

Feasibility of analysing archived Canadian prairie agricultural soils by near infrared reflectance spectroscopy

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Introduction

Collections of archived soils contain a great deal of information on soil quality over time and space. With declining budgets for soil mapping and environmental monitoring, not only are fewer samples being taken but, also, fewer analyses are being performed on the samples. Near infrared (NIR) spectroscopy has been shown to be effective for analysing soils for a number of important constituents and parameters. It may provide a cost-effective way to permit more complete analysis, not only of current, but also of archived samples. Furthermore, NIR spectroscopy may be useful in detecting and monitoring large-scale changes in soil acidity, salinity or organic matter content that may reflect practices that degrade land and reduce its productivity.¹

In this study we explored the feasibility of using NIR spectroscopy for the analysis of particle size fractions, nutrients and metals in soil samples ($n = 1100$) from the Canada–Manitoba Soil Survey. We report results for a group of 108 samples from the Duck Mountain Provincial Park, Manitoba, for organic C, total N, sand, silt, clay, cation exchange capacity and exchangeable Na, K, Ca and Mg. Secondly, preliminary results are given for 1000 samples, representative of agro-Manitoba, for organic C, organic N, total Fe, Mn, Zn, Cu, Co, Pb, Ni, Cd, Mo, Ag, V, Hg, and Cr.

Materials and methods

Collection of soil samples

Soil samples were collected by the Canada–Manitoba Soil Survey at selected locations within agricultural landscapes of Manitoba.² The soil samples ($n = 108$) were from 35 different soil profiles (maximum depth, 100 cm) at various locations in Duck Mountain Provincial Park, Manitoba. They were selected to represent distinct textural classes and a wide range of variable soil chemical proper-

Table 1. Physical and chemical characteristics of the soil samples used in this study. Concentrations are on a dry weight basis, except for pH and EC that were determined on wet soil.

Constituent or parameter	Duck Mountain			Agro–Manitoba	
	N	Mean \pm SD	Range	N	Range
% organic C	108	1.71 \pm 1.89	0.09–11.13	940	0.01–59.34
% total N	108	0.132 \pm 0.146	0.012–0.942	169	0–2.813
% sand	108	32.73 \pm 22.69	1–94	952	0.06–98
% silt	108	32.17 \pm 12.20	3–62	956	0.08–76
% clay	108	35.10 \pm 17.73	3–76	957	0.06–87
pH	108	—	4.4–7.9	1000	3.5–8.7
EC, mmohs cm ⁻¹	108	0.37 \pm 0.26	0.1–2.03	—	—
CEC, meq 100 g ⁻¹	108	27.23 \pm 12.13	2.60–63.94	118	2.63–70.93
exch. Ca, meq 100 g ⁻¹	108	13.87 \pm 6.87	0.5–31.1	—	—
exch. Mg, meq 100 g ⁻¹	108	6.78 \pm 3.5	0.3–16.4	—	—
exch. Na, meq 100 g ⁻¹	108	0.24 \pm 0.52	0–5.1	—	—
exch. K, meq 100 g ⁻¹	108	0.71 \pm 0.43	0.1–2.6	—	—
% Fe	—	—	—	829	0.17–4.5
Cu, μ g g ⁻¹	—	—	—	829	1–54
Cr, μ g g ⁻¹	—	—	—	829	5–142
V, μ g g ⁻¹	—	—	—	829	15–440

ties. Textural classes included clay, loam, fine sand, loamy sand, silty clay, silty clay loam, clay loam, silt loam, loamy sand, medium sandy loam, fine sandy loam and very fine sandy loam. The larger set of soil samples ($n = 1000$) represented agro–Manitoba archived samples.

Physical and chemical analyses

Analysis of soil physical and chemical parameters was done by Manitoba Agriculture, as described by Haluschak.³ The pipet method was used for particle size analysis. Fractionation of soil particles into distinct classes (% sand, % silt, % clay) was achieved by sieving and sedimentation. Soil pH was determined on field moist soil in 0.01 M CaCl₂ using a pH meter with glass–calomel electrodes. Electrical conductivity was measured in a saturation extract using a conductivity meter. Determination of nitrogen was done by the Kjeldahl method. The procedure used for determining organic carbon was the Walkley–Black method, modified for automatic titration. Ammonium acetate at pH 7.0 was used for cation exchange capacity (CEC) and extraction of exchangeable cations (Ca, Mg, Na, K). Air-dried soil samples were subject to determinations for particle size, CEC and exchangeable cations. Total N and organic carbon were done on oven-dried soil.

For heavy metal analysis, 1 g soil subsamples were dried, ground and digested in an HF-HClO₄-HNO₃ mixture. Total Fe, Mn, Zn, Cu, Co, Pb, Ni, Cd, Mo, Se, Hg, V, Cr and Ag content in soil samples were then measured using atomic absorption spectrophotometry.⁴

Mean, medians and ranges for number of physical and chemical parameters of soil samples used in this study are given in Table 1.

Preparation and scanning of soil samples by near infrared spectroscopy

Near infrared reflectance spectroscopy was performed on c. 5 g air-dried samples, in ordinary borosilicate glass scintillation vials, using an NIRSystems Model 6500 visible/NIR spectrophotometer (Foss NIRSystems, Silver Spring, MD, USA), equipped with a Rapid Content Sampler[®]. Using Near infrared Spectral Analysis Software (NSAS), provided with the instrument, absorbance at wavelength intervals of 2 nm was recorded over the wavelength range 1100 to 2498 nm as log 1/R, where R is reflectance. The samples were scanned three times, usually sequentially. Between scans, the sample was removed from the detector, shaken and replaced in order to obtain representative scans of the material. Prior to each scan of a sample, a ceramic reference was scanned and the reference spectrum was automatically subtracted from the sample scan.

Development of NIR calibrations—Multiple Linear Regression

Calibrations were developed using the stepwise multiple linear regression (MLR) option in the NSAS software. Separate calibration equations were computed using one-half of the spectral and constituent data and evaluated using the other, independent, half of the data. Calibrations were developed using several mathematical treatments: the raw optical data (log 1/R) smoothed over four, 10, 20 or 40 wavelength points (i.e. segment), or the first or second derivative of the smoothed log 1/R data with several combinations of segment and derivative (i.e. gap) sizes.

The best calibration was the one with the highest coefficient of determination, r^2 , and the lowest standard error of performance (*SEP*). The *RPD* (ratio of the *SD* of the constituent reference values in the prediction set to the *SEP*) and the *RER* (ratio of the range of the constituent reference values in the prediction set to the *SEP*) were also used to evaluate the success of the calibration process. In environmental applications, where samples are qualitatively much more variable than in applications involving agricultural commodities, “acceptable” values for *RPD* and *RER* have not been established.

Results

Duck Mountain

Calibrations developed for the Duck Mountain soil samples ($n = 108$) had $r^2 > 0.9$ for % clay [Figure 1(c)]; $r^2 \sim 0.9$ for % organic C and cation exchange capacity [Figures 1(a,d)]; $r^2 > 0.85$ for exchangeable Ca [Figure 1(e)]; $r^2 \sim 0.8$ for % total N [Figure 1(b)]; and $r^2 = 0.7\text{--}0.85$ for exchangeable Mg [Figure 1(f)], (Table 2). For most calibrations, *RPD* was 2.5–3.5 and *RER* was > 10 (Table 2). Concentrations were well distributed across the ranges for % clay, CEC, Ca and Mg, but less well distributed for % organic C or % total N (Figure 1).

Calibrations for % sand ($r^2 = 0.74$) and % silt ($r^2 = 0.45$), (data not shown) were less successful than for % clay. In this study, calibrations for pH ($r^2 = 0.6$) and exchangeable K ($r^2 = 0.55$) were less satisfactory than for the other constituents. No useful calibrations were obtained for exchangeable Na or conductivity.

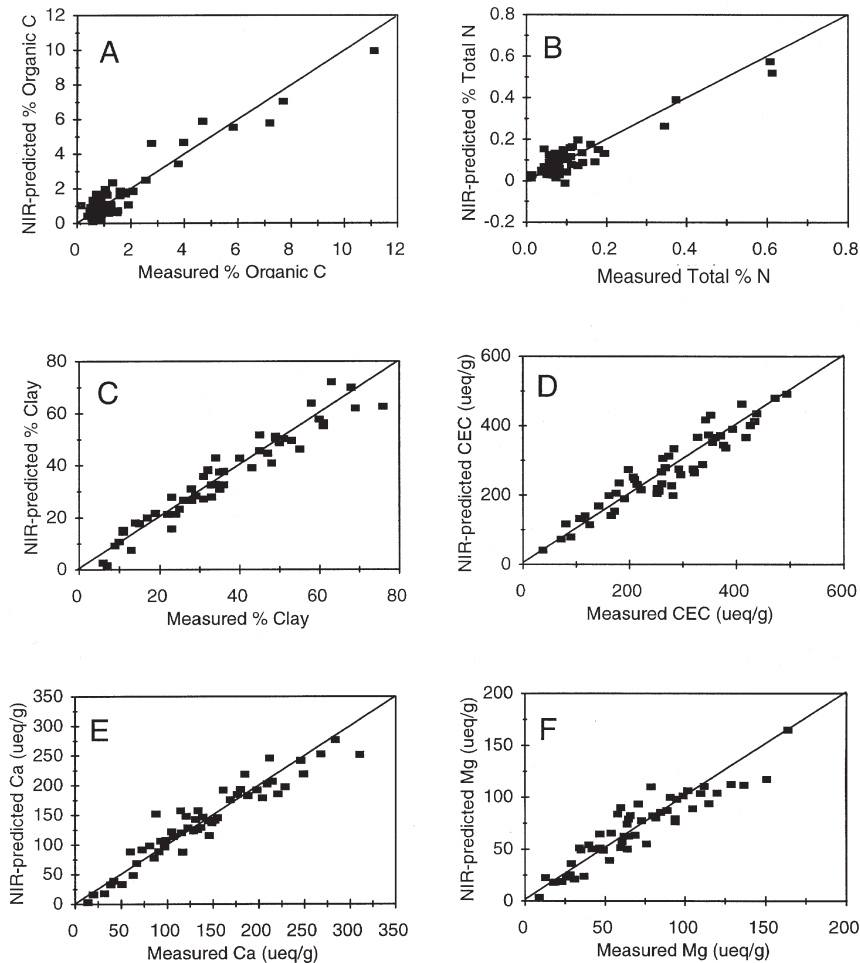


Figure 1. NIR-predicted values plotted against values measured by conventional methods in dry soil from the Duck Mountain Provincial Park for (a) % organic C, (b) % total N, (c) % clay, (d) cation exchange capacity, (e) exchangeable Ca, and (f) exchangeable Mg.

Agro-Manitoba

The numbers of samples analysed for the constituents in the agro-Manitoba soils varied between 118 to 1000 (Table 1). The ranges for % organic C, % total N, CEC, and the particle size fractions were larger than for the Duck Mountain samples (Table 1).

The calibration developed for % total N was the best in this sample set with $r^2 = 0.87$ and was similar to that for the Duck Mountain samples. Other calibrations were less successful than for the Duck Mountain samples, with $r^2 = 0.78$ for % organic C, 0.81 for % clay, 0.65 for % sand, 0.51 for CEC and 0.36 for % silt (Table 3). Calibrations for the metals were best for V with $r^2 = 0.78$ while those for %

Table 2. Accuracy of prediction, mathematical treatments and wavelengths for calibrations using the multiple linear regression procedure for the Duck Mountain soil samples. Wavelength range for all calibrations was 1100–2498 nm.

Statistic	% Organic C		% Total N		% Clay		CEC		Exch. Ca		Exch. Mg	
	A/B	B/A	A/B	B/A	A/B	B/A	A/B	B/A	A/B	B/A	A/B	B/A
r^2	0.91	0.88	0.79	0.85	0.92	0.92	0.89	0.93	0.90	0.85	0.85	0.72
SEP ^a	0.63	0.60	0.08	0.05	5.18	4.95	4.03	3.66	2.15	2.64	1.37	1.84
RPD ^b	3.3	2.7	2.2	2.6	3.5	3.6	3.0	3.8	3.3	2.6	2.6	1.9
RR ^c	17.5	14.0	12.1	13.2	13.5	13.5	14.9	15.9	13.8	10.8	11.3	8.2
Math ^d	D2OD	D2OD	D2OD	D2OD	D1OD	D1OD	D1OD	D1OD	D1OD	D1OD	D1OD	D1OD
Seg ^e /Gap ^f	10/4	20/10	10/20	4/4	4/4	40/20	20/10	20/40	10/4	40/40	4/4	4/4
1 ^h	2000	2100	1760	1660	2380	2460	2300	1980	2120	1900	2480	2400
2	1660	1700	1220	1640	1840	1640	2360	2340	2180	2400	2100	2100
3	—	2020	2000	2420	2480	2020	2440	2280	2000	1440	2340	2360
4	—	2160	1660	1680	2360	1880	2040	2300	2360	2020	2020	2040
5	—	1320	1240	1400	2100	2320	1500	1440	1500	1620	2360	2480
6	—	1660	—	2040	1680	1400	2420	2440	2420	2140	—	—
7	—	—	—	2340	2080	2420	1880	2000	1880	2300	—	—
8	—	—	—	—	1640	2340	1460	2360	1460	2080	—	—

^a standard error of prediction

^b ratio of standard deviation to SEP (SD/SEP)

^c ratio of range to SEP

^d mathematical treatments

^e D1OD = first derivative, D2OD = second derivative

^f segment = degree of smoothing, i.e., number of wavelength points averaged

^g gap = derivative size, i.e. distance in wavelength points between the beginning and end of the derivative

^h the wavelengths used in the calibration equation

Fe, Cu and Cr had r^2 of 0.62–0.73 (Table 3). Calibrations for the remaining constituents had $r^2 = 0.5$ or less (not shown).

Discussion

This study reports that % total N was predicted on both sets of samples with moderate success. Generally, with the possible exception of % total N, the results achieved for the smaller sample set from Duck Mountain Provincial Park were superior to those for the larger sample set from agro–Manitoba. This relationship of the quality of the calibrations being inversely related to the number of samples in the set is borne out by results reported on 28 samples from a single soil series. R^2 between reference and NIR-predicted values were >0.98 for Ca, Mg and Fe,⁵ with $r^2 > 0.92$ for Cu, Cr, and V.⁶

This trend with the number of samples suggests that sets with less variability in soil parameters may produce better calibrations than those with more variability. In an attempt to improve the performance of the calibrations for the agro–Manitoba soils in an on-going study, the 1000 samples will be

Table 3. Accuracy of prediction, mathematical treatments and wavelengths for calibrations using the multiple linear regression procedure for the agro-Manitoba soil samples. Wavelength range for all calibrations was 1100–2498 nm. Abbreviations are defined in Table 2.

Statistic	% Org C	% Tot N	% Sand	% Silt	% Clay	CEC	% Fe	Cu	Cr	V
r^2	0.78	0.87	0.65	0.36	0.81	0.51	0.62	0.69	0.73	0.78
SEP	2.95	0.25	17.6	13.2	8.6	8.87	0.53	5.79	14.10	18.40
RPD	2.6	2.7	1.7	1.3	2.26	1.4	1.64	1.8	1.9	2.5
RER	20.1	11.4	5.5	6.1	10.7	7.7	8.18	9.2	9.9	22.1
math	D1OD	D2OD	D1OD	D1OD	D1OD	D1OD	D1OD	D1OD	D2OD	D1OD
seg/gap	20/20	4/4	4/10	40/40	10/40	10/40	20/40	20/20	20/40	20/4
1	1760	2400	1660	1520	1380	2420	2340	1920	1620	1700
2	1660	2340	1900	2380	1520	2000	1200	2340	1200	1920
3	1480	2460	2400	1410	1960	2160	1500	2320	1720	2160
4	1320	2080	2380	2420	2320	2440	2320	1860	1180	2360
5	1500	2260	1480	1880	1100	2360	1240	1380	1840	2180
6	2040	1840	1880	1900	2400	—	1900	2360	1220	1440
7	1640	2000	2360	1440	2040	—	1960	1440	2140	2200
8	—	1460	—	2400	2360	—	2460	2440	1240	2440

segregated into groups and subject to further calibration. For example, soils will be divided by geographical location, by textural class, soil horizon (A or C), soil association and series designation, sample particle size uniformity (i.e. ground v. not ground), soil type classification and parent material designation (i.e. relating to mode of deposition).

Cationic forms of elements such as metals are not NIR spectrally-active. They may be predictable because of their associations with hydroxides, carbonates, sulphates, phosphates, organic matter or clays that are spectrally active. Work is continuing to determine whether there is sufficient knowledge of the chemical relationships of metals in soil so that metals can be expected to be predicted by NIR with reasonable certainty.

A number of the parameters studied here have been previously predicted in soil by NIR spectroscopy, some with similar success as obtained here.⁷ These include organic C,^{8,9} total N^{8,10–12} and exchangeable Ca and Mg.¹² Recently, Salgo *et al.*¹³ predicted a number of physical and chemical properties of 108 soil samples representing various soil types in Hungary by NIR spectroscopy. They obtained the best calibrations with Partial Least Squares regression. R² for organic matter content was 0.90; mechanical composition of soil, 0.88; hygroscopic water content, 0.88; and total N content, 0.66.

In conclusion, the results presented here show the feasibility of measuring a number of important parameters of Canadian Prairie soil by NIR spectroscopy. Even though the soil samples included various soil types and horizons, good to moderately good calibrations were developed using NIR spectroscopy for % C, N, % clay, CEC, Ca and Mg. Use of NIR spectroscopy in soil science promises to improve the rapidity and cost-effectiveness of sample analysis.

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