Feasibility of predicting phosphorus retention capacity and several forms of phosphorus in Canadian prairie soils by near infrared spectroscopy

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Introduction

Awareness is emerging that the global supply of easily-mineable rock phosphate used for the production of industrial fertilizers, that began in 1847, is running out.[1–5] All countries must soon thoroughly understand and actively manage phosphorus (P) dynamics in agricultural soils, and apply bio-wastes to the land if agriculture is to produce sufficient food to sustain global human populations into the indefinite future. Minimising the quantities of phosphorus wastefully running off land is a priority.

Methods to monitor P in agricultural soils in the context of precision agriculture are needed immediately. An important characteristic of soils that influences the transport of agricultural P from soil to water is the soil phosphorus retention capacity (PRC), a measure of the ability of the soil to retain added P.[6] The higher the capacity of the soil to retain P added either as organic or inorganic soil amendment (fertilizer), the lower is the risk of P loss from soil to water bodies, and eventually to the ocean.

The determination of PRC in the laboratory is tedious. An attempt is made in this study to use near-infrared (NIR) spectroscopy to predict PRC. Near-infrared technology has been used for about five decades for the analysis of soil.[7] Generally, total P in soil is not predictable by NIRS,[7] although some fractions of available P have been predicted with marginal acceptability. Apparently, the prediction of PRC by NIR spectroscopy has not previously been examined. In contrast, calcium (Ca) and magnesium (Mg) in soils from around the world have previously been predicted with moderate success. Aluminium (Al) in soil has been predicted by several workers, also with marginal success. The purpose of the present study was to evaluate the feasibility of predicting the Langmuir adsorption maximum, S_{max}, determined in the laboratory as a measure of PRC, as well as concentrations of Mehlich-3 extractable Ca and Mg, and oxalate-extractable Al. Also, potentially-available P content in soil, as measured by five chemical extraction methods, was predicted by NIR spectroscopy.

Materials and methods

Soil Sampling and soil analysis

Surface soil samples (0–15 cm) were collected from across Manitoba from five distinct soil groups, clay, regional till loam, high lime till, wet sand soils, and dry sand soils as described by Ige *et al*.[6] The samples were air-dried and gently crushed to pass a 2-mm sieve. In the laboratory, Mehlich-3 extractable Ca and Mg were determined using the method of Mehlich.[8] S_{max} is the calculated Langmuir adsorption maximum in mg P kg^{-1}, corrected for the native sorbed P, and determined by equilibrating the soil samples with 11 concentrations of P.

Phosphorus was extracted from 108 to 195 soil samples by five methods described by Ige *et al*.[9] These extractions were water extraction, Olsen P extraction, and extractions by the Mehlich-3 method, sodium nitrilotriacetate (NTA), and ammonium oxalate.

Near-infrared spectroscopy using a Zeiss Corona 45 vis-NIR spectrometer

The Zeiss Corona 45 VISNIR 1.7 Spectrometer was operated using CORA Version 3.2 software. This instrument records spectra as absorbance from 360 to 1690 nm and displays the spectral data at 2 nm intervals. For scanning, each sample in a glass scintillation vial was positioned in a sample holder that fitted over the sensor head of the spectrometer. Each vial was shaken and scanned three times in succession. A scan takes about 7 sec. Number of samples was 147.

Calibration procedure using The Unscrambler

Calibration was performed using multivariate analysis software, The Unscrambler version 9.7 (CAMO ASA Oslo, Norway). To avoid noise at the lower wavelengths, the spectral range was truncated to 520 to 1690 nm for analysis. Spectral data were pre-treated by several degrees of box-car smoothing, and transformation to first or second derivative. Calibration models between the spectral and constituent data were developed using principal component analysis/partial least squares regression (PCA/PLS), and the test set method using two-thirds of the samples as a calibration set and the remaining third as a validation set. Prior to dividing the samples into calibration and validation sets, they were sorted by each constituent value.

NIR-predicted values for the samples in the validation set were evaluated as a function of the calculated or chemically-measured values. The calibration that resulted in the highest r^2 between the NIR-predicted values and the chemically-measured values, and in the lowest root mean standard error of prediction (*RMSEP*), was selected as the most effective.

Results and discussion

Constituents

Composition of the 147 samples used for the determination of S_{max} is given in Table 1.

Table 1. Concentrations of the parameters and constituents in samples in this study.

	S_{max} mg P kg^{-1}	Mehlich-3 Ca mg kg^{-1}	Mehlich-3 Mg mg kg^{-1}	Oxalate Al mg kg^{-1}
Mean $\pm$ SD	690 $\pm$ 305	5337 $\pm$ 3804	788 $\pm$ 543	724 $\pm$ 358
Range	108 – 1523	558 – 21970	68 – 3266	145 – 1943

NIR predictions

The performance of calibrations for the three constituents is shown statistically in Table 2 and graphically for S_{max} in Figure 1. The calibrations for all three constituents were judged to be useable.

In this study, useful calibrations were not developed for any of the five P extractants. R^2 ranged from 0.20 for Olsen P and Mehlich 3 P, to 0.23 for H_2O P, 0.32 for NTA P and 0.35 for Oxalate P. Somewhat better results were obtained by Ryu et al.[10] with r^2 of 0.67 for Bray 1 extractant, 0.64 for Olsen, and 0.58 for Truog extractant in Korean soils.

In conclusion, NIR technology has been shown to be potentially effective for the rapid estimation of S_{max}, the Langmuir adsorption maximum, on dried, ground soil from 5 soil groups in Manitoba. Two of the most important parameters that correlate with S_{max} in these soils, Mehlich-3 Ca and Mehlich-3 Mg, were also predicted with a performance judged as moderately useful. Calibration success was slightly lower for the prediction of Oxalate Al. This appears to be the first attempt to predict S_{max} with NIR, but Ca and Mg in soils have usually been found to be predicted successfully in previous studies.[7] Mehlich-3 Ca and Mg have also been predicted with good results.[11,12]
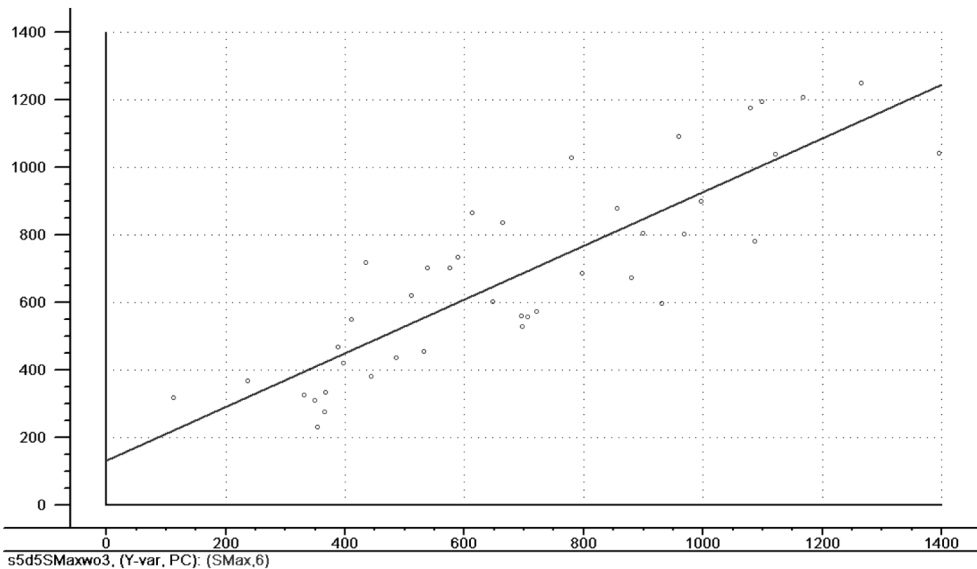

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Figure 1. Linear regression relationship between the NIR-predicted and measured values for S_{max}. The line is the best fit through the points, not the 1:1 line. Plot statistics are given in Table 2.

Table 2. Accuracy of prediction for PRC-related calibrations in this study.

Statistic	S_{max}	Mehlich-3 Ca	Mehlich-3 Mg	Oxalate Al
r^2	0.74	0.72	0.78	0.69
RMSEP	157	1762	236	224
Slope	0.80	0.59	0.80	0.62
Bias	−10.4	76.2	-27.5	-17.1
RPD	2.0	1.8	2.1	1.7
RER	8.2	9.1	8.0	7.7
No. components	6	7	4	8

Acknowledgements

References

1. P. Déry and B. Anderson, *Energy Bulletin* Aug 13 (2007). http://energybulletin.net/node/33164
2. J. Ward, *Energy Bulletin* Aug 26. (2008). http://www.energybulletin.net/node/46386
3. S. White and D. Cordell, *Sustainable Phosphorus Futures* (2008). http://phosphorusfutures.net/index.php?option=com_content&task=view&id=16&Itemid=30.
4. N. Gilbert, *Nature* **461,** 716 (2009).
5. D.A. Vaccari, *Scientific American* **300,** 54 (2009).
6. D.V. Ige, O.O. Akinremi and D.N. Flaten, *Can. J. Soil Sci*. **88,** 327 (2008).
7. D.F. Malley, P.D. Martin and E. Ben-Dor, Chapter 26, in *Near-Infrared Spectroscopy in Agriculture*. Ed. by C.A. Roberts, J. Workman, Jr and J.B. Reeves, III. Agronomy 44. American Society of Agronomy, Inc., Crop Science Society of America, Inc., Soil Science Society of America, Inc. Publishers, Madison WI, ISA, pp. 729–784 (2004).
8. A. Mehlich, *Commun. Soil Sci. Plant Anal*. **15,** 1409 (1984).
9. D.V. Ige, O.O. Akinremi, D.N. Flaten, B. Ajiboye and M.A. Kashem, *Can. J. Soil Sci*. **85,** 417 (2005).
10. K.S. Ryu, J.S. Park and B.J. Kim, in *Proceedings of the 10th International Conference*. Ed. by A.M.C. Davies and R.K. Cho. NIR Publications, Chichester, UK, 399 (2002).
11. C.-W. Chang, D.A. Laird, M.J. Mausbach and C.R. Hurburgh, *Soil Sci*. **167,** 110 (2001).
12. C. Nduwamungu, N. Ziadi, L.-E. Parent and G.F. Tremblay. *Can. J. Soil Sci*. **89,** 579 (2009).