

Soil spectroscopy with the use of chemometrics, machine learning and pre-processing techniques in soil diagnosis: Recent advances -A review

Issam Barra^{a,*}, Stephan M. Haefele^b, Ruben Sakrabani^c, Fassil Kebede^a

^{a.} *Center of Excellence in Soil and Fertilizer Research in Africa, Mohammed VI Polytechnic University, Benguerir, Morocco.*

^{b.} *Department of Sustainable Agriculture Sciences, Rothamsted Research, Harpenden, UK.*

^{c.} *School of Water, Energy and Environment, Cranfield University, UK.*

Corresponding author:

*I. Barra, Center of Excellence in Soil and Fertilizer Research in Africa, Mohammed VI Polytechnic University, Benguerir, Morocco, Email: Issam.barra@um6p.ma

ABSTRACT

Over the past two decades soil spectroscopy, particularly, in the infrared range, is becoming a powerful technique to simplify analysis relative to the traditional chemical methods. It is known as a rapid, cost-effective, quantitative and eco-friendly technique, which can provide hyperspectral data with narrow and numerous wavebands, both in the laboratory and in the field. In this context, the present article reviews the recent developments in mid and near infrared techniques coupled with chemometrics and machine learning tools in addition to the preprocessing transformations and variable selection strategies to diagnose soil physical and chemical properties. Both spectral techniques demonstrated a good ability to provide accurate predictions of specific properties. Moreover, the MIR spectroscopy outperformed NIR for the estimation of most indicators used for fertilizers recommendation. Herein, a detailed overview on the opportunities and challenges that soil spectroscopy offers as efficient diagnostic tool in soil science was provided.

Keywords: Soil diagnosis, infrared spectroscopy, chemometrics, machine learning, data preprocessing

1. Introduction

Quantitative and qualitative analyses of soil properties ensure acquiring proper knowledge and skills for managing soil fertility and productivity through development of adjusted fertilizer formulations and recommendations [1]. The conventional soil laboratory methods require the use of chemical reagents, which are often not eco-friendly, a whole range of sophisticated laboratory equipment, and, moreover, the protocols are time consuming and expensive. The use of infrared spectroscopy method has gained ground, not so much as a substitute of conventional soil measurements, but as an additional option providing efficient, rapid, robust and cheap methods for soil characterization.

Spectroscopic techniques are considered as physical methods of characterization that can be defined as the study of the interaction of electromagnetic waves in the ultraviolet, visible and infrared wavelengths with a the material under consideration [2]. Furthermore, these techniques have shown, when coupled with a multivariate data analysis, to be powerful tools for developing quantitative and classification models in many disciplines including food technology [3–5], petroleum engineering [6–11] and soil science [12–14] among many others. Nowadays, the application of chemometrics and machine learning techniques are among the most relevant tools to investigate the relationship between the chemical variables and the measured instrumental signals [15–17].

The present paper aims at bringing together the recent developments in the coupling of infrared spectroscopy in the medium and near ranges with chemometrics and machine learning including the preprocessing tools in soil spectroscopy to diagnose soil physical and chemical properties.

2. Spectroscopic fingerprints

Spectroscopic techniques operate at different ranges of electromagnetic radiation. Among the various techniques, in the field of soil analysis, spectroscopic application includes near infrared spectroscopy (NIR) between 4000 and 13000 cm^{-1} , visible-near infrared (Vis-NIR) spectroscopy (4000 to 28600 cm^{-1}), mid-infrared (MIR) analysis that comprises Fourier transform infrared spectroscopy (FTIR) and FTIR-ATR (attenuated total reflection) between (400 to 4000 cm^{-1}) and the Raman spectroscopy (500–1500 cm^{-1}). These non-destructive techniques are characterized by the ease of use since they only require minimal sample

preparation, they do not require sample treatments with chemicals and reagents, and they do not generate chemical wastes (i.e., eco-friendly) [18,19]. In this review a comparison was carried out between two common spectroscopic techniques i.e. NIR/Vis NIR and MIR in order to assess their usefulness in coupling with machine learning techniques to facilitate the prediction of key soil properties.

3. Chemometrics/Machine learning tools

Chemometrics is a discipline of analytical chemistry that uses mathematical, statistical and computer applications to reveal the hidden information from chemical analyses in order to optimize processes and/or products [20]. Most of the techniques used in this discipline aim at reducing the dimension of the data at hand to highlight the relationships between the group of samples or between the spectra and selected variables. There are two main categories of chemometrics tools, namely the unsupervised (generally for data visualization) and the supervised methods (prediction).

3.1. Preprocessing tools

Several factors can affect the quality of the infrared spectra. These factors include the particle size of the samples [21] and the variations of the optical path [22]. This is why it is necessary to have a well-defined sample preparation and analysis protocol for each spectrometer [23]. With the purpose of reducing these interferences, thereby improving the predictive ability of the models, a pre-treatment is highly recommended to be applied to the raw data (Figure 1). The most commonly used treatments in the vibrational spectroscopy are smoothing (remove the high-frequency noise from samples) [24], mean centering (include an adjustable intercept in multivariate models) [25], derivatives (reduce the drift of the baseline and highlight some parts of the spectral information) [26–28], normalization (minimize errors presented due to the samples preparation step) [29], standard normal variate (eliminate the effect of uncontrolled variations, viz, instrument optical path) [30] and multiplicative scatter correction (mitigate problems arising from scattered light) [31,32].

Figure 1 here

Figure 1. Effect of different preprocessing tools on MIR spectra. A: raw spectra, B: first derivative, C: standard normal variate, D: second derivative.

3.2.Data visualization

The most used visualization method is the principal component analysis (PCA). A well-known exploratory method which is used to unveil the underlying structure of the data. This is achieved by reducing the dimension of the data, from a very high number (in the thousands of variables) into a few orthogonal synthetic variables called Principal Components (PCs) whose aim is to recover as much variation as possible in the data at hand[33]. The number of PCs can be chosen on the basis of the explained total variance.

3.3.Regression tools

The supervised techniques are generally multivariate calibration techniques. This encompasses tools that involve setting up a relationship between two matrices; the predictor variables **X** (fingerprints), on the one hand, and the variables to be predict **Y** (quantitative response), on the other hand. The commonly applied multivariate calibration tools are the partial least squares regression (PLS) and orthogonal projections to latent structures [34,35], support vector machine regression (SVMR) [36], principal component regression (PCR) [35] and multiple linear regression [37].

4. Prediction of soil properties

As shown in Tables **1-3**, several studies were carried out using infrared fingerprinting (i.e., in the MIR and NIR/Vis-NIR infrared ranges) in combination with chemometric methods for rapid soil properties diagnosis.

4.1.Application of NIR and Vis-NIR spectroscopy

Relevant studies carried out for soil diagnostic using NIR/Vis-NIR spectroscopy techniques and chemometric/machine learning methods are listed in **Table 1** and discussed in the sections below.

4.1.1. Total and Organic carbon

Applications of NIR and Vis-NIR spectral techniques with the PLS algorithm were found to be efficient for evaluating the soil organic carbon (SOC) in soils [14,38–46], where the difference between all these studies are the type of soils, sample set representativeness, the number of soil samples, sample preparation, the preprocessing strategies and model validation methodologies.

Combining NIR and Vis-NIR spectral databases on the one hand and PLS regression on the other hand yielded results that showed a good agreement between measured and predicted values, indicating accurate SOC predictions. One study [47] evaluated the effect of dataset division methods on the model accuracy, i.e., 50 strategies for dividing the data into calibration and validation samples were tested with PLS-NIR as a calibration model to predict soil organic carbon. Several data preprocessing strategies were also compared. The results showed that the optimization of data set division combined with PLS could improve the model prediction. In addition, [48] studied the effect of the data size on the prediction of total carbon using three different algorithms, namely PCR, PLS and SVMR applied on the same Vis-NIR spectra. The results showed that the required minimum number of samples for calibration was 29 for PCR, 72 for SVMR and 130 for PLSR, which confirmed that the PCR was less sensitive to the sample size than PLS and SVMR. On the other hand, the three predictive models were better in terms of correlation and prediction errors RMSEP (Root Mean Squared Error of Prediction). [49] compared the performance of a miniaturized (mobile) and a conventional (bench-top) near infrared reflectance (NIR) spectrometer for characterizing soil carbon and nitrogen, concluding that the PLS model that was set up on the spectral data of the two instruments led to acceptable results. Furthermore, coupling Vis-NIR spectra with SVMR and using eight preprocessing methods led to an improvement of the prediction accuracy of soil organic carbon contents in soil samples [50]. The results indicated that the Savitzky-Golay (SG) derivative was the best preprocessing method to predict SOC from Vis-NIR-SVMR spectra. [51] investigated the prediction of SOC using PLS regression applied to Vis-NIR data belonging to three external soil spectral libraries at national, regional and field scales. The calibrated models based on the three datasets led to good results. Moreover, the field scale calibration using a local library led to more accurate predictions than calibrations using regional or national libraries, which nevertheless yielded good results when completed with some spiking samples (originating from the target fields). [51] explored the PLSR calibration method and its ability to predict SOC from Vis-NIR data. The results obtained confirmed that the proposed approach provided reliable estimates with a large coefficient of determination R^2 and small predictions errors. In [52] the performances of infield estimation of SOC using a portable Vis-NIR spectrometer and moist soils with a laboratory NIR instrument on dried soil samples were compared. The model on air-dry spectra outperformed the one obtained from fresh samples in terms of correlation between predicted and measured SOC values. The performance of a cheap, micro-electromechanical system NIR spectrometer coupled with PLS, SVM and Cubist tree model regressions for SOC and total carbon (TC) prediction was assessed by [53]. The results showed that the Cubist model

predicted SOC and TC more accurately than PLSR and SVMR. [54] evaluated the precision of Vis–NIRS, LIBS (Laser Induced Breakdown Spectroscopy), and combined Vis–NIRS - LIBS spectral data for simulated in-situ soil profile total C, inorganic C and SOC measurement. The calibrated Vis-NIR and LIBS models predicted soil C satisfactorily although not very accurately. Even data fusion of Vis–NIRS-LIBS did not consistently increase the accuracy of soil C prediction.

4.1.2. Soil pH

The applicability of Vis-NIR, pXRF and sensor data fusion (Vis-NIR+PXRF) for rapid characterization of soil pH was investigated by [55] comparing linear PLS method with a non-linear SVMR method. The results showed that Vis-NIR, pXRF and their fusion can be used to predict soil pH through SVMR more accurately.

4.1.3. Total Nitrogen

NIR spectroscopy was evaluated as a commercial pre-sowing test to estimate soil N supply of irrigated rice in south-eastern Australia [56]. The performance of the calibrated model was satisfactory in terms of prediction error and correlation between the predicted and measured N uptake. A similar study was conducted [58] to predict the soil total nitrogen (TN) content using NIR spectroscopic techniques along with two algorithms (i.e., PLS and SVMR). The study revealed that the calibrated SVMR model outperformed the PLS algorithm in terms of correlation (calibration and validation) and error values (RMSEP). [57] studied the effect of soil moisture on TN prediction using the Vis/NIR-PLS method, after applying four spectral preprocessing approaches, namely Savitzky–Golay (SG) smoothing, SG smoothing followed by first derivative (FD), orthogonal signal correction (OSC) and generalized least squares weighting (GLSW). The results demonstrated that the strength of OSC and GLSW in eliminating the effects of moisture when estimating TN is superior. Consequently, the GLSW-PLSR approach was recommended for improved Vis/NIR estimation of TN content under different soil moisture conditions.

4.1.4. Prediction of multiple soil properties

Several research studies investigated the predictive ability of PLS applied to Vis-NIR spectra for the prediction of four soil properties, namely pH, free iron oxide, clay and CaCO₃ [58–60]. Accordingly, the prediction performances of the PLSR models were stable and globally accurate for the four selected soil properties. [59] compared Vis-NIR Spectrometers of different

resolutions for the prediction of seven soil properties, namely extractable P, K, Ca, Mg, Al, SOC and CEC using PLS modeling. The two instruments (Veris and FieldSpec brands) yielded both good results, making it hard to conclude which one performed better. Other previous research [61] studied different modeling techniques, viz., PLS, MLR, RR (Regression Rules) and ANN (Artificial Neural Network) for predicting soil texture and the SOC. The study concluded that machine learning techniques such as RR and ANN combined with Vis-NIR spectral data can provide precise predictions. A similar study [62] tested the accuracy of combining PLS with NIR and Vis-NIR techniques as a soil multi-nutrient availability index. The coupling of PLS - Vis-NIR proved to be relevant since it accurately predicted plant available P, Ca, Mg and K. [63] confirmed that soil Vis-NIR spectroscopy can accurately estimate SOC, TN, pH and texture. [64] examined the effect of considering soil samples from different depths during calibration modelling on the accuracy using Vis-NIR spectroscopy for the prediction of SOC and SON. This study proved that collecting samples from various depths resulted in increasing the robustness of the developed models. A large, regional scale study was carried out to inspect the potential of the NIR spectroscopy coupled with modified partial least squares regression (mPLS) for measuring several mineralogical and physico-chemical properties of Brazilian soils [65]. The models gave good predictions of soil organic matter content, clay content and the amounts of kaolinite and gibbsite. In addition, Vis-NIR spectro-radiometers can be used to predict SOC and hot water-extractable C (HWE-C) contents accurately in a wide range of soil types and soil properties [66]. A comparison of four multivariate techniques (i.e., PCR, PLS, ANN and SVMR) was conducted for the rapid and accurate prediction of four soil properties, namely SOC, TN, total P (TP) and total K, using Vis-NIR spectral data [67]. It turned out that SVMR yielded the best predictions for SOC, TN, and TP, whereas ANN yielded the best predictions for TK. In [68] the applicability of Vis-NIR spectroscopic technique coupled with PLS for estimating eighteen different soil properties, namely coarse crumb, pH (H₂O), pH (KCl), cation exchange capacity, sand, silt, and clay contents, total nitrogen, soil organic carbon, total potassium, total phosphorus, soluble salts, free iron (Fe₂O₃), available phosphorus, aluminum saturation, exchangeable aluminum, bulk density (BD) and base saturation (BS) was tested. Good prediction values were found for pH, SOC, TN, Fe₂O₃, salt, and aluminum saturation whereas satisfactory results were found for sand, silt, clay, TP, TK, CEC, AP and Al_{ex} (**figure 2**). The study of a spectral data-mining system was designed to minimize or eliminate any subjective or random variation during model development for the prediction of SOC, CaCO₃ and CEC [69]. The effect of this algorithm was clear, and predictions of all parameters were successful with good correlations and low

prediction errors. [70] examined the potential of Vis-NIR spectroscopy for the prediction and mapping of sand and clay fractions of soils in one irrigated field with clayey texture in Turkey. The results showed a good prediction performance for both sand and clay. [71] compared four different portable near infrared sensors with different sizes for the prediction of soil characteristics, viz., $\text{pH}_{\text{CaCl}_2}$, CEC, TC, clay, sand, silt, K_{ex} , Ca_{ex} , Mg_{ex} , and Na_{ex} . The results showed that the four portable infrared sensors presented good prediction accuracy for clay, sand, total carbon, CEC, pH, exchangeable Mg and Ca, but were poor in predicting silt, exchangeable Na, and K. Moreover, the regression tree modeling (Cubist) outperformed PLSR. [12] provided an assessment of the performance of portable and miniature Vis-NIR spectrometer to predict soil properties (i.e., pH, SOC, TC, TN, CEC, Ca_{ex} , Mg_{ex} , Na_{ex} , K_{ex} , sand, silt and clay). The results showed that the small Vis-NIR spectrometer coupled with chemometrics tools was able to predict the proposed soil characteristics with acceptable correlations and errors. [72] studied the effect of soil particle size on the prediction of Na_{ex} by multivariate models (PLS and PCR) based on NIR spectroscopy. The results proved that particle sizes have an important effect on the multivariate predictions (particle sizes larger than 0.212 mm led to better predictive models). [73] applied the Vis-NIR spectroscopy combined with PLS, PCR and wavelet analysis for the prediction of SOC and TN in soil. The results suggested that wavelet analysis was a better method for capturing the absorption features of soil properties and determining SOC and TN content. [74] tested short wave Vis-NIR reflectance spectroscopy for the prediction of four soil properties, including SOC, Ca, K and Mg. The prediction models were successful for SOC estimation and less successful for the three remaining properties. [75] evaluated an in-field NIR instrument combined with the PLS algorithm to predict the contents of TN, SOC, K, S, P and the pH in soil. The obtained results in this work suggested that good predictions of TN, SOC, S, P, and pH were obtained using the portable NIR spectrometer. [76] developed a new MLR model for the proper estimation of soil potassium content. The calibrated model showed a high potential for soil potassium prediction. [77] studied the effect of six different soil-water contents on the Vis-NIR predictions of four soil properties. The results demonstrated that the contents of clay, silt, and sand were well predicted at different soil moisture levels, whereas the estimation of SOC was good at air-dry soil conditions. [78] evaluated the feasibility of Vis-NIR spectroscopy for rapid determination of the four Fe forms: total Fe (Fe_t), pyrophosphate-extractable Fe (Fe_p), dithionite-citrate-bicarbonate extractable Fe (Fe_d), and oxalate-extractable Fe (Fe_o). The results indicated that the nonlinear SVMR models performed better than PLSR models for the predictions of all Fe forms. Several other studies investigated the usefulness of NIR and Vis-NIR spectroscopy combined with chemometrics,

viz., PLS and SVMR for the prediction of soil fertility indicators [79–85], and the calibrated models were in most cases of good quality .

Figure 2 here

Figure 2. PLSR models of each soil property using Vis-NIR spectroscopy. Reused with permission [68]

Table1. A summary of recent applications of NIR and Vis-NIR techniques in combination with multivariate calibrations for the prediction of soil properties. A: well predicted ($R^2 > 0.8$), B: acceptable prediction ($0.6 < R^2 < 0.8$), C: poor prediction ($R^2 < 0.6$))

IR technique	Multivariate calibration	Sample size	Predicted properties	References
Vis-NIR	PCR, PLS, SVMR	216	TC ^{A(PCR)}	[48]
NIR	PLS	360	C ^A and TN ^B	[49]
Vis-NIR	PLS	291	SOC ^A	[38]
Vis-NIR	PLS	148	clay ^B , CaCO ₃ ^A and pH ^C	[58]
NIR	PLS	400	SOC ^B , TN ^B	[86]
Vis-NIR	PLS	798	P ^C , K ^C , Ca ^B , Mg ^B , Al ^C , SOC ^B , CEC ^C	[59]
Vis-NIR	PLS	201	SOC ^A	[14]
Vis-NIR	PLS	95	clay ^B , sand ^C , silt ^C , CaCO ₃ ^B , free iron ^B , CEC ^B , organic carbon ^C , pH ^B	[60]
Vis-NIR	PLS, MLR, ANN, RF, RR	850	bulk density, SOC ^{B(ANN,RF,RR)} , soil texture ^{B(ANN,RF,RR)}	[61]
Vis-NIR	PLS, Cubist	11213	SOC ^{A(cubist)}	[39]
NIR, Vis- NIR	PLS	36	TP ^A , clay ^A , pH ^B , SOC ^B , CEC ^B , Na ^C , K ^B , Mg ^A , Ca ^B , Fe ^A ,	[62]
Vis-NIR	SVMR	298	SOC ^B	[50]

NIR	PLS	22	Mineralizable N ^A	[56]
Vis-NIR	PLS	120	SOC ^A	[51]
Vis-NIR	PLS	83	SOC ^B , TN ^B , pH ^C , Silt ^B	[63]
Vis-NIR	PLS	324	SOC ^A , SON ^C	[64]
Vis-NIR	PLS, SVMR	96	SOC ^{A(PLS)} , pH ^C , TN ^{A(PLS)} , CEC ^{A(PLS)} , Sand ^{A(PLS)} , Silt ^C , Clay ^{A(PLS)}	[83]
Vis-NIR	PLS	255	pH ^C , CEC ^C , Sand ^A , Clay ^C , Silt ^C , TC ^C , TN ^C , K ^C , P ^C , S ^C , Fe ^C , Cu ^B , Mn ^C , Zn ^C	[84]
NIR	PLS	148	Clay ^B , Silt ^C , Sand ^B , pH (H ₂ O and KCl) ^C , TC ^B , P ^C , Mehlich III, Ca ^C , Mg ^C , K ^C , Al ^C , CEC ^B , Mineralogical properties ^B	[65]
Vis-NIR	PLS	48	SOC ^B , HWE-C ^B	[66]
Vis-NIR	PLS	138	pH ^B	[55]
Vis-NIR	PCR, PLS, ANN, SVMR	148	SOC ^{A(SVMR)} , TN ^{A(SVMR)} , TP ^{B(SVMR)} , TK ^{B(ANN)}	[67]
Vis-NIR	PLS	146	Sand ^B , Silt ^B , Clay ^C , pH(H ₂ O and KCl) ^A , SOC ^B ,	[68]

			TN ^B , K ^B , TP ^B , CEC ^B , Fe ₂ O ₃ ^B , AP ^C , Ex. Al ^C , AS ^B	
NIR	PLS, SVMR	90	TN ^{B(SVMR)}	[87]
Vis-NIR	PLS	7120	SOC ^B	[40]
Vis-NIR	PLS	514	TC ^B	[41]
Vis-NIR	PLS, SVMR	149	TC ^{B(SVMR)}	[88]
Vis-NIR	PLS	91	SOC ^A , CaCO ₃ ^A , CEC ^A	[69]
Vis-NIR	MLR	28	K ^A	[76]
Vis-NIR	PLS, SVMR	592	Fe ^{A(SVMR)}	[78]
Vis-NIR	PLS, CCR	113	SOC ^{B(PLS)} , Sand ^{B(PLS)} , Silt ^{B(PLS)} , Clay ^{B(CCR)}	[85]
NIR	Mowing window PLS	91	SOC ^A	[47]
NIR	PLS	431	SOC ^A , TN ^A , P ^B , K ^B	[79]
NIR	PLS	86	Clay ^A , Sand ^A	[70]
NIR	PLS, PCR	332	Exch. Na ^{B(PCR)}	[72]
NIR	PLS	179	TC ^A , TN ^A	[81]
NIR	PLS	60	SOC ^A , TN ^A , Nitrate ^A	[82]
NIR	PLS	384	TC ^A , TN ^A	[80]
NIR	PLS, SVM, Cubist tree model	151	SOC ^{B(Cubist)} , TC ^{B(Cubist)}	[53]

NIR vs LIBS	PLS, LASSO regression, MRCE	236	TC ^{B(PLS)} , SOC ^{B(PLS)} , IC ^{A(PLS)}	[54]
Vis-NIR, NIR	PLS	392	pH(CaCl ₂) ^B , CEC ^A , TC ^A , Clay ^A , Sand ^B , Silt ^C , Exch.(K ^B , Ca ^B , Mg ^B , Na ^B)	[71]
Vis-NIR	PLS	70	SOC ^B , Sand ^A , Silt ^A , Clay ^A	[77]
Vis-NIR	PLS	458	pH ^B , SOC ^A , TC ^A , TN ^A , CEC ^A , Ca ^B , Mg ^B , Na ^B , K ^C , Sand, Silt ^B , Clay ^A	[12]
Vis-NIR	PLS	62	TN ^B	[57]
Vis-NIR	PLS, PCR, wavelet analysis	60	SOC ^{A(WA)} , TN ^{A(WA)}	[73]
Vis-NIR	PLS	98	IC ^B , TOC ^B	[43]
Vis-NIR	PLS	20	SOC ^A	[52]
Vis-NIR	PLS	168	SOC ^B , Ca ^C , K ^B , Mg ^C	[74]
Vis-NIR	PLS	194	SOC ^B	[44]
Vis-NIR	PLS	173	SOC ^A	[45]
Vis-NIR	PLS	12128	SOC ^B	[46]
NIR	PLS	50	SOC ^B	[42]
NIR	PLS	70	TN ^B , SOC ^B , K ^B , S ^A , P ^B , pH ^B ,	[75]

4.2. The use of MIR spectroscopy

The coupling of MIR spectroscopy with chemometrics/machine learning modeling algorithms proved its capabilities to generate multivariate models that make it possible to rapidly perform a soil diagnosis. Relevant studies that were carried out using MIR spectroscopy and are summarized in **Table 2** and discussed in the sections below.

4.2.1. Soil organic carbon

[89] investigated data fusion strategies for laser-induced breakdown spectroscopy (LIBS) and attenuated total reflectance Fourier-transform mid-infrared spectroscopy (FTIR-ATR), as well as a combination of multivariate calibration methods (PLS, SVMR and ANN) for the prediction of soil organic carbon (SOC) content in soil samples. The findings from this work suggest that the use of LIBS and FTIR-ATR spectra in combination with multivariate calibration namely the ANN can be a fast and non-destructive approach to monitor SOC.

4.2.2. Phosphorus

[90] explored the application of MIR DRIFT in combination with chemometrics (PLS), for the prediction of one of the most important indicators of soil fertility and quality which is the P sorption property. The validation of the model to predict the P sorption index was satisfactory for most types of sorption.

4.2.3. Multi-prediction of more than one property

Recent work [12] proposed an effective approach based on portable MIR spectroscopy data modeled by machine learning techniques (Random Forest [RF] and PLSR) to predict TC, TN, CEC, clay, silt and Na_{ex} in 458 representative Australian soil samples. All models were proven to have a good performance with excellent results obtained by means of the RF algorithm. Early works [91] investigated the possibility of using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy to predict soil quality in the form of a soil quality index (SQI). To do this the infrared spectra were modeled using the PLS method for the prediction of the most important soil properties, namely pH both in water and KCl, CaCO_3 , SOC, CEC, sand, silt and clay. The study demonstrated that DRIFT data could be calibrated to estimate a soil quality index by directly predicting measurable soil parameters. [92] tested a small portable prototype MIR spectrometer to collect soil spectra from two agricultural fields (predominantly organic and mineral soils). Those spectra were used for setting up PLS multivariate models for the

prediction of pH, CEC, SOC, Ca, Mg, TN, TP, Fe, Cu, K, Na in Canadian soils. The results showed that in both organic and mineral soils, SOC, CEC, Ca and Mg were predicted with varying levels of accuracy. It was found that Fe in an organic soil field could be predicted with a moderate accuracy. [93] examined the ability of MIR to predict lime requirements (LR) of cultivated soils. The precision of the PLSR model was not sufficient to predict the spatial variability of LR. However, the authors suggested that MIR spectroscopy can be used to predict the averaged value of LR. [94] compared the coupling of mid-infrared spectroscopy with PLS and PLS-NN (Partial Least Squares combined with Neural Network) methods for the prediction of a wide range of chemical and physical soil properties. This study proved that the predictions using the novel PLS-NN approach appeared to be the most precise based on the coefficient of determination (R^2) and root-mean squared errors of prediction (RMSEP) values for total organic carbon (TOC) which were improved from $R^2 = 0.87$ and $RMSEP = 0.7\%$ by PLS, to an $R^2 = 0.94$ and $RMSEP = 0.5\%$ by PLS-NN. [95] The MIR spectroscopic technique combined with Random Forest was used to predict soil properties related to its fertility (pH, Mehlich-3 (i.e., Ca, K, Mg, Na, P, Al, B, Cu, Fe, Mn, Zn, S), P sorption, clay, sand, silt, TN and SOC). The prediction models from MIR spectra were good ($R^2 > 0.80$) for SOC and TN, pH and Mehlich-3 (Ca and Al); intermediate ($R^2 > 0.60$) for sand, silt, clay, P sorption index and extractable Mg and less satisfactory ($R^2 < 0.60$) for Mehlich-3 extractable K, Mn, Fe, Cu, B, Zn, P, S, and Na. The predictive performance of linear (PLS) and non-linear (SVM) multivariate regression models were evaluated by predicting four physico-chemical properties of soil (pH, sand, clay and TOC) using MIR spectral data [96]. The results showed that support vector machines outperformed PLS models for all soil properties tested. [97] compared the performance of the commercial OPUS Quant 2 software, which uses partial least squares regression (PLSR), with the PLS, ANN, and SVMR calibration algorithms. It turned out that, on the one hand, support vector machine regression slightly outperformed the other algorithms and resulted in better predictions and, on the other hand, the performance of SVMR and PLSR decreased when the sample size used for the calibration decreased. [98] used the diffuse reflectance spectroscopy (DRF), attenuated total reflectance spectroscopy (ATR) and Fourier transform infrared photoacoustic spectroscopy (PAS) coupled to the self-adaptive partial least squares model (SAM-PLS) to predict four soil properties and to explore their features in the Mid-Infrared range by the use of uninformative variable elimination (UVE) algorithm as a variable selection tool. The results showed that selected wavenumbers improved the accuracy of prediction for pH, SOC, TN and P contents. [99] proposed and developed simple methods for partitioning the African spectral library (Afsis) into subspaces from which local calibration

models were developed and assessed against global models. The results proved that the global models were more accurate than the local ones. Furthermore, several researchers studied the performance of coupling MIR and PLS for the prediction of important soil properties [100–108]. The results generally led to successful predictions, **figure 3** shows as an example the result obtained by Waruru et al. [105].

Figure 3 here

Figure 3. Scatterplot for measured vs predicted values of selected soil properties for mixed depth data sets using MIR spectroscopy. LL: liquid limit, PL: plastic limit, PI: plasticity index, LS: linear shrinkage, COLE: coefficient of linear extensibility, VS: volumetric shrinkage, tClay: total clay content, tSa: total sand content, W: air-dried moisture content, CEC: cation exchange capacity. Reused with permission [105]

Table 2. A summary of the recent applications of MIR technique in combination with multivariate calibrations for the prediction of soil properties. A: well predicted ($R^2 > 0.8$), B: acceptable prediction ($0.6 < R^2 < 0.8$), C: poor prediction ($R^2 < 0.6$)

IR technique	Multivariate calibration	Sample size	Predicted properties	References
MIR	PLS, SVMR	933	pH ^{A(SVMR)} , Clay ^{A(SVMR)} , Sand ^{A(SVMR)} , TOC ^{A(SVMR)}	[96]
MIR	PLS, RF	458	TC ^{A(RF)} , TN ^{B(PLS)} , CEC ^{B(PLS)} , Clay ^{B(PLS)} , Silt ^{B(RF)} , Na ^{B(RF)}	[12]
MIR	PLS	225	P sorption ^B	[90]
FTMIR-ATR	PLS	89	pH(H ₂ O, KCl) ^B , CaCO ₃ ^B , SOC ^B , CEC ^B , Sand ^B , Silt ^B , Clay ^B ,	[91]
MIR	PLS	300	pH ^C , CEC ^B , SOC ^A , Ca ^B , Mg ^B , TN ^C , TP ^C , Fe ^B , Cu ^C , K ^C , Na ^B	[92]
MIR	PLS	54211	SOC ^A , CEC ^A , pH ^B , TN ^A , Sand ^B , Silt ^B , Clay ^A	[100]
MIR	PLS, ANN, SVMR	144	SOC ^{A(SVMR)} , TN ^{B(SVMR)} , Sand ^{B(ANN)} , Silt ^{A(ANN)} , Clay ^{B(ANN)}	[97]
MIR	PLS, PLS-NN	964	pH (H ₂ O, CaCl ₂) ^{B(PLS-NN)} , Sand ^{B(PLS-NN)} , Clay ^{B(PLS-NN)} , Silt ^C , Exch (Al,Ca, Mg, Na) ^{A(PLS-NN)} , K ^C , P-Sorption ^{A(PLS-NN)} , TOC ^{A(PLS-NN)}	[94]

MIR	PLS	255	Clay ^B , Silt ^C , Sand ^B , Exch(Ca, Mg, Na, K) ^B , CEC ^A , SOC ^B ,	[105]
MIR	PLS	291	pH ^B , EC ^B , TC ^A , TN ^A , C/N ^C , P ^C , K ^C , Clay ^B , Silt ^C , Sand ^C	[104]
MIR	PLS	80000	TC ^A , OC ^A , CEC ^A , CaCO ₃ ^A , pH ^B , Clay ^A	[107]
MIR	RF	700	pH ^B , Mehlich-3(Ca ^B , K ^B , Mg ^B , Na ^C , P ^C , Al ^B , B ^B , Cu ^C , Fe ^C , Mn ^B , Zn ^C , S ^C), P sorption ^B , Clay ^B , Sand ^B , Silt ^B , TN ^A , SOC ^A	[95]
FTMIR, LIBS	PLS	204	SOC ^B	[89]
MIR	PLS	180	TOC ^A , TN ^A , TOC/TN ^A , TP ^A	[103]
MIR	PLS, ANN	20000	pH ^{A(ANN)} , SOC ^{A(ANN)} , IC ^{A(ANN)} , TC ^{A(ANN)} , TN ^{A(ANN)} , clay ^{A(ANN)} , silt ^{B(PLS)} , sand ^{B(PLS)} , M3 extractable (P) ^C , K ^{B(PLS)} , CEC ^{A(ANN)} , S ^{A(ANN)}	[108]
MIR	PLS	1456	pH ^A , SOC ^B , TN ^B , P ^C	[98]
MIR	PLS	307	pH ^A , clay ^B , sand ^B , Mehlich-3(Al, Ca) ^A , TC ^A	[99]

MIR	PLS	270	Clay ^A , sand ^A , organic C ^B , inorganic C ^A	[106]
MIR	PLS	68	TC ^A , SOC ^A , TN ^C , pH ^C , sand ^C , clay ^B , silt ^B	[101]
MIR	PLS	655	Lime Requirement (LR) ^A	[93]

4.3. Comparative studies between the NIR and MIR spectroscopy

As summarized in **table 3**, several researchers compared the performance of the two infrared techniques MIR and NIR in addition to the fusion of the two techniques [109–125], for the prediction of one soil property [111,114,117,119,125,126] (e.g. **figure 4** that shows the results obtained by Viscarra Rossel et al. [126]), two soil properties [110,124] or multi-predictions [109,112,113,115,116,118,120–123]. The results and conclusions differ depending on the case and the properties to be predicted and the quality of predictions can be affected by many factors, Viz. the presence of some outliers, the existence of chemical compound that hide the bonds corresponding to the desired property (e.g. Carbonate ion mask the ones corresponding to the organic C) [127]. Some researchers concluded that MIR spectroscopy is the best [111,112,114,119–123,125], others prefer NIR [115], and several studies have shown that combining and merging the two datasets can significantly improve the predictions [113,116,124].

Figure 4 here

Figure 4. Partial least-squares regression modelling and prediction output for soil lime requirements (LR) for each of the VIS, NIR, MIR and VIS–NIR–MIR methods used. Columns: (a) shows the cross-validated root mean squared errors of prediction (RMSEP) against the number of factors (NF); (b) shows selection of the model with the fewest number of factors, such that the RMSE for this model is equal to, or not significantly larger than $RMSE_{ref}$. The level of significance used was $\alpha = 0.1$; and (c) shows the observed (y) against the cross-validated PLSR predictions (\hat{y}) of soil LR with the validation statistics. Reused with permission [126]

Table 3. A summary of the recent studies that have compared the MIR and NIR techniques in combination with multivariate calibrations for the prediction of soil properties. A: well predicted ($R^2 > 0.8$), B: acceptable prediction ($0.6 < R^2 < 0.8$), C: poor prediction ($R^2 < 0.6$)

IR technique	Multivariate calibration	Sample size	Predicted properties	References
MIR vs NIR	PLS	111	$\text{SOC}^{\text{A(NIR)}}, \text{pH}^{\text{A(NIR)}}, \text{As}^{\text{A(NIR)}},$ $\text{Cu}^{\text{A(NIR)}}, \text{Zn}^{\text{A(MIR)}}, \text{Pb}^{\text{B(NIR)}},$ $\text{Cr}^{\text{B(MIR)}}$	[109]
MIR vs NIR	PLS	217	$\text{SOC}^{\text{A(MIR)}}, \text{TN}^{\text{A(MIR)}}$	[110]
MIR vs NIR vs MIR-NIR	PLS, SVMR	280	Available $\text{N}^{\text{A(NIR)}}, \text{P}^{\text{A(MIR)}},$ $\text{K}^{\text{A(MIR)}}$	[118]
MIR vs Vis- NIR	PLS, RF	305	$\text{TC}^{\text{A(MIR, RF)}}$	[119]
MIR vs Vis- NIR	PLS	--	$(\text{Clay, sand, silt})^{\text{B(MIR)}},$ $\text{TC}^{\text{A(MIR)}}, \text{TN}^{\text{A(NIR)}}, \text{C/N}^{\text{A(NIR-}$ $\text{MIR})}, \text{CEC}^{\text{A(MIR)}}, \text{Exch (Ca, K,}$ $\text{Mg, P, Cu, Fe, Mn, Na, Zn, Al,}$ $\text{Si})}^{\text{B(MIR)}}, \text{TP}^{\text{B(Vis-NIR)}}, \text{pH}^{\text{B(Vis-}$ $\text{NIR})}, \text{CaCO}_3^{\text{A(MIR)}}$	[120]
MIR vs Vis- NIR	PLS	60	$\text{SOC}^{\text{A(MIR)}}, \text{pH}^{\text{A(MIR)}}$	[121]
MIR vs Vis- NIR	PLS	198	$\text{CEC}^{\text{B(MIR)}}, \text{SOC}^{\text{A(MIR)}}, \text{pH}^{\text{C}},$ $\text{p}^{\text{B(MIR)}}, \text{exchCa}^{\text{B(MIR)}}$	[122]

MIR vs Vis-NIR	SVMR	1259	(pH(H ₂ O), sand, clay, TOC, CEC) ^{B(MIR)} , P ^C , K ^C , (Ca, Mg, Al, Cu, Fe, Zn, Mn) ^{B(MIR)} , B ^C	[123]
MIR vs Vis-NIR	PLS, RF	1014	TC ^{A(VisNIR-MIR)} , SOC ^{A(MIR)}	[124]
MIR vs NIR	PLS	150	TC ^{A(NIR)}	[125]
MIR vs Vis-NIR	PLS	3800	SOC ^{A(MIR)}	[111]
MIR vs Vis-NIR	PLS	458	(pH, CEC, sand, clay, silt, Na, Ca, Mg) ^{B(MIR)} , K ^C	[112]
MIR vs NIR	PLS	2845	pH (H ₂ O) ^{B(MIR)} , (TN, TC, Clay, sand, Silt, CEC) ^{B(NIR-MIR)} , Exch(P, K, Ca, Mg, Na) ^{B(MIR)} , S ^C , Cu ^C , Mn ^C , B ^{B(NIR-MIR)} , Zn ^C , (Al, Fe) ^{B(NIR-MIR)}	[113]
MIR vs NIR	PLS	90	SOC ^{A(MIR)}	[114]
MIR vs Vis-NIR	PLS	--	(N, P, K) ^{B(NIR)}	[115]
MIR vs NIR vs MIR-NIR	PLS, CNN	14594	(pH, clay, sand, CEC, TC, SOC) ^{A(MIR)}	[116]

MIR vs Vis- NIR	PLS	95	$\text{SOC}^{\text{A}(\text{Vis-NIR})}$	[117]
--------------------	-----	----	---	-------

4.4.Data preprocessing tools for soil properties prediction improvement

Spectral preprocessing techniques are mathematical transformations that aim to account for the noise in the spectrum or to eliminate some sources of variation that disturbs the prediction of the variables of interest, whether related to soil chemistry, physic or the biology of the analyzed samples. In the field of soil spectroscopy, several studies have been carried out to select the best preprocessing treatment to improve soil properties prediction. However, there is no general agreement about which pre-treatment is the most effective. Different options should be tested including the combination of several strategies of pre-treatment. [128] used the first-derivative transformation with a smoothing interval of 21 data points. [129] tested various transformations, each one having a specific effect: first-derivative transformation with a smoothing interval of 21 data points to minimize the variation in the data caused by sample grinding and optical setup, and the multiplicative scatter correction to correct the noise caused by the light scattering effects. [130] studied the effect of the six most used pretreatments, namely Savitzky–Golay smoothing, first derivative, $\log(1/R)$, mean centering, standard normal variate, and multiplicative scatter correction, the finding was that the first derivative transformation led to the best predictive models. [131] found that the first derivative preprocessing method gave the best results for the prediction of soil heavy metals, whereas multiplicative scatter correction and standard normal variate spectral preprocessing showed weak prediction for all the measured metals. [132]found that among the preprocessing techniques they studied, the scatter-correction group MSC and SNV showed improved prediction capability. [133] reduced the noise by smoothing the soil spectra using the Savitzky–Golay first-order polynomial across a moving window of five bands. Then, the first order detrending transformation was used to remove the baseline of the signals in the spectral data. This study confirmed the high potential of using spectral preprocessing techniques to predict soil properties. [38] proved that by combining more than one preprocessing strategy, namely, Savitzky–Golay smoothing with SNV and the first derivative yielded the best predictions of organic matter content in saline-alkali soils (**figure 5**).

Figure 5 here

Figure 5. Effect of applying different preprocessing techniques on predictive soil organic matter models based on Vis-NIR data. Reused with permission [38]

5. Conclusion & perspectives

This review has evidenced the effectiveness of infrared spectroscopy for soil characterization. Unlike the routine agrochemical analytical methods, which are time consuming, costly and which use hazardous chemical reagents, infrared spectroscopy is a rapid, inexpensive and eco-friendly alternative. Therefore, the advances in the instrumentation and the efforts to improve the machine learning and preprocessing tools should be considered as an opportunity to improve the effectiveness of these methods of diagnosis. In particular, the advances include the new generation of portable instrumentation available for the two discussed techniques (MIR and (Vis-)NIR) and the coupling of the generated spectral database with appropriate multivariate calibration strategies, which yield accurate predictions of several properties, especially when in-field measurements are needed.

Advanced multivariate models performed on infrared spectra in both ranges after applying appropriate data preprocessing tools can generate accurate predictions for most of the soil characteristics.

The studies cited in this paper showed that infrared spectroscopy especially in MIR led to predictive models that are able to give reasonable estimations of important key soil health indicators, namely, SOC, pH, sand, clay... etc. and offered several important advantages over the conventional soil laboratory methods where chemical reagents are ubiquitous.

The big challenges facing this new generation of dry chemistry laboratories are the model transfers from one instrument to another, between laboratories and countries. Future research must include as an important objective to standardize the working methods including the methods of sample preparation (drying and grinding), the spectral wave ranges (Vis-NIR, NIR, MIR) and even the brands of instruments used when scanning the samples. These efforts will undoubtedly contribute to solve the model transfer issue.

Funding: This work was funded by OCP Morocco as part of the FP02 project (New soil and plant diagnostics tools for better fertilizer recommendations) between CESFRA (Mohammed 6 Polytechnic University), Rothamsted Research and Cranfield University.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Soil Science:

AfSIS: Africa Soil Information Service

AS: Aluminum Saturation

B: Boron

C: Carbon

CEC: Cation Exchange Capacity

Cl: Chlorine

Cu: Copper

Al_{ex}: Exchangeable Aluminum

Fe: Iron

HWE-C: Hot-Water Extractable Carbon

IR: Infrared spectroscopy

K: Potassium

LR: Lime Requirement

Mn: Manganese

Mo: Molybdenum

N: Nitrogen

NIR: Near Infrared Spectroscopy

pH: potential Hydrogen

SOC: soil organic carbon

SOM: Soil organic matter

TC: Total carbon

TN: Total nitrogen

TP: Total Phosphorus

Vis-NIR: Visible and Near Infrared spectroscopy

Zn: Zinc

Chemometrics:

ANN: Artificial Neural Network

CCR: Correlated Components Regression

CNN: Conventional Neural Network

FD: First Derivative

GLSW: Generalized Least Squares Weighting

MC: Mean Centering

MIR: Mid Infrared Spectroscopy

MLR: Multiple Linear Regression

OSC: Orthogonal Signal Correction

PCA: Principal Components Analyses

PCs: Principal Components

PCR: Principal Components Regression

PLS: Partial Least Squares

PLS-NN: partial least-squares regression and neural networks

RF: Random Forest

RR: Regression Rules

SVMR: Support Vector Machine Regression

SG: Savitzky-Golay

References

- [1] M.L. Silveira, M.M. Kohmann, Maintaining soil fertility and health for sustainable pastures, in: J. Monte Rouquette, G.E. Aiken (Eds.), *Manag. Strateg. Sustain. Cattle Prod. South. Pastures*, Elsevier Inc., 2020: pp. 35–58. doi:10.1016/b978-0-12-814474-9.00003-7.
- [2] S.S. Zumdahl, S.A. Zumdahl, D.J. DeCoste, Molecular spectroscopy, in: S. Zumdahl (Ed.), *Chemistry (Easton)*, 10th editi, Cengage Learning, University of Illinois, 2016: p. A28.
- [3] M. De Luca, W. Terouzi, G. Ioele, F. Kzaiber, A. Oussama, F. Oliverio, R. Tauler, G. Ragno, Derivative FTIR spectroscopy for cluster analysis and classification of morocco olive oils, *Food Chem.* 124 (2011) 1113–1118. doi:10.1016/j.foodchem.2010.07.010.
- [4] M. Kharbach, R. Kamal, I. Marmouzi, I. Barra, Y. Cherrah, K. Alaoui, Y. Vander Heyden, A. Bouklouze, Fatty-acid profiling vs UV-Visible fingerprints for geographical classification of Moroccan Argan oils, *Food Control.* 95 (2019) 95–105. doi:10.1016/j.foodcont.2018.07.046.
- [5] M. Kharbach, I. Marmouzi, R. Kamal, H. Yu, I. Barra, Y. Cherrah, K. Alaoui, Y. Vander Heyden, A. Bouklouze, Extra virgin Argan oils' shelf-life monitoring and prediction based on chemical properties or FTIR fingerprints and chemometrics, *Food Control.* 121 (2021) 107607. doi:10.1016/j.foodcont.2020.107607.
- [6] I. Barra, M. Alaoui Mansouri, Mohammed Bousrabat, Y. Cherrah, M. Kharbach, A. Bouklouze, Discrimination and Quantification of Moroccan Gasoline Adulteration with Diesel Using Fourier Transform Infrared Spectroscopy and Chemometric Tools, *J. AOAC Int.* 102 (2019) 966–970.
- [7] I. Barra, M. Alaoui, Y. Cherrah, M. Kharbach, A. Bouklouze, FTIR fingerprints associated to a PLS-DA model for rapid detection of smuggled non-compliant diesel marketed in Morocco, *Vib. Spectrosc.* 101 (2019) 40–45. doi:10.1016/j.vibspec.2019.02.001.
- [8] I. Barra, M. Kharbach, M. Bousrabat, Y. Cherrah, M. Hanafi, E.M. Qannari, A. Bouklouze, Discrimination of diesel fuels marketed in Morocco using FTIR, GC-MS analysis and chemometrics methods, *Talanta.* 209 (2019) 120543. doi:https://doi.org/10.1016/j.talanta.2019.120543.
- [9] L.C. Gontijo, E. Guimarães, H. Mitsutake, F.B. De Santana, D.Q. Santos, W. Borges Neto, Quantification of soybean biodiesels in diesel blends according to ASTM E1655 using mid-infrared spectroscopy and multivariate calibration, *Fuel.* 117 (2014) 1111–1114. doi:10.1016/j.fuel.2013.10.043.
- [10] H.G. Aleme, L.M. Costa, P.J.S. Barbeira, Determination of gasoline origin by distillation curves and multivariate analysis, *Fuel.* 87 (2008) 3664–3668. doi:10.1016/j.fuel.2008.06.015.
- [11] I. Barra, M. Kharbach, E.M. Qannari, M. Hanafi, Y. Cherrah, A. Bouklouze, Predicting cetane number in diesel fuels using FTIR spectroscopy and PLS regression, *Vib. Spectrosc.* 111 (2020). doi:10.1016/j.vibspec.2020.103157.

- [12] R. Martínez-España, A. Bueno-Crespo, J. Soto, L.J. Janik, J.M. Soriano-Disla, Developing an intelligent system for the prediction of soil properties with a portable mid-infrared instrument, *Biosyst. Eng.* 177 (2019) 101–108. doi:10.1016/j.biosystemseng.2018.09.013.
- [13] M.R. Ehsani, S.K. Upadhyaya, D. Slaughter, S. Shafii, M. Pelletier, A NIR Technique for Rapid Determination of Soil Mineral Nitrogen, *Precis. Agric.* 1 (1999) 217–234. doi:10.1023/A:1009916108990.
- [14] M. Conforti, A. Castrignanò, G. Robustelli, F. Scarciglia, M. Stelluti, G. Buttafuoco, Laboratory-based Vis-NIR spectroscopy and partial least square regression with spatially correlated errors for predicting spatial variation of soil organic matter content, *Catena*. 124 (2015) 60–67. doi:10.1016/j.catena.2014.09.004.
- [15] P. Filzmoser, S. Serneels, R. Maronna, C. Croux, *Robust Multivariate Methods in Chemometrics*, 2nd ed., Elsevier Inc., 2019. doi:10.1016/b978-0-12-409547-2.14642-6.
- [16] J. Liu, J. Han, J. Xie, H. Wang, W. Tong, Y. Ba, Assessing heavy metal concentrations in earth-cumulic-orthic-anthrosols soils using Vis-NIR spectroscopy transform coupled with chemometrics, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 226 (2020) 117639. doi:10.1016/j.saa.2019.117639.
- [17] R. Chauhan, R. Kumar, P.K. Diwan, V. Sharma, Thermogravimetric analysis and chemometric based methods for soil examination: Application to soil forensics, *Forensic Chem.* 17 (2020) 100191. doi:10.1016/j.forc.2019.100191.
- [18] R. Linker, I. Shmulevich, A. Kenny, A. Shaviv, Soil identification and chemometrics for direct determination of nitrate in soils using FTIR-ATR mid-infrared spectroscopy, *Chemosphere*. 61 (2005) 652–658. doi:10.1016/j.chemosphere.2005.03.034.
- [19] B.G. Osborne, Near-infrared Spectroscopy in Food Analysis, in: Robert A. Meyers (Ed.), *Encycl. Anal. Chem.*, 2006th ed., 2006: pp. 1–14. doi:10.1002/9780470027318.a1018.
- [20] B. Caballero, P. Finglas, F. Toldra, *Encyclopedia of Food and Health*, 1st editio, Academic Press, Waltham MA 02451, 2016.
- [21] M.S. Dhanoa, S.J. Lister, R. Sanderson, R.J. Barnes, The link between Multiplicative Scatter Correction (MSC) and Standard Normal Variate (SNV) transformations of NIR spectra, *J. Near Infrared Spectrosc.* 2., 47 (1994) 43–47.
- [22] J.M. Olinger, P.R. Griffiths, Effects of Sample Dilution and Particle Size / Morphology on Diffuse Reflection Spectra of Carbohydrate Systems in the Near- and Mid-Infrared . Part I : Single Analytes, *Appl. Spectrosc.* 47 (1993) 687–694.
- [23] T. Isaksson, B.R. Kowalski, Piece-Wise Multiplicative Scatter Correction Applied to Near-Infrared Diffuse Transmittance Data from Meat Products, *Appl. Spectrosc.* 47 (1993) 702–709.
- [24] eigenvector, Advanced Preprocessing: Noise, Offset, and Baseline Filtering, (2019). http://wiki.eigenvector.com/index.php?title=Advanced_Preprocessing:_Noise,_Offset,_and_Baseline_Filtering#Derivative_.28SavGol.29.
- [25] Eigenvector, mean centring, (2012).

http://wiki.eigenvector.com/index.php?title=Advanced_Preprocessing:_Variable_Centering#Mean_Centering.

- [26] L.S.L. Arakaki, D.H. Burns, Multispectral Analysis for Quantitative Measurements of Myoglobin Oxygen Fractional Saturation in the Presence of Hemoglobin Interference, *Appl. Spectrosc.* 46 (1992) 1919–1928.
- [27] Y. Ozaki, A. Mizuno, H. Sato, K. Kawauchi, S. Muraishi, Biomedical Application of Near-Infrared Fourier Transform Raman Spectroscopy. Part I: The 1064-nm Excited Raman Spectra of Blood and Met Hemoglobin, *Appl. Spectrosc.* 46 (1992) 533–536.
- [28] P. Levillain, D. Pompeydie, Derivative spectrophotometry principles, advantages and limitations, applications, *Analysis*. 14 (1986) 1–20.
- [29] D. Bertrand, E. Vigneau, Prétraitement des données spectrales dans la spectroscopie infrarouge et ses applications analytique, in: B. Dominique, E. Dufour (Eds.), *La Spectrosc. Infrarouge Ses Appl. Anal.*, 2^o edition, Tech & doc, 2006: p. 248.
- [30] R.J. Barnes, M.S. Dhanoa, Susan J. Lister, Standard Normal Variate Transformation and De-trending of Near-Infrared Diffuse Reflectance Spectra, *Appl. Spectrosc.* 43 (1989) 772–777.
- [31] P. Geladi, D. Macdougall, Linearization and Scatter-Correction for Near-Infrared Reflectance Spectra of Meat, *Appl. Spectrosc.* 39 (1985) 491–500.
- [32] T. Naes, T. Isaksson, B. Kowalsky, Locally Weighted Regression and Scatter Correction for Near-Infrared Reflectance Data, *Anal. Chem.* 62 (1990) 664–673.
- [33] A.S. Luna, P. Arnaldo, J.S.A. Pinho, J. Ferré, R. Boqué, Rapid characterization of transgenic and non-transgenic soybean oils by chemometric methods using NIR spectroscopy, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 100 (2013) 115–119. doi:10.1016/j.saa.2012.02.085.
- [34] J. Trygg, S. Wold, Orthogonal projections to latent structures (O-PLS), *J. Chemom.* 16 (2002) 119–128. doi:10.1002/cem.695.
- [35] J.H. Kalivas, Calibration methodologies, in: S.D. Brow, R. Tauler (Eds.), *Compr. Chemom. Biochem. Data Anal.* 3, 1st editio, Elsevier B.V, 2009: pp. 1–32.
- [36] A.J. Smola, B. Scholkopf, A tutorial on support vector regression, *Stat. Comput.* 14 (2004) 199–222.
- [37] L.S. Aiken, S.G. West, S. C. Pitts, Multiple linear regression, in: I.B. Weiner (Ed.), *Hand B. Psychol.*, 2nd Editio, John Wiley & Sons, Inc., 2003: pp. 511–541.
- [38] Y. Ba, J. Liu, J. Han, X. Zhang, Application of Vis-NIR spectroscopy for determination the content of organic matter in saline-alkali soils, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 229 (2019) 1–11. doi:10.1016/j.apcatb.2019.118214.
- [39] S. Liu, H. Shen, S. Chen, X. Zhao, A. Biswas, X. Jia, Z. Shi, J. Fang, Estimating forest soil organic carbon content using vis-NIR spectroscopy: Implications for large-scale soil carbon spectroscopic assessment, *Geoderma*. 348 (2019) 37–44. doi:10.1016/j.geoderma.2019.04.003.

- [40] G.M. Vasques, S. Grunwald, W.G. Harris, Spectroscopic Models of Soil Organic Carbon in Florida, USA, *J. Environ. Qual.* 39 (2010) 923–934. doi:10.2134/jeq2009.0314.
- [41] D. V. Sarkhot, S. Grunwald, Y. Ge, C.L.S. Morgan, Comparison and detection of total and available soil carbon fractions using visible/near infrared diffuse reflectance spectroscopy, *Geoderma*. 164 (2011) 22–32. doi:10.1016/j.geoderma.2011.05.006.
- [42] J.T. Bushong, R.J. Norman, N.A. Slaton, Near-Infrared Reflectance Spectroscopy as a Method for Determining Organic Carbon Concentrations in Soil, *Commun. Soil Sci. Plant Anal.* 46 (2015) 37–41. doi:10.1080/00103624.2015.1048250.
- [43] C. Riefolo, A. Castrignanò, C. Colombo, S. Ruggieri, C. Vitti, G. Buttafuoco, Investigation of soil surface organic and inorganic carbon contents in a low-intensity farming system using laboratory visible and near-infrared spectroscopy, *Arch. Agron. Soil Sci.* 66 (2019) 1–13. doi:10.1080/03650340.2019.1674446.
- [44] I. Amin, F. Fikrat, E. Mammadov, M. Babayev, Soil Organic Carbon Prediction by Vis-NIR Spectroscopy : Case Study the Kur-Aras Plain , Azerbaijan, *Commun. Soil Sci. Plant Anal.* 51 (2020) 1–9. doi:10.1080/00103624.2020.1729367.
- [45] M. Ogrič, M. Knadel, S.M. Kristiansen, Y. Peng, L.W. De Jonge, K. Adhikari, M.H. Greve, M. Knadel, S.M. Kristiansen, Y. Peng, L.W. De Jonge, Soil organic carbon predictions in Subarctic Greenland by visible – near infrared spectroscopy, *Arctic, Antarct. Alp. Res.* 51 (2019) 490–505. doi:10.1080/15230430.2019.1679939.
- [46] F. Castaldi, S. Chabrilat, C. Chartin, V. Genot, A. R.Jones, B. van Wesemael, Estimation of soil organic carbon in arable soil in Belgium and Luxembourg with the LUCAS topsoil database, *Eur. J. Soil Sci.* 69 (2018) 592–603. doi:10.1111/ejss.12553.
- [47] H. Chen, T. Pan, J. Chen, Q. Lu, Waveband selection for NIR spectroscopy analysis of soil organic matter based on SG smoothing and MWPLS methods, *Chemom. Intell. Lab. Syst.* 107 (2011) 139–146. doi:10.1016/j.chemolab.2011.02.008.
- [48] F. Lucà, M. Conforti, A. Castrignanò, G. Matteucci, G. Buttafuoco, Effect of calibration set size on prediction at local scale of soil carbon by Vis-NIR spectroscopy, *Geoderma*. 288 (2017) 175–183. doi:10.1016/j.geoderma.2016.11.015.
- [49] B.G. Barthès, E. Kouakoua, M. Clairotte, J. Lallemand, L. Chapuis-Lardy, M. Rabenarivo, S. Roussel, Performance comparison between a miniaturized and a conventional near infrared reflectance (NIR) spectrometer for characterizing soil carbon and nitrogen, *Geoderma*. 338 (2019) 422–429. doi:10.1016/j.geoderma.2018.12.031.
- [50] X. Peng, T. Shi, A. Song, Y. Chen, W. Gao, Estimating soil organic carbon using VIS/NIR spectroscopy with SVMR and SPA methods, *Remote Sens.* 6 (2014) 2699–2717. doi:10.3390/rs6042699.
- [51] M. Seidel, C. Hutengs, B. Ludwig, S. Thiele-Bruhn, M. Vohland, Strategies for the efficient estimation of soil organic carbon at the field scale with vis-NIR spectroscopy: Spectral libraries and spiking vs. local calibrations, *Geoderma*. 354 (2019) 113856. doi:10.1016/j.geoderma.2019.07.014.
- [52] C. Hedley, P. Roudier, L. Maddi, VNIR Soil Spectroscopy for Field Soil Analysis,

- Commun. Soil Sci. Plant Anal. 46 (2015) 104–121.
doi:10.1080/00103624.2014.988582.
- [53] A. Sharififar, K. Singh, E. Jones, F.I. Ginting, B. Minasny, Evaluating a lowcost portable NIR spectrometer for the prediction of soil organic and total carbon using different calibration models, *Soil Use Manag.* 35 (2019) 607–616.
doi:10.1111/sum.12537.
 - [54] R.S. Bricklemyer, D.J. Brown, P.J. Turk, S. Clegg, Comparing vis–NIRS, LIBS, and Combined vis–NIRS-LIBS for Intact Soil Core Soil Carbon Measurement, *Soil Sci. Soc. Am. J.* 82 (2018) 1482–1496. doi:10.2136/sssaj2017.09.0332.
 - [55] M. Wan, M. Qu, W. Hu, W. Li, C. Zhang, H. Cheng, B. Huang, Estimation of soil pH using PXRF spectrometry and Vis-NIR spectroscopy for rapid environmental risk assessment of soil heavy metals, *Process Saf. Environ. Prot.* 132 (2019) 73–81.
doi:10.1016/j.psep.2019.09.025.
 - [56] C.A. Russell, J.F. Angus, G.D. Batten, B.W. Dunn, R.L. Williams, The potential of NIR spectroscopy to predict nitrogen mineralization in rice soils, *Plant Soil.* 247 (2002) 243–252. doi:10.1023/A:1021532316251.
 - [57] Y. Liu, Q. Jiang, T. Shi, T. Fei, J. Wang, G. Liu, Prediction of total nitrogen in cropland soil at different levels of soil moisture with Vis / NIR spectroscopy, *Acta Agric. Scand. , Sect. B — Soil Plant Sci.* 64 (2014) 267–281.
doi:10.1080/09064710.2014.906644.
 - [58] K.R.M. Adeline, C. Gomez, N. Gorretta, J.M. Roger, Predictive ability of soil properties to spectral degradation from laboratory Vis-NIR spectroscopy data, *Geoderma.* 288 (2017) 143–153. doi:10.1016/j.geoderma.2016.11.010.
 - [59] M. Marmette, V. Adamchuk, J. Nault, S. Tabatabai, R. Cocciardi, Comparison of the Performance of Two Vis-NIR Spectrometers in the Prediction of Various Soil Properties, 14th Int. Conf. Precis. Agric. June 24 – June 27, 2018, Montr. Quebec, Canada. (2018) 1–12.
<https://www.ispag.org/proceedings/?action=abstract&id=5404&search=types>.
 - [60] C. Gomez, P. Lagacherie, G. Coulouma, Regional predictions of eight common soil properties and their spatial structures from hyperspectral Vis-NIR data, *Geoderma.* 189–190 (2012) 176–185. doi:10.1016/j.geoderma.2012.05.023.
 - [61] S. Katuwal, M. Knadel, T. Norgaard, P. Moldrup, M.H. Greve, L.W. de Jonge, Predicting the dry bulk density of soils across Denmark: Comparison of single-parameter, multi-parameter, and vis–NIR based models, *Geoderma.* 361 (2019) 114080. doi:10.1016/j.geoderma.2019.114080.
 - [62] R. Recena, V.M. Fernández-Cabanás, A. Delgado, Soil fertility assessment by Vis-NIR spectroscopy: Predicting soil functioning rather than availability indices, *Geoderma.* 337 (2019) 368–374. doi:10.1016/j.geoderma.2018.09.049.
 - [63] P. Shi, F. Castaldi, B. van Wesemael, K. Van Oost, Vis-NIR spectroscopic assessment of soil aggregate stability and aggregate size distribution in the Belgian Loam Belt, *Geoderma.* 357 (2020) 113958. doi:10.1016/j.geoderma.2019.113958.
 - [64] N.J. Sithole, K. Ncama, L.S. Magwaza, Robust Vis-NIRS models for rapid assessment

of soil organic carbon and nitrogen in Ferralsols Haplic soils from different tillage management practices, *Comput. Electron. Agric.* 153 (2018) 295–301. doi:10.1016/j.compag.2018.08.036.

- [65] P.R.S. Vendrame, R.L. Marchão, D. Brunet, T. Becquer, The potential of NIR spectroscopy to predict soil texture and mineralogy in Cerrado Latosols, *Eur. J. Soil Sci.* 63 (2012) 743–753. doi:10.1111/j.1365-2389.2012.01483.x.
- [66] M. Vohland, C. Emmerling, Determination of total soil organic C and hot water-extractable C from VIS-NIR soil reflectance with partial least squares regression and spectral feature selection techniques, *Eur. J. Soil Sci.* 62 (2011) 598–606. doi:10.1111/j.1365-2389.2011.01369.x.
- [67] S. Xu, Y. Zhao, M. Wang, X. Shi, Comparison of multivariate methods for estimating selected soil properties from intact soil cores of paddy fields by Vis–NIR spectroscopy, *Geoderma* 310 (2018) 29–43. doi:10.1016/j.geoderma.2017.09.013.
- [68] D. Xu, W. Ma, S. Chen, Q. Jiang, K. He, Z. Shi, Assessment of important soil properties related to Chinese Soil Taxonomy based on vis–NIR reflectance spectroscopy, *Comput. Electron. Agric.* 144 (2018) 1–8. doi:10.1016/j.compag.2017.11.029.
- [69] N. Carmon, E. Ben-Dor, An Advanced Analytical Approach for Spectral - Based Modelling of Soil Properties, *Int. J. Emerg. Technol. Adv. Eng.* 7 (2017) 90–97. doi:10.1002/9781119043553.
- [70] Z. Tümsavaş, Y. Tekin, Y. Ulusoy, A.M. Mouazen, Prediction and mapping of soil clay and sand contents using visible and near-infrared spectroscopy, *Biosyst. Eng.* 177 (2019) 90–100. doi:10.1016/j.biosystemseng.2018.06.008.
- [71] Y. Tang, E. Jones, B. Minasny, Evaluating low-cost portable near infrared sensors for rapid analysis of soils from South Eastern Australia, *Geoderma Reg.* 20 (2020) e00240. doi:10.1016/j.geodrs.2019.e00240.
- [72] D. Cozzolino, Influence of Soil Particle Size on the Measurement of Sodium by Near-Infrared Reflectance Spectroscopy, *Commun. Soil Sci. Plant Anal.* 41 (2010) 2330–2339. doi:10.1080/00103624.2010.508097.
- [73] Z. Sun, Y. Zhang, J. Li, W. Zhou, Spectroscopic Determination of Soil Organic Carbon and Total Nitrogen Content in Pasture Soils, *Commun. Soil Sci. Plant Anal.* 45 (2014) 37–41. doi:10.1080/00103624.2014.883628.
- [74] L. Xuemei, L. Jianshe, Using Short Wave Visible – Near Infrared Reflectance Spectroscopy to Predict Soil Properties and Content, *Spectrosc. Lett. An Int. J. Rapid Commun.* 47 (2014) 729–739. doi:10.1080/00387010.2013.840315.
- [75] D. Cozzolino, W.U. Cynkar, R.G. Damberg, N. Shah, In Situ Measurement of Soil Chemical Composition by Near-Infrared Spectroscopy : A Tool Toward Sustainable Vineyard Management, *Commun. Soil Sci. Plant Anal.* 44 (2013) 37–41. doi:10.1080/00103624.2013.768263.
- [76] M.R. Mobasheri, M. Amani, R. Fathi-almas, H.R. Zabihi, Developing a model for soil potassium estimation using spectrometry data, *Commun. Soil Sci. Plant Anal.* 51 (2020) 1–10. doi:10.1080/00103624.2020.1733002.

- [77] L.P.M. Manage, M.H. Greve, M. Knadel, P. Moldrup, L.W. de Jonge, S. Katuwal, Visible-Near-Infrared Spectroscopy Prediction of Soil Characteristics as Affected by Soil-Water Content, *Soil Sci. Soc. Am. J.* 82 (2018) 1333–1346. doi:10.2136/sssaj2018.01.0052.
- [78] S. Xu, Y. Zhao, M. Wang, X. Shi, Quantification of Different Forms of Iron from Intact Soil Cores of Paddy Fields with Vis-NIR Spectroscopy, *Soil Sci. Soc. Am. J.* 82 (2018) 1497–1511. doi:10.2136/sssaj2018.01.0014.
- [79] J.B. Carra, M. Fabris, J. Dieckow, O.R. Brito, P.R.S. Vendrame, L. Macedo Dos Santos Tonial, Near-Infrared Spectroscopy Coupled with Chemometrics Tools: A Rapid and Non-Destructive Alternative on Soil Evaluation, *Commun. Soil Sci. Plant Anal.* 50 (2019) 421–434. doi:10.1080/00103624.2019.1566465.
- [80] M. Fuentes, C. Hidalgo, NIR Spectroscopy : An Alternative for Soil Analysis, *Commun. Soil Sci. Plant Anal.* 43 (2012) 346–356. doi:10.1080/00103624.2012.641471.
- [81] J. Dinakaran, A. Bidalia, A. Kumar, M. Hanief, A. Meena, K.S. Rao, Near Infrared-Spectroscopy for Determination of Carbon and Nitrogen in Indian Soils, *Commun. Soil Sci. Plant Anal.* 3624 (2016) 1503–1516. doi:10.1080/00103624.2016.1194990.
- [82] G.T. Freschet, B.G. Barthès, D. Brunet, E. Hien, D. Masse, Use of Near Infrared Reflectance Spectroscopy (NIRS) for Predicting Soil Fertility and Historical Management, *Commun. Soil Sci. Plant Anal.* 42 (2011) 37–41.
- [83] B. Ludwig, R. Murugan, V.R.R. Parama, M. Vohland, Use of different chemometric approaches for an estimation of soil properties at field scale with near infrared spectroscopy, *J. Plant Nutr. Soil Sci.* 181 (2018) 704–713. doi:10.1002/jpln.201800130.
- [84] C.M. Clingensmith, S. Grunwald, S.P. Wani, Evaluation of calibration subsetting and new chemometric methods on the spectral prediction of key soil properties in a data-limited environment, *Eur. J. Soil Sci.* 70 (2019) 107–126. doi:10.1111/ejss.12753.
- [85] O.A.R. Vlasova, L. Vlassova, F.P. Cabello, R. Montorio, E.N. Romero, Soil organic matter and texture estimation from visible – near infrared – shortwave infrared spectra in areas of land cover changes using correlated component regression, *L. Degrad. Dev.* 30 (2018) 544–560. doi:10.1002/ldr.3250.
- [86] R. Reda, T. Saffaj, B. Ilham, O. Saidi, K. Issam, L. Brahim, E.M. El Hadrami, A comparative study between a new method and other machine learning algorithms for soil organic carbon and total nitrogen prediction using near infrared spectroscopy, *Chemom. Intell. Lab. Syst.* 195 (2019). doi:10.1016/j.chemolab.2019.103873.
- [87] Y. Zhang, M.Z. Li, L.H. Zheng, Y. Zhao, X. Pei, Soil nitrogen content forecasting based on real-time NIR spectroscopy, *Comput. Electron. Agric.* 124 (2016) 29–36. doi:10.1016/j.compag.2016.03.016.
- [88] M. Vohland, J. Besold, J. Hill, H.C. Fründ, Comparing different multivariate calibration methods for the determination of soil organic carbon pools with visible to near infrared spectroscopy, *Geoderma.* 166 (2011) 198–205. doi:10.1016/j.geoderma.2011.08.001.

- [89] X. Xu, C. Du, F. Ma, Y. Shen, K. Wu, D. Liang, J. Zhou, Detection of soil organic matter from laser-induced breakdown spectroscopy (LIBS) and mid-infrared spectroscopy (FTIR-ATR) coupled with multivariate techniques, *Geoderma*. 355 (2019) 1–13. doi:10.1016/j.geoderma.2019.113905.
- [90] K.S. Dunne, N.M. Holden, S.M. O'Rourke, A. Fenelon, K. Daly, Prediction of phosphorus sorption indices and isotherm parameters in agricultural soils using mid-infrared spectroscopy, *Geoderma*. 358 (2020) 113981. doi:10.1016/j.geoderma.2019.113981.
- [91] T. Filep, D. Zacháry, K. Balog, Assessment of soil quality of arable soils in Hungary using DRIFT spectroscopy and chemometrics, *Vib. Spectrosc.* 84 (2016) 16–23. doi:10.1016/j.vibspec.2016.02.005.
- [92] W. Ji, V.I. Adamchuk, A. Biswas, N.M. Dhawale, B. Sudarsan, Y. Zhang, R.A. Viscarra Rossel, Z. Shi, Assessment of soil properties in situ using a prototype portable MIR spectrometer in two agricultural fields, *Biosyst. Eng.* 152 (2016) 14–27. doi:10.1016/j.biosystemseng.2016.06.005.
- [93] K. Metzger, C. Zhang, M. Ward, K. Daly, Mid-infrared spectroscopy as an alternative to laboratory extraction for the determination of lime requirement in tillage soils, *Geoderma*. 364 (2020) 114171. doi:10.1016/j.geoderma.2020.114171.
- [94] L.J. Janik, S.T. Forrester, A. Rawson, The prediction of soil chemical and physical properties from mid-infrared spectroscopy and combined partial least-squares regression and neural networks (PLS-NN) analysis, *Chemom. Intell. Lab. Syst.* 97 (2009) 179–188. doi:10.1016/j.chemolab.2009.04.005.
- [95] E.K. Towett, K.D. Shepherd, A. Sila, E. Aynekulu, G. Cadisch, Mid-Infrared and Total X-Ray Fluorescence Spectroscopy Complementarity for Assessment of Soil Properties, *Soil Sci. Soc. Am. J.* 79 (2015) 1375–1385. doi:10.2136/sssaj2014.11.0458.
- [96] L. Deiss, A.J. Margenot, S.W. Culman, M.S. Demyan, Tuning support vector machines regression models improves prediction accuracy of soil properties in MIR spectroscopy, *Geoderma*. 365 (2020) 114227. doi:10.1016/j.geoderma.2020.114227.
- [97] B. Ludwig, R. Murugan, P. V. R. ramakrishna, M. Vohland, Accuracy of Estimating Soil Properties with Mid-Infrared Spectroscopy: Implications of Different Chemometric Approaches and Software Packages Related to Calibration Sample Size, *Soil Sci. Soc. Am. J.* 83 (2019) 1542–1552. doi:10.2136/sssaj2018.11.0413.
- [98] F. Ma, C.W. Du, J.M. Zhou, Y.Z. Shen, Investigation of soil properties using different techniques of mid-infrared spectroscopy, *Eur. J. Soil Sci.* 70 (2019) 96–106. doi:10.1111/ejss.12741.
- [99] A.M. Sila, K.D. Shepherd, G.P. Pokhariyal, Evaluating the utility of mid-infrared spectral subspaces for predicting soil properties, *Chemom. Intell. Lab. Syst.* 153 (2016) 92–105. doi:10.1016/j.chemolab.2016.02.013.
- [100] J. Sanderman, K. Savage, S.R.S. Dangal, Mid-infrared spectroscopy for prediction of soil health indicators in the United States, *Soil Sci. Soc. Am. J.* 84 (2020) 251–261. doi:10.1002/saj2.20009.
- [101] H. Sepahvand, R. Mirzaeitalarposhti, K. Beiranvand, Prediction of soil carbon levels in

- calcareous soils of Iran by mid-infrared reflectance spectroscopy, *Environ. Pollut. Bioavailab.* 31 (2019) 9–17. doi:10.1080/09542299.2018.1549961.
- [102] C. Du, J. Zhou, Application of Infrared Photoacoustic Spectroscopy in Soil Analysis, *Appl. Spectrosc. Rev.* 46 (2011) 405–422. doi:10.1080/05704928.2011.570837.
- [103] D.B. Madhavan, M. Kitching, D.S. Mendham, C.J. Weston, T.G. Baker, Mid-infrared spectroscopy for rapid assessment of soil properties after land use change from pastures to *Eucalyptus globulus* plantations, *J. Environ. Manage.* 175 (2016) 67–75. doi:10.1016/j.jenvman.2016.03.032.
- [104] I. Aiko Fifi Djuuna, L. Abbott, C. Russell, Determination and Prediction of Some Soil Properties using Partial Least Square (PLS) Calibration and Mid-Infra Red (MIR) Spectroscopy Analysis, *J. Trop. Soils.* 16 (2011) 93–98. doi:10.5400/jts.2011.16.2.93.
- [105] B.K. Waruru, K.D. Shepherd, G.M. Ndegwa, A. Sila, P.T. Kamoni, Application of mid-infrared spectroscopy for rapid characterization of key soil properties for engineering land use, *Soils Found.* 55 (2015) 1181–1195. doi:10.1016/j.sandf.2015.09.018.
- [106] Y. Ge, J.A. Thomasson, C.L.S. Morgan, Mid-infrared attenuated total reflectance spectroscopy for soil carbon and particle size determination, *Geoderma.* 213 (2014) 57–63. doi:10.1016/j.geoderma.2013.07.017.
- [107] C.A. Seybold, R. Ferguson, D. Wysocki, S. Bailey, J. Anderson, B. Nester, P. Schoeneberger, S. Wills, Z. Libohova, D. Hoover, P. Thomas, Application of Mid-Infrared Spectroscopy in Soil Survey, *Soil Sci. Soc. Am. J.* 83 (2019) 1746–1759. doi:10.2136/sssaj2019.06.0205.
- [108] N. k. Wijewardane, Y. Ge, S. Wills, Z. Libohova, Predicting Physical and Chemical Properties of US Soils with a Mid-Infrared Reflectance Spectral Library, *Soil Sci. Soc. Am. J.* 82 (2018) 722–731. doi:10.2136/sssaj2017.10.0361.
- [109] Y.W. Dong, S.Q. Yang, C.Y. Xu, Y.Z. Li, W. Bai, Z.N. Fan, Y.N. Wang, Q.Z. Li, Determination of Soil Parameters in Apple-Growing Regions by Near- and Mid-Infrared Spectroscopy, *Pedosphere.* 21 (2011) 591–602. doi:10.1016/S1002-0160(11)60161-6.
- [110] H.T. Xie, X.M. Yang, C.F. Drury, J.Y. Yang, X.D. Zhang, Predicting soil organic carbon and total nitrogen using mid- and near-infrared spectra for Brookston clay loam soil in Southwestern Ontario, Canada, *Can. J. Soil Sci.* 91 (2011) 53–63. doi:10.4141/CJSS10029.
- [111] M. Clairotte, C. Grinand, E. Kouakoua, A. Thébault, N.P.A. Saby, M. Bernoux, B.G. Barthès, National calibration of soil organic carbon concentration using diffuse infrared reflectance spectroscopy, *Geoderma.* 276 (2016) 41–52. doi:10.1016/j.geoderma.2016.04.021.
- [112] J.M. Soriano-Disla, L.J. Janik, D.J. Allen, M.J. McLaughlin, Evaluation of the performance of portable visible-infrared instruments for the prediction of soil properties, *Biosyst. Eng.* 161 (2017) 24–36. doi:10.1016/j.biosystemseng.2017.06.017.
- [113] J.M. Johnson, E. Vandamme, K. Senthilkumar, A. Sila, K.D. Shepherd, K. Saito, Near-infrared, mid-infrared or combined diffuse reflectance spectroscopy for assessing soil

- fertility in rice fields in sub-Saharan Africa, *Geoderma*. 354 (2019) 1–24. doi:10.1016/j.geoderma.2019.06.043.
- [114] C. Hutengs, M. Seidel, F. Oertel, B. Ludwig, M. Vohland, In situ and laboratory soil spectroscopy with portable visible-to-near-infrared and mid-infrared instruments for the assessment of organic carbon in soils, *Geoderma*. 355 (2019) 113900. doi:10.1016/j.geoderma.2019.113900.
- [115] M.A.N. Coutinho, F. de O. Alari, M.M.C. Ferreira, L.R. d. Amaral, Influence of soil sample preparation on the quantification of NPK content via spectroscopy, *Geoderma*. 338 (2019) 401–409. doi:10.1016/j.geoderma.2018.12.021.
- [116] W. Ng, B. Minasny, M. Montazerolghaem, J. Padarian, R. Ferguson, S. Bailey, A.B. McBratney, Convolutional neural network for simultaneous prediction of several soil properties using visible/near-infrared, mid-infrared, and their combined spectra, *Geoderma*. 352 (2019) 251–267. doi:10.1016/j.geoderma.2019.06.016.
- [117] M. Allo, P. Todoroff, M. Jameux, M. Stern, L. Paulin, A. Albrecht, Prediction of tropical volcanic soil organic carbon stocks by visible-near- and mid-infrared spectroscopy, *Catena*. 189 (2020) 104452. doi:10.1016/j.catena.2020.104452.
- [118] Y. Shao, Y. He, Nitrogen, phosphorus, and potassium prediction in soils, using infrared spectroscopy, *Soil Res.* 49 (2011) 166–172. doi:10.1071/SR10098.
- [119] M.L. McDowell, G.L. Bruland, J.L. Deenik, S. Grunwald, N.M. Knox, Soil total carbon analysis in Hawaiian soils with visible, near-infrared and mid-infrared diffuse reflectance spectroscopy, *Geoderma*. 189–190 (2012) 312–320. doi:10.1016/j.geoderma.2012.06.009.
- [120] J.M. Soriano-Disla, L.J. Janik, R.A. Viscarra Rossel, L.M. MacDonald, M.J. McLaughlin, The performance of visible, near-, and mid-infrared reflectance spectroscopy for prediction of soil physical, chemical, and biological properties, *Appl. Spectrosc. Rev.* 49 (2014) 139–186. doi:10.1080/05704928.2013.811081.
- [121] M. Vohland, M. Ludwig, S. Thiele-Bruhn, B. Ludwig, Determination of soil properties with visible to near- and mid-infrared spectroscopy: Effects of spectral variable selection, *Geoderma*. 223–225 (2014) 88–96. doi:10.1016/j.geoderma.2014.01.013.
- [122] S.R. Araújo, M. Söderström, J. Eriksson, C. Isendahl, P. Stenborg, J.A.M. Demattê, Determining soil properties in Amazonian Dark Earths by reflectance spectroscopy, *Geoderma*. 237 (2015) 308–317. doi:10.1016/j.geoderma.2014.09.014.
- [123] F.S. Terra, J.A.M. Demattê, R.A. Viscarra Rossel, Spectral libraries for quantitative analyses of tropical Brazilian soils: Comparing vis-NIR and mid-IR reflectance data, *Geoderma*. 255–256 (2015) 81–93. doi:10.1016/j.geoderma.2015.04.017.
- [124] N.M. Knox, S. Grunwald, M.L. McDowell, G.L. Bruland, D.B. Myers, W.G. Harris, Modelling soil carbon fractions with visible near-infrared (VNIR) and mid-infrared (MIR) spectroscopy, *Geoderma*. 239–240 (2015) 229–239. doi:10.1016/j.geoderma.2014.10.019.
- [125] M.P.N.K. Henaka Arachchi, D.J. Field, A.B. McBratney, Quantification of soil carbon from bulk soil samples to predict the aggregate-carbon fractions within using near- and mid-infrared spectroscopic techniques, *Geoderma*. 267 (2016) 207–214.

doi:10.1016/j.geoderma.2015.12.030.

- [126] R.A. Viscarra Rossel, D.J.J. Walvoort, A.B. McBratney, L.J. Janik, J.O. Skjemstad, Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties, *Geoderma*. 131 (2006) 59–75. doi:10.1016/j.geoderma.2005.03.007.
- [127] V. Bellon-maurel, A. Mcbratney, *Soil Biology & Biochemistry* Near-infrared (NIR) and mid-infrared (MIR) spectroscopic techniques for assessing the amount of carbon stock in soils e Critical review and research perspectives, *Soil Biol. Biochem.* 43 (2011) 1398–1410. doi:10.1016/j.soilbio.2011.02.019.
- [128] T. Terhoeven-Urselmans, T.-G. Vagen, O. Spaargaren, K.D. Shepherd, Prediction of Soil Fertility Properties from a Globally Distributed Soil Mid-Infrared Spectral Library, *Soil Sci. Soc. Am. J.* 74 (2010) 1792–1799. doi:10.2136/sssaj2009.0218.
- [129] T.G. Vågen, K.D. Shepherd, M.G. Walsh, Sensing landscape level change in soil fertility following deforestation and conversion in the highlands of Madagascar using Vis-NIR spectroscopy, *Geoderma*. 133 (2006) 281–294. doi:10.1016/j.geoderma.2005.07.014.
- [130] Y. Liu, Y. Liu, Y. Chen, Y. Zhang, T. Shi, J. Wang, Y. Hong, T. Fei, Y. Zhang, The influence of spectral pretreatment on the selection of representative calibration samples for soil organic matter estimation using vis-NIR reflectance spectroscopy, *Remote Sens.* 11 (2019). doi:10.3390/rs11040450.
- [131] A. Gholizadeh, L. Boruvka, M.M. Saberioon, J. Kozák, R. Vašát, K. Nemecek, Comparing different data preprocessing methods for monitoring soil heavy metals based on soil spectral features, *Soil Water Res.* 10 (2015) 218–227. doi:10.17221/113/2015-SWR.
- [132] A.C. Dotto, R.S.D. Dalmolin, A. ten Caten, S. Grunwald, A systematic study on the application of scatter-corrective and spectral-derivative preprocessing for multivariate prediction of soil organic carbon by Vis-NIR spectra, *Geoderma*. 314 (2018) 262–274. doi:10.1016/j.geoderma.2017.11.006.
- [133] A.C. Dotto, R.S.D. Dalmolin, S. Grunwald, A. ten Caten, W. Pereira Filho, Two preprocessing techniques to reduce model covariables in soil property predictions by Vis-NIR spectroscopy, *Soil Tillage Res.* 172 (2017) 59–68. doi:10.1016/j.still.2017.05.008.

Soil spectroscopy with the use of chemometrics, machine learning and pre-processing techniques in soil diagnosis: recent advances - a review

Barra, Issam

2020-12-30

Attribution-NonCommercial-NoDerivatives 4.0 International

Barra I, Haefele SM, Sakrabani R, Kebede F. (2021) Soil spectroscopy with the use of chemometrics, machine learning and pre-processing techniques in soil diagnosis: recent advances - a review. Trends in Analytical Chemistry, Volume 135, February 2021, Article number 116166

<https://doi.org/10.1016/j.trac.2020.116166>

Downloaded from CERES Research Repository, Cranfield University