Reflectance Spectroscopy Detects Management and Landscape Differences in Soil Carbon and Nitrogen

V. P. Chaudhary
Indian Council of Agricultural Research
Modipuram
Meerut, UP 250 110, India

Kenneth A. Sudduth*
Newell R. Kitchen
Robert J. Kremer
USDA-ARS
Cropping Systems and Water
Quality Research Unit
269 Agricultural Engineering Bldg.
Univ. of Missouri
Columbia, MO 65211

Many studies have calibrated visible and near-infrared (VNIR) diffuse reflectance spectroscopy (DRS) to various soil properties; however, few studies have used VNIR DRS to detect treatment differences in controlled experiments. Therefore, our objective was to investigate the ability of VNIR DRS to detect treatment differences in topsoil organic C (SOC) and total N (TN) compared with standard dry combustion analysis. A long-term (since 1991) experiment in central Missouri, where cropping systems were replicated across a typical claypan soil landscape was studied. Soil samples from two depths (0–5 and 5–15 cm) were obtained in 2008 at summit, backslope, and footslope positions for three grain cropping systems. Estimates of SOC by VNIR DRS using oven-dried soil samples and an independent calibration set were very good, with R^2 = 0.87 and RMSE = 2.4 g kg^{-1}. Estimates of TN were somewhat less accurate (R^2 = 0.79, RMSE = 0.24 g kg^{-1}). Field-moist VNIR DRS results were also good, but with 13 to 17% higher RMSE. Trends in differences among treatment means were very similar for dry combustion, oven-dry soil VNIR, and field-moist VNIR. Dry combustion was best at separating treatment means, followed by dry soil VNIR and field-moist VNIR. Differences among methods were relatively minor for 0- to 5-cm depth samples but more pronounced for 5- to 15-cm samples. Efficiency of the VNIR method, particularly when applied to field-moist soil, suggests that it deserves consideration as a tool for determining near-surface SOC and TN differences in field experiments.

Abbreviations: CRP, conservation reserve program; DRS, diffuse reflectance spectroscopy; PLS, partial least squares; SOC, soil organic carbon; SQI, soil quality indicators; TN, total nitrogen; VNIR, visible–near-infrared.

The soil quality concept involves the capacity of a soil to function; included among the soil functions are water flow and retention, physical stability and support, retention and cycling of nutrients, and maintenance of biodiversity, habitat, and crop productivity (Doran and Parkin, 1994). Thus, soil quality not only includes sustaining crop productivity but also maintaining environmental quality, and it is likely that enhancement of soil quality would be a major barrier against the degradation of water and air quality (Kennedy and Papendick, 1995). Best management practices to improve soil quality encompass an array of strategies, including reduced or no tillage, crop rotation, cover crops, reduced chemical inputs, and more efficient use of chemical inputs, such as may be found with variable-rate application.

The evaluation of management impacts on soil quality is based on the measurement of soil quality indicators (SQI) (Karlen et al., 2003). Although SQI most directly portray the current state of management systems, assessments using selected SQI are perhaps most valuable to further improve future, sustainable land man-

Soil Sci. Soc. Am. J. 76:597–606
Posted online 27 Dec. 2011
doi:10.2136/sssaj2011.0112
Mention of trade names or commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the USDA or its cooperators.
Received 28 Mar. 2011.
*Corresponding author (Ken.Sudduth@ars.usda.gov).

agement practices. Measurements of SQI generally involve field collection of soil samples and laboratory analysis. The labor and expense involved make this approach more suited to research investigations than to monitoring production fields because many SQI can exhibit strong spatial dependence at the field scale (Cambardella et al., 1994; Jung et al., 2006), requiring dozens or hundreds of measurements per field for good representation. To transfer the soil quality approach to practice, methods that can efficiently map SQI across fields and landscapes are needed.

Soil organic matter (SOM) and SOC (the C within the SOM) are considered key SQI because of the integral role of SOM in soil biological, physical, and chemical processes (Carter, 2002). A technique that has been successfully used to estimate SOC and numerous other soil properties is DRS. Most commonly, soil sensing by DRS uses the visible (400–700 nm), near-infrared (NIR; 700–2500 nm), or combined VNIR (400–2500 nm) wavelength ranges (Sudduth et al., 1997; Viscarra Rossel et al., 2006). This method is based on the interaction of light with the surface at which it is directed. Characteristics of the reflected light are influenced by the chemical and physical properties of the target, such that these properties can be estimated through statistical analysis of the reflectance spectrum (Malley et al., 2004).

The DRS technique has been used to estimate SOC (or SOM), TN, and other soil properties in numerous studies, as reviewed by Malley et al. (2004), Viscarra Rossel et al. (2006), and Stenberg et al. (2010). Many of these studies have drawn soils from a wide geographic range and thus do not directly address the use of DRS to detect differences in soil properties within fields or landscapes. Studies that have investigated within-field DRS estimation of soil properties have had varying degrees of success. When variation in the parameter of interest was small, generally poor estimations of SOM (Sudduth et al., 2010) and SOC (Udelhoven et al., 2003) were obtained at the field scale. Brown et al. (2005) and Lee et al. (2010) reported inaccurate within-field SOC estimation when using an independent calibration data set. Wetterlind et al. (2010) found good estimation of SOM and TN in one field but poor results in another, suggesting that more than the 25 calibration samples they used might be necessary. McCarty and Reeves (2006) reported good estimation of both C and N within a 20-ha field. Thus, the question of whether VNIR DRS can accurately estimate SOC and TN within a particular site is unresolved.

The majority of soil DRS studies have been conducted with dried and sieved soil samples; however, the ability to collect valid data on field-moist samples would improve the efficiency of the data collection process by removing the drying and sieving step. Furthermore, the ability to obtain accurate estimations using moist soils is necessary for successful in situ DRS soil measurement (Christy, 2008). In previous research, calibrations using field-moist or rewetted soil have generally been less accurate than those with air- or oven-dried soil. Sudduth and Hummel (1993) obtained DRS estimates of SOC using rewetted soil samples in the laboratory. They found a 10 to 15% increase in SOC estimation errors when the data were obtained from soils at a range of water contents compared with oven-dried samples. Chang et al. (2005) applied NIR-DRS on sieved moist and air-dried soil samples. They found that total C, SOC, inorganic C, TN, moisture, CEC, and clay content could be estimated with reasonable accuracy for both the air-dried ($R^2 > 0.76$) and moist ($R^2 > 0.74$) soils. They stated that prediction using moist samples could be achieved as long as diverse soil samples from the same region were included in the calibration. Kusumo et al. (2008) developed a field method for measuring NIR DRS on a flat, sectioned horizontal surface of a field-moist soil core using a purpose-built contact probe attached by fiber optic cable to a spectrometer. Their best models estimated total C and N with R^2 values of 0.75 and 0.86, respectively. Morgan et al. (2009) estimated organic and inorganic C on soil cores with four different sample treatments: air-dried ground, air-dried intact, field-moist intact, and field-moist smeared samples. They reported similar results for the two air-dried treatments but a reduction in prediction accuracy with field-moist samples. Waiser et al. (2007) estimated soil clay content using the same samples and treatments used by Morgan et al. (2009). For total clay content, they found that air-dried intact samples provided the highest accuracy, followed by field-moist intact and air-dried ground samples, and finally field-moist smeared samples. They concluded that natural soil heterogeneity had little effect on the predictions but that smearing of the soil surface did reduce accuracy by creating specular reflectance and masking absorbance features. Bricklemyer and Brown (2010) compared in situ estimates of organic C and clay obtained with a commercial mobile spectrometer and those obtained using a laboratory spectrometer with dried and sieved samples. They found that the mobile spectrometer estimates were less accurate in all cases and suggested possible causes, including soil heterogeneity, variable field moisture content, and sample presentation issues.

Sensing of SOC and other SQI would be particularly advantageous for the claypan soils in north-central and northeastern Missouri and southern Illinois because many claypan soil properties can be extremely variable across the landscape and within the soil profile (Jung et al., 2006, 2008; Jiang et al., 2007a). These soils, classified as Epiaqualfs by Soil Survey Staff (1999) and Stagnic Luvisols by the IUSS Working Group WRB (2006), have a restrictive high-clay subsoil layer (the *claypan*) occurring at varying depth below the soil surface. Summit soils in claypan landscapes have a depth to the claypan horizon of around 30 to 40 cm, decreasing to as little as 5 to 15 cm on eroded backslopes and increasing to as deep as 100 cm or more on depositional footslope areas. Surface soil textures are silty clay loam to silty clay (Young and Geller, 1995). Variations in claypan profile properties across the landscape greatly influence the profile water holding capacity (Jiang et al., 2007b), hydraulic conductivity (Thompson et al., 1991; Yang et al., 2003; Jiang et al., 2007a), and plant root development (Wang et al., 2003; Myers et al., 2007).

In previous research on claypan soils, SOC and TN were responsive to differential management. An agroforestry system showed increases of up to 38 and 46% for SOC and TN, respectively, in permanent tree and grass buffer areas compared with adjacent annual cropping systems 8 yr after establishment (Bailey et al., 2009). Jung et al. (2008) reported little difference in soil quality properties, including SOC and TN, between tilled and no-till annual cropping systems 12 yr after initiation. They did find, however, that SOC increased significantly with 12 yr of Conservation Reserve Program (CRP) management. At the 0- to 7.5-cm depth, CRP system SOC increased during the period by 33% and TN increased by 34%. Jung et al. (2008) also reported an effect of landscape position, suggesting that a high sampling density may be needed to accurately characterize SOC and TN on claypan soil landscapes. Ideally, this intensive data acquisition would be accomplished using sensor-based measurements such as VNIR DRS.

Thus, the goal of this study was to determine the ability of VNIR DRS to distinguish differences in claypan soil quality among cropping systems and landscape positions on the basis of topsoil SOC and TN. Our specific objectives were to: (i) evaluate the performance of VNIR DRS analysis using both oven-dried and field-moist sieved soil samples; and (ii) compare the performance of VNIR DRS in detecting treatment differences with that of SOC and TN data from standard dry combustion laboratory analysis.

MATERIALS AND METHODS

Study Site

The study was conducted on a 12-ha site 2 km from Centralia, MO (39°13′ N, 92°7′ W) in Major Land Resource Area 113, the Central Claypan Region (NRCS, 2006). The site encompasses three landscape positions: summit, backslope, and footslope (Fig. 1). Soils were delineated on the basis of an Order 1 soil survey conducted in 1991. The summit landscape position was mapped as Adco (a fine, smectitic, mesic Vertic Albaqualf) silt loam with 0 to 1% slopes; the backslope position was mapped as Mexico (a fine, smectitic, mesic Vertic Epiaqualf) silty clay loam with 1 to 3% slopes; and the footslope landscape position was mapped as Mexico silt loam with 1 to 2% slopes and somewhat poorly drained (Fig. 1). The landscape was linear to slightly convex at the summit position and linear to slightly concave in the backslope and footslope landscape positions. The difference in elevation between the summit and footslope positions was about 2 to 3 m. The subsoil argillic horizon, typical of claypan soils, was characterized by the abrupt occurrence of silty clay loam, silty clay, or clay at varying depths.

Cropping systems were established in 1991 to investigate the effects of tillage, rotation, and other management practices on crop production and soil and water quality. The experimental design was a randomized complete block with three blocks (i.e., replications), where all rotation phases of each cropping system were present each year. Each of the 30 plots measured 18 by 189 m (0.35 ha) running east–west parallel to the slope direction (Fig. 1) and thus each landscape position was included within each plot. Three grain cropping systems were selected for study: mulch tillage corn (*Zea mays* L.)–soybean [*Glycine max* (L.) Merr.], no-till corn–soybean, and no-till corn–soybean–wheat (*Triticum aestivum* L.). Three grass systems were also studied: a CRP cool-season grass mixture (CRP-C), a warm-season CRP mixture (CRP-W), and mixed grass harvested as a hay crop (HAY). Unlike the other cropping systems, which were established in 1991, CRP-W and HAY were established in

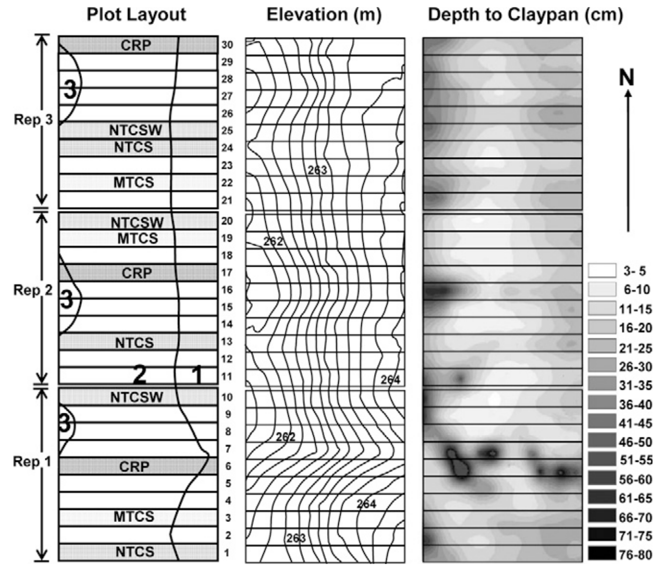

Fig. 1. Plot layout with soil series, elevation, and depth to the claypan horizon for the research site near Centralia, MO. Mapped soils include Adco silt loam, 0–1% slope (1), Mexico silty clay loam, 1–3%, eroded (2), and Mexico silt loam, 1–2% slope (3). Plots used for this study are labeled with the cropping system treatment: MTCS, mulch tillage corn–soybean rotation; NTCS, no-till corn–soybean rotation; NTCSW, no-till corn–soybean–wheat rotation; CRP, Conservation Reserve Program. The CRP plots were further split in thirds lengthwise for the three grass cropping systems of this study.

2001; previously, those areas had been in CRP-C. Background soil profile data were obtained from the experimental area in 1991 (Jung et al., 2010). Descriptions of the six management systems are given in Table 1, and additional information about the experimental area can be found in Ghidey et al. (2005).

Soil Sampling and Analysis

Soil samples were collected in November 2008 from each of the six cropping systems at the center of each of the three landscape positions (summit, backslope, and footslope) for a total of 18 treatments. All three replications were included. The grain cropping system plots sampled were in the soybean year of the rotation in 2008. Samples were obtained for two different depth increments, 0 to 5 and 5 to 15 cm. For each site and depth, a total of 20, 3-cm-diameter cores were collected to provide a reasonable field estimate. Cores were distributed evenly across row positions to equally sample between- and within-row effects. Samples were sealed in plastic bags and stored at 4°C before processing.

Field-moist soil samples were pushed through an 8-mm screen for moist-soil spectral data acquisition. After spectral scanning at room temperature, samples were dried at 105°C for 24 h, crushed and passed through a 2 mm screen, and then used for dry-soil spectral data acquisition. A subsample of the oven-dry soil was ground to a fine powder using a mortar and pestle. These ground samples were used to determine SOC and TN by dry combustion methods with a LECO Tru-Spec C/N Analyzer (LECO Corp., St. Joseph, MI) based on Nelson and Sommers (1996).

To provide an independent calibration data set for the VNIR DRS technique, additional soil samples were obtained

Table 1. Description of the six management systems used in the study. All systems were established in 1991 unless otherwise noted.

Cropping System	Description	Fertilizer input	Yield goal
MTCS	mulch tillage† with a corn–soybean rotation	190 kg N ha^{-1} for corn; lime, P, and K by soil test	10.1 Mg ha^{-1} for corn; 2.5 Mg ha^{-1} for soybean
NTCS	no-till with a corn–soybean rotation	151 kg N ha^{-1} for corn; lime, P, and K by soil test	7.5 Mg ha^{-1} for corn; 2.5 Mg ha^{-1} for soybean
NTCSW	mulch tillage (1991–1995) then no-till (1996–2004) with a corn–soybean–wheat rotation, with either hairy vetch (*Vicia villosa* Roth) (1994–1995) or red clover (*Trifolium pretense* L.) (1996–2008) cover crop following wheat; cover crop harvested as hay crop (2004–2008)	150 kg N ha^{-1} for corn, 101 kg N ha^{-1} for wheat; lime, P, and K: by soil test	8.7 Mg ha^{-1} for corn; 2.5 Mg ha^{-1} for soybean; 4.0 Mg ha^{-1} for wheat
CRP-C	cool-season grasses and legumes suitable for the Conservation Reserve Program: Orchard grass (*Dactylis glomerata* L.), smooth bromegrass (*Bromus inermis* Leyss.), timothy (*Phleum pratense* L.), tall fescue (*Festuca arundinacea* Schreb.), alfalfa (*Medicago sativa* L.) (1991); hairy vetch, red clover, lespedeza sp., birdsfoot trefoil (*Lotus corniculatus* L.) (1992).	lime, P, and K by soil test	none
CRP-W	established in 2001; warm-season grasses and legumes suitable for the Conservation Reserve Program: big bluestem (*Andropogon gerardi* Vitman), Indian grass [*Sorghastrum nutans* (L.) Nash], tall dropseed [*Sporobolus compositus* (Poir.) Merr.], little bluestem (*Andropogon scoparius* Michx.), lespedeza, ladino clover (*Trifolium repens* L.)	lime, P, and K by soil test	none
HAY	established in 2001; hay crop, including cool-season grasses Canada wild rye (*Elymus canadensis* L.) and Virginia wild rye (*Elymus virginicus* L.) and warm-season grasses big bluestem, eastern gama grass [*Tripsacum dactyloides* (L.) L.], Indian grass, ladino clover	90 kg N ha^{-1}; lime, P, and K by soil test	8960 kg ha^{-1} for hay; harvest 2–3 times yr^{-1}

† Tillage system that targets maximum retention of crop residues (30% or more) on the soil surface.

from other claypan-soil sites located within a few kilometers of the study site and under various management systems. These included no-till and tilled cropped fields, grass pastures, and a prairie site ($n = 107$). Soil sampling and analysis procedures were as described above.

Spectral Data Acquisition

Soil spectral reflectance data were obtained in the laboratory using an ASD FieldSpec Pro FR spectrometer (Analytical Spectral Devices, Boulder, CO). Spectra recorded between 400 and 2500 nm were output at a 5-nm interval. Each soil spectrum was obtained as the mean of 30 scans. The spectrometer data collection software automatically adjusted the data for dark current variations using dark current scans obtained at the beginning of each data collection session and at least every 30 min thereafter. A Spectralon (Labsphere Inc., North Sutton, NH) reflectance standard was scanned after every 10 soils and used to convert the raw spectral data to decimal reflectance.

Sample preparation varied between the oven-dry and field-moist samples. For the oven-dry reflectance measurements, approximately 15 cm^3 of soil was poured into a glass-bottomed sample cup and leveled with a metal spatula. The sample was placed on the ASD "mug lamp" sample stage, where it was illuminated from the bottom by a halogen lamp, and the reflected light from an approximately 12-mm-diameter area was transmitted to the spectrometer through a fiber optic bundle. In preliminary tests, this approach was not satisfactory for many of the field-moist samples, particularly those from high-clay backslope positions. These samples formed large plastic "clumps" that left many open voids against the glass cup bottom and thus did not provide a consistent surface for scanning through the glass. Field-moist samples were scanned from the top by inverting the mug lamp over the top of the sample cup. Less clayey samples were leveled with a metal spatula similarly to the oven-dry samples. For the higher clay samples, it was often necessary to smooth the samples with the spatula to obtain a flat surface for reflectance scanning. Thus, while some of the field-moist samples had a textured surface, others were smeared, similar to the samples used by Morgan et al. (2009).

Spectral Analysis

Partial least squares (PLS) regression, implemented in ParLeS version 3.1 (Viscarra Rossel, 2008), was applied to the separate 107-sample data set described above to develop calibration models relating SOC and TN to reflectance spectra collected at a 5-nm sampling interval. The PLS method is widely used in chemometrics, remote sensing, and spectral data processing to deal with large data sets containing highly correlated variables. It is a full-spectrum method in that it uses information from all the wavelengths in the original spectrum to develop a calibration using linear regression on a new set of variables (factors). The factors are statistically independent from one another and are constructed such that they capture the variation in both the response (soil) and predictor (spectral) variables (Beebe and Kowalski, 1987). As in all multivariate regression, it is important to select the number of factors that best represents the calibration data without overfitting. To do this, we applied a leave-one-out cross-validation procedure within the ParLeS software. The appropriate number of factors used was that which minimized the Akaike information criterion. The final calibration model was obtained from the full data set using this number of factors.

Many different preprocessing transformation methods that may be appropriate for PLS spectral analysis were available in the ParLeS software (Viscarra Rossel, 2008). Based on the results of our past research (La et al., 2008), we selected a number of transformations and combinations for preliminary analysis. Following the best results in this preliminary analysis, each spectral scan was (i) transformed from reflectance to absorbance

[$\log_{10}$(1/reflectance)], and (ii) mean normalized (i.e., divided by its mean value) for analysis.

The best cross-validated calibration models were applied to the spectral data sets from the cropping systems plots to estimate SOC and TN across cropping system and landscape position. Model evaluation was based on the R^2, RMSE, and the ratio of the standard deviation to the RMSE (RPD). The RPD is useful when comparing the results from data sets containing different degrees of variability, with a higher RPD indicating a more accurate prediction. Of the potential 108 samples (6 cropping systems × 3 landscape positions × 2 depths × 3 replications), five were deleted due to missing laboratory or spectral data, leaving a total of 103 for statistical analysis.

Statistical Analysis

The data were analyzed in a split-plot treatment arrangement, with cropping system as the main plot and landscape position as the split plot. Because landscape position was not randomized, a repeated measures analysis (Littell et al., 2002) was used to assess the response variables of SOC and TN using PROC MIXED in SAS (SAS Institute, 2005). Mean separations using LSD were determined for treatment main effects when F tests were significant at P values ≤ 0.05. Independent analyses were conducted for each data source (field-moist soil DRS, oven-dry soil DRS, and dry combustion laboratory analysis) and for each depth interval (0–5 and 5–15 cm).

RESULTS AND DISCUSSION

Estimating Soil Organic Carbon and Total Nitrogen by Visible–Near-Infrared Diffuse Reflectance Spectroscopy

Summary statistics for laboratory dry combustion SOC and TN analysis of the plot data set and independent calibration data set are given in Table 2. The two data sets were relatively similar in composition, although the means and standard deviations were somewhat higher in the plot data set. This was probably because approximately 50% of the plot data were from the grass systems, with generally higher SOC and TN, while only about 25% of the calibration data were from grass systems.

The performance of the cross-validated calibration models for reflectance estimation of SOC and TN using PLS regression was good for the oven-dry soil. The model performance with field-moist samples, however, was worse in terms of both R^2 and RPD (Table 3). Reflectance characteristics in VNIR wavelengths are primarily determined by chemical and physical characteristics of the sample surface. The physical structure of the oven-dry samples was much more consistent than that of the wet samples, where samples with higher clay content were somewhat smeared due to the manual manipulation necessary to obtain a flat surface. Morgan et al. (2009) stated that one possible reason for reduced accuracy with field-moist, intact, smeared samples was that cores with a high clay content smeared more than others, leading to greater variability. It seems likely that a similar effect occurred here with the field-moist sieved samples. Additionally, Lobell and Asner (2002) reported that the water content in wet samples may decrease accuracy because increasing water content can reduce the strength of an important absorption feature of C and N. Malley et al. (2002) also reported less accurate prediction of soil properties including organic matter and NH_4–N with field-moist soils than dry soils.

Application of the calibration models to the plot data set resulted in SOC and TN estimates that were of similar to slightly better accuracy than in the calibration set, with oven-dry sample results again of higher accuracy than field-moist sample results (Table 3). The most accurate estimation (R^2 = 0.87, RPD = 2.48, Fig. 2) was for SOC using oven-dry soil samples, but TN estimation was also good. Similar SOC and TN estimation accuracies were reported by Lee et al. (2009) and Chang et al. (2001). Field-moist soil estimates had 13 to 17% higher RMSE values than oven-dry soil estimates (Table 3). Estimation residuals (data not shown) were examined for trends related to cropping system or landscape position. In no case was there a significant effect of landscape position, suggesting that the calibration model was appropriate. There

Table 2. Descriptive statistics of measured soil organic C (SOC) and total N (TN) for the research plot data set and the spectral calibration data set.

Parameter	Mean	SD	Max.	Min.
	g kg^{-1}			
	Research plots (n = 103)			
SOC	16.8	6.02	31.0	9.3
TN	1.59	0.48	2.86	0.76
	Spectral calibration (n = 107)			
SOC	15.1	4.47	32.5	8.7
TN	1.45	0.40	3.02	0.79

Table 3. Partial least squares (PLS) calibration cross-validation and plot data estimation statistics for soil organic C (SOC) and total N (TN) of oven-dry and field-moist soil samples.

		Calibration cross-validation				Plot data estimation			
Parameter	NF†	R^2	RMSE	RPD‡	Bias	R^2	RMSE	RPD	Bias
			g kg^{-1}		g kg^{-1}		g kg^{-1}		g kg^{-1}
				Oven-dry sample analysis					
SOC	8	0.80	1.98	2.26	–0.01	0.87	2.43	2.48	–0.55
TN	8	0.71	0.22	1.85	0.00	0.79	0.24	2.01	–0.09
				Field-moist sample analysis					
SOC	9	0.58	2.90	1.54	0.02	0.81	2.75	2.19	–0.11
TN	7	0.49	0.29	1.40	0.00	0.68	0.28	1.71	–0.04

† Number of PLS factors used in model.

‡ Ratio of standard deviation to RMSE.

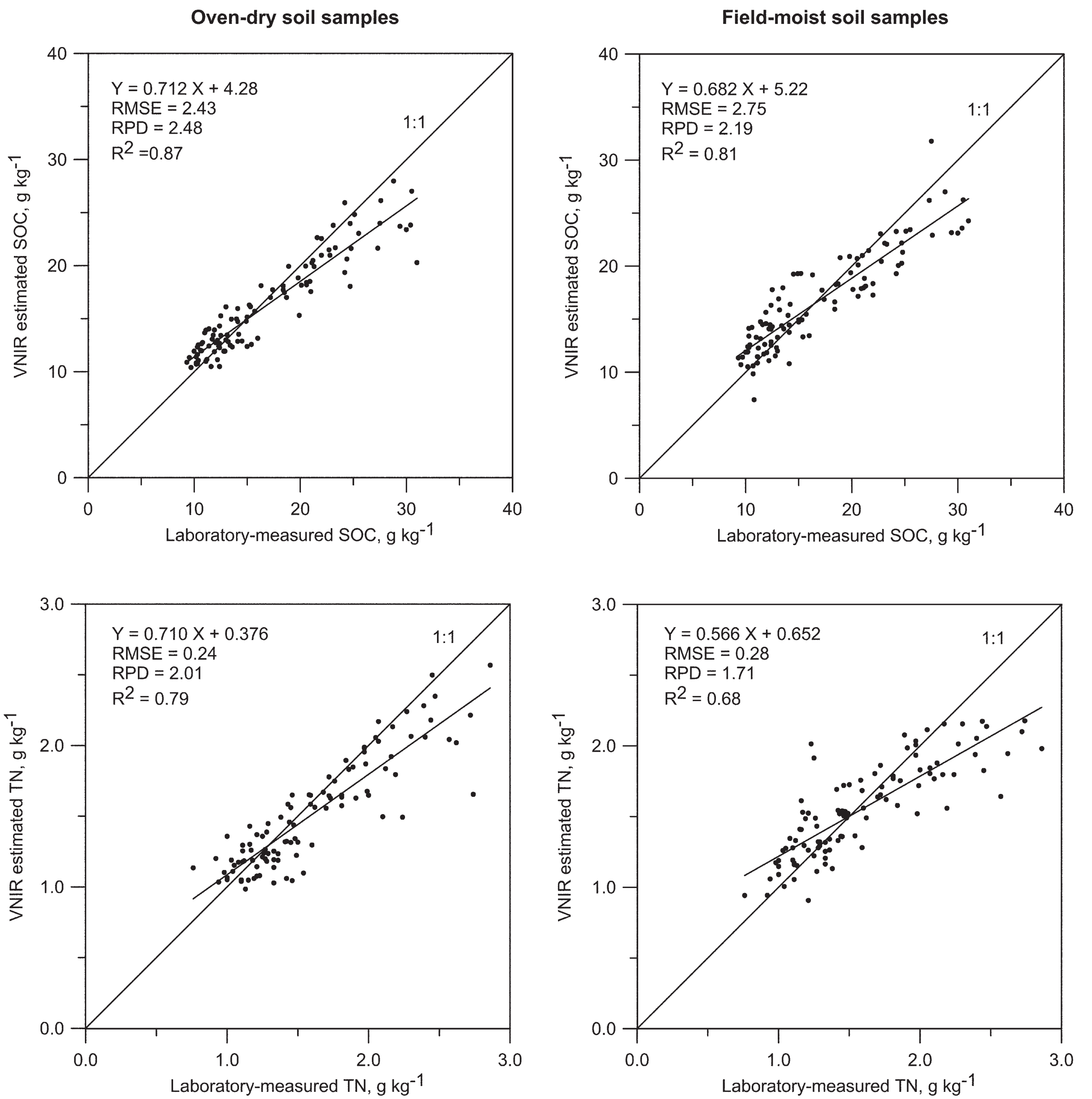

Fig. 2. Visible–near-infrared (VNIR) spectroscopy-estimated vs. laboratory-measured values of soil organic C (SOC) and total N (TN) for oven-dry and field-moist plot soil samples collected in 2008.

was a significant effect of cropping system, however, for both SOC and TN and for both oven-dry and field-moist calibrations. Thus, separate models by cropping system might be expected to provide more accurate information; however, we did not have a sufficient number of soil samples to implement and evaluate this approach.

According to classifications proposed by Chang et al. (2001) and Lee et al. (2009), oven-dry soil estimates of SOC and TN were in the good category, while field-moist estimates could be described as fair. It should be noted, however, that any such classification of VNIR DRS accuracy levels is somewhat arbitrary. The real test is whether the estimate is accurate enough for the task at hand—in this case, to provide a similar level of discrimination among cropping system and landscape position effects as was obtained with standard laboratory data.

Discriminating Treatment Differences in Soil Organic Carbon and Total Nitrogen

Analysis of variance results for estimates of SOC and TN at the two depth intervals and by all three analysis methods are given in Table 4. In all cases, both cropping system and landscape position were significant ($\alpha = 0.05$) sources of variation with laboratory dry combustion analysis. Estimates using VNIR with oven-dry sieved samples showed significant differences in seven of the eight combinations (soil property by depth by main effect), while with field-moist samples there were significant differences in only four combi-

Table 4. Analysis of variance of soil organic C (SOC) and total N (TN) data determined by dry combustion laboratory analysis, oven-dry-sample visible–near-infrared (VNIR), and field-moist VNIR measurements for two depth intervals.

Analysis method	Source of variation	df	ANOVA $P > F$ SOC 0–5 cm	SOC 5–15 cm	TN 0–5 cm	TN 5–15 cm
Laboratory analysis by dry combustion	block	2	–	–	–	–
	cropping system (CS)	5	<0.01	<0.01	<0.01	<0.01
	landscape position (LP)	2	<0.01	<0.01	0.02	<0.01
	CS × LP	10	0.12	0.91	0.19	0.78
VNIR estimation with oven-dry samples	block	2	–	–	–	–
	CS	5	<0.01	0.11	<0.01	0.04
	LP	2	<0.01	0.01	<0.01	<0.01
	CS × LP	10	0.37	0.89	0.33	0.67
VNIR estimation with field-moist samples	block	2	–	–	–	–
	CS	5	<0.01	0.08	<0.01	0.56
	LP	2	0.14	0.01	0.42	0.04
	CS × LP	10	0.21	0.17	0.95	0.18

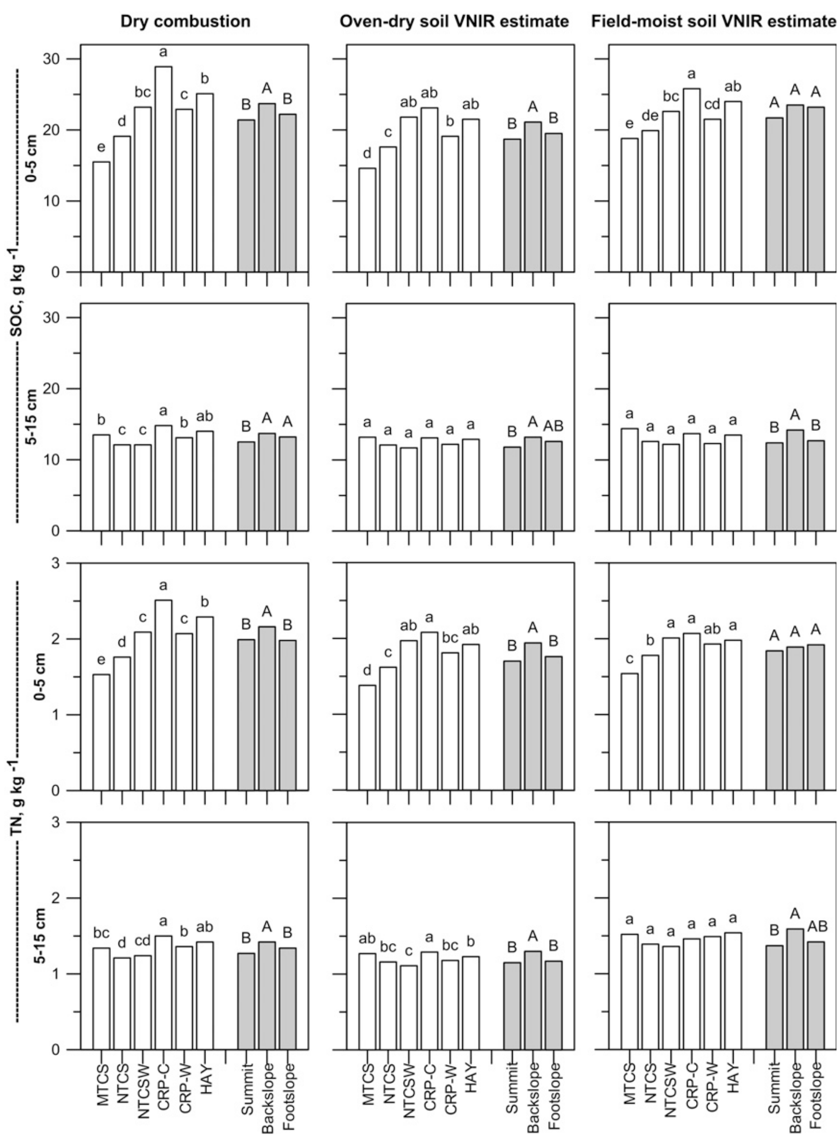

Fig. 3. Main effect means of soil organic C (SOC) and total N (TN) by dry combustion laboratory analysis, oven-dry soil visible–near-infrared (VNIR) spectroscopy estimation, and field-moist soil VNIR estimation at two depth intervals. Within a panel, treatments with the same lowercase or uppercase letters are not significantly different (α = 0.05). Management systems: MTCS, mulch tillage corn–soybean rotation; NTCS, no-till corn–soybean rotation; NTCSW, no-till corn–soybean–wheat rotation; CRP-C and CRP-W, Conservation Reserve Program cool-season and warm-season grasses, respectively; HAY, mixed-grass hay.

Table 5. Number of significantly different cropping system and landscape position pairs for each analysis method: dry combustion laboratory analysis (Lab), visible–near-infrared (VNIR) analysis of oven-dried and sieved samples (Dry), and VNIR analysis of field-moist samples (Moist). Maximum possible number of significant differences is 15 for cropping system and three for landscape position.

Parameter†	Cropping system			Landscape position		
	Lab	Dry	Moist	Lab	Dry	Moist
			0–5-cm soil depth			
SOC	13	10	10	2	2	0
TN	14	9	8	2	2	0
			5–15-cm soil depth			
SOC	10	0	0	2	1	2
TN	9	4	0	2	2	1

† SOC, soil organic C; TN, total N.

nations. As interactions were not significant in any case, main effect means by cropping system and landscape position, along with mean separation indicators, are presented in Fig. 3. Relative differences among cropping system and landscape position were consistent with the results and interpretation presented by Jung et al. (2008) based on soil samples collected in 2002 from the same plot area.

Similar relative differences in treatment means were seen among the different cropping systems and landscape positions for all three analysis methods (Fig. 3). The additional variability added by the VNIR calibration (Fig. 3), however, caused many differences that were significant by laboratory analysis to not be significant with VNIR estimation. Table 5 summarizes the number of significant differences detected by each method. Data obtained by standard laboratory dry combustion methods provided the highest number of significant differences (Table 5) among treatment means. Oven-dry soil VNIR estimates were less able to detect cropping system differences due to the scatter present in the calibration relationship (Fig. 2). This reduction in discrimination ability was greater for the deeper (5–15-cm) soil layer, where treatment differences were less. For example, there were no significant differences in the 5- to 15-cm SOC by oven-dry soil VNIR although standard laboratory analysis showed 10 treatment pairs to be significantly different. In all but one case (5–15-cm SOC), mean separations among landscape positions were identical for laboratory analysis and oven-dry soil VNIR.

Field-moist sample VNIR analysis exhibited a further reduction in ability to detect significant differences among cropping systems and landscape positions (Table 5). An exception was in differentiating cropping system effects in the 0- to 5-cm soil layer, where oven-dry soil and field-moist sample VNIR results were identical or very similar. To a large extent, the ability of the different VNIR methods to detect differences was explained by the estimation statistics of RMSE and RPD. Methods and soil depths with higher RPD (Table 6) generally showed greater separation of treatments (Table 5). Values of RPD <1 indicated poor separation of treatments by VNIR compared with laboratory methods. With values of RPD >1.5 (Table 6), most of the treatments shown as significantly different by laboratory methods were shown as significantly different by VNIR (Table 5).

Table 6. Root mean square error (RMSE) and the ratio of the standard deviation to the RMSE (RPD) for soil organic C (SOC) and total N (TN) by soil depth for each visible–near-infrared (VNIR) analysis data set: oven-dried and sieved samples (Dry) and field-moist samples (Moist).

Parameter	RMSE		RPD	
	Dry	Moist	Dry	Moist
	g kg^{-1}			
		0–5-cm soil depth		
SOC	3.02	3.19	1.61	1.53
TN	0.29	0.32	1.36	1.21
		5–15-cm soil depth		
SOC	1.56	2.17	0.98	0.70
TN	0.18	0.23	0.97	0.73

Consistent with this finding, an RPD value of 1.4 to 1.5 has been used as the lower limit for estimates of good accuracy in past research (Chang et al., 2001; Lee et al., 2009).

The results were consistent among methods. Differences significant by field-moist VNIR were also significant by oven-dry soil VNIR. With one exception, differences significant by oven-dry soil VNIR were also significant by standard laboratory analysis. Thus, it appears that VNIR SOC and TN analysis could be used to assess management differences, albeit with a reduced ability to discriminate among treatment means. Due to the smaller differences in subsoil samples, the technique would be more successful when applied to surface samples. Although others (Chang et al., 2005) have reported similar accuracy levels between VNIR analysis of moist and dry samples, the high-clay soils at the study site made it difficult to achieve a consistent surface for DRS scanning of the moist samples and may have been a large factor in the poorer results with the field-moist data set. While field-moist sample VNIR analysis provided the same mean separation as standard laboratory data with large treatment differences (e.g., 0–5-cm SOC among grain cropping systems, Fig. 3), it was not able to discriminate smaller differences (e.g., 0–5-cm SOC among landscape positions) that were found with oven-dry soil VNIR analysis and standard laboratory data. Thus, the question of whether samples should be dried and sieved before VNIR analysis would depend on the expected differences among treatments.

It is worthwhile to note that these results were obtained using the same number of samples for VNIR analysis as for standard laboratory analysis. Due to the higher efficiency of the VNIR analysis, however, spectral scans would probably be acquired at more sampling points than would be used for laboratory analysis. Thus, although the accuracy at individual sampling points might be lower as indicated by this study, the overall spatial variation in the properties of interest could be more accurately represented. Additionally, VNIR analysis can be completed at less cost and with less time than dry combustion laboratory analysis. This is particularly true if VNIR sample processing can be kept to a minimum. Waiser et al. (2007) and Morgan et al. (2009) reported that VNIR scanning of air-dried intact cores provided more accurate results than air-dried sieved samples. Perhaps intact core scanning, in either field-moist or air-dry condition, would be able to both improve accuracy and minimize sample processing. Another approach would be in situ scanning as described by Christy (2008) and Bricklemyer and Brown (2010). Although in situ scanning eliminates the need for sample collection, preparation, and analysis (except for calibration samples), this method has generally provided lower accuracy. For any particular experiment estimating near-surface SOC and TN, the choice of a method would need to be based on several factors, including the number of samples, the required accuracy, and the available resources. Based on the results of this and other studies, VNIR estimation of SOC and TN would be an acceptable methodology in some cases.

CONCLUSIONS

This study investigated the ability of VNIR DRS to distinguish differences in claypan soil quality among cropping systems and landscape positions on the basis of topsoil SOC and TN. Soil samples at two depths (0–5 and 5–15 cm) were obtained from long-term research plots encompassing six contrasting management systems across a representative claypan-soil landscape. Additional soil samples were obtained from nearby locations to provide an independent VNIR DRS calibration data set. Diffuse reflectance spectra of both field-moist and dried samples, across the 400- to 2500-nm spectral range, were obtained in the laboratory, and calibrations were established using PLS regression. Good results were obtained, with the accuracy of the VNIR estimates higher with oven-dry samples than with field-moist samples. Both VNIR analyses were able to discriminate among treatments but not as well as standard dry combustion methodology, with the oven-dry-sample VNIR analysis being more sensitive in detecting differences than the field-moist sample analysis. The results with VNIR were better in the surface layer, where differences among treatments were generally greater. Even with its lower accuracy, the efficiencies inherent in the VNIR method, particularly when applied to field-moist soil, suggest that it deserves consideration as a tool for evaluating near-surface SOC and TN differences in field experiments.

ACKNOWLEDGMENTS

The participation of V.P. Chaudhary in this project was supported by the National Agricultural Innovation Project sponsored by the Indian Council of Agricultural Research.

REFERENCES

Bailey, N.J., P.P. Motavalli, R.P. Udawatta, and K.A. Nelson. 2009. Soil CO_2 emissions in agricultural watersheds with agroforestry and grass contour buffer strips. Agrofor. Syst. 77:143–158. doi:10.1007/s10457-009-9218-x

Beebe, K.R., and B.R. Kowalski. 1987. An introduction to multivariate calibration and analysis. Anal. Chem. 59:1007A–1017A. doi:10.1021/ac00144a001

Bricklemyer, R.S., and D.J. Brown. 2010. On-the-go VisNIR: Potential and limitations for mapping soil clay and organic carbon. Comput. Electron. Agric. 70:209–216. doi:10.1016/j.compag.2009.10.006

Brown, D.J., R.S. Bricklemyer, and P.R. Miller. 2005. Validation requirements for diffuse reflectance soil characterization models with a case study of VNIR soil C prediction in Montana. Geoderma 129:251–267. doi:10.1016/j.geoderma.2005.01.001

Cambardella, C.A., T.B. Moorman, J.M. Novak, T.B. Parkin, D.L. Karlen, R.F. Turco, and A.E. Konopka. 1994. Field-scale variability of soil properties in central Iowa soils. Soil Sci. Soc. Am. J. 58:1501–1511. doi:10.2136/sssaj1994.03615995005800050033x

Carter, M.R. 2002. Soil quality for sustainable land management: Organic matter interactions that maintain soil functions. Agron. J. 94:38–47. doi:10.2134/agronj2002.0038

Chang, C.W., D.A. Laird, and C.R. Hurburgh, Jr. 2005. Influence of soil moisture on near-infrared reflectance spectroscopic measurement of soil properties. Soil Sci. 170:244–255. doi:10.1097/00010694-200504000-00003

Chang, C.W., D.A. Laird, M.J. Mausbach, and C.R. Hurburgh, Jr. 2001. Near-infrared reflectance spectroscopy: Principal component regression analysis of soil properties. Soil Sci. Soc. Am. J. 65:480–490. doi:10.2136/sssaj2001.652480x

Christy, C.D. 2008. Real-time measurement of soil attributes using on-the-go near-infrared reflectance spectroscopy. Comput. Electron. Agric. 61:10–19. doi:10.1016/j.compag.2007.02.010

Doran, J.W., and T.B. Parkin. 1994. Defining and assessing soil quality. p. 3–21. *In* J.W. Doran et al. (ed.) Defining soil quality for a sustainable environment. SSSA Spec. Publ. 35. SSSA and ASA, Madison, WI.

Ghidey, F., P.E. Blanchard, R.N. Lerch, N.R. Kitchen, E.E. Alberts, and E.J. Sadler. 2005. Measurement and simulation of herbicide transport from the corn phase of three cropping systems. J. Soil Water Conserv. 60:260–273.

IUSS Working Group WRB. 2006. World reference base for soil resources. 2nd ed. World Soil Resour. Rep. 103. FAO, Rome.

Jiang, P., S.H. Anderson, N.R. Kitchen, E.J. Sadler, and K.A. Sudduth. 2007a. Landscape and conservation management effects on hydraulic properties of a claypan-soil toposequence. Soil Sci. Soc. Am. J. 71:803–811. doi:10.2136/sssaj2006.0236

Jiang, P., S.H. Anderson, N.R. Kitchen, K.A. Sudduth, and E.J. Sadler. 2007b. Estimating plant-available water capacity for claypan landscapes using apparent electrical conductivity. Soil Sci. Soc. Am. J. 71:1902–1908. doi:10.2136/sssaj2007.0011

Jung, K.-Y., N.R. Kitchen, K.A. Sudduth, K.-S. Lee, and S.-O. Chung. 2010. Soil compaction varies by crop management system over a claypan soil landscape. Soil Tillage Res. 107:1–10. doi:10.1016/j.still.2009.12.007

Jung, W.K., N.R. Kitchen, K.A. Sudduth, and S.H. Anderson. 2006. Spatial characteristics of claypan soil properties in an agricultural field. Soil Sci. Soc. Am. J. 70:1387–1397. doi:10.2136/sssaj2005.0273

Jung, W.K., N.R. Kitchen, K.A. Sudduth, and R.J. Kremer. 2008. Crop management and landscape impact on claypan soil quality properties. Soil Sci. Plant Nutr. 54:960–971. doi:10.1111/j.1747-0765.2008.00314.x

Karlen, D.L., C.A. Ditzler, and S.S. Andrews. 2003. Soil quality: Why and how? Geoderma 114:145–156. doi:10.1016/S0016-7061(03)00039-9

Kennedy, A.C., and R.I. Papendick. 1995. Microbial characteristics of soil quality. J. Soil Water Conserv. 50:243–252.

Kusumo, B.H., C.B. Hedley, M.J. Hedley, A. Hueni, M.P. Tuohy, and G.C. Arnold. 2008. The use of diffuse reflectance spectroscopy for in situ carbon and nitrogen analysis of pastoral soils. Aust. J. Soil Res. 46:623–635. doi:10.1071/SR08118

La, W.-J., K.A. Sudduth, S.-O. Chung, and H.-J. Kim. 2008. Preprocessing and calibration of optical diffuse reflectance signal for estimation of soil physical and chemical properties in the central USA. J. Biosyst. Eng. 33:430–437. doi:10.5307/JBE.2008.33.6.430

Lee, K.S., D.H. Lee, K.A. Sudduth, S.O. Chung, N.R. Kitchen, and S.T. Drummond. 2009. Wavelength Identification and diffuse reflectance estimation for surface and profile soil properties. Trans. ASABE 52:683–695.

Lee, K.S., K.A. Sudduth, S.T. Drummond, D.H. Lee, N.R. Kitchen, and S.O. Chung. 2010. Calibration methods for soil property estimation using reflectance spectroscopy. Trans. ASABE 53:675–684.

Littell, R.C., W.W. Stroup, and R.J. Freund. 2002. SAS for linear models. 4th ed. SAS Inst., Cary, NC.

Lobell, D.B., and G.P. Asner. 2002. Moisture effects on soil reflectance. Soil Sci. Soc. Am. J. 66:722–727. doi:10.2136/sssaj2002.0722

Malley, D.F., P.D. Martin, and E. Ben-Dor. 2004. Application in analysis of soils. p. 729–784. *In* C.A. Roberts et al. (ed.) Near infrared spectroscopy in agriculture. Agron. Monogr. 44. ASA, CSSA, and SSSA, Madison, WI.

Malley, D.F., L. Yesmin, and R.G. Eilers. 2002. Rapid analysis of hog manure and manure-amended soils using near-infrared spectroscopy. Soil Sci. Soc. Am. J. 66:1677–1686. doi:10.2136/sssaj2002.1677

McCarty, G.W., and J.B. Reeves III. 2006. Comparison of near infrared and mid infrared diffuse reflectance spectroscopy for field-scale measurement of soil fertility parameters. Soil Sci. 171:94–102. doi:10.1097/01.ss.0000187377.84391.54

Morgan, C.L.S., T.H. Waiser, D.J. Brown, and C.T. Hallmark. 2009. Simulated in situ characterization of soil organic and inorganic carbon with visible near-infrared diffuse reflectance spectroscopy. Geoderma 151:249–256. doi:10.1016/j.geoderma.2009.04.010

Myers, D.B., N.R. Kitchen, K.A. Sudduth, R.J. Miles, and R.E. Sharp. 2007. Soybean root distribution related to claypan soil properties and apparent soil electrical conductivity. Crop Sci. 47:1498–1504. doi:10.2135/cropsci2006.07.0460

Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. p. 961–1010. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3. Chemical methods. SSSA Book Ser. 5. SSSA, Madison, WI.

NRCS. 2000. Land Resource Regions and Major Land Resource Areas of the United States, the Caribbean, and the Pacific Basin. Agric. Handbk. 296. 3rd. ed. U.S. Gov. Print. Office, Washington, DC.

SAS Institute. 2005. SAS OnlineDoc 9.1.3. SAS Inst., Cary, NC.

Soil Survey Staff. 1999. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. 2nd ed. Agric. Handbk. 436. U.S. Gov. Print. Office, Washington, DC.

Stenberg, B., R.A. Viscarra Rossel, A.M. Mouazen, and J. Wetterlind. 2010. Visible and near infrared spectroscopy in soil science. Adv. Agron. 107:163–215. doi:10.1016/S0065-2113(10)07005-7

Sudduth, K.A., and J.W. Hummel. 1993. Soil organic matter, CEC, and moisture sensing with a prototype NIR spectrometer. Trans. ASAE 36:1571–1582.

Sudduth, K.A., J.W. Hummel, and S.J. Birrell. 1997. Sensors for site-specific management. p. 183–210. *In* F.J. Pierce and E.J. Sadler (ed.) The state of site-specific management for agriculture. ASA, CSSA, and SSSA, Madison, WI.

Sudduth, K.A., N.R. Kitchen, E.J. Sadler, S.T. Drummond, and D.B. Myers. 2010. VNIR spectroscopy estimates of within-field variability in soil properties. p. 153–163. *In* R.A. Viscarra Rossel et al. (ed.) Proximal soil sensing. Springer Science + Business Media, Dordrecht, the Netherlands.

Thompson, A.L., C.J. Gantzer, and S.H. Anderson. 1991. Topsoil depth, fertility, water management, and weather influences on yield. Soil Sci. Soc. Am. J. 55:1085–1091. doi:10.2136/sssaj1991.03615995005500040032x

Udelhoven, T., C. Emmerling, and T. Jarmer. 2003. Quantitative analysis of soil chemical properties with diffuse reflectance spectrometry and partial least-square regression: A feasibility study. Plant Soil 251:319–329. doi:10.1023/A:1023008322682

Viscarra Rossel, R.A. 2008. ParLes: Software for chemometric analysis of spectroscopic data. Chemom. Intell. Lab. Syst. 90:72–83. doi:10.1016/j.chemolab.2007.06.006

Viscarra Rossel, R.A., D.J.J. Walvoort, A.B. McBratney, L.J. Janik, and J.O. Skjemstad. 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. Geoderma 131:59–75. doi:10.1016/j.geoderma.2005.03.007

Waiser, T.H., C.L.S. Morgan, D.J. Brown, and C.T. Hallmark. 2007. In situ characterization of soil clay content with visible near-infrared diffuse reflectance spectroscopy. Soil Sci. Soc. Am. J. 71:389–396. doi:10.2136/sssaj2006.0211

Wang, F., C.W. Fraisse, N.R. Kitchen, and K.A. Sudduth. 2003. Site-specific evaluation of the CROPGRO–Soybean model on Missouri claypan soils. Agric. Syst. 76:985–1005. doi:10.1016/S0308-521X(02)00029-X

Wetterlind, J., B. Stenberg, and M. Söderström. 2010. Increased sample point density in farm soil mapping by local calibration of visible and near infrared prediction models. Geoderma 156:152–160. doi:10.1016/j.geoderma.2010.02.012

Yang, J., R.D. Hammer, A.L. Thompson, and R.W. Blanchar. 2003. Predicting soybean yield in a dry and wet year using soil productivity index. Plant Soil 250:175–182. doi:10.1023/A:1022801322245

Young, F.J., and A.W. Geller. 1995. Soil survey of Audrain County, Missouri. U.S. Gov. Print. Office, Washington, DC.