Error propagation in spectrometric functions of soil organic carbon

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Abstract

Soil organic carbon (SOC) plays a major role concerning the chemical, physical and biological soil properties and functions. To get a better understanding how soil management affects the SOC content, the exact monitoring of SOC on long-term field experiments (LTFE) is needed. Visible and near infrared (Vis-NIR) reflectance spectrometry provides an inexpensive and fast possibility to enhance conventional SOC analysis and has often been used to predict SOC. For this study, 100 soil samples were collected at a LTFE in central Germany by two different sampling designs. SOC values ranged between 1.5 and 2.9%. Regression models were built using partial least square regression (PLSR). In order to build robust models, a nested repeated 5-fold cross-validation was used, that comprises model tuning and evaluation. Various aspects that influence the obtained error measure were analysed and discussed. Four preprocessing methods were compared in order to extract information regarding SOC from the spectra. Overall the best model performance which did not consider error propagation corresponds to a mean $RMSE_{MV}$ of 0.12 % SOC (R^2=0.86). This model performance is impaired by $\Delta RMSE_{MV}$ = 0.04% SOC while considering input data uncertainties (ΔR^2=0.09), and by $\Delta RMSE_{MV}$ = 0.12 (ΔR^2=0.17) considering an inappropriate pre-processing. The effect of the sampling design amounts to a $\Delta RMSE_{MV}$ of 0.02% SOC (ΔR^2=0.05). We emphasize the necessity of a transparent and precise documentation of the measurement protocol, the model building and validation procedure, including the calculation of the error measure, in order to assess model performance in a comprehensive way and allow for comparison between publications. The consideration of uncertainty propagation is essential when applying Vis-NIR spectrometry for soil monitoring.

1 Introduction

Soil is at the same time one of the most important and one of the most limited natural resources. Most of all it is needed for food production, but also for the production of energy and fibre or for the provision of fresh water (Johnson, 2008; Lorenz and Lal, 2016; Stenberg et al., 2010). All these aspects depend on the quality of the existing soil. This quality in turn is much influenced by its SOC content since it affects chemical, physical and biological soil properties and functions (Knadel et al., 2015; Lorenz and Lal, 2016). Additionally, SOC is also interesting when it comes to the global warming issue since soil is the largest terrestrial reservoir of organic carbon in the world (Conforti et al., 2015; Johnson, 2008; McBratney et al., 2014; Stockmann et al., 2013). The SOC content of soils can be increased through the sequestration of atmospheric CO_2 into long-living components of soils (Lal, 2004; McBratney et al., 2014). Thus, the SOC stock of soils could be used as a manageable sink for atmospheric carbon (Stockmann et al., 2013), achieving both food security and a strategy against the increasing CO_2-concentration in the global atmosphere (Lal, 2004; Lorenz and Lal, 2016; McBratney et al., 2014). As the SOC content of soils reacts very slowly to environmental changes (Meersmans et al., 2009), long-term field experiments (LTFE) are required to understand the impact of soil management and farming systems on the rate of SOC sequestration (Lal, 2004) as well as on yield and crop quality in the long run.

The precise monitoring of SOC on a LTFE with conventional lab analysis is labour-intensive and expensive (Adamchuk and Viscarra Rossel, 2010; Loum et al., 2016) as it requires the analysis of a rather high amount of samples. Visible and near infrared (Vis-NIR) reflectance spectrometry can facilitate this procedure. It is non-destructive, fast and economical (Mouazen et al., 2010; Tekin et al., 2014), requiring only a small number of soil samples and little sample preparation (Conforti et al., 2015). In addition, no chemicals are needed and one spectrum contains information about many different soil components (Conforti et al., 2015; Viscarra Rossel et al., 2006b). Spectral absorption features are caused by vibrational stretching and bending of structural molecule groups and electronic excitation (Ben-Dor et al., 1999; Dalal and Henry, 1986). Molecule vibrations from hydroxyl, carboxyl and amine functional groups produce soil absorption features related to soil organic matter in the mid-infrared (MIR) region of the spectra (Croft et al., 2012). In comparison, Vis-NIR spectra show only broad and unclear adsorption features related to overtone vibrations from the MIR, but instruments are less cost-intensive and available for field monitoring as well (Stenberg and Viscarra Rossel, 2010; Viscarra Rossel et al., 2006a). Furthermore, in diffuse reflectance spectroscopy, scattering properties depend on the particular wavelengths and can vary significantly over the VIS-NIR spectral range (Pilorget et al., 2016). Hence, pre-processing of Vis-NIR spectra is necessary in order to extract soil property related information (Stenberg and Viscarra Rossel, 2010).

Scattering and other effects attributed to within-sample variance can be addressed by repeated measurements of replicate samples (e.g. Pimstein et al., 2011). Alltogether, Vis-NIR soil spectrometry has been used on many occasions to build SOC prediction models (Jiang et al., 2016; Kuang and Mouazen, 2013; Nocita et al., 2013).

However, the application of Vis-NIR soil spectrometry for SOC determination involves a couple of uncertainties. The required calibration data are determined with standard lab analysis, e.g. dry combustion, with associated uncertainties. On the other hand side, the spectral measurements are affected by the sample preparation, e.g. drying, sieving, grinding (e.g. Nduwamungu et al., 2010). Furthermore, sensor noise and other spectrometer internal sources (electronic and mechanical) can affect the measurements (Schwartz et al., 2011). Finally, these two uncertain data sources are related by a regression model. And the model building procedure involves a couple of error sources itself. The development of robust models requires a resampling process to determine the model parameters and avoid overfitting; the applied resampling method impacts model performance (e.g. Molinaro et al., 2005, Beleites et al., 2005). Further aspects that impact model performance are the available dataset in concordance with the applied sampling design, the handling of outliers, spectral pre-processing, and last but not least the model evaluation procedure. In most studies dealing with SOC prediction from Vis-NIR spectra, no clear statement about input data uncertainties or their handling is made. The reported prediction errors only refer to the model building procedure, while uncertainties from lab measurements are neglected. Commonly, only a single SOC measurement per soil sample is available. In spectral soil sensing in lab applications, the general approach consistst in averaging the multiple measured spectra of one sample to one spectrum which is then used for model building (Ge et al., 2011; Stevens et al., 2013; Viscarra Rossel et al., 2003). But the number of measurements used to gain one averaged spectrum differs between studies. Jiang et al. (2016), for example, averaged 10 measurements to receive one spectrum, while Volkan Bilgili et al. (2010) and Wang et al. (2014) used four measurements. This difference is also assumed to have an influence on the uncertainties implemented in the input data.

Overall, to allow for comparision between studies, in terms of predictive uncertainty in % SOC, a modelling procedure is required that deals with the propagation of the input data uncertainites. For discussion of the general concept, please refer to Jansen (1998), for applications in soil modelling compare e.g. Heuvelink et al. (1999) and Poggio and Gimona (2014). Although, the problem of the involved uncertainties in Vis-NIR spectrometry is well-known (e.g. Gholizadeh et al., 2013, Nduwamungu et al., 2010, Mortensen, 2014), implementations of uncertainty propagation in Vis-NIR spectrometric modelling are lacking.
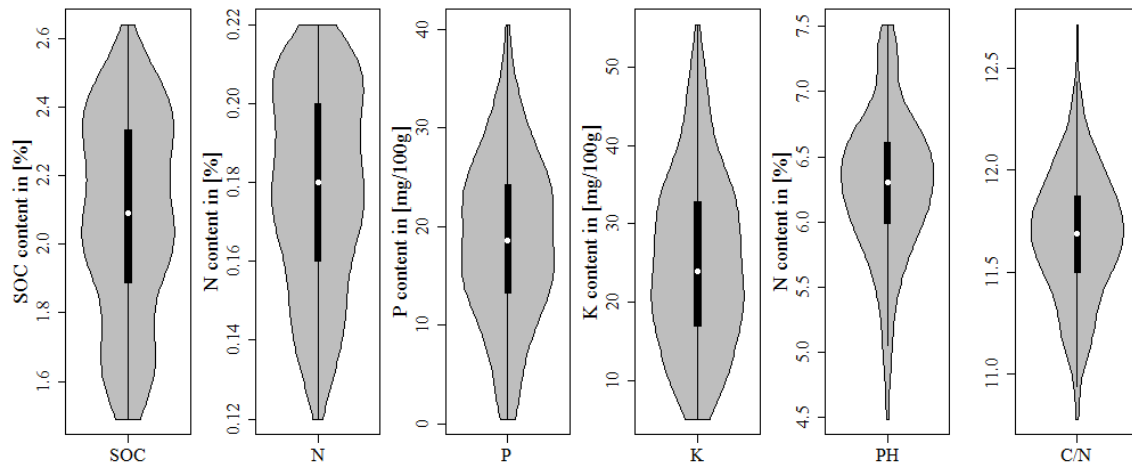
2 Material and Methods

2.1 The static fertilization experiment Bad Lauchstädt

The soil samples were taken at the LTFE site "Static Fertilisation Experiment" in Bad Lauchstädt in central Germany (Körschens and Pfefferkorn, 1998). Positioned at 51° 24' N, 11 ° 53' E and with an altitude of 113 m

95   (Körschens and Pfefferkorn, 1998), the climate is characterized by a mean annual precipitation of 470 – 540 mm and an average mean annual temperature of 8.5 – 9.0 °C. The soil type was characterized as a haplic Chernozem developed from loess (Altermann et al., 2005) with a soil texture of 21.1 ± 1.2 % clay, 72.1 ± 1.7 % silt, and 6.9 ± 1.9 % sand (Dierke and Werban, 2013). Saturated water conductivity and air capacity are medium to high in the top soil (Altermann et al., 2005). The Static Fertilization Experiment was initialized in 1902 by Schneidewind and

100   Gröbler and is about 4 ha in size (Merbach and Schulz, 2013) Its objective is to investigate the impact of organic and mineral fertilization on soil fertility as well as yield and quality of crops (Körschens and Pfefferkorn, 1998; Schulz, 2017). The experiment includes eight subfields with a width from 25.2 m to 28.5 m and a length of 190 m which are each divided into 18 plots that are treated with different mineral and organic fertilizer as well as planted with different crops following a crop rotation (Körschens and Pfefferkorn, 1998). The plots of subfields 4 and 5

105   are additionally parted into 5 smaller subplots.

2.2 Sampling design

A total of 100 soil samples were taken at the soil surface (0-10 cm) in September 2016. The exact location of the sampling points was determined by a differential GPS GNSS LEICA Viva GS08. It was decided to sample at precise point locations instead of taking samples representative for LTFE plots to allow for a direct comparison

110   with spectrometric field measurements for area-wide regionalisation (not included in this study). The sampling points were determined beforehand by two sampling designs. Based on the LTFE treatment factors and per-plot soil archive data including C_{org}, N_{tot}, plant available P, plant available K (both with DL-Method (VDLUFA, 2012)) and pH (Fig. 1) both designs strived to select a dataset of 50 samples representative for the soil variability of the entire LTFE. Categorical and continuous data first entered a factor analysis with mixed data (FAMD) performed

115   with R package FactoMineR (Lê et al., 2008) to allow for further joint analysis. For design 'A' the LTFE plots were then grouped by a k-means cluster analysis. R package NbClust (Charrad et al., 2014) automatically determines the optimal number of clusters making use of 30 indices. In the end, ten plots were randomly selected from each of the resulting five clusters making a total of 50 plots to be sampled. For design 'B' the Kennard-Stone algorithm was applied with R package prospectr (Kennard and Stone, 1969; Stevens and Ramirez Lopez, 2014).

120   50 LTFE plots were selected involving 5 repetitions of the algorithm to reduce inter-point dependence. Finally, one sampling point was randomly selected from each of the 50 LTFE plots from design A and B based on a 5 x 5 cm raster. Plot margins of 1.5 m (3 m between plots) were excluded. Fig. 2 shows the location of the so obtained 100 soil samples.

125   **Fig. 1 Soil archive data of the LTFE measured from 2004 to 2007 (Reports of the experimental station Bad Lauschstädt 2004-2007 (unpublished).**
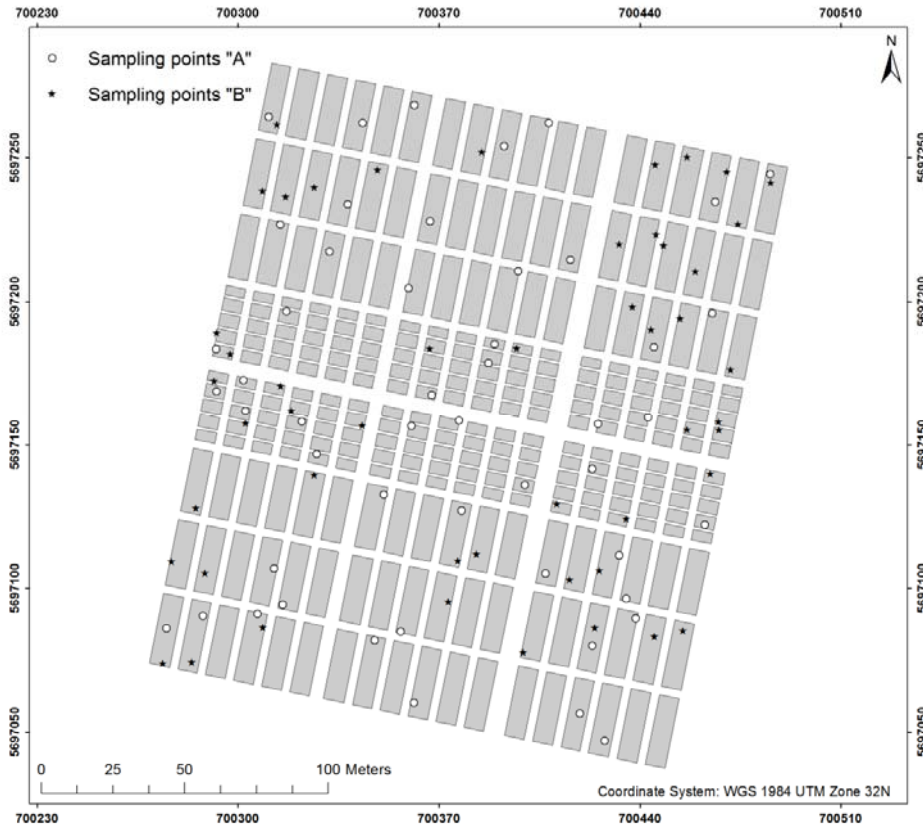
Fig. 2 Site of the Static Fertilisation Experiment in Bad Lauchstädt with LTFE plots and sampling points according to design A and B. Plot margins excluded from sampling are visible as 3 m wide stripes between plots.

130 **2.3   Laboratory measurements**

The soil samples were air-dried, sieved and grinded prior to C measurements with dry combustion. A High-end Elementaranalysator vario EL Cube-CN was used. Measurements were repeated in three replicate samples. C measurements were taken as organic carbon due to negligibly small carbonate contents (below detection limit). The Vis-NIR contact measurements were performed on air-dried and sieved (2 mm) samples in July 2017, using

135 Veris® VIS-NIR Spectrophotometer by Veris technologies, Inc. (hereinafter called Veris) containing an Ocean Optics USB4000 instrument (200 to 1100 nm) and a Hamamatsu Mini-spectrometer TG series (1100 to 2200 nm, resolution 6 nm). The device was warmed up for at least 20 minutes before performing measurements. All measurements were taken in a dark room to prevent daylight from affecting the outcome. The soil samples were scanned from the top. Before and between soil sample measurements, Veris was calibrated using four Avian

140 Technologies Fluorilon™ gray scale standards. Each soil sample was divided into three sub-samples filled into petri dishes (Schott Duran petri dishes; Duran Group, Mainz, Germany). These replicate samples were not related

to the three replicate samples used for C/N-measurements. For each replicate sample six spectra were gained by measuring each replicate sample three times, rotating it by 90 degrees and then measuring it three times again. This procedure resulted in 18 spectra for each soil sample. Internally the spectrometer averaged 25 scans for each

145   spectrometer reading (spectrometer setting).

2.4   Spectral pre-processing

Veris is equipped with two spectrometers. At the beginning and end of their respective wavelength ranges noise occurs in the measurements. Therefore, the spectra between these wavelengths (1000 to 1100 nm) had to be removed. Additionally, the spectra were cut at the beginning (402 nm) and the end (2220 nm) to remove noise. A

150   number of pre-processing methods were tested to enhance the information regarding SOC in the Vis-NIR spectra. The spectra were tested for outliers using R package mvoutlier (Filzmoser and Gschwandtner, 2017). For this procedure a PCA is performed, using then the first two obtained PCs for outlier detection with function aq.plot. Out of the tested pre-processing methods, four different combinations are shown in this study in order to demonstrate their different effects on the prediction model. Their application resulted in spectra with different

155   wavelength ranges (Table 1) and different appearance (Fig. 3). These pre-processing techniques include the Savitzky-Golay algorithm (SG), continuum removal (CR), the standard normal variate (SNV), the first derivative (d1) and the gap-segment algorithm (gapDer). The SG algorithm fits a polynomial regression on the spectral data to find the derivative at a center point i of a defined smoothing window (w) (Rinnan et al., 2009; Savitzky and Golay, 1964; Swarbrick, 2016). CR can be seen as a spectra normalization technique which enables to compare

160   different absorption characteristics from a mutual baseline (Kokaly, 2001; Mutanga and Skidmore, 2003). It identifies the local reflectance spectra maximum points and connects those points to form a convex hull (Mutanga and Skidmore, 2003; Stevens and Ramirez Lopez, 2014). Calculating

$$\phi_i = \frac{x_i}{c_i} \qquad\qquad (1)$$

for i = {1, ... , p} with x_i and c_i being the initial and the continuum reflectance values at wavelength i of a set of p

165   wavelengths then gives the continuum-removed reflectance value ϕi (Stevens and Ramirez Lopez, 2014). All other data have values between 1 and 0 (Mutanga and Skidmore, 2003; Schmidt and Skidmore, 2001). Thus the absorption peaks are enhanced (Schmidt and Skidmore, 2001). SNV is a scatter-corrective pre-processing method (Rinnan et al., 2009). The basic formula is as follows

$$x_{corr} = \frac{x_{org} - a_0}{a_1} \qquad (2)$$

with a_0 as the measured spectrum's average value which shall be corrected and a_1 being the sample spectrum's standard deviation. x_{org} are the original spectra and x_{corr} the corrected spectra after applying SNV. SNV operates row-wise, so each observation is processed on its own (Rinnan et al., 2009; Stevens and Ramirez Lopez, 2014). d1 represents the slope of the spectrum, showing peaks where the spectrum displays its maximum slope and crossing zero where the spectrum shows peaks (Leone et al., 2012). According to Knadel et al. (2015) and Smith (2002), d1 can be used to remove baseline offsets from the spectra. The estimation of d1 is done by computing the difference between two batched spectral points x_i and x_{i-1} (Eq. 3)
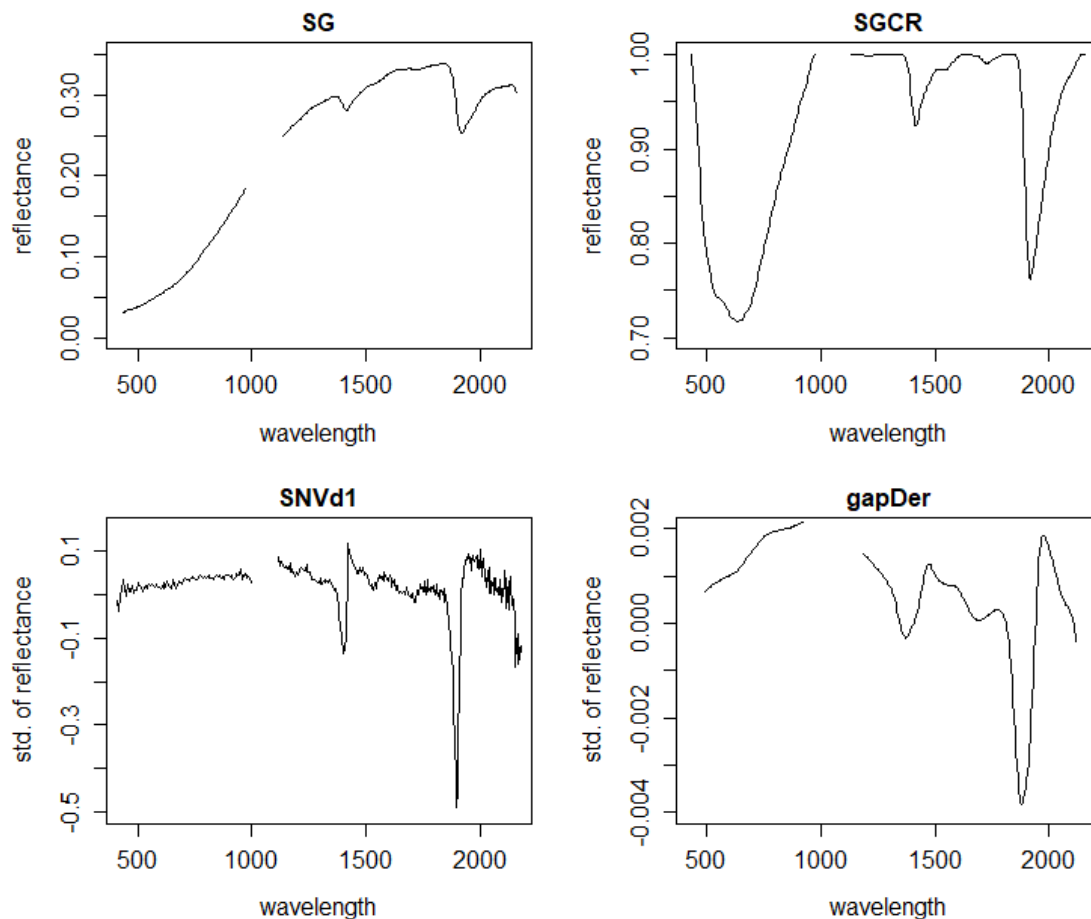
$$x_i' = x_i - x_{i-1} \qquad (3)$$

with x_i' as the value of the first derivative at the ith wavelength (Rinnan et al., 2009). The downside of using derivative spectra is their tendency to over-fit the calibration model (Stevens and Ramirez Lopez, 2014). Moreover, derivatives may increase noise so that a smoothing of the data is required (Leone et al., 2012; Stevens and Ramirez Lopez, 2014). With the gapDer a smoothing is performed under a chosen segment size (s) and then a derivative follows (Stevens and Ramirez Lopez, 2014). The application of the different pre-processing methods for this study was conducted using R package prospectr (Stevens and Ramirez Lopez, 2014).

Table 1 Combinations of pre-processing techniques used in this study; w = window size, s = segment size.

Pre-processing methods	Wavelength range	Abbr.
Savitzky-Golay (w =11 nm)	432 – 2201 nm	SG
Savitzky-Golay (w=11 nm) and continuum removal	432 – 2201 nm	SGCR
Standard normal variate and 1st derivative	408 – 2186 nm	SNVd1
Gap-segment algorithm (w = 11 nm, s = 10 nm)	490 – 2163 nm	gapDer

185

Fig. 3 Impact of different pre-processing techniques on a spectrum; SG = Savitzky-Golay, CR = continuum removal, SNV = standard normal variate, d1 = 1ˢᵗ derivative, gapDer = Gap-segment algorithm.

2.5   Error propagation

A problem occurring in every model building process is uncertainty propagation. Uncertainties of the input data and model result in uncertainties in the output (Brown and Heuvelink, 2006). Uncertainties in the input data are caused by errors in data acquisition (e.g. measurement errors) as well as variation in the data themselves (e.g. within-sample variability) (Heuvelink, 1999). For this study, there are two different sources for errors in data acquisition: the measurement of the spectral data and the measurement of the SOC content of the soil samples. In order to investigate the influence of these errors, different datasets were built in this study. Fig. 4 gives an overview. From the measured Vis-NIR spectra, three different spectral data variants were created (Fig. 4, step 1). For the first variant, all 18 spectra were retained. The inclusion of all 18 spectra reveals the influence of the error implemented in the spectral measurements as well as the influence of the within-sample variability. For the second,

10

the three measurements obtained before and after sample rotation were averaged separately resulting in 6 spectra per sample showing the influence of within-sample variability. For the third data variant, all 18 spectra were averaged to 1 mean spectrum per sample, removing the influence of the measurement error as well as the within-sample variability. The different spectra obtained through this procedure can be seen in Fig. 5. Only parts of the spectra are depicted in order to show their differences. The three different spectral data variants were then pre-processed with the different pre-processing methods from Table 1 (Fig. 4, step 2), resulting into 12 different spectral datasets (Fig. 4, step 3). These were then combined with single and averaged SOC values in step 4 so that altogether 24 datasets were obtained (Fig. 4, step 5). In order to compare the two sampling designs, this procedure was carried out for the 50 soil samples labelled "A" and "B" and also for the complete set of soil samples. In this way, three different soil sample sets ("A", "B" and "all samples") were achieved.
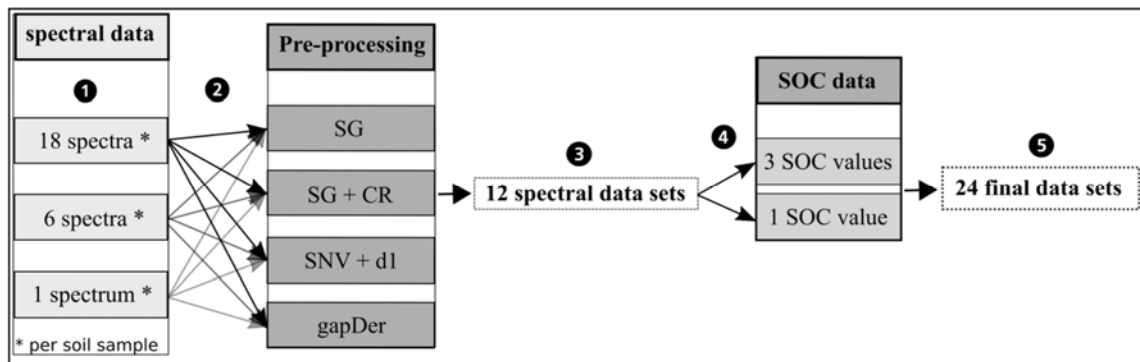

Fig. 4 Datasets to investigate the uncertainty propagation. SG = Savitzky-Golay, CR = continuum removal, SNV = standard normal variate, d1 = 1st derivative, gapDer = Gap-segment algorithm.
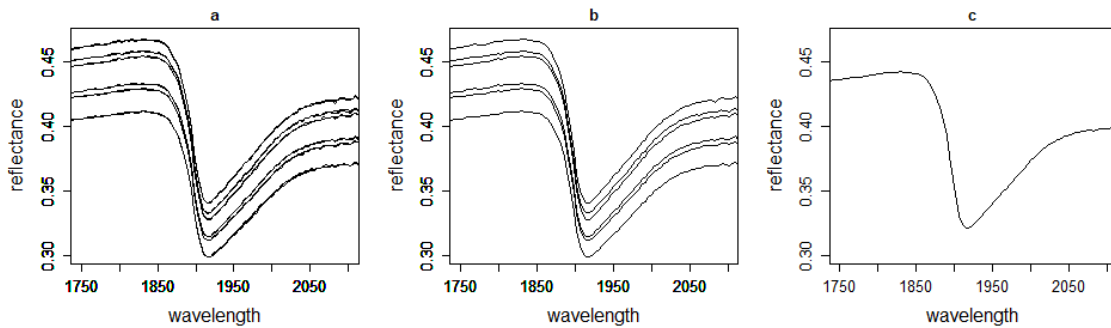

Fig. 5 Zoom-in to a sample's spectral dataset: a) 18 spectra comprised of 6 replicate sample measurements with 3 scans each, b) 6 spectra related to replicate sample measurements (average of three scans each) and c) 1 averaged spectrum.
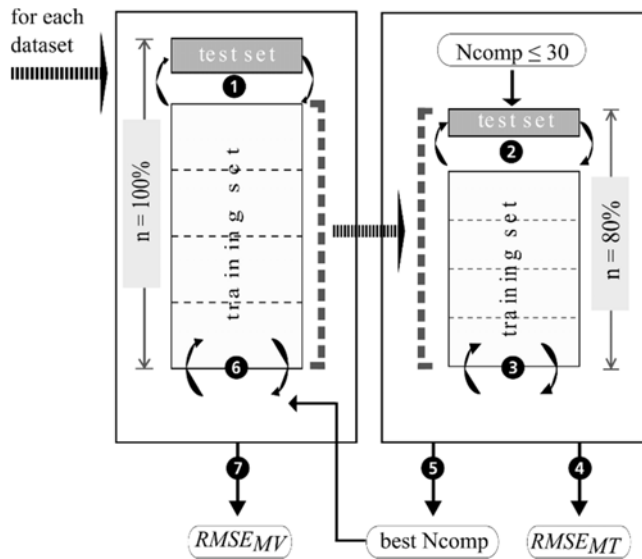
2.6   Model building and validation

Regression models were built using partial least square regression (PLSR). Out of the many algorithms, PLSR is seen as a standard method for spectral calibration and prediction (Mouazen et al., 2010; Tekin et al., 2014; Viscarra Rossel et al., 2006b). For applications to predict SOC from Vis-NIR soil spectra see (Conforti et al., 2015; Jiang

et al., 2016; Kuang and Mouazen, 2013; Nocita et al., 2013). PLSR is described in detail by Martens and Næs (1989) and Naes et al. (2002). It incorporates characteristics from principle component analysis (PCA) and multiple regression (Abdi, 2007). The concept behind PLSR is to seek a small number of linear combinations (components or latent factors) obtained from the measured spectral data and to use them in the regression equation to predict SOC instead of the initial values (Martens and Næs, 1989; Naes et al., 2002). These components are constructed so that they account for most variance in the measured spectral data (X) and the SOC content (Y) and at the same time maximize the correlation between X and Y. In other words, PLSR leads to the covariance between X and Y being maximized (Bjørsvik and Martens, 2008; Summers et al., 2011; Tekin et al., 2014; Wehrens, 2011).

In order to receive a robust model, it is important not to include too many components in model building as this will lead to over-fitting (Hastie et al., 2009; Kuhn and Johnson, 2013). On the other hand, the inclusion of too few components comprises the risk of building an under-fitted model which is too small to cover the variability existing in the soil spectral data (Naes et al., 2002). The selection of the optimal number of components is hereinafter referred to as *model tuning*. In order to receive a robust model, resampling is commonly applied for model building and validation. But resampling can also be used for *model tuning* to receive robust tuning parameters (Guio Blanco et al., 2018; Hastie et al., 2009; Kuhn and Johnson, 2013). For small datasets, k-fold cross-validation is recommended (Hastie et al., 2009).

In this study, model building, *model validation* and *model tuning* was done using a nested repeated 5-fold cross-validation (CV) (e.g. Varma and Simon, 2006, Guio Blanco et al., 2018). Repeated 5-fold CV can increase the precision of the prediction while maintaining a small bias (Kuhn and Johnson, 2013). Five Repetitions of 5-fold CV were conducted in this case.

Fig. 6 M*odel tuning* and *model validation* **procedure with a nested k-fold cross validation approach. The right box shows the *model tuning*, the left one the *model validation* procedure; Ncomp = number of components; adapted from Guio Blanco et al. (2018).**
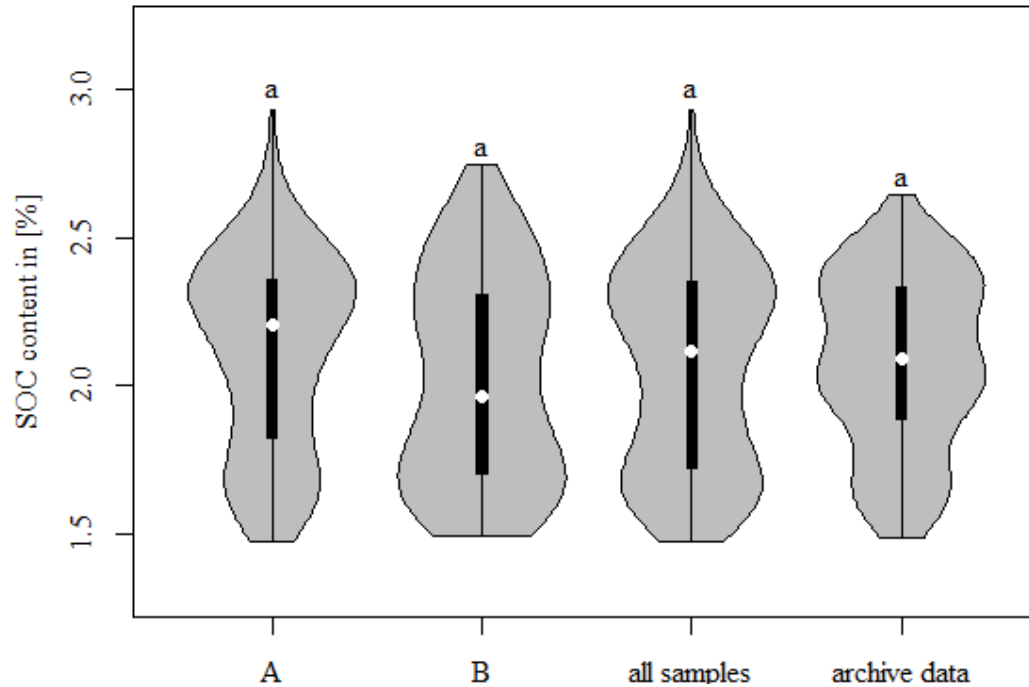
Fig. 6 shows the various steps of the modelling procedure involving repeated 5-fold CV for *model tuning* (right box) and *validation* (left box). In the process the dataset (n = 100%) is randomly subdivided into 5 folds of equal size (step 1). One of the 5 folds is held out as test set and the other four are used as training set and partitioned again into 5 folds for *model tuning* (step 2). The optimal number of components (*best Ncomp*) is then determined by computing a PLSR on the resampled data testing 1 to 30 components (step 3) calculating the repeatedly 5-fold cross-validated RMSE of *model tuning* (RMSE$_{MT}$) (step 4). This was implemented with the trainControl() function in package caret (Kuhn, 2017). The optimal number of components (step 5) is then used in model building (step 6). The resulting model's test set RMSE of model validation (RMSE$_{MV}$) is determined in step 7. The whole procedure is repeated until all folds in the boxes have once been used as test set.

In this study, the subdivsision of the spectral data into the folds for 5-fold CV had to account for repeated scans and replicate measurements per sample. All spectra for one sample were assigned to the same fold during k-fold CV, i.e. k-fold group CV. The folds contained always the same sample IDs for the various data variants described in Figure 4. For model validation, folds were created following a repeated stratified group CV approach (5-fold). The data were primarily subdivided into 5 equal probability strata based on their density function. The data from each of the strata were then randomly assigned to the 5 folds. Neighbouring points of ≤ 5 m distance were assigned to the same fold to avoid spatial autocorrelation and too optimistic error measures.

3 Results and Discussion

3.1 Soil organic carbon content

Fig. 7 shows the distribution of the SOC content of the three soil sample sets, consisting of 50 soil samples labelled "A" and "B" and 100 soil samples referred to as "all samples". The measurement error existing in the SOC measurements, here defined as the difference between replicate measurements, ranges from 0.003 to 0.229 % SOC with a mean of 0.048 % SOC. The aim of this study was not to compare the two different sampling designs among each other, but to test whether they are representative of the SOC values existing on the LTFE. For this purpose, per-plot soil archive data from the years 2004 to 2007 are also displayed. The statistics of the data are given in Table 2. In order to compare distributions between the archive SOC data and "A", "B" and "all samples", a Mann–Whitney U test was applied to the data, testing the "A", "B" and "all samples" against the archive data, respectively. In all cases, no significant difference between the different sample sets and the archive data could be found. This shows that all soil sample sets used in this study are representative for the SOC values existing in the LTFE. Nevertheless, the SOC distribution of "A" and "B" samples differ, with the "A" samples resembling the distribution of all 100 samples more than the "B" samples. The "A" samples contained more samples representing higher SOC values, whereas the "B" samples show a higher representation for lower SOC values. This difference in the distribution of SOC values may have an influence on the prediction results of the models built with "A" and "B" samples. "A" models may be better in predicting higher SOC values, while simultaneously failing to estimate lower SOC values in an appropriate way. To the contrary, "B" models may predict lower SOC values more accurate than higher SOC values. The violin plots of all three soil sample sets do not resemble the archive violin plot very much. The plots for "A" and all samples show higher and lower SOC values than the archive data due to the fact that those data are obtained from compound samples for one plot. The "B" samples share the same minimum value with the archive data, but display slightly higher SOC values. This indicates that the choice of the sampling design might have an influence on the model outcome, even if both designs represent the SOC values on the experimental field in an appropriate way.

Fig. 7 Soil organic carbon (SOC) content of the three soil sample sets "A" (left), "B" (middle), and all (middle) and of archive data measured from 2004 to 2007 (right); The thin line shows the 95 % confidence interval, the bar the interquartile range and the dot the median; Mann–Whitney U test was used to compare "A", "B", and all samples to the archive data; the three soil sample sets were not compared among each other.

Table 2 Statistics of soil organic carbon in [%] for the three different soil sample sets and the per-plot soil archive data.

Samples	Min.	1st Qu.	Median	Mean	3rd Qu.	Max.
"A"	1.47	1.82	2.21	2.11	2.36	2.93
"B"	1.49	1.70	1.97	2.02	2.31	2.74
all	1.47	1.72	2.12	2.01	2.35	2.93
Archive data	1.49	1.89	2.09	2.08	2.33	2.64

3.2   Comparison of datasets and pre-processing methods

According to Filzmoser (2005), the Mahalanobis distance of normally distributed data follows a chi-square distribution. Observations which lay beyond a certain quantile of this distribution are marked as outliers and removed from the data (Filzmoser and Gschwandtner, 2017). In this study, no outliers were detected.

15

Table 3 displays the different combinations of soil spectra and SOC values per soil sample. The resulting models are then named after the following scheme: Dataset$_{x1\ x2\ x3}$ with the SOC measurement error (x1), the spectral measurement error (x2) and the within-sample variability (x3). The number 1 indicates that the respective error is included into the model, the number 0 shows that the error was removed beforehand by averaging the data.

Table 3 Data basis per soil sample

	Number of SOC values per sample	Number of measured spectra per sample	Resulting size of the dataset per sample
Dataset$_{111}$	3	18	54
Dataset$_{101}$	3	6	18
Dataset$_{100}$	3	1	3
Dataset$_{011}$	1	18	18
Dataset$_{001}$	1	6	6
Dataset$_{000}$	1	1	1

Fig. 8 shows boxplots of the RMSE$_{MV}$. The six datasets are displayed in one panel. The models using "A" samples are shown in the 1st column (a), "B" samples in the 2nd column (b) and all samples in the 3rd column (c); Figure lines 1 to 4 refer to the used pre-processing method. As 5-fold CV with five repetitions was performed, five RMSE$_{MV}$ are shown in each boxplot. The model results are now compared based on their mean RMSE$_{MV}$ and their interquartile range. It is not surprising that the dataset of 3 SOC replicate measurements with 1 averaged spectrum (Dataset$_{100}$) results in low model performance, as the within-sample variance concerning SOC cannot be explained by the contained predictor information; the input data uncertainty propagates through the model building process. This model performance is impaired in some cases by Dataset$_{101}$ which combines the 3 SOC measurements with 6 replicate spectral measurements (Figures 8b$_1$, a$_2$, a$_3$, b$_3$, c$_3$) but not always. It seems that the within sample variation concerning soil spectra can somehow compensate the within sample variability concerning SOC within the model building process, although replicate measurements do not match. Considering the dataset with 18 spectra and 3 SOC measurements, model performance improves even further (Dataset$_{111}$). In contrast to this, we find the expected pattern while only 1 SOC measurement is considered: model performance results display an increase of RMSE values from Dataset$_{000}$ to Dataset$_{001}$ to Dataset$_{011}$ due to the fact that more spectral variance is related to the same target information concerning SOC. This applies for three of the four spectral preprocessing variants (SG, SGCR, gapDer), while SNVd1 preprocessing displays an unexpected pattern with datasets including replicate measurements and multiple scans even outperforming those with averaged data. Overall SGCR resulted in the best model performance for data 'A' (Figure 8a$_2$) and all samples (Figure 8c$_2$), while SG preprocessing resulted best

for data 'B' (Figure 8b$_1$). However, the latter does not apply for Dataset$_{000}$ where gapDer preprocessing resulted in the best model performance with RMSE$_{MV}$= 0.13. Comparing the mean RMSE$_{MV}$ for samples 'A' and 'B', models build on samples 'B' resulted in better model performance whith the exception of Dataset$_{100}$. The locations of the 'B' samples were determined using the Kennard-Stone-algorithm, those of the 'A' samples with k-means clustering algorithm. Fig. 7 allows an assessment of the data collected by those two sampling designs and shows no clear resemblance between the violin plots of 'A', 'B' , all samples, and the archive violin plot. But the Mann–Whitney U test did not show a significant difference between the archive data and the sample sets used in this study. 'A' samples as well as 'B' samples seem to represent the LTFE SOC data in an adequate way. As already mentioned above, the difference in the distribution of SOC values of 'A' and 'B' samples might have led to a different predictive capability in certain SOC value ranges. If this difference is the reason for the better performance of the 'B' models cannot be stated with certainty.

Comparing Dataset$_{111}$ with Dataset$_{000}$ shows how the inclusion of all input data uncertainties affects the model results. It can be seen that a model without error propagation (Dataset$_{000}$) reaches a mean RMSE$_{MV}$ of 0.12 % SOC and mean R^2 0.86 using the pre-processing method which delivered the best results. A model with error propagation (Dataset$_{111}$) on the other hand reaches a mean RMSE$_{MV}$ of 0.16 % SOC and R^2 0.77. This is further illustrated in Fig. 9 and could be expected, as Dataset$_{000}$ contains no input data uncertainties, the RMSE$_{MV}$ values therefore only correspond to the model building process. Overall the best model performance which does not consider error propagation corresponds to a mean RMSE$_{MV}$ of 0.12 % SOC (R^2=0.86). This model performance is impaired by ΔRMSE$_{MV}$ = 0.04% SOC while considering input data uncertainties (ΔR^2=0.09), and by ΔRMSE$_{MV}$ = 0.12 (ΔR^2=0.17) considering an inappropriate pre-processing. The effect of the sampling design amounts to a ΔRMSE$_{MV}$ of 0.02% SOC (ΔR^2=0.05).
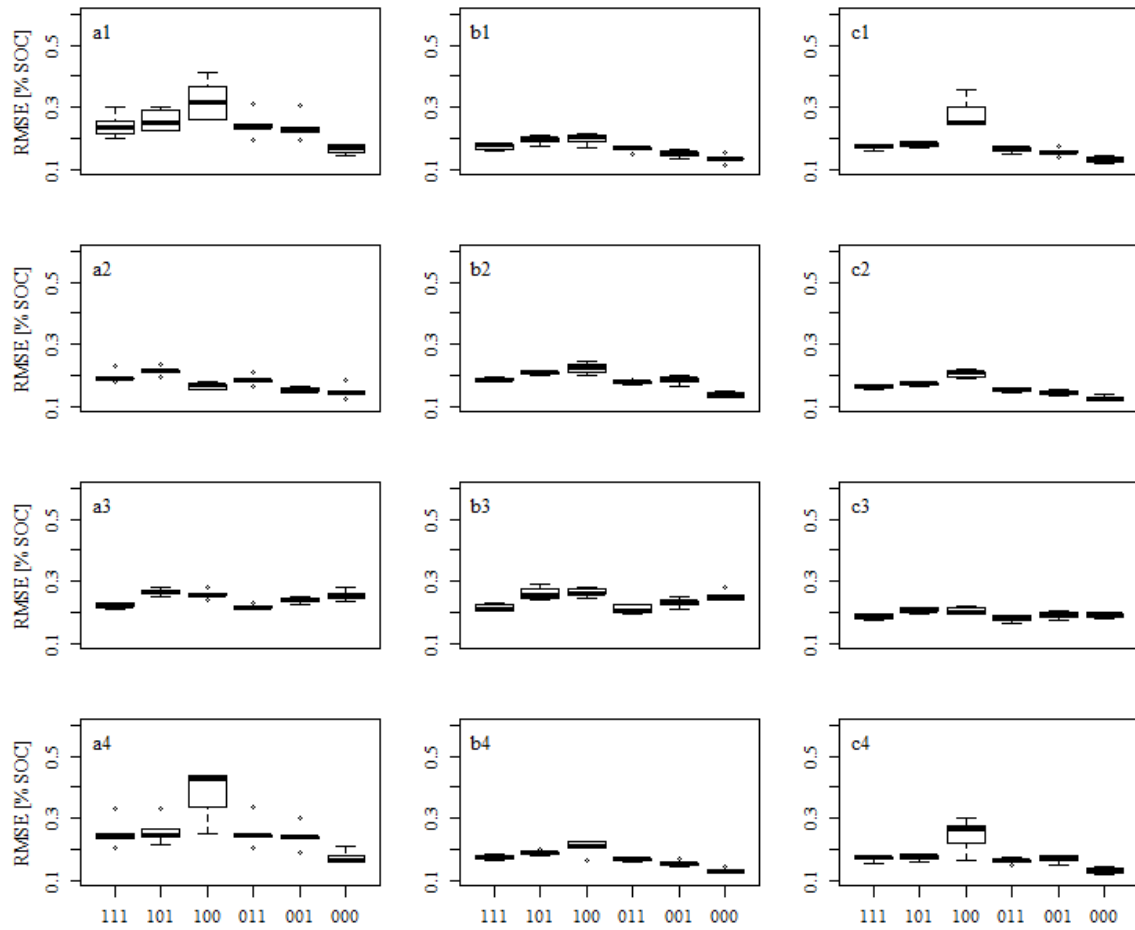
Fig. 8 Boxplots of testset RMSE$_{MV}$ (5 repetetions) obtained with the various datasets; Figure columns refer to datasets using a) 'A' samples, b) 'B' samples and c) all samples; figure rows refer to the applied pre-processing, 1 = SG, 2 = SGCR, 3 = SNVd1, 4 = gapDer.
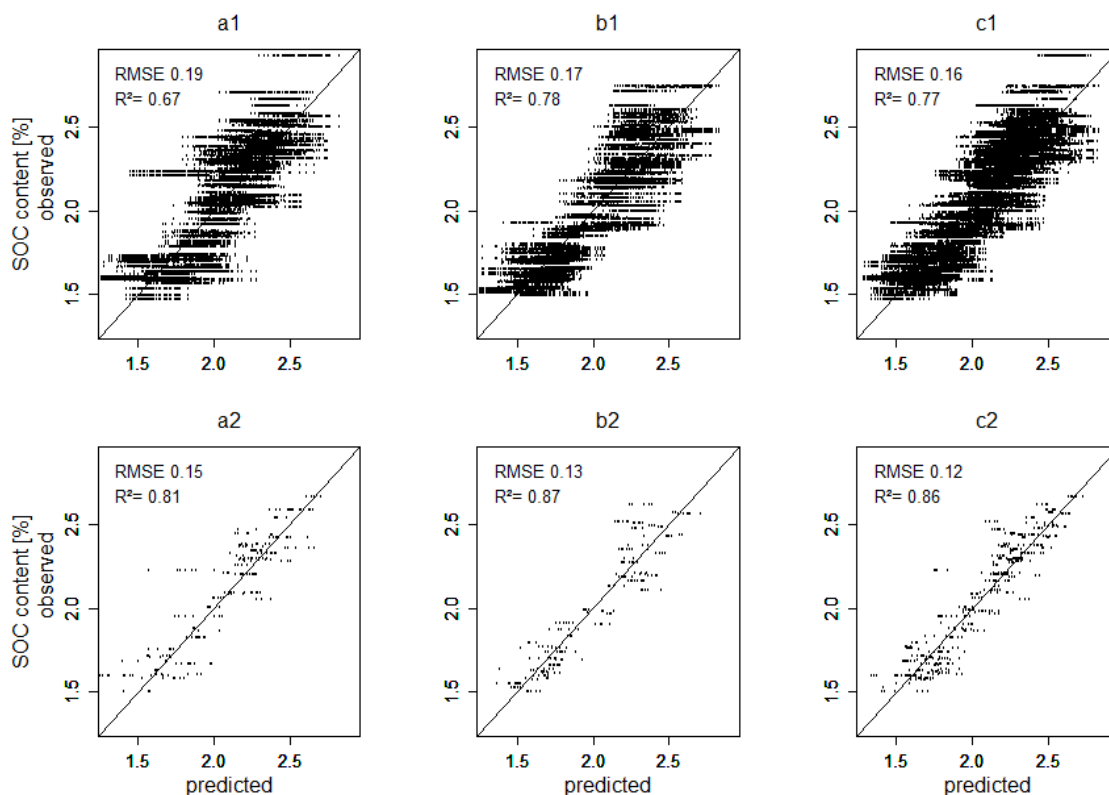
Fig. 9 Comparison of predicted and observed soil organic carbon (SOC) values for Dataset$_{111}$ (a1 to c1) and Dataset$_{000}$ (a2 to c2) for five repetitions with the corresponding best pre-processing (SGCR for data 'A' and all ADATA, SG for data 'B'); a) shows results for 'A' samples, b) for 'B' samples and c) for all samples. The depicted RMSE and R² values refer to the mean of 5 repetitions.

Examples of other studies using Vis-NIR spectra to predict SOC are listed in Table 4. Most studies used a different number of scans and replicate samples to get an averaged spectrum to predict SOC, so the error implemented in the respective input data is assumed to be different. Pimstein et al. (2011) propose a number of 3-5 replicate measurements as standard protocol for measurering Vis-NIR spectra of soil samples under laboratory conditions. Figure 5b indicated the high impact of within sample variance determined by the measurements of replicate samples, whereas the effect of the repeated scans per replicate is comparatively small (compare Figures 5a and b). We dried and sieved the samples before spectral measurements but did not grind them to fine powder. The latter might reduce spectral variance in replicate measurements, but the benefit of Vis-NIR spectroscopy as a fast and inexpensive method is reduced. One might argue that samples have to be grinded for SOC analysis, anyway. However, this requires a tiny fraction of the large amount that would have to be grinded for Vis-NIR measurements. In addition, comparison to measurements under field conditions is further distorted while grinding the samples for lab measurements. As shown in Figure 8, the input data error has a major influence on the model

19

outcome. In none of these studies the error in SOC measurements is mentioned to be considered during model building. Also, in most studies the available dataset is randomly parted into calibration and validation set, using different percentages of the data for the two sets. Jeong et al., 2017 and Beleites et al. (2005) showed that different validation strategies lead to different error measures.

The overall best pre-processing methods in this study were the combination of SG and CR as well as SG alone. SG was used successfully by many authors before for spectral pre-processing (Bogrekci and Lee, 2006; Nocita et al., 2013; Stevens et al., 2013; Viscarra Rossel et al., 2006a). CR was used by e.g. Viscarra Rossel et al. (2016) or Loum et al. (2016) with acceptable success. The combination of SG and CR could not be found in literature, though. SNV was applied before by other authors in order to remove baseline effects (Knadel et al., 2015; Minasny et al., 2011; Viscarra Rossel et al., 2006a). The pre-processing technique d1 was found to lead to poorer model results and rather unexpected performance patterns in this study. The former may have its cause in the tendency of d1 to over-fitting and the increasing of noise in the data as reported by some authors before (Leone et al., 2012; Stevens and Ramirez Lopez, 2014). We do not have an explanation for the latter, though. Leone et al. (2012) suggests the usage of SG in combination with d1 to solve the problem. For the usage of gapDer no comparison could be found in literature. As there is no standard pre-processing technique which works on all spectral data (Stenberg and Viscarra Rossel, 2010), it is recommended to always test various techniques and to choose the one which performs best for the respective data.

Table 4 R^2 from literature for soil organic carbon prediction models.

Author	number of samples	averaged scans per sample	calibration and validation set	R^2
(Reeves and Smith, 2009)	720	64	a) Cross-validation with all samples b) Independent validation set	a) 0.534 b) 0.335
(Islam et al., 2003)	161	-	Randomly selected from dataset (121 / 40)	0.76
(Wang et al., 2014)	156	4	Randomly selected from dataset (116 / 40)	0.67 - 0.88
(Volkan Bilgili et al., 2010)	512	100	Randomly selected from dataset (70 % and 30 %)	0.80

(Kuang and Mouazen, 2013)	174	10	60 % and 40 %	-
(Jiang et al., 2016)	98	10	Dataset parted into calibration and validation set	0.58 - 0.85
(Conforti et al., 2015)	201	30	-	-
(Leone et al., 2012)	374	4	Randomly selected from dataset (2/3 and 1/3)	0.84 - 0.92

4   Conclusions

This study aimed to investigate the influence different aspects have on the model building process and the
385   calculation of error measures. Those aspects included the input data uncertainties, the number of measurements
per sample and the chosen pre-processing method. Furthermore, the effect of sampling design, model tuning and
validation procedure was discussed. The applied nested cross validation approach that includes resampling in
model tuning as well as evaluation can be recommended in general. The fact that replicate measurements and scans
as well as geographically near samples have to be assigned to the same fold (k-fold group CV) in order to obtain
390   unbiased error measures is often neglected, and, therefore, has to be emphasized. Overall the best model
performance which does not consider error propagation corresponds to a mean $RMSE_{MV}$ of 0.12 % SOC (R^2=0.86).
This model performance is impaired by $\Delta RMSE_{MV}$ = 0.04% SOC while considering input data uncertainties
(ΔR^2=0.09), and by $\Delta RMSE_{MV}$ = 0.12 (ΔR^2=0.17) considering an inappropriate pre-processing. The effect of the
sampling design amounts to a $\Delta RMSE_{MV}$ of 0.02% SOC (ΔR^2=0.05). The rather high within-sample variance of
395   spectral replicate measurements of field-scale soil samples of very similar mineral composition requires a
reconsideration of the number of replicate measurements per sample. 3-5 replicates as suggested for Vis-NIR soil
measurements might simply not be enough. In general, this within-sample variability depends on the soil treatment
and possibly also on the origin of the samples (e.g. agricultural or forest soils). Overall, this study showed that it
is important to clarify which information the reported error measure contains. We are aware that the consideration
400   of stratified group CV for model evaluation but only partly for tuning (spectral replicate measurements and scans
per sample were always assigned to the same fold) might impair model performance as suboptimal model
parameters might be selected. This will be adapted in future studies. We emphasize the necessity of a transparent
and precise documentation of the measurement protocol, the model building and validation procesdure, including

21

the calculation of the error measure, in order to assess model preformance in a comprehensive way and allow for comparison between publications. Particularly, when Vis-NIR spectrometry is used for soil monitoring, the aspect of uncertainty propagation in the involved modelling procedure becomes essential.

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