

IMPROVING PHOSPHORUS SENSING BY ELIMINATING SOIL PARTICLE SIZE EFFECT IN SPECTRAL MEASUREMENT

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ABSTRACT. *This study investigated the effects of soil particle size on the reflectance spectra of sandy soils using ultraviolet, visible, and near-infrared spectroscopy in sensing phosphorus (P) concentration. Pure sandy soil was graded into three particle sizes. Sieve sizes were 125, 250, and 600 μm for fine, medium, and coarse, respectively. Phosphorus application rates for the soil samples were 0.0, 12.5, 62.5, 175.0, 375.0, 750.0, and 1000.0 mg kg^{-1} . Concentrations of P in the soil samples were analyzed. The reflectance of the samples was measured between 225 and 2525 nm at 1 nm intervals. Overall, soils with coarse particles absorbed light more than those with medium and fine particles. Detection analysis for soil particle sizes was conducted using ratio and discriminant analysis methods. Prediction analyses for P concentration were performed using multiple linear regression (MLR; stepwise and maximum R^2 methods) and linear partial least squares (PLS). Results showed that detection of the particle size in a spectrum and then the prediction of P using individual calibration models for each soil particle size produced lower prediction errors. For the maximum R^2 MLR, stepwise MLR, and linear PLS analyses, respectively, the standard errors of prediction (SEPs) for determining P concentration without removing the particle size effect were 105.8, 106.2, and 69.8 mg kg^{-1} and after removing the particle size effect were 52.8, 73.4, and 64.4 mg kg^{-1} .*

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

Phosphorus (P) is currently measured by methods including chemical analysis, atomic spectroscopy, and chromatography that require sampling, handling, sample preparation, and use of chemical agents. Current P measurement methods are costly, labor intensive, and time consuming. Developing a portable P sensor using diffuse reflectance could provide efficiencies for agricultural and environmental research and applications by reducing the cost, labor, and time required to determine P concentrations of soils in the field. Absolute reflectance properties of many solid and liquid materials in the visible (VIS), near-infrared (NIR), and shortwave infrared (SWIR) regions (0.4 to 2.5 μm) have significant correlations with many chemical and physical parameters under laboratory and field conditions (Ben-Dor et al., 2004). Reflectance from a soil sample varies with its soil particle size in the ultraviolet (UV), VIS, and NIR regions of the electromagnetic spectrum (Bogrekci and Lee, 2004). This photo-physical property of the soil sample is useful in determining the particle size distribution (Zhang et al., 1992). 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 variation into the reflectance intensity at different wavelengths. Therefore, the

effect of particle size on the reflectance spectra of a soil sample should also be calibrated when the chemical properties of the soil sample are to be determined. Particle size is not the only contributor of variation to the soil spectra; among other factors are moisture content, soil reaction, and soil orders.

Zhang et al. (1992) studied the spectral properties of soils in order to improve the prediction of soil particle size fractions in the NIR band (0.76 to 0.90 μm). Reflectance in the NIR band was used as an auxiliary variable in the prediction of soil particle size fractions on a 100 \times 100 m grid in a 2200 \times 1300 m field. With cokriging, soil texture was predicted successfully in a 1300 \times 220 m field using reflectance data in the NIR region as an auxiliary variable. The mean square error between the actual and estimated values was reduced up to 18% and 33% for estimations in 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. The conclusion was that spectral contrast features in the emittance spectrum of a particulate mineral were controlled by both particle size and packing density.

Salisbury and D'Aria (1992) studied infrared (8 to 14 μm) remote sensing of soil particle size, suggesting that particle sizes of dry and quartz-dominated soils with low organic matter content and lack of overlaying 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.

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Measurements of pristine and disturbed soils were conducted to determine spectral contrast differences between field and laboratory data (Johnson et al., 1998).

Merry and Janik (2001) used mid-infrared (MIR) spectroscopy for rapid and cheap analysis of soils. After minimal sample preparation, they found that the MIR spectrum of a soil required 2 min to acquire and analyze. Their study demonstrated that the technology could predict soil properties (carbonate and organic carbon, total nitrogen, cation exchange capacity, some exchangeable cations, electrical conductivity, pH, soil texture, and a number of other properties) very well. Some of these were expensive to measure by conventional methods and not usually available.

In order to improve the capability of P prediction models, the effects of soil particle size on reflectance spectra of soils should be studied.

OBJECTIVE

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

MATERIALS AND METHODS

SOIL SAMPLE PREPARATION

In order to study the effects of soil particle size on the reflectance spectra of soils, pure sandy soil was obtained from Florida. The soil was graded into three particle sizes using a sieve shaker (Ro-Tap, W. S. Tyler, Inc., Mentor, Ohio). Sieve sizes of 125, 250, and 600 μm were selected to categorize fine, medium, and coarse samples, respectively. Sample preparation with different P concentrations and particle sizes is described in table 1. Four replications of seven P application rates and three particle sizes generated 84 samples for this study.

Soil samples were leached using 0.1 molar HCl acid solutions and deionized water in order to remove existing P. After leaching, the pH and P concentration of the samples were analyzed. Soil pH was measured using a pH/temperature meter (HI 991000, Hanna Instruments, Woonsocket, R.I.), and soil P was determined using a soil test kit (Luster Leaf Products, Inc., Woodstock, Ill.). If P was detected in the soil samples, further leaching was applied. The soil samples were incubated for seven days for all P rates. Phosphorus solution was prepared from potassium phosphate monobasic (KH_2PO_4 , Fisher Scientific, Fairlawn, N.J.). Phosphorus rates were 0.0 (no P), 12.5 (very low), 62.5 (low), 175.0 (medium), 375.0 (high), 750.0 (very high), and 1000.0 (extremely high) mg kg^{-1} . Phosphorus solution was added to

the soil. The samples were wetted to the field capacity level of 8% moisture, chosen to simulate the moisture content in soils in the Lake Okeechobee drainage basin, Okeechobee County, Florida. After spectral measurement of the wet soil, the samples were dried at 104 °C for 24 h. The samples were sent to Waters Agricultural Laboratories, Inc., Camilla, Georgia, for analysis of P concentrations. All samples were analyzed for total P (acid digestion method).

DIFFUSE REFLECTANCE MEASUREMENT

A spectrophotometer (Cary 500 Scan UV-VIS-NIR, Varian, Inc., Palo Alto, Cal.) equipped with an integrating sphere (DRA-CA-5500, Labsphere, Inc., North Sutton, N.H.) was used to collect spectral reflectance data for each soil sample. The spectral bandwidth (SBW) for data collection was 2 nm. Spectral bandwidth, the width in nanometers of light at half peak height exiting the monochromator, is determined by the physical width of the entrance and exit slits of the monochromator and the dispersion of the grating. A 27.5 g sample was placed into a sample holder. A 50 mm diameter polytetrafluoroethylene (PTFE) disk (Spectralon, Labsphere, Inc., North Sutton, N.H.) was used to obtain the optical standard of the system before spectral measurements. The reflectance of each sample was measured in the 225-2525 nm region with an increment of 1 nm using baseline correction mode. Reflectance of the samples was measured before and after drying.

SPECTRAL SIGNAL PROCESSING AND DATA ANALYSIS

Before further analysis, the reflectance values of all samples were converted into absorbance to calculate the relationship between P concentration and absorbance at different wavelengths using Beer-Lambert's law (Williams and Norris, 2001). The data were filtered using a Savitzky-Golay polynomial convolution filter to remove the noise in the signal. This method used a convolution approach, which performed a least squares fit to a specified window of data points. Smoothing was controlled by the degree of polynomial (2) and the number of points (50). In order to find significant bands for each particle size fraction, correlation coefficients and standard deviation spectra were computed. Correlation coefficients were computed between the absorbance and actual total P concentration of the samples. Two methods (ratio and discriminant analysis) were used to predict the particle size of the samples. The ratio of absorbance at 345 and 1323 nm was computed to obtain accurate classification of particle sizes, as shown in equation 1. These wavelengths were selected because standard deviation spectra (fig. 2) produced very good discrimination of the three particle sizes. Half of the data was used for calibration and half for validation.

The absorbance ratio (R) was calculated as follows:

$$R = \frac{A_{\lambda 345}}{A_{\lambda 1323}} \quad (1)$$

where

R = absorbance ratio

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

$A_{\lambda 1323}$ = absorbance at 1323 nm.

In the discrimination method, the SAS STEPDISC and SAS REG procedures were used to select the significant wavelengths to determine the particle size of the samples.

Table 1. Sample preparation with different phosphorus concentrations and sieve sizes.

Sieve Size (μm)	P Application Rates (mg kg^{-1})	Moisture Content (w.b.)		pH	Spectral Range
Fine 125	No P	0.0	8%	6	225-2525 nm
	Very low	12.5			
	Low	62.5			
	Medium	175.0			
Medium 250	High	375.0			
Coarse 600	Very high	750.0			
	Extremely high	1000.0			

Then, the SAS DISCRIM procedure was used to predict the particle size of the samples (SAS, 1999).

Two methods predicted phosphorus concentrations of the samples. The first method used a particle size effect-removing (PSER) equation (eq. 2) and predicted P concentrations of the soil samples with the SAS REG and SAS PLS procedures (SAS, 1999). Multiple linear regressions were executed using two techniques, stepwise and maximum R². Particle size effect removal was calculated as follows:

$$A_{PSER} = \frac{(A_{\lambda_i} - \bar{A}_{\lambda_i})}{(A_{\lambda_{345}}/A_{\lambda_{1325}})} \quad (2)$$

where

A_{PSER} = absorbance after particle size effect removal

A_{λ_i} = absorbance at present wavelength

\bar{A}_{λ_i} = average absorbance

$A_{\lambda_{345}}$ = absorbance at 345 nm

$A_{\lambda_{1325}}$ = absorbance at 1325 nm.

The second method predicted particle size and then calculated P concentration using different prediction models for each particle size class. Standard errors of prediction (SEPs) and root mean square errors (RMSEs) for the validation data sets were calculated based on formulas in Williams and Norris (2001). The percentage error rate was computed as the number of misclassified samples over the total number of samples multiplied by 100.

RESULTS AND DISCUSSION

This section first describes the chemical analysis results and the effect of particle size on sensing P concentrations using reflectance spectroscopy for sandy soils. Next, the prediction of particle size of samples with different P concentrations using the ratio and discriminant analysis methods is presented. Finally, the prediction of P concentration for soils with different particle sizes is discussed with two approaches.

CHEMICAL ANALYSIS

Total P results for soils with different particle sizes and P concentrations are listed in table 2. The chemical analysis showed a wide range of P concentrations in the samples needed for the statistical analysis. Seven different P clusters were obtained for coarse, medium, and fine particles. Leaching the samples with HCl acid and deionized water did not completely remove the P. The amount and type of acid and the duration of leaching determine the extent of P removal.

THE EFFECT OF PARTICLE SIZE ON ABSORBANCE SPECTRA OF SANDY SOILS

Figure 1a shows average absorbance spectra in the 225-2525 nm region for the four wet soil samples without P for the three particle sizes. Average absorbance spectra of the four dry soil samples are shown in figure 1b. Overall, soils with coarse particles absorbed light more than those with medium and fine particles.

Soil particle size distribution had a considerable effect on the reflectance of the soil samples. Consequently, the absorbance of the soil samples varied with regard to particle size, which was desirable for determining particle size distribution, but not for determining P concentration. This

Table 2. Chemical analysis results of the soil samples for total P in mg kg⁻¹.

Particle Size	P Levels	Range	Mean	Std. Dev.
Coarse (600 µm)	No P	10-14	12.2	1.9
	Very low	32-40	34.9	3.7
	Low	58-65	62.2	3.0
	Medium	161-216	192.2	26.7
	High	358-425	393.5	27.7
	Very high	629-745	683.2	48.2
Medium (250 µm)	Extremely high	828-893	854.2	29.9
	No P	10-28	18.3	7.6
	Very low	34-49	43.2	7.1
	Low	66-95	76.6	12.8
	Medium	142-177	163.2	17.2
	High	347-392	368.3	18.3
Fine (125 µm)	Very high	683-737	703.7	23.4
	Extremely high	842-955	892.0	46.9
	No P	20-57	38.1	16.4
	Very low	56-66	60.0	4.3
	Low	82-89	85.5	3.4
	Medium	184-198	189.9	6.8
	High	395-417	407.5	11.2
	Very high	729-742	735.5	5.7
	Extremely high	670-872	759.5	85.4

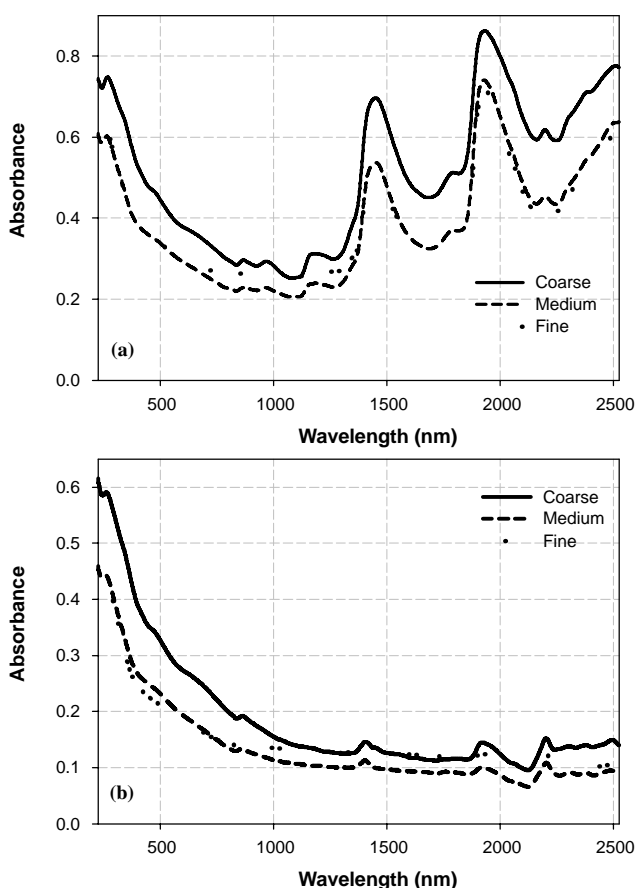


Figure 1. Average absorbance spectra of four sandy soil samples without P: (a) wet samples with 8% moisture content, and (b) dry samples.

variation introduces an error that must be corrected. The absorbance spectra in figure 1 proved that soil spectra changed with soil particle size. Comparing the absorbance values of dry and wet samples with different particle sizes revealed that overall absorbance values for the dry samples decreased con-

siderably in the NIR region. However, the absorbance values of coarse soil were higher than those of medium and fine soil at almost all wavelengths for both the dry and wet samples. Therefore, the effect of soil particle size on soil spectra either should be removed to predict P concentrations using spectroscopy or should be identified by using the appropriate model for P prediction.

Figure 2a shows the standard deviation spectra of absorbance of the dry soil samples with different P concentrations for individual soil particle sizes in the 225-2525 nm region. Large standard deviations in the 1775-2525 nm region indicated that significant absorption bands for predicting P concentration might be observed in this range. Standard deviations were larger for wavelengths above 1775 nm, showing that significant wavelengths for P in the soil samples could be found in the 1775-2525 nm region. Standard deviation spectra of the dry samples (fig. 2b) with different P concentrations and particle sizes (all 84 samples) in the 225-2525 nm region clearly showed the effects of both soil particle size and P concentration on soil spectra when average absorbance spectra of soil samples with no P concentration (fig. 1) and average absorbance spectra of soil samples with different P concentrations for individual soil particle sizes were considered. These results are presented later in this section. Variability in the 225-1775 nm region was related to soil particle size and in the 1775-2525 nm region to both soil particle size and P concentration.

The correlation coefficient spectra of absorbance with P concentrations of the dry sandy soil samples are shown in

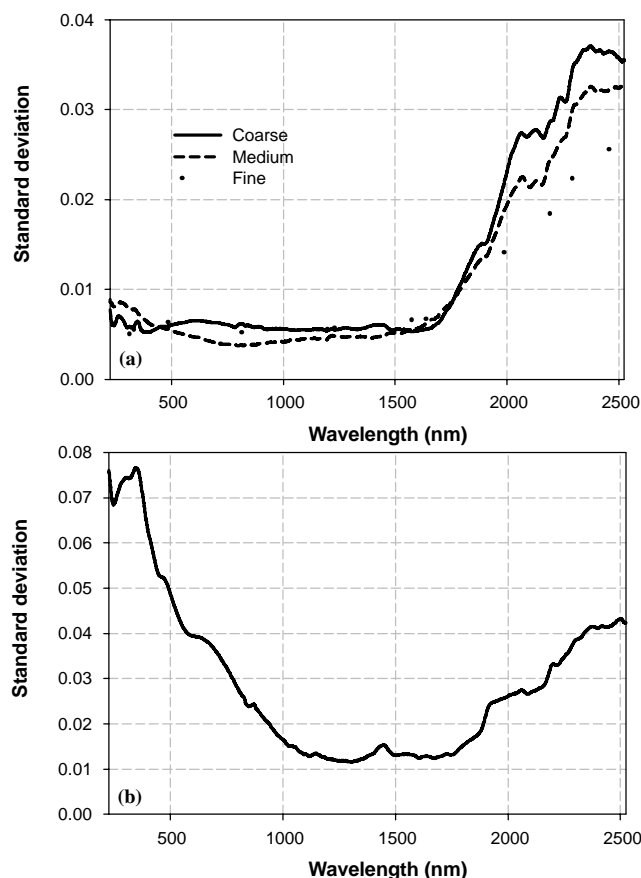


Figure 2. Standard deviation spectra of the sandy soil samples: (a) within different soil particle size classes, and (b) for all soil particle size classes.

figure 3 for three different particle sizes in the 225-2525 nm region. Higher correlations between absorbance and P concentrations were observed in the 225-400 nm and 1775-2525 nm regions. High correlations indicated that wavelengths in these regions might be utilized to develop P prediction models.

Figure 4a shows average absorbance spectra of the four dry coarse soil samples with different P concentrations in the 225-2525 nm region. Figure 4b is an enlarged portion of figure 4a in the 1500-2525 nm region. Absorbance values increased with an increase in P concentration between 1500 and 2525 nm. We observed that the absorbance range for determining P concentration increased from 1500 to 2525 nm.

Figure 4c shows average absorbance spectra of the four dry medium soil samples with different P concentrations in the 225-2525 nm region, and figure 4d presents an enlarged portion of figure 4c in the 1500-2525 nm region. Absorbance increased with an increase in P concentration between 1500 and 2525 nm; in addition, a gradual range increase was observed with the increase in wavelength.

Figure 4e shows average absorbance spectra of the four dry fine soil samples with different P concentrations in the 225-2525 nm region, and figure 4f is an enlarged portion of figure 4e in the 1500-2525 nm region. Particle size effect on P detection for the dry soil samples produced a bias effect on the signal. Depending on the wavelength, the particle size had either a positive or a negative effect. Thus, particle size effects on absorbance spectra should be removed in order to predict P concentrations of soil samples, or a number of particle size clusters should be generated to produce different P prediction models for each cluster.

The first derivative spectra of absorbance for coarse, medium, and fine dry soils with no P content are shown in 225-325 nm (fig. 5a), 400-700 nm (fig. 5b), and 1900-2200 nm (fig. 5c). The second derivative spectra of absorbance for coarse, medium, and fine dry soils with no P content are presented in 230-325 nm (fig. 6a), 380-420 nm (fig. 6b), and 2300-2400 nm (fig. 6c). If the first and second derivatives of absorbance could remove the particle size effect on the absorbance spectra, then we can conclude that the first and second derivatives of the absorbance spectra for different particle sizes would have been very similar when there was no P content in samples (figs. 5 and 6).

Derivative intensity variation in signals for three particle sizes showed that the first derivative of absorbance of the dry samples did not remove the effect of particle size. Therefore,

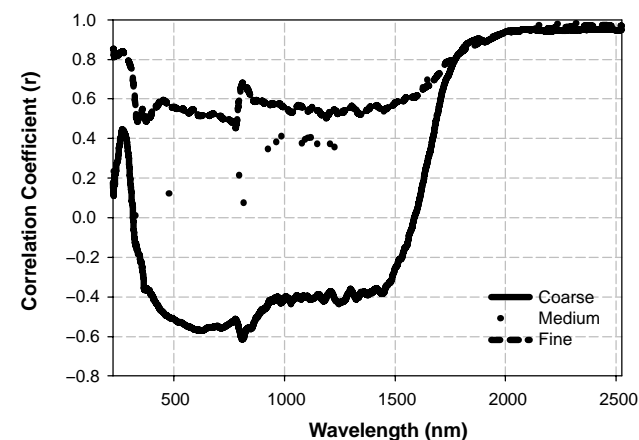


Figure 3. Correlation coefficient spectra of absorbance with P concentrations in sandy soil samples.

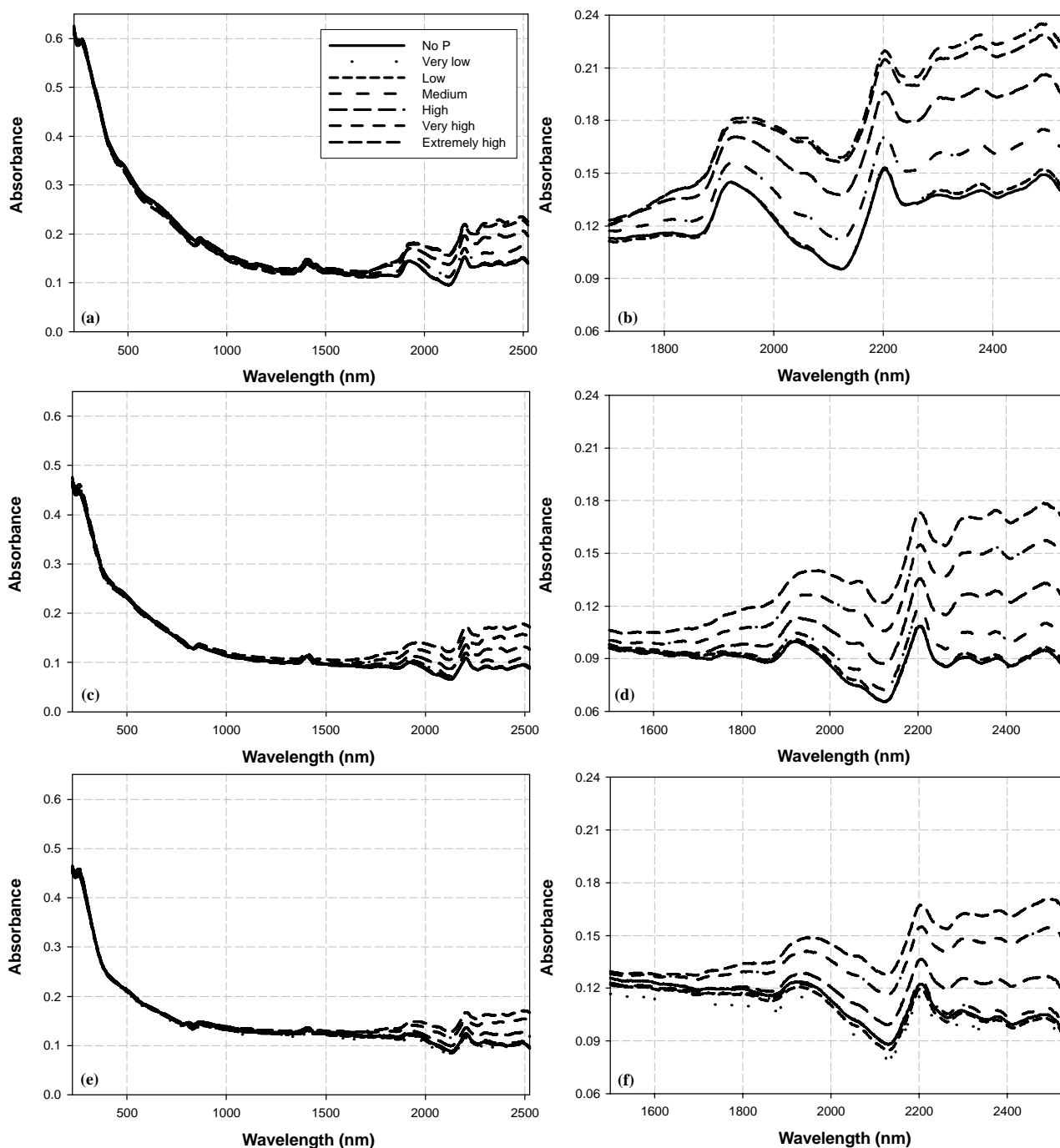


Figure 4. Average absorbance spectra of the four dry sandy soil samples: (a) coarse in 225-2525 nm (the legend applies to all graphs), (b) coarse in 1500-2525 nm, (c) medium in 225-2525 nm, (d) medium in 1500-2525 nm, (e) fine in 225-2525 nm, and (f) fine in 1500-2525 nm.

the first derivative of absorbance should not be used as a particle size effect removal method in sensing P concentration of soils. Furthermore, the second derivative of the absorbance spectra for different particle sizes with no P concentration appeared different in the UV, VIS, and NIR regions (figs. 6a, 6b, and 6c). The second derivative pretreatment in the NIR range with soils disagrees with the study done by Hruschka (1987), who demonstrated the capability of second derivative pretreatment to reduce the particle size effect on NIR absorbance spectra of wheat samples.

PARTICLE SIZE PREDICTIONS

Table 3 compares error rates for the ratio and discriminant analysis methods for detecting soil particle sizes in the validation data. Tables 4 and 5 show the number and percentage of samples classified into sample particle sizes for the validation data using the discriminant analysis and ratio methods, respectively. As shown in table 3, the maximum detection error was 2.38% when wavelengths for soil particle size detection were selected using stepwise discriminant analysis. The other methods for wavelength selection, soil

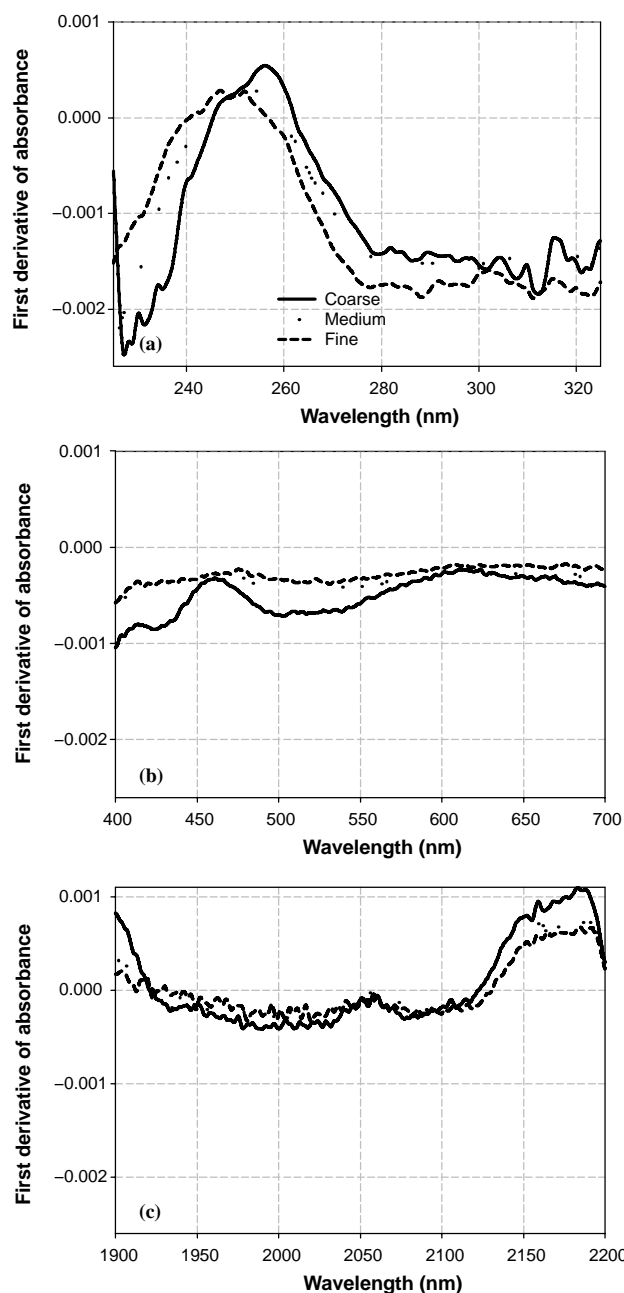


Figure 5. First derivative of average absorbance of the four dry sandy soil samples with no phosphorus for different soil particle sizes: (a) 225-325 nm, (b) 400-700 nm, and (c) 1900-2200 nm.

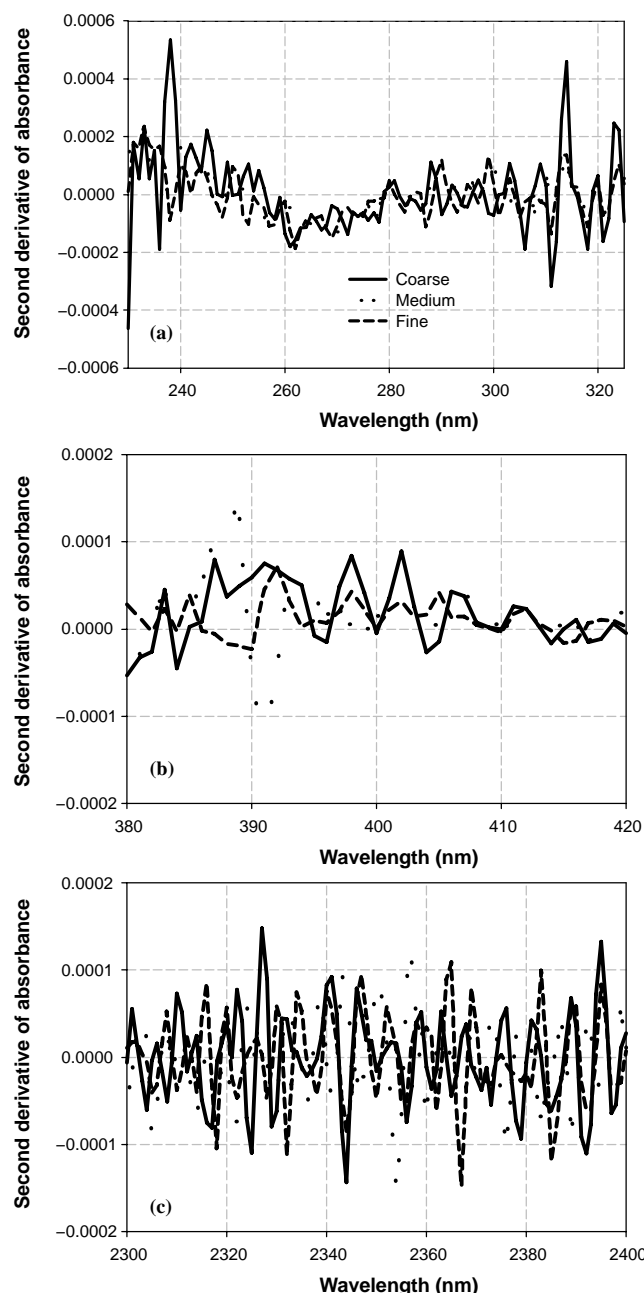


Figure 6. Second derivative of average absorbance of the four dry sandy soil samples with no phosphorus for different soil particle sizes: (a) 230-325 nm, (b) 380-420 nm, and (c) 2300-2400 nm.

Table 3. Comparison of error rates for ratio and discriminant analysis methods for detection of soil particle size in the validation data set.

Wavelength Selection Method	Selected Wavelengths (nm)	Particle Size Detection Method	Error Rate (%)
Stepwise linear discriminant analysis	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	Discriminant analysis	2.38
Stepwise multiple linear regression analysis	2021, 2022, 2025, 2081	Discriminant analysis	0.00
Stepwise linear discriminant analysis and stepwise multiple linear regression	2021, 2081	Discriminant analysis	0.00
Standard deviation	345, 1323	Ratio	0.00

particle size detection, and prediction of soil particle sizes produced successful classifications.

PHOSPHORUS CONCENTRATION PREDICTIONS

Because particle size has an effect on reflectance spectra, it is logical to remove the particle size effect before

Table 4. Number and percentage of samples classified into sample particle sizes using the discriminant analysis for the validation data set.

	Coarse	Medium	Fine	Total
Coarse	14	0	0	14
14	100%	0%	0%	100%
Medium	0	14	0	14
14	0%	100%	0%	100%
Fine	0	0	14	14
14	0%	0%	100%	100%

Table 5. Number and percentage of samples classified into sample particle sizes using the ratio method for the validation data set.

	Coarse	Medium	Fine	Total
Coarse	14	0	0	14
14	100%	0%	0%	100%
Medium	0	14	0	14
14	0%	100%	0%	100%
Fine	0	0	14	14
14	0%	0%	100%	100%

performing any analysis of P concentration of the samples. This study investigated techniques both with and without removing the soil particle size effect on P concentration predictions.

The multiple linear regression (MLR) and partial least squares (PLS) results for predicting P concentrations of the soil samples by soil particle size are tabulated in table 6. These techniques required soil particle size detection first and then determined the P concentration of the soil sample. The number of selected wavelengths was between 12 and 14 for coarse, medium, and fine particles with the stepwise and maximum R² methods. The selected number of wavelengths did not change considerably between the two regression methods and among the three particle sizes. The maximum R² method produced R² values of 0.983, 0.997, and 0.994 for coarse, medium, and fine, respectively. The stepwise method yielded R² values of 0.990, 0.995, and 0.988 for coarse, medium, and fine, respectively. The PLS method produced R² values of 0.988, 0.999, and 0.975 for coarse, medium, and fine, respectively. Stepwise multiple linear regression was able to yield a very high R² of 0.944 and an SEP of 75.94 mg kg⁻¹ with one wavelength (902 nm).

Table 7 lists the MLR and PLS results for predicting P concentrations of soil samples before and after the effect of soil particle size was removed. Calibration models for the three soil particle sizes predicted soil P concentrations better than those with the particle size effect removed when

Table 6. Multiple linear regression results for predicting P concentrations by soil particle size (SEP and RMSE are in mg kg⁻¹).

Particle Size	Regression Analysis	Method	Selected Wavelengths (SW) (nm)	No. of SWs	Calibration		Validation		
					R ²	RMSE	R ²	SEP	RMSE
Coarse	MLR	Maximum R ²	226, 233, 276, 381, 1036, 1430, 1458, 1478, 1481, 1491, 1674, 1699, 1703, 1707	14	0.993	26.57	0.983	43.35	41.88
		Stepwise selection	814, 821, 943, 1096, 1114, 1370, 1379, 1407, 1604, 1811, 1842, 1841	12	0.992	28.80	0.990	32.36	31.18
	PLS	PLS	225-2525	6	0.991	29.04	0.988	34.71	33.45
Medium	MLR	Maximum R ²	338, 340, 606, 815, 821, 1350, 2107, 2186, 2405, 2417, 2434, 2459, 2510, 2525	14	0.995	25.13	0.997	19.30	18.60
		Stepwise selection	797, 821, 1348, 1355, 1424, 1457, 1459, 1857, 1870, 1898, 1955, 2508	12	0.995	24.83	0.995	23.64	23.22
	PLS	PLS	225-2525	8	0.999	9.87	0.999	9.89	9.53
Fine	MLR	Maximum R ²	232, 807, 2163, 2200, 2207, 2213, 2214, 2215, 2375, 2501, 2502, 2514, 2523	13	0.993	28.18	0.994	25.26	24.37
		Stepwise selection	2046, 2232, 2253, 2262, 2270, 2501, 2502, 2503, 2504, 2508, 2510, 2523	12	0.981	47.22	0.988	37.74	36.37
	PLS	PLS	225-2525	5	0.971	66.98	0.975	55.82	53.83

Table 7. Multiple linear regression results for predicting P concentrations before and after the effect of soil particle size was removed (SEP and RMSE are in mg kg⁻¹).

Signal Processing	Regression Analysis	Method	Selected Wavelengths (SW) (nm)	No. of SWs	Calibration		Validation		
					R ²	RMSE	R ²	SEP	RMSE
Original (Before)	MLR	Maximum R ²	2022, 2025, 2084	3	0.948	72.20	0.882	105.83	104.62
		Stepwise selection	2021, 2022, 2025, 2081	4	0.951	69.94	0.881	106.16	104.96
	PLS	PLS	225-2525	6	0.973	52.00	0.949	69.84	69.03
Normalized (After)	MLR	Maximum R ²	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	42	0.985	38.25	0.971	52.75	52.14
		Stepwise selection	902	1	0.946	74.00	0.944	73.41	72.75
	PLS	PLS	225-2525	3	0.961	62.74	0.957	64.37	63.60

compared in terms of SEP (tables 6 and 7). High R^2 values indicated that both methods might be used to predict P concentration of soils with an acceptable error for environmental measurement. The results from both before and after particle size effect removal show the performance of the PSER formula in spectral signal processing and data analysis. The multivariate analysis with MLR and PLS for the validation data sets yielded better predictions when the particle size effect was removed (table 7). Average SEPs were 63.5 and 93.9 mg kg⁻¹ in soil P prediction for techniques with and without removing the effect of soil particle size, respectively.

CONCLUSIONS

Significant differences existed between the reflectance spectra of coarse, medium, and fine soil particles because coarse sand particles absorbed more light than medium and fine sand particles. The maximum soil particle size detection error was 2.38% using stepwise discriminant analysis as the wavelength selection method. Furthermore, implementing standard deviation as a wavelength selection method and predicting sand particle size with a ratio method produced very successful results with 0% error. The individual prediction method for each soil particle size produced better soil P predictions with lower SEPs for coarse, medium, and fine sand particles than the method that removed the effect of particle size on absorbance spectra and predicted P concentration of the soil samples.

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REFERENCES

- Arnold, G. 1991. Measurement of the spectral emittance of particulate minerals and some remote sensing implications. *Vib. Spectrosc.* 2(4): 245-249.
- Ben-Dor, E., B. Kindel, and A. F. H. Goetz. 2004. Quality assessment of several methods to recover surface reflectance using synthetic imaging spectroscopy data. *Remote Sens. Environ.* 90(3): 389-404.
- Bogrekci, I., and W. S. Lee. 2004. Spectral signatures for the Lake Okeechobee soils using UV-VIS-NIR spectroscopy and predicting phosphorus concentrations. ASAE Paper No. 041076. St. Joseph, Mich.: ASAE.
- Hruschka, W. R. 1987. Data analysis: Wavelength selection methods. In *Near-Infrared Technology in the Agricultural and Food Industries*, 39-58. 2nd ed. P. C. Williams and K. H. Norris, eds. St. Paul, Minn.: American Association of Cereal Chemists.
- Johnson, J. R., P. G. Lucey, K. A. Horton, and E. M. Winter. 1998. Infrared measurement of pristine and disturbed soils: 1. Spectral contrast differences between field and laboratory data. *Remote Sens. Environ.* 64(1): 36-46.
- Merry, R. H., and L. J. Janik. 2001. Mid-infrared spectroscopy for rapid and cheap analysis of soils. In *Proc. 10th Australian Agronomy Conf.*, CD-ROM. Hobart, Australia: Australian Society of Agronomy.
- Ristori, G. G., E. Sparvoli, M. de Nobili, and L. P. D'Acqui. 1992. Characterization of organic matter in particle-size fractions of Vertisols. *Geoderma* 54(1-4): 295-305.
- Salisbury, J. W., and D. M. D'Aria. 1992. Infrared (8-14 μ m) remote sensing of soil particle size. *Remote Sens. Environ.* 42(2): 157-165.
- SAS. 1999. SAS/STAT User's Guide. Ver. 8. Cary, N.C.: SAS Institute, Inc.
- Williams, P., and K. Norris. 2001. *Near-Infrared Technology in the Agricultural and Food Industries*. 2nd ed. St. Paul, Minn.: American Association of Cereal Chemists.
- Zhang, R., A. W. Warrick, and D. E. Myers. 1992. Improvement of the prediction of soil particle size fractions using spectral properties. *Geoderma* 52(3-4): 223-234.