

Visible-near infrared reflectance spectroscopy for assessment of soil properties in a semi-arid area of Turkey

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ABSTRACT

Reflectance spectroscopy can be used to nondestructively characterize materials for a wide range of applications. In this study, visible-near infrared reflectance spectroscopy (VNIR) was evaluated for prediction of diverse soil properties related to four different soil series of the Entisol soil group within a single field in northern Turkey. Soil samples were collected from 512 locations in a 25×25 m sampling grid over a 32 ha (800×400 m) area. Air-dried soil samples were scanned at 1 nm resolution from 350 to 2500 nm, and calibrations between soil physical and chemical properties and reflectance spectra were developed using cross-validation under partial least squares regression (PLSR) and multivariate adaptive regression splines (MARS). Raw reflectance and first derivative reflectance data were used separately and combined for all samples in the data set. Data were additionally divided into two random subsets of 70 and 30% of the full data, which were each used for calibration and validation. Overall, MARS provided better predictions when under cross-validation. However, PLSR and MARS results were comparable in terms of prediction accuracy when using separate data sets for calibration and validation. No improvement was obtained by combining first derivative and raw data. Strongest correlations were obtained with exchangeable Ca and Mg, cation exchange capacity, and organic matter, clay, sand, and CaCO_3 contents. When soil data were classified into groups, VNIR spectroscopy estimated class memberships well, especially for soil texture. In conclusion, VNIR spectroscopy was variably successful in estimating soil properties at the field scale, and showed potential for substituting laboratory analyses or providing inexpensive co-variable data.

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1. Introduction

1.1. Use of reflectance spectroscopy for soil analyses

Soil characteristics often exhibit high spatial variability, even across single agricultural fields. Mapping soil fertility indicators and quantifying soil parameters that control the fate of chemicals are therefore important for site-specific soil management and protection of the environment. Typically, large numbers of samples must be collected and analyzed in order to capture this spatial variability and adequately estimate soil properties. Conventional methods may be expensive and require large amounts of labor and chemicals for performing these tasks (Viscarra Rossel and McBratney, 1998a,b). Visible and near infrared reflectance (VNIR) spectroscopy

shows promise as a low-cost method that can be used to substitute or complement traditional soil characterization methods. Once calibrated, it can be used to predict multiple soil characteristics simultaneously and explain within-field spatial variability (Bowers and Hanks, 1965; Ben-Dor and Banin, 1995; Chang et al., 2001; Islam et al., 2003; Shepherd and Walsh, 2002).

The scale of application for this method can affect its utility. Shepherd and Walsh (2002) and Brown et al. (2006) used VNIR spectroscopy based on samples from many soil types over large geographical areas. This type of sampling generally provides a wide range of soil indicator values, which promotes good regressive results. On the other hand, wide distribution of soils in a sample set challenges the methodology by requiring greater universality in the statistical prediction relations, especially when including different parent materials (Reeves and van Kessel, 1999; Shepherd and Walsh, 2002). In precision agriculture, the interest is often limited to characterizing single or multiple fields within a relatively small geographical area. This poses different challenges in that the data

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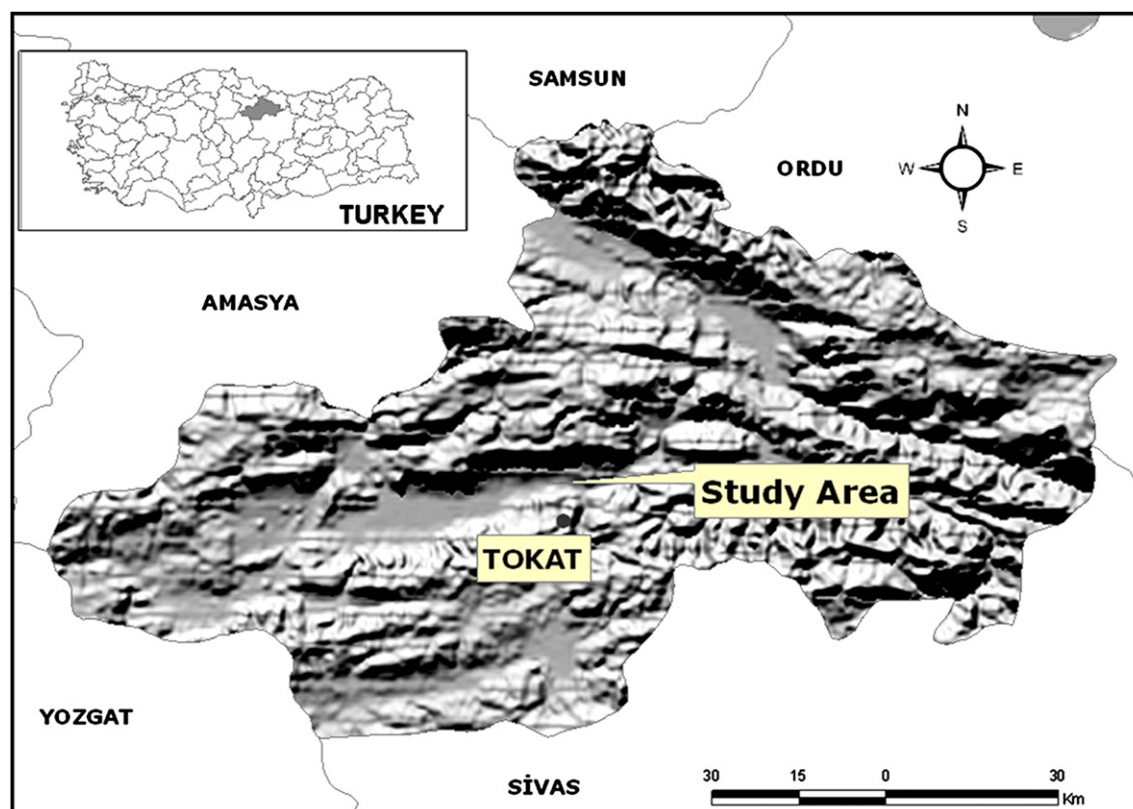


Fig. 1. Location of study area in northern Turkey.

ranges for soil properties are generally small, but the prediction equation may only need to be locally applicable.

With VNIR, soil reflectance characteristics are determined over the entire visible (350–700 nm) and near infrared (700–2500 nm) region with the use of a monochromator. Raw data, first-, and second-derivatives each provide valuable information that can be analyzed separately or combined using multivariate statistical methods or data mining techniques. Soil constituents have unique absorption features in these wavelength regions due to overtones related to stretching and bending vibrations in molecular bonds such as C–C, C–H, N–H and O–H (Dalal and Henry, 1986).

Chang et al. (2001) predicted more than thirty soil properties simultaneously with variable levels of success using a principal component analysis method with cross-validation. They reported successful predictions ($R^2 > 0.80$) for total organic carbon and nitrogen (g kg^{-1}), gravimetric soil water content, soil water content at -1.5 Mpa, exchangeable calcium, cation exchange capacity (CEC) and silt and sand content. Brown et al. (2006) used over 4100 surface and subsurface soils from across the United States, Africa and Asia to evaluate the accuracy of VNIR empirical models for global soil characterization and reported strong predictability for kaolinite, montmorillonite, clay content, as well as CEC, soil organic carbon, inorganic carbon, and extractable Fe.

Others also used VNIR spectroscopy to successfully predict organic carbon and nitrogen (Reeves et al., 2002), Fe_2O_3 , Al_2O_3 , CaCO_3 (Ben-Dor and Banin, 1995), potentially mineralizable nitrogen (Morón and Cozzolino, 2002; Reeves and Van Kessel, 1999), heavy metals, micronutrients (Cozzolino and Morón, 2003; Kooistra et al., 2001; Udelhoven et al., 2003), C:N ratio and soil biological properties (Chodak et al., 2001; Ludwig et al., 2002). Additionally, the prediction of soil constituents that do not absorb

within the VNIR range may be possible through their correlations with spectrally active constituents (Ben-Dor and Banin, 1995).

1.2. Processing hyperspectral data

Different mathematical pre-processing techniques have been applied to either raw reflectance spectra or soil absorbance spectra ($\log 1/\text{reflectance}$) to remove noise within spectra originating from effects of illumination or non-homogeneous distributions of particle sizes. The most commonly used are first- and second-derivatives with or without smoothing, which have provided optimum predictions in some studies (Chang et al., 2001; Reeves et al., 2002; Shepherd and Walsh, 2002). However, Kooistra et al. (2001) reported best predictions for clay, organic matter, Cd and Zn without pre-processing of spectra. Soil reflectance and soil variables have been calibrated using statistical methods like Multiple Linear Regression, Polynomial Regression, Principal Component Regression (Chang et al., 2001; Daniel et al., 2004; Islam et al., 2003; Udelhoven et al., 2003) and data mining techniques (Brown et al., 2006; Shepherd and Walsh, 2002). Partial least squares regression (PLSR) has been the most commonly used multivariate statistical method in calibrating soil reflectance to individual soil parameters and the estimation of those parameters, mainly due to its superiority over traditional methods in dealing with high dimensional multicollinearity. It is superior to Principal Component Regression in that it uses the information in both predictor and response variables.

Multiple Adaptive Regression Splines (MARS) is a non-parametric multivariate regression method. It is capable of modeling both linear and nonlinear relationships between response and predictor variables by fitting local regression curves to spectral subregions and including higher order interactions among

Table 1

Data ranges for measured soil variables.

	Sample set I (n = 359)				Sample set II (n = 153)			
	Min	Max	Mean	St. dev	Min	Max	Mean	St. dev
CaCO ₃ (g kg ⁻¹)	25.7	98.7	55.1	11.4	29.3	98.7	53.8	11.6
SOM (g kg ⁻¹)	3.9	68.7	15.9	5.9	5.0	33.8	15.7	5.6
Ca (me100 g ⁻¹)	20.6	35.8	30.7	2.7	21.1	35.0	30.6	2.6
K (me100 g ⁻¹)	0.07	1.84	0.79	0.24	0.08	1.94	0.81	0.26
Mg (me100 g ⁻¹)	1.17	5.15	3.41	0.66	1.54	4.34	3.37	0.57
Na (me100 g ⁻¹)	0.02	0.18	0.06	0.02	0.02	0.13	0.06	0.02
CEC (me100 g ⁻¹)	21.8	42.9	34.9	3.1	22.7	41.5	34.8	3.3
pH	7.53	8.26	7.95	0.14	7.55	8.31	7.94	0.15
EC (dS m ⁻¹)	0.14	0.56	0.26	0.07	0.13	0.63	0.26	0.07
Clay (g kg ⁻¹)	73.0	477.9	280.8	91.9	106.8	502.3	282.1	104.5
Silt (g kg ⁻¹)	185.6	556.7	379.6	60.2	206.2	553	375.7	60.2
Sand (g kg ⁻¹)	153	700.2	338.3	100.4	154.6	659	343.5	110.9

predictors. It has been successfully applied in various fields (Deichmann et al., 2002; Luoto and Hjort, 2005; Shepherd and Walsh, 2002; Yang et al., 2003) and generally provides better results in modeling compared to other linear and non-parametric regression techniques like Generalized Linear Models (GLM), Artificial Neural Networks (ANN), and Classification and Regression Trees (CART).

The objectives of this study were to (i) determine whether VNIR spectroscopy can be used as a rapid, inexpensive alternative or supplement to traditional methods for measuring soil properties collected from a single field in northern Turkey, (ii) to evaluate whether the combined use of raw and first derivative spectra can help improve the estimations of parameters, (iii) to compare the predictive abilities of MARS with the more commonly used PLSR method, and (iv) to evaluate the utility of VNIR for single field characterization compared to other scales.

2. Materials and methods

2.1. Study site and sampling

Soil samples were collected from a study area on the experimental farm of the Tokat Province Research Institute in northern Turkey (40° 32' N lat, 36° 32' E long), located at an average elevation of 580 m above sea level. The study area has a semi-arid climate with a mean annual precipitation, evaporation, temperature and relative humidity of 445 mm, 881 mm, 12 °C and 61%, respectively (Tokat Research Institute, 2000).

The study area (Fig. 1) covers 32 ha (800 m × 400 m), which was divided into 25 × 25 m grid squares. The soils are classified as Mollic Ustifluvent, Typic Ustifluvent and Typic Ustorthent (Yildiz, 1997). They are mostly finely textured (clay loam), contain various amounts of organic matter (3.9–68.7 g kg⁻¹), and a moderate amount of CaCO₃ (25.7–98.7 g kg⁻¹). A total of 512 soil samples

(16 × 32) were collected in 2000 from the midpoint of each grid square and a depth of 0–30 cm.

2.2. Chemical analyses

Soil samples were air-dried and passed through a 2 mm sieve. Particle size distributions were determined by the hydrometer method (Bouyoucos, 1926); organic matter content by the Walkley–Black method (Nelson and Sommers, 1982); carbonates using a calcimeter (Kacar, 1994); soil pH with a 1:2 soil/water suspension using a glass electrode pH meter (McLean, 1982); electrical conductivity (EC) in soil extraction using a conductivity meter (Janzen, 1993). Exchangeable bases (Ca, Mg, K and Na) were determined after NH₄OAc extraction and measured using an ICP-AEAS (Varian-Vista, Palo Alto, CA, USA); and CEC was determined by summing of the measured exchangeable bases.

2.3. Hyperspectral reflectance

Soil samples were scanned and Absolute Reflectance (decimal percent) of samples was recorded for 350–2500 nm at 1 nm spectral resolution, yielding a total of 2150 data points per spectrum, using a FieldSpec Pro hyperspectral sensor (Analytical Spectral Devices, Inc., Boulder, Colorado: ASD, 1997). Air-dried soil samples were placed into 4 cm diameter optical quality petri dishes and illuminated with a Tungsten Quartz halogen lamp light source that was held inside a Muglight sensor attachment (<http://www.asdi.com/products-accessories-hisp.asp>). Reflectance was recorded through the glass bottom of each dish with a constant angle (55 degrees from horizontal) at a distance of 4 cm from the sensor. After five consecutive readings, each average of ten sequential reflectance spectra, the sample was rotated 90° and five additional

Table 2

Pearson correlation coefficients between measured soil variables.

	CaCO ₃	SOM	Ca	K	Mg	Na	CEC	pH	EC	Clay	Silt	Sand
CaCO ₃	1.00											
SOM	−0.34**	1.00										
Ca	−0.23**	0.46**	1.00									
K	−0.27**	0.62**	0.38**	1.00								
Mg	−0.04	0.39**	0.62**	0.45**	1.00							
Na	0.26**	−0.13**	0.18**	−0.04	0.32**	1.00						
CEC	−0.22**	0.51**	0.98**	0.48**	0.75**	0.21**	1.00					
pH	0.03	−0.20**	0.04	−0.12**	0.02	0.05	0.03	1.00				
EC	−0.18**	0.31**	0.34**	0.37**	0.41**	0.13**	0.39**	−0.27**	1.00			
Clay	−0.58**	0.55**	0.69**	0.46**	0.60**	−0.01	0.72**	0.12**	0.40**	1.00		
Silt	0.44**	0.03	0.16**	0.07	0.41**	0.15**	0.22**	−0.01	0.06	−0.17**	1.00	
Sand	0.28**	−0.53**	−0.73**	0.46**	−0.79**	−0.08	−0.79**	−0.10*	−0.40**	−0.83**	−0.41**	1.00

**Significant at the level of <0.01.

* At the level of ≤0.05.

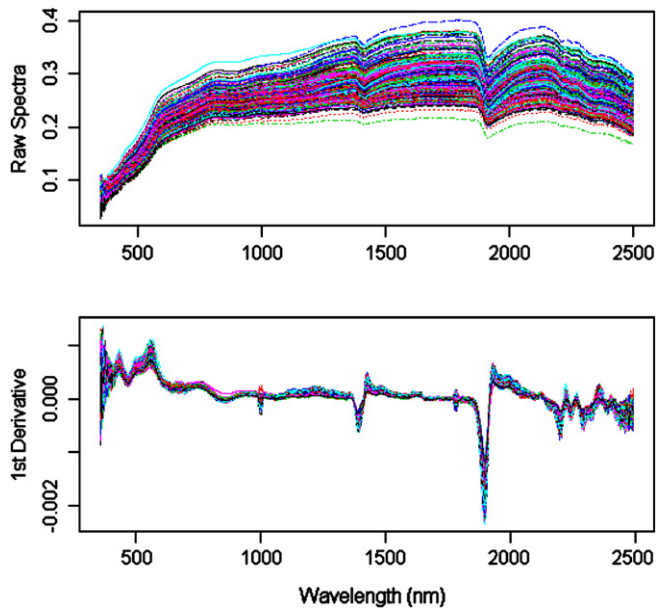


Fig. 2. Raw spectra and first derivative equivalents for all soils of the study.

readings were collected to avoid possible spectral differences originating from particle size variations within soil samples. The signal was optimized and the accuracy and detector responses were calibrated using a Spectralon standard. If the white (Spectralon) reading was not stable, the instrument was reset.

2.4. Data processing

Reflectance data were translated from binary to ASCII and exported in batches using ViewSpecPro (Analytical Spectral Devices, Inc., Boulder, CO, 80301). The 10 sequential reflectance readings obtained from each sample (100 scans total) were averaged using Splus, producing a master data file with one representative reflectance spectrum per soil sample. Spectral data were transformed with first derivative processing using the Savitsky–Golay transformation procedure (Savitzky and Golay, 1964) with mathematical treatment of 1 4 1 2, which refers to the order of derivative, first smoothing, second smoothing and order of polynomial, respectively, using Unscrambler®V.8.05 (CAMO Process, Oslo, Norway, 2003). The first derivative spectra generally amplify the absorption features indicative of the contents of the soil materials, and also reduce variation among samples (Martens and Naes, 1989). First derivative and raw spectra were tested both separately and jointly in predicting soil variables.

2.5. Statistical modeling

The prediction approach was to first use cross-validation with all samples used in the calibration, and subsequently to test the prediction accuracy using separate validation sample subsets. Prior to calibration, the samples were randomly divided into two subsets containing 30 and 70 percent of the total data ($n = 153$ and $n = 359$, respectively). Each subset was used once for both calibration and validation. Calibrations between soil reflectance and soil parameters were performed using both partial least square (PLSR) regression and multivariate adaptive regression splines (MARS) analysis.

2.5.1. Partial least square regression

Partial least square regression is a method for relating two data matrices X and Y through a linear multivariate model, and is widely

used in reflectance spectroscopy data analyses. PLSR decomposes both X and Y variables and finds new components, called latent variables, which are both orthogonal and weighted linear combinations of X variables. These new X variables are then used for prediction of Y variables where X is soil reflectance and Y is a measured soil property. Unlike multiple linear regression, it can handle data with strong co-linearity in independent (X) variables, which can also be more numerous than observations. Variables X and Y are centered by subtracting column averages from each observation in the column before the analysis. In PLSR, the selection of the number of latent variables is critical to preventing over or under fitting of the data, which would create models with poor prediction capability.

Proper fitting was achieved using cross-validation where the models were constructed each time by leaving some samples out of the calibration data set for use in the validation process until all samples or groups were tested. PLSR was performed using Unscrambler®V.8.0.5 software.

2.5.2. Multivariate adaptive regression splines

Multivariate adaptive regression splines (MARS) is an explanatory data analysis (data mining) technique developed by Friedman (1991). Recently, it has been applied to several disciplines as a regression method (Deichmann et al., 2002; Shepherd and Walsh, 2002; Yang et al., 2003), where it was generally reported to perform better than conventional statistical methods.

MARS uses basis functions to model predictor and response variables. For constructing the basis functions, MARS splits the data into subregions (splines) with different interval ending knots, which are the points in the slopes where the regression coefficients change, and fits the data in each sub region using a set of adaptive piecewise linear regressions. These basis functions are then used as new predictor variables for modeling purposes. Each basis function may contain nonlinear and interaction factors (second and third order) among variables, as well as linear combinations.

Basis functions take two forms, one for the values on the left of the knot (negative) and one for the values on the right of knot (positive):

$$Y = \max(0, Xf - cf)$$

$$Y = \max(0, cf - Xf)$$

where cf is the threshold value for a predictor, or knot, and Xf denotes a predictor variable.

The number of knots and basis functions are determined by using a forward stepwise procedure where first a deliberately over-fitted model is constructed. Then, backward stepwise elimination is used, where the basis functions which do not contribute sufficiently to the accuracy of the fit are discarded to get a final model of the proper size (Friedman, 1991). A final MARS model consists of a collection of basis functions and may also include nonlinear and interaction relationships among the predictor variables. A maximum of 15 basis functions were used in this study, as suggested by Friedman (1991).

In order to measure lack of fit and avoid overfitting the data, MARS uses a modified form of the generalized cross-validation (GCV) criterion as follows:

$$GCV = \frac{\frac{1}{n} \sum_{i=1}^n [y_i - f(x_i)]^2}{\left[1 - \frac{C(m)}{n}\right]^2}$$

where n is the number of observations. The numerator is the sum of squared errors as a measure of the lack of fit on the m basis function models and the denominator represents the penalty to account for the increased variance associated with higher model complexity

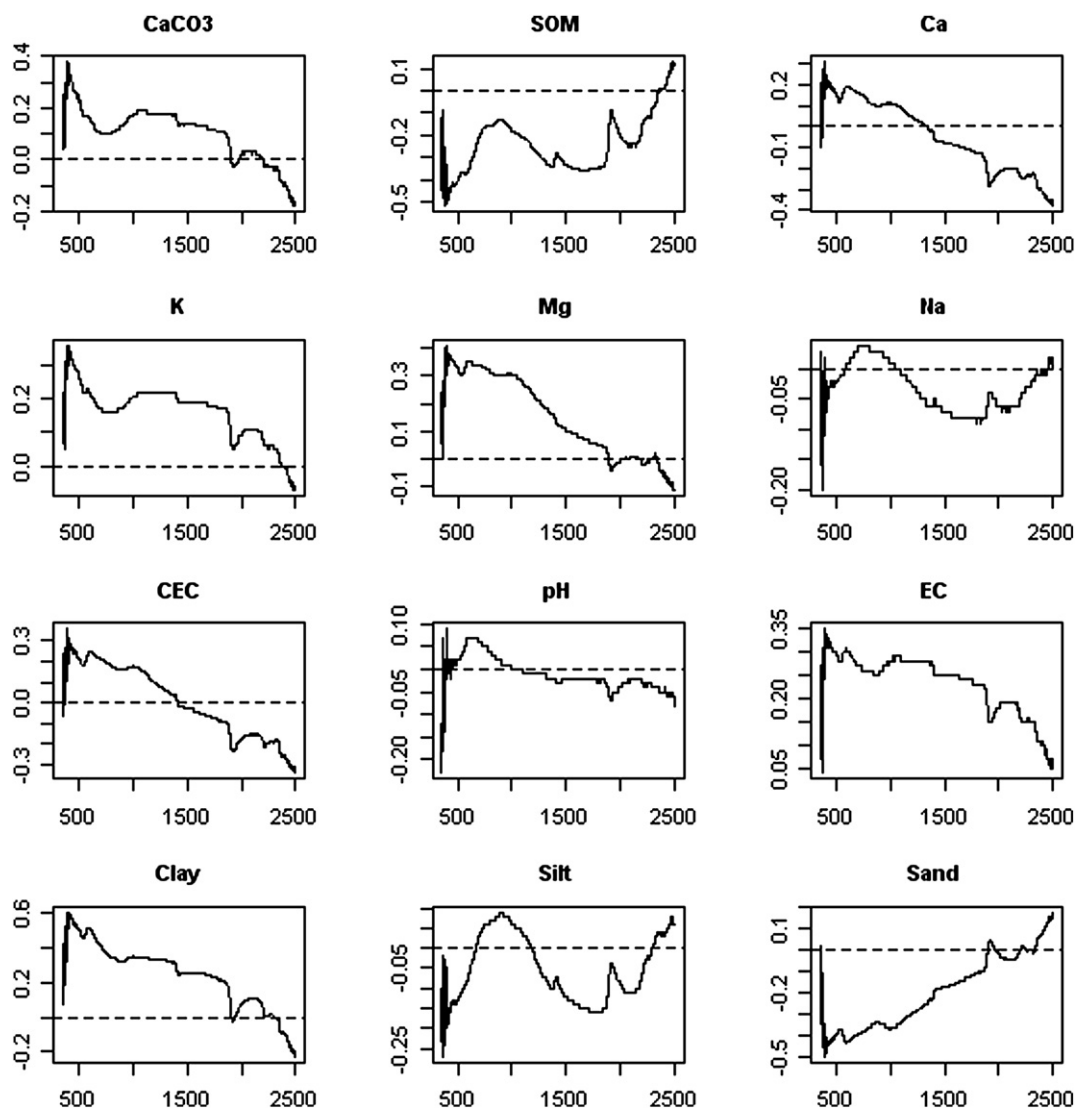


Fig. 3. Correlations between soil variables and average reflectance at each wavelength.

and a larger number of basis functions in the model. $C(m)$ is the cost-complexity measure of a model containing m basis functions, used to penalize the model complexity to avoid overfitting by introducing a cost for the added basis functions into the model. More basis functions in the model provide both greater flexibility but also more complexity, and MARS attempts to minimize model complexity, selecting the optimum model based on the lowest generalized cross-validation value. MARS™ software, Windows (V.2; Salford Systems, San Diego, CA) was used in this study.

2.5.3. Prediction accuracy

The ability of each VNIR technique to predict a soil property was evaluated using the coefficient of determination (R^2) of measured and predicted values of samples, and the root mean square error of prediction (RMSEP), which is defined as:

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^n (Y_{\text{pred.}} - Y_{\text{meas.}})^2}{n - 1}}$$

Other statistical parameters used to evaluate prediction accuracy were the ratio of standard error of prediction to standard

deviation (RPD), which is calculated by dividing the SD of reference values used in the validation set by the RMSEP, and the ratio error range (RER), computed by dividing the range in the reference values of the validation set by the RMSEP:

$$\text{RPD} = \text{SD}/\text{RMSEP}$$

$$\text{RER} = \text{Range}/\text{RMSEP}$$

2.5.4. Classification accuracy

Having classified information regarding soil properties may suffice for many applications. The kappa statistic (κ) can be used to judge accuracy of classification or the level of agreement between methods (Cohen, 1960). Kappa measures the degree of agreement between two raters (two analysis methods in our case) and tests the hypothesis that the agreement between two methods is only by chance. We categorized the continuous soil variables of CaCO_3 , SOM, K and Mg of samples both in the calibration set from lab analysis and in the validation set predicted using VNIR spectroscopy as low, moderate and high according to standard ranges for the soil fertility parameters in the study area. Soils were also classified based on texture. We measured the degree of agreement

Table 3

Statistics of cross-validation of VNIR predictions with PLSR and MARS using raw reflectance data, first derivative data, or combined.

	Raw		First		First + raw	
	R^2	RMSEP ^a	R^2	RMSEP	R^2	RMSEP
PLSR						
CaCO ₃	0.65	6.80	0.68	6.50	0.65	6.80
SOM	0.75	2.90	0.73	3.00	0.75	2.90
Ca	0.68	1.48	0.71	1.44	0.68	1.48
K	0.38	0.2	0.35	0.20	0.39	0.19
Mg	0.55	0.42	0.57	0.41	0.56	0.42
Na	0.19	0.02	0.18	0.02	0.19	0.02
CEC	0.73	1.66	0.73	1.65	0.72	1.67
pH	0.29	0.12	0.28	0.12	0.30	0.12
EC	0.27	0.07	0.34	0.07	0.30	0.06
Clay	0.84	38.20	0.83	33.90	0.84	38.10
Silt	0.38	46.80	0.34	48.20	0.37	46.80
Sand	0.8	46.30	0.79	47.60	0.8	46.50
	R^2	GCV ^b	R^2	GCV	R^2	GCV
MARS						
CaCO ₃	0.71	6.20	0.79	5.70	0.79	5.20
SOM	0.73	3.00	0.80	2.70	0.79	2.50
Ca	0.69	1.46	0.74	1.37	0.74	1.35
K	0.43	0.19	0.47	0.19	0.48	0.18
Mg	0.63	0.37	0.61	0.40	0.63	0.39
Na	0.18	0.02	0.23	0.02	0.23	0.02
CEC	0.73	1.64	0.77	1.54	0.76	1.54
pH	0.28	0.12	0.35	0.11	0.35	0.11
EC	0.27	6.53	0.39	0.06	0.39	5.94
Clay	0.86	35.10	0.89	31.10	0.89	31.8
Silt	0.43	44.7	0.49	42.40	0.49	42.2
Sand	0.80	45.4	0.82	43.70	0.84	41.0

^a Root mean square error of prediction by cross-validation.

^b Gross cross-validation.

between the two methods (lab vs VNIR) for soil parameter determination using both κ and the percentage of correctly classified samples. Kappa statistics were obtained using SPSS version 11 for windows, 2001 (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Soil properties

Summary statistics of soil variables and Pearson correlation coefficients between them are provided in Tables 1 and 2, respectively. The variables pH, K, EC and Na generally have narrow ranges in the data set as opposed to clay, sand, organic matter, CaCO₃, CEC, and exchangeable Ca and Mg contents. Among exchangeable cations, Ca content was the highest (avg. 30.7 me 100 g⁻¹) and made up the largest part of the CEC of soil samples. Soil EC was low for all soil variables.

Significant correlations existed among soil variables. Clay was strongly correlated with CaCO₃, SOM, exchangeable Ca and Mg, CEC and sand ($r = -0.58, 0.55, 0.69, 0.60, 0.72$ and -0.83 , respectively). Sand content was strongly correlated with SOM, CEC, and exchangeable Ca and Mg ($r = -0.53, -0.73, -0.79$ and -0.79 , respectively). Similarly, SOM was strongly correlated with CEC ($r = 0.51$) and K ($r = 0.62$). The other strong correlations were between CEC and Ca and Mg ($r = 0.98, 0.75$, respectively), not surprisingly considering they are used in its estimation.

3.2. Soil reflectance

Basic soil constituents affecting soil reflectance characteristics are soil water, clay type and content, organic matter, and Fe–Al

oxides (Bowers and Hanks, 1965). Fig. 2 shows raw reflectance spectra and their first derivatives for all soil samples. Soil reflectance was generally lower in the visible range (Islam et al., 2003; Shepherd and Walsh, 2002) and higher in the near infrared with specific absorbance bands around 1400, 2200 and 2400 nm. These are strongly associated with OH features of free water at 1400 and 1900 nm and clay lattice OH features at 1400 and 2200 nm (Hunt, 1980). Absorption peaks were generally enhanced in the first derivative graphs (Fig. 2).

Correlation coefficients between soil variables and reflectance spectra showed both positive and negative correlations at various wavelengths across the spectrum (Fig. 3). The highest correlation for soil clay content ($r = 0.61$) was found at 450 nm, and overall reflectance also increased with clay content. Other relatively high correlations were obtained for CaCO₃ ($r = -0.52$) and soil organic matter ($r = 0.38$) within the visible range.

Overall reflectance magnitude (albedo) was relatively low (maximum = 39%). Ben-Dor and Banin (1995) obtained comparable findings for similar Israeli soils formed under equivalent semi-arid climate conditions (Entisols and Aridisols). Clay content correlated positively with reflectance within the visible range and negatively within the NIR range, where most minerals are optically active. Bowers and Hanks (1965) similarly reported a decrease in reflectance with increasing particle size, but Skidmore et al. (1975) and Viscarra Rossel and McBratney (1998a,b) obtained lower reflectance values. They suggested that this discrepancy can be explained by mineralogical differences among soil samples investigated.

We obtained both negative and positive correlations for soil organic matter and CaCO₃ across the spectrum. However, in general, soil reflectance decreases with increasing SOM, while CaCO₃ increases the reflectance. Soil with organic matter contents greater than 2% may also have a masking effect on other soil properties (Stoner and Baumgardner, 1981). The opposite results obtained for soil organic matter can be attributed to low amounts of organic matter (on average 15.6 g kg⁻¹) and higher positive and negative correlations between soil organic matter and CaCO₃ with clay content ($r = 0.55, r = -0.57$, respectively). Therefore, the effect of these soil variables can apparently be masked by soil particle size effects.

Correlations between reflectance and the secondary soil variables K, Ca, Mg (i.e. those not directly measured through C–H, O–H and N–H bonds) showed patterns similar to those of the primary soil variables to which they are presumably correlated, mostly clay and SOM contents. This suggests that these secondary soil variables can be assessed with reflectance data based on primary soil variables to which they are correlated, but with due consideration of the lack of physical causality.

3.3. Prediction of soil properties

The ten-out cross-validation approach was used with both PLSR and MARS to test the prediction accuracy for soil variables based on the entire sample data set ($n = 512$). Methods were compared using cross-validation R^2 and RMSEP for various soil properties. Table 3 summarizes PLSR and MARS cross-validation statistics for chemical and particle size indicators using raw and first derivative spectra separately (2150 data points), as well as combined spectra (4300 data points). Both PLSR and MARS provided good correlations between soil spectra and various soil properties. No significant improvement was obtained by combining raw spectra and first derivatives with a larger data set. The best prediction was generally achieved using first derivative spectra with MARS. Reeves et al. (2002) stated that the prediction results may change based on different mathematical processing methods and derivatives of spectra. First derivative processing is justified to remove the

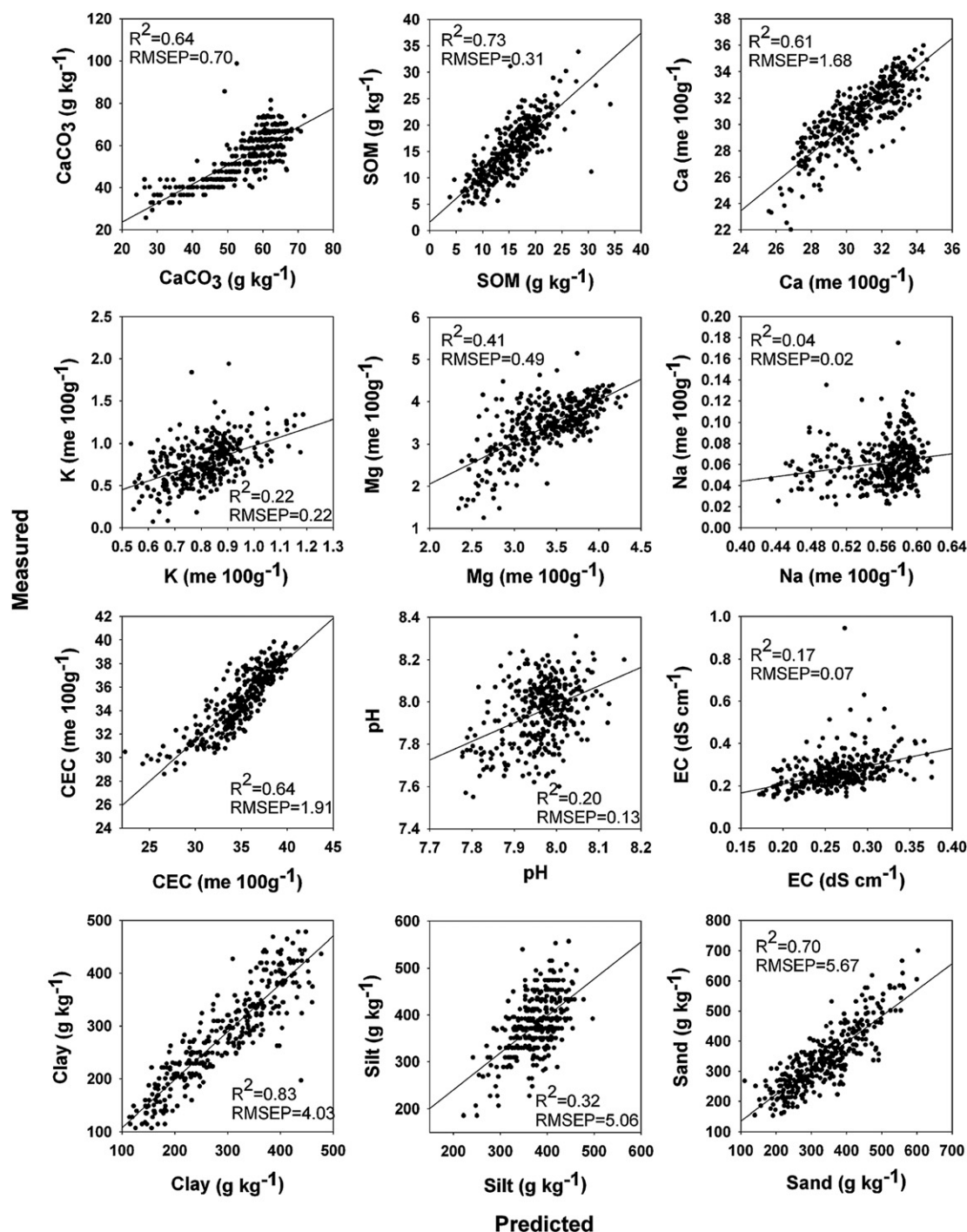


Fig. 4. Regression between measured values and VNIR predictions for all soil variables.

particle size effects and illumination differences (Tsai and Philpot, 1998). In this study, the illumination source was practically constant and soils were scanned by rotating the sample 90° after ten readings.

The best predictive models were obtained for organic matter ($R^2 = 0.80$), CaCO_3 ($R^2 = 0.79$), Ca ($R^2 = 0.74$), CEC ($R^2 = 0.77$), clay content ($R^2 = 0.89$), sand content ($R^2 = 0.84$) and Mg ($R^2 = 0.63$). Inadequate models ($R^2 < 0.50$) were obtained for K, Na, pH, EC and silt content using both PLSR and MARS.

The n -out cross-validation approach can give over-optimistic results in terms of predictions for new unknown samples. Models

constructed through VNIR spectroscopy are empirical so validation is better performed using separate sample sets that are independent of the calibration data set. Indicator parameters on the prediction performance of VNIR spectroscopy using PLSR and MARS are shown in Fig. 4 and Table 4. The values of R^2 in the validation set were lower and RMSEP values higher than corresponding values in the calibration set, but statistical performance was not much different. It is uncommon to get similar prediction levels when independent samples are used for validation (Dardanne et al., 2000), although the data sets were both from the same spatial domain. Prediction quality decreased when using more samples in

Table 4
Statistics for VNIR predictions with PLSR and MARS.

	Validation set I (ncal = 359, nval = 153)						Validation set II (ncal = 153, nval = 359)					
	R ² cal.	RMSEP ^a	R ² val.	RMSEP ^b	RPD	RER	R ² cal.	RMSEP ^a	R ² val.	RMSEP ^b	RPD	RER
<i>PLSR</i>												
CaCO ₃	0.73	6.00	0.71	6.30	1.84	11.02	0.74	5.90	0.64	7.00	1.63	10.44
SOM	0.79	2.70	0.76	2.88	1.94	10.01	0.84	2.20	0.73	3.06	1.93	21.18
Ca	0.73	1.28	0.74	1.29	2.05	10.83	0.76	1.28	0.65	1.61	1.67	9.43
K	0.44	0.19	0.32	0.21	1.21	8.77	0.30	0.20	0.25	0.22	1.11	8.15
Mg	0.66	0.36	0.60	0.37	1.54	7.57	0.60	0.41	0.43	0.50	1.33	8.05
Na	0.24	0.02	0.12	0.02	1.05	5.41	0.03	0.02	0.09	0.02	0.99	7.79
CEC	0.77	1.50	0.79	1.42	2.31	13.17	0.79	1.46	0.68	1.88	1.67	11.21
pH	0.35	0.11	0.27	0.13	1.18	5.89	0.50	0.11	0.21	0.13	1.04	5.53
EC	0.41	0.06	0.36	0.06	1.23	9.02	0.28	0.06	0.30	0.06	1.19	7.18
Clay	0.82	38.30	0.87	40.50	2.58	9.76	0.88	35.40	0.83	40.30	2.28	10.04
Silt	0.41	46.30	0.40	44.30	1.36	7.83	0.51	39.90	0.32	50.60	1.19	7.33
Sand	0.81	43.30	0.84	44.50	2.49	11.33	0.84	44.80	0.70	56.70	1.77	9.65
<i>MARS</i>												
CaCO ₃	0.81	5.20	0.73	6.00	1.93	11.57	0.83	4.70	0.62	7.30	1.56	10.01
SOM	0.79	2.60	0.74	2.90	1.92	9.94	0.78	2.60	0.72	3.12	1.90	20.77
Ca	0.76	1.35	0.74	1.31	2.02	10.67	0.77	1.24	0.63	1.67	1.61	9.10
K	0.45	0.18	0.34	0.22	1.19	8.65	0.52	0.16	0.21	0.23	1.06	7.69
Mg	0.69	0.39	0.63	0.36	1.61	7.89	0.66	0.38	0.47	0.49	1.35	8.20
Na	0.28	0.02	0.19	0.02	1.14	5.89	0.23	0.02	0.12	0.02	0.96	7.57
CEC	0.78	1.48	0.79	1.44	2.29	13.04	0.83	1.35	0.70	1.74	1.81	12.13
pH	0.36	0.11	0.26	0.12	1.28	6.39	0.50	0.11	0.18	0.14	0.99	5.25
EC	0.43	0.04	0.31	0.06	1.15	8.40	0.41	0.05	0.25	0.07	1.06	6.42
Clay	0.89	31.90	0.90	33.90	3.08	11.66	0.91	31.70	0.85	36.60	2.51	11.06
Silt	0.51	42.20	0.35	47.20	1.28	7.35	0.55	38.70	0.29	53.20	1.13	6.98
Sand	0.84	39.80	0.82	47.60	2.33	10.60	0.86	41.00	0.72	53.90	1.86	10.15

^a Root mean square error of prediction by cross-validation.

^b Root mean square error of prediction by validation using separate sample set.

the validation set than in the calibration set (70–30 vs 30–70) using either PLSR or MARS (Table 4). Ben-Dor and Banin (1995) obtained R^2 values of 0.69 for CaCO₃, 0.55 for organic matter and 0.86 for clay content with associated standard error of prediction values of 11.6, 1.34 and 10.3 using a separate sample set to test the prediction accuracy. Similar results were obtained in this study for CaCO₃ and organic matter, but the latter was predicted more accurately.

No critical values exist for RPD and RER levels for agriculturally-related soil predictions, in part because these statistics change based on the range and standard deviation of reference samples in the validation set. Chang et al. (2001) grouped the prediction quality of soil properties using VNIR spectroscopy into three categories based on RPD values in the ranges >2.0, 1.4–2.0, and <1.4 to indicate excellent, acceptable and poor predictions, respectively. They suggested that the predictions in the middle category could be improved using different calibration strategies, but the properties in the poor category may not be reliably predicted using reflectance spectroscopy. According to this classification, excellent predictions were obtained for clay content (RPD = 3.08) and acceptable predictions for CaCO₃, organic matter, sand, CEC, Ca, Mg and silt (RPD values of 1.93, 1.94, 2.49, 2.31, 2.05, 1.61 and 1.36, respectively). Poor predictions were obtained for K, pH, Na, and EC, with RPD values between 0.99 and 1.28. Chang et al. (2001) obtained RPD values of 2.79 for organic carbon, 1.71 for clay content, 2.32 for sand content, 2.28 for CEC, 1.94 for Ca and 1.75 for Mg. Some of our RPD values are lower, but their strategy in the prediction set was cross-validation, which is considered to yield an over-optimistic assessment of the actual performance of the model (Dardanne et al., 2000). Islam et al. (2003) used the same validation strategy as in our study (a separate sample set to validate the calibration) and obtained the RPD values for pH of 1.8, clay content of 1.9, sand content of 1.5, CEC of 1.6, exchangeable Ca of 1.7 and exchangeable Mg of 1.7.

Good prediction results were obtained for CEC and exchangeable Ca and Mg, but predictions for exchangeable Na and K were weak. The better predictions of the former may be attributable to

the relatively higher correlations of these variables with CEC ($r = 0.98$ and 0.75 for Ca and Mg, respectively) and clay content ($r = 0.69$, 0.60 for Ca and Mg, respectively) which were well predicted using VNIR spectroscopy. Chang et al. (2001), reported that accurate predictions for some soil properties without any direct physical connection to VNIR processes could be explained by the correlation with clay and organic matter.

The poor predictions of the Na, pH, K and EC could be attributable to a narrow chemical range, high skewness of these variables in data sets (Table 1), or poor correlations with primary soil variables such as CaCO₃, clay content and organic matter that are more directly assessed by VNIR spectroscopy. Similar poor predictability for K and Na was found by Islam et al. (2003) and Chang et al. (2001).

The poor prediction for pH in this study could be attributable to its narrow range, as with Viscarra Rossel et al. (2006). Although this property may be inherently poorly predicted by VNIR spectroscopy, Shepherd and Walsh (2002) achieved good predictions for pH (1:2.5 soil/solution, range = 4.2–10, $n = 758$) with $R^2 = 0.83$, RMSE = 0.34 and RER = 17.1 using soils from eastern and southern Africa. Dunn et al. (2002), obtained $R^2 = 0.80$, SEP = 0.32 and RPD = 2.3 for 0–10 cm depth for Australian soils covering more than 550 sites in the Riverine Plain of southeastern Australia with a range of 3.8–7.3 (1:5 soil/CaCl₂ extract). Similarly, Islam et al. (2003), obtained a higher level of prediction $R^2 = 0.71$, SEP = 0.61 and RPD = 1.8 for pH with a range of 3.7–9.7 using soil samples collected from different soil locations representing eleven soil orders of Australia. The study of these researchers covered larger areas and the soils had much wider ranges in pH as compared to this study.

3.4. MARS vs PLSR

In the case of 10-out cross-validation, models constructed using MARS performed better than those from PLSR in nearly all cases (Table 3). PLSR with cross-validation has been successfully used to

Table 5

Texture classification on samples in validation set by two methods (Lab. – VNIR).

Laboratory	VNIR								Total
	Sandy loam	Silt loam	Loam	Sandy clay loam	Silty clay loam	Clay loam	Silty clay	Clay	
Sandy loam	6 ^a		7						13
Silt loam			3						3
Loam	1		54	1		8			64
Sandy clay loam				1					1
Silty clay loam						2	1		3
Clay loam			7			45			52
Silty clay									0
Clay					1	5	2	9	17
Total	7	0	71	2	1	60	3	9	153

^a Number of samples categorized into one of the texture classes based on Laboratory and VNIR estimations.**Table 6**

Kappa statistics as an indicator of similarity between laboratory and VNIR results.

Property	Po ^a	κ^b	P value
Soil type	71.8	0.61	<0.001
Soil texture	75.1	0.68	<0.001
SOM	76.15	0.52	<0.001
CaCO ₃	86.27	0.68	<0.001
Mg	84.6	0.53	<0.001
K	82.78	0.36	<0.001

^a Proportion of agreement (%) = # of cases that both methods agree upon divided by total cases (numbers along the diagonal/n, i.e. as in Table 5).^b Kappa statistics = $P_o - P_c / 1 - P_c$; where P_c is agreement by chance (%) and equals to multiplication of sum of numbers in each rows with sums of the numbers in corresponding columns divided by square of total cases (i.e. as in Table 5).

calibrate many soil variables including metal concentrations (Udelhoven et al., 2003), and organic and inorganic carbon contents (McCarty et al., 2002). MARS' superior performance over PLSR can be explained by the inclusion of nonlinear and interactions effects as well as linear combinations of variables. MARS has been used with other materials (Put et al., 2004; Srivastava and Solanky, 2003) and was used by Shepherd and Walsh (2002) to calibrate spectra to various properties of soils sampled in eastern and southern Africa. They achieved cross-validated R^2 values between 0.79 and 0.91 for pH, exchangeable Ca, exchangeable Mg, effective cation exchange capacity, and silt, clay and sand contents. In a recent study, Brown et al. (2006) found Boosted Regression Trees (BRT), another data mining technique, to outperform PLSR and attributed this to its ability to include interactions and nonlinear relationships. Nonlinear relationships between spectra (in mid-infrared) and soil variables often occur with data containing wide ranges and can be the result of distortions of strong signals, and different mineralogical values with high and low soil variable values in the calibration data sets (Janik and Skjemstad, 1995). A locally linear approximation similar to the basis function procedure of MARS method was suggested to address regression nonlinearities.

Unlike the cross-validation approach, MARS was not the best prediction method for many soil variables when using the split data set validation method. PLSR results were close to MARS, and in some cases better. This can be related to MARS' statistical procedure which is more localized than PLSR. Therefore, as the sample size in the validation set was increased, the global models may be more successful. Also, MARS is more sensitive to outliers in the validation set and multi-collinearity among the predictors (Friedman, 1991).

3.5. Classification

The actual lab results and the VNIR estimations of soil parameters were categorized into groups and the agreement between

categorical classifications by the two methods was evaluated using the κ statistics. An example of cross-classification for soil texture is given in Table 5. The majority of samples were classified correctly (values along the diagonal) and the samples which were not classified exactly fell into a neighboring class.

The values of κ for selected parameters and associated P values are given in Table 6. κ values equaling $|-1|$ indicate perfect agreement and if κ is different than 0, the agreement among two methods is more than chance. Significant P values ($P < 0.001$) were found for all parameters, indicating that the agreement with respect to ordinal classification of samples between laboratory and VNIR results is more than chance. The highest κ values were obtained for soil texture and soil CaCO₃ content while the lowest was obtained for K ($\kappa = 0.35$).

The results showed that VNIR could classify various soil parameters successfully, assisting with soil management and understanding soil parameter status. Some soil parameters cannot be predicted precisely by the VNIR method, but they can still be classified with reasonable agreement. This can be especially helpful for soil variables that do not have direct relationships with reflectance. For example, although the estimation quality for K (cmol/kg) was low (Table 4.), it could still be categorized successfully ($P < 0.01$).

4. Conclusion

This study focused on the use of VNIR for predicting soil properties within a single agricultural field, and evaluated several different methods of spectral pretreatment and data analysis. Important environmental soil variables such as clay and SOM content were well predicted using hyperspectral VNIR spectroscopy. The results were generally in line with those of the other studies, even though they were conducted at different scales and in other geographic regions. The comparison of MARS and PLSR analyses showed that in the case of cross-validation, MARS provided the better prediction results for almost all variables. However, the results between the two were not much different when using separate sample sets for calibration and validation. The accuracy of the calibration models appears to depend more on the range of data values and their degree of autocorrelation than on model selection or spectral pretreatment of the reflectance data. Considering the high spatial variability, and the expensive and time consuming measurements of soil properties, VNIR spectroscopy proved to be a useful method to substitute or complement traditional soil analyses and reduce the number of samples to be analyzed for precision management applications in fields. It can also be used as auxiliary information in combination with spatial statistic methods to improve the estimation quality of the parameters and characterization of soil constituents.

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References

- Ben-Dor, E., Banin, A., 1995. Near infrared analysis as a rapid method to simultaneously evaluate several soil properties. *Soil Science Society of America Journal* 59, 364–372.
- Bouyoucos, G.J., 1926. The hydrometer method as a new and rapid method for determining the colloidal content of soils. *Soil Science* 23, 319–330.
- Bowers, S.A., Hanks, R.J., 1965. Reflection of radiant energy from soils. *Soil Science* 100, 130–137.
- Brown, D.J., Shepherd, K.D., Walsh, M.G., Mays, M.D., Reinsch, T.G., 2006. Global soil characterization with VNIR diffuse reflectance spectroscopy. *Geoderma* 132, 273–290.
- Chang, C.W., Laird, D.A., Mausbach, M.J., Maurice, J., Hurburgh, J.R., 2001. Near-Infrared reflectance spectroscopy – principal components regression analyses of soil properties. *Soil Science Society of America Journal* 65, 480–490.
- Chodak, M., Ludwig, B., Khanna, P., Beese, F., 2001. Use of near infrared spectroscopy to determine biological and chemical characteristics of organic layers under spruce and beech stands. *Journal of Plant Nutrition and Soil Science* 165, 27–33.
- Cohen, J., 1960. A coefficient of agreement for nominal scales. *Educational and Psychological Measurement* 20, 37–46.
- Cozzolino, D., Morón, A., 2003. The potential of near-infrared reflectance spectroscopy to analyse soil chemical and physical characteristics. *Journal of Agricultural Science* 140, 65–71.
- Dalal, R.C., Henry, R.J., 1986. Simultaneous determination of moisture, organic carbon, and total nitrogen by near infrared reflectance spectrophotometry. *Soil Science Society of America Journal* 50, 120–123.
- Daniel, K.W., Tripathi, N.K., Honda, K., Apisit, E., 2004. Analysis of VNIR (400–1100 nm) spectral signatures for estimation of soil organic matter in tropical soils of Thailand. *International Journal of Remote Sensing* 25, 643–652.
- Dardanne, P., Sinnaeve, G., Baeten, V., 2000. Multivariate calibration and chemometrics for near infrared spectroscopy: which method? *Journal of Near Infrared Spectroscopy* 8, 229–237.
- Deichmann, J., Eshghi, A., Houghton, D., Sayek, S., Teebag, N., 2002. Application of multiple adaptive regression splines (MARS) in direct response modeling. *Journal of Interactive Marketing* 16, 15–27.
- Dunn, B.W., Beecher, H.G., Batten, G.D., Ciavarella, S., 2002. The potential of near-infrared reflectance spectroscopy for soil analysis – a case study from the Riverine Plain of south-eastern Australia. *Australian Journal of Experimental Agriculture* 42, 607–614.
- Friedman, J.H., 1991. Multivariate adaptive regression splines. *Annals of Statistics* 19, 1–67.
- Hunt, G.R., 1980. Spectroscopic properties of rock and minerals. In: Stewart, C.R. (Ed.), *Handbook of Physical Properties of Rocks*. CRC Press Inc., Florida, p. 295.
- Islam, K., Singh, B., McBratney, A., 2003. Simultaneous estimation of several soil properties by ultra-violet, visible, and near-infrared reflectance spectroscopy. *Australian Journal of Soil Research* 41, 1193–1202.
- Janik, L.J., Skjemstad, J.O., 1995. Characterization and analysis of soils using mid-infrared partial least squares. II. Correlations with some laboratory data. *Australian Journal of Soil Research* 33, 637–650.
- Janzen, H.H., 1993. Soluble salts. In: Carter, M.R. (Ed.), *Soil Sampling and Methods of Analysis*. CRC Press Inc., Florida, pp. 161–166.
- Kacar, B., 1994. *Soil and Plant Analysis III: Soil Analysis*. Ankara University Agricultural Faculty, Ankara, Turkey.
- Kooistra, L., Wehrens, R., Leuven, R.S.E.W., Buydens, L.M.C., 2001. Possibilities of visible-near-infrared spectroscopy for assessment of soil contamination in river floodplains. *Analytica Chimica Acta* 446, 97–105.
- Ludwig, B., Khanna, P.K., Bauhus, P., Hopmans, P., 2002. Near infrared spectroscopy of forest soils to determine chemical and biological properties related to soil sustainability. *Forest Ecology and Management* 171, 121–132.
- Luoto, M., Hjort, J., 2005. Evaluation of current statistical approaches for predictive geomorphological mapping. *Geomorphology* 67, 299–315.
- Martens, H., Naes, T., 1989. *Multivariate Calibration*, second ed. John Wiley and Sons Ltd, Chichester, UK, 419 pp.
- McCarty, G.W., Reeves, J.B., Reeves, V.B., Follett, R.F., Kimble, J.M., 2002. Mid-infrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. *Soil Science Society of America Journal* 66, 640–646.
- McLean, E.O., 1982. Soil pH and lime requirement. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), *Methods of Soil Analysis. Part 2. Agronomy Monograph*, vol. 9. American Society of Agronomy, Madison, WI, pp. 199–223.
- Morón, A., Cozzolino, D., 2002. Application of near infrared reflectance spectroscopy for the analysis of organic C, total N and pH in soils of Uruguay. *Journal of Near Infrared Spectroscopy* 10, 215–221.
- Nelson, D.W., Sommers, L.E., 1982. Total carbon, organic carbon, and organic matter. In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), *Methods of Soil Analysis (Part II)*. Agronomy Monograph, vol. 9. ASA and SSSA, Madison, WI, pp. 570–571.
- Put, R., Xu, Q.S., Massart, D.L., Heyden, Y.V., 2004. Multivariate regression splines (MARS) in chromatographic quantitative structure–retention relationship studies. *Journal of Chromatography A* 1055, 11–19.
- Reeves, J.B., Van Kessel, J.S., 1999. Investigations into near-infrared analysis as an alternative to traditional procedures in manure N and C mineralization studies. *Journal of Near Infrared Spectroscopy* 7, 195–212.
- Reeves, J., McCarty, G., Mimmo, T., 2002. The potential of diffuse reflectance spectroscopy for the determination of carbon inventories in soils. *Environmental Pollution* 116, 277–284.
- Savitzky, A., Golay, M.J.E., 1964. Smoothing and differentiation of data by simplified least square procedure. *Analytical Chemistry* 36, 1627–1639.
- Shepherd, K.D., Walsh, M.G., 2002. Development of reflectance spectral libraries for characterization of soil properties. *Soil Science Society of America Journal* 66, 988–998.
- Skidmore, E.L., Dickerson, J.D., Schimelpfenning, H., 1975. Evaluating surface soil water content by measuring reflectance. *Soil Science Society of America Journal* 39, 238–242.
- Srivastava, M.S., Solanky, T.K., 2003. Predicting multivariate response in linear regression model. *Communications in Statistics* 32, 389–409.
- Stoner, E.R., Baumgardner, M.F., 1981. Characteristic variations in reflectance of surface soils. *Soil Science Society of America Journal* 45, 1161–1165.
- Tokat Research Institute, 2000. *Rural Service's Hydrometeorological Data of the Year in 2000*. Tokat Research Institute, Tokat, Turkey.
- Tsai, F., Philpot, W., 1998. Derivative analysis of hyperspectral data. *Remote Sensing Environment* 66, 41–51.
- Udelhoven, T., Emmerling, C., Jarmer, T., 2003. Quantitative analysis of soil chemical properties with diffuse reflectance spectrometry and partial-least square regression: a feasibility study. *Plant Soil* 251, 319–329.
- Viscarra Rossel, R.A., McBratney, A.B., 1998a. Soil chemical analytical accuracy and costs: implications from precision agriculture. *Australian Journal of Experimental Agriculture* 38, 765–775.
- Viscarra Rossel, R.A., McBratney, A.B., 1998b. Laboratory evaluation of a proximal sensing technique for simultaneous measurement of soil clay and water content. *Geoderma* 85, 19–39.
- Viscarra Rossel, R.A., Walvoort, D.J.J., McBratney, A.B., Janik, L.J., Skjemstad, J.O., 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. *Geoderma* 131, 59–75.
- Yang, C.C., Prasher, S.O., Lacroix, R., Kim, S.H., 2003. A multivariate adaptive regression splines model for simulation of pesticide transport in soils. *Bio-systems Engineering* 86, 9–15.
- Yildiz, H., 1997. *Detailed soil survey and mapping of Tokat fruit production stations soils*. MSc thesis, Gaziosmanpaşa University, Tokat, Turkey.