Research article

Determination of petroleum hydrocarbon contamination in soil using VNIR DRS and PLSR modeling

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ABSTRACT

Visible near infrared diffuse reflectance spectroscopy (VNIR DRS) is being proposed as a rapid and cheaper alternative to conventional soil analysis. This approach to soil analysis will be especially useful when conducting an environmental risk management for petroleum contamination in soil. This study evaluated the potential of VNIR diffuse reflectance spectra for rapid non-destructive quantitative analysis of extractable total petroleum hydrocarbon (ETPH) in soils. It also assessed the effect soil organic carbon (SOC) has on the performance of partial least square regression (PLSR) models developed for characterizing ETPH in soils. Model performance was evaluated based on the coefficient of determination ($R^2$), ratio of performance to deviation (RPD) and the root means square error (RMSE). Result show that VNIR DRS can be a potentially viable analytical tool for petroleum hydrocarbon contamination in soils. However, model quality was found to be affected by spatial variations within soil samples. Models developed from contaminated soils from highly variable geological origins had fair but promising model statistics ($R^2 = 0.72$, RPD = 1.4) as against excellent predictions obtained from contaminated soils with similar geology ($R^2 = 0.97$, RPD = 4.5) implying that the VNIR DR approach to characterizing petroleum hydrocarbon contamination in soils will be better suited to development of local prediction models. PLSR models developed for soil groups with SOC range (0.94–26.5% OC) gave quite robust prediction ($R^2 = 0.90–0.97$, RPD = 2.7–4.5), though a high SOC content slightly lowered PLSR model statistics. These results suggest that VNIR DRS can be quite useful for rapid characterization of petroleum hydrocarbon contamination especially when low budgets and reduced timelines are desirable for remediation purposes.

1. Introduction

Petroleum contamination of soils is an inevitable occurrence during exploration/transport of petroleum and its products with attendant adverse environmental and human health consequences (Ahmed and Fakhruddin, 2018). When soil contamination occurs, there is a need for sustainable remediation techniques to restore the soil to a healthy productive condition. There is therefore need for a rapid but robust characterization of the extent of hydrocarbon contamination to ensure appropriate techniques are deployed for remediation.

Characterization of petroleum hydrocarbon is conventionally done using highly sensitive and specific wet chemistry analytical procedures that involve extraction and consequent gravimetric or chromatographic techniques (Brassington et al., 2010). These procedures are laborious, costly, time consuming and inadequate when high spatial and temporal resolutions of petroleum hydrocarbon contents are required (Chakraborty et al., 2012). There is no doubt that management and clean up of petroleum hydrocarbon contaminated soils will benefit from a less laborious, rapid and reliable detection technique such as visible near infrared diffuse reflectance spectroscopy (VNIR DRS).

The use of spectroscopy such as the VNIR DRS is been proposed as a potential alternative to expensive laboratory procedures for soil analysis. This approach has the advantage of being non-destructive so that samples can be preserved for future comparisons. It requires little to no soil preparation takes less time and has the potential to give information on other soil properties with a single scan (Forrester et al., 2010). Considerable number of studies have made attempts to characterize a number of soil properties such as pH, organic carbon and nutrients in the laboratory using a combination of VNIR spectra and Regression modelling (Abdul Munnaf et al., 2019; Vasques et al., 2009; Brown et al., 2005; Madari et al., 2006; ViscarraRossel et al., 2006). A few studies have also used this rapid scanning procedure on-site with portable equipments such as a portable version of the ASD spectrometer, to quantify soil organic and inorganic carbon (Ge et al., 2007; Waiser et al., 2007; Morgan et al., 2009).

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To date, few studies have reported on the use of VNIR DRS to characterize petroleum hydrocarbons in soils. These studies have reported promising models (Okparanma et al., 2014; Okparanma and Mouazen, 2013; Chakraborty et al., 2010; Analytical Spectral Devices, 2007). However, there is less information on what effect varying conditions such as soil organic content can have on the potentials of using VISNIR DRS as a rapid quantitative tool for petroleum hydrocarbons in contaminated soils. Soil organic carbon is particularly important during petroleum hydrocarbon spectral characterization as it contains similar functional groups that co-absorb at regions of the visible near infrared spectrum. How this soil property influences spectral quantification of SOC is yet to be understood. To the best of our knowledge, no previous study has attempted to evaluate the contributions of SOC to petroleum hydrocarbon estimation using VNIR DRS. Therefore, this study aims to (i) assess the potential of estimating petroleum hydrocarbon contamination in soils using VNIR DRS, and (ii) investigate the effect of SOC on the performance of partial least square regression (PLSR) models developed for characterizing petroleum hydrocarbon contamination in soil.

2. Methodology

This study comprise of two experiments. The first experiment assessed the viability of the VNIR DRS approach to petroleum hydrocarbon characterization in soil while the second part examined the effect of soil organic carbon on performance of models developed for petroleum hydrocarbon characterization. Both experiments were done under using laboratory contaminated soil samples with spectral measurements taken under laboratory controlled conditions.

2.1. Soil collection and processing

2.1.1. Soil sampling in Wisley

Agricultural soil was collected within a depth of 15 cm at the Royal Horticultural Society experimental plots at Wisley, Surrey, United Kingdom (51°19’24.34”N; 0°28’27.81”W). According to the UK soil observatory, soils within this area are freely draining acidic sandy and loamy soils with high groundwater. Most of the land is used for arable and root cropping but this is also replaced by grass where soils are excessively stony or too wet. After collection, soils were air-dried, thoroughly mixed to ensure maximum homogeneity, sieved through a 2mm mesh and labeled ‘WIS’ prior to contamination with diesel fuel.

2.1.2. Soil sampling in southwest England

A total of 96 topsoil samples were collected from different areas in 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. After collection, each soil sample was air-dried, sieved through a 2mm mesh and labeled ‘SWEn’ prior to contamination with diesel fuel.

2.1.3. Analysis of basic soil properties

Soil samples were analyzed for basic properties using standard methods. pH was determined using an HI98129 electrode which had been calibrated with buffers pH 4.0 and 9.0 prior to measurement. Percentage moisture content was determined gravimetrically. Total organic carbon content was determined in 10mg of ball milled soil subsamples using a Thermo Scientific Flash 2000 organic elemental analyzer with a reproducibility of 0.07% while the particle size distribution was assessed using the Mastersizer 3000 Laser Diffraction Particle Size Analyzer.

2.1.4. Characterisation of ETPH in soil using VNIR DRS

Fixed quantities of WIS soil (100 g) were spiked with increasing aliquots of diesel stock to give contaminated soils with spiking concentration ranging from 205 mg/kg to 20000 mg/kg. Samples were thoroughly mixed by hand and allowed to integrate for 24 h prior to spectral and laboratory analysis.

2.1.5. Effect of SOC on the performance of VNIR DRS - PLSR models

To investigate the effect of SOC content on the performance of VNIR DRS – PLSR models, three groups of soils (LOW, MED and HIG) were created from homogenized agricultural soil by amending with different amounts of market grade compost (made from peat, horse manure, composted bracken and mushroom compost). This soil processing technique aims to ensure that the three groups of soils had similar geologic composition and are expected to differ only with respect to organic carbon contents thereby reducing variability in spectrally active components within soils groups. 20 subsamples from each group were analyzed for pH and SOC content.

For each group, fixed quantities of soil (100 g) were spiked with aliquots of diesel fuel to give a range of contaminated soils. Samples were then allowed to integrate for 24 h prior to spectral and laboratory analysis. Details about sample sets are presented in Table 1.

2.2. Spectral analysis

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° 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 3 nm at (350–1050 nm), 7 nm at (1050–1900 nm) and 9.5 nm 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 according to the Labsphere Reflectance Calibration Laboratory (LRCL, 2009). Scans were taken from diesel fuel spiked soil, tightly packed and levelled in borosilicate petri - dishes (9 cm diameter). Replicate measurements were collected at four positions by carefully rotating the Petri dish at an angle of 90° clockwise for each successive scan to increase precision of measurements. Each scan was an average of 16 internal scans. The 64 replicate scans were then averaged to produce a single spectrum for each sample in line with the recommendations Fiorio et al. (2010).

2.3. Laboratory quantification of ETPH

Extractable total petroleum hydrocarbon (ETPH) content of soils were determined by solvent extraction coupled with gas chromatographic (GC/FID) quantification of 14 aliphatic and 16 polynuclear aromatic hydrocarbon analytes in the extract (MADEPH, 2009). The percent recoveries of all ETPH marker compounds ranged between 68.6%–94% with an average overall efficiency of 69.4%.

The quantitative results of ETPH from GC-FID analysis were combined with spectral data generated from the visible near infrared diffuse reflectance scans of contaminated soils to generate partial least square regression models.

2.4. Data processing and partial least square regression modeling

Each curve of the spectral data was subjected to processing using mathematical techniques to improve spectral quality. Multiplicative interferences from particle size and baseline shifts were corrected with the standard normal variate/detrending techniques according to Verbouven et al. (2012). For noise reduction, a 1st order polynomial Savitsky-Golay Smoothing with five smoothing points was used. All spectra processing and multivariate calibration validations were carried out using the Unscrambler-X 10 (CAMO, Incorporation, Oslo, Norway).

A principal component analysis (PCA) analysis was performed on data sets to observe groupings within soil samples and to identify the presence of outliers. Possible outliers were identified as samples with very high
livers and residuals. Partial least square regression (PLSR) models were developed from VNIR DR spectra (x, predictor variables) and log_{10} transformed ETPH data (y, dependent variables), that approximated a Gaussian distribution after stabilizing the variance. 76% of each dataset were selected for model calibration using the Kennard – Stone algorithm while the remaining 24% were used for model validation.

The predictive ability of PLSR models are reported in terms of coefficient of determination ($r^2$), root mean-square error (RMSE; Eq.1), percentage prediction error (%PE; Eq. 2), ratio of prediction deviation (RPD; Eq 3) (Cezar et al., 2019; Janik et al., 2007; Brown et al., 2005)

$$RMSE = \sqrt{\frac{\sum (ETPH_{p} - ETPH_{m})^2}{n}} \quad (1)$$

$$%\text{PE} = \frac{RMSE_{P}}{X_{hp}} \times 100 \quad (2)$$

$$RPD = \frac{SD}{RMSE_P} \quad (3)$$

where $n$ is the number of validation samples, SD is the standard deviation of the predicted validation values and $X_{hp}$ is the largest measured data point within the validation set. According to ViscarraRosel 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.

3. Results and discussion

3.1. Characterization of ETPH using VNIR DRS

WIS soil used for this study has a pH of 5.9 and an average TOC content of 2.02% obtained from an analysis of 10 grab samples. SWE soils have a wider range of pH and TOC. Details about particle size distribution content of 2.02% obtained from an analysis of 10 grab samples. SWE soils have a wider range of pH and TOC. Details about particle size distribution

| No. of Samples | pH     | TOC (%) | ETPH Range (mg/Kg) |
|----------------|--------|---------|--------------------|
| **LOW**        | 57     | 5.4     | 2.02               | 320-8770 |
| **MED**        | 50     | 6.1     | 12.41              | 428-9330 |
| **HIG**        | 50     | 7.4     | 21.07              | 360-8580 |

Table 1. Descriptive statistics of sets of samples used for PLSR modeling.

During calibration, the PLSR model for WIS presented a high coefficient of determination $R^2 = 0.87$ and a RMSE of 1.23 mgKg$^{-1}$. On the other hand, SWE model presented a lower coefficient of determination and a higher RMSE ($R^2 = 0.46$ and 742.4 mgKg$^{-1}$ respectively). Diffuse reflectance spectra of soils are a combination of responses from all spectrally active components within the soil. The high geologic variability within SWE soils may present interferences, reducing the relationship between overall soil spectra and measured ETPH in the soils, leading to lower model performance. However, subsoil samples used for WIS model were geologically similar and differed only in the degree of diesel contamination.

Upon validation, it is evident that PLSR model developed from WIS soils presented better results to that developed using the SWE soils (Figure 2). The WIS model had a validation $R^2 = 0.97$, %PE = 1.5, and an RPD value of 4.5 considered to be of excellent analytical quality for predicting petroleum hydrocarbon in soils (Forrester et al., 2010). The SWE model had a lower validation statistics, %PE = 9.8 and an RPD = 1.4 classified as of poor predictive quality (ViscarraRosel et al., 2006). These results implies that the quality of prediction models developed for characterizing petroleum hydrocarbons in soils using visible near infrared diffuse reflectance spectroscopy may reduce with an increase in the variations within soils used for model calibrations/validation. Therefore, future soil analysis during clean-up and remediation activities of petroleum hydrocarbon contaminated soils using the VNIR DR spectroscopic approach will benefit more from the development of local calibration models.

The RMSE for validation were higher when compared to those obtained during calibration, decreasing 0.08 mg kg$^{-1}$ and 125.84 mg kg$^{-1}$ for WIS and SWE models respectively. The observed improved prediction statistics despite using an independent validation set that is not included in model calibration is due to a careful selection process that ensures that the calibration set covers the spectral and contamination range of the proposed validation set in agreement with Opkaranma and Mouazen (2013) and Guerrero et al. (2014).

Table 2. Descriptive statistics of soil properties.

| No. of Samples | pH     | Moisture | SOC    | PSD | ETPH |
|----------------|--------|----------|--------|-----|------|
|                |        |          |        | Sand|      |
|                |        |          |        | %   | 63   |
|                |        |          |        | Silt| 29   |
|                |        |          |        | Clay| 8    |
| **WIS**        | 57     | 5.9      | 3.4    | 2.02| 8    |
| **SWE**        | 96     | 3.9-7.7  | 3.0-4.7| 1.87-30.9 | 8 |

$^a$ Number of samples.

$^b$ Particle size distribution.
It is worth noting that PLSR models developed from the SWE soils also showed promising model quality statistics. A RPD value of 1.4 indicates that there is room for model enhancement (Chang et al., 2001). Similar model statistics for total petroleum hydrocarbons predictions in soils (validation R²: 0.64 and RPD: 1.76; validation R²: 0.68 and RPD: 1.76; validation R²: 0.77–0.89 and RPD: 1.86–3.12) were reported by Chakraborty et al. (2010) and Okparanma and Mouazen (2013) respectively. Forrester et al. (2010) also reported a R² = 0.93 and RMSE = 564 mg kg⁻¹ using a partial least squares (PLS) cross-validation approach for infrared spectroscopic identification of TPH in soils.

### 3.2. Effect of soil organic carbon on VNIR DR - PLSR model performance

A principal component analysis of VNIR spectra obtained from the three groups of soils (LOW, MED, HIG) show soils clearly separated within the spectral space based on both the SOC content as well as the degree of petroleum hydrocarbon contamination (Figure 3). This resulted in a reduction of the initial dimension of the datasets, with the first component (PC-1) explaining 92% of the variation in the spectral data the second component (PC-2) explains 6% of the variation most probably associated with the SOC content. This is indicative that visible near

**Figure 1.** Mean reflectance (straight lines) and continuum removed (broken lines) VNIR spectra of diesel spiked soils indicating wavelength regions where absorptions are strongly correlated with ETPH concentrations.

**Figure 2.** Predicted vs Measured Extractible total petroleum hydrocarbon (ETPH) of the validation data set for WIS and SWE data sets, Calibration samples (faint boxes); validation samples (blue boxes).

### Table 3. Effect of organic carbon content on performance of ETPH – VNIR partial least square regression models of diesel contaminated soils.

| Data set | Optimum factor | Calibration | Validation |
|----------|----------------|-------------|------------|
|          | R² | RMSE (mg/Kg) | R² | RMSE (mg/Kg) | RPD | %PE |
| LOW(57)  | 2  | 0.87 | 1.23 | 0.97 | 1.15 | 4.5 | 1.5 |
| MED (50) | 1  | 0.94 | 1.29 | 0.97 | 1.2 | 5.5 | 2.1 |
| HIG (50) | 2  | 0.89 | 1.32 | 0.91 | 1.29 | 3.3 | 2.7 |
| Composite (157) | 3  | 0.85 | 1.45 | 0.90 | 1.45 | 2.7 | 4.0 |
infrared diffuse reflectance spectra is able to capture inherent information within soils and can be a very important qualitative tool for distinguishing soils with respect to organic carbon content and degree of petroleum hydrocarbon contamination.

Table 3, summarizes the model statistics for PLSR models from the three data sets. PLSR models developed from all data sets gave very robust prediction performances with RPD values greater than 2. The coefficient of determination $R^2$ and the ratio of performance to deviation were highest in the LOW model. Similarly the RMSE and %PE for the LOW model were 1.15 mg/kg and 1.5% respectively, the lowest for all three models. It is evident that model quality parameters reduced as the contents of SOC in soils increased (Figure 4). This implies that, although spectral energy reflected by soil samples is a function of all soil constituents, SOC can be a significant soil parameter which overlaps with petroleum hydrocarbons, influencing spectral responses and ultimately the predictive performance of models developed from visible near infrared diffuse reflectance spectra of soils for characterizing petroleum hydrocarbon contamination.

Absorptions due to soil organic carbon are as a result of stretching and bending of C–H, N–H, S–H and O–H bonds of functional groups. These bonds are also responsible for the spectral absorptions associated with petroleum hydrocarbons (Okparanma and Mouazen, 2013) and a high organic carbon content could potentially increase the overall spectral absorption by a soil sample. While this may lower the validation statistics of the models developed, it does not have a considerable effect on the robustness of models calibrated for ETPH when all soils used with the calibration have similar organic carbon contents (Table 3). PLSR model developed from a composite of all three data sets with a wider range of organic carbon content (2.02–21.07 mg/kg) but with similar geologic composition also has validation statistics ($R^2 = 0.90$; RPD = 2.7), considered to be of excellent analytical quality for predicting petroleum hydrocarbon in soil (Forrester et al., 2010). This can be especially useful during local remediation activities on soils with similar geologic compositions but varying SOC contents due to land use.

This paper assessed the viability of the VNIR DR approach to quantifying ETPH using laboratory contaminated soil samples with spectral measurements taken under laboratory controlled conditions. However, spectral measurements in the field are usually affected by interferences such as atmospheric moisture and other light sources which may ultimately impact on the quality of modeling. Therefore further research is essential to enhancing the understanding of the VNIR DRS approach to characterizing petroleum hydrocarbon contamination in soils.

4. Conclusion

Quantitative predictions of extractible petroleum hydrocarbon content in soils were achieved using a combination of VNIR spectra and PLSR modeling. Quality of models was found to be affected by the spatial geologic variations within soil samples, though PLSR model developed from contaminated soils with a highly variable geological origin gave fair model statistics (RPD = 1.4). All three models developed within the SOC range (2.02–21.07 %) were robust and gave quite excellent prediction statistics. A slight reduction in validation statistics was observed for soils with high SOC. Considering the high costs and analytical time associated with current wet chemistry procedures, the prospect of using this relatively cheaper and faster procedure is particularly promising. It will be of particular utility during soil remediation activities at oil polluted sites in developing countries where lower budgets and extended remediation timelines are a constant source of civil unrest.
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Declarations

Author contribution statement

Olatunde K.A.: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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