

Estimating the soil clay content and organic matter by means of different calibration methods of vis-NIR diffuse reflectance spectroscopy

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Abstract

The selection of calibration method is one of the main factors influencing measurement accuracy of soil properties estimation in visible and near infrared reflectance spectroscopy. In this study, the performance of three regression techniques, namely, partial least-squares regression (PLSR), support vector regression (SVR), and multivariate adaptive regression splines (MARS) were compared to identify the best method to assess organic matter (OM) and clay content in the salt-affected soils. One hundred and two soil samples collected from Northern Sinai, Egypt, were used as the data set for the calibration and validation procedures. The dry samples were scanned using a FieldSpec Pro FR Portable Spectroradiometer (Analytical Spectral Devices, ASD) with a measurement range of 350–2500 nm. The spectra were subjected to seven pre-processed techniques, e.g., Savitzky–Golay (SG) smoothing, first derivative with SG smoothing, second derivative with SG smoothing, continuum removed reflectance, standard normal variate and detrending (SNV-DT), multiplicative scatter correction (MSC) and extended MSC. The results of cross-validation showed that in most cases MARS models performed better than PLSR and SVR

models. The best predictions were obtained using MARS calibration methods with CR pre-processing, yielding R^2 , root mean squared error, and ratio of performance to deviation values of 0.85, 0.19 %, and 2.63, respectively, for OM; and 0.90, 5.32 %, and 3.15, respectively, for clay content.

Keywords: Organic matter; clay content; reflectance spectroscopy; PLSR; SVR; MARS.

1. Introduction

Diffuse reflectance spectroscopy is considered as a promising method for the estimation of soil properties and a low cost alternative to traditional soil analysis methods because of its efficiency. Furthermore, determination of soil organic matter (OM) and clay content is complex and requires more chemical reagents and caution especially in salt-affected soils (Richards, 1954; Jackson, 1973). Whereas, visible and near infrared reflectance spectroscopy (VNIRRS) requires little sample preparation and provides accurate estimation of several soil properties from one spectral reading (Viscarra Rossel et al., 2006; Vohland et al., 2011). VNIRRS reflects the compositional and structural information of molecules at spectral wavelengths of 350–2500 nm. The analytical ability of VNIRRS depends on the repetitive and broad absorption of VNIRRS light by C–H, O–H and N–H bonds (Li et al., 2008; Xuemei and Jianshe, 2013), determined as overtones and combinations in the NIR range.

Different spectral pre-processing methods have been used to transform soil spectra, remove noise due to light scattering, emphasise features, and extract useful data for quantitative predictive models. Spectral pre-processing methods represent an important phase in multivariate calibration (Buddenbaum and Steffens, 2012) and have enhanced the accuracy of predictive models (Bilgili et al., 2010; 2011; Mashimbye et al., 2012). Typical spectral pre-processing includes smoothing, normalisation, scatter correction, continuum removal, and derivative

algorithms. For instance, first- and second-derivative absorption spectra have been used by [Ben-Dor et al. \(1997\)](#) to enhance spectral information and demonstrate spectral changes during a decomposition process. [Stevens et al. \(2010\)](#) used derivatives and Savitzky–Golay (SG) smoothing to enhance the performance of their models to predict soil organic carbon level. [Rinnan et al. \(2009\)](#) reviewed the most common spectral pre-processing methods for near-infrared spectroscopy. They concluded that, the optimal pre-processing method for a spectral data set in a calibration model is the signal transformation that gives the best regression performance after rigorous and comprehensive validation for all possible variation in the data.

The prediction mechanisms that may be used in a spectral calibration model depend on the corresponding spectral interaction of the predominant soil chromophores ([Vohland et al., 2011](#)). Therefore, selection of the calibration method and its performance in modelling reflectance spectra is one of the main factors for calibration success ([Mouazen et al., 2010](#)). Several calibration methods based on VNIRRS have been used to predict soil properties, including organic matter (OM) and clay content, among them partial least-squares regression (PLSR) is the standard method used for its simplicity and robustness ([Farifteh et al., 2007](#); [Vasques et al., 2008](#)). The PLSR approach has inference capabilities, which are useful to model a probable linear relationship between the measured reflectance spectra and soil attributes ([Farifteh et al., 2007](#); [Viscarra Rossel and Behrens, 2010](#)). Further, this approach enables the modelling of several response variables simultaneously, while effectively addressing strongly collinear and noisy predictor variables ([Wold et al., 2001](#)). However, the complex and non-linear reflectance behaviour in soils suggests that the use of linear models such as PLSR may be insufficient ([Vohland et al., 2011](#)).

Compared to linear and non-parametric regression methods, multivariate adaptive regression splines (MARS), a nonparametric method that estimates complex nonlinear relationships among

independent and dependent variables (Friedman, 1991), has been effectively applied in different fields (Luoto and Hjort, 2005; Bilgili et al., 2010; Felicísimo et al., 2012; Samui, 2012) and generally exhibits higher performance results. Bilgili et al. (2010) used MARS to model soil properties, including soil OM and clay content, and reported that MARS provided better soil property estimations than those by PLSR method. The support vector regression (SVR), a nonlinear method based on the statistical learning theory, which was proposed by Vapnik (1998), is capable of using fewer training data for learning in high-dimensional feature space and employs a set of linear equations to obtain the support vectors (Xuemei and Jianshe, 2013). In addition, SVR is capable of modelling linear and nonlinear relationships and solving calibration problems with high performance (Suykens and Vandewalle, 1999). Recently, Viscarra Rossel and Behrens (2010) successfully used SVR for modelling soil OM and clay content based on reflectance spectroscopy. SVR has gained extensive application in soil spectroscopy, because of its advantages and high performance (Viscarra Rossel and Behrens, 2010; Vohland et al., 2011).

A robust method for estimating the OM and clay content must provide sufficiently accurate measurements and be cost-effective without excessive complexity, and applicable at different spatial scales and in different environments (Stevens et al, 2008; Reeves, 2010). Numerous studies have shown the potential of VNIRRS for digital soil mapping (Viscarra Rossel and McBratney, 2008; Viscarra Rossel and Chen, 2011; Sidiki et al., 2014). Moreover, remote sensing (RS) and VNIRRS combined together could be more efficient and cost-effective than traditional soil mapping techniques (Lu et al., 2013; Nawar et al., 2014b). In particular, RS and VNIRRS should be suitable for digital large-scale mapping studies where soil data are sparse such as in the case of salt-affected soils. Although several of the studies estimated OM and clay content using VNIRRS, effective and reliable methods for the accurate estimation in salt-affected soils have not been implemented to date. This research aims to fill this gap and to advance the use

of diffuse reflectance spectroscopy for assessing OM and clay content in the salt-affected soils based on spectral library with limited soil samples. The main goals of this study were (1) to investigate the feasibility of using VNIRRS to predict OM and clay content in salt-affected soils; (2) to select the most effective pre-processing methods for OM and clay content estimation; and (3) to compare between PLSR, SVR, and MARS models for optimal estimation of OM and clay content.

2. Materials and methods

2.1. Study area

The study area is the El-Tina Plain, which is located on the north-western Sinai Peninsula in Egypt between longitudes 32°20'35" and 32°33'10" E and latitudes 30°57'25" and 31°04'28" N and has an area of approximately 175 km² (Fig. 1). The El-Tina Plain is characterised by arid conditions, with annual rainfall ranging from 33.4 mm to 70.3 mm. The mean air temperatures ranged from 7.5°C to 23.3°C in winter and between 16.3°C and 35.6°C in summer. The mean evaporation is high and ranges from 3.6 mm/day to 7.3 mm/day. The land surface is nearly flat and ranges in elevation, from below sea level to 5 m above sea level. Nawar et al. (2014a, b) found that soil texture varied from loamy sand to clay, and the soil salinity (EC_e) ranged from 3.3 to 166 dSm⁻¹ and the mean salinity value was 33.03 dSm⁻¹, indicated that the soils in the study area were highly salt-affected. Nawar et al. (2011) classified the soils of the El-Tina Plain into two orders—Entisols and Aridisols, which include eight subgroups: Typic Aquisalids, Typic Haplosalids, Aquic Torriorthents, Typic Torriorthents, Aquic Torripsamments, Typic Torripsamments, Gypsic Aquisalids, and Gypsic Haplosalids.

(Fig. 1)

2.2. Soil sampling and analysis

One hundred and two topsoil samples (depth, 0–20 cm) were collected in the study area between 28 August and 12 September 2012 (Fig. 1). The collected soil samples were air-dried, crushed, and passed through a 2-mm sieve and the resulting fine earth (<2 mm) was retained for analysis. OM content was determined using the modified Walkley and Black method (Page et al., 1982). Particle size distribution was measured using the pipette method (Kilmer and Alexander, 1949). Samples (20 g) were dispersed in 400 ml of distilled water containing 10 ml of 10 percent sodium hexametaphosphate by stirring with high-speed mixer for 30–60 m, and then settled for 30 seconds. Suspensions were poured through 325 mesh sieves, and delivered into 1000-mL graduated cylinders. Aliquots of 10 ml were taken at a 10-cm depth following a settling time as calculated by Stokes' equation (Baver, 1965). Water from the aliquots was evaporated, the fines dried at 105° C and the amount of suspended solids weighed. The remaining dispersed sample was passed through a 300-mesh sieve; the retained sands were washed, dried at 105° C, and fractionated using a nest of sieves. For pretreatment, OM, soluble salts and gypsum in the samples were removed prior to particle-size analysis. OM was removed using hydrogen peroxide, H₂O₂, 30%. Gypsum was removed by heating the sample to 105° C and dialysis (Rivers et al., 1982). Soluble salts were removed by dialysis against water.

2.3. Spectral measurements

Diffuse reflectance spectra of soil samples were measured using a portable spectroradiometer (FieldSpec-FR, ASD), with a measurement range of 350–2500 nm and a resolution of approximately 10 nm and sampling interval of 3 nm in the short-wave infrared domain (Hatchell, 1999). The measurements were conducted in a dark laboratory environment. Plastic dishes were

used to keep the soil samples, which were levelled off to a thickness of 2.0 cm (Mouazen et al., 2007). A light source (halogen lamp) illuminated the sample surface with a 45° zenith angle from a distance of 30 cm. Spectral measurements were taken from nadir at 1.5 cm height above the sample. . Three spectra were collected from the central area of each sample. The final spectrum measurement was attained by averaging the three representative spectra of each sample. The reflected radiance from a white reference panel with known reflectance was recorded before scanning each sample. To calculate the absolute reflectance of the samples, the radiance from each sample was divided by the radiance from the white reference panel and multiplied by the reflectance of the reference panel.

2.4. Pre-processing transformations

Seven types of spectra pre-processing were used , including (1) raw spectra (R), (2) Savitzky–Golay (SG) smoothing, (3) first-derivative spectra with SG smoothing (FD-SG), (4) second-derivative spectra with SG smoothing (SD-SG), (5) continuum removed reflectance (CR), (6) standard normal variate and detrending (SNV-DT), 7) multiplicative scatter correction (MSC), and (8) extended MSC (EMSC). The details about this spectral transformation can be found in the review by Rinnan et al. (2009) and Buddenbaum and Steffens (2012). The continuum removal was performed using ENVI 5.0 software (Exelis Visual Information Solutions, Inc.). All the remaining pre-processing methods were carried out in MATLAB (Version 8.0; The Mathworks, Natick, MA, USA).

2.5. Multivariate calibration models

Three models, PLSR, SVR and MARS, were constructed based on the measured reflectance spectra (R) with seven spectral pre-processing methods and the measured values of OM and clay

content of the 70 soil samples. In addition to cross-validation, 32 samples (neither used in the calibration of the models nor in the cross-validation) were used for the independent validation.

2.5.1. Partial least-squares regression

PLSR is a popular regression method that is often applied in chemometrics, and it was introduced and statistically described by [Geladi and Kowalski \(1986\)](#) and [Wold et al. \(2001\)](#). This method is frequently used to conduct quantitative spectral analyses ([Viscarra Rossel and Behrens, 2010](#)), and the algorithm follows a linear multivariate model to relate the predictor (X) and response (Y) variables and select successive orthogonal (latent) factors, thereby maximising the X and Y covariance or the covariance between the spectra (X) and a measured soil property (Y). Compared to multiple linear regression, PLSR is an appropriate method for managing data with severe collinearity in the independent variables, particularly in cases where the sample size is small. To determine the number of latent factors when using PLSR, leave-one-out cross-validation (LOOCV) was used ([Efron and Tibshirani, 1994](#)) to prevent over- or under-fitting the data, which may produce models with poor performance. The root mean squared error (RMSE) of the predictions and the coefficient of determination (R^2) were ascertained to identify the optimal cross-validated calibration model. Generally, the model with the highest cross-validated R^2 value and lowest RMSE value is selected. The PLSR process was performed using MATLAB (Version 8.0; [The Mathworks, Natick, MA, USA](#)).

2.5.2. Support vector regression (SVR)

SVR is a powerful calibration model based on the kernel learning methods ([Vapnik, 1999](#)). This method utilises an implicit mapping of the input data into a high dimensional feature space defined by a kernel function ([Karatzoglou and Feinerer, 2010](#)). The epsilon-SV regression (ϵ -

SVR) uses training data to obtain a calibration model as the so-called ε -insensitive loss function, which is able to map independent data with deviation smaller or equal to the ε deviation from dependent training data. Errors within the predetermined distance ε from the true value are ignored, whereas errors greater than ε are penalised using parameter C (Vohland et al., 2011). Consequently, SVR reduces the complexity of the training data to an optimal number of so-called support vectors.

In this study, the models were developed using the LIB-SVR algorithm with type epsilon-SVR and radial basis function (RBF) kernel. The optimal parameters of SVR, namely, cost, epsilon, gam (γ), and sig² (σ^2) were adopted to regulate the models. For each combination of cost, γ , and σ^2 parameters, the RMSE of cross-validation was calculated, and the optimum parameters were selected, which resulted in the smallest RMSE. Further, we optimised cost in the range of 1–10 and epsilon and γ in the range of 0.01–0.1. X-block compression using PLS with 4 components were selected to process the data. The LOOCV was used for the validation process. The LIB-SVR model was built by utilising PLS Toolbox (Version 7.9; Eigenvector, Wenatchee, Washington) and MATLAB (Version 8.0; The Mathworks, Natick, MA, USA).

2.5.3. Multivariate adaptive regression splines

MARS is an explanatory data analysis (data mining) technique developed by Friedman (1991). Recently, MARS was applied as a regression method in several disciplines (Shepherd and Walsh, 2002; Yang et al., 2003; Bilgili et al., 2010; 2011; Nawar et al., 2014) and was generally reported to show better performance than that by conventional statistical methods. The MARS analysis uses basis functions to model the predictor and response variables (Hastie et al., 2009). To construct the basis functions, MARS splits the data into sub-regions (splines) with different interval ending knots where the regression coefficients change and fits the data in each sub-

region by using a set of adaptive piecewise linear regressions. These basis functions are subsequently used as new predictor variables for modelling purposes. Each basis function may contain nonlinear and variable interaction factors of the second and third order as well as linear combinations. The basis functions take two forms, one for the values on the left of the knot (negative) and one for the values on the right of the knot (positive):

$$Y = \max(0, Xf - cf)$$

$$Y = \max(0, cf - Xf)$$

where cf is the threshold value for a predictor or knot and Xf denotes a predictor variable (Bilgili et al., 2010). The number of knots and basis functions are determined using a forward stepwise procedure in which a deliberately over-fitted model is first constructed. Next, backward stepwise elimination is applied during which the basis functions that do not contribute sufficiently to the accuracy of the fit are discarded to obtain a final model of the proper size (Friedman, 1991).

To measure lack of fit, avoid over-fitting, and improve prediction, the redundant basis functions are removed one at a time using a backward stepwise procedure. To determine which basis functions should be included in the model, MARS uses a modified form of the generalised cross-validation method (GCV, Vidoli, 2011). The GCV is the mean squared residual error divided by a penalty dependent on the model complexity and is expressed as follows:

$$GCV = \frac{\frac{1}{n} \sum_{i=1}^n [y_i - f(x_i)]^2}{\left[1 - \frac{C(m)}{n}\right]^2}$$

where n is the number of observations, $f(x_i) = \hat{y}_i$ and $C(m)$ is the cost-complexity measure of a model containing m basis functions used to penalise the model complexity to avoid over-fitting

by introducing a cost for the added basis functions in the model. Additional basis functions in the model provide greater flexibility but also add complexity, and MARS attempts to minimise model complexity by selecting the optimal model based on the lowest generalised cross-validation value. The MARS analysis was performed using the ARESLab toolbox (Jekabsons, 2011) with selected adaptations based on MATLAB 8.0 software.

2.6. Prediction accuracy

The R^2 , RMSE, and ratio of performance to deviation (RPD), which is the standard deviation divided by RMSE were used to assess the performance of the OM and clay content prediction models. The RPD was classified into three classes by Chang et al. (2001): category A (RPD > 2) includes models that accurately predict a given property; category B ($1.4 < \text{RPD} < 2$) has limited predictive ability and category C ($\text{RPD} < 1.4$) has no predictive ability. These classes were considered in the current work to compare the performance of different modelling approaches to predict OM and clay content.

3. Results

3.1. Soil data

The results of the descriptive statistical analyses for 70 soil samples were shown in Table 1. The OM content of the samples was low with the mean and maximum values of 0.85% and 2.3%, respectively (Table 1). The OM content >1.0% accounted for 66% of all samples. Clay content ranged between 0.02% and 54.3%, with a mean value of 27.22%, and samples with clay content >40% comprised 71% of all soil samples, indicating that clay texture is dominant among the soil samples. Further, a high correlation was noted between soil OM and clay content ($r = 0.63$).

(Table 1)

3.2. Effects of pre-processing methods on modelling

Results showed that the different pre-processing methods had considerable effects on the performance of OM and clay content regression models (Table 2). Compared with the PLSR model without pre-processing (raw [R] spectra), CR, FD-SG, and SD-SG improved the model performance. Models based on CR showed the best accuracy ($R^2 = 0.52$ and 0.82 , RMSE = 0.36% and 7.10% , and RPD = 1.45 and 2.34 for OM and clay content, respectively), followed by FD-SG ($R^2 = 0.45$ and 0.67 , RMSE = 0.38% and 9.6% , and RPD = 1.35 and 1.46 for OM and clay, respectively) and SD-SG ($R^2 = 0.42$ and 0.53 , RMSE = 0.39% and 11.44% , and RPD = 1.31 and 1.46 for OM and clay, respectively). In contrast, PLSR models based on SNV-DT, MSC, and EMSC spectra resulted in lower estimation accuracies. For OM, the worst performance was with EMSC ($R^2 = 0.33$, RMSE = 0.42% and RPD = 1.23), and SNV-DT produced the worst performance ($R^2 = 0.18$, RMSE = 15.42% and RPD = 1.08) for clay content. Even though, the performance for OM with SG ($R^2 = 0.51$) was better than raw spectra, the results with for clay ($R^2 = 0.50$) were lower than FD-SG and SD-SG ($R^2 = 0.67$ and 0.53). Furthermore, both FD-SG and SD-SG included smoothing step. Thus, the calibrations of the three spectral types that achieved better results with PLSR (CR, FD-SG, and SD-SG) besides raw spectra were used for calibrating the SVR and MARS models.

Figure 2 presents PLS regression coefficients for both OM and clay content PLSR models, and shows the correlation between both OM and clay content and reflectance spectra of the selected four pre-processing methods. The regression coefficients showed both positive and negative correlations at various wavelengths across spectra. The highest correlation for OM was found at 600 nm for raw spectra and at 1900 nm for CR, FD-SG, and SD-SG spectra. For clay content, the highest correlation observed is at 600 nm for raw spectra. The spectrum for CR showed positive

correlation at 700 and 1400 nm, and negative correlation at 1900 and 2200 nm. Positive correlations were obtained for FD-SG and clay content at 1400 nm, but at 1900 and 2270 nm, the correlation was negative. The highest reflectance magnitude (albedo) of samples was low (maximum 35%), except for five sandy samples (40–60%).

(Table 2)

(Fig. 2)

3.3. Performance of PLSR, SVR, and MARS for estimating OM and clay content

The calibration methods considered in this study provided different prediction accuracies of OM (Table 3, Figures 3 and 4). For the calibration data set, the best results were obtained using MARS based on CR ($R^2_{\text{Cal}} = 0.85$, $\text{RMSE}_{\text{Cal}} = 0.19\%$, and $\text{RPD}_{\text{Cal}} = 2.63$; Table 3; Fig. 3), whereas the least acceptable results for OM were shown by PLSR and SD-SG spectra ($R^2_{\text{Cal}} = 0.42$, $\text{RMSE}_{\text{Cal}} = 0.39\%$, and $\text{RPD}_{\text{Cal}} = 1.31$; Table 3; Fig. 3). Thus, the MARS model outperformed the SVR and PLSR models with respect to the R, CR, and SD-SG, but for FD-SG, the SVR model showed better result ($R^2_{\text{Cal}} = 0.74$, $\text{RMSE}_{\text{Cal}} = 0.26\%$, and $\text{RPD}_{\text{Cal}} = 1.96$). In addition, SVR showed good performance for modelling OM, and all the calibration models had RPD above 1.4. The worst results for SVR was with R and SD-SG ($\text{RPD}_{\text{Cal}} = 1.52$ and 1.44 , respectively).

(Table 3)

(Fig. 3)

Using the validation dataset, the prediction of OM content was close to the calibration results for MARS and SVR with improvement for PLSR results. The results of MARS and PLSR with CR were the better accuracy ($R^2 = 0.81$, $\text{RMSE}_{\text{Val}} = 0.22\%$ and $\text{RPD} = 2.27$ for MARS, and $R^2 = 0.79$, $\text{RMSE}_{\text{Val}} = 0.28\%$ and $\text{RPD} = 2.16$ for PLSR). The validation for SVR was close to the

calibration results yet not as good with $R^2 = 0.65$, $RMSE_{Val} = 0.29\%$ and $RPD = 1.69$. The better results for SVR were received with FD-SG $R^2 = 0.75$, $RMSE_{Val} = 0.26\%$ and $RPD = 2.00$. Considering a relatively large number of samples in the calibration step, MARS, PLSR and SVR were found to be suitable methods for determining OM content of salt-affected soils. The slopes for the MARS and PLSR models with CR as well as SVR with FD-SG using the validation data set were well distributed along the 1:1 line, indicating good validations, whereas the slopes for MARS, SVR and PLSR with R, FD-SG (except SVR) and SD-SG spectra with the validation dataset were under the 1:1 line, indicating under-estimation of OM (Fig. 4).

(Fig. 4)

Compared to OM, clay content was determined with higher accuracy. CR transformed spectra produced the best calibration models for clay estimation with PLSR, SVR, and MARS models. The MARS results outperformed PLSR and SVR models, with all spectra pre-processing types, and the best results were recorded with CR ($R^2 = 0.9$, $RMSE_{Cal} = 5.32\%$, $RPD = 3.15$; Table 4; Fig. 5). The clay content results of MARS with raw spectra showed good performance ($RPD = 2.41$), and those of the SVR were good with all spectra types and RPD ranged from 1.44 to 2.13. The best result for SVR was obtained with CR ($R^2=0.78$, $RMSE_{Cal} = 7.7\%$ and $RPD = 2.13$; Table 4; Fig. 5). PLSR generated good results and the RPD ranged between 1.44 and 2.34. The best result for PLSR was with CR and achieved R^2 of 0.82 , $RMSE_{Cal}$ of 7.1% and RPD of 2.34.

(Table 4)

(Fig. 5)

For clay content, validation results with CR were the best among all models with $R^2 = 0.79$, $RMSE_{val} = 7.60\%$ and $RPD = 2.24$, $R^2 = 0.72$, $RMSE_{val} = 7.75\%$ and $RPD = 1.90$, and $R^2 = 0.64$, $RMSE_{val} = 8.84\%$ and $RPD = 1.67$ for MARS, PLSR and SVR, respectively (Figure 6 and Table 4). Validation accuracy of SVR was the worst and slightly lower than the calibration results, however still reasonable for a relatively small validation data set (R^2 between 0.52 and 0.64, $RMSE_{val}$ between 8.84 and 11.35%, RPD between 1.44 and 1.67). The slopes for MARS, PLSR and SVR models with CR using the validation dataset were well distributed along the 1:1 line of the calibration models, indicating good fit, whereas the slopes for MARS, SVR and PLSR with R, FD-SG and SD-SG spectra using the validation dataset were over the 1:1 line, indicating over-estimation of clay content (Fig. 6).

(Fig. 6)

4. Discussion

4.1 Soil spectra

Significant absorbance features around 1400, 1900, 2200, and 2400 nm were observed. These are strongly associated with free water OH features at 1400 and 1900 nm and clay lattice OH features at 1400 and 2200 nm (Vicente and Souza, 2011). The strong absorptions near 1416 nm and 1911 nm in the spectra indicate the presence of water bound in the interlayer lattices (Bishop et al., 2008). The absorption feature near 2200 nm may be likely associated with the absorption of Al–OH, and the small absorption feature near 2280 nm may appear because of Fe–OH, as Fe is exchanged in the octahedral sheet, e.g. in montmorillonite. In the spectra, the slight shoulder at 2340 nm may represent illite or mixtures of muscovite minerals (Post and Noble, 1993).

Many studies have concentrated on sensitive spectral wavebands and their relationship with OM content (Viscarra Rossel et al., 2006; Bartholomeus et al., 2008; Wang et al., 2010; Tekin et

al., 2012; Nocita et al., 2014). For instance, Viscarra Rossel et al. (2006) reported that the wavelengths 410, 570, and 660 nm in the Vis range showed good correlations with soil OM. Furthermore, Wang et al. (2010) reported 5 wavelength bands (440, 560, 625, 740, and 1336 nm) as the optimal spectral bands for the estimation of soil OM under laboratory conditions. Bartholomeus et al. (2008) found the highest correlation between absorption and soil organic carbon at wavelengths between 640 nm and 690 nm. In addition, Nacita et al. (2014) reported an absorption peak centred at 600 nm that was associated with the high estimation of soil organic carbon. The results of the present work also showed that the highest correlation for OM was found at a region between 550 and 680 nm of the raw spectrum, which may be associated with soil colour (Mouazen et al., 2007). This is consistent with the results of Bartholomeus et al. (2008) and Nacita et al. (2014), suggesting that the raw spectral reflectance in the 550–680 nm is sufficiently sensitive for evaluating the OM content in soil.

Viscarra Rossel and McBratney (1998) found that the significant wavelengths for estimating clay content in the NIR range were 1600, 1800, 2000, and 2100 nm. Lagacherie et al. (2008) reported that the wavelength 2206 nm of CR was the optimal band for quantifying clay content. A similar result has been confirmed by Viscarra Rossel et al. (2009), who reported that the absorption features at 2206 and 2207 nm of the CR spectrum are the optimal wavelengths for estimating defined clay minerals. Our study results are in line with the results achieved in these previous studies, showing that the features at wavelengths 1900, 2000, and 2200 of the CR had strong correlation with clay content (Figs. 2b).

4.2. Influence of pre-processing methods on estimation models

In this study, the pre-processing methods significantly affected the results of calibration models (Table 2 and Fig. 2). For OM, CR pre-processing achieved the best performance followed

by SG and FD-SG methods. Similarly, CR pre-processing achieved the best performance for clay content models followed by FD-SG and SD-SG methods. Although PLSR results with SG for OM ($R^2=0.50$ and $RMSE=0.37\%$) were better than models with the raw spectra ($R^2=0.44$ and $RMSE=0.39\%$), the results of clay content modelling, contrary to OM models, were better for the raw spectra ($R^2=0.56$ and $RMSE=11.08\%$) than for the spectra processed with SG technique ($R^2=0.50$ and $RMSE=12.42\%$). Furthermore, smoothing using SG technique was included in FD-SG, and SD-SG pre-processing methods. Using SG, SNV-DT, MSC, and EMSC led to the deterioration of the models accuracy as compared to the PLSR model based on raw spectra. SNV-DT is sensitive to the noise in the spectrum (Rinnan et al., 2009).

CR was the best pre-processing method for the PLSR, SVR, and MARS estimation models in this study. CR has also been successfully used in some other studies for predicting soil properties (Lagacherie et al., 2008; Weng et al., 2008; Nawar et al., 2014a). For example, Lagacherie et al. (2008) recorded improvements in the estimation of the clay content by using reflectance spectroscopy after implementing CR pre-processing on the soil spectra. On the other hand, FD-SG was used to improve the estimation of OM (Vasques et al. 2008). The reason of better performance of CR, as well as FD-SG and SD-SG pre-processing methods was effective noise removal and enhanced signal-to-noise ratio, beneficial for OM and clay content estimation.

4.3. Comparison of PLSR, SVR, and MARS estimation models

In our study, the PLSR, SVR, and MARS methods were used to compare the estimation of soil OM and clay content. Generally, the accuracy of the PLSR, SVR, and MARS models is affected by variations in the soil texture and moisture content (Farifteh et al., 2007), and a successful pre-processing method for the spectral data may improve the performance of such models (Vasques et al., 2008; Rinnan et al., 2009). Amongst the three investigated multivariate techniques, MARS

performed best. Compared to MARS, the two other multivariate techniques (SVR and PLSR) showed a noticeable decrease in accuracy with PLSR performing somewhat better than SVR in the validation data set for OM and clay content estimation.

For OM estimation, MARS provided very good calibration accuracies depending on the pre-treatment method used with R^2 between 0.70 and 0.85, $RMSE_{Cal}$ ranged between 19% and 28%, and all RPD higher than 2.0, except with FD-SG (RPD=1.86). The best model performance ($R^2 = 0.85$ and $RMSE_{Cal} = 0.19\%$) was obtained using MARS with CR. The accuracy of the test set validation is good and in the same range as the calibration (RPD close to 2.0). These models particularly showed good $RMSE_{Val}$ around 0.35%. The validation accuracy was slightly lower but reasonable (R^2 between 0.49 and 0.62, $RMSE_{Val}$ between 0.43% and 0.54%, RPD between 1.26 and 1.57).

As shown in Table 3, the PLSR model with CR pre-processing performed relatively well compared to MARS and better than SVR with CR as well as with SD-SG and R for the validation data set. The good accuracy of PLSR with validation data set may be attributed to the fine texture of the soil samples (75% of samples had clay texture). The best results among SVR models were with FD-SG ($R^2 = 0.76$ and $RMSE = 0.25\%$). CR generally emphasises the spectral absorption features (Clark and Roush, 1984) and may improve the estimations. Weng et al. (2008) recorded improvements in the estimation of the soil salinity content by using reflectance spectroscopy after implementing CR pre-processing on the soil spectra. Our study results showed that CR generally improved these estimations compared to estimations from the raw spectra. SVR produced good results with FD-SG ($R^2 = 0.76$ and $RMSE = 0.25\%$), which was better than that by PLSR, but not as good as the results obtained by using the MARS model.

Compared to published results obtained using MARS ($R^2_{\text{Cal}} = 0.79\text{--}0.91$) (e.g. Shepherd et al., 2002; Bilgili et al., 2010; Viscarra Rossel and Behrens, 2010), SVR ($R^2_{\text{Cal}} = 0.73\text{--}0.89$ (e.g. Viscarra Rossel and Behrens, 2010; Vohland et al., 2011; Peng et al., 2014), and PLSR ($R^2_{\text{Cal}} = 0.79\text{--}0.85$) (e.g. Vasques et al., 2008; Bilgili et al., 2010; Viscarra Rossel and Behrens, 2010), the OM models used in the present study may be considered as good according to the standard by Chang et al. (2001). The estimation quality of the OM was dependent on the different pre-treatment and calibration methods. For instance, the MARS model developed with raw spectra, CR and SD-SG produced better results than the PLSR and SVR (Table 3). However, the results of SVR with FD-SG were better than the MARS and PLSR. Similarly, averaging the spectra consistently optimised the calibrations with PLSR. Averaging and smoothing of the spectra removes noise and may eliminate factors that lead to nonlinearities (Bilgili et al., 2010). The MARS method typically yields better results when a nonlinear relationship between absorption and concentration exists, whereas the PLSR model fits only linear relationships (Brown et al., 2006; Mouazen et al., 2010; Viscarra Rossel and Behrens, 2010).

Very good predictions for clay content were obtained using MARS ($R^2_{\text{Cal}} = 0.90$) and good performances were obtained with PLSR ($R^2_{\text{Cal}} = 0.82$) and SVR ($R^2_{\text{Cal}} = 0.78$). Table 4 shows that the calibration models with CR performed well and provided the best results for MARS, PLSR, and SVR, respectively. These results were consistent with previous studies for estimating clay content based on reflectance spectroscopy ($R^2_{\text{Cal}} = 0.82\text{--}0.91$) (Shepherd and Walsh, 2002; Lagacherie et al., 2008; Bilgili et al., 2010; Viscarra Rossel and Behrens, 2010). For example, Bilgili et al. (2010) obtained good results for estimating clay content of 512 soil samples collected from northern Turkey, by using MARS and PLSR and reported R^2_{Cal} of 0.89 and 0.82,

respectively. According to [Chang et al. \(2001\)](#), the predictive performance of the MARS model in this study was high.

In line with findings of [Kuang and Mouazen \(2011\)](#), it is believed that a fundamental factor that improved the performance of the models in this study was a wide range of clay content (0.0–54.3). Furthermore, the model performance depends to a large extent on variability encountered in the data set, including soil types ([Stenberg, 2010; Wang et al., 2010](#)).that due to variety of parent material can have considerably different physical and chemical characteristics influencing soil spectra. Thus, if soil heterogeneity increases regression can be more successful and this may influence the model accuracy. [Kuang and Mouazen \(2011\)](#) confirmed that although R^2 and RPD increase with variability measured as SD and range, RMSE also increased. The high performance for estimating clay content in the current research obtained with MARS and SVR may be attributed to the wide range of variation of clay content as shown in Table 1.

The performance of the MARS, SVR, and PLSR models to predict soil properties is evaluated by R^2 , RMSE, and RPD. Of all models, MARS showed higher performance than PLSR and SVR for estimating clay content and OM, except SVR with FD-SG in calibration and PLSR with CR in validation step. According to [Chang et al. \(2001\)](#), estimation models of soil properties with RPD >2 are considered as accurate calibration models. The performance of OM and clay content predictive models were good in terms of RPD. MARS provided very good models for clay content estimation ($RPD_{Cal} = 3.15$) with CR. Good models were also received for PLSR ($RPD_{Cal} = 2.34$) and SVR ($RPD_{Cal} = 2.13$) with CR. For OM, a good model was achieved by MARS with CR ($RPD_{Cal} = 2.63$), and a satisfactory model by SVR with FD-SG spectra ($RPD_{Cal} = 1.96$).

The predictive models used in this study have not been tested on digital hyperspectral airborne or satellite images. They will be tested using airborne or satellite imagery at a selected study site

where further work is currently being conducted. Future research should focus on possible integration between spectra obtained in the field or in the laboratory, and spectra from airborne or satellite imagery. This integration could be useful for accurate OM and clay content mapping that employs predictive models (Lu et al., 2013; Nawar et al., 2015). These estimation models should be subjected to further examination and optimisation before broad application in soil mapping, as the estimation accuracy of OM and clay contents in the field could be negatively affected by several factors that are well controlled in laboratory conditions, such as spectral mixture, atmospheric conditions, and spatial variability of soil moisture content (Gomez et al., 2008; Ben-Dor et al., 2009).

5. Conclusions

In this study, different pre-processing methods were utilised for the estimation of OM and clay content in salt-affected soils based on VNIRRS, and the accuracies were compared between PLSR, SVR, and MARS models. The CR and FD-SG pre-processing methods had strong positive influence on the performance of most models. Overall, MARS was the most reliable method for estimating the OM and clay content under laboratory conditions and provided better estimations than the SVR and PLSR at both the calibration validation steps. The main strengths of MARS method, besides accuracy of modeling OM and clay content in salt-affected soils, are the lower costs compared to the conventional field-based approaches and simplicity to transfer models to image pixels for digital soil mapping. It is proposed that these estimation models undergo further testing and optimization before broad application in soil mapping. For instance, appropriate methods of atmospheric correction and elimination of spectral noise (e.g., vegetation influences) are needed to advance laboratory-based models to operational soil mapping of large areas.

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Estimating the soil clay content and organic matter by means of different calibration methods of vis-NIR diffuse reflectance spectroscopy

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