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## Predicting extractable soil phosphorus using visible/near-infrared hyperspectral soil reflectance measurements

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**ABSTRACT** Phosphorus is added to agriculture soils by applying chemical fertilizers and manure; if not completely consumed by crops and plants, it can mobilize in reduced conditions and end up in ground water and, ultimately, in surface water bodies due to leaching and/or runoff. Soil reflectance spectroscopy (SRS) shows promise in providing for the rapid assessment of various physical and

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chemical properties of soil in both laboratory conditions and directly in the field. While conventional analyses of soil test phosphorus (STP) are laborious and time-consuming, hyper-spectral soil reflectance measurements provide a portable, and low-cost, alternative that can be performed in situ. The objective of this study was to evaluate the capability of a commercial, combined visible/near-infrared spectrometry system, covering a spectral range from 342-1023 nm and 1070-2220 nm, to predict soil test phosphorus using samples obtained from an agricultural field that received 45 kg P ha<sup>-1</sup> from inorganic P fertilizer alone, composted cattle manure alone or a mixture of the two fertilizer sources. Three repeated measurements of soil absorbance were collected using 86 homogenized air-dried soil samples. Using a spectrometer calibration procedure, each 376-band spectrum was transformed into a digital array of soil reflectance measurements. A Partial-leastsquares regression (PLSR) method was used to relate the averages of the three repeated spectra of each of the 86 soil samples with the STP measurements (Mehlich-3 extractable P concentration). The results of the leave-one-out-cross-validation of the spectral calibration model yielded a linear relationship between the predictions from the model and the reference measurements, with a coefficient of determination equal 0.86 and a standard error of prediction of 31 mg/kg. However, these results could be biased due to the residual or re-formed organic and/or in organic P compounds, from experiments undergoing P fertility trials. The next step in this research will involve applying a similar data processing procedure to *insitu* measurements.

**Keywords:** Soil reflectance spectroscopy, soil test phosphorus, proximal soil sensing.

**INTRODUCTION** Phosphorus (P) is an essential plant nutrient, along with nitrogen and potassium. Due to an inadequate supply of plant-available P in most soils, chemical fertilizers and manure are often applied to meet crop P requirements. The P in all fertilizing material is originally derived from sedimentary phosphate rock that contains P-rich apatite minerals. A conservative estimate, based on industry data, indicates that the peak in global P extraction could occur by 2033 (Cordell et al., 2009; Jasinski, 2011). Industry analysts predict that after we reach "peak P", the lower quality and difficulty in accessing the remaining rock phosphate reserves will make them uneconomical to mine and process. Given that demand for P fertilizers continues to grow to support global food production and the supply of P fertilizer is constrained by finite resources, we need to be proactive in developing technologies that maximize the fertilizer P use efficiency in agroecosystems.

Another reason to improve fertilizer P use efficiency is to protect surface water from pollution. There is no doubt that fertilizer P applied to agricultural land is susceptible to transport into aquatic systems, leading to contamination and eutrophication of inland freshwater bodies in Canada (Chambers et al., 1997) and around the world (Carpenter et al., 2008). The problem of accelerated eutrophication due to agricultural nonpoint source pollution is not limited to freshwater lakes; it is also linked to eutrophication in Canadian estuaries, inlets and marine coastal ecosystems. The increasing supply of N and P to coastal waters stimulates phytoplankton and microalgae growth, leading to changes in the ecosystem and biota as both light penetration and dissolved oxygen beginning to decline. Low oxygen areas in the Lower St. Lawrence Estuary are "dead zones" that pose a risk to cod, halibut and other fish (Fisheries and Oceans Canada, 2013), and nutrient enrichment from agricultural runoff threatens near-shore marine systems across Canada (Canadian Council of Ministers for the Environment, 2007).

It is clear that fertilizer P inputs need to be applied in as precise a manner as possible. This is done by evaluating the soil available P concentration with a chemical extractant (soil test P, STP, Condron *et.al.* (2005)), which is related to crop tissue P at critical growth stages and crop yields to predict the probability of crop response to fertilizer P. Accurate quantification of STP can be done by taking large numbers of real-time ground measurements. But, currently, there is no commercial

service available which is capable of measuring STP in real-time and on-the-go. Soil reflectance spectroscopy (SRS) shows promise in providing for the rapid assessment of various physical and chemical soil properties in both laboratory conditions and directly in the field. While conventional analyses of STP are laborious and time-consuming, hyper-spectral soil reflectance measurements provide a portable, and low-cost, alternative that can be performed *in situ*. A spectrophotometric method employs the interactions of visible and near infrared radiation with the sample under investigation; the VIS/NIR system is based on the sample's absorption of electromagnetic radiation at wavelengths in the range of 400-2500 nm.

A number of studies to determine soil attributes by this method have resulted in the successful use of near infrared spectrophotometry to quantify soil organic matter, moisture, total carbon, total nitrogen and cation exchange capacity. Dalal and Henry (1986) simultaneously determined soil organic carbon, moisture and total nitrogen by near infrared spectrophotometry. Initially, there were a number of unsuccessful attempts to predict STP by NIR spectroscopy. Krischenko et al. (1991) reported very weak correlations between predicted P and actual P (R<sup>2</sup>=0.42). Similarly, Williams (2003) reported the poor prediction of P using NIR spectroscopy. Chang et. al. (2001) reported the weakest result with an R<sup>2</sup>=0.4. Thomson et al., 2001, reported a similar value (R<sup>2</sup>=0.49), noting that there were several spectral overtones for P in the wavelength range from 275 to 2475 nm in sandy loam, clay and silt clay soils. He et. al. (2005) reporting R<sup>2</sup>=0.46, offered the explanation that this low correlation could be the result of a significant overlap in the signals for both P and C-H-O-N bonds. On the other hand, Bogrekci and Lee (2005) investigated the effects of common soil P compounds on reflectance spectra of sandy soils using UV, VIS and NIR reflectance spectroscopy. They added P to the sandy soils in four different forms (FePO<sub>4</sub>.2H<sub>2</sub>O, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O, CaPO<sub>4</sub>, and AIPO<sub>4</sub>) and in 7 different proportions. They reported successfully predicting soil P in sandy soils for all 4 compounds  $(0.48 \le R^2 \le 0.73)$ . The strongest absorption peaks for FePO<sub>4</sub>.2H<sub>2</sub>O, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.2H<sub>2</sub>O, CaPO<sub>4</sub>, and AlPO<sub>4</sub> occurred at 286, 2548, 2516, and 228 nm, respectively. Maleki et. al. (2006) reported soil P prediction for 2 different data sets of R<sup>2</sup>=0.75 and R<sup>2</sup>=0.73, with soil texture classes ranging from silt loam, to sandy loam and loamy sand.

The objective of this study was to evaluate the capability of a commercial, combined visible/near-infrared spectrometry system covering a spectral range from 400 to 2220 nm to predict STP in the lab using samples obtained from an agricultural field in Quebec that received variable inputs of fertilizer P (up to 45 kg P ha<sup>-1</sup>) from inorganic fertilizer or composted cattle manure.

## **MATERIALS AND METHODS**

**Data collection** A combined, dual type spectrophotometer instrument, operating in the visible and near-infrared regions of the spectrum, was used in this project (Figure 1). The vis-NIR instrument (P4000, Veris Technologies, Inc., Salina, Kansas, USA) was ready for both in-situ and ex-situ measurements. One of the two spectrometers was used to collect soil reflectance data between 342 and 1023 nm, and the other spectrometer measured between 1070 and 2200 nm. The instrument included its own light source and was capable of maintaining a constant distance between measured soil surfaces and detectors.

Soil samples (1440 in total) were archived during a study conducted from 2000-2004 and described by Carefoot *et.al.* (2003) and Jiao et al. (2006). Soil samples were collected in the fall after harvest, but before fall tillage, at 0- to 15-cm, 15- to 30-cm, and 30- to 60-cm depths using a tractor-mounted soil auger. Soil samples for each depth were composites of two cores (7.5-cm diameter) removed from each split plot (Carefoot *et.al.*, 2003). Soils were then dried in a forced-air oven (60°C for 48 h), ground and sieved (<2 mm mesh).

Phosphate ions were extracted using Mehlich-3 (1:10, soil:solution ratio) after shaking for 5 min at 130 rpm. Phosphate concentrations in Mehlich-3 extracts were evaluated by the molybdenum blue



Figure 1: Setup-vis-NIR in bench top configuration.

reaction. A uniform distribution of narrow ranges was observed between  $P_{\text{Mehlich-3}}$  concentrations at each soil sampled depth and the concentrations were also observed to be decreasing with an increase in soil sampling depths, therefore covering a wide range of measurements. From these, a small subset consisting of 86 soils samples were selected (Figure 2). Depth wise statistical results on  $P_{\text{Mehlich-3}}$  concentrations for the selected 86 soil samples are summarized in Table 1

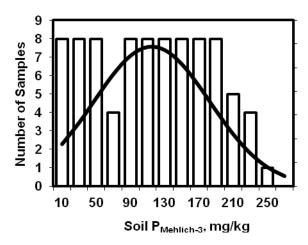


Figure 2: Distribution of  $P_{\text{Mehlich-3}}$  concentration in 86 soil samples from an agricultural field receiving fertilizer P inputs.

Three repeated ex-situ measurements of soil absorbance were collected using 86 aforementioned soil samples. Using a spectrometer calibration procedure, each 376-band spectrum was transformed into a digital array of soil reflectance measurements. A Partial-least-squares regression (PLSR) method was used to relate the averages of the three repeated spectra for each of the 86 soil samples with the Mehlich-3 extractable P measurements.

Table 1: Soil sampling depth-wise statistical results on P<sub>Mehlich-3</sub> (mg/Kg) for 86 soil samples.

Number of samples	Texture	Depth	Minimum	Mean	Maximum	Standard deviation
31	silty- loam	0-15 cm	96	177	244	38
33	sandy-silty- loam	15-30 cm	44	109	196	40
22	sandy-clay	30-60 cm	4	32	154	32

## Data Processing

The ParLeS software (version 3.1, 2007, University of Sydney, Sydney, Australia) was used for model development. Initially, three similar soil spectra replicates were averaged for all 86 soil samples to represent average and smoothed (median filter of window size=3) soil spectra of each soil sample. Later spectra noise was filtered out by removing the noisy parts (generally the tails) observed in the averaged spectra corresponding to wavelengths 342-373, 1018, 1023, 1070, 1075, 2216 and 2220 nm. Noise could be present due to the low reflectance of soils or lower sensitivity of the instruments in these wavelengths. Spectra from both instruments with wavelengths from 379-1014 and 1081-2212 were selected, where the spectra showed clearly noticeable reflectance peaks and dips in both vis and NIR ranges. Finally, the raw averaged and smoothed spectral data were divided randomly into two data sets consisting of 70 random training examples and 16 random test examples. Table 2 shows the statistical results with even distribution for P<sub>Mehlich-3</sub> in both examples.

Table 2: Statistical results on P<sub>Mehlich-3</sub> for training and test data sets.

Number of samples	Set	Minimum	Mean	Maximum	Standard deviation
70	Training	4	112	244	67
16	Testing	4	127	228	71

A variety of statistical data pre-processing and pre-treatment options were used on training examples while developing calibration equations. A tentation process was followed to find out the best pre-processing's and pre-treatments and the final selection of a pre-processing and pre-treatment was based on comparing the statistical results of the different models. This process resulted in two models as will be discussed henceforward.

In a first and second effort to develop a P<sub>Mehlich-3</sub> model, no pre-treatment after de-noising of spectra (Model-1) and first derivative of spectra using Savitzky and Golay (1964), pre-treated by mean centering technique (Model-2) resulted with best results.

**Modeling** Partial least-squares is a bilinear regression technique that extracts a small number of latent factors, which are a combination of the independent variables of reflectance (at spectral wavelengths), and uses these factors as a regression producer for the dependent variables or chemical laboratory measured values (Geladi, P. and Kowalski, B. (1986), de Jong, S. and Kiers, H. (1992)). A soil P (P<sub>Mehlich-3</sub>) calibration equation was generated using the PLS regression whereby soil spectra were related to the measured soil P<sub>Mehlich-3</sub> concentration. The PLS analysis was evaluated using the leave-one-out cross-validation technique.

Model performances were evaluated using the root mean squared error (RMS<sub>E</sub>), coefficient of determination (R<sup>2</sup>) and Akaike Information Criterion (AIC) (Akaike, H.,1974). An additional statistical

quality parameter; the residual prediction deviations (RPD) was used to evaluate the calibration models of Williams and Norris (2001). The RPD is the ratio of standard deviation (SD) of the measured value of soil properties to the value for RMSE of prediction or the RMSE of validation (Stenberg et al., 2004 and Nduwamungu *et al.*, 2009c). For samples of heterogeneous material such as soil, the following levels of performance are defined. Calibrations of those yield values for R<sup>2</sup>>0.95 and RPD>4 are outstanding, values for R<sup>2</sup> of 0.90-0.95 and RPD of 3–4 are high, values for R<sup>2</sup> of 0.8-0.9 and RPD of 2.25-3 are moderately high and values for R<sup>2</sup> of 0.7-0.8 and RPD of 1.75-2.25 are moderate.

## RESULTS AND DISCUSSION

Figure 3 depicts the averaged vis-NIR spectrum between 400-2200 nm when using the 86 soil samples in the laboratory where the narrow gap or missing values represent a separation between the two spectrometer measurements. Figure 4, depicts the Pearson coefficient of correlation (R) for all vis-NIR transformed factors (averaged raw, de-noised, first derivative and second derivative spectra), where no difference in R values was observed between the averaged and the de-noised spectrum, and a weak value of R=0.4 can be observed around 600 nm. However, significantly strong values of R >0.6, can be observed at many parts of the other transformed vis-NIR spectra.

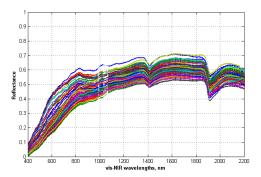


Figure 3: Average vis-NIR soil reflectance measurements taken on 86 soil samples.

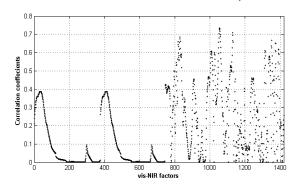


Figure 4:  $P_{Melich-3}$  correlations observed on vis NIR wavelengths and their transformations.

The explanation could be similar to that reported by Maleki *et. al.* (2006) where all the correlations for P<sub>Mehlich-3</sub> in the vis and NIR region would be indirect correlations with the soil components that bind with P and show spectral activity. Phosphorus binds with oxides present in sandy soils, whereas in sandy loam soils, calcium carbonate will bind P as calcium phosphate. The soil samples used in this experiment were taken from an archived set, that were stored in bottles at room temperature, and those soils could have adsorbed air moisture over time (up to 3%). The presence of the absorbed moisture could darken the color of these complexes which in turn would be responsible for a better correlation between the P complex and the spectral signal in the NIR ranges. On the other hand, since the soils were treated with inorganic fertilizer (Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>), the presence of P and its reformed complexes with Al, Fe and Ca minerals, could be derived from the source and should be detected by the NIR spectrometer for their corresponding wavelengths, and similarly, since the soils were also treated with organic P fertilizers (manure), the presence of carbon and its organic complexes, which formed with phosphorus, would also be responsible for a better correlation between the organic P complex and the spectral signal in the vis range.

For this present research, in the vis range, the higher peaks for P<sub>Mehlich-3</sub> for soils used in the training set were observed at wavelengths of 439, 457, 463, 545, 596, 635 and 738 nm whereas, in the NIR

range, most high peaks were observed at wavelengths of 806, 1000, 1009, 1374, 1418, 1873, 1911, 2032 and 2174 nm (Figure 6).

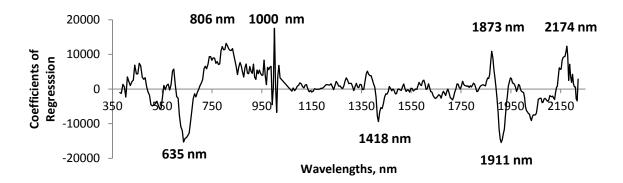


Figure 5: Coefficients of Regression, used for soil P (P<sub>Mehlich-3</sub>) calibration; data pre-processing with first Savitzky–Golay derivative followed by mean centering (model 1).

The highest peaks in the vis region were at 635 nm and in the NIR region 1418, 1911 and 2174 nm, respectively. Among these wavelengths, 439-457 and 1418 could be compared with 421, 441, 448, 454 and 1464 found by Maleki *et.al.* (2006). However, in future research, a detailed analysis of each suggestive wavelength and P<sub>Meblish-3</sub> concentration needs to be carried out.

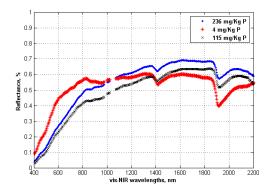


Figure 6: vis-NIR spectra illustrating differences when collected on soil samples having three different  $P_{\text{Melich-3}}$  concentrations

Figure 7 shows the AIC values over a different number of PLS factors, where the best number chosen by both models corresponded to the lowest AIC values. Table 3 shows the PLS statistical results on two  $P_{\text{Mehlich-3}}$  models in both the training and test data sets. Both models produce a first-class prediction for  $P_{\text{Mehlich-3}}$  concentration in both the training and the test samples; however, model two is simpler as it uses only 4 PLS factors in comparison to model one which uses 7 PLS factors.

In the present study, RPD and  $R^2$  were 2.42 and 0.84, respectively, when no pre-treatment was applied (Model-1) and RPD and  $R^2$  were 2.37 and 0.86, respectively, when data was pre-treated by the first Savitzky–Golay derivative followed by mean centering (Model-2); however, the later pre-treatment showed the highest coefficient of determination ( $R^2$ ) value between the predicted and measured values, the lowest value for the standard error ( $ST_E$ ) of prediction and lowest number (four) of PLS latent factors. Both models were developed for the prediction of  $P_{Mehlich-3}$  Concentrations in air dried soils; they can be classified in the category of moderately useful (Nduwamungu *et al.*, 2009c).

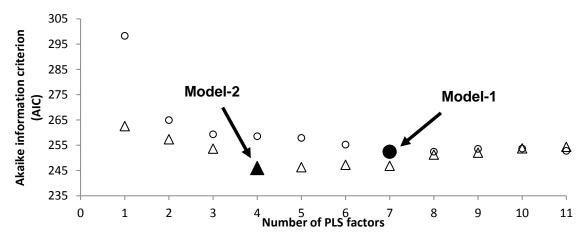


Figure 7: Solid symbols representing number of PLS factors selected; Circles-averaged raw training data; Triangles-first derivatives and mean centered on averaged raw data.

As an additional quality, these P models are useful for at least three types of soil texture (silt-loam, to sandy-silty-loam and sandy-clay). However, these results would be limited to predict soil P locally on the same fields, and to offer its concrete usefulness, on a global perspective it would have been more of an interest to train and test this service on soil samples originating from different fields.

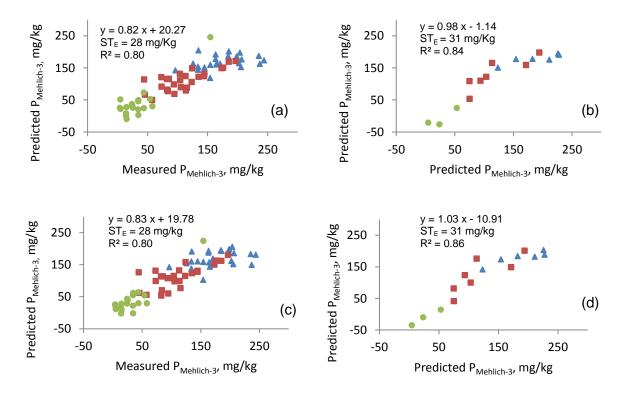


Figure 8: Predicted versus laboratory chemical measurement of soil phosphorus ( $P_{\text{Mehlich-3}}$ ), including: a) calibration, averaged training raw data; b) prediction, averaged test raw data; c) calibration, first derivative and mean-centered on averaged training data; d) prediction, first derivative and mean-centered on averaged test data;  $R^2$ , coefficient of determination;  $ST_E$ , standard error in prediction.

Table 3: Statistical results of partial least-squares model for P<sub>Mehlich-3</sub> resulting from aforementioned data pre-processing.

Data process	Model-1		Model-2	Model-2		
Statistics	Training	Test	Training	Test		
$R^2$	0.80	0.84	0.80	0.86		
Model Factors	7	7	4	4		
RMSE, mg/kg	30.16	29.38	29.98	29.94		
L CI RMS <sub>E,</sub> mg/kg	-	21.71	-	22.12		
H CI RMS <sub>E,</sub> mg/kg	-	45.45	-	46.31		
RPD	2.22	2.42	2.23	2.37		

In Figure 8, symbols (triangles, squares and circles) represent soil  $P_{\text{Mehlich-3}}$  concentrations of samples taken from depths 1, 2 and 3 respectively. The performance of the two models, discussed above, is also demonstrated in Figure 8, which shows the linear correlation between laboratory measurements and predicted soil P by the vis–NIR model in the calibration (training) and validation (test) stage.

**CONCLUSION** In this study, soil absorbance measured using a combined dual spectrophotometer in the range of 342-2220 nm of the visible (vis) and near infrared (NIR) spectrum was combined with a partial least squares (PLS) cross-validation technique to correlate soil reflectance with soil test P (P<sub>Mehlich-3</sub>) on a well organized calibration (training) data set of readily available oven-dried soil samples. Two methods of pre-processing the averaged spectral data resulted in two distinct models. The results of the leave-one-out cross-validation of the spectral calibration model yielded a linear relationship between the predictions from the model and the reference measurements, with a coefficient of determination of 0.86 and a standard error of prediction of 31 mg/kg. However, firstly these results would be limited to predict soil P locally on the same fields, and to offer its concrete usefulness, on a global perspective it would have been more of an interest to train and test this service on soil samples originating from different fields and secondly, these results could be biased due to the residual or re-formed organic and/or in organic P compounds, from experiments undergoing P fertility trials and in future research, a detailed analysis of each suggestive wavelength and P<sub>Mehlich-3</sub> concentration needs to be carried out. The next step in this research will involve applying a similar data processing procedure to vis-NIR in-situ measurements on the same and on different fields.

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