# Estimation of soil organic carbon using chemometrics: a comparison between mid-infrared and visible near infrared diffuse reflectance spectroscopy

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## Abstract

Analysis for soil organic carbon (SOC) content is a key component of sustainable soil fertility management. Estimating this parameter using traditional methods is time – consuming and may be inappropriate for large scale monitoring. This study assessed the potential of a combined application of diffuse reflectance spectroscopy and the partial least square regression (PLSR) to analyse and predict SOC in soils. Fifty three (53) topsoil samples were collected from areas with differing land use activities, and then analysed for SOC using a Flash 2000 organic elemental analyzer. Diffuse reflectance spectra of soil samples were measured in the visible near infrared (VNIR) and the mid-infrared (MIR) wavelength ranges using a Ger3700 VNIR spectrophotometer and a FT-IR spectrometer respectively. Partial least squares regression (PLSR) was used to develop prediction models. Models developed from both spectra predicted SOC with accuracy close to the elemental analyzer ($R^2 > 0.80$) and offers a reliable alternative to the traditional laboratory analyses. On comparison using the coefficient of determination ($R^2$), ratio of performance to deviation (RPD) and the root mean square error (RMSE), VNIR spectra offer better accuracy with an $R^2 = 0.90$, RPD = 3.12 and RMSE = 0.07 Log10 %SOC compared to the MIR spectra with an $R^2 = 0.85$, RPD = 3.09 and RMSE = 0.08 Log10 %SOC.

**Keywords:** Soil organic carbon; VNIR spectroscopy; MIR spectroscopy; SOC estimation; PLSR

## Introduction

Quantification of soil organic carbon (SOC) content is crucial component of soil fertility management. SOC enhances soil structure and water retention. It serves as the driving force of all biological activities providing energy and nutrients for the teeming soil organisms (Craswell and Lefroy, 2001). Most often, decisions whether or not to plant and/or to deploy specific soil management procedures are usually made based on the results of quantitative soil SOC analysis.

Traditional procedures for quantifying SOC such as chromate oxidation and combustion are expensive and time consuming (McCarty and Reeves, 2006). The 'loss-on-ignition' analytical procedure though cheaper and rapid has also been shown not to be totally accurate due to the decomposition of certain mineral fractions such as kaolinite, and iron oxyhydroxides at high temperatures required by this method (Lal et al., 2001). One of the emerging alternatives which permits rapid and cost-effective quantification, and can

potentially yield comparable results to the traditional methods is chemometrics (Cezar et al., 2019; Bellon-Maurel and McBratney, 2011; Schwartz et al., 2009; Brown et al., 2006; Wetterlind et al., 2008).

The predictive accuracies of models developed for SOC estimation reported by researchers have been varied. The mid-infrared (MIR) spectra of soil are characterised by well-defined features due to fundamental vibrations of functional groups and may be well suited for SOC prediction purposes due to their higher specificity (Chen et al., 2016; Knox et al., 2015; Bellon-Maurel and McBratney, 2011; Reeves, 2010). However, while MIR spectroscopy has been a major tool for qualitative analysis, it has been argued that its use for quantitative analysis in undiluted samples such as soils may be complicated due to the presence of spectral distortions and nonlinearities (Culler, 1993).

Quantitative predictions of SOC using visible near infrared (VNIR) diffuse reflectance spectroscopy requires little to no sample

preparation compared to the MIR which requires additional sample preparation and the use of spectrometers that are considerably expensive (Knadel et al., 2013). Also, despite weak absorptions by organic functional groups in the VNIR, the general absorption due to soil organic matter in the visible region is obvious (Gholizadeh et al., 2013). SOC content of soils influences soil colour, an important factor for prediction in the visible region (Udelhoven et al., 2003), implying that the VNIR region of the electromagnetic spectrum may interact better with SOC than the infrared region alone. Consequently, VNIR spectra could have improved predictive potentials when used in calibrating models for SOC estimations (McDowell et al., 2012; Viscarra Rossel et al., 2006).

Some studies have been carried out to estimate SOC in the laboratory and under field conditions using VNIR and MIR diffuse reflectance spectroscopy. However, to the best of our knowledge, there have been few studies comparing the accuracies of SOC predictions using VNIR and MIR diffuse reflectance spectroscopy on the same set of samples. The VNIR diffuse reflectance approach is non-destructive and can be suitable for large scale soil monitoring where large number of samples are required for assessments. This study therefore sought to compare the predictive capabilities of MIR and VNIR diffuse reflectance spectra for prediction of SOC using spectra obtained from the same soil sample.

## Materials and Methods

A total of 53 soil samples were collected at a depth of 10 cm from differing land use and land management activities within southwest England, a region delimited by the geographic coordinates 50°58' to 50°96' North and 3°13' to 3°22' West. The geology of this region contains light to medium textured soils characterized by slate, granite, gravel, kaolin and limestone (UKSO, 2021). The samples were collected from different landscape areas

and draining conditions. Each soil sample was air-dried and passed through 2 mm mesh sized sieves before all further analysis. pH was determined using an HI98129 electrode which had been calibrated with buffers pH 4.0 and 9.0 prior to measurement. The particle size distribution (PSD) was assessed using the Mastersizer 3000 Laser Diffraction Particle Size Analyzer.

*Soil Chemical Analysis*
Total SOC was determined in 10 mg of ball milled soil subsamples using the Thermos Scientific Flash 2000 organic elemental analyzer with a reproducibility of 0.07% calculated using the equation (Fearn, 2008):

$$SEL = \sqrt{\frac{\sum_{i=0}^{n} E_i^2}{2n}}$$

Where *SEL* is the standard error of laboratory, $E_i$ is the difference between measurements and the estimated true value of a certified reference material.

Prior to analysis using the Flash 2000 organic elemental analyzer, a simple test for carbonates was done by checking the pH of soil samples. When soil samples possess pH less than 7.4, it is concluded that the samples contain none to insignificant quantities of carbonates (Schumacher, 2002). Otherwise, samples are initially dried at $105^0$C overnight and treated with a combination of $H_2SO_4$ and $FeSO_4$ to remove carbonates. All soils within this study have pH less than 7.4. Therefore:

$$\% \text{ Total carbon} \cong \% \text{ Total organic carbon}$$

*Spectral Measurement*
*VNIR*
VNIR spectra of soil samples were obtained in a dark room with a Ger3700 VNIR spectrophotometer (350 - 2500nm) coupled with a light source made of a quartz-halogen bulb, and projected at $45^0$ to the detector. The spectrophotometer has one Si array (350 - 1050 nm) and two Peltier-cooled InGaAs detectors (1050 - 1900 nm and 1900 - 2500 nm). Spectral

sampling interval of the instrument was 3nm at (350 - 1050 nm), 7nm at (1050 - 1900 nm) and 9.5nm at (1900 - 2500 nm).

A white reference panel of Spectralon calibrated for 100% of reflectance was scanned before each measurement to optimize the instrument in accordance with the Labsphere Reflectance Calibration Laboratory (LRCL, 2009). Scans were taken from soil, tightly packed and levelled in petri – dishes at four positions by carefully rotating the petri dish at an angle of 900clockwise to increase precision of measurements. The replicate scans were then averaged to produce a single spectrum for each sample in line with the recommendations of Fiorio et al. (2010).

*MIR*
MIR spectra of soils were collected from ball milled subsamples using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific Inc., Madison, WI, USA). Spectral acquisition was performed by diamond attenuated total reflectance (MIR-ATR) spectroscopy over the spectral range 2500 – ~15400nm (4000–650 cm$^{-1}$), with spectral resolution of 4 cm$^{-1}$ and 16 scans per replicate.

*Data Analysis and Model Development*
Due to scatter effects and path length variations inherent in diffuse spectra, four common spectra pre-processing techniques were applied to the spectra. Techniques tested include Log10(1/B) transformation (where B is reflectance), standard normal variate coupled with the detrending (SNV-DT) which reduces scatter effects and linearizes the spectra. Other tools tested include the Savitzky- Golay smoothing of the spectra (SG), and a combination of Savitzy-Golay and derivatisation which smoothens, enhances resolution and eliminates baseline drift between spectra (Verboven et al., 2012). Spectra processing and statistical modeling were done using the Unscrambler-X 10 (CAMO, Incorporation, Oslo, Norway).

Partial least square regression (PLSR) models were developed from VNIR and MIR diffuse reflectance spectra (x, predictor variables) and log10-transformed ETPH data (y, dependent variables), that approximated a Gaussian distribution after stabilizing the variance. Twenty four percent (24%) of the dataset was set aside for model validation while only 76% of each dataset selected using the Kennard – Stone algorithm was used for model calibration. Potential outliers were identified as samples with very high leverages and residuals.

The predictive ability of PLSR models is reported in terms of coefficient of determination ($R^2$), root mean-square error (RMSE; Eq.1), percentage prediction error (% PE; Eq. 2), ratio of performance to deviation (RPD; Eq 3) (Cezar et al., 2019; Janik et al., 2007; Brown et al., 2006).

$$RMSE = \sqrt{\frac{\sum(ETPHp - ETPHm)^2}{n}} - - - (1)$$

$$\% PE = \frac{RMSEp}{Xh_p} \times 100 - - - - - - - (2)$$

$$RPD = \frac{SD}{RMSEp} - - - - - - - - (3)$$

where *n* is the number of validation samples, *SD* is the standard deviation of the predicted validation values and *Xhp* is the largest measured data point within the validation set. According to Viscarra Rossel et al. (2006), very poor models show RPD < 1.0; poor models: $1.0 \leq RPD \leq 1.4$; fair models: $1.4 \leq RPD \leq 1.8$; good models: $1.8 \leq RPD \leq 2.0$ and very good models: $2.0 \leq RPD \leq 2.5$; and excellent models have RPD > 2.5.

**Results**

*Laboratory Analysis*
The results of laboratory analyses show a wide variation in soil pH and a highly skewed SOC distribution (1.87-30.9%). The data was Log10 –transformed to make it normal. Consequently, all PLSR models were developed based on

Log10 – transformed SOC. Details about pH, particle size and laboratory measured SOC concentrations of soil samples are presented in Table 1.

wavelengths of measurement. MIR spectra of soil samples covered a spectral range of 2500 −16660 nm (4000 – 600 cm$^{-1}$) and contained prominent features than the VNIR spectra.

**TABLE 1**
Descriptive statistics of soil properties

|  | n[a] | pH | PSD[b] | | | SOC | SD[c] | Skewness |
|---|---|---|---|---|---|---|---|---|
|  |  |  | Sand | Silt | Clay |  |  |  |
|  |  |  |  |  | % |  |  |  |
| Calibration | 40 | 4.9 – 7.2 | 54 - 60 | 26 - 30 | 7 – 12 | 1.87 – 30.9 | 5.15 | 1.81 |
| Validation | 13 | 4.7 – 7.1 | 53 - 60 | 26 - 29 | 7 – 10 | 2.02 – 21.4 | 5.45 | 1.54 |
| Total | 53 | 4.9 – 7.2 | 54 - 60 | 26 - 30 | 7 – 12 | 1.87 – 30.9 | 5.18 | 1.72 |

[a] Number of samples

[b] Particle size distribution

[c] Standard deviation

*Qualitative Description of Spectra*
Figure I illustrates the shape and variations observed in both the VNIR and MIR spectra. VNIR Spectra of all samples follow a similar shape with absorptions observed at ~400 – 900, ~1400–1450 nm, 1626 – 1750 nm, 1910–1930 nm and at ~2100 and 2500 nm. In general, samples with higher SOC content were observed to be relatively darker in tone and had lower reflectance across the total

Prominent absorption features present in the MIR spectra include the steeped absorption at ~7812 – 9852nm, absorptions around 5680 - 6200 nm, at ~3500 – 3850 nm and at ~ 3070 - 3360 nm. MIR spectra of soils used in this study can be seen to be less affected by shifting baselines and are clearly separable at 2760 – 3730 nm and at 5540 – 8470 nm (Figure 2).
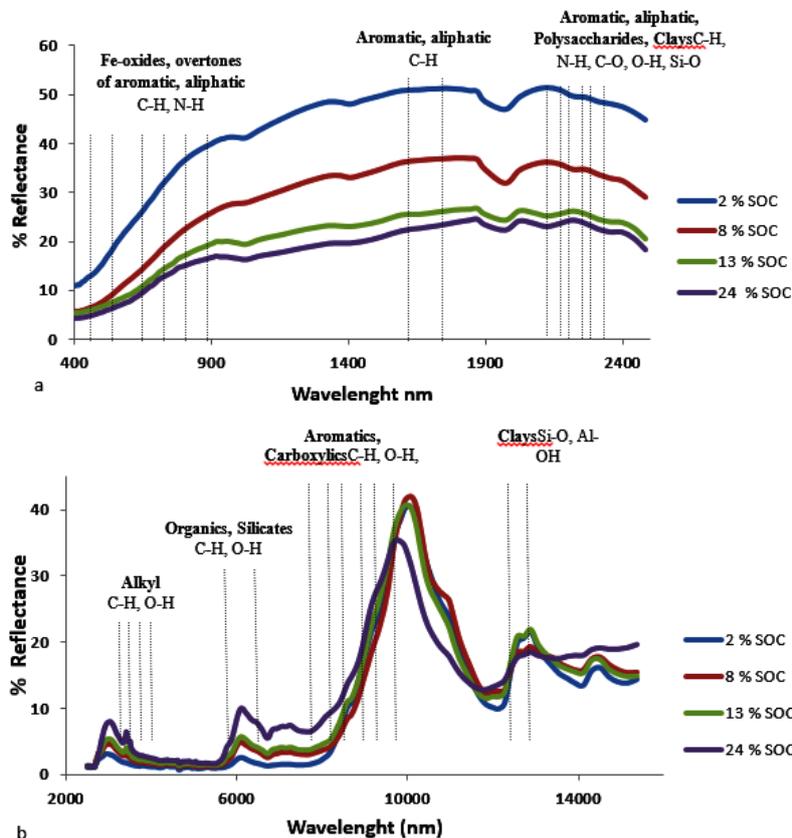


**Figure 1** a) VNIR and b) MIR diffuse reflectance spectra of some of the soil samples used for this study showing absorbing functional groups

*Spectra Pre-processing*

A total of five (5) PLS models were generated each for both VNIR and MIR spectra using different pre-processing approaches. Predictive accuracy and stability of PLSR models (evaluated using the $R^2$, RPD, RMSE and optimum number of latent factors) indicate that only $Log_{10}(1/R)$ transformation significantly improved model quality. In particular, the SNV-DT, a standard pre-processing technique used to normalise spectral data, remove scatter effect, and correct for baseline effect lowered the RPD value for VNIR spectra (from 1.60 to 1.53) as opposed

to improving the MIR spectra (Table II).

*Partial Least Square Regression (PLSR)*

The results of the model performance are summarized in Figure II, a scatter plot that compares the measured and predicted SOC concentrations using PLSR analysis for the calibration and validation data sets. PLSR models to predict SOC from both the VNIR and MIR spectra performed excellently with validation statistics $R^2$ =0.90 and 0.90; and RPD = 3.12 and 3.09 for VNIR and MIR respectively (Table II). The PLSR- VNIR models showed a lower RMSE (0.07 $Log_{10}$

**TABLE 2**

Partial least square model evaluation statistics from different spectral pre-processing methods applied to VNIR and MIR diffuse reflectance spectra

| Pre-processing | VNIR | | | MIR | | |
|---|---|---|---|---|---|---|
| | $R^2_v$ | $RMSE_v$ | RPD | $R^2_v$ | $RMSE_v$ | RPD |
| | | $Log_{10}$ %SOC | | | $Log_{10}$ %SOC | |
| RAW | 0.62 | 0.16 | 1.60 | 0.80 | 0.12 | 2.03 |
| $Log_{10}(1/R)$ | 0.90 | 0.07 | 3.12 | 0.90 | 0.08 | 3.09 |
| SG | 0.61 | 0.16 | 1.57 | 0.80 | 0.12 | 2.06 |
| SG-1st D | 0.64 | 0.14 | 1.32 | 0.77 | 0.14 | 2.12 |
| SNV-DT | 0.73 | 0.13 | 1.53 | 0.86 | 0.09 | 2.69 |

RAW = averaged raw spectra; $Log_{10}(1/R)$ = Absorbance, where R is the reflectance value; SG = 5 window smoothing Savitzky–Golay filter; SG-1st D = first derivative of 5 windowsmoothing Savitzky–Golay filter; SNV-DT = standard normal variate coupled with detrend correction. The best PLSR models are boldened
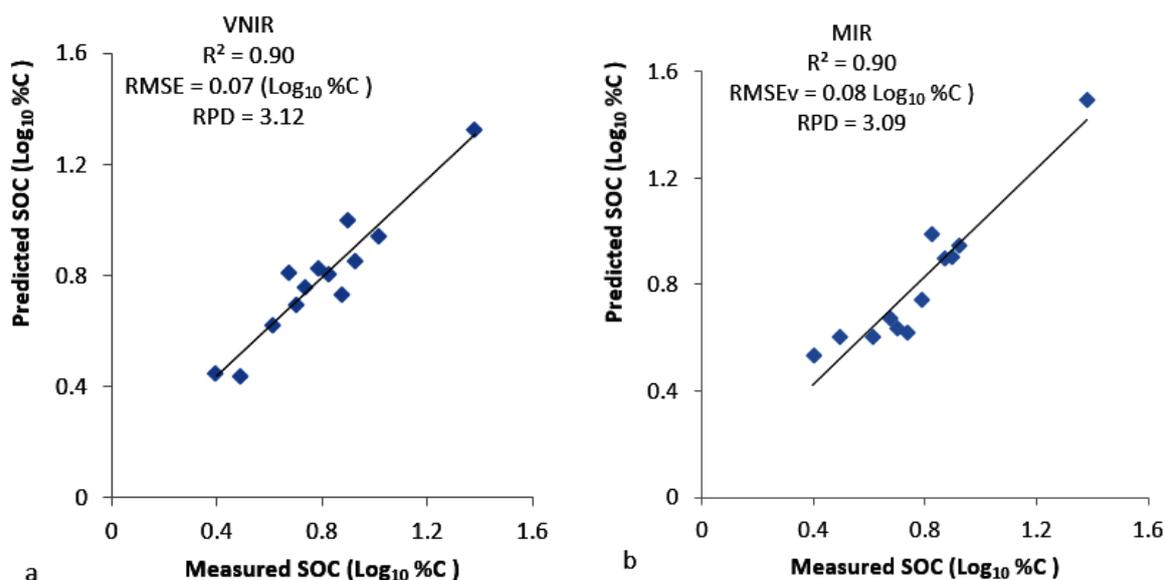


**Figure 2** Scatter plots of measured vs. Predicted SOC values based on PLSR modeling of a) VNIR and b) MIR diffuse reflectance spectra of soil
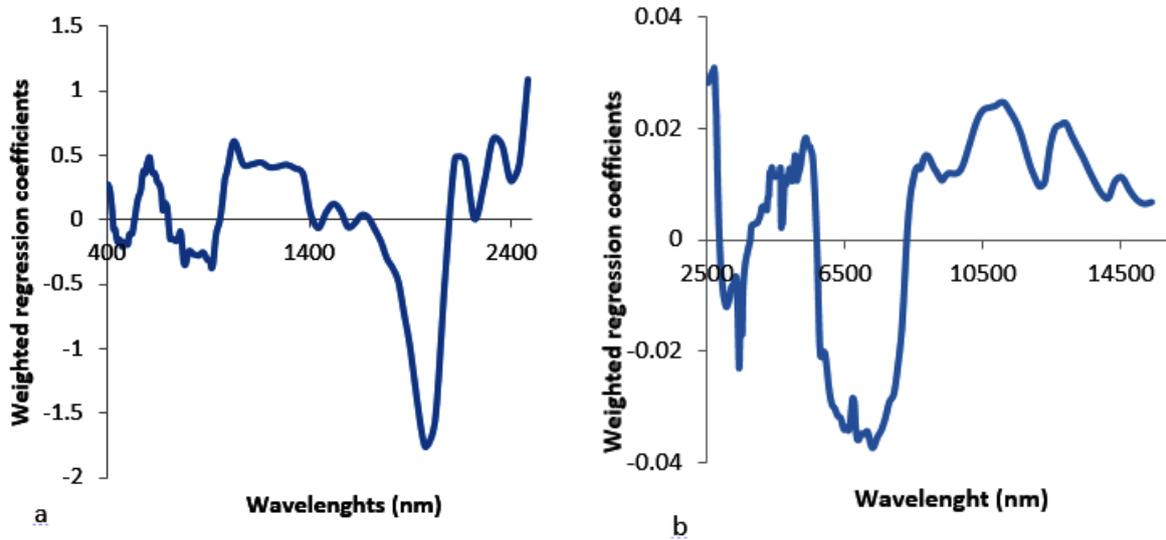
**Figure 3** Regression coefficient curves obtained from PLSR models
a) VNIR, and b) MIR diffuse reflectance spectra of soil

%SOC) compared to and 0.08 $Log_{10}$ %SOC for PLSR-MIR (12.5% lower than MIR). Overall, this result demonstrates that estimations of SOC using the VNIR and MIR spectra produce similar results though validation parameters are comparatively better for the PLSR - VNIR model.

*Correlation Coefficients of Wavelengths*
A plot of regression coefficients illustrating the importance of wavelength variables within the PLSR models developed for the estimation of SOC illustrated in Figure III. Each coefficient within this plot summarizes the association between each predictor variable (wavelength) and a given response (SOC).

The most important peaks used to predict SOC in the PLSR-VNIR model include 436, 478, 499, 521 and 607 nm in the visible range and 789, 843, 921, 1025, 1286, 1366, 1444, 1970, 2020, 2308 and 2481 nm in the near-infrared range. Concerning the PLSR-MIR model, the important peaks appear at 2698, 3429, 4387, 5390, 5879, 6631, 7334, 8907, 11103, 12899 and 14525 nm.

**Discussion**

The distinct absorption minima at ~1400–1450 nm and ~1910–1930 nm observed within the VNIR spectra of soil samples are characteristic of hydroxyl and water (Fortes and Dematte, 2006) while the steep slope found at ~400 - 900 nm has been associated with iron and iron oxide minerals such as goethite and hematite (Vaughan, 1996) but can also contain overtones of C-H, N-H absorptions of alkyls, aromatics and amines (Viscarra Rossel and Behrens, 2010). Absorption band around 1626 – 1750 nm is reflective of C-H bonds (Stuart, 2004) while features at ~2100 and 2500 nm may be attributed to C-O absorptions of polysaccharides; $C-H_2$, $C-H_3$, NH3 absorptions of alkyls and aromatics; and Si-OH and –OH absorptions in minerals(Clark et al., 1990).

Within the MIR spectra of soil samples, absorption feature at ~7812 – 9852 nm may be associated with clay minerals such as smectite, illite, kaolinite and silica (Byrappa and Suresh Kumar, 2007). Absorptions around 5680 - 6200 nm can be due to C-H and C-O bonds of organic compounds such as amides, carboxyl, and/or silicate minerals such as quartz and kaolinite (Stuart, 2004) while absorptions at ~3500 – 3850 nm and at ~ 3070 3360 nmare likely associated with C-H bonds in alkyl groups (Gaffey et al., 1993; Stuart, 2004).

Spectral quality is the most important factor in VNIR and MIR spectroscopy calibrations because reliable predictions cannot be made from poor spectra (Gholizadeh, 2013). Pre-processing spectra is therefore required prior to calibrations to reduce interferences caused by variations in particle-size distribution,

noise or any other inappropriate information that cannot be accommodated by modeling techniques (Brunet et al., 2007; Van Waes et al., 2005). Results from pre-processing of soil spectra show that there is no "best" spectral data pre-processing technique and soil spectra should be carefully studied to identify which technique best suits the spectra/ soil property under investigation. This will ensure that absorption features that are important to the modeling of the soil property under investigation is not screened out.

PLSR models built from VNIR and MIR diffuse reflectance spectra within this study compares favourably with results of models developed for SOC by similar studies (Mcdowell et al., 2012; McCarty et al., 2010; Mouazen et al., 2010; Vasques et al., 2010; ViscarraRossel and Behrens, 2010; Vasques et al., 2009). Lower $R^2$ and RPD values have also been reported by Knox et al. (2015): (0.86/ 2.60), Sarkhot et al. (2011): (0.85 /2.59) and Vasques et al. (2008): (0.79 / 2.14) for $R^2$ and RPD respectively.

RMSE values recorded in past studies vary considerably, with some lower and others higher than the values obtained in this study. The range and composition of SOC in soils used for the various studies also varied widely i.e. <1% - 56% (Mcdowell et al., 2012), ~10% (McCarty et al., 2002; Sarkhot et al., 2011), ~27% (Vasques et al., 2008) and ~2 – 31% within this study. RMSE values are unique to each calibration/validation (Neill and Hashemi, 2018) and will most likely reflect the range of values used in the modeling, contributing to the differences in RMSE values across studies. Irrespective, a robust model is that with the lowest RMSE.

This study demonstrates that the VNIR wavelength range can perform just as well or better than the MIR wavelength region for estimation of SOC. Similar position was held by Jia et al., (2017) and Mcdowell et al. (2012) who concluded that VNIR PLSR models have excellent prediction qualities. More so, assessing SOC quality in most agricultural and industrial applications does not always require precision, but rather a classification of the soil condition. The VNIR spectra used in this study were obtained from air-dried and sieved soils. However, some studies have also generated fair regression models from VNIR spectra of field intact soils (Li et al., 2015; Charkraborty et al., 2010) implying that measurements can be taken insitu with lesser effects of interferences from soil properties such as moisture and particle size distribution on the modeling. MIR spectra are however obtained from processed ball milled homogenous soils increasing the time and cost of sample collection and/or preparation.

In the VNIR region, important absorptions around 436, 478, 499 nm can be attributed to blue colour absorption (Tekin et al., 2012), while absorbance peak near 521, 607, 789, 843 nm can be due to the presence of iron hydroxides or oxides found in goethite and hematite (Ben-Dor et al., 2008; Viscarra Rossel & Behrens, 2010). Absorption band found around at 843 nm has been associated with the functional groups present in soil organic matter (BenDor et al., 1999). The featured absorption bands around 1444, 1970, 2020, 2308 nm have also been discussed for their relationships with clay minerals, soil moisture content, and organic matter content (Hong et al., 2018; Nocita et al., 2014; Viscarra Rossel & Behrens, 2010; Thomasson et al.,, 2001). Absorption peaks around 2308 and 2481 nm in the near-infrared are diagnostic of Al-OH bend and O-H stretch absorptions in clay mineral (Clark et al., 1990).

In the MIR region, important spectral signatures around 8907, 11103, 12899 nm can be from Si–O stretching vibrations from quartz while bands around 2698 nm are associated Al-OH present in kaolinite clays (Viscarra Rossel et al., 2006). Absorptions around 2900 – 3300 nm resonates strongly with C-H and O-H bonds in organic components (Viscarra Rossel et al., 2006).

## Conclusion

This study demonstrated the ability of the combined application of diffuse reflectance spectroscopy and the PLSR method to

analyse and predict SOC concentrations in soils using the VNIR and the MIR regions of the electromagnetic spectrum. The main conclusions are:

Both the VNIR and the MIR diffuse reflectance spectroscopy are useful tools for the prediction of SOC in soils. They both offer a reliable alternative to the traditional laboratory analyses.

VNIR diffuse reflectance spectra give a more robust model quality for SOC content compared to the MIR diffuse reflectance spectra. They offer a reliable alternative to the MIR and to the traditional laboratory analyses which are expensive, complex and time consuming.

The PLSR gives strong correlated results of SOC from a combination of diffuse reflectance spectra and traditional laboratory measurements.

Not all pre-processing tools improved spectral quality. The Log10(1/B) transformation was more effective and significantly improved both the VNIR and the MIR spectra within this study.

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