Environmental Pollution 184 (2014) 298–305

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Analysis of petroleum-contaminated soils by diffuse reflectance spectroscopy and sequential ultrasonic solvent extraction–gas chromatography

Reuben N. Okparanma, Frederic Coulon, Abdul M. Mouazen*

Department of Environmental Science and Technology, Cranfield University, Cranfield, MK43 0AL Bedfordshire, United Kingdom

A R T I C L E I N F O

Article history:
Received 8 June 2013
Received in revised form
28 August 2013
Accepted 30 August 2013

Keywords:
Chemometrics
Near-infrared spectroscopy
Hydrocarbon
Soil

A B S T R A C T

In this study, we demonstrate that partial least-squares regression analysis with full cross-validation of spectral reflectance data estimates the amount of polycyclic aromatic hydrocarbons in petroleum-contaminated tropical rainforest soils. We applied the approach to 137 field-moist intact soil samples collected from three oil spill sites in Ogoniland in the Niger Delta province (5.317°N, 6.467°E), Nigeria. We used sequential ultrasonic solvent extraction–gas chromatography as the reference chemical method. We took soil diffuse reflectance spectra with a mobile fibre-optic visible and near-infrared spectrophotometer (350–2500 nm). Independent validation of combined data from studied sites showed reasonable prediction precision (root-mean-square error of prediction = 1.16–1.95 mg kg^{-1}, ratio of prediction deviation = 1.86–3.12, and validation r^2 = 0.77–0.89). This suggests that the methodology may be useful for rapid assessment of the spatial variability of polycyclic aromatic hydrocarbons in petroleum-contaminated soils in the Niger Delta to inform risk assessment and remediation.

1. Introduction

Rapid measurement of polycyclic aromatic hydrocarbons (PAHs) in soils can reduce the costs associated with their management, and the likely impacts of future pollution incidents through early identification. For effective management of PAHs in the environment, knowledge of their concentration and compositional distribution in the environment is vital. The information is essential to be able to identify the origin or source of the PAH (Hites and Gschwend, 1982; Okoro and Ikolo, 2007; Yunker and MacDonald, 1995) for risk-based assessment and remediation purposes (Askari and Pollard, 2005). In the analysis of petroleum-contaminated soils for PAH, gas chromatography–mass spectrometry (GC–MS) is mostly preferred because of their relative selectivity and sensitivity (Brassington et al., 2010; Wang and Fingas, 1995). Nevertheless, GC–MS method is relatively expensive, involves time-consuming sample preparation protocols, and relies on the use of noxious extraction solvents (Okparanma and Mouazen, 2013a). This has prompted increased research activity recently by scientists to evolve simpler, faster, and cost-effective methods of measuring PAH in contaminated soils to complement the conventional methods.

Among these innovative methods are techniques based on vibrational spectroscopy, particularly those employing diffuse reflectance sample interfaces. These techniques include Fourier transform infrared (FTIR) spectroscopy and visible and near-infrared (VIS–NIR) spectroscopy. Diffuse reflectance in the IR spectrum came to limelight in 1976, and became known as diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy (Willey, 1976). Before its advent in the IR spectrum, diffuse reflectance has been commonly available in the visible and NIR spectrum (Willey, 1976). Early applications of DRIFT have been widely reported (e.g., Fuller and Griffiths, 1978). Both DRIFT and VIS–NIR are very much similar in many ramifications, but maybe more importantly are the differences between the two of them. Both techniques are now available in portable devices that can be deployed for in-field measurements without sample preparation. In terms of capital equipment cost, the prices of their latest portable models are comparable. The commercially available DRIFT (portable) system developed by Forrester et al. (2011), the 4100 ExoScan FTIR (Agilent Technologies, CA, USA), currently costs $61 301 while the latest portable model of VIS–NIR analyser, the LabSpec 5000 (Analytical Spectral Devices, Inc., CO, USA), costs $61 078

---

* Corresponding author.
E-mail addresses: a.mouazen@cranfield.ac.uk, mouazen2002@yahoo.com (A.M. Mouazen).

0269-7491/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envpol.2013.08.039

(Okparanma and Mouazen, 2013a). The former system predicted TPH with root-mean-square error of 903 mg kg^{-1} in cross-validation for TPH ranging from 0 to 11 000 mg kg^{-1} (Forrester, 2010). On the other hand, VIS–NIR spectroscopy has been successfully used for on-line (tractor-mounted) measurement of soil properties (e.g., Mouazen et al., 2007a; Kuang and Mouazen, 2013), which opens the possibility for on-line measurement of PAHs using the technology. So far, no reports about the use of DRIFT for on-line measurement can be found in the literature.

In VIS–NIR spectroscopy (350–2500 nm), energy absorption by hydrocarbon derivatives is due to overtones and combinations of fundamental vibrational C–H stretching modes of saturated CH_2 and terminal CH_3, or aromatic C–H (ArCH) functional groups (Aske et al., 2001). The difficulty in interpreting VIS–NIR spectra because of broad and overlapping bands (Stenberg, 2010), to a large extent has been overcome by the use of advanced chemometrics and data-processing techniques (Pasquini, 2003). In the analysis of spectroscopic data, multivariate calibration generally solves the problem of interference from compounds closely related to the analyte thereby eliminating the need for selectivity (Naes et al., 2002). VIS–NIR spectroscopy has been used in conjunction with various multivariate analytical techniques to predict TPH in contaminated soils (Chakraborty et al., 2010, 2012; Forrester et al., 2010; Graham, 1998; Malley et al., 1999; Schwartz et al., 2012). However, studies on the application of the methodology to predict PAH in contaminated soils are few in literature (e.g., Bray et al., 2010; Okparanma and Mouazen, 2013b). High false positive rates were reported for PAH prediction by Bray et al. (2010), which underscore the need for further research on the application of the approach. On the other hand, models reported by Okparanma and Mouazen (2013b) for PAH prediction appear to be local models. This limits extrapolation of the models to studied soil types. Moreover, none of these two studies considered contaminated tropical rainforest soils in their applications. Therefore, to set up a VIS–NIR-based methodology to model VIS–NIR spectra for broader environmental application, it is essential to expand the approach to cover a wider range of soil types and environmental conditions.

The objective of this study was to evaluate the performance of VIS–NIR-based methodology in the prediction of PAH in contaminated tropical rainforest soils. To do this we used sequential ultrasonic solvent extraction–gas chromatography (SUSE–GC) as the benchmark method. Sites investigated in this study are in the tropical rainforests of the oil-rich Niger Delta province in Nigeria. To the best of our knowledge this study is the first attempt to adopt VIS–NIR spectroscopy for the determination of hydrocarbons in contaminated arable lands in Nigeria.

2. Materials and methods

2.1. Brief description of the study area

Available geological data for the study area show that Ogoniland is located within the Niger Delta basin with soils that are broadly classified as tropical rainforest soils, which occur in the southern part of Nigeria (SPDC, 2006). Niger Delta province covers a total land area of 70 000 km^2 (Niger Delta Environmental Survey, 1995). According to the United States Department of Agriculture (USDA) soil taxonomic order, soils in the Niger Delta belong to the Oxisols. In this study, soils were collected from within the shallow geology (top-soils) of Ogoniland, which consists of sandy clay (UNEP, 2011). Typical ranges of soil nutrients concentrations at all soil depths reported for similar ecosystems in the Niger Delta show that nitrate-nitrogen range from 0.01 to 1.96 mg kg^{-1}, phosphorous range from 0.21 to 6.92 mg kg^{-1}, sulphate range from 0.20 to 10.91 mg kg^{-1} and soil pH range from 5.2 to 6.4 (SPDC, 2006). Total organic carbon range from 3.63 to 4.11% (Tanee and Albert, 2011).

2.2. Sample collection

In this study, we collected soil samples from three oil spill sites located at Baraboo (4.652°N, 7.249°E), Bomu 1 (4.662°N, 7.277°E), and Bomu 2 (4.662°N, 7.249°E) all in K-Dere, Ogoniland in the Niger Delta province of Nigeria (Fig. 1). By directed sampling method, we collected soil samples from the top 15-cm depth in plastic containers and preserved them in a cooler containing ice blocks until shipment. We adopted directed sampling method because of the need to cover as much of the visible hot-spots in the contaminated sites as possible. Sample management was done according to the standards of the Nigerian Government's Department of Petroleum Resources (2002). We carried out both reference SUSE–GC analysis and VIS–NIR optical scanning of soil samples in the Environmental Analytical Facility of Cranfield University, United Kingdom.

2.3. Reference chemical analysis of PAHs

We used SUSE–GC method to determine the concentrations of PAH compounds in the soil samples as described by Risdon et al. (2008). But, in place of acetone we used dichloromethane (Rathburn Chemicals Ltd., Walderburn, UK). Analysis of PAHs was carried with a 6890N Network GC system coupled to a 5973 Network mass selective detector (Agilent Technologies Inc., USA) operated at 70 eV in positive ion mode. Each PAH compound was quantified by the internal standard method. In this study, we adopted the same limit of quantitation (LOQ) of 0.02 mg kg^{-1} routinely used by laboratories in Nigeria for PAH quantitation in Nigerian soils because our soil samples were collected from Nigeria. LOQ is the lowest concentration at which an analyte can be reliably detected (Mitra, 2003). Consequently, concentrations less than the LOQ were removed from the total PAH computation as they were considered unreliable. A priori 5-level calibration was carried out with a calibration solution mix. The calibration solution mix was made up with EPA 525 PAH Mix-A standard solution (Sigma–Aldrich Co. Ltd., Dorset, UK), surrogate standard solution

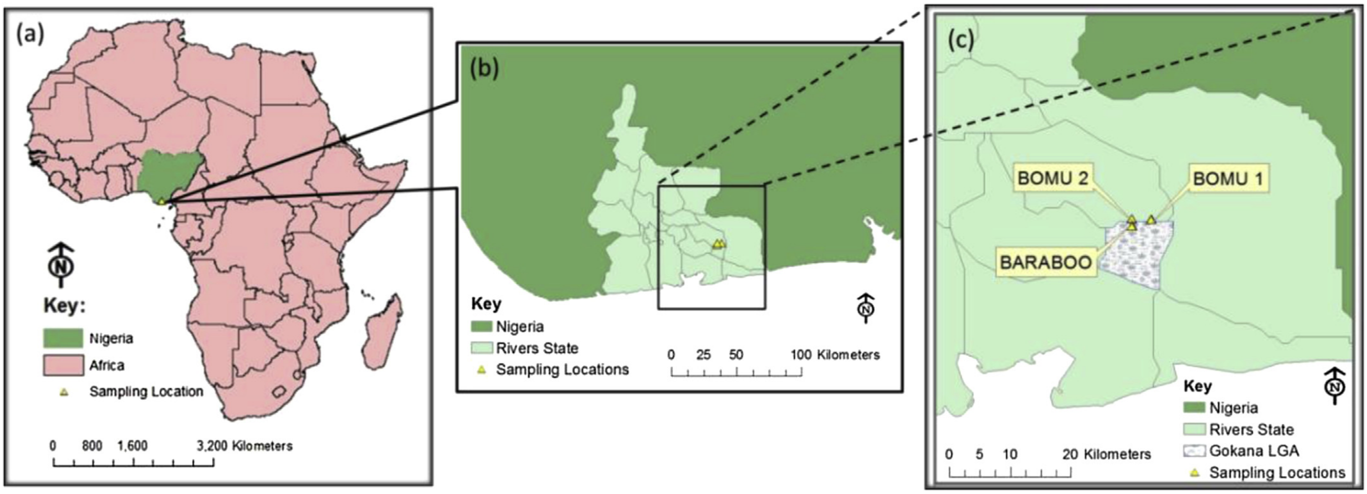

Fig. 1. Sampling locations: (a) Nigeria, (b) Rivers State in the Niger Delta province, and (c) Gokana Local Government Authority in Ogoniland (Datum and Projection: GCS WGS 1984. Shape files source: ESRI®, CA, USA).