Spectral Signatures for the Lake Okeechobee Soils
Using UV-VIS-NIR Spectroscopy and Predicting Phosphorus Concentrations

Ismail Bogrekci, PhD, Postdoctoral Research Associate, bogrekci@ufl.edu.
Won Suk Lee, PhD, Assistant Professor, wslee@ufl.edu.
Juan Herrera, Graduate Research Assistant, jherrera@ufl.edu.

Agricultural and Biological Engineering, Frazier Rogers Hall, PO Box 110570, IFAS, University of Florida, Gainesville, FL 32611-0570

Written for presentation at the 2004 ASAE/CSAE Annual International Meeting
Sponsored by ASAE/CSAE
Fairmont Chateau Laurier, The Westin, Government Centre
Ottawa, Ontario, Canada
1 - 4 August 2004

Abstract. Developing a phosphorus sensing system using UV, VIS and NIR provides a non-contact, cost & time effective, less laborious measurement of phosphorus (P) concentration in a soil sample. The determination of soil spectral signatures in the Lake Okeechobee basins in Florida improves the prediction accuracy of calibration models produced for the determination of soil P concentration for Okeechobee originated soils. This study aimed to obtain spectral signatures of soil samples collected from the Lake Okeechobee basins and find the significant absorption bands for sensing P concentration in a soil sample. A total of 345 soil samples were collected from the surrounding area of the Lake Okeechobee to obtain broad range of P concentrations from very low to very high (1.1-2709 mg/kg). Thirty-eight soil samples from different fields were sub-sampled and leached in order to remove existing nutrient content. The reflectance spectra of leached and un-leached soil samples were measured using UV, VIS and NIR spectroscopy. P concentrations of the samples were correlated with the absorbance of the same sample. Leached soil signatures were subtracted from those of un-leached soil samples to obtain only nutrient spectrum. Data analysis for P concentration determination was conducted with and without soil signature corrected. For each set, two-third of data was used for calibration while one-third of data was for validation. PLS analysis (partial least squares) was applied to data set.

Keywords. Spectral reflectance, Soil spectra, Sensor, Phosphorus, Lake Okeechobee, UV, VIS, NIR

The authors are solely responsible for the content of this technical presentation. The technical presentation does not necessarily reflect the official position of ASAE or CSAE, and its printing and distribution does not constitute an endorsement of views which may be expressed. Technical presentations are not subject to the formal peer review process, therefore, they are not to be presented as refereed publications. Citation of this work should state that it is from an ASAE/CSAE meeting paper. EXAMPLE: Author's Last Name, Initials. 2004. Title of Presentation. ASAE/CSAE Meeting Paper No. 04xxxx. St. Joseph, Mich.: ASAE. For information about securing permission to reprint or reproduce a technical presentation, please contact ASAE at hq@asae.org or 269-429-0300 (2950 Niles Road, St. Joseph, MI 49085-9659 USA).
Introduction

Developing a phosphorus-sensing system using ultraviolet (UV), visible (VIS), and near infrared (NIR) provides a non-contact, cost & time effective, less laborious measurement of phosphorus (P) concentration in a soil sample. Electromagnetic spectrum of a soil sample holds information about soil, water content, nutrients, and particle size etc. Therefore, the determination of pure soil spectral signatures in the Lake Okeechobee basin in Florida improves the prediction accuracy of calibration models produced for the determination of soil P concentration for the Lake Okeechobee originated soils. In order to reach the aim of this project, the following objectives were established. Specific objectives of this study were:

- to collect soil samples with wide range of P concentrations
- to measure diffuse reflectance spectra of soil samples
- to remove the nutrients and water from soil samples
- to measure diffuse reflectance of both dried and leached soil
- to obtain the nutrient reflectance spectrum
- to analyze nutrient spectra with actual P concentrations
- to analyze original soil spectra with P concentrations
- to compare results of the two analysis techniques

Reflectance measurements of soils using VIS and NIR spectroscopy to investigate the soil properties were conducted by many researchers (Ehsani et al., 1999; Varvel et al., 1999; Ingleby and Crowe, 2000; Millmier et al., 2000; Lee et al., 2001; Thomasson et al., 2001; Bogrekci et al., 2003; Montross et al., 2003). Ehsani et al. (1999) used NIR technique for rapid determination of soil mineral nitrogen. Varvel et al. (1999) investigated the relationships between spectral data from an aerial image and soil organic matter as well as P levels. Lee et al. (2001) conducted a study on soil properties and spectral characteristics in Florida. Thomasson et al. (2001) studied the soil reflectance sensing for determining soil properties. Hummel et al. (2001) studied soil moisture and organic matter prediction of surface and subsurface soils using an NIR soil sensor. Bogrekci et al. (2003) used VIS and NIR spectroscopy to determine P concentrations of soil samples from the Lake Okeechobee Basins.

Spectrum of soils in different wavelengths has been reported by many previous research activities. However, in the past, no study reported the removal of nutrient from soil sample before reflectance measurement using UV-VIS-NIR spectroscopy. This research is aiming to obtain pure spectrum of a sandy soil sample by both removing the nutrient and moisture of a soil sample and measuring the reflectance spectrum.

Material and Methods

Soil Sampling and Leaching

Soil samples were collected from 10 different sites in the Lake Okeechobee drainage basins in Florida. Grid center method was used to collect soils from each site. Soil samples were collected using a soil-sampling auger at a 15 cm depth at each sampling point. Each soil sample weighed between 200-400 grams. Geo-coordinates of each sampling point for each site
were recorded using a DGPS receiver (March II, Corvallis Microtechnology, Inc.). A total of 345 soil samples were collected. After reflectance measurement of the wet soils, the wet soil samples were oven-dried at 104°C for 24 hours. Soil samples were analyzed for Mehlich-1 P to determine P concentrations for all fields and for total P, total organic P, and water soluble P for three different sites.

Thirty-eight soil samples from different fields were sub-sampled and leached in order to remove existing nutrient content. 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 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.). When P was detected in the soil samples, further leaching was applied to remove existing nutrients.

**Reflectance Measurement, Spectral Signal Processing and Statistical Analysis**

A spectrophotometer (Cary 500, Varian Inc.) equipped with a diffuse reflectance accessory (DRA-CA-5500, Labsphere) was used to collect spectral reflectance for each soil sample. Reflectance for each wet soil sample was measured in 400-2500 nm with an increment of 1 nm. However, reflectance for each dry soil sample was measured in 175-2550 nm in order to investigate the spectral properties of soil samples in ultraviolet (UV) regions as well as visible (Vis) and near infrared (NIR).

Dry soil reflectance spectra had noise both in 175-225 and 2525-2550 nm, so data at both ends of dry soil reflectance spectra was removed. Reflectance of all samples was converted into absorbance 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. Absorbance spectra of leached soils in individual fields were averaged to obtain a pure soil spectrum for each field. Absorbance spectra of the leached soils for each field were subtracted from absorbance spectra of the un-leached soils for individual field in order to obtain nutrient spectrum for each sample in individual field.

Following correlation coefficient computation between absorbance and P concentrations of soil samples, data for original soils was divided into two sets as calibration and validation datasets. Calibration data set had 230 soil samples and validation data set had 115 soil samples. After calculating nutrient spectra for each soil sample, data for nutrients was also divided into two sets as calibration and validation datasets. Calibration data set had 230 soil samples and validation data set had 115 soil samples. Then quantitative analysis was conducted. A partial least squares (PLS) analysis (Proc PLS, SAS/STAT, SAS Inc.) was used to predict P concentrations. Tukey’s means test was performed (Proc ANOVA, SAS/STAT, SAS Inc.) in order to compare the means of P in the soil samples from different fields.

**Results and Discussion**

Chemical analysis results, spectral signal processing techniques and P predictions are discussed under three subsections; wet chemistry, spectral analysis, and P predictions.
Wet Chemistry

Table 1 shows the range, mean, standard deviation, coefficient of variance, and Tukey’s grouping of double acid extracted P (mg/kg) in the 345 soil samples from the ten study sites. The results showed that P concentrations of the soil samples varied from very low (1.1 mg/kg) to extremely high (2708.7 mg/kg) from the Okeechobee region. Spray field and Palaez Ranch (artesian well) had very low P concentrations, on the other hand, MacArthur 5-2 and Candler farm had P concentration from very low to extremely high. The standard deviations also proved that some fields did not have P variability whereas some fields had extremely high variability for P concentration. In addition to this, results from Tukey’s grouping in means test expressed that Candler farm was actually different than the others and the rest of the fields were not significantly different from each other.

Table 1. Soil Mehlich-1 P results (mg/kg) for the study sites.

<table>
<thead>
<tr>
<th>Field</th>
<th>Range</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Coefficient of Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray Field</td>
<td>4.0-10.5</td>
<td>6.2 a*</td>
<td>1.9</td>
<td>30.6</td>
</tr>
<tr>
<td>NPA (New Palm Site Abandoned)</td>
<td>8.0-844.0</td>
<td>207.9 a</td>
<td>220.3</td>
<td>105.8</td>
</tr>
<tr>
<td>Larson 6&amp;7-1</td>
<td>3.1-654.3</td>
<td>90.0 a</td>
<td>170.0</td>
<td>188.9</td>
</tr>
<tr>
<td>Larson 6&amp;7-2</td>
<td>2.7-160.3</td>
<td>36.3 a</td>
<td>36.8</td>
<td>101.4</td>
</tr>
<tr>
<td>MacArthur 5-1</td>
<td>1.1-54.2</td>
<td>10.8 a</td>
<td>15.0</td>
<td>138.9</td>
</tr>
<tr>
<td>MacArthur 5-2</td>
<td>1.9-1390.7</td>
<td>267.3 a</td>
<td>380.9</td>
<td>142.5</td>
</tr>
<tr>
<td>Palaez Ranch (artesian well)</td>
<td>1.5-6.6</td>
<td>3.4 a</td>
<td>1.4</td>
<td>41.2</td>
</tr>
<tr>
<td>Candler Farm</td>
<td>13.6-2708.7</td>
<td>1329.3 b</td>
<td>889.1</td>
<td>66.9</td>
</tr>
<tr>
<td>Palaez Ranch (south)</td>
<td>4.1-174.1</td>
<td>28.6 a</td>
<td>31.1</td>
<td>108.7</td>
</tr>
<tr>
<td>Woody Larson</td>
<td>4.1-158.6</td>
<td>43.7 a</td>
<td>42.0</td>
<td>96.1</td>
</tr>
</tbody>
</table>

* Means within a column followed by the same letter are not significantly different (P>0.0001).

Figure 1 shows the relationships among soil P extraction methods, i.e., (a) total P versus water soluble P, (b) total P versus total organic P, and (c) total P versus Mehlich-1 P for the soil samples in Candler farm, Palaez Ranch (south), and Woody Larson. A good correlation ($R^2=0.80$) exists between total P and water-soluble P. Relationship between total P and total organic P did not seem to be consistent. The best correlation ($R^2=0.98$) was obtained between total P and Mehlich-1 P (double acid method). Since the relationship is so strong between total P and double acid method, they can be used interchangeably for soils in the Lake Okeechobee drainage basins when cost of chemical analysis is an issue, knowing that double acid method underestimates P concentrations of soils and underprediction originally comes from the method itself.
Figure 1. Relationships between soil P extraction methods: (a) total P versus water soluble P, (b) total P versus soil total organic P, and (c) total P versus Mehlich-1 P.
Spectral Analysis

Figure 2 shows absorbance of the original and average leached soils for corresponding field and subtracted spectra. Subtracted spectrum was assumed to indicate nutrient content of a soil sample. Therefore, it was named as nutrient spectrum. Absorbance of original soils was higher than leached soils in 225-2525 nm wavelengths since reflectance of the leached soils were higher due to the fact that organic material and nutrients were removed.

![Absorbance of original and leached soils](image)

**Figure 2.** Absorbance of the original and average leached soils for corresponding field and subtracted nutrient content in soils.

Absorbance of original and the leached soil samples in UV and VIS region decreased more than those in NIR region. Absorbance spectra of original and leached soils showed that the highest absorbance was observed in UV whereas the lowest absorbance occurred in NIR. Absorbance of soils in VIS region was smaller than those in UV but higher than those in NIR.

Averages of leached soil absorbance signatures for individual field were depicted in figure 3. The pattern of soil signatures for each field is similar. However, magnitudes of absorbance of soil signatures for each field are different. The differences in magnitudes of absorbance could come from soil properties. There should not be any acidity effect on leached spectra since soil pH was measured and they were the same for all soil samples. Since soil was dried, there was no moisture effect on the spectra of leached soils. However, the difference in absorbance for each field could originate from the particle size differences.
**Figure 3.** Average leached soil absorbance signature of sandy soils itself in different fields.

**P Predictions**

Figure 4 shows PLS calibration results between actual Mehlich-1 P and original absorbance-derived P for the 230 original soil samples. Calibration yielded higher correlations between actual and predicted P concentrations (R²=0.874). The root mean square (RMSE) was 221.7 mg/kg for validation. As prediction results of both calibration and validation using PLS indicated, locations with very high P concentrations (“hot spots”) in the Lake Okeechobee drainage basins could be identified using diffuse reflectance spectroscopy in UV, VIS, and NIR. Therefore, this calibration model can identify hot spots in the Lake Okeechobee drainage basins and improve the rapid data collection and management of P loadings into the Lake Okeechobee.
Figure 4. PLS calibration results of actual soil Mehlich-1 P and original absorbance spectra-derived P concentrations for 230 original dry soil samples.

\[ y = 0.8741x + 38.392 \]

\[ R^2 = 0.8741 \]

Figure 5. PLS validation results of actual soil Mehlich-1 P and original absorbance spectra-derived P concentrations for 115 original dry soil samples.

\[ y = 0.8999x + 39.04 \]

\[ R^2 = 0.8691 \]
Figure 6. PLS calibration results of actual soil Mehlich-1 P and nutrient absorbance spectra-derived P concentrations for 230 nutrient spectra.

Figure 7. PLS validation results of actual soil Mehlich-1 P and nutrient absorbance spectra-derived P concentrations for 115 nutrient spectra.
PLS calibration result of actual soil Mehlich-1 P and absorbance spectra derived P concentrations for the 230 nutrient spectra is plotted in figure 6. Figure 7 shows PLS validation results of actual soil Mehlich-1 P and absorbance spectra derived P concentrations for the 115 nutrient spectra. Predictions results for nutrient spectra showed higher correlations than original soil spectra. Coefficients of determination ($R^2$) were 0.900 and 0.925 for calibration and validation, respectively. Table 2 tabulated PLS results for the calibration and validation data sets using both original soil spectra and nutrient spectra for all soil samples. The results showed that obtaining nutrient spectra produced higher $R^2$ and lower RMSE. The results also proved that using soil signatures and obtaining nutrient spectra improved the prediction performance of calibration for P concentrations for soils collected from the Okeechobee drainage basins.

Table 2. PLS results for the calibration and validation data sets using both original soil absorbance spectra and nutrient absorbance spectra for the 345 samples.

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Calibration</th>
<th>Validation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>RMSE (mg/kg)</td>
</tr>
<tr>
<td>Original dry soils</td>
<td>0.874</td>
<td>223.2</td>
</tr>
<tr>
<td>Nutrients</td>
<td>0.900</td>
<td>198.8</td>
</tr>
</tbody>
</table>

Conclusion

Soils from the Lake Okeechobee drainage basins were collected and reflectance of soils was measured using diffuse reflectance spectroscopy in UV, VIS, and NIR regions. Sub samples of soils from each field were leached. Consequently, soil signatures of each field were obtained and nutrient spectra were calculated using the original soil samples and the leached soil samples. Results showed that soil samples with very high P concentrations in the Lake Okeechobee drainage basins could be identified using soil signatures and nutrient spectra in UV, VIS, and NIR diffuse reflectance spectroscopy. Therefore, identifying soil samples with very high P concentrations could be used to identify high P spots in the Lake Okeechobee drainage basins. Also this study proved that use of soil signatures and nutrient spectra could yield better relationship between absorbance and Mehlich-1 P, and low prediction errors than using original soil spectra.

Acknowledgements

The authors would like to thank to the Florida Department of Agriculture and Consumer Services for funding this project.
References


