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Visible-Near-Infrared Spectroscopy Prediction of Soil Characteristics as Affected by Soil-Water Content

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Soil physical characteristics are important drivers for soil functions and productivity. Field applications of near-infrared spectroscopy (NIRS) are already deployed for in situ mapping of soil characteristics and therefore, fast and precise in situ measurements of the basic soil physical characteristics are needed at any given water content. Visible-near-infrared spectroscopy (vis-NIRS) is a fast, low-cost technology for determination of basic soil properties. However, the predictive ability of vis-NIRS may be affected by soil-water content. This study was conducted to quantify the effects of six different soil-water contents (full saturation, pF 1, pF 1.5, pF 2.5, pF 3, and air-dry) on the vis-NIRS predictions of six soil physical properties: clay, silt, sand, water content at pF 3, organic carbon (OC), and the clay/OC ratio. The effect of soil-water content on the vis-NIR spectra was also assessed. Seventy soil samples were collected from five sites in Denmark and Germany with clay and OC contents ranging from 0.116 to 0.459 and 0.009 to 0.024 kg kg⁻¹, respectively. The soil rings were saturated and successively drained/dried to obtain different soil-water potentials at which they were measured with vis-NIRS. Partial least squares regression (PLSR) with leave-one-out cross-validation was used for estimating the soil properties using vis-NIR spectra. Results showed that the effects of water on vis-NIR spectra were dependent on the soil-water retention characteristics. Contents of clay, silt, and sand, and the water content at pF 3 were well predicted at the different soil moisture levels. Predictions of OC and the clay/OC ratio were good at air-dry soil condition, but markedly weaker in wet soils, especially at saturation, at pF 1 and pF 1.5. The results suggest that in situ measurements of spectroscopy are precise when soil-water content is below field capacity.

Abbreviations: clay/OC ratio, clay/organic carbon ratio; NIRS, near-infrared spectroscopy; OC, organic carbon; OM, organic matter; PC, principal component; pF, matric potential in log₁₀ (| -cm H₂O |); PLSR, partial least squares regression; R², coefficient of determination; RMSECV, root mean square error of cross-validation; RPIQ, ratio of performance to inter-quartile range; RPD, ratio of performance to deviation; vis-NIR, visible-near-infrared; vis-NIRS, visible-near-infrared spectroscopy.

Core Ideas

- The soil-water retention characteristics govern the water effect on soil vis-NIR spectra.
- Soil clay, silt, sand content, and the water content at pF3 can be predicted with high degree of accuracy using spectroscopy at any field moisture condition.
- The OC and the derived properties of OC showed poorer prediction when the soil-water content exceeds field capacity (pF<2).

Soil physical characteristics are important drivers for soil functions and productivity. Soil texture and soil OC are important soil characteristics that affect soil structure and quality, and have important implications for agricultural productivity, soil degradation, water retention, hydraulic conductivity, and fertility of soil. Both clay and OC in the soil can be present in complexed and non-complexed forms and the quantification of these forms is more important in terms of soil degradation and soil functions than the absolute contents of clay or OC (Dexter et al., 2008). Dexter et al. (2008) introduced a threshold limit for the Dexter ratio of total clay to OC of between 8 and 11 (average of 10), which means that one unit of OC can complex with approximately 10 units of clay and the excess clay or OC is present in non-complexed form. The concept of “clay saturation” by OC is important for understanding the soil structure, functional behavior, and

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the ability of soil to self-organize the structure after a breakdown (de Jonge et al., 2009; Dexter et al., 2008). However, the analysis of these soil characteristics is very time-consuming and labor-intensive. Hence, there is a strong need to devise fast and precise methods for measuring soil characteristics both in the lab and in the field.

Visible-near-infrared spectroscopy (vis-NIRS) has gained huge popularity in soil science research both in laboratory and field applications (Bellon-Maurel and McBratney, 2011; Knadel et al., 2011; Sørensen and Dalsgaard, 2005; Stenberg et al., 2010; Viscarra Rossel et al., 2006) as a fast and low-cost alternative to conventional soil analysis (Stenberg et al., 2010; Viscarra Rossel et al., 2006). The main attraction is that a single measurement can be used for assessing multiple soil properties and thus a large number of samples can be analyzed within a short time period. The most common application of vis-NIRS includes estimations of basic soil characteristics such as clay, sand, silt, organic matter (OM), OC, and water content (Ben-Dor and Banin, 1995; Chang et al., 2001; Knadel et al., 2011; Nawar et al., 2016; Stenberg et al., 2010; Viscarra Rossel et al., 2006). Recently, Hermansen et al. (2016) utilized vis-NIRS in the laboratory for determining the clay/OC ratio for a wide range of soils.

The application of vis-NIRS in estimation of soil properties is possible because the vis-NIR spectrum is affected by the soil constituents. For example, the absorption in the visible region of the spectrum from 400 to 700 nm is related to the color of the soil because of OM, soil moisture, and iron oxides (Stenberg et al., 2010). Soil minerals containing iron, like hematite and goethite, result in concave shapes in the visible region of the spectra (Demattê et al., 2004; Sherman and Waite, 1985). Clay minerals, OM, and soil water dominate most of the absorption in the NIR region from 700 to 2500 nm (Hunt, 1977; Stenberg et al., 2010; Viscarra Rossel et al., 2006). Each soil characteristic has a specific absorption feature in the vis-NIR spectrum. For instance, major absorption regions of clay minerals are located between 1300 and 1400, 1800–1900, and 2200–2500 nm and are associated with the spectrally active OH group present either as part of a mineral lattice or as part of a water molecule adsorbed to the mineral surface (Ben-Dor, 2002; Roberts and Cozzolino, 2016). These absorption regions can vary slightly depending on the different chemical groups, such as Al-OH, Mg-OH, and Fe-OH, present in clay minerals (Ben-Dor, 2002). The spectral bands at 1100, 1600, 1700, 1800, and 2000 nm and the bands between 2220 and 2400 nm in the NIR region are important for OC estimation (Ben-Dor and Banin, 1995; Clark 1999; Jiang et al., 2016; Roberts and Cozzolino, 2016) as they are related to various functional groups present in OC or OM such as N-H, C-H, and C=O groups (Stenberg et al., 2010). However, lack of specificity of the spectral features in the spectrum may arise because of overlapping bands of soil constituents and scatter effects caused by the different particle sizes present in the soil (Stenberg et al., 2010).

Absorption related to water in the soil is attributed to the overtones and combinations of three fundamental vibrations of

the water molecule: symmetric O-H stretching, asymmetric O-H stretching, and O-H bending (Hunt, 1977). Fundamentally, the spectrally active water can be present in the soil in three forms: hydration water, which is incorporated in the lattice of clay minerals and has strong absorption peaks near 1400 and 2200 nm; hygroscopic water, which is adsorbed to the soil surface especially on the surface areas of clay minerals and organic matter in thin layers and has absorption features near 1900 nm; and free water, which is present in soil pores and has two pronounced absorptions near 1400 and 1900 nm and weaker absorptions near 760, 980, and 1200 nm (Ben-Dor, 2002; Stenberg, 2010). However, the vibration properties of the OH group related to hydrated water and hygroscopic water vary slightly depending on the composition and structure of clay minerals, and their absorption features may shift at 1400, 1900, and 2200 nm (Ben-Dor, 2002). As the soil moisture increases from a dry state, the thickness of the water film around soil particles increases, changing the reflective properties of soil (Nolet et al., 2014; Stenberg et al., 2010). The increase in water film thickness results in a decrease in soil reflectance (Baumgardner et al., 1986; Knadel et al., 2014; Nocita et al., 2013) by increasing the forward light scattering in the medium (Baumgardner et al., 1986; Nolet et al., 2014; Stenberg et al., 2010). This increase in scattering causes darkening of the wet soil and affects the visible part of the spectra between 500 and 800 nm (Viscarra Rossel et al., 2006). The largest effect of moisture on vis-NIR spectra occurs at the change from adsorptive surface forces to capillary forces, corresponding to the dry and wet soils, respectively (Knadel et al., 2014). However, when the moisture content is above 20% (volumetric water), the reflectance is not as sensitive to changes in soil moisture content (Liu et al., 2003; Lobell and Asner, 2002; Rienzi et al., 2014).

The reduction in spectral reflectance because of water and the overlap of absorbance bands with other soil properties may conceal important spectral features of other soil constituents thus reducing their prediction accuracy. Several studies have reported weaker prediction of soil properties such as total C, OC, and texture using spectra of moist soils as compared with air-dried soils (e.g., Bogrekcı and Lee, 2005; Chang et al., 2005; Stevens et al., 2006; Udelhoven et al., 2003). Rienzi et al. (2014) observed that the characteristic absorption peaks for H-C aromatics (i.e., 1142 nm) and alkene (1170 nm), corresponding to OC prediction, were overlaid by the adjacent water peak (1180 nm), thus reducing the prediction accuracy for moist soils. Similarly, Lobell and Asner (2002) demonstrated that absorption features of clay at 2200 nm had been superimposed by the broader absorption features of water near 1900 nm and resulted in a lower prediction performance of the soil clay content. Contradictory to the negative effects of soil moisture, Stenberg et al. (2010) reported that clay prediction could be enhanced by rewetting of soil samples from 12.5 to 30% (volumetric water content) because of increasing water retention capacity of clay-rich soils with clay content. Their study also showed a positive effect of rewetting on OC prediction, but a clear reason related to moisture effect was not suggested. Furthermore, Rienzi et al. (2014) reported that

the decrease in OC predictions was not linearly proportional to the increase in soil moisture, which might be caused by interactive effects between OC, moisture, and soil texture. Therefore, few studies have examined the effect to understand their influence on the predictive ability of vis–NIRS in field applications (Demattê et al., 2010; Kuang and Mouazen, 2013a).

The effect of variable moisture content in the field is one of the crucial limiting factor during in situ measurements. It would be even a bigger issue when we want to use the dry spectral library data for the local prediction of “field-moist data” without making local calibrations. Several approaches have been applied with different degrees of success to eliminate the effect of soil moisture on the spectra, such as spectral pre-processing (Wu et al., 2009), spiking with local field-moist samples (Knadel et al., 2012; Kuang and Mouazen, 2013b) and application of different spectral transformation algorithms like External Parameter Orthogonal (EPO) algorithm, Direct Standardization (DS) algorithms (Ji et al., 2015a; Minasny et al., 2011; Roger et al., 2003; Wijewardane et al., 2016) and Piecewise Direct Standardization (PDS; Ji et al., 2015b). However, the important question is to what extent the different moisture levels affect the soil spectra and how they influence the predictive ability of different soil properties. Few studies have examined the effects of moisture on the vis–NIR spectroscopy prediction of soil properties focusing only on a narrow range in variation in soil moisture (Chang et al., 2005; Minasny et al., 2011; Morgan et al., 2009; Wäiser et al., 2007; Rienzi et al., 2014; Stenberg, 2010; Wang et al., 2016). At different matric potentials, water-retention capacity of soils vary across the different soil types and OC content. Therefore, it is important to understand the effect of moisture in terms of different matric potentials. That would provide a better understanding of interaction between moisture, texture, and OC and how they can influence the predictive ability of vis–NIRS in field applications. None of these studies have looked into the variation in water-retention capacity of soils and its effect on the soil moisture and spectra. Therefore, interaction between moisture and soil properties needs to be further studied to understand how they can influence the predictive ability of vis–NIRS in field applications. The water content at pF 3 or the amount of water which is adsorbed to soil particles is also interesting to estimate using spectroscopy as it is an important functional attribute to determine soil hydraulic properties. The adsorbed water film influences the residual water saturation and hydraulic conductivity in soil at low saturation (Tokunaga, 2009).

The primary objective of this study was to quantify the effect of variable soil-water contents on vis–NIR spectroscopy prediction of six soil properties including soil texture properties (clay, silt, and sand), OC, soil-water content at water potential at pF 3 and the clay/OC ratio, using five soil types with a wide variation in soil texture. For the first time, six different soil-water contents in terms of different matric potentials, which varied from fully saturated to air-dry, have been investigated to quantify this effect. Furthermore, this study evaluated the effects of variable soil-water contents on soil vis–NIR spectra for gradients in clay and OC content.

MATERIALS AND METHODS

Soil Samples

Soil samples were collected from five different locations—four in Denmark: Aarup, Juelsminde, Lerbjerg, and Slæggerup, and one in Germany (Bad Lauchstädt). The characteristics of these soils are presented in Table 1 and Fig. 1. The Aarup field site (55°22′45″ N lat., 10°02′54″ E long.) has a sandy loam soil and is an arable field characterized by a natural clay gradient from 0.097 to 0.233 kg kg⁻¹. The soil at this site is classified as Stagnic Luvisol (Vendelboe et al., 2012). The Lerbjerg field site (56°20′54″ N lat., 9°59′17″ E long.) has sandy clay loam soil with a high gradient in clay content (0.12–0.46 kg kg⁻¹). The soils from the Juelsminde site (55°42′31″ N lat., 9°59′55″ E long.) has a sandy loam soil and were collected from two neighboring fields with different management histories, the details of which are provided in Vendelboe et al. (2013). The Slæggerup field site (55°40′14″ N lat., 12°08′53″ E long.) has a loamy soil with the lowest OC among the fields studied and is classified as Luvisol (Lindhardt et al., 2001). The agriculture field in Bad Lauchstädt (51°23′32″ N lat., 11°49′13″ E long.) is located in the central part of Germany where a long-term fertilizer experiment has been conducted using organic and mineral fertilizers. The soil has the highest OC gradient among the studied soils. It has silt loam soil and classified as Haplic Chernozem (Eden et al., 2012).

Seventy intact soil samples (100 cm³) were collected from the topsoil (0–25 cm) in replicates of two from each sampling point, except for the Juelsminde soils with only one sample per sampling point. Bulk soil was also collected from each sampling point. Particle-size distribution was determined using the sieving and hydrometer method (Gee and Bauder, 1986). Clay was defined as particles smaller than 0.002 mm, silt as 0.002 to 0.05 mm and sand as 0.05 to 2 mm. Soil C was measured by combustion in the laboratory using a LECO induction furnace coupled to CO₂ infrared detector (CN-2000 instrument, LECO Corp.). Soil OC was obtained as the difference between the total soil C and inorganic C.

Soil Moisture Retention

To examine the effects of moisture on soil vis–NIR reflectance and predictions, six different moisture levels were used (full saturation, pF 1, pF 1.5, pF 2.5, pF 3, and air-dry). To obtain the different moisture levels, the intact soils were saturated in a sandbox for about 24 h and gradually drained to different matric potentials: -10 cm (pF 1), -30 cm (pF 1.5), -300 cm (pF 2.5), and -1000 cm (pF 3) by applying suction. To obtain pF 2.5 and pF 3, the soil rings were drained on pressure plates for 15 h and 1 mo, respectively. The water content at the corresponding matric potentials (from pF 1 to pF 3) was determined for all the rings. To obtain air-dried soil, the bulk soil was air-dried at room temperature for 7 d and sieved to 2 mm. At each moisture level, the soils were scanned using a vis–NIR sensor.

Vis–NIR Spectral Measurement

A Labspec5100 spectrometer (ASD Inc.) was used following a standard laboratory protocol for instrument control and

Table 1. Descriptive statistics of the soil characteristics for five investigated soils.

Location	No. of samples	Soil property	Min.†	Max.‡	Mean	Std. dev.§	Q1¶	Q3#
Aarup (Denmark)	16	Clay, kg kg ⁻¹	0.097	0.233	0.164	0.047	0.132	0.198
		Silt, kg kg ⁻¹	0.151	0.375	0.274	0.075	0.23	0.325
		Sand, kg kg ⁻¹	0.358	0.73	0.533	0.126	0.445	0.604
		OC, kg kg ⁻¹	0.012	0.022	0.017	0.003	0.014	0.019
		Soil-water content at pF 3, cm ³ cm ⁻³	0.16	0.31	0.23	0.05	0.20	0.26
		Clay/OC ratio, <i>n</i>	8.0	11.3	9.6	1.0	9.1	10.4
Lerbjerg (Denmark)	12	Clay, kg kg ⁻¹	0.116	0.459	0.29	0.122	0.199	0.382
		Silt, kg kg ⁻¹	0.092	0.142	0.114	0.019	0.101	0.133
		Sand, kg kg ⁻¹	0.388	0.773	0.580	0.138	0.468	0.679
		OC††, kg kg ⁻¹	0.014	0.016	0.015	0.001	0.014	0.016
		Soil-water content at pF 3, cm ³ cm ⁻³	0.16	0.44	0.32	0.09	0.28	0.40
		Clay/OC ratio, <i>n</i>	8.4	28.5	18.9	7.9	12.6	26.9
Juelsminde (Denmark)	18	Clay, kg kg ⁻¹	0.166	0.207	0.183	0.014	0.169	0.195
		Silt, kg kg ⁻¹	0.219	0.265	0.243	0.013	0.234	0.254
		Sand, kg kg ⁻¹	0.539	0.565	0.551	0.007	0.547	0.556
		OC, kg kg ⁻¹	0.012	0.018	0.014	0.001	0.013	0.015
		Soil-water content at pF 3, cm ³ cm ⁻³	0.25	0.30	0.27	0.02	0.26	0.28
		Clay/OC ratio, <i>n</i>	9.5	16.2	13.4	2.1	11.4	15.3
Slæggerup (Denmark)	12	Clay, kg kg ⁻¹	0.188	0.284	0.220	0.032	0.198	0.220
		Silt, kg kg ⁻¹	0.202	0.361	0.292	0.063	0.242	0.359
		Sand, kg kg ⁻¹	0.337	0.593	0.469	0.093	0.395	0.533
		OC, kg kg ⁻¹	0.009	0.014	0.011	0.002	0.010	0.012
		Soil-water content at pF 3, cm ³ cm ⁻³	0.19	0.26	0.23	0.02	0.21	0.25
		Clay/OC ratio, <i>n</i>	16.3	24.1	20.3	2.8	18.3	23.3
Bad Lauchstädt (Germany)	12	Clay, kg kg ⁻¹	0.246	0.257	0.253	0.005	0.247	0.257
		Silt, kg kg ⁻¹	0.589	0.642	0.626	0.018	0.626	0.641
		Sand, kg kg ⁻¹	0.023	0.036	0.032	0.005	0.028	0.036
		OC, kg kg ⁻¹	0.015	0.024	0.020	0.003	0.018	0.022
		Soil-water content at pF 3, cm ³ cm ⁻³	0.25	0.30	0.28	0.02	0.26	0.29
		Clay/OC ratio, <i>n</i>	10.4	16.8	12.8	2.24	11.1	14.1
All	70	Clay, kg kg ⁻¹	0.097	0.459	0.217	0.077	0.17	0.247
		Silt, kg kg ⁻¹	0.092	0.642	0.304	0.167	0.209	0.361
		Sand, kg kg ⁻¹	0.023	0.773	0.447	0.216	0.369	0.561
		OC, kg kg ⁻¹	0.009	0.024	0.015	0.004	0.013	0.018
		Soil-water content at pF 3 (cm ³ cm ⁻³)	0.16	0.44	0.27	0.06	0.24	0.29
		Clay/OC ratio (<i>n</i>)	8.0	28.5	14.6	5.1	10.8	16.8

† Minimum value.

‡ Maximum value.

§ Standard deviation.

¶ First quartile.

Third quartile.

†† Soil organic carbon.

scanning of the samples (Knadel et al., 2013). The spectrometer covers the spectral region from 350 to 2500 nm, with a 3-nm spectral resolution at 700-nm and 6-nm spectral resolution at 1400 and 2100 nm. Depending on the moisture level of the soil samples, either a contact probe or a mug light device was used for scanning. The contact probe was used for the intact wet soils ensuring that the probe was in proper contact with the sample being scanned, and the mug light with sample holder was used for dry and loose soils. Calibration of the instrument was done by scanning a white reference at the beginning and after every five scans. For each sample the vis-NIR spectra that was analyzed was an average of two scans.

Multivariate Data Analysis

Principal Component Analysis (PCA) was used to explore the patterns and internal structure of the spectral data using score and loading plots. Score plots were used to represent the similarities and differences in the spectra of the samples in different principal component spaces. Loading plots were used to examine the importance of different wavelengths for the patterns present in each principal component. The chemometric data analysis was performed using the Unscrambler X 10.5 software (Camo ASA). The spectral regions from 350 to 500 nm and from 2400 to 2500 nm were excluded from the analysis to remove the effect of noise. The reflectance values (*R*) in the spectral data were transformed to absorbance values ($A = \log [1/R]$).

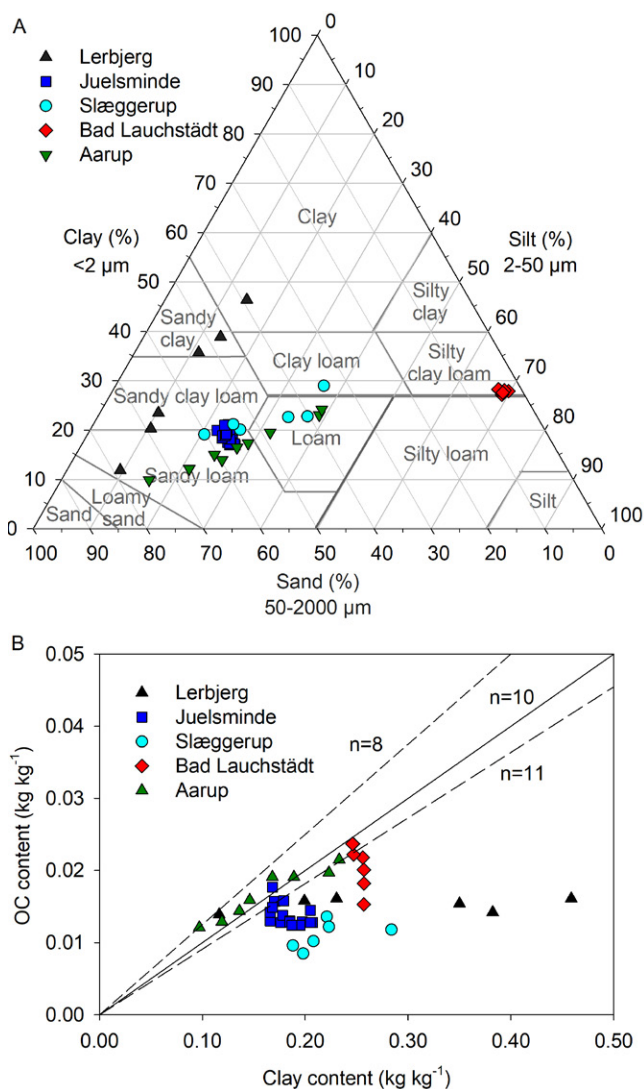


Fig. 1. Distribution of soil samples from the five investigated sites. (A) across USDA soil texture triangle; (B) in the ratio of clay to organic carbon, (OC; lines of $n = \text{clay}/\text{OC} = 8, 10, 11$ suggested by Dexter et al., 2008).

Savitzky–Golay smoothing (Savitzky and Golay, 1964) and gap-segmented second-derivative (gap size = 30, segment size = 29) were used as the pre-treatments to remove noise and improve model performance. The soil properties at different moisture levels were estimated using PLSR (Wold et al., 1984) using leave-one-out cross-validation.

The performance of the PLSR models (predicted against measured values) was evaluated with the coefficient of determination (R^2), root mean square error of cross-validation (RMSECV) and ratio of performance to inter-quartile range (RPIQ). The RMSECV was calculated as:

$$\text{RMSECV} = \sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{n}} \quad [1]$$

where y_i is the measured value, \hat{y}_i is the predicted value and n is the total number of samples.

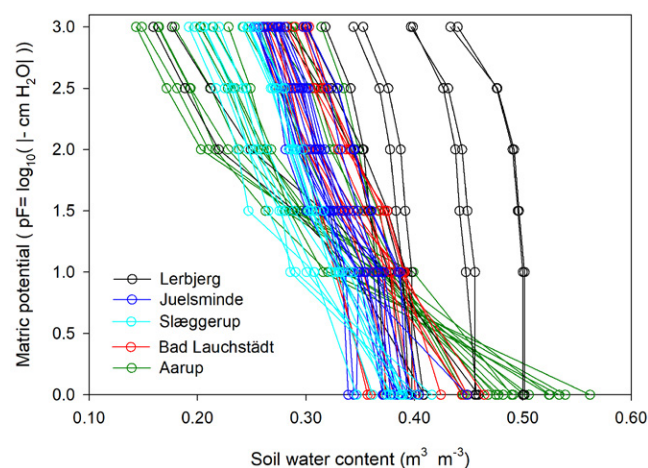


Fig. 2. Water retention curves for soils from the five investigated sites.

RPIQ was calculated using the first and the third quartiles (Q_1 and Q_3 , respectively) and RMSECV as:

$$\text{RPIQ} = \frac{Q_3 - Q_1}{\text{RMSECV}} \quad [2]$$

The ratio of performance to deviation (RPD), which is the ratio of standard deviation to RMSECV, is often used to assess the performance of models and to classify them (Chang et al., 2001). However, RPD is suitable only for variables which are normally distributed (Minasny and McBratney, 2013). The RPIQ index, proposed by Bellon-Maurel et al. (2010), is a better index than RPD in terms of representing the model performance regardless the distribution of variable, and thus used in the study.

RESULTS AND DISCUSSION

Soil Properties

Figure 1B shows the relationship between the clay content and OC content in the soils. Except for the Aarup soils, most of the soils were below the Dexter ($n = 10$) line, suggesting that OC in these soils was present in the complexed form and a large fraction of clay was present as non-complexed clay. Large amounts of non-complexed clay in the soil can result in extensive clay dispersibility (Dexter et al., 2008; Schjønning et al., 2012) and degradation of the soil structure (de Jonge et al., 2009).

Soil-Water Retention Curve

The relationship between the soil moisture content and the matric potential ($pF = \log_{10}|-cm H_2O|$) is explained by the water retention curves. Figure 2 shows the water retention curves for the studied soils for the wet part, that is, from full saturation to pF 3. The soils exhibited large variation in moisture content at each pF. The Lerbjerg soils exhibited the largest variation in water retention capacity at each matric potential, which can be attributed to the large variation in clay content in the soils. In a fine-textured soil (Lerbjerg soil), capillary and adsorptive forces are facilitated because of the presence of a larger number of micropores and larger surface area, which results in a significant increase in water retention at all pF values. The greater water retention capacity of the Bad Lauchstädt soils can be attributed to the

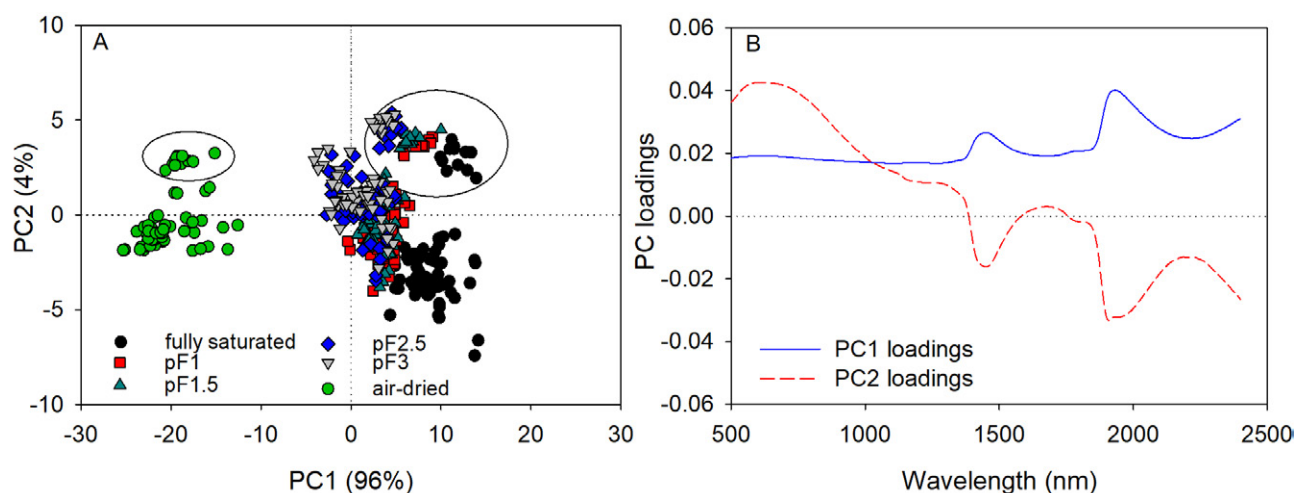


Fig. 3. Principal component analysis of soil spectra with score plot and the loadings plot. (A) Score plot of the first two principal components (PC1 and PC2) colored according to moisture content. The two ellipses demarcate the soil samples from Bad Lauchstädt, which are discriminated from the samples obtained from four Danish fields. (B) Loadings plot of principal component PC1 and PC2.

higher silt and OM/OC contents. The differences in the water retention capacity of Bad Lauchstädt soils can be related to the gradient in OC content in the soils. The lowest water retention capacity was found in the Aarup soils, basically because of the high sand content and low OC content.

At different pF values, different forms of water can be present in soil matrix. When the soil is fully saturated, free water is readily available and macro-pores dominate the water retention, whereas when the soil-water content varies from pF 1 to pF 3, adsorption and capillary forces dominate water retention and water is available in micro- and medium pores in the soil matrix (Tuller and Or, 2005). In dry soil, adsorptive forces begin to dominate and water can be present as a water film around soil particles (Tuller and Or, 2005).

PCA Analysis on Spectral Data

The first two principal components (PC1 and PC2) explained the total spectral variability (100%) in the total data set at all moisture levels. In the principal components (PC) space, the wet soil samples (fully saturated—pF 3) were clearly separated from the air-dry soil samples (Fig. 3A). According to the loading plot of PC1 (in blue), the variables responsible for this separation were allocated near 1443 and 1932 nm, which can be assigned to two characteristic water bands (Fig. 3B; Hunt, 1977). Grouping within the wet soils in the principal components space was also observed with fully-saturated samples separated clearly from the other wet samples (pF 1 and pF 3) which could be related to the large amount of free water present in soil macropores (Fig. 2).

Distinct separation could also be observed along PC2 (Fig. 3A) between the Bad Lauchstädt and the Danish soils on both sides of PC1 possibly because of differences in the OC quantity and/or quality, and/or the clay content and mineralogy between the two soils. The loading plot of PC2 (in red) shows a positive peak near 600 nm, which can be attributed to the soil OM (Fig. 3B) (Nocita et al., 2013). There are subsequent dips at 1400 nm

and 1900 nm that are negatively correlated to spectrally active OH group in clay minerals (Ben-Dor, 2002). The clay minerals in the Danish soils are dominated by illite, smectite, kaolinite, and vermiculite (Mørberg et al., 1988) whereas, Bad Lauchstädt soils are dominated by smectite and vermiculite (Leinweber and Reuter, 1989).

Effect of Moisture on Soil Spectra

The spectral features of soil depend on the basic soil constituents such as soil texture, clay mineralogy, water content, OM content (quality and quantity), and their interactions (Ben-Dor, 2002; Stenberg et al., 2010). Two soils with different soil characteristics (Lerbjerg with a natural clay gradient [Fig. 4A–C] and Bad Lauchstädt with an OC gradient [Fig. 4D–F]) were selected to study the effect of soil-water content on soil vis–NIR spectra. A decrease in reflectance with an increase in matric potential/water content was observed for all soils, which is in agreement with previous studies (Baumgardner et al., 1986; Bishop et al., 1994; Knadel et al., 2014; Liu et al., 2003; Lobell and Asner, 2002; Nocita et al., 2013). However, the biggest difference in vis–NIR spectra was found at the change from dry (air-dry) to wet soil (\leq pF 3) (Fig. 4), where water retention forces change from adsorptive to capillary forces. Similar results were also reported by Knadel et al. (2014).

For the Lerbjerg soil, pronounced absorption occurred at characteristic clay bands near 1400, 1900, and 2200 nm which can be linked to OH stretches, combinations of OH stretches and H–O–H bends, and Al–OH bend plus OH stretch combinations, respectively (Clark, 1999; Viscarra Rossel et al., 2006), and they were clearly visible in air-dried soil. The absorption dips near 1410 and 1910 nm (Fig. 4A–C) reflect the tightly bound water on the surface of clay minerals, specifically 2:1 clay minerals (Bishop et al., 1994; Demattè et al., 2004; Stenberg, 2010). Clay minerals, especially those with 2:1 configuration, have large specific surface areas which increase the attraction of water molecules to the clay mineral surface (Ben-Dor, 2002; Stenberg et al.,

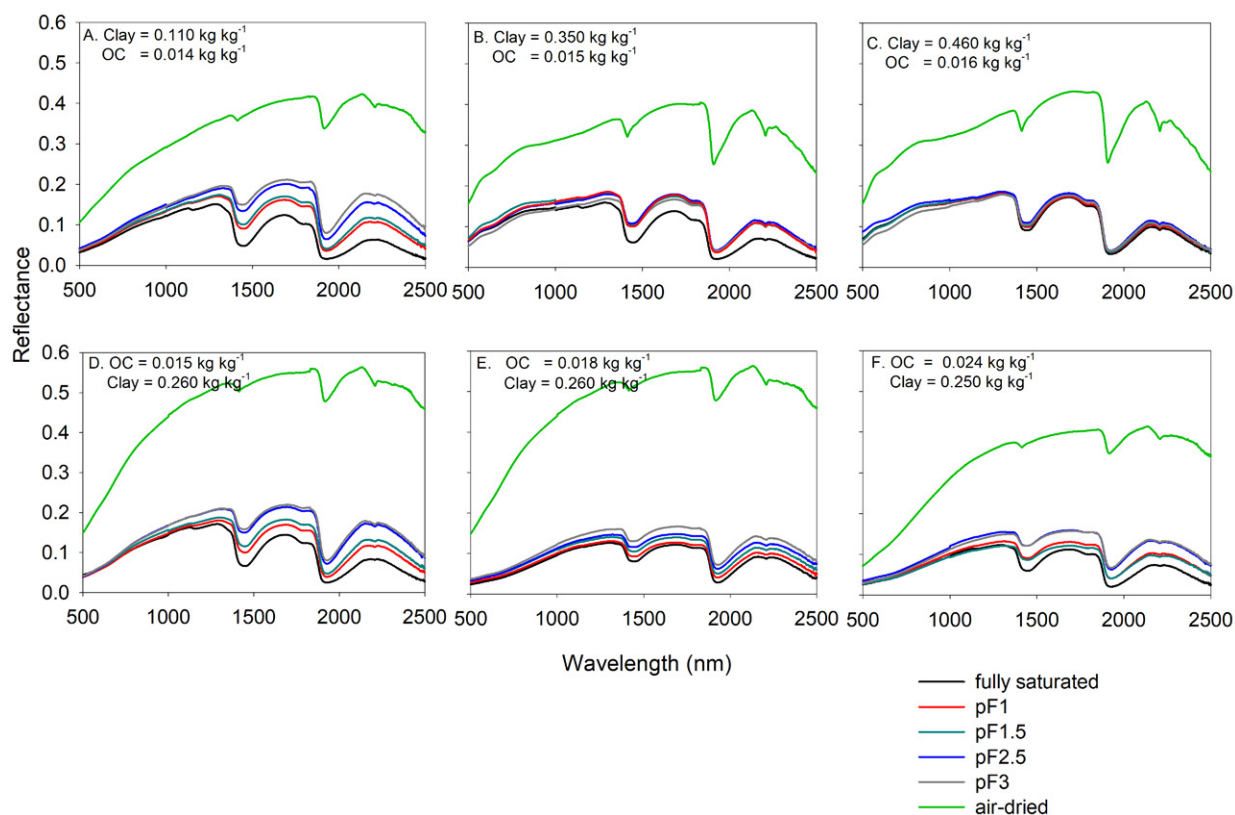


Fig. 4. Influence of soil-water content on vis-NIR spectra of soils with different textures. Upper: Lerbjerg soils with varying clay contents: (A) 0.110 kg kg^{-1} , (B) 0.350 kg kg^{-1} , (C) 0.460 kg kg^{-1} . Lower: Bad Lauchstädt soils with varying OC (organic carbon) contents: (D) 0.015 kg kg^{-1} , (E) 0.018 kg kg^{-1} , and (F) 0.024 kg kg^{-1} .

2010), thus increasing the absorption near 1410 and 1910 nm with increasing clay content for the air-dried Lerbjerg soil. The similarity in the reflectance spectra for the wet soils with high clay contents can be explained by the similar moisture contents at the different pFs in the wet region (Fig. 2 and 4C). However, a clear deviation in the vis-NIR spectra for the wet soils was observed for the soil with the lowest amount of clay content (Fig. 4A). This could be because of the differences in moisture content at different pFs resulting from the weaker water retention capacity of the soil with less clay.

The absorption feature of clay at 2200 nm is because of lattice water which is incorporated in the clay mineral structure. The absorption dips at 2200 nm increases with increasing clay content for the dry soils. However, this absorption feature was more evident in dry soil, as the broad water absorption peak at 1900 nm superimposed this feature in the wet soils (Fig. 4A–C). Similar results were reported by Bowers and Hanks (1965). However, the impact of the broad absorption peak near 1900 nm on the absorption feature of clay at 2200 nm decreased with increasing water retention capacity of the soils (Fig. 4A–C). Stenberg (2010) also found that when soil contained less clay, free water dominated absorption near 1900 nm and this effect was more pronounced. Moreover, the reflectance of the soil with a high clay content exhibited a concave shape between 500 and 800 nm, which could be attributed to the presence of iron oxides of goethite and hematite (Ben-Dor, 2002; Stenberg et al., 2010).

For the Bad Lauchstädt soils, the overall reflectance for the air-dried soils was greater than for the Lerbjerg soils with similar OC values, which could be because of differences in clay mineralogy, texture (especially the high silt content and low sand content in the Bad Lauchstädt soils) and/or OM quality. The deviation of the spectral reflectance of Bad Lauchstädt soils from Lerbjerg soils was further explained in the PC space by the score plot given in the PCA analysis of this study (Fig. 3). The overall reflectance was lower for the high OC soil (Fig. 4D–F), which is in agreement with the finding of Baumgardner et al. (1986) that the spectral responses to OC are more prominent for soils containing at least 2.0% of OM. A more convex-like shape of the reflectance spectra of the air-dried soil was observed between 500 and 800 nm for soils high in OC (Fig. 4F). Previous studies have found that some of important OC spectral features can appear near 1100, 1600, 1700, 1800, and 2000 nm and between 2220 and 2400 nm in the NIR region (Ben-Dor and Banin, 1995; Clark, 1999; Jiang et al., 2016; Roberts and Cozzolino, 2016). However, these important spectral regions of OC were not evident in the NIR region in our results possibly because of relatively low quantity ($<2.4\%$) of OC.

The deviation in vis-NIR spectra for wet soils at different pFs was more evident for Bad Lauchstädt soils than for Lerbjerg soils especially when clay was $<0.250 \text{ kg kg}^{-1}$, resulting possibly from the differences in clay content in the soils (Fig. 4). However, the difference in spectral reflectance for the Bad Lauchstädt soil was higher for the wet soils with the low OC content (Fig. 4D)

than for high OC contents (Fig. 4F) likely because of the lower water retention potential of soils with low OC than with high OC content (Hudson, 1994).

Effect of Moisture on Predictive Ability of vis-NIRS Models

The calibration performance of PLSR with leave-one-out cross-validation is shown in Table 2. The predictions of clay, silt, sand, and water content at pF 3 were obtained with high accuracies regardless of soil moisture level ($R^2 = 0.74$ – 0.95 ; RPIQ = 1.7 – 4.3 ; Table 2), whereas for OC and clay/OC ratio better prediction results were obtained at high pFs and for air-dried soils. The best predictive ability of the clay models was found for fully saturated and air-dried soils ($R^2 = 0.87$ and 0.88 ; RPIQ = 3.1 and 3.2 , respectively). Among all the soil properties investigated, the models for silt produced the best predictive results with $R^2 = 0.88$ – 0.95 for all the moisture levels. The sand models had the best predictive ability for air-dried soils and pF 1.5 soils ($R^2 = 0.92$ – 0.93). The model performance for the prediction of clay at different moisture levels are comparable and the performances for silt and are better than reported for air-dried soils in the literature (Chang et al., 2005; Waiser et al., 2007; Stenberg, 2010). Sørensen and Dalsgaard (2005) have shown that the accuracy of the vis-NIRS models are dependent on several factors

such as spectral region used for model calibration, the spectral pretreatment process, and on the range of the soil property within the calibration data set. The high R^2 and RPIQ values for silt and sand in our study at all moisture levels could possibly be because of the high range of values in the dataset resulting from the inclusion of the Bad Lauchstädt soils (Table 1). The measured versus predicted plots for the investigated soil properties at two moisture levels, pF 1 (Fig. 5), and air-dry (Fig. 6), show that there were improvements in the prediction of all the properties with the air-dried soils as compared with pF 1. While the improvement in the prediction performance for clay, sand, and soil-water content at pF 3 were minimal, the improvement in the prediction was considerable for silt, OC, and clay/OC ratio. The high R^2 and RPIQ for the prediction of silt/sand content at pF 1, despite having a higher scatter along 1:1 line for the silt/sand content, could possibly be because of the larger range in silt/sand content as a result of the inclusion of the silt loam soil from Bad Lauchstädt. Recalibration of the models for silt and sand content excluding Bad Lauchstädt soils resulted to lower R^2 (for silt: $R^2 = 0.64$ and 0.78 at pF 1 and air-dry respectively, and for sand: $R^2 = 0.60$ and 0.66 at pF 1 and air-dry models, respectively). However, the scatter along the 1:1 line (figure not shown), RMSECV and RPIQ values both at pF 1 and air dry condition were similar with and without Bad Lauchstädt soils

Table 2. Results of partial least squares (PLS) regression for clay, silt, sand, OC, soil-water content at pF 3 and clay/OC ratio, at different soil-water contents.

Soil properties	Model statistics	Fully saturated	pF 1	pF 1.5	pF 2.5	pF 3	Air-dried
Clay	R^2 †	0.88#	0.82	0.86	0.81	0.85	0.87
	RMSECV‡, kg kg ⁻¹	0.025	0.030	0.027	0.031	0.027	0.026
	NF§	7	3	3	3	2	3
	RPIQ¶	3.2	2.7	3.0	2.6	3.0	3.1
Silt	R^2	0.88	0.89	0.94	0.91	0.91	0.95
	RMSECV, kg kg ⁻¹	0.056	0.054	0.040	0.048	0.050	0.035
	NF	5	2	6	6	5	5
	RPIQ	2.7	2.8	3.8	3.1	3.0	4.3
Sand	R^2	0.89	0.90	0.93	0.87	0.89	0.92
	RMSECV, kg kg ⁻¹	0.070	0.065	0.056	0.076	0.071	0.058
	NF	5	3	6	4	3	4
	RPIQ	2.7	2.9	3.4	2.5	2.7	3.3
OC	R^2	0.48	0.52	0.70	0.76	0.68	0.82
	RMSECV, kg kg ⁻¹	0.0026	0.0025	0.0019	0.0017	0.0020	0.0015
	NF	7	2	5	6	5	10
	RPIQ	1.9	2.0	2.6	2.9	2.5	3.3
Soil-water content at pF 3	R^2	0.84	0.74	0.79	0.78	0.75	0.78
	RMSECV, cm ³ cm ⁻³	0.022	0.029	0.026	0.026	0.028	0.026
	NF	7	3	3	3	5	3
	RPIQ	2.3	1.7	1.9	1.9	1.8	1.9
Clay/OC ratio	R^2	0.65	0.63	0.70	0.68	0.70	0.82
	RMSECV	3.19	3.27	2.95	3.03	2.94	2.25
	NF	9	2	4	6	7	9
	RPIQ	1.9	1.8	2.0	2.0	2.0	2.7

† Coefficient of determination.

‡ Root mean square error of cross-validation.

§ Number of factors.

¶ Ratio of performance to inter-quartile range.

Values in bold show the two best predictions observed from the models.

(for silt: RMSECV = 0.049 and 0.037, RPIQ = 3.1 and 4.1, at pF 1 and air-dry condition, respectively; and for sand: RMSECV = 0.066 and 0.061, RPIQ = 2.9 and 3.1, at pF 1 and air-dry con-

dition, respectively), suggesting that the models were stable and without any overfitting resulting from the Bad Lauchstädt soils.

Contradictory results are reported in the literature regarding the effects of moisture on the predictive ability of vis-NIR

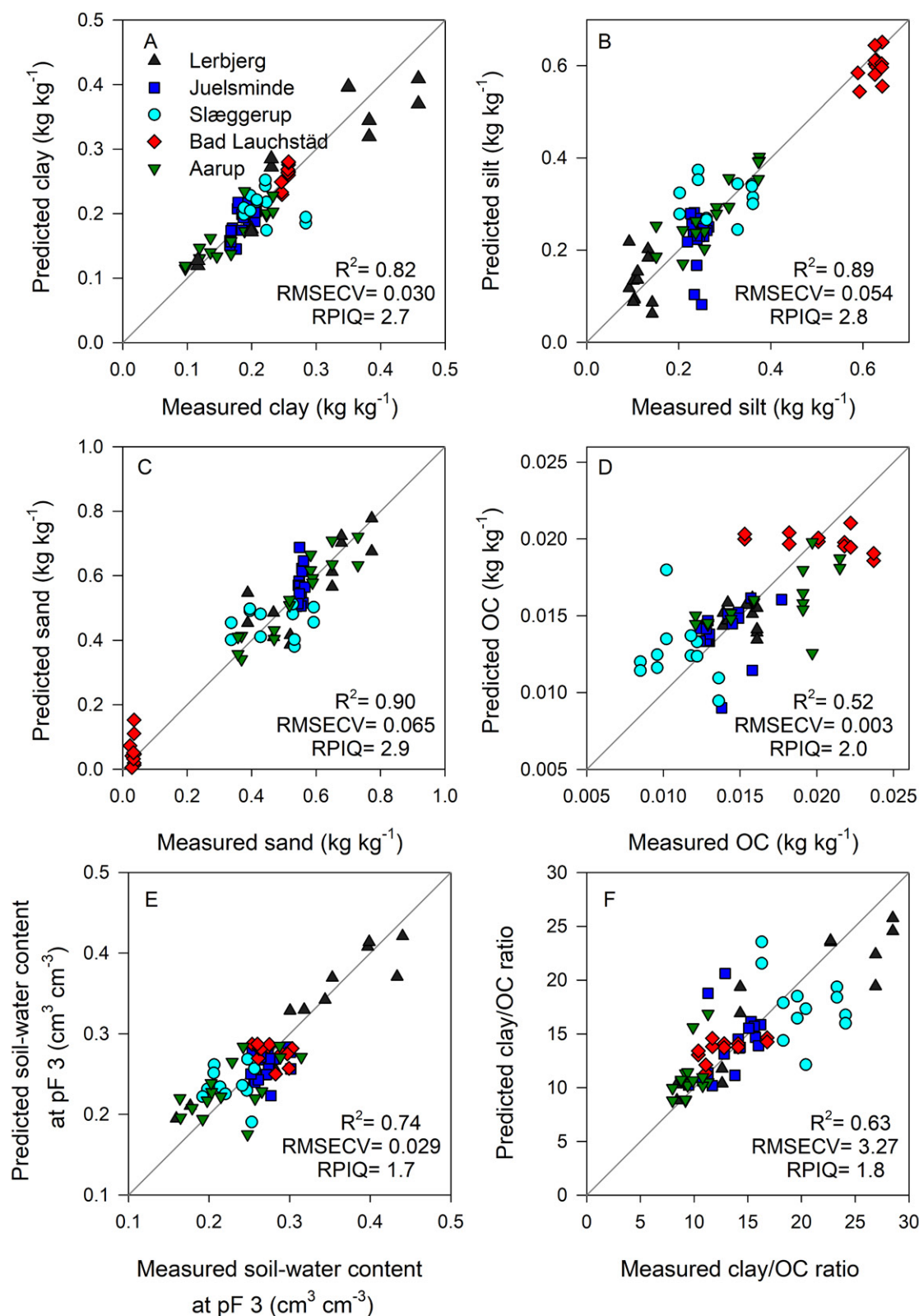


Fig. 5. Performance of vis-NIR models developed for soil samples at wet (pF 1) conditions. Predicted vs. measured values from Partial Least Square Regression for soil properties (A) Clay, (B) Silt, (C) Sand, (D) OC, (E) soil-water content at pF 3 and (F) Clay/OC ratio. The PLSR were developed using vis-NIR spectra for pF 1 condition with leave-one-out cross-validation. R², coefficient of determination; RMSECV, root mean square error of cross-validation; RPIQ, ratio of performance to inter-quartile range.

models for clay content. Stenberg (2010) observed slight improvements in the prediction performance of clay content by rewetting the soil samples to volumetric water contents between 12.5 and 30% as compared with air-dry soils. Wang et al. (2016)

predicted clay content at nine different moisture contents (0–450 g kg⁻¹) with different prediction accuracies (R^2 values between 0.66 and 0.78), however, with no distinct pattern between moisture content and the corresponding prediction accu-

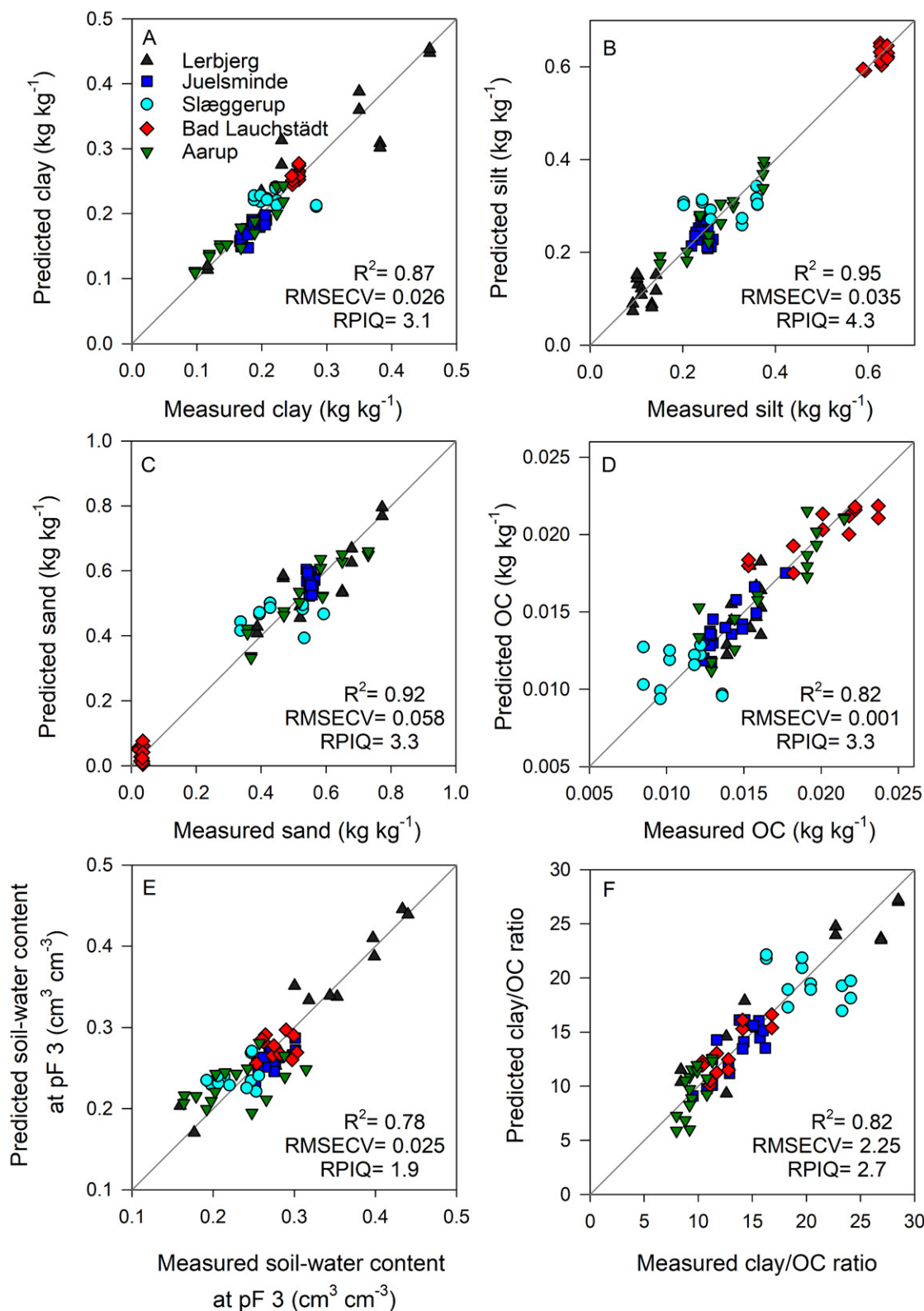


Fig. 6. Performance of vis-NIR models developed for soil samples at dry (air-dry) conditions. Predicted vs. measured values from Partial Least Square Regression for soil properties A: Clay, B: Silt, C: Sand, D: OC, E: soil-water content at pF 3 and F: Clay/OC ratio. The PLSR were developed using vis-NIR spectra for air-dry condition using leave-one-out cross-validation. OC, organic carbon; R^2 , coefficient of determination; RMSECV, root mean square error of cross-validation; RPIQ, ratio of performance to inter-quartile range.

racy. In contrast, a negative effect of water on the prediction of clay content with better prediction results for air-dried soil than for moist intact soils were obtained by Ackerson et al. (2015) and Waizer et al. (2007). The inconsistency in the effect of moisture content on the prediction accuracy of clay content in the aforementioned studies could be resulting from the differences in sample pretreatments, the range in soil properties or the use of calibration model developed for different soil moisture level. It

should also be noted that despite the inconsistency in the effect of moisture content in prediction performance of clay content, the prediction accuracies for clay content in these studies were high when the calibration models were developed using spectra from the corresponding moisture level, which is in agreement with the findings of this study.

The results of our study showed that prediction performance of clay, silt, and sand are similar. This could be because

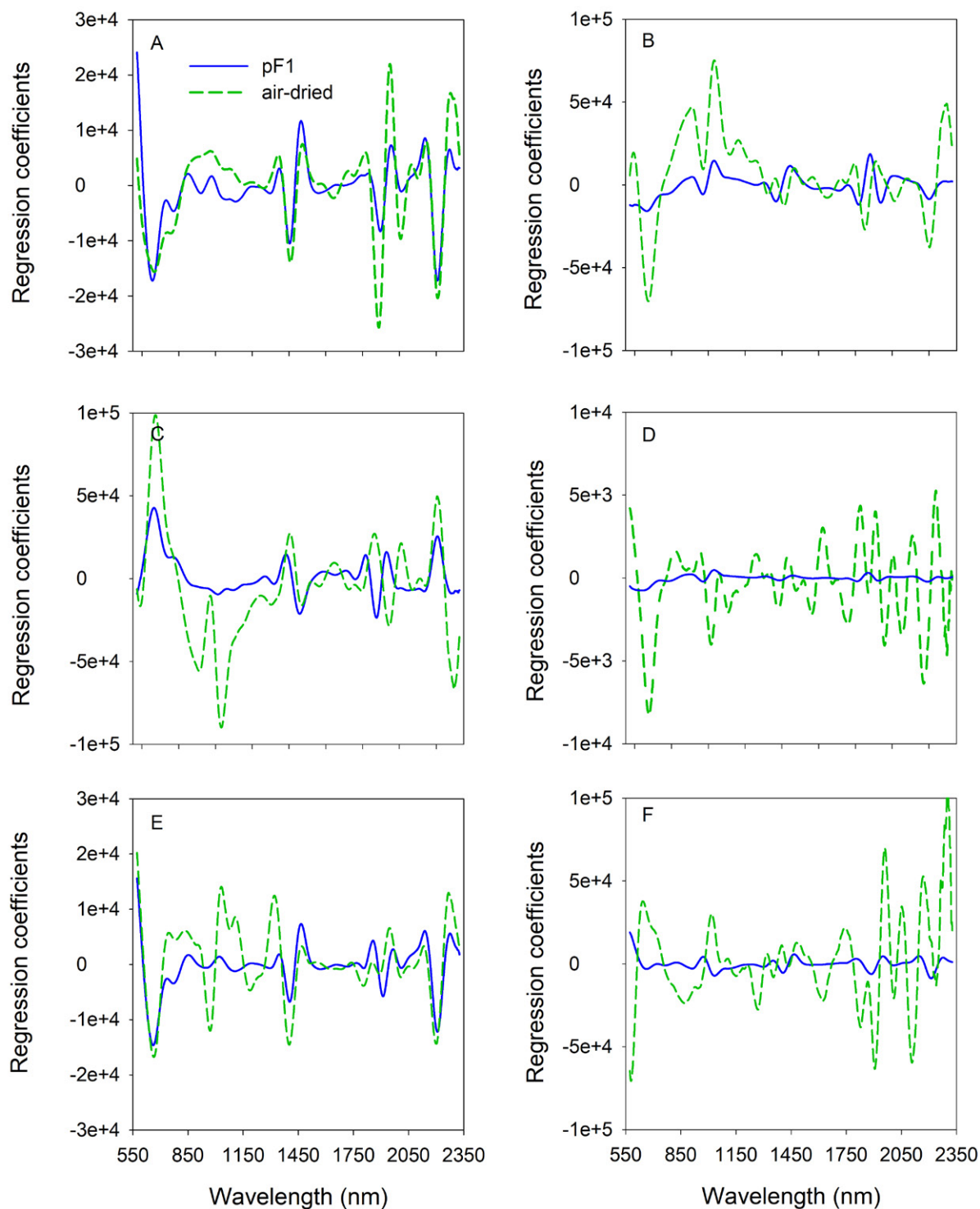


Fig. 7. Comparison of regression coefficients at different wavelengths for soil properties A: Clay, B: Silt, C: Sand, D: OC (organic carbon), E: soil-water content at pF 3 and F: Clay/OC ratio at two different moisture conditions (pF 1 and air-dry). The PLSR (partial least squares regression) were developed using vis-NIR spectra for pF 1 and air-dry condition using leave-one-out cross-validation.

clay, silt, and sand absorb in similar spectral regions in vis-NIR spectrum (Santra et al., 2009), which is also confirmed by the regression plots for clay, silt, and sand in Fig. 7A-C. The present study is the also first ever to investigate the predictive ability of water content specifically at pF 3 and using six different soil moisture levels. The models for water content at pF 3 resulted to predictions with R^2 values of 0.74 to 0.84 and RPIQ values of 1.7 to 2.3 which is comparable with previous findings using air-dried soils ($R^2 = 0.83-0.98$) (Chang et al., 2005; Demattê et al., 2006; Feyziyev et al., 2016).

The models for OC and Clay/OC ratio resulted in lower prediction accuracies especially at high moisture levels ($R^2 = 0.48-0.82$) compared with other soil properties (Table 2). The best prediction for OC and Clay/OC ratio was obtained for air-dried soil. The prediction results of OC at air-dry condition are comparable with the findings of previous studies ($R^2 = 0.73-0.78$; Jiang et al., 2016; Knadel et al., 2012; Minasny et al., 2011; Morgan et al., 2009), whereas, that for Clay/OC ratio is poorer than reported by Hermansen et al. (2016) ($R^2 = 0.97$) possibly because of the lower variation in OC content and/or the non-complexed OC in this study. The comparison between the models at pF 1 (Fig. 5) and air-dried soils (Fig. 6) indicates that prediction accuracy of OC can be negatively affected by water content in soil, consistent with previous studies (Morgan et al., 2009; Stevens et al., 2006). The results of our study showed that deviation in vis-NIR spectra for wet soils at different pFs was more evident for soils with less OM content (Fig. 4D). Therefore, soils with less clay and OM content might be greater effected by water at different pFs compared with soils with high clay and OM content (Fig. 4).

The comparison of the regression coefficient values of the models developed for two selected moisture conditions (pF 1 and air-dry) is presented in Fig. 7. The important spectral regions for the prediction of clay were found near 540 and 680 nm, attributed to the iron oxides present in the soil (Demattê et al., 2004; Stenberg et al., 2010) and near 1400, 1900, and 2200 nm, associated with the OH groups in mineral lattice or adsorbed water to the clay surface surface (Ben-Dor, 2002; Roberts and Cozzolino, 2016) (Fig. 7A). The important spectral regions for prediction of silt and sand obtained from the two models were similar to those of clay (Fig. 7A-C). However, the intensities of regression coefficient values from the wet model (pF 1) were lower for silt and sand than for clay. Further, the important spectral regions for predicting sand and silt between 800 and 1200 nm were masked by absorptions of water at pF 1, which was reflected in a higher predictive ability of the dry models of silt and sand as opposed to the models based on pF 1. The important spectral regions for water content at pF 3 between the two models were comparable (Fig. 7E). The spectral regions for prediction of clay and water content at pF 3 were similar resulting possibly from the strong correlation between the two soil properties ($r = 0.80$). Therefore, the prediction performance of texture properties and water content at pF 3 did not decline significantly when soil moisture increased.

The important spectral regions for OC was found in the visible region between 500 and 800 nm and in the NIR region between 1700 and 2300 nm (Fig. 7D). Several wavelengths, such as 1100, 1600, 1700 to 1800, 2200, and 2300 nm are reported to be important for predicting OC (Stenberg et al., 2010; Morgan et al., 2009). Figure 7D and 7F shows that the absorption regions for OC and Clay/OC ratio in the vis-NIR region were extensively camouflaged by the absorption peaks of water when soil-water content was at pF 1. Therefore, their prediction performance declined in wet soil as compared with dry soil. Rienzi et al. (2014) found that the characteristic water peak near 1180 nm could overlap with the defined peaks for H-C aromatics (1142 nm) and alkene (1170 nm) in the NIR region, which are important for OC prediction. Furthermore, Stenberg (2010) and Knadel et al. (2014) found that the important spectral features of OC near 1700 nm had a tendency to be superimposed by the broader water absorptions of free water in the NIR region. Counter to the negative effect of water we found in our study, Stenberg (2010) found a positive effect of rewetting on the prediction of OC. However, his results were obtained with a higher range in SOC content of 0.4 to 6.9% compared with the 0.9 to 2.4% in our study and with different type of soil. Neither have any consistent results been found in the literature on the effect of moisture on the predictive ability of soil clay content and OC/OM content using vis-NIRS. A possible reason could be that moisture can interact with other soil properties such as soil texture, particularly clay content and mineralogy, sand content, OM content and iron content and alter this effect (Knadel et al., 2014; Demattê et al., 2010; Stenberg, 2010; Kuang and Mouazen, 2013a; Rienzi et al., 2014).

CONCLUSIONS

This study investigated the effect of soil-water content at different moisture levels on the soil vis-NIR spectral reflectance and quantified their effects on the predictive ability for six different soil properties: clay, silt, sand, water content at pF 3, OC and the clay/OC ratio using vis-NIR spectroscopy. The results show that the water retention characteristics of soil govern the water effect on the soil vis-NIR spectra. The presence of water decreased the vis-NIR spectral reflectance and this effect was higher when the soil contained a larger amount of free water. The biggest difference in water effect on vis-NIR spectra was found at the change from capillary to absorptive surface forces, related to the changes between wet and dry soil. The moisture effect on the soil vis-NIR spectra for the high moisture levels was smaller when the water absorption potential was higher. In contrast, the proportion of free water affected the spectral features in the vis-NIR region when water adsorption capacity of the soil was low. Subsequently, pronounced water peaks in the vis-NIR region masked the important spectral features of other soil components.

Clay, silt, sand content, and the water content at pF 3 were well predicted by vis-NIR models at all soil moisture levels, suggesting that these properties can be predicted with high de-

gree of accuracy using spectroscopy under field conditions at any moisture level. However, the predictions of OC and clay/OC ratio were good only for air-dried soils likely because of the interference of free water on the spectral features important for the prediction of OC and clay/OC ratio when the water content is above field capacity. Therefore, the results suggest that poorer predictions of OC and OC-derived properties can be expected when the soil-water content exceeds field capacity ($pF < 2$). For field application, the results suggest that attention should be taken to deploy soil sensors only at relative dry soil conditions for the prediction of OC and clay/OC ratio. However, this study was limited by the low variability in OC content in soil. Therefore, further research is needed to determine the water effect on the prediction accuracy of vis-NIR models for a wider variation in soil properties including soil texture and OC.

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