



# Mapping polycyclic aromatic hydrocarbon and total toxicity equivalent soil concentrations by visible and near-infrared spectroscopy



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## ARTICLE INFO

### Article history:

Received 27 February 2014

Received in revised form

20 May 2014

Accepted 22 May 2014

Available online 19 June 2014

### Keywords:

Near-infrared spectroscopy

Generic assessment criteria

Hydrocarbon

Mapping

## ABSTRACT

In this study, we used data from spectroscopic models based on visible and near-infrared (vis-NIR; 350–2500 nm) diffuse reflectance spectroscopy to develop soil maps of polycyclic aromatic hydrocarbons (PAHs) and total toxicity equivalent concentrations (TTEC) of the PAH mixture. The TTEC maps were then used for hazard assessment of three petroleum release sites in the Niger Delta province of Nigeria (5.317°N, 6.467°E). As the paired *t*-test revealed, there were non-significant ( $p > 0.05$ ) differences between soil maps of PAH and TTEC developed with chemically measured and vis-NIR-predicted data. Comparison maps of PAH showed a slight to moderate agreement between measured and predicted data (Kappa coefficient = 0.19–0.56). Using proposed generic assessment criteria, hazard assessment showed that the degree of action for site-specific risk assessment and/or remediation is similar for both measurement methods. This demonstrates that the vis-NIR method may be useful for monitoring hydrocarbon contamination in a petroleum release site.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed organic pollutants. The [EU Water Framework Directive \(2000\)](#) identified them as priority hazardous substances (PHS), and listed five key indicator compounds including benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene. Anthracene and naphthalene have been recently added to the list of PHS. In the EU, the cost of PAH decontamination is estimated to be approximately €17.3 billion per year ([CEC, 2006](#)).

Risk assessment is an established requirement for effective management of contaminated land, and now a widely-used support tool for environmental management decisions. It is employed as a means of assessing and managing potential impacts to human and ecosystem health ([Vegter et al., 2002](#)). Assessing the risk of PAH at contaminated sites is complicated because of the profiles of compounds present. Specific indicator compounds (genotoxic

carcinogens and non-carcinogens) should be assessed because these are often the key risk drivers at petroleum contaminated sites ([Brassington et al., 2007](#)). Genotoxic carcinogens are assumed not to have a threshold concentration as even very small concentrations (or doses) are assumed to pose some (albeit small) risk of cancer. There are cases in which carcinogenicity can be assumed to occur only after some dose or threshold concentration is reached, depending on the mode of action by which the contaminant is thought to cause cancer. To carry out such assessment, the United States Environmental Protection Agency (US EPA) developed the toxicity equivalency factor (TEF) methodology for a mixture of structurally related chemical compounds with a common mechanism of action such as PAHs ([WSDE, 2007](#)). A TEF is an estimate of the relative toxicity of an individual PAH to benzo[a]pyrene, which is usually chosen as the reference chemical compound since its toxicity is well characterized ([WSDE, 2007](#)). The TEF approach aims to give a single concentration number (e.g., total toxicity equivalent concentration – TTEC), to environmental matrixes like soil with highly complex nature. To determine compliance for a particular soil sample, the deduced TTEC for the PAH mixture is compared with the applicable target value for benzo[a]pyrene ([WSDE, 2007](#)).

In petroleum release sites, mapping the spatial and temporal variation of PAH and the toxicity levels are required for a broad range of environmental applications. Mapping the toxicity of PAHs,

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which equates with hazard assessment or tier 1 Risk-Based Corrective Action (RBCA) for petroleum release sites (ASTM, 1995), helps in the delineation of potential management zones within the site. This also provides vital information for quantitative risk assessment and/or remediation (if action is required). Traditional methods of hazard assessment in petroleum release sites involve prior soil sampling, extraction of PAH compounds from the soil sample using various extraction solvents, and analysis of the liquid extract by gas chromatography–mass spectrometry (GC–MS) (EPA, 1999). Soil sampling and solvent extraction of PAHs are tedious, labour-intensive, time consuming and require expert operators. Therefore, PAH analysis by GC–MS is hazardous and uneconomical; particularly when large-scale contamination is involved and dense sampling is required for high-resolution soil contaminant mapping (Peterson et al., 2002; Okparanma and Mouazen, 2013). This has prompted increasing demand for rapid and cost-effective methods capable of high-sampling resolution essential for spatial mapping to complement the conventional methods.

In response to this demand, scientists have recognized the potential of visible and near-infrared (vis-NIR) diffuse reflectance spectroscopy as a cost-effective tool for rapid identification of hydrocarbon contamination in soils (e.g., Malley et al., 1999). Over the years, several attempts have been made to use reflectance spectroscopy as an approach for mapping hydrocarbons in soils. Two studies employed airborne remote sensing with Landsat Thematic Mapper (TM) and Daedalus scanner to map hydrocarbons in soil (Bannert et al., 1994; Kuhn and Horig, 1995). Both studies yielded limited results because of the overly poor spectral resolution of the multispectral Landsat TM and Daedalus scanner (Horig et al., 2001). A later study employed airborne hyperspectral remote sensing using HyMap scanner in conjunction with a field GER Mark V IRIS<sup>®</sup> infrared spectroradiometer (385–2548 nm) to identify hydrocarbon-contaminated soils (Horig et al., 2001). However, this approach was amenable only to high hydrocarbon concentrations (2.5% w/w), and typical hydrocarbon absorption features in the pixel spectra were not very well pronounced (Horig et al., 2001). In a similar study, Kuhn et al. (2004) developed the Hydrocarbon Index approach for mapping hydrocarbon bearing materials with the HyMap scanner. However, the approach was limited to sensors with very high signal-to-noise ratio like the HyMap scanner. Moreover, airborne hyperspectral remote sensing relies on bare earth imagery, which is affected by land cover and vegetation (Schwartz et al., 2011). Even then, the application of the methodology for soil investigation is still at the rudimentary stages. As a result, studies adopting airborne hyperspectral remote sensing are rarely found in literature since only few of the sensors are available worldwide (Schwartz et al., 2011). Consequently, investigation into the possibility of using reflectance spectroscopy for mapping hydrocarbons and the level of toxicity in petroleum release sites is needed. Even though the methodology has been proven to map soil properties for precision agriculture applications (e.g., Mouazen et al., 2007; Kodaira and Shibusawa, 2013; González et al., 2013; Quraishi and Mouazen, 2013), only one study could be found in the literature on mapping hydrocarbon contamination in soils using vis-NIR diffuse reflectance spectroscopy. Even then, the study focused on mapping total petroleum hydrocarbon (TPH) contamination in soil using kriging interpolation method (Chakraborty et al., 2012). It is known that complex TPH mixture measured as a single concentration number inherently is not a direct indicator of risk to either the environment or humans but, may give an indication of the degree of hydrocarbon contamination in soil (Weisman, 1998). Thus, for risk-based assessment of petroleum contaminated sites, the literature recommends the determination of the PAH fractions (Askari and Pollard, 2005).

Recently, the application of vis-NIR spectroscopy for the prediction of PAH in petroleum contaminated tropical rainforest Oxisols of the Niger Delta province in Nigeria was reported by Okparanma et al. (2014). They used a total of 137 field-moist intact soil samples for their study. Using partial least squares (PLS) regression analysis with full cross-validation, they developed vis-NIR-based models to predict PAH in the soil samples. The site-specific calibration and generalized prediction models developed demonstrated reasonable accuracy with coefficient of determination ( $r^2$ ) ranging from 0.69 to 0.89, root mean square error (RMSE) ranging from 1.16 to 1.98 mg kg<sup>-1</sup>, and ratio of prediction deviation (RPD) ranging from 1.81 to 3.12 (Okparanma et al., 2014). This result and the successful application of vis-NIR spectroscopy in the mapping of soil properties (e.g., Mouazen et al., 2007; Kodaira and Shibusawa, 2013; González et al., 2013; Quraishi and Mouazen, 2013) as well as soil TPH content (e.g., Chakraborty et al., 2012) prompted this study. Mapping PAH and TTEC of the PAH mixture using vis-NIR method is expected to reduce the amount of time, energy and money usually expended in hazard assessment of petroleum release sites by the conventional methods.

The objectives of the current study were: (1) to develop maps of PAH and TTEC of the PAH mixture using data from vis-NIR-based models developed and reported in our previous study (Okparanma et al., 2014), and (2) to use the soil maps of TTEC of the PAH mixture for hazard assessment of the studied sites using Generic Assessment Criteria (GAC) established in this study for the three petroleum release sites in Ogoniland in the Niger Delta province of Nigeria.

## 2. Materials and methods

### 2.1. The study area

The Niger Delta province (5.317°N, 6.467°E) covers a total land area of 70,000 km<sup>2</sup>, and is home to Nigeria's oil and gas industries with most of the country's oil and gas fields located in the area (Niger Delta Environmental Survey, 1995). Ogoniland, covering some 1000 km<sup>2</sup>, is located within the Niger Delta province in southern Nigeria. Top soils of Ogoniland are mainly sandy clay (UNEP, 2011), which is consistent with Oxisols that characterise tropical rainforest soils of southern Nigeria (USDA, 2005). In Ogoniland, soil total organic carbon range from 3.63 to 4.11% (Tanee and Albert, 2011), and typical soil pH at all soil depths range from 5.2 to 6.4, according to studies reported for similar ecosystems in the Niger Delta (SPDC, 2006). The increased oil and gas activities in recent years make the Niger Delta province most vulnerable to environmental pollution. For example, in Ogoniland alone, there are over 69 contaminated land sites (UNEP, 2011). Of this number, we selected three sites with various levels of contamination for this study. Site A is located at Baraboo (4.652°N, 7.249°E); site B is at Bomu 1 (4.662°N, 7.277°E); and site C is at Bomu 2 (4.662°N, 7.249°E); all in Gokana Local Government Authority (LGA) in Ogoniland (Fig. 1).

### 2.2. Soil sampling

From the three oil spill sites in Ogoniland, we collected a total of 137 soil samples from the top 15-cm depth in plastic containers and preserved them in a cooler containing ice blocks until shipment to the UK for analysis. The number of samples collected from site A, B, and C were 43, 58, and 36 respectively. We adopted targeted sampling method to cover as much of the potentially contaminated spots as possible. Targeted sampling method is purely judgemental sampling, which is the subjective selection of sampling locations at a site on the basis of visual inspection, and on best professional judgement of the sampling team (IAEA, 2004). This sampling method was adopted because of security situations in Ogoniland at the time and restricted access to contaminated sites by community and youth leaders, which did not permit us to implement the intended sampling design. The twin problems of insecurity and restricted access also dictated the total number of samples. Sample management was strictly in line with the standards of the Department of Petroleum Resources (DPR, 2002).

### 2.3. Soil chemical PAH analysis, optical measurement and development of PLS calibration models

Soil chemical analysis for PAHs was carried out by sequential ultrasonic solvent extraction–gas chromatography. Sequential ultrasonic solvent extraction was used to extract the PAH compounds from the soil samples as described by Risdon et al. (2008). Identification and quantification of the PAH compounds were carried by gas chromatography–mass spectrometry (GC–MS) as described in Okparanma et al.

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