

DETERMINATION OF SOIL ORGANIC CARBON VARIATION WITH ON-LINE Vis-NIR SENSOR

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Abstract— Vis-NIR spectroscopy was reported by many researchers confirming the possibility of successful measurement of soil organic carbon (SOC) which was attributed to the direct spectral response of carbon in the NIR range. In this research, SOC variability was measured in two cropping seasons with an on-line vis-NIR sensor in a field with a clay soil, 10 ha area in Karacabey Farm in Bursa, Turkey. The performance and accuracy of the SOC calibration model was evaluated in cross-validation after partial least squares regression (PLSR) and independent validation. Model performance was evaluated by means of coefficient of determination (R^2), root mean square error of prediction (RMSEP) and ratio of prediction deviation (RPD). Three categories of SOC maps were developed: 1) reference laboratory analyses maps based on 92 points 2) Full-data point maps based on all 6486 on-line points Vis-NIR predicted in 2013 and 3) full-data point maps based on all 2496 on-line points Vis-NIR predicted in 2015. Results show that SOC calibration model in cross-validation results is fairly accurate ($R^2 = 0.75$, RMSEP = 0.17 % and RPD=1.81). According to the classification of RPD values, the performance of the SOC in cross-validation is classified as good. Based on 3297 points map shows the variation of the SOC at high sampling resolution. According to the SOC level of the field, 80 ton/Ha manure has been applied to the field. A year later the manure influence on SOC was measured with the on-line vis-NIR soil sensor.

Keywords— On-line soil sensor, Proximal soil sensing, Soil organic carbon, Vis-NIR spectroscopy.

I. INTRODUCTION

One of the most rapid and promising technique of soil analysis for precision agriculture (PA) applications is the visible and near infrared (vis-NIR) spectroscopy. This non-destructive analytical method can be applied to enhance or replace conventional methods of soil analysis. Vis-NIR spectroscopy is one of the main methods that have been explored. Soil organic carbon (SOC), the major component of soil organic matter, is extremely important in all soil processes. There is a continuous cycle of SOC in soils that is not uniform and dependent mostly on land use and land management systems. Therefore, even small changes in SOC stocks cause important CO₂ fluxes between terrestrial ecosystems and the atmosphere [1]. The conventional analytical methods used for the determination of SOC are expensive, complex and time-consuming. Consequently, researchers have been attempting to find alternative solutions that are fast, simple and cost-effective. Vis-NIR spectroscopy was reported by many researchers [2-5] confirming the possibility of successful measurement of SOC which was attributed to the direct spectral response of carbon in the NIR range. This can be attributed to the fact that, by using suitable chemometric methods, large sets of spectral information can be extracted from the Vis-NIR spectra of soils. The complex relationship between spectral signatures and soil properties can be better modeled via multivariate regression methods, which have an advantage over the simple bivariate relationships, e.g., those based on peak intensity measurements [6]. Partial least squares (PLS) regression is the most common technique

adopted today to model the relationships between the infrared spectral intensity characteristics of the soil components and the soil properties through derived PLS loadings, scores, and regression coefficients [7]. The PLS regression establishes a series of components or latent vectors that provide a simultaneous reduction or decomposition of X and Y such that these components explain, as much as possible, the covariance between X and Y [8]. One of the advantages of PLS regression compared to other chemometric methods, such as principal component regression analysis, is the possibility of interpreting the first few latent variables, because these show the correlations between the property values and the spectral features [9]. The calibration samples should cover the variability expected in the full sample set, and the future unknown data and the validation (test) set must be independent of the calibration set in order to avoid an optimistic assessment of predictive performance [6, 10, 11].

Although Vis-NIR is an analytical technology adapted to specifications and becoming a very popular analytical technology in soil science, it is still steps away from being used as a routine analytical tool, both in field and laboratory [12]. Recent advances in proximal soil sensing techniques indicate that on-line sensors are capable of providing trustful and high resolution data on some fundamental soil properties including SOC. Among available techniques, vis-NIR spectroscopy proved to be the most capable technology for on-line characterization and quantification of within field variation in soil properties [13-16]. The aim of this study was to explore the potential of a Vis-NIR on-line sensor to

measure SOC. Laboratory-measured and on-line Vis-NIR predicted maps were produced and used with independent validation sample sets. Based on 3297 points, maps of SOC were produced after manure applications, and these maps were then compared to corresponding maps from the previous year. This comparison showed variations in SOC that were attributed to the manure application implemented in the preceding year.

II. DETAILS EXPERIMENTAL

2.1. On-line sensor

A simple metal frame for the on-line sensor was manufactured at Uludag University using the patented design [17] of A.M. Mouazen. The optical unit was attached to the backside of the subsoiler chisel in order to acquire soil spectra from the smooth bottom of the trench in the diffuse reflectance mode. The subsoiler (acting as a soil-cutting tool) and the optical probe were set on the metal frame. The on-line soil sensor was then mounted on the three-point linkage of a tractor for collecting soil spectra under mobile conditions. The sensor was equipped with an AgroSpec mobile, fiber-type vis-NIR spectrophotometer (Tec5 Technology for Spectroscopy, Germany) to measure the soil spectra. A differential global positioning system (DGPS) (EZ-Guide 250, Trimble, USA) was used to record the position of the on-line-measured spectra with sub-meter accuracy

2.2. Experimental site

This study was carried out in the irrigated field of 10.06 ha area located in Karacabey village, in Bursa Province. For laboratory analysis total of 92 soil samples were collected from the field, respectively, from the bottom of the trench opened by the subsoiler (Fig 1a). The 92 soil samples were equally divided into two parts. The first half was used for laboratory reference measurements of SOC and particle size distribution (PSD) and the second half was used for optical scanning in the laboratory. SOC was measured with help of the Walkley-Black method [18]. The PSD was measured by sieving and sedimentation method [19]. PSD analyses result were used to determine the texture class using the United State Department of Agriculture classification system (Table 1).

Table 1: Particle size distribution

Crop	Sand, %	Silt, %	Clay, %	Texture Type
Wheat	26.6	30.4	43	Clay

In the year 2013, raw spectra were collected along with parallel transects at a speed of approximately 3 km h⁻¹ (Fig. 1b). Same application were done in year 2015. Sampling lines and sampling positions are shown in Fig 1c.

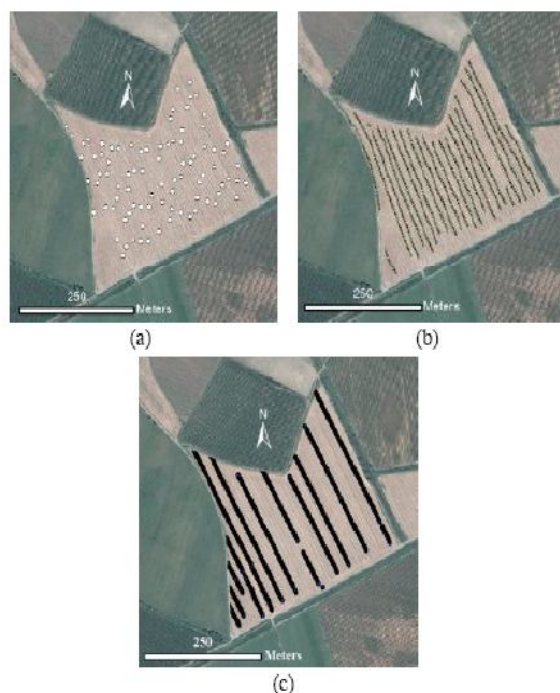


Fig. 1. Field location in Karacabey, Turkey: (a) soil sampling positions, (b) on-line soil measurement points (2013), and (c) on-line soil measurement points (2015)

2.3. Laboratory analyses

The 92 soil samples (Fig. 1a) were equally divided into two parts. The first half was used for laboratory reference measurements of SOC and particle size distribution (PSD), and the second half was used for optical scanning in the laboratory. Soil samples were scanned in the laboratory using the same Vis-NIR spectrophotometer employed during the on-line field measurements. Each sample was put into three plastic cups (1.2 cm deep and 1.2 cm in diameter) and carefully levelled to form a smooth scanning surface. A white reference was scanned before the soil scanning, which was repeated every 30 min. Each cup was scanned 10 times, and the readings were averaged. The final spectrum for each sample, to be used for further analysis, was the average of the three spectra obtained for the three cups.

2.4. Model establishment

Since the number of soil samples collected in the field was relatively small to build a field scale calibration, 324 external soil samples collected from other fields across Europe were used. These samples were divided as follows: 147 samples were collected from Vindumovergaard Farm (Denmark), 82 samples from Duck End farm (UK), 21 samples from Shrewsbury field (UK), 34 samples from Ten Acre Meadow Farm (UK), 16 samples from Ely Farm (UK), 10 samples from MespølMedlov, A.S. (Czech Republic) and 14 samples from Wageningen University experimental farm (Netherlands) [20, 21]. A total of 67 samples from the Karacabey field were pooled together in one matrix with the 324 external samples. The remaining 25

samples were used for validation of the laboratory scanned vis-NIR measurements. The calibration matrix set of 391 (67+324) was used to develop the SOC calibration model. The calibration spectra were pretreated. Firstly, the raw spectra at both edges were trimmed to get the final wavelength range of spectra (370 to 2150 nm). Secondly, soil spectra were averaged for three and fifteen neighboring wavelengths in the ranges of 370-1000 nm and 1001-2150 nm, respectively. This was followed by maximum normalization, 1st Savitsky-Golay derivation, and smoothing with Savitsky-Golay method [4]. The pre-treated spectra and the results of laboratory chemical analyses were used to develop the calibration model for SOC. PLS regression with one-leave-out cross validation was carried out using the calibration set to develop SOC calibration model using Unscrambler 7.8 software (Camo Inc.; Oslo, Norway).

Table 2. Sample statistics of laboratory and on-line measured SOC (%) of the calibration and independent validation sets

Karacabey Field	Sample number	Min, %	Max, %	Mean, %	SD, %
All field samples	92	0.81	1.93	1.41	0.22
Cross-validation set	391	0.79	2.64	1.41	0.31
Laboratory validation set	25	0.98	1.66	1.44	0.17
On-line validation set	25	0.85	2.01	1.29	0.28

The performance and accuracy of the SOC calibration model was evaluated in cross-validation and independent validation. The independent on-line validation was carried out using the on-line soil spectra of the validation set of 25 soil samples. Model performance was evaluated by means of coefficient of determination (R^2), root mean square error of prediction (RMSEP) and ratio of prediction deviation (RPD) that is standard deviation divided by RMSEP. Sample statistics of the calibration and independent validation sets for SOC model are shown in **Table 2**.

2.5. Map development

All maps were developed using ArcGis 10 (ESRI, USA) software. Three maps were used for the comparison of chemical properties. The first one was for the laboratory measurement points based on 92 soil samples measured in 2013. The second one was for the on-line measurement in 2013 based on 6486 points. The inverse distance weighing (IDW) interpolation method was used to develop the laboratory-measured maps. The full-point maps were developed via the Kriging interpolation. Kriging is a statistical method used in diverse application modeling. Kriging is most appropriate when you

know there is a spatially correlated distance or directional bias in the data.

2.6. Fertilizer applications

Amount of N, P₂O₅, K₂O(kg) applied for the entire field are shown in **Table 3**.

Table 3. Total amount of N, P₂O₅, K₂O application for the entire field.

Years	Manure (ton)	N (kg)	P ₂ O ₅ (kg)	K ₂ O (kg)
2013	-	3264	712	950
2014	800	9740	2710	0
2015	-	8700	6600	2100

III. RESULTS AND DISCUSSION

3.1. Model performance

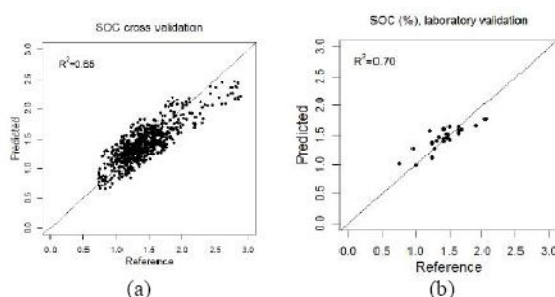
The model performances in cross-validation, laboratory and on-line predictions of SOC for the field are shown in **Table 4**.

Table 4. Summary of SOC model performance in cross-validation, laboratory and on-line validations.

Karacabey Field	R ²	RMSEP, %	RPD	intercept
Cross-validation	0.65	0.17	1.81	0.03
Laboratory validation	0.70	0.15	1.78	0.61
On-line validation	0.60	0.20	1.41	0.25

ViscarraRossel et al., [22] classified RPD values as follows: RPD < 1.0 indicates very poor model predictions and their use is not recommended; RPD between 1.0 and 1.4 indicates poor model predictions, where only high and low values are distinguishable; RPD between 1.4 and 1.8 indicates fair model predictions, which may be used for assessment and correlation; RPD values between 1.8 and 2.0 indicates good model predictions, where quantitative predictions are possible; RPD between 2.0 and 2.5 indicates very good, quantitative model predictions; and RPD > 2.5 indicates excellent model predictions. This classification system was adopted in this study.

Fig. 2 shows the scatter plots of reference versus predicted SOC in cross-validation, laboratory validation and on-line validation.



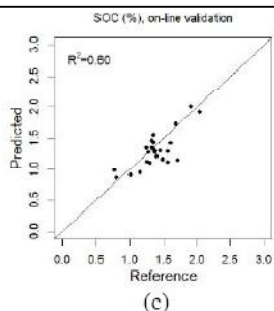


Fig. 2. Scatter plot of predicted versus reference measured SOC (%) for cross-validation (a), laboratory validation (b) and on-line (c) validation sets.

Results show that SOC calibration model in cross-validation results is fairly accurate ($R^2 = 0.65$, RMSEP = 0.17 and RPD=1.81). According to the classification of RPD values proposed by Viscarra-Rossel *et al.* [22], the performance of the SOC in cross-validation is classified as good. This finding is in coherence with earlier reports by Udelhoven (with $R^2 = 0.60$ and RMSEP = 1.4 %) [23] and by Dunn *et al.* (with $R^2 = 0.66$ and RMSEP = 2.5) [24]. However, better results were reported by Chang *et al.*, ($R^2 = 0.89$, RMSEP = 6.2) [25] and Islam *et al.* ($R^2 = 0.81$, RMSEP = 3.5) [26].

3.2. Mapping

From the Fig. 3, SOC ratio has been increased in 2015. The reason for this is the manure application of 80-90 ton/Ha.

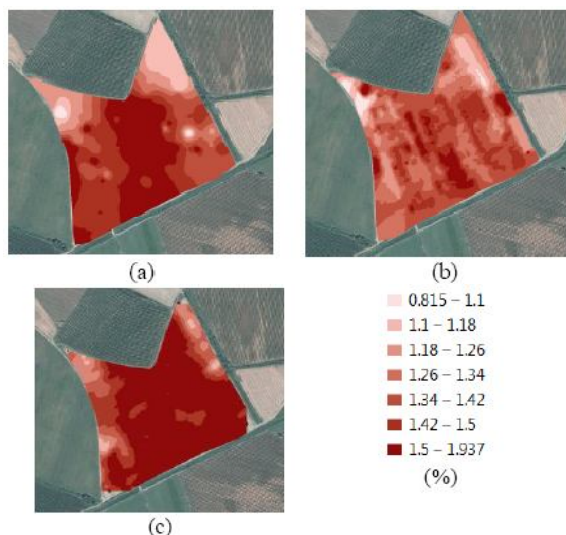


Fig. 3. SOC Comparison maps between laboratory measured based on 92 samples (a), on-line vis-NIR predicted (6486 points) measured in 2013 (b) and on-line vis-NIR predicted (2496 points) measured in 2015 (c)

CONCLUSIONS

This study described the potential of visible and near infrared (Vis-NIR) spectroscopy for the measurement of soil organic carbon in fields with clay soils in a semiarid environment in Turkey. The results were evaluated under laboratory and on-line field

measurement conditions. Major conclusions are as follows:

1. Vis-NIR spectroscopy can be successfully used for the measurement of SOC in clay soils under semiarid conditions.
2. The Vis-NIR prediction maps of SOC were similar to the corresponding measured maps. However, with the full-point maps, more details showing different spatial distribution were observed compared to the maps developed with a limited number of points.

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