Published August 25, 2014

Sensing of Soil Organic Carbon Using Visible and Near-Infrared Spectroscopy at Variable Moisture and Surface Roughness

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Variations in soil moisture and surface roughness are major obstacles for the proximal sensing of soil organic C (SOC) using visible and near-infrared spectroscopy (VIS-NIRS). We gained a significant improvement of SOC prediction under field conditions with a stepwise approach. This comprised of (i) the estimation of these disturbing factors and (ii) the subsequent use of this information in multivariate SOC prediction. We took 120 surface soil samples (SOC contents 6.55–13.40 g kg^{-1}) from a long-term trial near Bonn, Germany. To assess soil moisture, we recorded VIS-NIR spectra on <2-mm sieved disturbed samples at seven different moisture levels (air-dried to 30% w/w). The impact of roughness on VIS-NIRS performance was studied with undisturbed samples (air-dried and at different moisture levels), which were scanned with a laser profiler after fractionation into six aggregate size classes. The results confirmed that it was possible to include VIS-NIRS based assessments of soil moisture [R^2_{adj} = 0.96; root mean square error of cross validation ($RMSE_{cv}$) = 1.99% w/w] into the prediction of SOC contents for sieved samples <2 mm (R^2_{adj} = 0.81–0.94; $RMSE_p$ = 0.41–0.72 g SOC kg^{-1}). However, for rough soil surfaces, SOC contents were overestimated, and the prediction of roughness indices using VIS-NIRS failed. Fortunately, surface roughness did not impair the VIS-NIRS assessment of soil moisture. Hence, we could directly estimate moisture via VIS-NIRS in undisturbed field samples and then incorporate this information into a moisture-dependent prediction of SOC contents. This provided accurate SOC estimates for field-moist, undisturbed samples (R^2_{adj} = 0.91). Deviations from the reference method (elemental analysis) were below 2 g SOC kg^{-1}.

Abbreviations: AIC, Akaike information criterion; PLSR, partial least square regression; R_a, arithmetical mean roughness; $RMSE_{cv}$, root mean square error of cross validation; $RMSE_P$, root mean square error of prediction; RPD, relative percent deviation; *Rz*, surface roughness depth; S^2/L, ratio of the mean variance of the height over the projected sampling length; SOC, soil organic C; VIS-NIRS, visible and near-infrared spectroscopy.

Many soil properties including SOC exhibit pronounced heterogeneity in the field. The accurate assessment of SOC patterns, traditionally using elemental analysis or wet digestion, is time-consuming and costly. Hence, sensor techniques are increasingly used for rapid determination of soil properties in the field. Among them, VIS-NIRS (350–2500 nm) combined with multivariate calibrations have proven their potential for a rapid assessment of SOC heterogeneities (Bellon-Maurel and McBratney, 2011; Ladoni et al., 2010). Yet, variations in soil moisture and surface roughness are still major obstacles for VIS-NIRS applications in the field. The commercially available Veris device is designed to flatten the subsurface to assist measurement. However, the shank-based

Soil Sci. Soc. Am. J. 78:949–957
doi:10.2136/sssaj2013.07.0264
Received 5 July 2013.
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systems operating in the plow layer have limitations (Reeves, 2010; Kuang et al., 2012): The sapphire window and the steel housing are mechanically stressed (Reeves, 2010); mechanical impacts like vibrations and varying contact angles influence the results; and gravels, stable macroaggregates, clods, and roots may inhibit a close and smooth contact between sensor and soil (Kuang et al., 2012). Further, difficulties arise in taking samples for a proper calibration when taking spectra on-the-go and beneath the surface.

Any VIS-NIR prediction of soil properties relies on calibrations with data acquired in the laboratory, such as the quantitative assessment of SOC on selected dry samples using, for example, using elemental analysis. The moisture content in the field, however, is variable and interferes with spectral reflectance and the correct VIS-NIRS assessment of soil properties (Bogrekci and Lee, 2006; Lobell and Asner, 2002; Udelhoven et al., 2003). Nocita et al. (2013), thus, recommended the use of normalized soil moisture indices (NMSI; Haubrock et al., 2008) for predicting SOC in imaging spectroscopy. Soil surface is also rarely smooth, particularly when roughness is not manipulated. Rough surfaces change spectral reflectance (Fontán et al., 2010; Wu et al., 2009) and interfere with the spectral assessment of SOC. To advance the on-site or even remote assessment of SOC using VIS-NIR spectroscopy, one option is to limit the spectral information to those regions that mainly determine the target variable (Stenberg and Viscarra Rossel, 2010). This, however, is difficult when the disturbing impact is fairly unspecific. One further option is to improve current prediction models so as to include spatiotemporal variations of soil moisture and surface roughness.

The presence of water generally reduces the VIS-NIR reflectance. Wetting induces a darkening of the soil and smoothes the spectra, particularly brightness in the shortwave VIS region (Stenberg, 2010). Nevertheless, the related overtoning of O-H stretching near 1400 nm and combinations of H-O-H bending and O-H stretching near 1900 nm can be used for a NIRS based assessment of soil moisture content (Daughtry and Hunt, 2008; Mouazen et al., 2005; Viscarra Rossel and Behrens, 2010). Spectra from moist samples were included into the prediction models of SOC (Viscarra Rossel et al., 2009) or additional orthogonalization algorithms could be applied to remove the soil moisture effects from spectra (Minasny et al., 2011; Roger et al., 2003). All these analyses still required that the soil sample was smooth.

Soil surface roughness causes light scattering effects and therewith also decreases the reflectance in the VIS-NIR region, which then adds to the loss of reflectance when the sample is moist. In the laboratory it is possible to quantify soil surface roughness using noninvasive mechanical or laser profiler techniques with a subsequent calculation of roughness indices (e.g., Mattia et al., 2003; Sun et al., 2006; Zribi and Dechambre, 2003). These indices are computed from field height measurements of the soil microrelief within a one-dimensional transect or a two-dimensional grid. However, it might also be possible to predict surface roughness indices using VIS-NIR spectra (Fontán et al., 2010; Wu et al., 2009), therewith opening the chance to categorize and include this information into VIS-NIRS based calibration models for sensing SOC in the field. The computing of roughness certainly depends on the distance between the VIS-NIR sensor and the soil surface and covers a huge range from proximal sensing applications up to remote sensing purposes. In any case, as both soil moisture and surface roughness vary in space and time, any SOC survey in the field must be able to cope with these disturbing factors.

The main objective of this study was to classify moisture and roughness via VIS-NIR spectra and to use this information for the prediction of SOC contents under field conditions. To do so, we concentrated on the variation of SOC contents within a given long-term agricultural field trial (Luvisols). Samples from this field were manipulated in the laboratory (aggregate fractionation, moistening) to get a sound basis for analyzing the mutual reactions between variable moisture and roughness conditions, SOC level, and the shape of the corresponding VIS-NIR spectra.

MATERIALS AND METHODS

Field Site and Sampling

We sampled a long-term fertilization trial of approximately 3.7 ha installed in 1904 at the Dikopshof experimental station near Bonn, Germany (Lower Rhine Basin, 50°48′29″ N lat; 6°57′11″ E long; Körschens, 1997; Mertens, 1952). The soils comprised Haplic Luvisols from loess. The overall trial comprised 24 independent variants and five replications (total n = 120 plots; plot size 18.5 by 7 m) with variable combinations of organic manuring and inorganic fertilizer applications as described by Schellberg and Hüging (1997).

Sampling was performed in different campaigns, also depending on the purpose of analyses. Overall we sampled 2 × 2 different sample sets:

1. Sample Set A: Disturbed samples across all plots, sieved to <2 mm, for spectral acquisitions without pronounced roughness effects. This set was later randomly subdivided into set A1 for calibrating soil moisture content, and set A2, which was ground to obtain truly smoothed surfaces.

2. Sample Set B: Undisturbed samples from 24 experimental plots, which maintained their original surface roughness. This set was later randomly subdivided to set B1, which was dried for roughness assessment with a laser profiler, and set B2, in which this analysis was repeated for variable moisture contents.

In detail:

We first collected disturbed topsoil samples (0–30 cm) in a radial sampling scheme from each of the 120 plots using a Pürckhauer soil corer (internal diameter 0.018 m). These samples were air-dried, sieved to <2 mm and then placed in petri dishes without exerting pressure or particle size stratifications at the sample surface. They were then used for testing the moisture effects on VIS-NIR reflectance (Sample Set A1). A subset of the sieved samples was ground and the surface was additionally smoothed with a stamp (Sample Set A2).

For the estimation of surface roughness and its effect on VIS-NIR reflectance, we took undisturbed field surface samples by carefully preparing soil blocks with a spade (approximately 30 by 20 cm surface area, approximately 2 kg weight) from 24 plots of the Dikopshof fertilization trial. These 24 plots comprised all experimental variants, that is, the full range of SOC contents. The undisturbed soil surface after field cultivation was visually differently aggregated, but the estimated size of clods and other agglomerations maintained a size of up to 30 mm. Two independent samples per plot were carefully transported in cardboard boxes to the laboratory. The first set of the 24 samples (Sample Set B1) was dried at 40°C for roughness index estimation with a laser profiler (see below, Roughness Determination with a Laser Profiler) and subsequent VIS-NIR spectra acquisitions (section VIS-NIR Reflectance Acquisition). Sample Set B2 was subjected to eleven air-drying steps over 2 wk, and the VIS-NIR spectra were concomitantly taken from the undisturbed rough surface of the samples. The latter procedure allowed us to record the spectral reflectance of identical samples at a wide range of moisture content. This helped us to improve our calibrations and to evaluate the impact of soil moisture on VIS-NIR performance using undisturbed, that is, rough samples.

Sample Pretreatment for Estimating Soil Moisture Contents

The air-dried, sieved samples from Sample Set A1 were stepwise wetted to 5, 10, 15, 20, 25, and 30% w/w, respectively, for the subsequent VIS-NIRS based prediction of soil moisture content. The water was carefully added with a spray flask to achieve a uniform, dispersal wetting of the samples without inducing any changes of the smooth surface. Each sample was stored until the added water was absorbed by the soil; thereafter, samples were allowed to equilibrate for approximately 20 min before recording the VIS-NIR spectra for each moisture class. Care was taken that the added water close to the upper moisture limit (30% w/w) did not form an aqueous phase on the scanned sample surface.

The final sample set (B2) comprised field-fresh samples. Their initial moisture content varied between 21.6 and 29.2% w/w (24.7 ± 1.9% w/w mean ± SD). The samples were then subjected to 11 air-drying steps over 2 wk with a gravimetrically monitoring of the soil moisture contents. After each step of air-drying, the VIS-NIR spectra were recorded as outlined above. The scanned area had the same size as that used for the sieved samples of Set A1. To account for roughness variations on the soil surface, we recorded five VIS-NIR spectra, each in random positions of the scanned spots.

Sample Pretreatment for Estimating Soil Surface Roughness

The air-dried samples from Sample Set B1 were dry sieved into six aggregate classes (<2, 2 to <5, 5 to <8, 8 to <16, 16 to <20, and 20 to <25 mm). A seventh class was prepared by grinding aggregates of the finest class. Thus, 7 × 24 = 168 samples with diverse soil surface roughness conditions were made available. The air-dried aggregate classes were carefully but tightly placed in petri dishes. After scanning with a laser-profiler (section Roughness Determination with a Laser Profiler) each sample was analyzed with the VIS-NIR spectrometer (section VIS-NIR Reflectance Acquisition). This procedure allowed for evaluating the VIS-NIR performance on a controlled range of surface roughness. Afterwards, the aggregate class samples were wetted as described for the sieved and ground samples. The ground samples were used as controls for smooth surfaces, with a surface roughness below the detection limit of the finest 1 by 1 mm resolution of the laser profiler.

Chemical Analyses as Reference Measurements in the Lab

Total C contents were determined by elemental analysis (Fisons NA 2000, Germany; ISO, 1995). The samples were free of carbonates; hence, total C contents corresponded to SOC. These conventionally measured SOC contents of the plow layer (ground-truth data set) varied from 6.55 to 13.40 g SOC kg^{-1} soil. We did not assess the C content of the different aggregate classes, particularly as the sensor only detects the aggregate surface. The C content of the aggregate surface was reported to be similar to that of aggregate cores in cultivated fields (see, e.g., Amelung and Zech, 1996).

Visible and Near-Infrared Reflectance Acquisition

Diffuse reflectance spectra of the soil samples were recorded with a full range VIS-NIR spectrometer (ASD AgriSpec, Analytical Spectral Devices Inc., Boulder, CO) from 350 to 2500 nm with an approximate 3-nm spectral resolution from 350 to 700 nm and a 10-nm spectral resolution at higher wavelengths, respectively. The spectrometer was used in a bare fiber optic configuration with a 25° view angle and an adjusted distance of 5 cm to the soil surface. This resulted in a scan spot of 2.2 cm in diameter (approximately 3.8 cm^2). The illumination was conducted with three lamps, which were calibrated for the sensor unit and adjusted to 24° beam angle (Pro Lamp, Analytical Spectral Devices Inc., Boulder, CO). The lamps were arranged in a triangle position at a height of 35 cm above the sample with a 45° incidence angle. The resulting beam distance between the lamp and the sample surface was approximately 50 cm. At the beginning of each analytical session, the baseline was corrected and the instrument was optimized on a dark current followed by white standard reference measurements (Spectralon II, Labsphere, North Sutton, NH). The VIS-NIR scanning was performed in a dark and climate-controlled room (20°C and 50% relative humidity). For each sample, 50 scans were conducted for the acquisition of a single VIS-NIR spectrum. The total time for gathering the spectra was standardized to approximately 15 to 20 s per sample to avoid heating and drying of the sample. Three replicate spectra per sample were taken (unless otherwise stated) with a slightly modified sample position for each spectrum.

Data Preprocessing and Spectra Transformations for Partial Least Square Regression Analyses

The repeated VIS-NIR spectral acquisitions of each sample (except for calibrations of roughness indices) were merged to a mean diffuse reflectance spectrum. Before partial least square regression (PLSR) modeling, the spectral range was narrowed to 410 to 2300 nm to exclude noisy ranges of the VIS-NIR spectra. For the spectra preprocessing and PLSR modeling, the software ParLes 3.1 was used (Viscarra Rossel, 2008). There have been different spectra preprocessing methods proposed for subsequent data evaluation (e.g., Barnes et al., 1989; Stenberg and Viscarra Rossel, 2010; Viscarra Rossel and Lark, 2009). For this paper, the original reflectance spectra were transformed to absorbance spectra [log (1/R)]. The software ParLes 3.1 allowed the combination of standard normal variate (SNV) transformation, which was used for light scattering and baseline corrections, and the Daubechies wavelet filter with four vanishing moments and mean centering was applied for denoising, enhancement of spectral resolution, and to eliminate background effects (ParLes 3.1; Viscarra Rossel, 2008).

For each sample set, we conducted calibration procedures employing a leave-one-out cross validation. The accuracy and the goodness of fit were expressed by the $RMSE_{cv}$ and the adjusted coefficient of determination (R^2_{adj}), respectively. In accordance with Li et al. (2002) and Viscarra Rossel (2008) the number of factors (also equated with "ranks"), which was calculated by the PLSR model was selected by comparing the minimum of $RMSE_{cv}$ and lowest Akaike information criterion (AIC; Akaike, 1974; Viscarra Rossel, 2008). The AIC (Akaike, 1974) does not only reward goodness of fit but also indicates when the number of selected factors is too high. The best model is the one with the lowest, the most negative AIC value. To avoid the risk of overfitting, the factors for PLSR modeling were kept preferably parsimonious, that is, the procedure minimized the residual variance to keep $RMSE_{cv}$ and AIC low. An iterative reduction was performed to achieve a conservative minimum of factors.

The accuracy of the calibrations and validations for the soil properties were assessed using the RMSE and the relative percent deviation (RPD) (ParLes 3.1; Viscarra Rossel, 2008). The prediction models were verified by test-set validation, meaning that we randomly selected a sample subset that was one-third in volume and that was, thus, not used for PLSR calibration (prediction PLSR; Table 1). All spectra were included in the analyses; no outliers were removed.

Roughness Determination with a Laser Profiler

The three-dimensional surface roughness of the air-dried Sample Sets B1 and B2 was measured with a laser-profiler, manufactured by the Institute of Agricultural Engineering at the University of Bonn (Sun et al., 2006). The scan area was 27 by 27 mm, with a lateral and vertical resolution of 1 by 1 mm, respectively, resulting in 729 three-dimensional data points per scan. The area scanned with the laser profiler was almost identical with the surface area used for VIS-NIR spectra acquisition.

On the basis of the laser-profiler measurements, three different roughness indices were calculated: (i) the ratio of the mean variance of the height over the projected sampling length (S^2/L; Zribi and Dechambre, 2003), (ii) the arithmetical mean roughness, that is, the arithmetical means of the altitude deviations in all one-dimensional transects across the scanned grid divided by surface length (R_a; De Chiffre et al., 2000; Thomas, 1999), and (iii) the surface roughness depth, that is, the averaged arithmetical means from five sequences with constant length inside of each one-dimensional transect, calculated for the whole two-dimensional grid (R_z; De Chiffre et al., 2000; Thomas, 1999).

Table 1. Chemometric parameters of the applied partial least square regression (PLSR) models for the prediction of soil moisture content and soil organic C (SOC) at different moisture levels.

	Predicted variable	Number of samples		Moisture	Aggregate size class	Cross-validation						Prediction				
										Equation$_{CV}$					Equation$_{P}$	
		CV†	P‡	% w/w		R^2_{adj}§	$RMSE_{cv}$¶	RPD#	Rank††	Slope	Offset	R^2_{adj}	$RMSE_{p}$	RPD	Slope	Offset
1	Moisture	560	280	air-dry to 30	<2 mm	0.95	2.32	4.32	2	0.95	0.77	0.95	2.24	4.48	0.96	0.79
2	SOC	80	40	air-dry	ground	0.91	0.63	3.33	8	0.93	0.76	0.90	0.51	3.25	0.93	0.63
3	SOC	80	40	air-dry	<2 mm	0.91	0.62	3.37	7	0.93	0.71	0.94	0.41	4.04	0.99	0.06
4	SOC	80	40	5	<2 mm	0.87	0.74	2.83	8	0.90	1.05	0.87	0.63	2.64	0.97	0.42
5	SOC	80	40	10	<2 mm	0.86	0.76	2.74	8	0.88	1.21	0.83	0.69	2.40	0.93	0.78
6	SOC	80	40	15	<2 mm	0.89	0.68	3.09	8	0.90	0.99	0.81	0.72	2.31	0.86	1.49
7	SOC	80	40	20	<2 mm	0.89	0.67	3.11	8	0.91	0.92	0.79	0.73	2.25	0.80	1.91
8	SOC	80	40	25	<2 mm	0.87	0.75	2.79	8	0.88	1.20	0.83	0.67	2.48	0.89	1.09
9	SOC	80	40	30	<2 mm	0.87	0.73	2.85	8	0.88	1.19	0.89	0.54	3.07	0.94	0.63

† Sample number in leave-one-out cross-validation set (CV).

‡ Sample number in test set for prediction (P).

§ Adjusted goodness of fit.

¶ Root mean square error of cross-validation $RMSE_{cv}$ and prediction $RMSE_{p}$.

Relative Percent Deviation; prediction accuracy excellent (RPD > 2.5), good (RPD 2.0–2.5), and poor (RPD < 2.0; Chang and Laird, 2002; Viscarra Rossel, 2007; Gomez et al., 2008; Stevens et al., 2008).

†† Optimal number of PLSR factors.

RESULTS AND DISCUSSION

The SOC contents were successfully estimated in air-dried, sieved (<2 mm) or ground samples using VIS-NIR spectroscopy and PLSR modeling with excellent accuracy (Table 1; Lines 2 and 3). These results confirmed previous findings of Viscarra Rossel et al. (2006), Stevens et al. (2008), and Stenberg and Viscarra Rossel (2010). When rewetted, as expected, this situation changed and SOC contents were not well estimated.

Impacts of Soil Moisture on Visible and Near-Infrared Spectra Acquisition

Increasing soil moisture content resulted in an increased VIS-NIR absorbance [log (1/R)] of the samples as illustrated in Fig. 1, and consistent with previously reported results (Hummel et al., 2001; Stenberg, 2010; Stenberg and Viscarra Rossel, 2010). This absorption is mainly caused by water based molecular vibrations at wavelengths around 1440 to 1455 nm and 1915 to 1950 nm (Lobell and Asner, 2002; Mouazen et al., 2005; Wu et al., 2009) causing the signal intensities used for prediction of SOC content to be displaced (1100–2500 nm; Lee et al., 2010; Minasny et al., 2011; Morgan et al., 2009; Viscarra Rossel et al., 2006). Furthermore, the soil lightness index (brightness of the sample) used to assess the SOC contents and quality of organic matter in the visible spectral range (400–700 nm; Hummel et al., 2001; Stenberg, 2010; Viscarra Rossel and Behrens, 2010) was displaced (Fig. 1). Consequently, when the model developed for air-dried samples was used to predict SOC under variable moisture conditions, it was not possible to predict SOC contents of the moist samples (Fig. 2; R^2_{adj} = 0.31; RMSE = 5.35 g SOC kg^{-1}).

However, as suggested previously (e.g., Hummel et al., 2001; Stenberg, 2010), the strong influence of water on the spectral reflectance allowed the development of a model for the prediction of soil moisture (Table 1; Line 1). Thus, the spectral data from gradually wetted soil samples (Set A1) were consolidated to a set for moisture prediction (air-dry to 30% w/w). The resulting PLSR model exhibited excellent goodness of fit ($R^2_{adj.}$ = 0.95). The optimal number of ranks for moisture prediction was only two and, thus, much smaller compared with the number of ranks needed for prediction of SOC content (Table 1; Line 1), demonstrating the dominant impact of few water vibrations and soil brightness on the shape of the spectrum.

In a next step, the VIS-NIRS based moisture predictions were then used to develop moisture-dependent PLSR calibrations for SOC prediction. Indeed, it was possible to predict the SOC content for each distinct class of moisture content in the sieved samples (Table 1, SOC prediction, Lines 4–9).

Hummel et al. (2001) suggested that it might be possible to adjust the NIRS assessment of SOC to the water content of the samples. Similarly, Nocita et al. (2013) pointed out that when soil moisture can be estimated from spectra by airborne imaging spectroscopy, SOC contents could be accurately predicted. Nevertheless, in all cases, the simple moisture-dependent assessment of SOC contents, as described in this paper so far and as also suggested by Hummel et al. (2001) or Nocita et al. (2013) still requires that surface roughness to be smooth.

Impacts of Surface Roughness on Visible and Near-Infrared Spectra Acquisition

To test the performance of a VIS-NIR based SOC calibration at different levels of soil surface roughness, we fractionated 24 undisturbed samples (Set B1) into seven aggregate classes. The effect of different degrees of surface roughness on VIS-NIR spectra is shown in Fig. 3. A larger aggregate size, that is, increasing roughness, resulted in an increase in noise by light scattering and, therewith, a loss of total signal intensity (Fig. 3). The general shape of the absorbance curves was comparable, indicating that

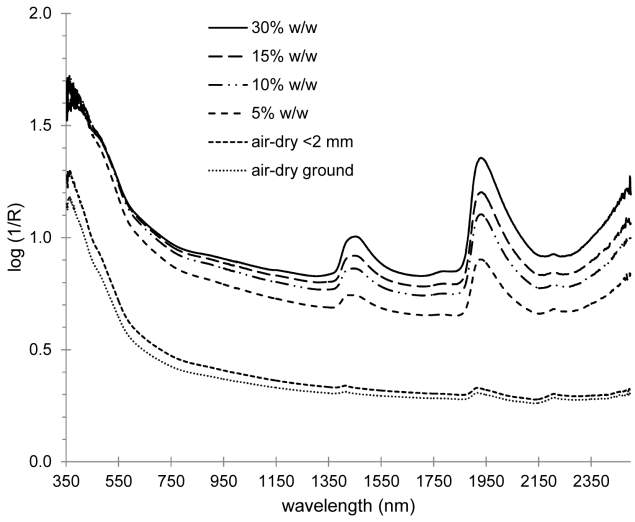

Fig. 1. Effect of grinding and different moisture levels in a sieved (<2 mm) soil sample [soil organic C (SOC) 6.6 g kg^{-1}] on the absorbance spectra [log (1/R)].

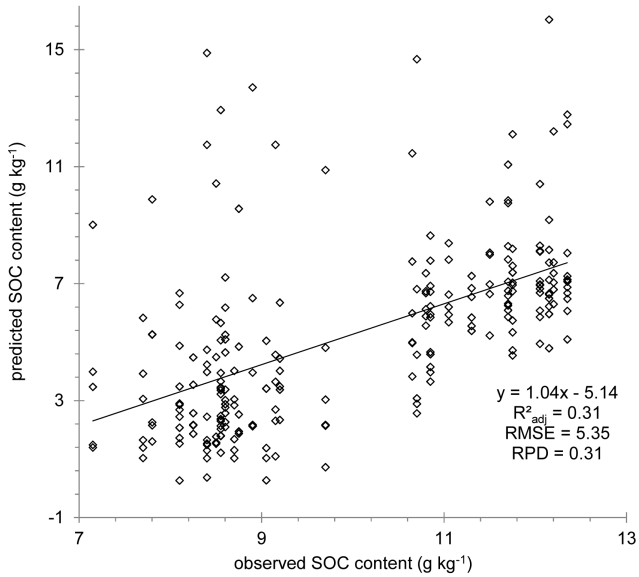

Fig. 2. Predicted SOC contents of moist, sieved (<2 mm) samples (Set A1, stepwise wetted to 5, 10, 15, 20, 25, 30% w/w) vs. observed (= elemental analysis) soil organic C (SOC) contents, based on a SOC calibration using a PLSR model established with air-dried, sieved (<2 mm) soil samples.

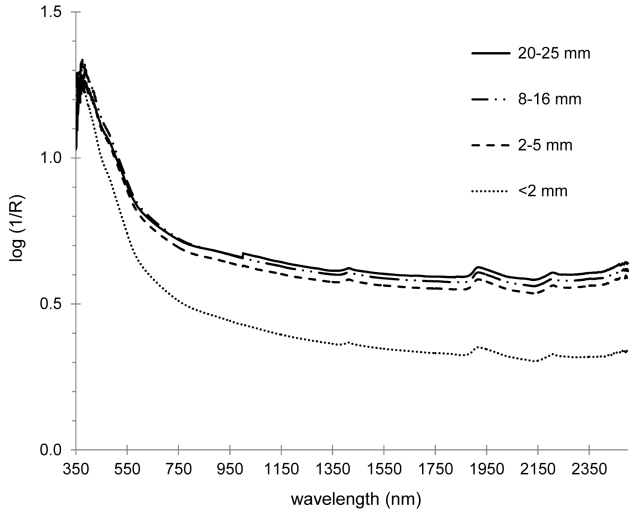

Fig. 3. Effect of increasing aggregate size diameters on the absorbance spectra [log (1/R)] of an air-dried soil sample (10.2 g SOC kg^{-1} soil). SOC, soil organic C.

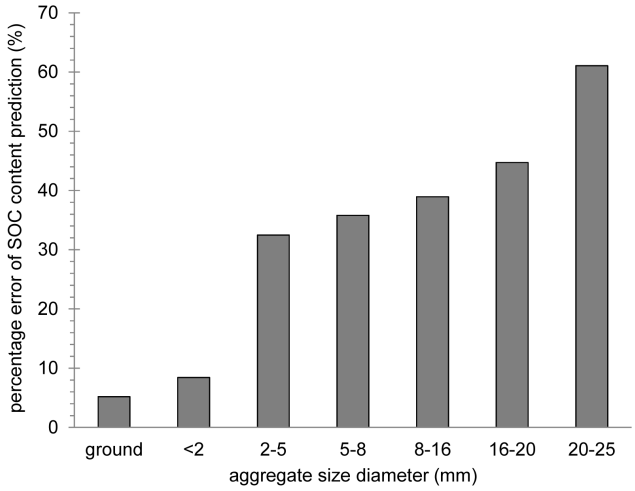

Fig. 4. Effect of grinding and an increasing aggregate size diameter on the percentage deviation of predicted soil organic C (SOC) contents from reference values (= elemental analysis), based on a SOC calibration using a partial least square regression (PLSR) model established with air-dried, sieved (<2 mm) soil samples.

surface roughness induced only a loss of diffuse reflectance and did not alter the different vibrations of the molecules themselves. Nevertheless, when a SOC model calibrated on dry smooth soil surfaces was applied to our aggregated samples (Set B1), the prediction quality decreased strongly with increasing aggregate size. The SOC contents were accurately predicted only for the dried, ground samples, but when aggregate size increased, the model finally produced a bias: the SOC contents were overestimated by up to 61% relative to the reference values determined by conventional elemental analysis for the fraction comprising aggregates of 20 to 25 mm (Fig. 4).

To quantitatively account for roughness differences in Sample Set B1, we first calculated various roughness indices using data from a laser profiler (see section Roughness Determination with a Laser Profiler). Table 2 summarizes the mean values of the indices and their standard deviation for the six aggregate size classes (no roughness calculation performed for ground samples). All tested indices increased with increasing aggregate diameter. Within the given aggregate classes the S^2/L index revealed the highest variability (see SD values in Table 2). The correlations of the roughness indices to the mean aggregate diameters were linear for R_a, but logarithmic [$y = 0.96 \ln(x)$] for R_z ($R^2 = 0.88$ and 0.86, respectively; Table 2). The S^2/L index was also highly variable among the different size classes (see above) and, thus, rather weakly correlated with the mean aggregate diameter ($R^2 = 0.41$; Table 2).

In the next step, we tried to estimate the roughness parameter using PLSR analyses of the spectra. Although the indices represented different approaches to characterize surface roughness, we failed to produce precise and robust PLSR models for their VIS-NIRS based prediction (Table 3, roughness indices prediction, Lines 2–7). Independent of moisture level, this modeling resulted only in an adjusted goodness of fit of $R^2_{adj} = 0.56$ to 0.81 (Table 3, Lines 2–7). Hence, soil surface roughness may be parameterized by different indices using a laser profiler, but these indices cannot be predicted using PLSR analyses of VIS-NIR spectra.

The PLSR modeling of SOC contents for air-dried samples separated in aggregate size diameters showed good results for rough surfaces (Table 3; Line 8), but as indicated this modeling

Table 2. Mean roughness indices of air-dried aggregate size classes (standard deviations are shown in parentheses).

Roughness Index	Aggregate Size Class, Diameter in mm						Correlation†		
	<2	2 to <5	5 to <8	8 to <16	16 to <20	20 to <25	R^2	Slope	Offset
S^2/L‡	0.09 (0.03)	0.28 (0.13)	0.43 (0.14)	0.64 (0.27)	0.83 (0.36)	1.25 (0.99)	0.41	0.05	0.07
R_a§	0.56 (0.09)	0.88 (0.07)	1.34 (0.12)	1.95 (0.20)	2.51 (0.54)	3.11 (0.51)	0.88	0.12	0.50
R_z¶	1.11 (0.18)	2.08 (0.17)	2.90 (0.26)	3.42 (0.34)	3.78 (0.54)	4.11 (0.68)	0.86	0.96#	1.04

† Linear correlation between mean aggregate diameter of the respective aggregate size class and roughness indices with coefficient of determination and equation parameters.

‡ S^2/L, the ratio of the mean variance of the height over the projected sampling length; Zribi and Dechambre, 2003; Fontán et al., 2010).

§ R_a, the arithmetical mean roughness with $R_a = \frac{1}{n}\sum_{i=1}^{n}|Zi|$ where Zi is the deviation of a single measurement from the mean of all measurements, and n is the number of measurements (De Chiffre et al., 2000; EN ISO, 1998; Thomas, 1999).

¶ R_z, the surface roughness depth: mean of five Z values from five sampling lengths over the total measured length (De Chiffre et al., 2000; EN ISO, 1998; Thomas, 1999) with $R_z = \frac{Z_1 + Z_2 + Z_3 + Z_4 + Z_5}{5}$ where Zi is the maximum profile height difference in a single sampling length.

Logarithmic relation [$y = 0.96 \ln(x)$].

Table 3. Chemometric parameters of the applied partial least square regression (PLSR) models for the prediction of soil moisture content, soil surface roughness, and soil organic C (SOC) in samples with different moisture contents. Calibrations rely on all aggregate size classes under study (ground, <2, 2 to <5, 5 to <8, 8 to <16, 16 to <20, 20 to <25 mm).

	Predicted variable	Number of samples†	Moisture	Cross-validation PLSR					
								Equation	
			% w/w	R^2_{adj}‡	$RMSE_{cv}$§	RPD¶	Rank#	Slope	Offset
1	Moisture	1176	air-dry to 30	0.96	1.99	5.03	2	0.96	0.59
2	S^2/L††	504‡‡	air-dry	0.73	0.09	1.74	4	0.92	0.02
3	R_a††	504‡‡	air-dry	0.56	0.31	1.07	4	0.98	0.13
4	R_z††	504‡‡	air-dry	0.80	0.45	1.65	3	0.83	0.44
5	S^2/L††	1032	air-dry to 30	0.68	0.21	1.79	5	0.68	0.18
6	R_a††	1032	air-dry to 30	0.57	0.31	1.08	4	0.97	0.13
7	R_z††	1032	air-dry to 30	0.81	0.45	1.65	3	0.83	0.44
8	SOC	504	air-dry	0.86	0.69	2.70	7	0.82	1.72
9	SOC	1176	air-dry to 30	0.84	0.75	2.49	8	0.84	1.53
10	SOC	504	air-dry to 10	0.84	0.73	2.53	8	0.85	1.44
11	SOC	504	10 to 20	0.86	0.70	2.65	8	0.87	1.32
12	SOC	504	20 to 30	0.88	0.64	2.92	8	0.89	1.11

† Sample number in leave-one-out cross-validation set (CV).

‡ Adjusted goodness of fit.

§ Root mean square error of cross-validation $RMSE_{cv}$ and prediction $RMSE_p$.

¶ Relative percent deviation, see Table 1.

Optimal number of PLSR factors.

†† Roughness indices, see Table 2.

‡‡ 168 aggregate class samples, with three separate spectral acquisitions from different sample spots on rough surface.

was absolutely insufficient in the case of moist samples (Test Set B2; $R^2_{adj} = 0.02$; RMSE = 14.44 g SOC kg^{-1}). Intriguingly, the assessment of soil moisture by VIS-NIR spectroscopy was not affected by soil surface roughness, and almost identical moisture predictions on undisturbed soil surface (Test Set B2; Table 3, moisture calibration, Line 1) were received regardless of whether calibration was performed with sieved samples (<2 mm; two factors needed for calibration; Table 1, Line 1) or with the aggregate classes up to 25 mm in diameter (again only two factors needed for calibration; Fig. 5; Table 3, moisture prediction, Line 1).

As a first summary, the implementation of rough samples did not result in an elevated number of factors in the PLSR calibration, but it even decreased the deviations of the moisture prediction (test set B2). Hence, splitting the samples into different aggregate size classes resulted in a different PLSR model for moisture prediction. However, it did not affect the quality of moisture prediction in comparison to that performed for smooth (<2 mm sieved) samples. When the moisture content was smaller than approximately 10% (w/w), the predicted results differed from the 1:1 line (Fig. 5), likely because the sample surface scanned by the VIS-NIR sensor had dried out relative to the remaining bulk of the sample (cf. Hummel et al., 2001). Similarly, larger deviations from the 1:1 line occurred at higher moisture contents, likely because not all of the added water had really reached all inner pores. We, therefore, attribute these findings to a general problem in spectroscopic sensing: the water detected by VIS-NIRS is not identical with that determined by gravimetric analysis (see also Mouazen et al., 2006; Nocita et al., 2013). With respect to the objectives of this study, however, it was sufficient to subdivide the samples into sets with intervals of different moisture levels, in our case 0 to <10, 10 to <20, and 20 to <30% (w/w) soil moisture, respectively (Table 3, Lines 10–12).

Due to the lacking impact of surface roughness on the quality of moisture assessment using VIS-NIRS this information allowed us to combine the impacts of moisture and aggregate size classes on spectral signatures of soils and to use both sets of information for PLSR modeling of SOC contents. This means that we predicted the water contents from rough rather than from smooth surfaces, and used this spectral information for SOC prediction. In both cases, we used the statistical procedures needed for PLSR analyses.

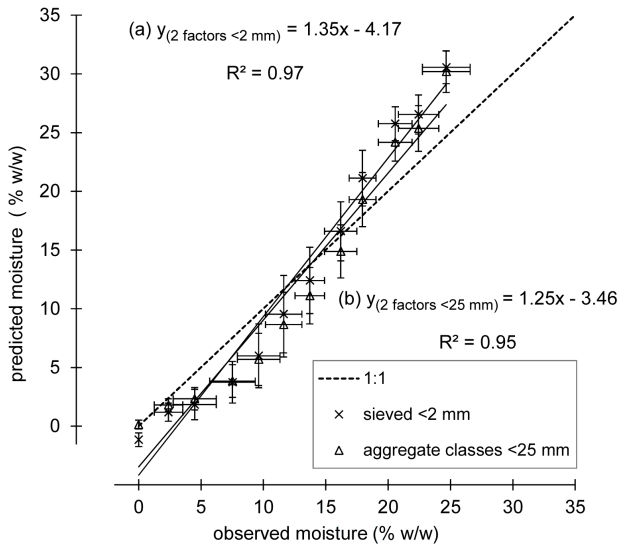

Fig. 5. Predicted moisture in undisturbed surface samples from the field (Set B2) vs. observed moisture (= gravimetric analysis) based on partial least square regression (PLSR) calibration models established with (a) sieved samples (<2 mm) and (b) samples with aggregate size diameters up to 25 mm.

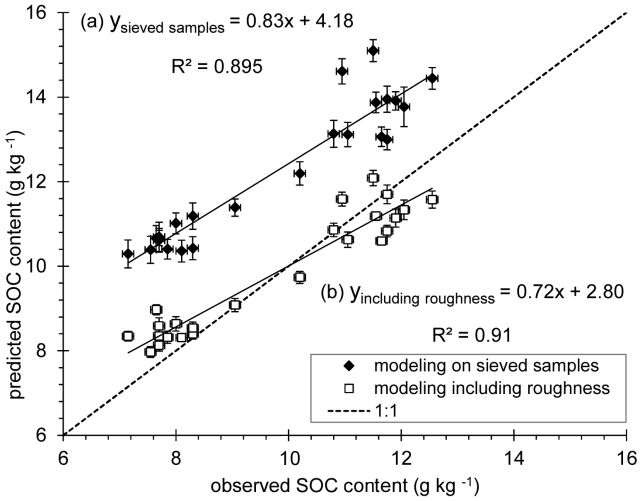

Fig. 6. Predicted soil organic C (SOC) contents in undisturbed field samples (Set B2) after foremost prediction of moisture content in the sample vs. observed (= elemental analysis) SOC contents, based on partial least square regression (PLSR) calibration models with (a) sieved samples (<2 mm) and (b) aggregate classes up to 25 mm. For the SOC calibration models soil moisture was split into three levels [<10, 10 to <20, and 20 to <30% (w/w)].

However, when working with rough instead of smoothed samples, the PLSR analysis accounted for the impact of different surface roughnesses (represented by the different aggregate classes) on the spectral shape and, thus, on the PLSR model. This procedure finally avoided a constant overestimation of SOC contents (of about 4 g SOC kg^{-1}) as occurred if only disturbed samples were used for moisture calibration (Fig. 6).

Overall, we tested four different models with either the full moisture range (Table 3, Line 9) or different moisture classes (Table 3; Lines 10–12), all including aggregates from <2 up to 25 mm. All goodness criteria were satisfactory (R^2_{adj} = 0.84–0.88), but the deviation from the reference values (offset from the 1:1 line) was smaller for higher moisture contents than for lower ones, and the deviation was also smaller when splitting into moisture classes rather than using the whole moisture range for prediction (Table 3).

The moisture- and roughness-dependent PLSR calibration established with Sample Set B1 was finally applied to undisturbed surface samples from the field (Set B2). After prediction of actual moisture contents, the samples were allocated to one of the moisture classes, and the related SOC model was applied to the sample. In all cases, we received satisfactory fits (R^2_{adj} = 0.72–0.83; RMSE = 0.84–0.98 g SOC kg^{-1}). Our data obtained for the disturbed samples, subdividing the samples into intervals of different moisture levels, exhibited better predictions of SOC contents (R^2 = 0.91; Fig. 6) than using a calibration across the full range of soil moisture levels and roughness (R^2_{adj} = 0.66; RMSE = 1.25 g SOC kg^{-1}).

CONCLUSIONS

Variable soil moisture and surface roughness in the field disturb the VIS-NIRS based acquisition of soil parameters like SOC. Here, it was shown that we also may take advantage of these variations to calibrate our models and then include this information into the prediction of SOC contents. The procedure proposed involves, in a first step, the use of VIS-NIR spectroscopy for estimating soil moisture contents in samples of varying surface roughness to use this information for a moisture-dependent calibration of SOC models in field-fresh samples. The estimation of SOC contents was achieved on the basis of PLSR calculations within a spectral range between 410 and 2300 nm, still allowing for evaluating disturbing effects on the shape of VIS-NIR spectra within a single run. All data presented here were obtained on an experimental trial with different fertilizer management but the same soil. The next steps could now be to utilize VIS-NIR spectroscopy as a field technique for SOC assessment under variable moisture and roughness conditions, as well as to extend the algorithms to other soil types and climate regions.

ACKNOWLEDGMENTS

We would like to thank Moni Kasten for her kind assistance in the laboratory. We would also like to thank the associate editor and three anonymous reviewers for their thoughtful comments, which helped to improve the revised version of our manuscript. The project was funded by the German Federal Ministry of Education and Research (BMBF), and the Ministry of Innovation, Science, Research and Technology of the State of North Rhine-Westphalia (Germany). This study was part of the networking sensor technology for plant breeding and crop management (CROP.SENSe.net) research project.

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