DETERMINING THE CLAY/ORGANIC CARBON RATIO BY VISIBLE NEAR INFRARED SPECTROSCOPY

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ABSTRACT

The recently presented Dexter et al. (2008) threshold (ratio of clay to organic carbon (OC) of 10 kg/kg⁻¹) is a good indicator for soil functional properties. However, the conventional analysis of OC and clay are costly and time consuming, thus an alternative method to quantify OC, clay or clay/OC ratio directly would be valuable. Visible near infrared spectroscopy (vis-NIRS) is a cost-effective method for soil analysis and was tested here for the prediction of clay/OC ratio. Soil samples from two agricultural fields in Denmark (N=115) were analyzed. Partial Least Squares regression (full cross-validation) was performed on 80% randomly selected samples to correlate soil spectra with OC, clay and clay/OC. The robustness of calibration models was tested on the remaining 20% of the samples. The soil from the two study sites vary greatly presenting clay/OC ratio between 1.20 and 10.43. Successful calibration results for OC, clay and clay/OC ratio were generated. The OC content was predicted with a RMSEP of 0.23%, R² of 0.96, whereas the prediction of clay resulted in RMSEP=0.94%, and R²=0.94. The most successful predictive ability reported was of the clay/OC ratio (RMSEP=0.42, and R²=0.97) with the most important absorption bands related to both clay minerals (1421, 1910 and 2206 nm – OH bonds and 429, 720 nm – Fe oxides) and organic carbon (1730, 2160 nm and 2310 nm). The results of this study show that vis-NIRS can provide very successful and direct determination of Dexter index on a field scale through its correlation to both OC and clay.

KEYWORDS: NIRS, soil quality, clay/organic carbon ratio

INTRODUCTION

The recently presented Dexter et al. (2008)¹ threshold (ratio of clay to organic carbon (OC) of 10 kg/kg⁻¹) is a good indicator for numerous soil functional properties. For soils with a clay/OC < 10, non-complexed OC is available for soil structure buildup and important biophysical functions. Soils with clay/OC > 10 have critically high clay to OC ratio and reduced functionality which may cause reduced aggregate stability and potentially have a negative effect on yields of agricultural crops.

Conventional analysis of OC and clay are costly and time consuming, thus an alternative method to quantify OC, clay or clay/OC ratio directly would be valuable. Visible near infrared spectroscopy (vis-NIRS) is a cost-effective analytical method which has been applied to soil analysis since the mid-1990's. The absorption in the vis region are associated with minerals containing iron (related to clay due to metal-OH bend) and with organic matter (due to color)². The NIR region is dominated by bonds characteristic of both organic and inorganic matter. Thus, there is a rationale for using vis-NIRS to OC and clay estimation. Here, for the first time the feasibility of using vis-NIRS to predict clay/OC ratio by utilizing Partial Least Squares regression (PLSR) was tested.

MATERIALS AND METHODS

Soil samples originated from two agricultural fields (Silstrup and Sørvad) in north-western and western Denmark (Fig. 1). In Silstrup, 65 topsoil samples were collected on a 15 m grid. In order to select representative locations for soil sampling in Sørvad, a conditioned Latin Hypercube sampling (cLHs) strategy was applied. The use of cLHs in digital soil mapping was suggested by Minasny et al. (2006)³.

This method ensures a full coverage of the range of each variable by maximally stratifying the marginal distribution. It can represent the complicated nature of a landscape variation well. cLHs sampling was based on the electrical conductivity (EC) data available for this field and terrain attributes⁴. In total 50 samples were collected at this site (Fig. 1).

Figure 1. Location of the study sites.

Collected soil samples analyzed with the conventional laboratory methods for soil texture and organic carbon (OC). Soil texture was determined by a combination of wet-sieving and hydrometer methods. Soil organic carbon was determined on a FLASH 2000 organic elemental analyzer coupled to a thermal conductivity detector (Thermo Fisher Scientific, Waltham, MA, USA).

Spectral measurements were conducted on air dried and 2 mm sieved soils using vis-NIR (400-2500 nm) spectrometer DS2500 (Foss, Hillerød, Denmark). Approximately 40 g of soil were placed in a sample holder which rotated seven times during the analysis. At each position four spectra were collected and averaged into one representative spectrum per sample.

Partial Least Squares regression (full cross-validation) was performed on 80% randomly selected samples to correlate soil spectra with OC, clay and clay/OC. The precision and robustness of calibration models was tested on the remaining 20% of the samples and evaluated using: root mean square error of prediction (RMSEP); R^2 ; and a ratio of performance to inter-quartile range (RPIQ). Analysis of regression coefficients was also performed.

RESULTS AND DISCUSSION

The soil from the two study sites vary from very sandy (90% sand) to clayey (24% clay) and from lower (1.5% OC) to high in OC content (>6%), giving clay/OC ratio between 1.20 and 10.43 (Table 1).

Table 1. General statistics for the calibration and the validation datasets

	clay (%)		OC (%)		clay/OC	
	cal. (N=92)	val. (N=23)	cal. (N=92)	val. (N=23)	cal. (N=92)	val. (N=23)
Mean	13.6	12.1	2.8	2.6	5.9	5.6
Max	24.9	18.5	6.3	7.5	10.2	10.4
Min	5.9	5.6	1.6	1.7	1.6	1.2
SD	3.9	4.4	1.4	1.4	2.8	2.9
Skewness	-0.3	-0.1	1.3	2.7	-0.3	0.04
Kurtosis	0.2	-1.5	0.1	7.4	-1.5	-1.4
Median	14.8	14.3	2.0	2.1	7.2	6.9
Q1	10.6	8.5	1.9	1.9	2.8	3.3
Q3	16.2	15.2	3.2	2.4	8.1	7.8

Where: cal: calibration data set; val: validation data set; OC: organic carbon; SD: standard deviation;
Q1: the first inter- quartile; Q3: the third inter-quartile

Successful calibration and validation results for OC, clay and clay/OC ratio were generated (Table 2 and Fig. 2). The prediction of clay resulted in RMSEP=0.9%, $R^2=0.94$, and a high RPIQ (7). The highest values of the regression coefficient in the clay model were located at 541 and 640 nm (Fe oxides) and at 1412, 1910 and 2208 nm (OH bond) (Fig. 2).

Table 1. The results of Partial Least Squares regression for clay, OC and Dexter n.

	clay (%)		OC (%)		clay/OC	
	cal. (N=92)	val. (N=23)	cal. (N=92)	val. (N=23)	cal. (N=92)	val. (N=23)
RMSECV/ RMSEP	1.2	0.9	0.3	0.2	0.5	0.4
R2	0.91	0.94	0.94	0.96	0.97	0.97
RPIQ	6	7	4	5	11	11
LVs	6	-	8	-	6	-
Q3	16.2	15.2	3.2	2.4	8.1	7.8

Where: cal: calibration data set; val: validation data set; OC: organic carbon; RMSECV: room mean square error of calibration; RMSEP: root mean square of prediction; RPIQ: Q1-Q3/RMSEP; LV's: number of latent variables

The OC content was predicted with a RMSEP of 0.2%, R^2 of 0.96 and RPIQ of 5. The important wavebands were related to soil organic matter (780, 1727, 2311 and 2330 nm), Fe oxides (442, 490, 560 nm) and OH bonds (1908 and 2208 nm) (Fig. 2). The most successful predictive ability reported was interestingly of the clay/OC ratio (RMSEP=0.4, $R^2=0.97$, RPIQ=11). The most important absorption bands were related to both clay minerals (1421, 1910 and 2206 nm – OH bonds and 429, 720 nm – Fe oxides) and organic carbon (1730, 2160 nm and 2310 nm) (Fig. 2).

Figure 2. Regression coefficients from clay, OC and clay/OC ratio PLSR models.

CONCLUSION

The results of this study show that vis-NIRS can provide very successful and direct determination of clay/OC ratio on a field scale through its correlation to both OC and clay. Further studies across different soil types will be conducted.

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