Evaluation of rapid determination of phosphorous in soils by near infrared spectroscopy

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Introduction

Phosphorous in soil is one of the most difficult elements to assess for plant needs. Phosphorous compounds commonly found in soils are mostly unavailable for plant uptake because they are highly insoluble. When soluble sources of phosphorous, such as those in fertilizer and manure, are applied to soil, they are easily fixed to less available, sparingly soluble forms. Reactions that fix phosphorous in relatively unavailable forms differ from soil to soil and are closely related to soil pH. In acid soils the reactions predominantly involve Al, Fe and Ca either as dissolved ion, as oxides, or as hydrous oxides. Many Korean soils contain such hydrous oxides as coatings on soil particles and as interlayer precipitate in silicate clays. Some of the added phosphorous may also be changed to organic forms and become temporarily unavailable.[1]

Determination of total phosphorous of the soil commonly uses an oxidation and dissolution method with suitable acids to oxidise organic forms and dissolve phosphorous imbedded in the soil minerals. The basic function of a soil phosphorous test depends on both test methods and soil characteristics. The commonly known phosphorous availability indices are dissolution methods with water or unbuffered salt solution, diluted weak acid, diluted strong acid and buffered alkaline. Interpretation of the data from those methods vary with regional preference, consideration of soil characteristics and efficiency of operation.[2]

Davies mentioned the potential of NIR technique and this has been shown a useful technique in determining soil moisture,[3] organic matter and total nitrogen in the soil.[4,5] Krischenko showed a possible near infrared (NIR) technique for soil phosphorous analysis.[6] This study investigated the capability to estimate total and available phosphorous extracted by various extractants from Korean soils.

Materials and methods

Soils

A total of 148 soil samples with a wide range of soil characteristics were collected from paddy, upland, orchard and others over the Kyong book province in Korea. Soil sample were air-dried and prepared to pass 2.0 mm sieve openings.

Determination of soil phosphorous

Total phosphorous in the soil was determined by ICP after four hours digestion with 60% $HClO_4$ – conc HNO_3. Available phosphorous was also determined by ICP after extraction with Bray 1

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extractant for one minute and Olsen and Truog extractants for 30 minutes, respectively. All results were expressed on the basis of dry weight.

Measurement of NIR spectra

The NIR reflectance spectra of soils were measured using a scanning NIR spectrometer (Foss, NIR5000) with the wavelength ranging from 1100 to 2500 nm. Functional groups of Ca, Fe and Al bounded phosphates on the NIR spectrum were compared after adding 3% of phosphorous solution with Ca, Fe and Al phosphate to a soil. The difference in the functional groups of the remaining phosphate in the soil was also compared after being extracted by the Bray 1, Olsen and Truog extractants. 99 soil samples were used for the calibration equation and 49 samples were used for prediction. The multiple linear regression was adopted for making the calibration.

Results and discussion

The data in Table 1 shows the various types of phosphorous in the soils used in this study. The average total phosphorus by $HClO_4$ digestion used for calibration was 1384.7 mg kg^{-1} ranged from 227.2 to 3675.9 mg kg^{-1} of the soil and that used for prediction was 1376.0 mg kg^{-1} ranged from 326.1 and 511.3 mg kg^{-1} of the soil. Total phosphorous in the soil was mainly determined by the Na_2CO_3 fusion, H_2SO_4 digestion, $HClO_4$ digestion and NaOBr oxidation methods. Kuo mentioned that the latter two methods were known not to readily dissolve phosphorous in silicate minerals and, therefore, underestimate the total phosphorous in the soils.[2]

Available phosphorous data of the soils used for calibration and prediction by Bray 1, Olsen and Truog extractant showed big differences (Table 1). This seemed mainly due to the different values of the soil pH, time of extraction and different extractants which extracted different types of phosphate. Shin *et al*. showed the composition rate of Ca–P, Al–P and Fe–P in Korean soil.[1] Ca–P was far below average when soil pH was less than 5.5. It was far higher than average when soil pH was more than 5.5. Al–P was increased slightly with the decrease of soil pH and Fe-P had the smallest value when soil pH was below 4.5 and above 6.5. The difference in Al–P and Fe–P to soil pH was smaller compared with Ca-P. After a soil was mixed with Ca, Fe and Al phosphate solution (3% as phosphorous), change in NIR reflectance spectra to the functional group for Ca, Fe and Al–P was not clear as shown in Figure 1. The minor change on raw and 2nd derivatives of the spectrum to these groups was barely identifiable. Therefore, it is difficult to interpret exactly what the main composition for the complicated bands was. After the soil was extracted by Olsen, Bray 1 and Truog extractant, minor changes in NIR reflectance spectra for these functional groups, shown in Figure 2, were of the same order as the functional groups of Al, Ca and Fe bounded phosphates but the magnitude was different near the 1930 nm range. Diluted

Table 1. Total and available phosphorus (mg/kg of soil) by various extractants used for calibration and prediction in the soil.

	Calibration (99)		Prediction (49)	
	Mean (mg kg^{-1})	Range (mg kg^{-1})	Mean (mg kg^{-1})	Range (mg kg^{-1})
Total P	1384.7	227.2–3675.9	1376.0	326.1–3511.3
Bray 1	213.7	16.9–911.6	205.5	8.0–888.3
Olsen	102.0	4.2–317.4	103.7	6.4–292.7
Truog	101.9	0.0–717.6	111.7	0.0–564.1

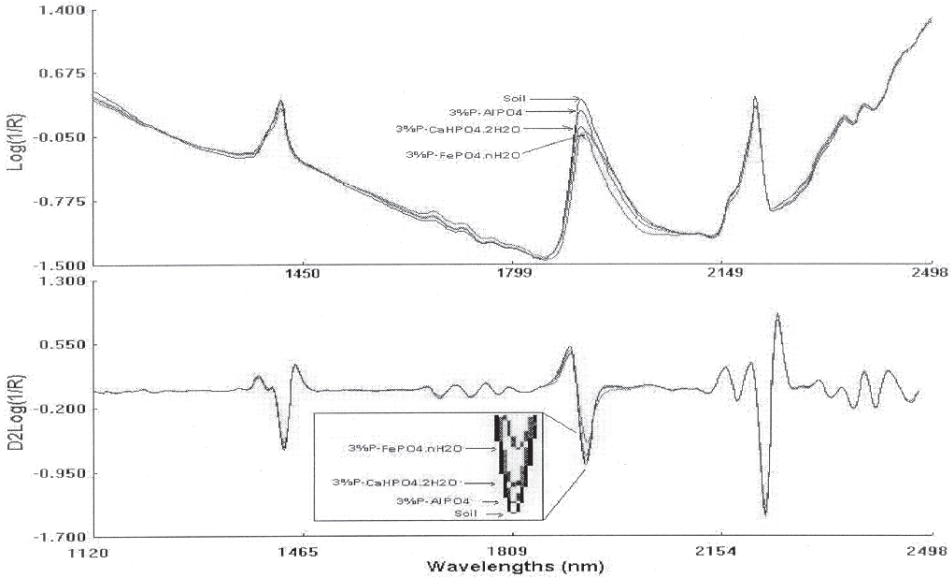

Figure 1. Raw and corresponding 2nd derivative spectra after adding various phosphate (as 3% of phosphorous) compound solutions to a soil and mixed through.

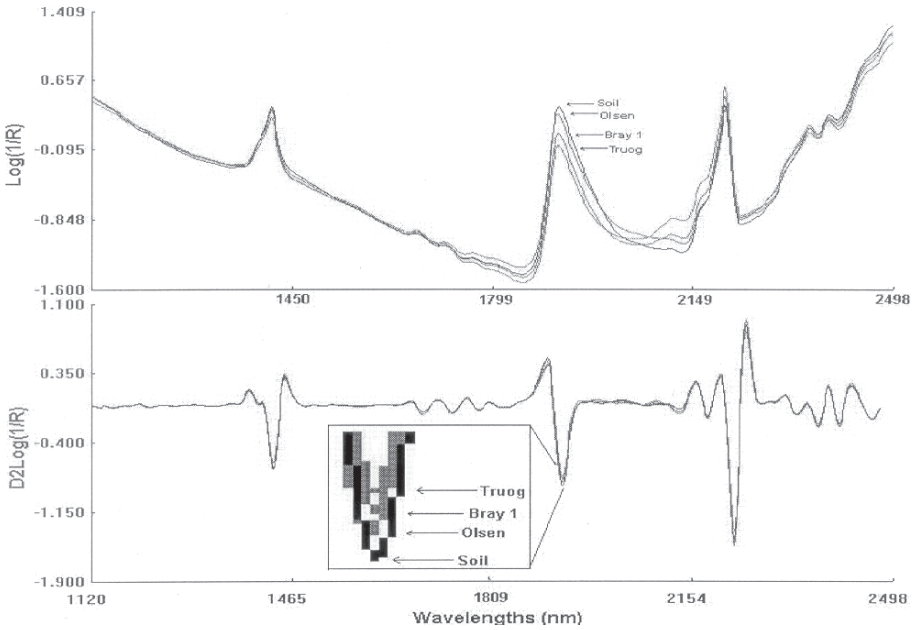

Figure 2. Raw and corresponding 2nd derivative spectra of a soil after extraction by different extractants and washed with distilled water.

strong acid solution such as Bray 1extractant solubilised Ca, Al–P and, to a lesser extent, Fe–P Al–P were the primary soil phosphorous fractions by the Bray 1 test. The Olsen test extracted less phosphorous than the Bray 1 test and correlated well with Al–P P.[2] Mean available phosphate was in the order of Bray 1, Olsen or Truog extractant phosphates but the range of these phosphates in the soil used for calibration and prediction was in the order of Bray 1, Truog and Olsen extractant phosphates. Figure 3 shows the actual measured phosphorous used for this study by means of wet chemistry and predicted value by NIR on a 1 : 1 line.

Scattering of each measurement and prediction on a 1 : 1 line seemed to be a function of a complicated effect of phosphorous compounds on the various extractants, time of extraction and various soil characteristics. As seen, the actually measured values showed relatively good agreement with the predicted value in spite of the complicated soil phosphorous analyses but the Truog P test showed very poor agreement when the P value was less than 200 mg k^{-1} of soil. The calibration developed for phosphorous was the best for total phosphorous with $R = 0.91$, then Bray 1 P with $R = 0.82$ and Olsen P with $R = 0.80$. The poorest one was the Truog P with $R = 0.76$.

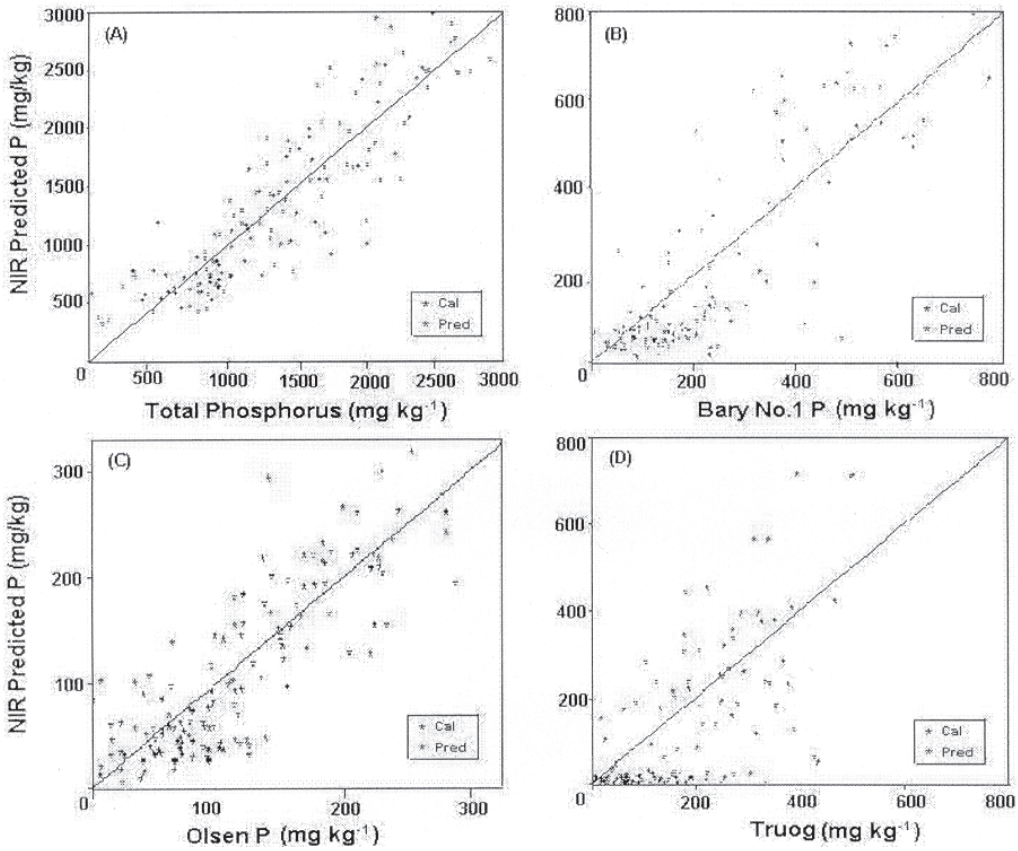

Figure 3. Relationship between measured phosphorous by $HClO_4$ (a) digested total phosphorousand (b) Bray 1, (c) Olsen and (d) Truog available phosphorous and predicted value by NIR in soils.

Table 2. Calibration and prediction statistics of mutiple linear regression for total and available phosphorus(mg kg^{-1} of soil) by the various extractants.

Extaractant	Spectrum	Terms	*R*	*SEE*	*SEP*	Bands used for calibration
Total P	Raw	9	0.91	329.0	429.7	1100,1920,1978,2160,2172,2284,2300,2308,2464
Bray 1	2D	9	0.82	146.4	162.3	1242,1252,1330,1742,1962,1990,2140,2252,2344
Olsen	2D	9	0.80	54.9	54.1	1188,1202,1216,1624,1678,1890,1982,2142,2228
Truog	1D	9	0.76	162.7	152.3	1464.1896,1922,1942,2026,2194,2212,2294,2304

Terms: number of wavelengths used for calibration, *R*: Multiple correlation coefficient
Raw: raw spectrum, 1D: 1st derivative spectrum, 2D: 2nd derivative spectrum
SEE: standard error of estimation, *SEP*: standard error of prediction

Conclusion

NIR spectroscopy is increasingly used as a means of rapid and accurate determination of the properties and qualities of food and agricultural products. However, the NIR technique may not exceed the referenced laboratory analytical method in accuracy due to the calibration equation being based on the referenced analytical data. Phosphorous in the soil is one of the most difficult elements to assess for plant needs mainly due to the various soil characteristics. However, the NIR method could also be used as a routine method to estimate or screen total phosphorous, and Bray 1 and Olsen type of available phosphorous because of ease of operation. Often research requires more accurate soil data for fertilizer recommendations than is achieved by present NIR calibrations. With improvments in accuracy, NIR spectra may become a suitable technique for reliable soil testing.

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