Quantification of organic carbon concentrations and stocks of tidal marsh sediments via mid-infrared spectroscopy

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Tidal marshes are coastal ecosystems that store large amounts of sedimentary organic carbon (OC). Reducing the current uncertainty on the amount of OC stored these sediments requires the analysis of a large number of sediment samples. Soil sensing techniques, using mid-infrared (MIR) spectroscopy combined with partial least squares regression (PLSR), have been proven to be a valid alternative for standard OC measurements in a wide range of terrestrial ecosystems. However, the application of these techniques to tidal marsh sediments has been very limited and the error associated with calculated sedimentary OC stocks using MIR spectroscopy/PLSR data has up till now not been evaluated. Therefore, we assessed the potential of MIR spectroscopy/PLSR to predict the OC concentration and OC stock of tidal marsh sediments in a temperate estuary (Scheldt estuary, Belgium and The Netherlands). Based on a cross-validation procedure, the results show that MIR spectroscopy/PLSR predicts the OC concentration of tidal marsh sediments along the entire estuary with a high accuracy ($R^2 = 0.94$, RMSE = 0.56 % OC). Similar accuracies were obtained for the prediction of sedimentary OC concentrations from independent tidal marshes. Organic carbon concentrations from tidal marshes in the salt portion of the estuary were, however, predicted more accurately using a PLSR model trained exclusively with sediment samples from this salinity zone. Combining depth profiles of predicted OC concentrations with measured bulk densities resulted in predictions of total OC stocks with a relative error < 4 % for freshwater and brackish marshes, while errors for salt marshes were up to 30 %. As MIR spectroscopy/PLSR is not able to accurately predict bulk density or OC density, standard field measurements of bulk density remain necessary to reliably predict sedimentary OC stocks in tidal marshes.

MIR spectroscopy; soil sensing; tidal wetlands; sedimentary organic carbon; organic carbon stocks

1. Introduction

Tidal marshes are highly productive vegetated coastal ecosystems that store large amounts of sedimentary organic carbon (OC) (Duarte et al., 2013; Mcleod et al., 2011). Because of their presence in climatologically and geomorphologically diverse settings (Mcowen et al., 2017), large variations in the characteristics of OC stored in tidal marsh sediments exist, while OC concentrations vary substantially with depth (Hayes et al., 2017; Kelleway et al., 2016; Van de Broek et al., 2016) as well as in space (Chen et al., 2016; Choi et al., 2001; Elschot et al., 2015). As a result, total OC stocks in tidal marsh sediments show large variations (Duarte et al., 2013; Ewers Lewis et al., 2017; Schile et al., 2017) and data on the OC concentration of a large number of soil samples are required to accurately estimate the amount of OC stored in these sediments.

Multiple studies have shown the potential of diffuse reflectance spectroscopy in the visible and near (vis-NIR) or the mid infrared (MIR) domain, also referred to as soil sensing, as a fast and cost-efficient method for the prediction of multiple physical and chemical soil properties (Baldock et al., 2013; Bellon-Maurel and McBratney, 2011; Minasny et al., 2008; Reeves III, 2010; Reeves et al., 1999; Viscarra Rossel et al., 2006; Viscarra Rossel and Bouma, 2016). Soil sensing involves the acquisition of a soil spectrum, which is a measure for the amount of reflected radiation in a part of the electromagnetic spectrum. These spectra are subsequently processed using linear regression methods (e.g. principal component regression (PCR) or partial least squares regression (PLSR)) or machine learning techniques (e.g. support vector machines (SVM) or artificial neural networks (ANN)) to predict soil properties based on a calibration dataset for which measured data is available (Dotto et al., 2018; Igne et al., 2010; Kang et al., 2017; Vasques et al., 2008). These methods have been applied at a wide range of spatial scales, from regional (Bornemann et al., 2010; Jia et al., 2017) to continental (Baldock et al., 2013; Reeves and Smith, 2009; Stevens et al., 2013), to successfully predict soil properties. In addition, the construction of large libraries of soil spectra (e.g. Stevens et al., 2013; Viscarra Rossel et al., 2016), combined with the development of methods to

efficiently sample these libraries (e.g. Lobsey et al., 2017) significantly contributes to the potential of soil sensing as a valuable alternative to analyze soil properties.

Despite the fact that soil sensing techniques have been shown to provide reliable estimates of soil OC concentrations in terrestrial ecosystems, their application to intertidal sediments has been limited (e.g. Ewers Lewis et al., 2017; Hayes et al., 2017; Macreadie et al., 2017). Moreover, the potential error associated with MIR predictions of the OC concentration of tidal marsh sediments, and how this error affects calculated sedimentary OC stocks, has to date not been investigated. Although the accuracy of MIR predictions has been assessed for terrestrial soils (e.g. Baldock et al., 2013; Bellon-Maurel and McBratney, 2011), these findings cannot be directly transferred to tidal marsh environments for two main reasons. First, OC concentrations found in tidal marsh sediments exhibit a range that is substantially larger compared to most terrestrial soils (Bouillon and Boschker, 2006). Second, and more important, the quality of OC in tidal marsh sediments is substantially different from terrestrial soils. Tidal marsh OC is a mixture of terrestrial, marine and estuarine OC, which are found in different ratios in tidal marsh sediments depending on their location along an estuary (Van de Broek et al., 2018). In addition, the physical mechanisms that stabilize OC in tidal marsh sediments vary. On the one hand, freshwater marsh sediments can contain a substantial amount of particulate organic matter (POM) and aggregation can efficiently preserve sedimentary OC. In salt marshes, on the other hand, in contrast, POM can be rapidly mineralized upon burial and aggregates contribute little to the protection of OC against mineralization (Van de Broek et al., 2018). It is also unclear whether a single calibration model can be used to predict the variation in OC concentration in tidal marsh sediments along an entire estuary, or if different calibration models have to be used for regions with distinct sedimentary OC characteristics.

In this study, we assessed to which extent MIR spectroscopy can provide reliable estimates of the OC concentration and sedimentary OC stock of tidal marsh sediments along a temperate macro-tidal estuary. More specifically, our aims were (i) to assess the accuracy of predictions of sedimentary OC concentration,

bulk density and OC density using MIR spectroscopy, (ii) to determine the minimum size of the calibration dataset needed to obtain an optimal PLSR model, (iii) to use the optimal calibration model to assess the accuracy with which the OC concentration of independent tidal marsh sediments can be predicted and (iv) to determine the optimal spatial scale along the estuary for which a calibration model has to be constructed.

2. Materials and methods

2.1. Study site and sample processing

Soil depth profiles from 10 tidal marshes along the Scheldt estuary (Belgium and The Netherlands, salinity 0.3 – 30, , unitless according to UNESCO (1985)) were used for this study (Figure 1). The dataset included 325 soil samples from 4 freshwater marshes (salinity 0 – 5, n = 141, 6 depth profiles), 2 brackish marshes (salinity 5 – 18, n = 84, 4 depth profiles) and 4 salt marshes (salinity > 18, n = 100, 8 depth profiles). For all but two tidal marshes, we sampled both a location with a low and a high elevation. The location with a low elevation is currently located below the local mean high water level (MHWL), or was located below this level during the past decades. The location with a high elevation is currently located above the local MHWL .The study sites and the sample collection methodology are described in detail in Van de Broek et al. (2018, 2016). In short, at every sampling location soil cores were collected using a gouge auger for the analyses of (i) bulk density (3 replicate depth profiles) and (ii) general soil properties (3 replicate depth profiles). Samples for general soil properties were collected at a depth resolution of 0.03 m, while soil samples for bulk density were collected at depth increments of 0.05 m (0 - 0.05 m, 0.10- 0.15 m etc.). The maximum sampling depth ranged from 0.2 to 1.8 m, depending on the thickness of the tidal marsh sediments.

Soil samples for bulk density were dried at 105 °C for 24 hours. The soil samples for the determination of other soil properties were dried at 50 °C and crushed to < 2 mm using a mortar and pestle, after which

macrovegetation residues and roots were removed manually using tweezers. At every sampling site, samples from one of the three replicate soil profiles were analyzed for OC using an Elemental Analyzer (FlashEA 1112 HT, Thermo Scientific), after the removal of carbonates using a 10 % HCl solution. These data will be referred to as OC%_{meas}. For two locations in each salinity zone, samples from the other two replicate soil cores were also analyzed for OC concentration using the Elemental Analyzer (Figure 1).

Figure 1. Map of the Scheldt estuary showing the locations of the studied salt (blue rectangles), brackish (orange rectangles) and freshwater marshes (green rectangles). For the marshes depicted with dashed rectangles, sedimentary OC concentrations have been determined with the elemental analyzer for three replicate depth profiles, samples from these marshes have been used to calculate the total sedimentary OC stocks using MIR data. Adapted from Van de Broek et al. (2018).

2.2. Spectroscopy measurements

For each soil sample, soil spectra were obtained for five subsamples for wavenumbers between 4000 and 400 cm^{-2} at a resolution of 4 cm^{-2} , using a PerkinElmer® Frontier FT-IR spectrometer which was coupled to a PIKE® XY autosampler. Before scanning, the soil samples were ground to a powder and transferred to a well plate with 96 wells without pressing or flattening the surface. The average reflectance spectrum of the 5 replicates of each soil sample was then combined with the average reflectance spectrum of 5 replicates of a KBr power, which served as a background, to calculate the absorbance spectrum for further analyses (absorbance = $\log(R^{-1})$, R being the ratio of the soil reflectance over the KBr reflectance). Predicted OC concentrations using MIR spectroscopy/PLSR are referred to as $\text{OC}\%_{\text{MIR}}$.

2.3. Data analyses

We used PLSR to predict the OC concentration from the spectral information. PLSR analyses were performed in R (R Core Team, 2017) using the *prospectr* package (Stevens and Ramirez Lopez, 2014). No spectral smoothing was applied before the analyses, as e.g. proposed by Vasques et al. (2008), as preliminary analyses showed that this did not impact the results (data not shown).

2.3.1. Finding the optimal PLSR model

Several approaches were tested to obtain the optimal PLSR model. First, the analyses using $\text{OC}\%_{\text{meas}}$ as the dependent variable were complemented with analyses using a square root- and a logarithmic transformation of $\text{OC}\%_{\text{meas}}$, as proposed by Baldock et al. (2013). Second, analyses were performed using different spectral pre-processing methods: (i) no pre-processing, (ii) a scatter-corrective pre-processing (Standard Normal Variate; SNV) and (iii) a spectral-derivative pre-processing (Savitsky Golay Filtering, 1st derivative, 1st order polynomial; SG). We justify the comparison of only three methods by the fact that multiple studies have shown that the effect of pre-processing on the accuracy of OC concentration predictions is very limited (Baldock et al., 2013; Dotto et al., 2018; Igne et al., 2010). Third, the number of latent variables included in the PLSR model was varied from 1 to 20. The choice of the optimal number of

latent variables was based on a visual analysis of the goodness of fit (GOF) measures (see below) in function of the number of latent variables included in the model. It was made sure that the optimal number of latent variables resulted in good GOF values, while not unnecessarily including more latent variables than needed to avoid overfitting. Finally, as the source of OC in tidal marsh sediments in the Scheldt estuary shows a clear gradient from mainly terrestrial-derived OC in freshwater marshes to mainly marine-derived OC in salt marshes (Van de Broek et al., 2018), separate analyses were performed for samples from (i) freshwater marshes, (ii) brackish marshes, (iii) salt marshes (referred to as 'local models') and (iv) all tidal marshes combined (referred to as 'general model'). The GOF measures used to quantify the performance of each combination of parameters are the coefficient of determination (R^2), the root mean square error of prediction (RMSE), ratio of performance to interquartile distance (RPIQ), the percentage of variance explained by the PLSR model ($\%var_{exp}$) and the average absolute and relative deviation between measured and predicted values (e_{abs} and e_{rel} respectively). For every combination of model parameters as described above, a cross-validation procedure was applied, with 100 runs being performed with randomly chosen calibration (2/3 of the dataset) and validation samples (1/3 of the dataset). The resulting GOF measures are expressed as the mean $\pm$ standard deviation (σ) based on the results from these 100 runs. Transformed values of OC were re-transformed to OC concentration before calculation of the GOF measures.

2.3.2. Finding the optimal number of calibration samples

The minimum number of soil samples with measured OC concentrations necessary to construct the optimal PLSR model was determined. Therefore, the optimal general model, as determined in the first part of this study, was ran using an increasing number of calibration samples (from $n+1$ to 100, with n being the number of PLSR latent variables). The calibration samples were determined using the Kennard-Stone algorithm with mahalanobis distances (Kennard and Stone, 1969) to include the maximum amount of variance in the calibration dataset. This was done for each salinity zone separately and for all tidal

marshes along the entire estuary combined. To create a representative validation dataset for the entire estuary, an equal number of validation samples were chosen from freshwater, brackish and salt marshes (n = 40 for each salinity zone).

2.3.3. Assessing the error of predicted soil organic carbon stocks

In a final step, the accuracy of predicted OC stocks using MIR spectroscopy/PLSR was determined. Three different strategies involving MIR spectroscopy/PLSR were applied to calculate total sedimentary OC stocks:

1. Combining depth profiles of $OC\%_{MIR}$ with measured bulk density data, referred to as OC_{MIR}
2. Combining depth profiles of $OC\%_{MIR}$ with MIR spectroscopy/PLSR predictions of bulk density (BD_{MIR}) values, referred to as $OC-BD_{MIR}$
3. MIR spectroscopy/PLSR predictions of the OC density, the known value of which is calculated by multiplying measured BD data [$kg\ m^{-3}$] with measured OC concentrations, referred to as $OCdens_{MIR}$ [$kg\ OC\ cm^{-3}$]

Total sedimentary OC stocks were calculated for both the low- and high portion of one tidal marsh in every salinity zone, for which measured depth profiles of OC concentration and bulk density were available in three replicates (Figure 1). The PLSR model for the prediction of the OC concentrations was constructed using the general model with the minimum number of necessary calibration samples. The procedures applied for the prediction of $OC-BD_{MIR}$ and $OCdens_{MIR}$ were identical to the above-described methods for OC_{MIR} . Prior to the construction of the PLSR model, the soil samples that were being predicted were removed from the calibration dataset. This way, the 6 locations for which these characteristics were predicted were assumed to be independent from the calibration dataset. This approach complements the cross-validation that was applied earlier, as sediment samples from all tidal marshes were used to construct the training dataset during cross-validation, thereby not being independent from the validation

dataset. The propagation of uncertainty associated with PLSR predictions to the uncertainty of the calculated sedimentary OC stock was calculated as:

$$\sigma_{tot} = \sqrt{(\sigma_{spat}^2 + \sigma_{MIR}^2)}$$

Where σ_{tot} is the calculated standard deviation of the total sedimentary OC stock, σ_{spat} is the standard deviation associated with spatial differences based on the three replicate soil cores and σ_{MIR} is the calculated standard deviation associated with the uncertainty on the PLSR predictions. As the aim of this exercise was to assess the difference between sedimentary OC stocks calculated using standard methodologies (bulk density determination and OC analyses using an Elemental Analyzer) and MIR spectroscopy/PLSR, it was assumed that sedimentary OC stocks calculated using standard procedures were free from errors. The extent to which the measured and predicted sedimentary OC stocks were significantly different was assessed using an ANOVA for summary data at a confidence level of 0.05 in R (*ind.oneway.second* function, *rpsychi* package (Okumura, 2015)).

In addition to the MIR spectroscopy/PLSR predictions of the OC concentrations and OC stocks of these independent samples using the general model, an identical procedure was used to predict the OC concentration using the local models. As the calculations of the OC stocks using MIR spectroscopy/PLSR predictions of bulk density and OC density were not satisfactory (see section 3.1), only the OC concentration of the independent samples was predicted. This analysis was performed to assess the effect of calibration models constructed using different spatial scales along the estuary (local versus general models) on calculated OC stocks.

The uncertainty of predicted OC concentrations using MIR spectroscopy/PLSR (σ_{MIR}) was calculated using the residuals of the OC concentrations predicted with the general model for all available soil samples, after doing 100 runs with randomly chosen calibration (2/3 of total samples) and validation samples (1/3

of total samples). First, the residuals (measured - predicted OC concentration) were sorted according to increasing predicted OC concentration. Next, the standard deviation of the residuals was calculated for neighboring samples using a moving average (window size = 21), as a measure of the spread of the measured values around the predictions. Subsequently, a linear relationship between the modelled OC concentrations and these standard deviations was constructed to report the error on predicted OC concentration as a standard deviation around the predicted value (Figure S1).

3. Results and discussion

3.1. Characterization of the dataset

The average ($\pm$ standard deviation) OC concentration of the freshwater, brackish and salt marsh samples was 6.09 ± 1.96 , 3.77 ± 2.42 and 2.88 ± 1.6 % OC respectively (Figure S2). The freshwater data was left-skewed (Skewness = -0.41), while the brackish- and salt marsh data were right-skewed (Skewness = 2.63 and 1.99 respectively). A visual representation of the data can be found in Figure S2.

3.2. Determination of the optimal PLSR model

The optimal predictions of OC concentration were obtained when no pre-processing was applied to the spectra, although differences with SNV pre-processing were minimal (Table 1). SG pre-processing resulted in unsatisfactory models in all cases (results not shown). For all models, a square root transformation of the OC data lead to optimal results, although the differences with a logarithmic transformation and no transformation of the data were minimal. Furthermore, the performance of the general model ($R^2 = 0.96$, RMSE = 0.48 % OC) was similar to the performance of the local models ($R^2 = 0.87 - 0.97$; RMSE = 0.28 – 0.68 % OC). This shows that a model calibrated on sediment samples along the entire estuary on average resulted in accurate predictions of OC concentration. In contrast, the accuracy of both bulk density and OC density predictions was substantially lower, with optimal RMSE values of 0.64 ± 0.09 g cm⁻³ and 8.28 ± 3.41 kg OC m⁻³ respectively (Table 1).

Table 1 Results of the determination of the optimal PLSR model, shown for the different salinity zones (fresh – brackish – salt) and all data combined - the general model - (all), for OC concentration (OC), bulk density (BD) and OC density (OCdens). ‘sqrt’ and ‘log’ refer to the transformation of the data, ‘No’ indicates the set-up using no spectral pre-treatment. GOF measures show the average $\pm$ standard deviation for 100 runs with randomly chosen calibration and validation samples. The model with the best performance per salinity zone is indicated in bold.

	Pre-processing method	# of latent variables	R ²	RMSE	RPIQ	% var _{exp}
Fresh OC	No	7	0.86 $\pm$ 0.04	0.71 $\pm$ 0.10	2.45 $\pm$ 0.65	97.11 $\pm$ 0.29
Fresh OC – sqrt	No	6	0.87 $\pm$ 0.04	0.68 $\pm$ 0.10	2.57 $\pm$ 0.70	96.44 $\pm$ 0.19
Fresh OC – log	No	6	0.86 $\pm$ 0.04	0.69 $\pm$ 0.09	2.53 $\pm$ 0.64	96.45 $\pm$ 0.24
Brackish OC	No	8	0.94 $\pm$ 0.03	0.46 $\pm$ 0.09	4.00 $\pm$ 1.25	98.50 $\pm$ 0.15
Brackish OC – sqrt	No	5	0.97 $\pm$ 0.02	0.41 $\pm$ 0.12	4.30 $\pm$ 1.48	97.07 $\pm$ 0.42
Brackish OC – log	No	6	0.95 $\pm$ 0.03	0.48 $\pm$ 0.28	4.71 $\pm$ 2.38	97.5 $\pm$ 0.29
Salt OC	No	9	0.94 $\pm$ 0.04	0.34 $\pm$ 0.06	4.44 $\pm$ 1.00	98.07 $\pm$ 0.17
Salt OC – sqrt	No	9	0.96 $\pm$ 0.02	0.28 $\pm$ 0.06	5.65 $\pm$ 1.17	98.06 $\pm$ 0.18
Salt OC – log	No	9	0.95 $\pm$ 0.03	0.33 $\pm$ 0.07	4.80 $\pm$ 0.99	98.02 $\pm$ 0.21
All OC	No	10	0.95 $\pm$ 0.01	0.54 $\pm$ 0.09	7.25 $\pm$ 1.29	98.15 $\pm$ 0.12
All OC – sqrt	No	10	0.96 $\pm$ 0.01	0.48 $\pm$ 0.07	8.00 $\pm$ 1.18	98.14 $\pm$ 0.15
All OC – log	No	10	0.95 $\pm$ 0.02	0.55 $\pm$ 0.09	6.93 $\pm$ 1.19	96.18 $\pm$ 0.14
BD	No	4	0.64 $\pm$ 0.09	0.13 $\pm$ 0.02	2.45 $\pm$ 0.41	88.4 $\pm$ 1.72
BD – sqrt	No	4	0.64 $\pm$ 0.08	0.13 $\pm$ 0.01	2.45 $\pm$ 0.41	87.7 $\pm$ 2.15
BD – log	No	4	0.66 $\pm$ 0.08	0.13 $\pm$ 0.02	2.50 $\pm$ 0.37	87.6 $\pm$ 1.95
OCdens	No	5	0.51 $\pm$ 0.12	8.28 $\pm$ 3.41	1.86 $\pm$ 0.59	91.5 $\pm$ 1.31
OCdens – sqrt	No	5	0.53 $\pm$ 0.15	8.74 $\pm$ 3.97	1.85 $\pm$ 0.76	91.76 $\pm$ 1.58

OCdens – log	No	5	0.53 ± 0.19	8.94 ± 4.31	1.85 ± 0.84	91.64 ± 2.11
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The optimal models (in bold in Table 1) were subsequently used to assess the accuracy of predictions of OC concentration using cross-validation. The results confirmed the good fit of between OC%_{MIR} and OC%_{meas} for the local (Figure 2a, b and c) and general models (Figure 2d), with an absolute average error (e_{abs}) of 0.39 % OC for the general model. The e_{abs} of OC predictions for samples from the freshwater and brackish marshes was similar when using the local and general models, while the e_{abs} for salt marshes was substantially higher when using the general model (0.23 and 0.30 % OC respectively, Figure 2d). Analysis of the residuals for the general model showed a linear relationship with OC%_{MIR} (heteroscedasticity), which can be expressed as $\sigma_{MIR} = 0.067 + OC\%_{MIR} \times 0.097$, with σ_{MIR} being the standard deviation of measured values around OC%_{MIR} (section 2.3.3, Figure S1). The RMSE (0.56 % OC) and R^2 (0.94) of the optimal general model are very similar to characteristics obtained for MIR spectroscopy/PLSR predictions of sedimentary OC concentrations in terrestrial ecosystems. Baldock et al. (2013) reported an R^2 of 0.92 based on a dataset spanning a large portion of Australia, Jia et al. (2017) obtained a R^2 and RMSE of 0.82 and 0.92 % OC respectively in an alpine landscape, Stevens et al. (2013) found RMSE values between 0.4 and 1.5 % OC for a dataset covering 23 European countries and Dotto et al. (2018) found R^2 and RMSE values of 0.81 and 0.49 % OC respectively for a large region in southern Brazil (ca. 1800 km²). Moreover, these results are in line with R^2 measures of models developed for Australian tidal marshes, which are in the range of 0.91 – 0.95 (Hayes et al., 2017; Macreadie et al., 2017).

The accuracy of predicted bulk density and OC density values was much lower, with absolute average errors of 0.1 g cm⁻³ and 5.18 kg OC m⁻³ (Figure 2e and f). The bulk density of a soil is generally controlled by multiple factors (e.g. Rawls, 1983; Ruehlmann and Körschens, 2009). Some of these are represented in the MIR spectra of dried and ground soil samples, such as soil organic matter content and grain size (Baldock et al., 2013; Minasny et al., 2008). In contrast, other factors are not represented in the spectra,

such as soil moisture content (as soil samples are dried) and root density (as roots were removed prior to sample crushing). As tidal marsh sediments typically have a high soil moisture content due to periodic flooding (Howes and Goehring, 1994; Nuttle, 1988) and can have a high root biomass (e.g. Van de Broek et al., 2018), the absence of these characteristics in the soil spectra could explain why the PLSR model fails to predict bulk density and OC density with a reasonable accuracy. Similar difficulties in predicting soil bulk density were encountered in terrestrial soils using both NIR (Cambou et al., 2016; Moreira et al., 2009) and MIR spectroscopy (Minasny et al., 2008). Alternatively, Lobsey and Viscarra Rossel (2016) have shown that a combination of gamma-ray attenuation and vis-NIR spectroscopy allows to accurately predict bulk density values of both wet and dried soil cores. The predicted OC densities also showed a weak relationship with modelled values (Figure 2f, $R^2 = 0.44$, RMSE = 7.09 kg OC m⁻³). A relatively low accuracy of predicted OC densities has also been reported by Cambou et al. (2016) ($R^2 = 0.70$) while Vågen and Winowiecki (2013) used MIR spectroscopy to predict OC densities but did not report accuracy measures.

Figure 2 Modelled versus measured soil characteristics based on the optimal PLSR models. Plots a), b) and c) show the results for OC concentration for different salinity zones using the local models. Plot d), e) and f) show the validation results for OC concentrations, bulk density and OC stock respectively, using the general model. ‘ e_{abs} ’ and ‘ e_{rel} ’ are the average absolute and relative differences between modelled and measured values. Error bars show the standard deviation based on results with 100 randomly chosen calibration (2/3) and validation (1/3) datasets.

3.3. Minimal size of the calibration dataset

The relationship between the number of samples included in the calibration dataset, identified using the Kennard-Stone algorithm, and the model fit showed a decreasing model error when the size of the calibration set was increased up to 70 samples, while including more samples did not improve the accuracy of the predictions (Figure 3). This is in contrast with the commonly applied practice whereby ca. 2/3 of the total dataset is used for calibration while the remaining samples are used for validation,

independent of the number of available samples (e.g. Dotto et al., 2018; Jia et al., 2017; Kuang and Mouazen, 2011). Similarly, Lucà et al. (2017) found that including 130 samples in the calibration dataset resulted in optimal vis-NIR spectroscopy/PLSR predictions of the OC concentration of forest soils in southern Italy. These results show that an optimal PLSR model can be constructed using a relatively low number of samples, thereby increasing the efficiency and further reducing the analysis cost. Identical analyses showed that the optimal number of calibration samples for the prediction of bulk density and OC density values were 70 and 80 samples respectively, while they were 55, 35 and 40 for the OC concentration of the freshwater- brackish- and salt marsh local models (data not shown).

Figure 3 R^2 , root mean square error (RMSE) and the average absolute difference between $OC\%_{meas}$ and $OC\%_{MIR}$ in function of the number of calibration samples used to construct the general PLSR model. Shadings represent the spread around the average (as a standard deviation) based on 100 runs with different randomly chosen validation datasets.

3.4. Predicting OC concentrations and stocks for independent tidal marsh sediments

In the final step, the OC concentration was calculated for sediment samples from a low- and high-lying location on 3 tidal marshes along the estuary. These samples were removed from the calibration dataset

298 prior to the analyses and were considered to be independent from the rest of the dataset. This was done
299 with PLSR models constructed using (i) sediment samples from along the entire estuary (the general
300 model) and (ii) sediment samples from the salinity zone in which the predicted samples were located (the
301 local models). Predicted depth profiles of OC concentration using the general and local models are shown
302 in Figure 4 and Figure 5, respectively. A visual analysis shows that for the freshwater marshes, the fit of
303 the predicted OC concentrations with measured values is better when using the global model compared
304 to the local model. For the brackish marshes, similar results are obtained for both models, while for the
305 salt marshes the local model results in the most optimal predictions of OC concentrations. The results for
306 bulk density values (using the global model) were substantially worse, as predicted depth patterns and
307 absolute values showed a poor match with measured bulk densities (Figure S3).

308 These visual interpretations are confirmed by the statistical analyses performed on predicted OC
309 concentrations using the local and general models (Figure 6). On average, the OC concentration of the
310 independent samples at the freshwater marshes were predicted better using the global model (average
311 absolute error (e_{abs}) = 0.58 % OC) compared to the local model (e_{abs} = 0.71 % OC). At the brackish marshes,
312 the difference is limited, while the OC concentration of samples at the independent salt marshes was
313 predicted with a higher average accuracy using the local model (e_{abs} = 0.46 % OC) compared to the general
314 model (e_{abs} = 0.62 % OC). There was thus no consistency in the accuracy with which OC concentrations are
315 predicted at the independent freshwater-, brackish- and salt marshes using either the local or the general
316 model. When all samples are combined, the difference between the accuracy using both models was very
317 limited (Figure 5d, e_{abs} = 0.51 % OC when using the local models, e_{abs} = 0.48 % OC when using the general
318 model). The choice of the spatial scale along the estuary at which the calibration model is constructed is
319 thus of little importance when the aim is to obtain OC concentrations which provide good overall results
320 across all sites. In contrast, when one aims to obtain the best predictions of the OC concentration of
321 sediment samples at one location, a local calibration might result in better results, as was evident at the

322 salt marshes (Figure 6c). The total number of sediment samples with a known OC concentration to
323 construct the general model ($n = 70$) was, however, substantially smaller compared to when the three
324 local models needed to be trained ($n = 130$).

325 A possible explanation for the lower quality of predictions of the OC concentration of the salt marsh
326 sediments when using the global model could be related to the characteristics of this sedimentary OC. A
327 previous study has shown that the amount of unprotected POM in the sediments of the studied brackish
328 and freshwater marshes is substantially larger compared to the salt marsh sediments (Van de Broek et al.,
329 2018). In the latter, the majority of subsoil OC is associated with minerals, as POM has been shown to
330 rapidly decompose upon burial in these saline environments. Therefore, the general PLSR model has to a
331 large extent been calibrated using sediment samples from brackish and freshwater marshes, which
332 contain a substantial amount of unprocessed POM. This could at least partly explain why the local
333 calibration model, constructed using only samples from salt marsh sediments low in unprotected POM
334 (Van de Broek et al., 2018), outperforms the general model for the salt marsh sediments. Prior knowledge
335 on the protection mechanisms of OC in tidal marsh sediments (e.g. the importance of unprocessed plant
336 material versus mineral-associated OC), can thus be used to divide the total dataset into multiple portions
337 based on the main stabilization mechanism of sedimentary OC. The effect of different protection
338 mechanisms on the capacity of MIR spectroscopy/PLSR to predict OC concentrations needs, however,
339 more research before the proposed data processing strategy can be reliably applied to other estuaries.

Figure 4 Depth profiles of $OC\%_{MIR}$ (predicted) and $OC\%_{meas}$ (measured), calculated using the general model. Error bars for the measured values show the standard deviation representing the spatial variation between 3 replicate soil cores, the error bars for the modelled values show the standard deviation for spatial variations plus the uncertainty associated with the MIR spectroscopy/PLSR predictions.

Figure 5 Depth profiles of $OC\%_{MIR}$ (predicted) and $OC\%_{meas}$ (measured), calculated using the local models, error bars are calculated similar to Figure 4.

Figure 6 Measured versus predicted sedimentary OC concentration for the independent freshwater (a), brackish (b) and salt marsh sediments (c), in addition to a combination of all independent samples (d). Predictions of OC concentration were performed using the local (filled circles) and global (open circles) models. The statistical measures are identical to Figure 2.

The residuals of the predictions were analyzed to gain more insights into the error associated with the prediction of the OC concentration of tidal marsh sediments using MIR spectroscopy/PLSR. This was done for the residuals of predictions using the general model for (i) the cross-validation method (Figure 2d) and (ii) the predicted OC concentrations for the independent tidal marshes (Figure 6d). As the residuals were not distributed normally, they were analyzed using box plots (Figure 7). The interquartile range of the cross-validation residuals (0.56 % OC; range between -0.28 and 0.27) was smaller compared to residuals for the predictions of the independent tidal marsh sediments (0.68 % OC, range between -0.49 and 0.19). The error for predictions of independent tidal marsh sediments can thus be expected to be higher compared to errors calculated using a cross-validation procedure. The errors calculated here can thus

provide an indication of the expected error on MIR spectroscopy/PLSR predictions of the OC concentration of tidal marsh sediments.

Figure 7 Boxplots of the residuals of predicted OC concentrations using the general model for the cross-validation method (Figure 2d) and the predictions of the OC concentration of the independent tidal marshes (Figure 6d).

Mid-infrared spectroscopy has been put forward as a fast and cost-efficient alternative for the determination of different soil properties. When applying this technique to predict the sedimentary OC stock of the studied tidal marshes, the gain in efficiency was substantially reduced because this technique does not allow to predict accurate bulk density or OC density values. Combining the MIR spectroscopy/PLSR predictions of bulk density and OC density with predictions of the OC concentration resulted in relative differences with measured stocks of -16.1 to +67.0 % and -43 to +64 % respectively (Figure S4). Although other soil sensing techniques (e.g. gamma-ray attenuation combined with vis-NIR spectroscopy) have been shown to hold the potential to reduce the need for standard analyses of bulk density (Lobsey and Viscarra Rossel, 2016), measured bulk density profiles still need to be obtained in order to calculate accurate OC stocks using MIR spectroscopy/PLSR. The advantage of MIR

spectroscopy/PLSR to predict OC stocks of the tidal marsh sediments studied here is thus generally limited to a reduction in the cost of sample processing.

The uncertainty associated with predicted OC stocks was relatively low when MIR spectroscopy/PLSR predictions of OC concentration were combined with measured bulk density profiles (Figure 8). Using the local model resulted in relative differences of $< 4\%$ between measured and predicted OC stocks for the freshwater and brackish marshes, while the error for the low and high salt marsh were 48 and 19 % respectively. When using OC concentrations obtained by the general model to predict sedimentary OC stocks, the relative error ranged between 2 and 13 % at the freshwater and brackish marshes, and was 30 and 15 % at the low and high salt marsh respectively (Figure 8). The high relative error at the low salt marsh can at least partly be attributed to its low OC stock. The general model thus outperformed the local models at the freshwater marshes, while differences were very limited at the brackish marshes. At the salt marshes, in contrast, the local model resulted in more accurate predictions of the OC stocks.

A strategy to obtain the lowest error on calculated sedimentary OC stocks using MIR spectroscopy/PLSR predictions of OC concentration would thus ideally use different PLSR calibration models for portions of an estuary in which OC is protected using different mechanisms. If this is applied in the studied estuary, i.e. using the general model for the freshwater and brackish marshes and the local model for the salt marshes, the relative differences between predicted and measured OC stocks would be $< 31\%$. When only freshwater and brackish marshes are being considered, the relative error would be $< 4\%$. The uncertainties we report here can be used by future studies as guidelines on the expected uncertainty when using MIR spectroscopy/PLSR predictions of OC concentration to calculate tidal marsh OC stocks.

Figure 8 Modelled and measured sedimentary organic carbon stocks using different methods. Error bars for the measured values show the standard deviation (σ) representing the spatial variation between 3 replica soil cores, the error bars for the modelled values show the σ for spatial variations plus the uncertainty associated with the MIR predictions. Δ is the relative difference between measured and modelled OC stocks, while significant differences between modelled and measured OC stocks are denoted with an * ($p = 0.05$).

4. Conclusion

Our results show that MIR spectroscopy/PLSR is a reliable method to predict the OC concentration of tidal marsh sediments at a high accuracy. At the scale of the estuary, predictions of sedimentary OC concentrations using PLSR models trained using sediment samples covering the entire estuary or for different salinity zones separately resulted in similar absolute errors (0.48 % and 0.51 % OC respectively). However, optimal predictions of the OC concentration of salt marsh sediments were improved by using a PLSR model trained by sediment samples for the same salinity zone only. Sedimentary OC stocks of tidal marsh sediments can be predicted at a high accuracy (error < 4 %) when predictions of OC concentration are combined with measured bulk density profiles, although this error can be higher for individual tidal marshes (15 – 30 %). The inability of MIR spectroscopy/PLSR to predict bulk density or OC density values at a reasonable accuracy limits the advantage of this soil sensing technique to a reduction of the processing cost. Predicting bulk density values using soil sensing techniques would lead to a major reduction in sample collection and processing time.

Data statement

The mid-Infrared spectra and organic concentrations of the sediment samples can be found on <https://data.mendeley.com/datasets/8n6vkv3r9y/draft?a=41898564-88ec-4116-9735-b5c2009e5094> (preview dataset)

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Supplementary figures

Figure S1 Analysis of the absolute residuals (measured - modelled organic carbon concentration) for the independent validation results of the general model (calibrated based on 70 samples). Plot A) shows the residuals, the moving average (window size (w) = 21) and the standard deviation (w = 21) in function the predicted OC concentration. Plot B) shows the standard deviation in function of the predicted OC concentration.

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Figure S2 Frequency histograms and descriptive statistics of the organic carbon concentration of the sediment samples in the studied freshwater (a), brackish (b) and salt marshes (c) .

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Figure S3 Depth profiles of predicted and measured bulk density values (g cm^{-3}) using the general model. Error bars for the measured values show the standard deviation (σ) representing the spatial variation between 3 replicate soil cores, the error bars for the modelled values show the σ for spatial variations plus the uncertainty associated with the m-IR predictions.

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583 **Figure S4** Modelled and measured sedimentary organic carbon stocks using different methods. Error bars for the
 584 measured values show the standard deviation (σ) representing the spatial variation between 3 replica soil cores,
 585 the error bars for the modelled values show the σ for spatial variations plus the uncertainty associated with the m-
 586 IR predictions. Δ is the relative difference between measured and modelled OC stocks, while significant differences
 587 between modelled and measured OC stocks are denoted with an * ($p = 0.05$). Predicted OC stocks using OC_{m-IR} and
 588 measured bulk densities used m-IR spectroscopy/PLSR predictions with the general model.