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Rapid prediction of total petroleum hydrocarbons in soil using a hand-held mid-infrared field instrument

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Highlights

- We present a novel field technique for the rapid prediction of TPH.
- Accurate predictions of TPH were obtained.
- Technique tested across different soil types and TPH concentrations.
- Technique suitable for commercial use and number of applications.
- Results pave the way for using hand-held mid-infrared instruments in the field.

Abstract

This manuscript reports on the performance of a hand-held diffuse reflectance (mid)-infrared Fourier transform (DRIFT) spectrometer for the prediction of total petroleum hydrocarbons (TPH) in three different diesel-contaminated soils. These soils include: a carbonate dominated clay, a kaolinite dominated clay and a loam from Padova Italy, north Western Australia and southern Nigeria, respectively. Soils were analysed for TPH concentration using a standard laboratory methods and scanned in DRIFT mode with the hand-held spectrometer to determine TPH calibration models. Successful partial least square regression (PLSR) predictions, with coefficient of determination (R^2) ~0.99 and root mean square error (RMSE) <200 mg/kg, were obtained for the low range TPH concentrations of 0 to ~3,000 mg/kg. These predictions were carried out using a set of independent samples for each soil type. Prediction models were also tested for the full concentration range (0–60,000 mg/kg) for each soil type model with R^2 and RMSE values of ~0.99 and <1,255 mg/kg, respectively. Furthermore, a number of intermediate concentration range models were also generated for each soil type with similar R^2 values of ~0.99 and RMSE values <800 mg/kg. This study shows the capability of using a portable mid-infrared (MIR) DRIFT spectrometer for predicting TPH in a variety of soil types and the potential for being a rapid in-field screening method for TPH concentration levels at common regulatory thresholds.

A novel hand-held mid-infrared instrument can accurately detect TPH across different soil types and concentrations, which paves the way for a variety of applications in the field.

Graphical abstract

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Introduction

Total petroleum hydrocarbons (TPH) comprise a mixture of short and long-chain aliphatic hydrocarbons and aromatic compounds (mixture of alkyl and mono/polycyclic) derived from crude oil. However, the aromatics group is a minor component in crude oil. The environmental occurrence of aliphatic short-chain fraction and mid-range fraction (particularly C_{10}–C_{36} compounds) in soil, sediment and water can adversely affect biological and human health [1], [2]. The main sources of pollution by TPH are spills from the production, storage and distribution of petroleum products [1].

Assessment of TPH contamination in soil requires rapid, accurate, on-site and cost-effective methods to facilitate risk assessment processes and to assist with pollutant management and remediation. However, the traditional laboratory method for the determination of TPH concentration using the capillary GC/FID method is time consuming and expensive. There are some portable methods available for the analysis of TPH [3], but they are still time consuming, and most require the extraction of the contaminant using chemical reagents.

A recent study by Forrester et al. [4] demonstrated that diffuse reflectance (mid)-infrared Fourier transform (DRIFT) spectroscopy using benchtop instrumentation, coupled with multivariate modelling such as partial least squares regression (PLSR) methods, could provide accurate and much more rapid predictions of TPH concentrations. In the article by Forrester et al. [4], the authors used the mid-infrared (MIR) region 3000–2600 cm^{-1}, which was identified to be sensitive to TPH concentration and capable of minimising interferences from natural soil organic matter and carbonates. While that study showed accurate and viable models for the prediction of TPH using a benchtop instrument, prediction of TPH using a portable hand-held instrument would be even more advantageous. However, there may be concerns about the performance of such instruments (e.g. noise level) relative to laboratory-based benchtop instrumentation, considered to be a crucial factor for the development of reliable and precise models [5].

As discussed in a recent review [6], only a small percentage of the publications on the use of visible and infrared (IR) spectroscopy in soil analysis refer to hand-held instruments. Most studies reporting regression models using hand-held instruments for soil analysis were based on the visible-near infrared (vis-NIR), with MIR based devices rarely used [7], [8]. This can be partially attributed to the historically poor portability of MIR instruments in the field [9]. This issue has now been solved with the emergence of true hand-held DRIFT MIR spectrometers suitable for in-field analysis.

Successful models have been reported using portable/hand-held vis-NIR to predict increasing concentrations of oil spiked into standard soils [10], [11]. Conversely, worse results are obtained when using field samples [12], [13], in agreement with Okparanma and Mouazen [14] with regard to MIR outperforming vis-NIR for the determination of TPH. Hitherto, there has only been one attempt to develop models for the prediction of TPH in soils using an MIR-DRIFT hand-held spectrometer [7]. However, those samples were sourced from a single unique site and comprised a relatively low TPH concentration range (0–11,000 mg/kg). In that study, an independent set of samples was not collected for validation and did not report on the influence of different soil types and TPH concentration ranges on calibration development. As previously determined by Forrester et al. [4], soil type and different TPH concentration ranges have been shown to influence the performance of MIR calibrations.

The present study reports on the performance of a portable hand-held DRIFT spectrometer for the prediction of TPH in a range of contaminated soils. This would allow for the practical/routine use of the MIR technique for accurately predicting TPH concentrations in the field. Thus, the practical use of this device in the field is discussed, as well as the impact of different soil types and TPH concentrations on the calibration models.

Section snippets

Total petroleum hydrocarbon contaminated soils

Three sets of contrasting soils, contaminated by diesel spills or spiked in the laboratory, were used in this study. These soils were chosen to address site contamination issues and because they represented a good spread of TPH with which to build calibration models. The three soil sample sets can be described as follows: Set 1 comprised 67 uncontaminated samples collected from a site in Padova (Italy) and were individually spiked in the laboratory with diesel covering a range of concentrations …

Spectra of soils

Soil samples, collected from the three different site locations, were characterised by the PCA loadings as well as the mean spectra and standard deviations (Fig. 1, Fig. 2, Fig. 3). Each score on a given scores plot represents a spectrum in multi-dimensional space. The individual variances calculated for each spectrum, based on the variability in the molecular vibrations detected in each sample scanned, contribute to the position of each score (spectrum) on a scores plot. The loadings plots …

Comparison with previous studies

It can be challenging to put these results into context with other studies since, to the best of the authors' knowledge, there have been no reported previous studies available on the use of hand-held MIR instrumentation for the prediction of TPH across various soil types and concentration ranges. If we compare with previous studies using vis-NIR for the prediction of TPH in field samples (Chakraborty et al. [12], R^2=0.63 and RPD=1.94; Chakraborty et al. [13], R^2=0.78 and RPD=2.19) our results …

Conclusions

In this article we have demonstrated the successful performance of a hand-held MIR spectrometer for the accurate prediction of TPH concentrations in soils, irrespective of the soil type and TPH concentration. Models with R^2~0.99 and RMSE <200 mg/kg were obtained for the prediction of <3,000 mg/kg TPH. High TPH concentration samples (0–60,000 mg/kg) were also accurately predicted (R^2~0.99, RMSEP 1,225 mg/kg) when combining NIR and MIR regions in the model. The prediction of TPH using the proposed …

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