



# Rapid assessment of petroleum-contaminated soils with infrared spectroscopy



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## ABSTRACT

Soil sensing using infrared spectroscopy has been proposed as an alternative to conventional soil analysis to detect soil contamination. This study evaluated the use of field portable and laboratory benchtop infrared spectrometers in both the near infrared (NIR) and mid infrared (MIR) region for rapid, non-destructive assessment of petroleum contaminated soils. A laboratory study of soils spiked with petroleum products showed that several factors can affect the infrared absorbance. These include soil texture, organic matter content, and the types and concentrations of contaminants. Despite these factors, infrared regions that are affected by hydrocarbon contamination can be readily found in  $2990\text{--}2810\text{ cm}^{-1}$  in the MIR range, and  $2300\text{--}2340\text{ nm}$  in the NIR range. Using continuum-removed spectra, the effects of soil and contaminant factors on the absorbance peaks were isolated. This study also created statistical models to predict total recoverable petroleum hydrocarbons concentration in soils by utilizing the absorption features found in the mid-infrared region spectra. Subsequently, three different approaches were tested for the prediction of Total Recoverable Hydrocarbon (TRH) concentration on 72 field contaminated samples: (i) linear regression using only 1 infrared region, (ii) multiple linear regression (MLR) using 4 regions in the MIR, and (iii) partial least square regression (PLSR) which use the whole spectra. The model created using MLR approach for portable MIR spectrometer outperformed the benchtop MIR spectrometer with a coefficient of determination ( $R^2$ ) of 0.71 and 0.53 respectively. While PLSR model for portable spectrometer show a better prediction for TRH prediction ( $R^2 = 0.75$ ), the MLR can also achieve a similar performance ( $R^2 = 0.71$ ) by using only 4 regions in the MIR spectra as predictors.

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## 1. Introduction

Petroleum contamination in soil has been recognized as a globally significant issue. It poses health risks to humans and wildlife in the surrounding environment. Petroleum contamination in soil is mostly due to the process of production, storage and distribution of the petroleum products. If the contamination levels exceed regulatory standards, clean-up measures need to be considered. Health Screening Levels (HSL) and Ecological Screening Levels (ESL) for petroleum products have been developed to address the risks associated with petroleum contamination on human health and ecosystems respectively (NEPC, 2011a). With millions of potentially contaminated soil sites in the world (CRCCARE, 2015), there needs to be rapid and efficient on-site assessment technologies that are able to analyse the concentration of the petroleum hydrocarbons.

Conventional methods to analyse soil contamination in the laboratory is not only time consuming, but also expensive (Viscarra Rossel et al., 2011; Okparanma and Mouazen, 2013a; Chakraborty et al., 2015; Horta

et al., 2015). The most commonly used analytical method for determining petroleum hydrocarbons in soil is extraction using chemical solvents, where the extracts are subjected to a gas chromatography (GC) system equipped with a flame ionization detector (FID) following US EPA method 8015B (Sadler and Connell, 2003). The cost to analyse a sample using this conventional method starts from \$100 per sample, and requires a significant investment of time and technical skills (Chakraborty et al., 2015). Furthermore, it is often found for repeated measurements that there can be considerable variation within lab, and particularly inter-lab variability for the same phenomena (Schwartz et al., 2012; Chakraborty et al., 2015).

To successfully distinguish petroleum contamination in soil, sensing with optical and radiometric sensors is preferred (Viscarra Rossel et al., 2010). Optical and radiometric sensors utilize electromagnetic energy to characterize soil, particularly those in the near-infrared and mid-infrared region. Infrared (IR) spectroscopy could be a viable alternative in soil sensing to provide measurements in a timely and cost-effective manner (Chakraborty et al., 2015; Horta et al., 2015). A number of studies have investigated the feasibility of infrared technologies for the rapid assessment of Total Petroleum Hydrocarbons (TPH) concentration in soil. Some of these include studies conducted by Forrester et al.

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(2013), Okparanma and Mouazen (2013a), Schwartz et al. (2012), and Horta et al. (2015). Although the infrared technologies had been used since the 1960s, it has gained much popularity in the last 20 years. This trend has coincided with the development of portable infrared instruments, chemometrics and statistical methods (Viscarra Rossel et al., 2011; Okparanma and Mouazen, 2013a). Sample scanning with infrared spectrometers only takes a matter of seconds, requires no chemicals, and facilitates the possibility to infer a number of soil properties simultaneously (Okparanma and Mouazen, 2013b; Horta et al., 2015).

TPH is a term used to describe the quantity of petroleum-based hydrocarbon products in the environment, such as crude oil and its derivatives. Currently in Australia, hydrocarbon contamination is reported as Total Recoverable Hydrocarbons (TRH) instead of TPH. This change is adopted to provide reliable site contamination assessments because TRH reflects what can be extracted, while TPH indicates what is actually present in the soil (NEPC, 2011b). Different soil components create unique interactions with the hydrocarbons, preventing them to be extracted completely. The strength of hydrocarbon sorption in the soil is affected by the nature of the hydrocarbon, organic matter content and soil minerals (Sadler and Connell, 2003).

The objectives of this study were to: 1) determine which spectrum range could be used to quantitatively assess petroleum hydrocarbons using the laboratory mid-infrared (MIR), portable MIR (pMIR), and portable Visible-NIR (pNIR) spectrometers, 2) observe the effect of soil texture and organic matter on the peak intensities of spectra, 3) observe the effect of various types and concentrations of petroleum hydrocarbons on the spectra, 4) monitor the degradation of petroleum hydrocarbons through time, 5) construct theoretical models to quantify the amount of petroleum hydrocarbon contamination based on significant NIR and/or MIR spectra bands, and validate them with field contaminated samples.

## 2. Materials and methods

This study comprised of two experiments. The first experiment examined the effect of soil type, organic matter content, and concentration of two types of petroleum on the near- and mid-infrared reflectance spectra. The study was done under laboratory conditions, where a known concentration of hydrocarbon material was added to the soil. In the second part of the experiment, we used field contaminated soils which had been contaminated with petroleum, with the aim to create and validate models which can predict TRH concentration from infrared spectra data.

### 2.1. Laboratory contaminated soils

The soil samples used in this part of experiment were obtained from University of Sydney Lansdowne Farm (34°02'S, 150°66'E) in NSW, Australia. This study was conducted on a total of 126 samples with factors and levels as follows: 2 soil texture types (clayey, sandy), 3 levels of organic matter addition (0%C, 1%C, 3%C), 2 types of organic contaminants (diesel, motor oil) at 3 concentration levels (0 ppm, 5000 ppm, 10,000 ppm, 30,000 ppm) in replicates of three.

The clayey soil (Red Chromosols according to Australian Soil Classification System (ASC) or Alisols according to World Reference Base for Soil Resources (WRB)) contained 48% sand (20–2000  $\mu\text{m}$ ), 13% silt (2–20  $\mu\text{m}$ ), and 39% clay (<2  $\mu\text{m}$ ) by mass, with clay mineralogy dominated by kaolinite. The sandy soil (Orthic Tenosols (ASC) or Arenosols (WRB)) contained 88% sand, 4% silt, and 9% clay by weight, dominated by  $\text{SiO}_2$  and kaolinite.

Soil samples were first air-dried at 40 °C for 3 days, then ground and sieved to pass through a 2-mm sieve. Moisture content of the samples was determined by drying the soil at 105 °C for 16 h in the oven. From the moisture content analysis, the dry weight of the soil is determined. An equivalent of 25 g of oven-dry soil of each soil type was then placed into the designated petri dishes.

Soil organic carbon content was determined using Vario MAX CNS Analyzer (Elementar, Langensfeld, Germany). The clayey soil and the sandy soil contained 0.60% and 0.15% organic carbon by mass, respectively. Organic matter in the form of organic compost (PMR0320, RichGro, Jandakot, WA, Australia) was added onto the samples until the increase of 1, and 3% in C was achieved.

These soil samples were then wetted to 75% field capacity to maintain their moisture and incubated for 3 weeks before being spiked with the petroleum hydrocarbons. Aliquots of 0, 0.15, 0.30 and 0.60 mL of motor oil and diesel fuel were mixed with 10 mL of cyclohexane (Sigma Aldrich, Castle Hill, NSW, Australia) to give soils with TPH concentration ranging from 0, 5000, 10,000 to 30,000 ppm. Cyclohexane was used as a solvent to ensure even distribution of petroleum hydrocarbons throughout the samples (Forrester et al., 2010). The petri dishes were left open to allow spiked samples dry overnight to remove traces of cyclohexane. The motor oil used was Valvoline 2-stroke engine oil. The experiment was carried out at a room temperature of ~25 °C for 11 weeks after soil was spiked. Measurement using infrared spectrometers was conducted every 2–3 weeks. After each measurement, the samples were re-wetted and covered to observe the effect of time on the petroleum degradation.

### 2.2. Spectral measurements

The reflectance spectra of each sample were obtained using a benchtop MIR, a portable MIR and a portable NIR spectrometer. To remove the effect of moisture, the samples were left open to dry overnight at laboratory temperature of ~25 °C prior to measurement. The samples were then mixed thoroughly and tamped flat. The spectra were obtained as an average of 2 replicate scans in a different spot to ensure the heterogeneity of samples was captured.

#### 2.2.1. MIR spectral acquisition

The MIR spectrum covers the range of 4000–400  $\text{cm}^{-1}$  (2500–25,000 nm). Resulting spectra from the absorbed and transmitted infrared radiation by the sample correspond to the fundamental molecular vibration of the sample. Laboratory benchtop MIR spectra were obtained from FTIR TENSOR 37 (Bruker Optics, Ettlingen, Germany) equipped with HTX-XT micro-plate reader automated sampler, with a spectral range acquisition between 3996 and 599  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  resolution and ~2  $\text{cm}^{-1}$  sampling interval. Potassium bromide (KBr) was used as a standard in this MIR spectrometer. The portable MIR spectra were obtained from the RemScan (Ziltek Pty Ltd., Adelaide, Australia) or equivalent to Agilent 4100 ExoScan (Agilent Technologies, Santa Clara, CA, United States) which collected reflectance between 6000  $\text{cm}^{-1}$  and 650  $\text{cm}^{-1}$  at 8  $\text{cm}^{-1}$  resolution and ~2  $\text{cm}^{-1}$  sampling interval. This instrument was calibrated with the standard background and a reference cap provided by the manufacturer.

#### 2.2.2. NIR spectral acquisition

The NIR region covers the range between 780 and 2500 nm. Spectra in this region correspond to combinations and overtones of the fundamental molecular vibration bands (2000–2500 nm) found in the mid

**Table 1**  
Band assignments observed in the MIR spectra.

Wavenumber ( $\text{cm}^{-1}$ )	Band assignments
1630–1580 <sup>a</sup>	Aromatic C, C=C conjugated with C=O
1930–1840 <sup>a</sup>	Aromatic CH, C=O acid anhydrides
2060–1930 <sup>a</sup>	Cumulative C =C bonds, aromatic CH
2990–2810 <sup>a</sup> (2930–2850 <sup>b</sup> , 3000–2600 <sup>c</sup> )	Aliphatic $-\text{CH}_2$ or $-\text{CH}_3$
3630–3620 <sup>b</sup>	Clay minerals (smectite and illite)
3690–3620 <sup>b</sup>	Clay minerals (kaolinite)

<sup>a</sup> Band assignments after Hobley et al. (2014).

<sup>b</sup> Band assignments after Soriano-Disla et al. (2014).

<sup>c</sup> Band assignments after Forrester et al. (2013).

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