2525-2550 nm, the spectra of soil samples between 225 and 2525 nm were used. Reflectance of the soil samples was measured before and after drying. After each experiment soil samples were oven-dried at 104°C for 24 hours. The soil samples were sent to a laboratory for chemical analysis of P concentrations. All soil samples were analyzed for total P.

Reflectance of all samples were converted into absorbance before further analysis in order to find relationship between P concentrations and absorbance of the samples at different wavelengths using the Beer-Lambert’s law (Williams and Norris, 2001). The data was filtered using Savitzky-Golay polynomial convolution filter to remove the noise in the signal. In order to find the significant bands for each particle size fractions, correlation coefficient and standard deviation spectra were computed. Correlation coefficients were computed between absorbance and actual total P concentration of the soil samples. Two methods (ratio and discrimination) were developed in order to predict the particle size of sandy soil samples. In the ratio method, a ratio of 345 and 1323 nm was computed to obtain accurate classification of soil particle sizes shown in equation 1. Half of data was used to develop calibration models and another half was used for validation.

Absorbance ratio is calculated as follows:

\[ R = \frac{A_{\lambda=345}}{A_{\lambda=1323}} \]  

(1)

where

\( R = \) Absorbance ratio
\( A_{\lambda=345} = \) Absorbance at 345 nm
\( A_{\lambda=1323} = \) Absorbance at 1323 nm.

In the discrimination method, stepwise discriminant analysis (Proc STEPDISC, SAS/STAT, SAS Inc.) and multiple linear regressions (Proc REG, SAS/STAT, SAS Inc.) were used to select the significant wavelengths to determine the particle size of soil samples. Then, discriminant analysis (Proc DISCRIM, SAS/STAT, SAS Inc.) was used to predict the particle size of soil.
samples. Also two methods were used to predict P concentrations of soil samples. First method removed the particle size effect using the particle size effect removing (PSER) equation and predicted phosphorus concentrations of soil samples using stepwise multiple linear regressions (Proc REG, SAS/STAT, SAS Inc.). Second method predicted particle size concentration and used the appropriate prediction model developed earlier for prediction of phosphorus concentration for individual particle size class. Multiple linear regressions were computed using two methods, i.e., maximum $R^2$ (MAXR) and stepwise.

PSER is calculated as follows:

$$A_{PSER} = \frac{(A_{345} - \bar{A}_\lambda)}{(A_{\lambda 345} / A_{\lambda 1325})}$$

where

$A_{PSER}$ = Absorbance after particle size effect removal

$A_{\lambda}$ = Absorbance at present wavelength

$\bar{A}_\lambda$ = Average absorbance

$A_{\lambda 345}$ = Absorbance at 345 nm

$A_{\lambda 1325}$ = Absorbance at 1325 nm.

Standard error of calibration (SEC) and standard error of prediction (SEP) for calibration and validation data sets were calculated based on formulas used in Williams and Norris (2001).

**Results and Discussion**

Soil particle size distribution has considerable effect on reflectance of the soil samples. Consequently, absorbance of the soil samples varies with regard to particle size distribution of the soil sample. This variation is advantage for the determination of soil particle size distribution. However, it is not desirable for the determination of P concentration and this introduces an error that should be corrected. This section discusses firstly the effect of particle size on sensing P concentrations using reflectance spectroscopy for sandy soils. Then the prediction of particle size of sandy soil samples with different P concentrations is presented using ratio and discriminant analysis methods. Lastly, the prediction of P concentration for sandy soils with different particle sizes is discussed with two approaches.

![Figure 1](image-url)  
**Figure 1.** Average absorbance spectra of four sandy soil samples without P: (a) wet samples with 8% moisture content, and (b) dry samples.
Figure 1a shows average absorbance spectra of four wet sandy soil samples without P for three different particle sizes in 225-2525 nm. Overall soil with coarse particles absorbed light more than those with medium and fine particles. Average absorbance spectra of four dry soil samples are shown in figure 1b. Comparing dry and wet absorbance values of soil samples with different particle sizes, overall absorbance values for dry samples decreased considerably in the NIR region. However, absorbance for coarse sandy soil samples was higher than those for medium and fine sandy soil samples in almost all wavelengths. Absorbance spectra in figure 1a and b proved that soil spectra changed with the change in soil particle size. Therefore, soil particle size effect on soil spectra either should be removed to predict P concentrations using spectroscopy or should be identified by using appropriate model for P prediction.

Figure 2. Standard deviation spectra of the sandy soil samples: (a) within different soil particle size classes, and (b) for all soil particle size classes.

Standard deviation spectra of absorbance of the dry soil samples with different P concentrations for individual soil particle sizes in 225-2525 nm are presented in figure 2a. Low standard deviations in 225-1775 nm indicated that significant absorption bands for predicting P concentration was not observed in this range. However, standard deviations increased with an increase in wavelengths after 1775 nm and showed that significant wavelengths for P in soil samples could be found in 1775-2525 nm. Standard deviation spectrum (figure 2b) of the dry soil samples with different P concentrations and particle sizes (all 84 samples) in 225-2525 clearly showed the effect of both soil particle size and P concentration on soil spectrum when average absorbance spectra of soil samples with no P concentration (figure 1) and average absorbance spectra of soil samples with different P concentrations for individual soil particle size (these results are presented later in this section in figure 4) were considered. High standard deviations in 225-1775 nm caused by soil particle sizes and deviations in 1775-2525 nm caused by both soil particle size and P concentrations.
Figure 3 shows the correlation coefficient spectra of absorbance with P concentrations of the dry sandy soil samples for three different particle sizes in 225-2525 nm. Highest correlations between absorbance and P concentrations were observed in 1775-2525 nm. High correlations mean that wavelengths in this regions can be used to predict P concentrations.

![Correlation coefficient spectra](image)

Figure 3. Correlation coefficient spectra of absorbance with P concentrations in sandy soil samples.

Figure 4a shows average absorbance spectra of four dry soil samples with different P concentrations in 225-2525 nm for coarse soil samples. The zoomed portion of the figure 4a in 1500-2525 nm is given in figure 4b. Absorbance values increased with an increase in P concentration between 1500 and 2525 nm. Absorbance range to determine P concentration was observed to be gradually increasing from 1500 to 2525 nm. Figure 4c shows average absorbance spectra of four dry medium soil samples with different P concentrations in 225-2525 nm and the zoomed portion of the figure 4c in 1500-2525 nm is presented in figure 4d. Figure 4d showed that absorbance increased with an increase in P concentration between 1500 and 2525 nm. Also, a gradual range increase was observed with the increase in wavelengths. Figure 4e shows average absorbance spectra of four dry fine soil samples with different P concentrations in 225-2525 nm and figure 4f indicates the zoomed portion of the figure 4e in 1500-2525 nm.
Figure 4. Average absorbance spectra of four sandy soil samples (the same legend in (a) applies to all figures): (a) coarse in 225-2525 nm, (b) coarse in 1500-2525 nm, (c) medium in 225-2525 nm, (d) medium in 1500-2525 nm, (e) fine in 225-2525 nm, and (f) fine in 1500-2525 nm.
Table 1. Comparison of error rates for ratio and discriminant analysis methods for detection of soil particle size in validation data set.

<table>
<thead>
<tr>
<th>Wavelength selection method</th>
<th>Selected wavelengths (SW)(nm)</th>
<th>Particle size detection method</th>
<th>Error rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stepwise linear discriminant analysis</td>
<td>326, 328, 368, 445, 469, 533, 544, 588, 589, 631, 632, 715, 718, 728, 864, 874, 953, 971, 981, 996, 1036, 1438, 1470, 1829, 1834, 1912, 1919, 2049, 2079</td>
<td>Discriminant analysis</td>
<td>2.38</td>
</tr>
<tr>
<td>Stepwise multiple linear regression analysis</td>
<td>2021, 2022, 2025, 2081</td>
<td>Discriminant analysis</td>
<td>0.00</td>
</tr>
<tr>
<td>Stepwise linear discriminant analysis and stepwise multiple linear regression</td>
<td>2021, 2081</td>
<td>Discriminant analysis</td>
<td>0.00</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>345, 1323</td>
<td>Ratio</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 2. Multiple regression results for predicting P concentrations for individual soil particle sizes (SEC and SEP are in mg/kg).

<table>
<thead>
<tr>
<th>Regression analysis</th>
<th>Calibrated</th>
<th>Validation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calibration</td>
<td>Validation</td>
</tr>
<tr>
<td></td>
<td>No. SW</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Coarse</td>
<td>Maximum R-square</td>
<td>226, 233, 276, 381, 1036, 1430, 1458, 1478, 1481, 1491, 1674, 1699, 1703, 1707</td>
</tr>
<tr>
<td>Coarse</td>
<td>Stepwise selection</td>
<td>814, 821, 943, 1096, 1114, 1370, 1379, 1407, 1604, 1811, 1842, 1841</td>
</tr>
<tr>
<td>Medium</td>
<td>Maximum R-square</td>
<td>338, 340, 606, 815, 821, 1350, 2107, 2186, 2405, 2417, 2434, 2459, 2510, 2525</td>
</tr>
<tr>
<td>Medium</td>
<td>Stepwise selection</td>
<td>797, 821, 1348, 1355, 1424, 1457, 1459, 1857, 1870, 1897, 1955, 2508</td>
</tr>
<tr>
<td>Fine</td>
<td>Maximum R-square</td>
<td>232, 807, 2163, 2200, 2207, 2213, 2214, 2215, 2375, 2501, 2502, 2514, 2523</td>
</tr>
<tr>
<td>Fine</td>
<td>Stepwise selection</td>
<td>2046, 2232, 2253, 2262, 2270, 2501, 2502, 2503, 2504, 2508, 2510, 2523</td>
</tr>
</tbody>
</table>
Table 1 shows comparison of error rates for ratio and discriminant analysis methods for detection of soil particle sizes in the validation data. The maximum detection error was 2.38% when wavelengths for soil particle size detection were selected by stepwise discriminant analysis (Proc STEPDISC, SAS/STAT, SAS Inc.). The other methods for both wavelength selections for soil particle size detection and prediction of soil particle sizes produced successful classifications.

Most research methods use the technique to remove the effect of an input (noise) on measurand. However, this study investigated both techniques with and without removing the soil particle size effect on P concentration predictions. Table 2 shows the MLR results for predicting P concentrations of the soil samples for individual soil particles. In other words, the technique requires soil particle size detection first and determines P concentrations of soil sample.

Table 3 tabulates the MLR results for predicting P concentrations of soil samples after the effect of soil particle size was removed. Calibration models for individual soil particle sizes predicted soil P concentrations better than those for particle size effect removed when compared in terms of SEP. Average SEP were 63.2 and 30.37 mg/kg in soil P prediction for techniques with and without removing the effect of soil particle sizes, respectively.

Table 3. Multiple regression results for predicting P concentrations after soil particle size effect was removed (SEC and SEP are in mg/kg).

<table>
<thead>
<tr>
<th>Regression analysis</th>
<th>Calibration</th>
<th>Validation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method</strong></td>
<td><strong>Selected Wavelengths (SW)(nm)</strong></td>
<td><strong>No. SW</strong></td>
</tr>
<tr>
<td>Maximum R-square</td>
<td>226, 352, 620, 672, 678, 679, 690, 708, 709, 713, 722, 724, 760, 790, 860, 868, 879, 921 961 966 968 993, 1008, 1050, 1100, 1102, 1116, 1217, 1232, 1417, 1419, 1429, 1430, 1434, 1435, 1570, 1571, 1658, 1667, 1742, 2155, 2468</td>
<td>42</td>
</tr>
<tr>
<td>Stepwise selection</td>
<td>902</td>
<td>1</td>
</tr>
</tbody>
</table>

**Conclusion**

Significant differences exist between the reflectance spectra of coarse, medium, and fine soil particles since coarse sand particles absorbed more light than medium and fine sand particles. Maximum soil particle size detection error was 2.38% using stepwise discriminant analysis as a wavelength selection method. However, implementing standard deviation as a wavelength selection method and predicting soil particle size with ratio method produced very successful results with 0% error.
Using individual P prediction models for each soil particle size produced better soil P predictions with low SEP such as 43.46, 19.30, and 25.26 mg/kg for coarse, medium, and fine soil particles than removing the effect of particle size and predicting P concentration.

Acknowledgements

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References


