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Chang-Wen Chang
National Tsinghua University

David A. Laird
United States Department of Agriculture

Charles R. Hurburgh Jr.
Iowa State University, tatory@iastate.edu

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Abstract

Near-infrared reflectance spectroscopy (NIRS), a nondestructive analytical technique, may someday be used to rapidly and simultaneously quantify several soil properties in agricultural fields. The objectives of this study were to examine the influence of moisture content on the accuracy of NIRS analysis of soil properties and to assess the robustness of a NIRS multivariate calibration technique. Four hundred agricultural soil samples (<2 >mm) from Iowa and Minnesota were studied at two moisture levels: moist and air-dried. The soil properties tested included total C, organic C, inorganic C, total N, CEC, pH, texture, moisture, and potentially mineralizable N. About 70% of the Iowa samples were selected for the calibration set, and the rest of the Iowa samples and all of the Minnesota samples were assigned to validation set I and validation set II, respectively. Calibrations were based on partial least-squares regression (PLSR), using the first differentials of $\log(1/R)$ for the 1100 to 2500-nm spectral range. The results for the calibration set and validation set I indicated that NIRS-PLSR was able to predict many soil properties (total C, organic C, inorganic C, total N, CEC, % clay, and moisture) with reasonable accuracy for both the air-dried ($R^2 > 0.76$) and moist ($R^2 > 0.74$) soils. The results for validation set II showed that NIRS-PLSR was able to predict some properties of soils (total C, organic C, total N, and moisture content) from a different geographic region, but other soil properties in validation set II were not accurately predicted. Although NIRS-PLSR predictions are slightly more accurate for air-dried soils than for moist soils, the results indicate that the NIRS-PLSR technique can be used for analysis of field moist samples with acceptable accuracy as long as diverse soil samples from the same region are included in the calibration database.

Keywords

NIRS, near-infrared reflectance spectroscopy, soil testing, precision farming, soil sensing, calibration transfer, moisture, organic carbon, total nitrogen, CEC

Disciplines

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INFLUENCE OF SOIL MOISTURE ON NEAR-INFRARED REFLECTANCE SPECTROSCOPIC MEASUREMENT OF SOIL PROPERTIES

Cheng-Wen Chang¹, David A. Laird², and Charles R. Hurburgh, Jr.³

Near-infrared reflectance spectroscopy (NIRS), a nondestructive analytical technique, may someday be used to rapidly and simultaneously quantify several soil properties in agricultural fields. The objectives of this study were to examine the influence of moisture content on the accuracy of NIRS analysis of soil properties and to assess the robustness of a NIRS multivariate calibration technique. Four hundred agricultural soil samples (<2 mm) from Iowa and Minnesota were studied at two moisture levels: moist and air-dried. The soil properties tested included total C, organic C, inorganic C, total N, CEC, pH, texture, moisture, and potentially mineralizable N. About 70% of the Iowa samples were selected for the calibration set, and the rest of the Iowa samples and all of the Minnesota samples were assigned to validation set I and validation set II, respectively. Calibrations were based on partial least-squares regression (PLSR), using the first differentials of $\log(1/R)$ for the 1100 to 2500-nm spectral range. The results for the calibration set and validation set I indicated that NIRS-PLSR was able to predict many soil properties (total C, organic C, inorganic C, total N, CEC, % clay, and moisture) with reasonable accuracy for both the air-dried ($R^2 > 0.76$) and moist ($R^2 > 0.74$) soils. The results for validation set II showed that NIRS-PLSR was able to predict some properties of soils (total C, organic C, total N, and moisture content) from a different geographic region, but other soil properties in validation set II were not accurately predicted. Although NIRS-PLSR predictions are slightly more accurate for air-dried soils than for moist soils, the results indicate that the NIRS-PLSR technique can be used for analysis of field moist samples with acceptable accuracy as long as diverse soil samples from the same region are included in the calibration database. (Soil Science 2005;170:244-255)

Key words: NIRS, near-infrared reflectance spectroscopy, soil testing, precision farming, soil sensing, calibration transfer, moisture, organic carbon, total nitrogen, CEC.

SOIL testing is an important component of modern precision farming systems. However, standard procedures for soil testing are often too complex, time-consuming, and expensive for many precision farming applications. Specifically, grid soil sampling requires a substantial amount of labor to individually collect soil samples at known

locations in a field, label the samples, transport them to a laboratory, and analyze each sample typically using multiple analytical techniques. The development of technology capable of providing simultaneous, real-time, on-the-go, in-field analysis of multiple soil properties would be a major advance allowing economical integration of information on the spatial distribution of soil properties into the decision-making process for precision farming. Near-infrared reflectance spectroscopy (NIRS) is an analytical technique with the potential to achieve this dream.

NIRS is a fast, convenient, and nondestructive analytical technique for characterization and quantification of chemical and physical proper-

¹Department of Computer Science, National Tsing Hua University, Hsinchu, Taiwan, ROC. D. A. Laird is corresponding author. E-mail laird@nstl.gov

²USDA, ARS, National Soil Tilth Laboratory, Ames, IA.

³Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA.

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ties of materials. This technique is widely used in the agricultural and food industries as a quality assessment tool (Williams and Norris, 1987). NIRS is also used in the pharmaceutical, petrochemical, polymer, textile, and many other industries (Martin, 1992; McClure, 1994; Wetzel, 1983). The advantage of NIRS over midinfrared spectroscopy, which can also be used for rapid multicomponent analysis of materials, is that NIRS is generally less expensive and is both portable and rugged enough to be used in a factory or in an agricultural field.

NIRS is the study of interactions between incident light and a material's surface. Near-infrared (NIR) spectra are dominated by weak overtones and combinations of fundamental vibrational bands from the midinfrared region for H-C, H-N, and H-O bonds (Wetzel, 1983). Assignment of NIR absorption peaks to organic functional groups and minerals was summarized by Workman (1996) and Hunt (1989). Because of the nature of overtones and combinations, absorption peaks in the NIR range are often weak and overlapping. Furthermore, diffuse reflectance in the NIR region is influenced by a material's physical properties, such as the size and arrangement of particles. Because of these problems, it is usually impossible to relate a property of a material to a specific adsorption peak; rather, multivariate statistics are used to build calibration models.

NIRS has been used in laboratory studies to estimate various soil properties, including organic C, N, moisture, CEC, % clay, carbonate, specific surface area, and soil N availability (Ben-Dor and Banin, 1995; Chang and Laird 2002; Chang et al., 2001; Dalal and Henry, 1986; Krishnan et al., 1980; Morra et al., 1991; Reeves et al., 1999; Shepherd and Walsh, 2002; Sudduth and Hummel, 1993). Typically, these researchers have used multivariate models that were calibrated with air-dried soil samples collected from the same field or region as the samples being analyzed. However, before NIRS can be routinely used for soil analysis, it is important to know the robustness of multivariate calibration models; for example, whether a calibration model developed for analysis of soils in one region can be successfully used to predict properties of similar soils in a neighboring region.

Many soils have similar NIR spectra, with a major absorption peak near 1900 nm and two small but distinct peaks around 1400 and 2200 nm. The peak around 1400 nm is related to the first overtone of O-H stretching, and the peak around 1900 nm is related to the combination of O-H stretching, HOH deformation, and the sec-

ond overtone of O-H bending; these two peaks are strongly affected by soil moisture. The peak around 2200 nm, due to a combination of metal-OH and O-H stretching, is less affected by soil moisture (Clark et al., 1990, and references therein). Unfortunately, the strong H₂O absorption bands often mask peaks associated with organic functional groups. Therefore, soil water may adversely affect the ability of NIRS to predict soil properties under field conditions and limit field applications of NIRS technology.

The overall goal of the project was to test the potential application of NIRS for analysis of field moist soils. The specific objectives of this study were to evaluate the influence of soil moisture on the accuracy of NIRS predictions of soil properties and to assess the robustness of a NIRS multivariate calibration technique.

MATERIALS AND METHODS

Soil Samples

Two groups of agricultural soils were chosen to study the influence of soil moisture on the accuracy of NIRS predictions of soil properties. The first group of soils was from an agricultural field in Story County, IA. The 10 sampling sites that were selected included five soil series: one site each for the Canisteo and Nicollet series, two sites for the Harps and Webster series, and four sites for the Clarion series. Five soil cores were collected at each site. The average length for the soil cores was 78.4 cm; however, the length ranged from 38 to 108 cm. The soil from each core was divided into 15-cm increments, for a total of 277 samples. The second group of soils was from the nitrogen, tillage, and residue management plots (NTRM plots) on the University of Minnesota Agricultural Experimental Station near Rosemont, MN (Clapp et al., 2000; Clay et al., 1989). Treatments for the NTRM plots included three N application rates (0, 100, and 200 kg ha⁻¹), three tillage methods (chisel, moldboard, and no till), and three methods of residue management (incorporate, surface, and no residue). All of the soils in the NTRM plots are in the Waukegan series. Soil samples were collected at three depth intervals (0 to 5, 5 to 15 and 15 to 30 cm), and a total of 123 samples were obtained. The taxonomic classification of the studied soils is summarized in Table 1.

Measurement of Soil Properties

Air-dried soils were crushed to pass through a 2-mm sieve. Portions of the air-dried soils were

TABLE 1
Taxonomic classification of studied soils

Soil series	Classification
Iowa	
Nicollet	Fine-loamy, mixed, superactive, mesic Aquic Hapludoll
Harps	Fine-loamy, mixed, superactive, mesic Typic Calciaquoll
Webster	Fine-loamy, mixed, superactive, mesic Typic Endoaquoll
Clarion	Fine-loamy, mixed, superactive, mesic Typic Hapludoll
Canisteo	Fine-loamy, mixed, superactive, calcareous, mesic Typic Endoaquoll
Minnesota	
Waukegan	Fine-silty over sandy or sandy-skeletal, mixed mesic Typic Hapludoll

ground using an agate mortar and analyzed for total C and N by the dry combustion method using a Carlo Erba NA 1500 NSC¹ elemental analyzer (Maake Buchler Instruments, Paterson, NJ). About 40% of the Iowa soils contained significant levels of carbonate, and the amount of inorganic C in these samples was measured by the titrimetric method of Bundy and Bremner (1972). For soils containing carbonate, organic C was calculated by subtracting inorganic C from total C. For soils without carbonate, organic C was assumed to equal total C. Soil pH was measured using 1:2.5 soil-CaCl₂ suspensions. Cation exchange capacity for soils without carbonate was measured by the pH 7 NH₄OAc method (USDA-NRCS, 1996). For soils with carbonate, CEC was measured by quantitative saturation and subsequent displacement of Na from the exchange sites at pH 8.2 according to Polemio and Rhoades (1977). The particle size distribution was analyzed for all samples in the Iowa group and 18 representative soil samples for the Minnesota group (six for each depth interval). Particle size distribution was measured using the pipette method (Walter et al., 1978). Ammonium production during an anaerobic incubation at 40 °C for 7 days (Keeney, 1982) was used to represent the potentially mineralizable N. The potentially mineralizable N was measured for all Minnesota soils, whereas samples from only two or three soil cores for each site were tested for the Iowa soils. Soil moisture was determined gravi-

¹Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that might also be suitable.

metrically using subsamples collected and analyzed immediately after the NIR spectra were acquired. The subsamples (about 1 g) were weighed moist, oven-dried (105 °C for 12 h), cooled in a desiccator, and then weighed again.

NIRS Measurement

Two reflectance spectra were obtained for each sample, one for the moist soils and one for the air-dried soils. The soils used for NIRS measurements were prepared by crushing and passing the moist soils through a 2-mm sieve. Some soils at the field moist condition were too wet to be crushed, so these samples were put on a laboratory bench to dry for 1 or 2 days before sieving. After the reflectance spectra for the moist soils were measured, the soils were dried at room temperature for several days and then spectra for the air-dried soils were measured.

The spectral reflectance of soil samples in the visible and near-infrared regions was measured with a Perstorp NIRSystem 6500 scanning monochromator (Foss NIRSystems, Silver Spring, MD). To obtain a reflectance spectrum, about 20 g of soil was put into a small rectangular sample holder having a quartz window, and the spectral reflectance was recorded as the logarithm of the inverse of reflectance [$\log(1/R)$] with a 2-nm interval from 400 to 2498 nm.

NIRS Predictions

The soil samples were separated into three sets; the calibration set, validation set I, and validation set II. The calibration set consisted of 190 Iowa soil samples from seven sampling sites (one site each for Nicollet and Harps, two sites for Webster, and three sites for Clarion soils). Validation set I consisted of 87 Iowa soil samples from the three remaining sampling sites (one site each for Harps, Clarion, and Canisteo soils). Validation set II consisted of all 123 Minnesota soil samples. Properties of the soils in the calibration and validation sets are summarized in Table 2.

A multivariate statistical technique, known as partial least-squares regression (PLSR) (Haaland and Thomas, 1988; Martens and Naes, 1989), was used to relate the near-infrared reflectance spectra to the measured values of soil properties. PLSR is a variation of principal component regression in which factor analysis is performed for both the matrix containing the spectral data and the matrix containing the chemical data, and then each pair of factors of the same rank (one each from the spectral and chemical data matrices) is adjusted to maximize the fit of the linear regres-

TABLE 2
Statistics for soil properties of the samples in the calibration and validation sets^a

Soil group	Soil properties	Sample size	Mean	Standard deviation	Range	
Calibration set	Total C (g kg ⁻¹)	162	17.8	10.3	1.9–43.9	
	Inorganic C (g kg ⁻¹) ^b	86	9.23	9.3	0.0–25.6	
	Organic C (g kg ⁻¹)	161	15.1	10.0	0.5–40.8	
	Total N (g kg ⁻¹)	161	1.2	0.8	0.0–2.9	
	pH	184	6.6	1.0	4.5–7.8	
	CEC (cmol _c kg ⁻¹) ^c	179	22.4	8.1	6.3–39.5	
	Mineralizable N (mg kg ⁻¹)	76	44.9	41.8	0.2–199.2	
	Sand (%)	187	39.3	11.6	6.7–60.7	
	Silt (%)	187	35.8	6.6	20.9–52.0	
	Clay (%)	187	24.9	6.5	3.8–43.3	
	Water-moist soils (g kg ⁻¹)	190	124	43	28–220	
	Water-dry soils (g kg ⁻¹)	189	35	14	12–90	
	Validation set I	Total C (g kg ⁻¹)	85	20.8	9.4	4.8–38.4
		Inorganic C (g kg ⁻¹) ^b	42	8.3	9.6	0.0–24.7
Organic C (g kg ⁻¹)		83	15.8	10.4	0.7–38.0	
Total N (g kg ⁻¹)		85	1.2	0.8	0.1–3.0	
pH		84	7.0	0.6	5.2–8.5	
CEC (cmol _c kg ⁻¹) ^c		82	26.9	8.4	10.5–39.6	
Mineralizable N (mg kg ⁻¹)		34	50.2	47.3	5.8–211.5	
Sand (%)		87	29.5	10.3	9.3–50.7	
Silt (%)		87	41.8	7.4	28.9–71.6	
Clay (%)		87	28.7	8.1	13.5–43.8	
Water-moist soils (g kg ⁻¹)		87	146	35	57–233	
Water-dry soils (g kg ⁻¹)		87	35	12	13–58	
Validation set II		Total C (g kg ⁻¹)	123	24.4	4.3	16.2–44.7
		Organic C (g kg ⁻¹)	122	24.3	3.9	16.2–40.6
	Total N (g kg ⁻¹)	123	2.1	0.4	1.4–4.0	
	pH	123	5.8	0.5	3.7–6.7	
	CEC (cmol _c kg ⁻¹)	123	20.9	1.4	17.8–24.6	
	Mineralizable N (mg kg ⁻¹)	123	41.1	27.5	4.9–190.4	
	Sand (%) ^d	18	15.0	2.4	11.2–20.1	
	Silt (%) ^d	18	63.1	2.0	59.3–66.0	
	Clay (%) ^d	18	21.9	0.9	20.4–23.4	
	Water-moist soils (g kg ⁻¹)	122	205	37	87–254	
	Water-dry soils (g kg ⁻¹)	122	31	8	20–49	

^aStatistics are based on all samples from Calibration set, Validation set I, and Validation set II, for which the indicated soil property was measured.

^bOnly samples with inorganic C greater than 0.05 mg kg⁻¹ were included.

^cTwo methods were used to measure CEC, one for soils containing carbonate and one for soils without carbonate. Data represent the values from both methods.

^dEighteen samples for the Minnesota soils (six from each depth interval) were used to measure the particle size distribution.

sion between projections of the spectral and soil property data on their respective factors. Calibration models for predictions of soil properties are based on multiple linear regressions between projections of the spectra on the spectral factors and projections of soil property values on the soil property factors of the same rank. Because factor analysis concentrates most of the information in a data matrix into the first few factors (low rank), little information is lost when high-ranking factors are excluded from the calibration models. An

easily understood description of PLSR was given by Kramer (1998).

Several pretreatments were used on the spectral data before the PLSR analysis. First, to reduce the size of the spectral data matrix, every five adjacent spectral data points were averaged such that each new data point represented a 10-nm interval. Second, the 1100 and 2498-nm spectral region was used rather than the full 400 and 2498-nm spectral region because preliminary studies indicated that more accurate predictions of soil prop-

erties were achieved. And, third, first differentials for the spectral data were used again because preliminary work indicated that more accurate predictions of soil properties were achieved.

Cross-validation analysis was performed on the calibration set. To do so, separate PLSR analyses were conducted and calibration models developed for each sample in the calibration set using data for all samples in the calibration set except the one being analyzed. The number of PLSR factors (N_f) giving the smallest root-mean-square error of cross-validation (RMSECV is analogous to a standard deviation) between measured and predicted values was chosen for the PLSR calibration models. For example, Fig. 1 shows the relations between R^2 and N_f and between RMSECV and N_f for total C using the NIR spectra of the air-dried soils. As shown in Fig. 1, the best predictions for the cross-validation, largest R^2 and smallest RMSECV, occur when N_f is 10. The best predictions for validation sets I and II occur when N_f is 7 and 4, respectively. However, during an actual application

of the NIRS-PLSR technique measured data would be known for only the calibration set. Therefore, to simulate an actual application, the N_f values used in the calibration models to analyze the validation sets were based on analysis of cross-validation for the calibration set. Use of too many factors in PLSR may cause overfitting and reduce the ability of the calibration model to predict soil property values for samples from an independent validation set. To avoid overfitting, N_f was always $<1/10$ of the number of samples in the calibration set for a specific soil property. Samples in validation sets I and II with measured soil properties outside of the range of measured soil property values for the calibration set were excluded from the validation process.

Diagnostic statistics used to evaluate the accuracy of NIRS-PLSR predictions of soil properties included R^2 values for the relation between the measured and predicted soil property values, RMSECV, RMSEP (root-mean-square error of prediction), and RPD (the ratio of standard deviation for measured values to either RMSECV or RMSEP). Both RMSECV and RMSEP are calculated as the square root of the sum of squares of measured minus predicted soil property values divided by the number of samples minus one. They differ, however, in the source of the data used for the calculations. RMSECV is calculated by using measured and predicted values for the calibration set, in which the predicted values were obtained by the cross-validation procedure. RMSEP is calculated by using measured and predicted values for a completely independent validation set.

All calculations were performed by using code written and executed in MATLAB (The Mathworks, Inc. Natick, MA).

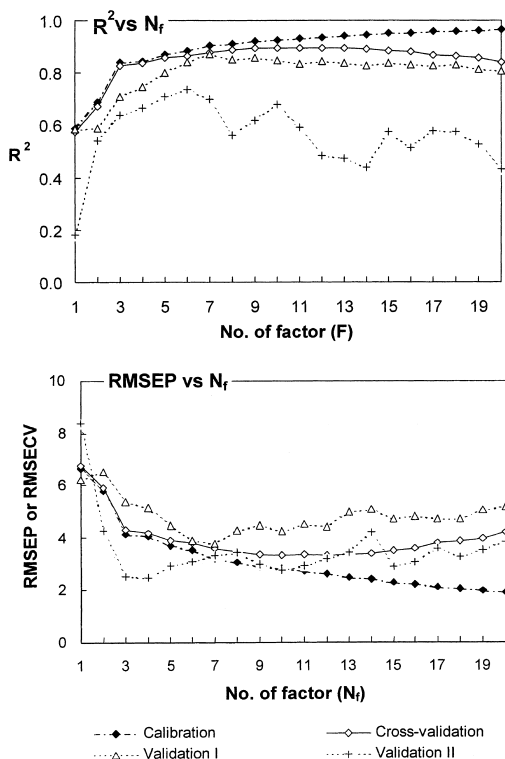


Fig. 1. Influence of the number of factors used in the NIRS-PLSR calibration model on the accuracy (R^2 , RMSEP, and RMSECV) of predictions of total C using the air-dry spectra.

RESULTS AND DISCUSSION

The impact of moisture on NIR spectra of soils is illustrated for an example soil (Nicollet, 0 to 15 cm) in Fig. 2. For the example, a relatively small increase in moisture (from 2.7% to 9.8%) caused a substantial increase in the baseline of the spectra and increases in both the intensity and breadth of the 1400 nm and 1900-nm peaks. Most prior studies of the ability of NIRS to predict soil properties have been conducted using air-dried soils. However, real-time, in-field use of NIRS will require analysis of field moist soils. Thus, an understanding of the impact of moisture on the ability of multivariate calibrations to predict soil properties is critical to the development of NIRS technology for in-field soil analysis.

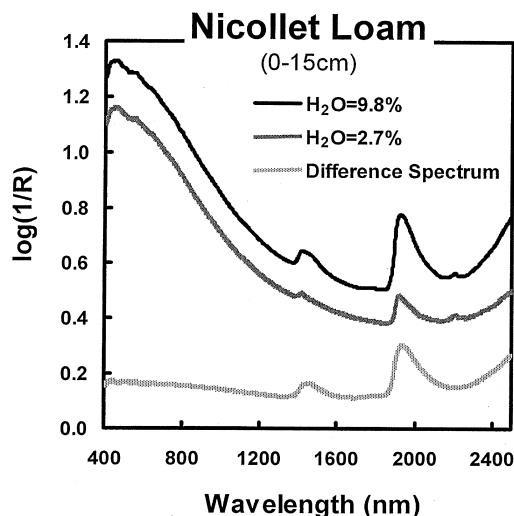


Fig. 2. NIR spectra of a Nicollet soil obtained air-dried and moist and the difference spectrum obtained by subtracting the air-dry spectrum from the moist spectrum.

Table 3 summarizes the ability of the NIRS-PLSR technique to predict total C, organic C, inorganic C, total N, soil moisture, CEC, pH, mineralizable N, and percentages of sand, silt, and clay for the air-dry and moist soils. Statistics reported in Table 3 for inorganic C in the calibration set and validation set I are based on samples containing more than 0.05 mg kg^{-1} inorganic C. Samples in validation set II did not contain inorganic C; therefore, the organic C content of these samples is equal to the total C content. The silt content for samples in validation set II was outside of the range of silt values in the calibration set and therefore was not determined.

The cross-validation analysis of the calibration set showed that the ability of NIRS-PLSR to predict soil moisture, total C, organic C, inorganic C, total N, CEC, and pH was good for both air-dried ($R^2 \geq 0.89$; $\text{RPD} \geq 2.89$) and moist soils ($R^2 \geq 0.88$; $\text{RPD} \geq 2.84$). Although the accuracy of the predictions was better for the air-dried soils (higher R^2 and RPD) than for the moist soils (lower R^2 and RPD), the differences were minimal. The cross-validation analyses for % sand and % clay were more accurate than those for % silt for both air-dried and moist soils. Like other properties, the NIRS-PLSR predictions of soil texture were better for the air-dried soils (% sand, $R^2 = 0.83$, $\text{RPD} = 2.44$; % silt, $R^2 = 0.68$, $\text{RPD} = 1.76$; % clay, $R^2 = 0.76$, $\text{RPD} = 2.02$) than for the moist soils (% sand, $R^2 = 0.78$, $\text{RPD} = 2.11$; % silt, $R^2 = 0.50$, $\text{RPD} = 1.40$; % clay, $R^2 = 0.74$, $\text{RPD} =$

1.94). The R^2 s between the measured and predicted values for mineralizable N were 0.63 and 0.57 for air-dried and moist soils, respectively. Predictions of mineralizable N were less accurate than predictions for other soil properties, and soil moisture had a larger influence on the accuracy of the predictions.

Results for validation set I (Table 3) were generally consistent with those obtained from cross-validation analysis of the calibration set. Predictions for validation set I for moisture, total C, organic C, inorganic C, total N, and CEC were good for both air-dried ($R^2 \geq 0.85$, $\text{RPD} \geq 1.71$) and moist soils ($R^2 \geq 0.74$, $\text{RPD} \geq 1.63$). Predictions for soil pH, which were good under the cross validation procedure, were much weaker for validation set I (air-dry soil, $R^2 = 0.67$, $\text{RPD} = 1.50$; moist soil, $R^2 = 0.66$, $\text{RPD} = 1.55$). Predictions for mineralizable N, % sand, % silt and % clay, which were moderate for the cross-validation procedure, ranged from moderate to poor for validation set I. These results indicate that NIRS-PLSR technique is able to accurately predict moisture, total C, organic C, inorganic C, total N, and CEC for both moist and air-dry samples but that texture, mineralizable N, and pH may be more difficult to predict with consistent accuracy.

Analyzing the soils in validation set II, which were from a different geographic region from the soils used to calibrate the model, challenged the robustness of the NIRS-PLSR technique. Results for validation set II (Table 3) indicate that total C, organic C, and total N were predicted with moderate accuracy for both the air-dry ($R^2 \geq 0.67$, $\text{RPD} \geq 1.22$) and moist soils ($R^2 \geq 0.31$, $\text{RPD} \geq 1.00$). Predictions of soil moisture were also moderately accurate for the moist soils ($R^2 = 0.36$, $\text{RPD} = 1.03$) but not the air-dry soils ($R^2 = 0.06$, $\text{RPD} = 0.61$). The NIRS-PLSR technique was not able to accurately predict other measured soil properties for validation set II. Because the distributions of soil property values for validation set II are different from those for the calibration set and validation set I, the R^2 and RPD values may not show the prediction ability of NIRS-PLSR as clearly as scatterplots (Fig. 3). Fig. 3 shows that NIRS-PLSR was able to predict total C, organic C, and total N for both air-dried and moist samples from validation set II with accuracy comparable to that achieved for validation set I. The accuracy of prediction of moisture content for the moist samples from validation set II was also comparable to that achieved for validation set I. However, the distributions of data points in the scatterplots for validation set II indicate that the NIRS-PLSR technique is less ro-

TABLE 3
Statistics for relation between measured and predicted (NIRS-PLSR) soil properties

Soil property	N _f ^a	Cross-validation			Validation set I			Validation set II		
		R ²	RMSECV	RPD ^b	R ²	RMSEP	RPD ^b	R ²	RMSEP	RPD ^b
Air-dried soils										
Moisture	13	0.89	0.005	2.89	0.88	0.005	2.36	0.06	0.013	0.61
Total C	10	0.90	3.34	3.10	0.85	4.24	2.21	0.68	2.77	1.42
Organic C	10	0.91	3.07	3.26	0.88	3.81	2.72	0.67	2.53	1.55
Inorganic C	8	0.97	1.53	6.06	0.98	1.92	4.99	—	—	—
Total N	11	0.94	0.20	3.99	0.91	0.27	3.00	0.68	0.25	1.22
pH	13	0.91	0.31	3.26	0.67	0.40	1.50	0.22	1.33	0.30
CEC	14	0.90	2.62	3.10	0.86	4.85	1.71	0.07	3.99	0.35
Mineralizable N	7	0.63	25.63	1.63	0.43	29.08	1.32	0.28	92.07	0.30
Sand	15	0.83	4.77	2.44	0.57	12.20	0.85	0.01	20.26	0.12
Silt	14	0.68	3.73	1.76	0.27	7.14	0.68	—	—	—
Clay	11	0.76	3.21	2.02	0.79	4.82	1.58	0.13	5.19	0.17
Moist soil										
Moisture	11	0.89	0.014	2.96	0.74	0.020	1.63	0.36	0.030	1.03
Total C	11	0.89	3.43	3.01	0.85	4.26	2.20	0.31	3.54	1.11
Organic C	9	0.90	3.14	3.19	0.91	3.28	3.16	0.48	3.04	1.29
Inorganic C	7	0.97	1.66	5.61	0.95	2.46	3.90	—	—	—
Total N	9	0.93	0.22	3.59	0.92	0.23	3.45	0.39	0.31	1.00
pH	14	0.88	0.35	2.92	0.66	0.39	1.55	0.31	1.13	0.35
CEC	10	0.88	2.86	2.84	0.89	3.57	2.33	0.30	3.41	0.41
Mineralizable N	6	0.57	27.36	1.53	0.31	32.08	1.20	0.01	99.50	0.28
Sand	18	0.78	5.53	2.11	0.49	12.44	0.83	0.00	22.57	0.11
Silt	11	0.50	4.69	1.40	0.13	6.04	0.80	—	—	—
Clay	13	0.74	3.35	1.94	0.76	5.25	1.45	0.25	7.45	0.12

^aN_f is the number of factors used in the NIRS-PLSR model to predict the value of the tested soil properties.
^bRPD equals the ratio of standard deviation to RMSECV (or RMSEP) (standard deviation for each validation set is based on the samples within the range of calibration set).

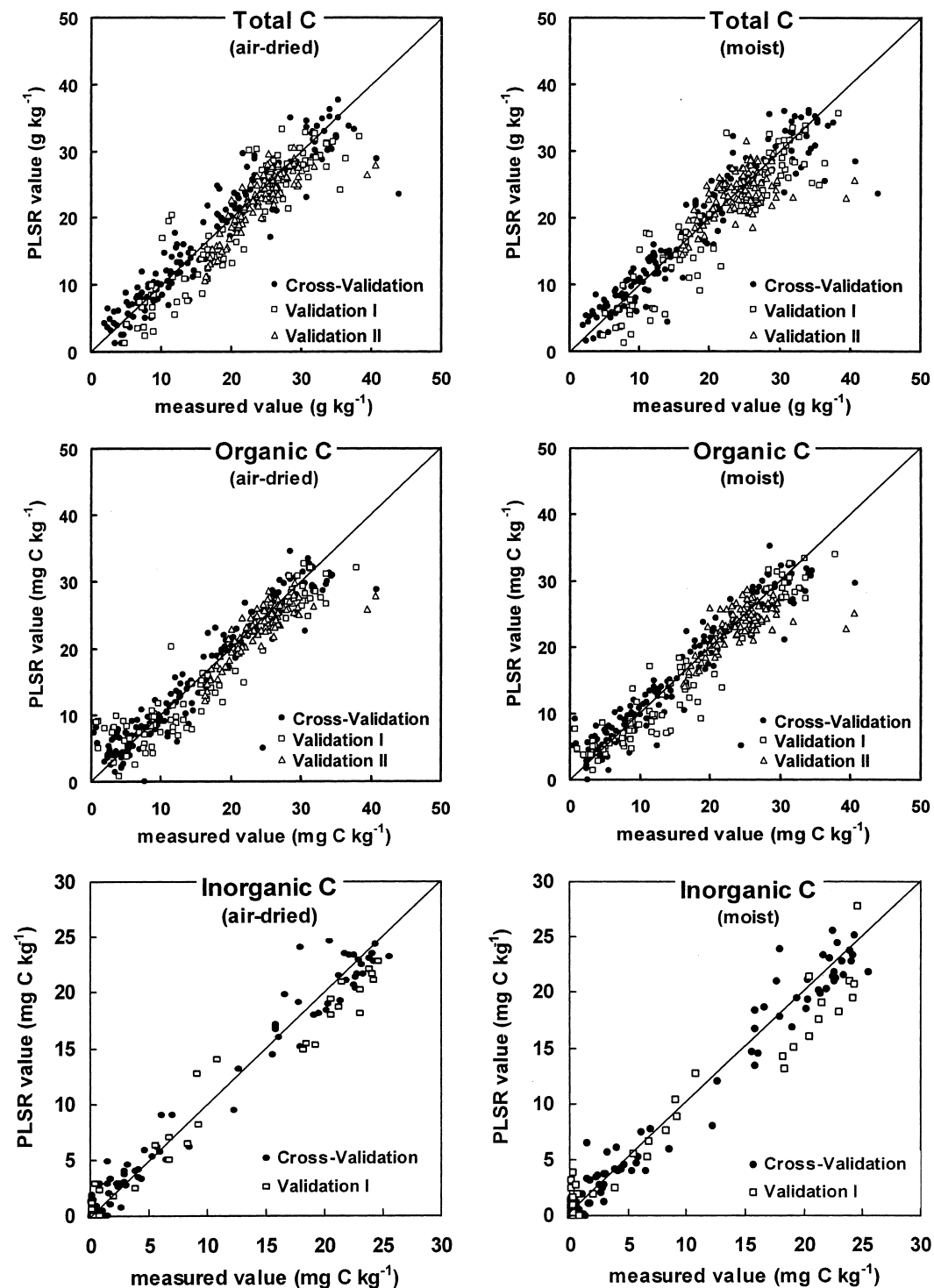


Fig. 3. Relation between values of soil properties measured by standard laboratory procedures and predicted by the NIRS-PLSR technique. The 1:1 line is shown for all plots.

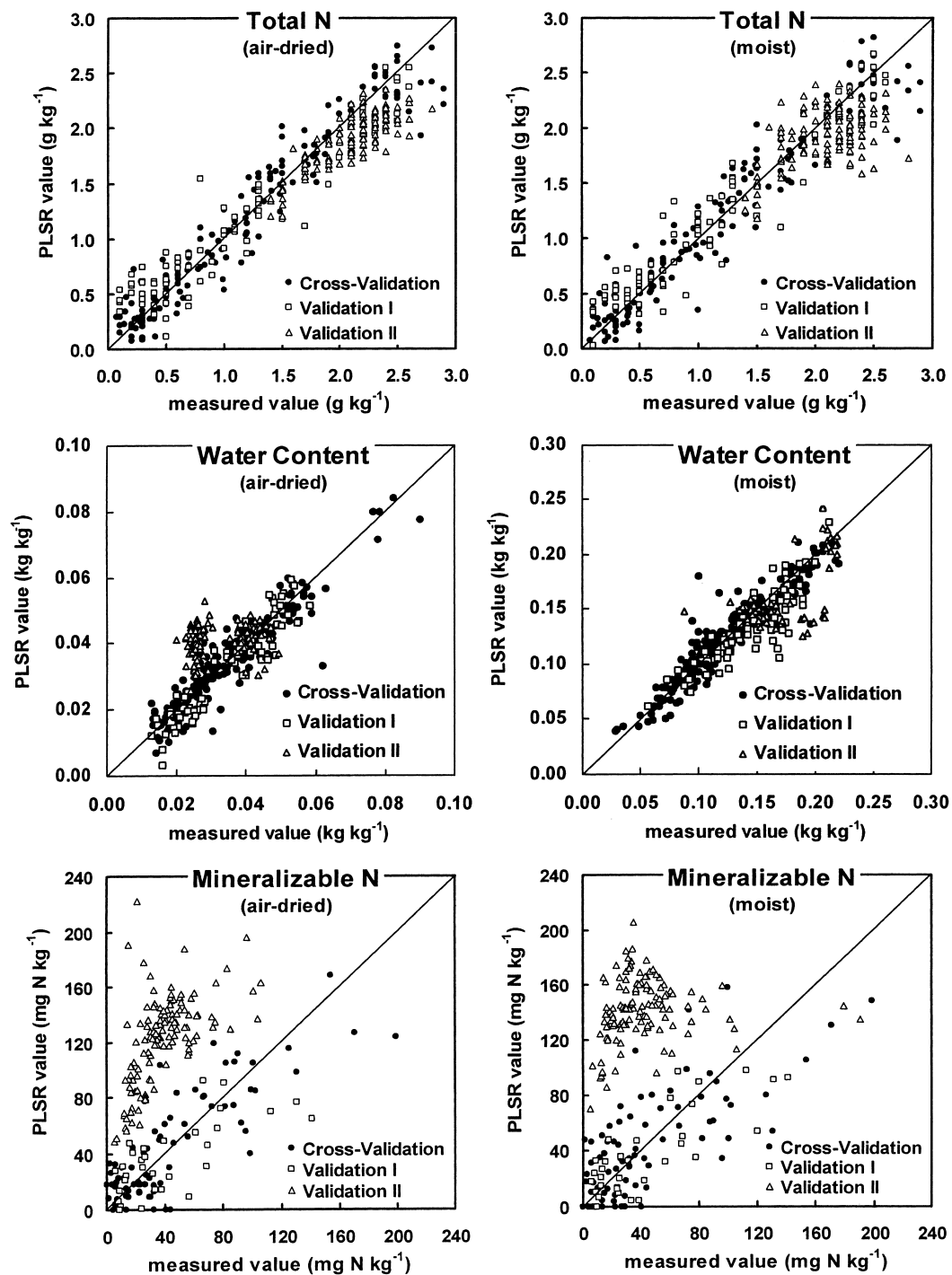


Fig. 3. (Continued)

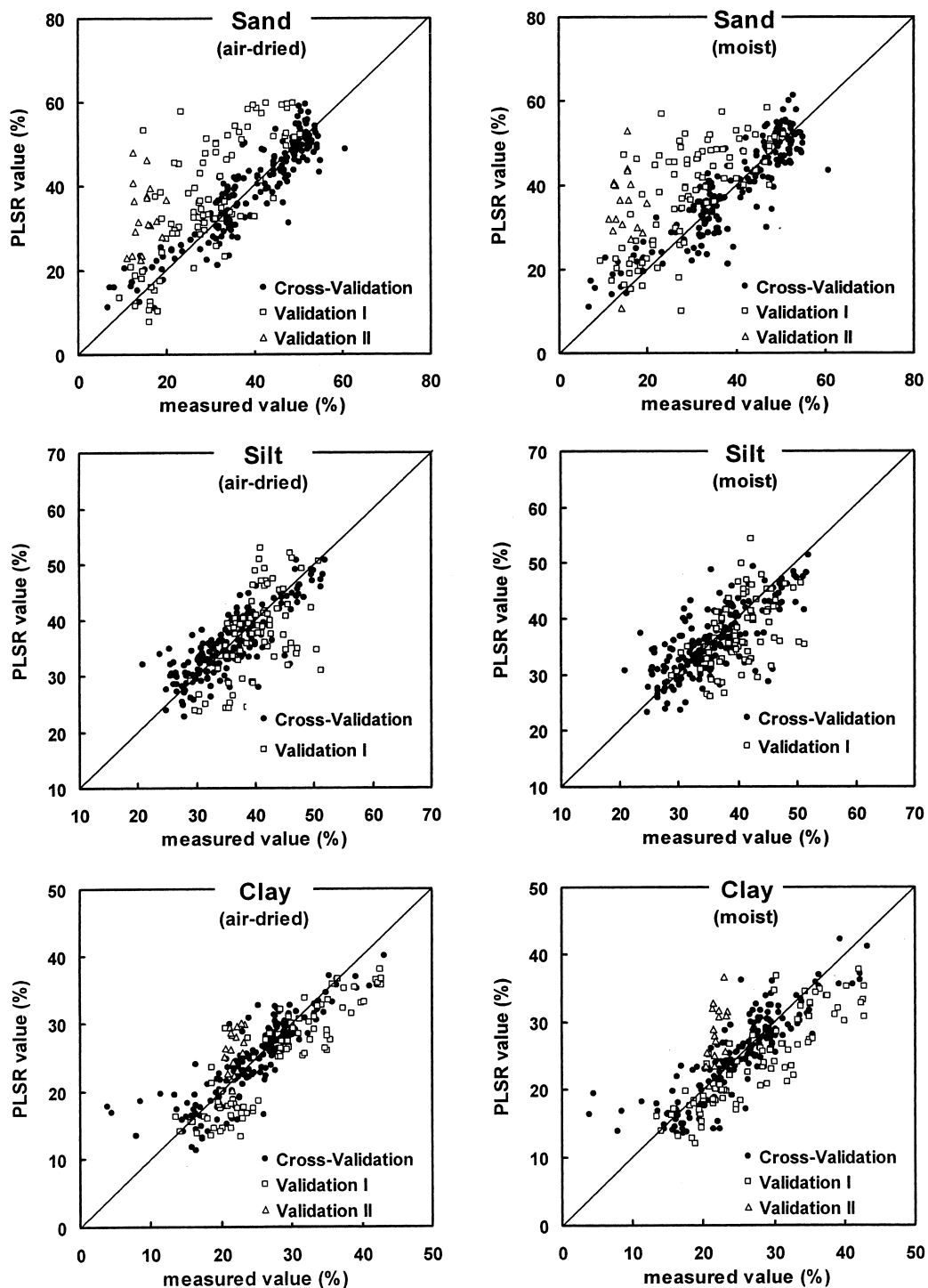


Fig. 3. (Continued)

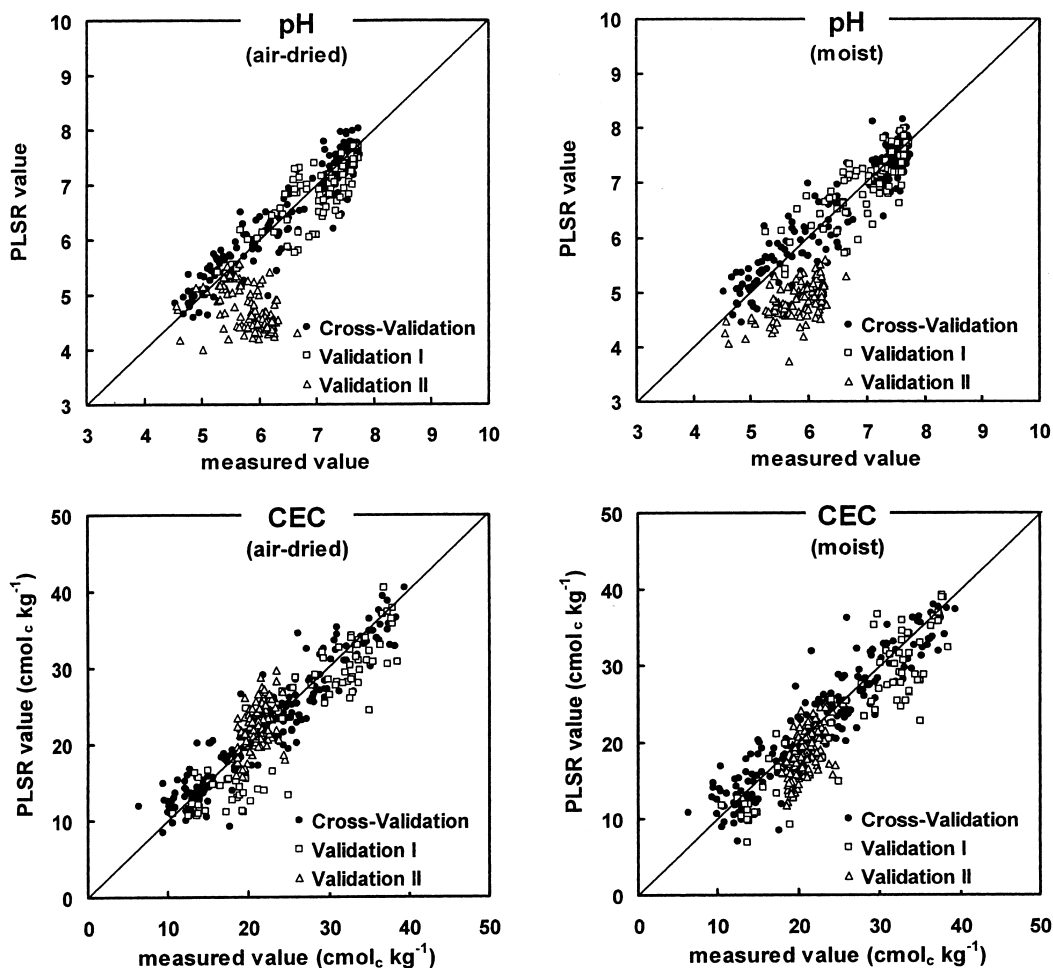


Fig. 3. (Continued)

but for the other soil properties. Water content (air-dry soils only), mineralizable N, and % sand are seriously over predicted and pH is under predicted for both air-dry and moist samples in validation set II. The errors for predictions of CEC (air-dry RMSEP = 3.99; moist RMSEP = 3.41) and % clay (air-dry RMSEP = 5.19; moist RMSEP = 7.45) associated with validation set II are relatively small (Table 3); however, the scatterplots (Fig. 3) reveal that the slopes for validation set II data points deviate substantially from the 1:1 line.

The analysis of soil properties for validation set I is a "best case scenario" in which the calibration set contains similar samples collected from different regions of the same field as those being analyzed. By contrast, validation set II is a "worst case scenario" because the samples in validation set II are from a different geographic re-

gion from the samples in the calibration set. That the NIRS-PLSR technique was able to provide reasonable estimates of total C, organic C, and total N for both the wet and air-dry samples and water content for the moist sample in validation set II demonstrates that the technique is robust for these analyses. The results for the other analytes, however, demonstrate the wisdom of using calibration sets populated with similar samples obtained from the same geographic region as the samples being analyzed.

CONCLUSIONS

The development of robust calibration models is likely to be a key issue challenging commercial development of in-field NIRS systems for soil analysis. In this study, we demonstrated that NIRS-PLSR was able to predict with reasonable

accuracy total C, organic C, inorganic C, total N, moisture, CEC, and % clay for both air-dry and moist soils. These results suggest that the necessity of analyzing field moist soils is not a major impediment to the deployment of commercial NIRS soil analysis technology. Furthermore, the NIRS-PLSR technique was able to predict total C, organic C, total N, and water content with reasonable accuracy from a different geographic region from that used to develop the calibration models, suggesting that the technique is robust for these analyses. On the other hand, the NIRS-PLSR technique was less accurate for predictions of % sand, % silt, pH, and mineralizable N; and the calibration models for pH, CEC, mineralizable N, % sand, and % clay were not robust when transferred from one geographic region to another. Thus, we conclude that the NIRS-PLSR technique can be used to rapidly and accurately estimate several important properties of field moist soils as long as diverse soil samples from the same region are included in the calibration database.

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