

Mapping polycyclic aromatic hydrocarbons and total toxicity equivalent soil concentrations for hazard assessment by visible and near infrared spectroscopy

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## Abstract

In a previous study, we have shown that spectroscopic models based on visible and near-infrared (vis-NIR) spectroscopy (350–2500 nm) predicts polycyclic aromatic hydrocarbons (PAHs) in tropical rainforest soils with reasonable accuracy. In this study, we used these models to develop soil maps of PAHs and total toxicity equivalent soil concentrations (TTEC) of the PAH mixture. We used the soil maps of TTEC for hazard assessment of three petroleum release sites in Ogoniland in the Niger Delta province of Nigeria from where the soils were collected. Inverse distance weighting soil maps show a near-perfect match of high and low PAH and TTEC zones between measured and predicted maps. There were non-significant ( $p < 0.05$ ) differences between measured and predicted soil maps as the ANOVA revealed. Hazard assessment results showed that the degree of action for site-specific risk assessment and/or remediation differs among the different management zones. Only one zone, covering some 20 m<sup>2</sup> in site C, showed very high levels of PAH with significant and unacceptable risk to specified targets. These results are indications that vis-NIR spectroscopy has the potential for mapping PAH and TTEC of the PAH mixture for hazard assessment of petroleum release sites in the Niger Delta province of Nigeria.

**Key words:** Near-Infrared Spectroscopy; Generic Assessment Criteria; Hydrocarbon; Soil Map

## **Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed organic pollutants. The Water Framework Directive (WFD, 2000/60/EC) 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, 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, 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 (Okparanma and Mouazen, 2013a). 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 recognised 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 point reflectance spectroscopy for mapping hydrocarbons and the level of toxicity in petroleum release sites is needed. To the best of our knowledge, none of the studies reported in the literature on mapping hydrocarbon contamination in soils adopted vis-NIR spectroscopy – although 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).

Recently, the application of vis-NIR spectroscopy for the prediction of total 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, and reported extraction efficiency ranging from 48 to 78 % for the chemical PAH extraction protocol used in the study, which were said to be within recommended standards (Okparanma et al., 2013). They also reported that a total of 13 United States Environmental Protection Agency (US EPA) priority PAHs were identified and quantified in the three studied sites as shown in Table 1 (Okparanma et al., 2014). Using partial least squares (PLS) regression analysis with full cross-validation, they developed vis-NIR-based models to predict total PAH in the soil samples. The site-specific calibration and generalised 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., 2013). This result and the successful use of vis-NIR spectroscopy to map soil properties as reported by previous researchers prompted further studies leading to the development of soil maps of PAH and TTEC of the PAH mixture for hazard assessment of the three petroleum release sites in Nigeria. Mapping PAH and TTEC of the PAH mixture using vis-NIR method should 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 in our previous study (Okparanma et al., 2013), and (2) to use the soil maps of TTEC of the PAH mixture for hazard assessment of the studied sites based on Generic Assessment Criteria established in this study for the three petroleum release sites in Ogoniland in the Niger Delta province of Nigeria.

Table 1: Statistics of the chemical analysis result showing the sum of individual polycyclic aromatic hydrocarbons (PAHs) quantified for each site by reference sequential ultrasonic solvent extraction–gas chromatography (SUSE–GC). (Modified after Okparanma et al., 2013)

| PAH                    | LOQ<br>(mg<br>kg <sup>-1</sup> ) | Site A   |                                   |                                   |                                   |                                    | Site B   |                                   |                                   |                                   |                                    | Site C   |                                   |                                   |                                   |                                    |
|------------------------|----------------------------------|----------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|----------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|----------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
|                        |                                  | <i>N</i> | Min.<br>(mg<br>kg <sup>-1</sup> ) | Max.<br>(mg<br>kg <sup>-1</sup> ) | Mean<br>(mg<br>kg <sup>-1</sup> ) | Range<br>(mg<br>kg <sup>-1</sup> ) | <i>N</i> | Min.<br>(mg<br>kg <sup>-1</sup> ) | Max.<br>(mg<br>kg <sup>-1</sup> ) | Mean<br>(mg<br>kg <sup>-1</sup> ) | Range<br>(mg<br>kg <sup>-1</sup> ) | <i>N</i> | Min.<br>(mg<br>kg <sup>-1</sup> ) | Max.<br>(mg<br>kg <sup>-1</sup> ) | Mean<br>(mg<br>kg <sup>-1</sup> ) | Range<br>(mg<br>kg <sup>-1</sup> ) |
| Acenaphthylene         | 0.02                             | 43       | 0.07                              | 3.06                              | 0.83                              | 2.98                               | 58       | 0.02                              | 2.40                              | 0.46                              | 2.38                               | 36       | <0.02                             | 8.53                              | 1.41                              | 8.53                               |
| Fluorene               | 0.02                             | 43       | <0.02                             | 4.80                              | 0.73                              | 4.80                               | 58       | <0.02                             | 2.70                              | 0.45                              | 2.70                               | 36       | <0.02                             | 6.25                              | 0.88                              | 6.25                               |
| Phenanthrene           | 0.02                             | 43       | <0.02                             | 3.64                              | 0.47                              | 3.64                               | 58       | 0.02                              | 3.15                              | 0.81                              | 3.13                               | 36       | <0.02                             | 6.86                              | 0.76                              | 6.86                               |
| Anthracene             | 0.02                             | 43       | <0.02                             | 4.22                              | 0.41                              | 4.22                               | 58       | <0.02                             | 2.57                              | 0.36                              | 2.57                               | 36       | <0.02                             | 6.86                              | 0.75                              | 6.86                               |
| Pyrene                 | 0.02                             | 43       | <0.02                             | 1.03                              | 0.30                              | 1.03                               | 58       | <0.02                             | 2.83                              | 0.56                              | 2.83                               | 36       | <0.02                             | 1.73                              | 0.52                              | 1.73                               |
| Benz[a]anthracene      | 0.02                             | 43       | <0.02                             | 0.88                              | 0.18                              | 0.88                               | 58       | <0.02                             | 2.61                              | 0.39                              | 2.61                               | 36       | <0.02                             | 1.01                              | 0.15                              | 1.01                               |
| Chrysene               | 0.02                             | 43       | <0.02                             | 1.17                              | 0.18                              | 1.17                               | 58       | <0.02                             | 1.07                              | 0.22                              | 1.07                               | 36       | <0.02                             | 0.55                              | 0.09                              | 0.55                               |
| Benz[b]fluoranthene    | 0.02                             | 43       | <0.02                             | 0.15                              | 0.03                              | 0.15                               | 58       | <0.02                             | 1.33                              | 0.23                              | 1.33                               | 36       | <0.02                             | 0.18                              | 0.04                              | 0.18                               |
| Benzo[k]fluoranthene   | 0.02                             | 43       | <0.02                             | 0.15                              | 0.03                              | 0.15                               | 58       | <0.02                             | 1.23                              | 0.19                              | 1.23                               | 36       | <0.02                             | 0.18                              | 0.04                              | 0.18                               |
| Benzo[a]pyrene         | 0.02                             | 43       | <0.02                             | 0.73                              | 0.17                              | 0.73                               | 58       | <0.02                             | 1.80                              | 0.14                              | 1.80                               | 36       | <0.02                             | 9.36                              | 0.68                              | 9.36                               |
| Indeno[1,2,3-cd]pyrene | 0.02                             | 43       | <0.02                             | 0.22                              | 0.02                              | 0.22                               | 58       | <0.02                             | 1.48                              | 0.23                              | 1.48                               | 36       | <0.02                             | 0.82                              | 0.06                              | 0.82                               |
| Dibenzo[a,h]anthracene | 0.02                             | 43       | <0.02                             | 0.15                              | 0.03                              | 0.15                               | 58       | <0.02                             | 1.82                              | 0.22                              | 1.82                               | 36       | <0.02                             | <0.02                             | -                                 | -                                  |
| Benzo[g,h,i]perylene   | 0.02                             | 43       | <0.02                             | 0.22                              | 0.02                              | 0.22                               | 58       | <0.02                             | 1.48                              | 0.22                              | 1.48                               | 36       | <0.02                             | 0.33                              | 0.02                              | 0.33                               |

LOQ, Limit of quantitation. It is the lowest concentration at which an analyte can be reliably detected (Mitra, 2003).

*N*, Number of samples

PAH, Polycyclic aromatic hydrocarbons

## Materials and Methods

### *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 1 000km<sup>2</sup>, is located within the Niger Delta province in southern Nigeria. Topsoils 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). In this study, we selected three oil spill sites in Gokana Local Government Authority (LGA) in Ogoniland – site A is located at Baraboo (4.652°N, 7.249°E); site B at Bomu 1 (4.662°N, 7.277°E); and site C is at Bomu 2 (4.662°N, 7.249°E) (Figure 1).

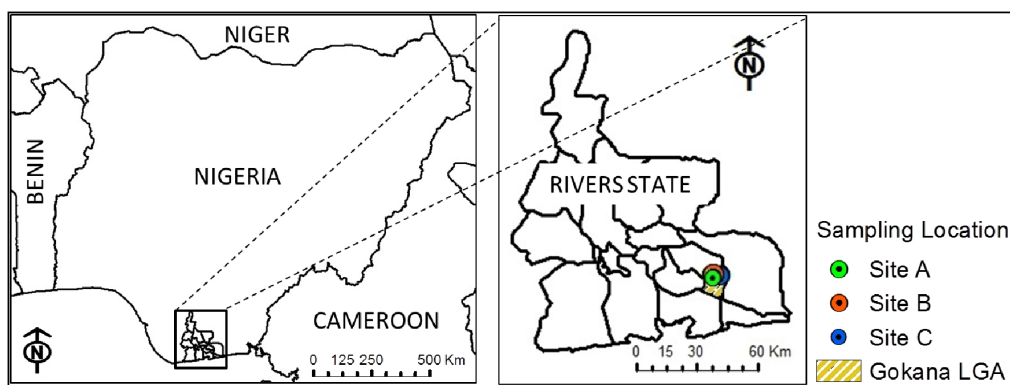


Figure 1: Sampling locations in Gokana Local Government Authority (LGA) in Ogoniland, Rivers State in the Niger Delta province of Nigeria. (Projection: Geographic Coordinate System –World Geographic System 1984 in ArcGIS® 10.1; ESRI™, CA, USA)

### *Soil sampling*

From 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. 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. Sample management was strictly in line with the standards of the Nigerian Government's Department of Petroleum Resources (2002).

### *Soil chemical PAH analysis*

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 by Okparanma et al. (2014).

### *Soil optical measurement and development of PLS calibration models*

Optical scanning of soil samples in diffuse reflectance mode was carried out with a mobile fibre-optic LabSpec2500<sup>®</sup> vis-NIR spectrophotometer (350–2500 nm) (Analytical Spectral Devices Inc., CO, USA). Soil scanning protocols, pre-processing of soil spectra, and establishment of PLS calibration models were carried as described by Okparanma et al. (2014). Spectral pre-processing and PLS regression analysis were carried out with the Unscrambler<sup>®</sup> X version 10.2 (CAMO Software AS, Oslo, Norway).



*Establishment of Generic Assessment Criteria (GAC) and delineation of potential management zones*

The decision on the likely need for site-specific assessment and/or site-specific remediation of a petroleum release site following hazard assessment is done using GAC (Petts et al., 1997). This has the advantage of saving time and money that would otherwise be expended in developing site-specific assessment criteria (Ferguson et al., 1998; Cheng and Nathanail, 2009).

In this study, the threshold–action concept, which is the underlying concept for establishing GAC (Petts et al., 1997), was used to delineate potential management zones within the studied sites. To do this, the first step was to transform individual PAH concentrations to toxicity equivalent concentrations (TEC in  $\text{mg kg}^{-1}$ ) using Equation 1, and compute the TTEC ( $\text{mg kg}^{-1}$ ) for the PAH mixture using Equation 2 as follows (WSDE, 2007):

$$TEC = C \times TEF \quad (1)$$

$$TTEC = \sum C_n \times TEF_n \quad (2)$$

Where  $C$  = PAH concentration (in  $\text{mg kg}^{-1}$ ),  $n$  = the individual PAH in the mixture, and  $TEF$  = toxicity equivalency factor (dimensionless).  $TEF$  values for PAHs are freely available on the internet. Table 2 shows  $TEF$  values of US EPA priority PAHs relevant to this study.

Table 2: Toxicity Equivalency Factor for selected United States Environmental Protection Agency (US EPA) priority polycyclic aromatic hydrocarbons (PAHs)

| PAHs                   | TEF <sup>a</sup> |
|------------------------|------------------|
| Acenaphthylene         | 0.01             |
| Fluorene               | 0.001            |
| Phenanthrene           | 0.001            |
| Anthracene             | 0.01             |
| Pyrene                 | 0.001            |
| Benzo[a]anthracene     | 0.1              |
| Chrysene               | 0.01             |
| Benzo[b]fluoranthene   | 0.1              |
| Benzo[k]fluoranthene   | 0.1              |
| Benzo[a]pyrene         | 1                |
| Indeno[1,2,3-cd]pyrene | 0.1              |
| Dibenzo[a,h]anthracene | 0.1              |
| Benzo[g,h,i]perylene   | 0.01             |

TEF, Toxicity Equivalency Factor

<sup>a</sup>Data from Nisbet and LaGoy (1992), De Meulenaer (2006), WSDE (2007).

The second step was to compare the TTEC for the PAH mixture with applicable target value (screening level) for benzo[a]pyrene. In Nigeria, the screening level for TPH is 50 mg kg<sup>-1</sup> while for monocyclic aromatic hydrocarbons including benzene, toluene, ethylbenzene, and xylene (BTEX) the screening level is 0.05 mg kg<sup>-1</sup> (DPR, 2002). But, there are currently no screening levels for PAHs in Nigeria. As a result, in this study, we considered the screening levels for benzo[a]pyrene used among 9 European countries (Table 3) and used the average value as a guide.

Table 3: Soil screening levels for benzo[a]pyrene for selected European countries

| European country | Screening value for agricultural/special/natural/sensitive land use (mg kg <sup>-1</sup> ) <sup>a</sup> |
|------------------|---|
| Belgium          | 0.5   |
| Czech Republic   | 0.1   |
| Denmark          | 0.1   |
| Finland          | 0.2   |
| Germany          | 1   |
| Lithuania        | 0.1   |
| Poland           | 0.03  |
| Slovakia         | 0.1   |
| Spain            | 0.02  |
| <i>Average</i>   | <i>0.24</i>   |

<sup>a</sup> Data from Carlon (2007).

Before adopting the European screening level for benzo[a]pyrene, we ensured as much as we possibly could that the end-use of the sites and exposure scenarios in Nigeria were comparable to those considered when developing the applicable screening level for benzo[a]pyrene in the selected European countries. From our investigation, the studied sites in Nigeria are largely used for agricultural purposes for which several soil outdoor exposure pathways can be considered. Of these exposure pathways, majority of the European countries within the assessment considered oral ingestion of soil (Carlon, 2007). Since this exposure scenario is applicable to the system of agriculture in Nigeria, we assumed that soil outdoor exposure in the studied sites was through oral ingestion by an adult human. By this assumption, we were able to apply the TEF approach directly since the assumption is the same as the one used in developing the TEF method by the US EPA (WSDE, 2007).

Therefore, the average screening level for benzo[a]pyrene of 0.24 mg kg<sup>-1</sup> (Table 3) was adopted as the screening threshold of benzo[a]pyrene for the three sites in Nigeria. In Deutschland, when screening data against guidelines or standards, the acceptable risk level

for excess lifetime cancer risk (ECLR) is  $1 \times 10^{-4}$  for which a site-specific risk assessment is mandatory (Petts et al., 1997). On the other hand, it has been recently proposed that the unacceptable risk level for ECLR is  $1 \times 10^{-3}$  for which site-specific remediation is required (Kibblewhite, M. [2013], National Soil Resources Institute, Cranfield University, England – personal communication). This implies that the acceptable and unacceptable risk levels for ECLR differ by 10 orders of magnitude. Therefore, we adopted an action value (i.e., threshold of acceptability) of  $2.40 \text{ mg kg}^{-1}$  for benzo[a]pyrene in the three studied sites in Nigeria. Using the threshold–action concept (Petts et al., 1997), three management zones were delineated as follows. The actual number of management zones created for each site was based on the range of their TTEC.

- 1) Zone 1 ( $\text{TTEC} < 0.24 \text{ mg kg}^{-1}$ ). In this zone, no action is required because there is no unacceptable risk to specified target;
- 2) Zone 2 ( $0.24 \leq \text{TTEC} \leq 2.40 \text{ mg kg}^{-1}$ ). In this zone, site-specific assessment may be required because there may be additional risk to some targets; and
- 3) Zone 3 ( $\text{TTEC} > 2.40 \text{ mg kg}^{-1}$ ). Here, action is required because there is unacceptable risk to specified target.

#### *Development of full-data point soil maps*

The GC–MS-measured and vis-NIR-predicted soil maps for PAH, TTEC of the PAH mixture, and management zones were prepared using ArcGIS<sup>®</sup> 10.1 (ESRI Inc., USA). The full-data point soil maps were drawn using chemical GC–MS-measured soil data as follows: site A (43 samples), site B (58 samples), and site C (36 samples). The predicted maps were drawn using 401 vis-NIR spectral data. Data points were interpolated by the inverse distance weighting (IDW) method using the default Power function of 2 and standard neighbourhood type. IDW is a quick deterministic interpolator that is exact and can be a good way to take a first look at an interpolated surface, and there are no assumptions required of the data (ESRI,

2012). For both PAH and TTEC soil maps, seven classes were used. The classification method used for the PAH and TTEC maps was geometrical interval because it was designed to accommodate continuous data (ESRI, 2012). These classes were represented with colour ramps. For the management zones, between two and three classes were used depending on the TTEC range of the site. The area in m<sup>2</sup> of each zone was determined by converting the geographic coordinates of the data points in decimal degrees from geographic coordinate system (GCS) to projected coordinate system (PCS) of Nigeria mid belt national grid using ArcGIS<sup>®</sup>.

#### *Statistical data analysis*

We used one-way analysis of variance (ANOVA) available in Microsoft<sup>®</sup> Excel 2010 to evaluate the significance of differences between soil maps of PAH and TTEC of the PAH mixture developed by reference GC–MS and vis-NIR spectroscopic methods. Differences were considered significant at  $p < 0.05$ .

## **Results and Discussion**

#### *Full-data point soil maps*

Figure 2 shows the full-data point IDW soil maps developed for the three petroleum release sites using measured and predicted PAH and TTEC data. For fair comparison between measured and predicted maps, equal number of classes (7 classes) was used for the three maps in each site with identical class intervals (Mouazen et al., 2007). As shown in Figure 2, there is a large spatial similarity between the measured and predicted maps for both PAH and TTEC with a near-perfect match of high and low concentrations zones. However, some differences are observed around some interpolated surfaces of the predicted maps as shown in the error maps (Figure 2).

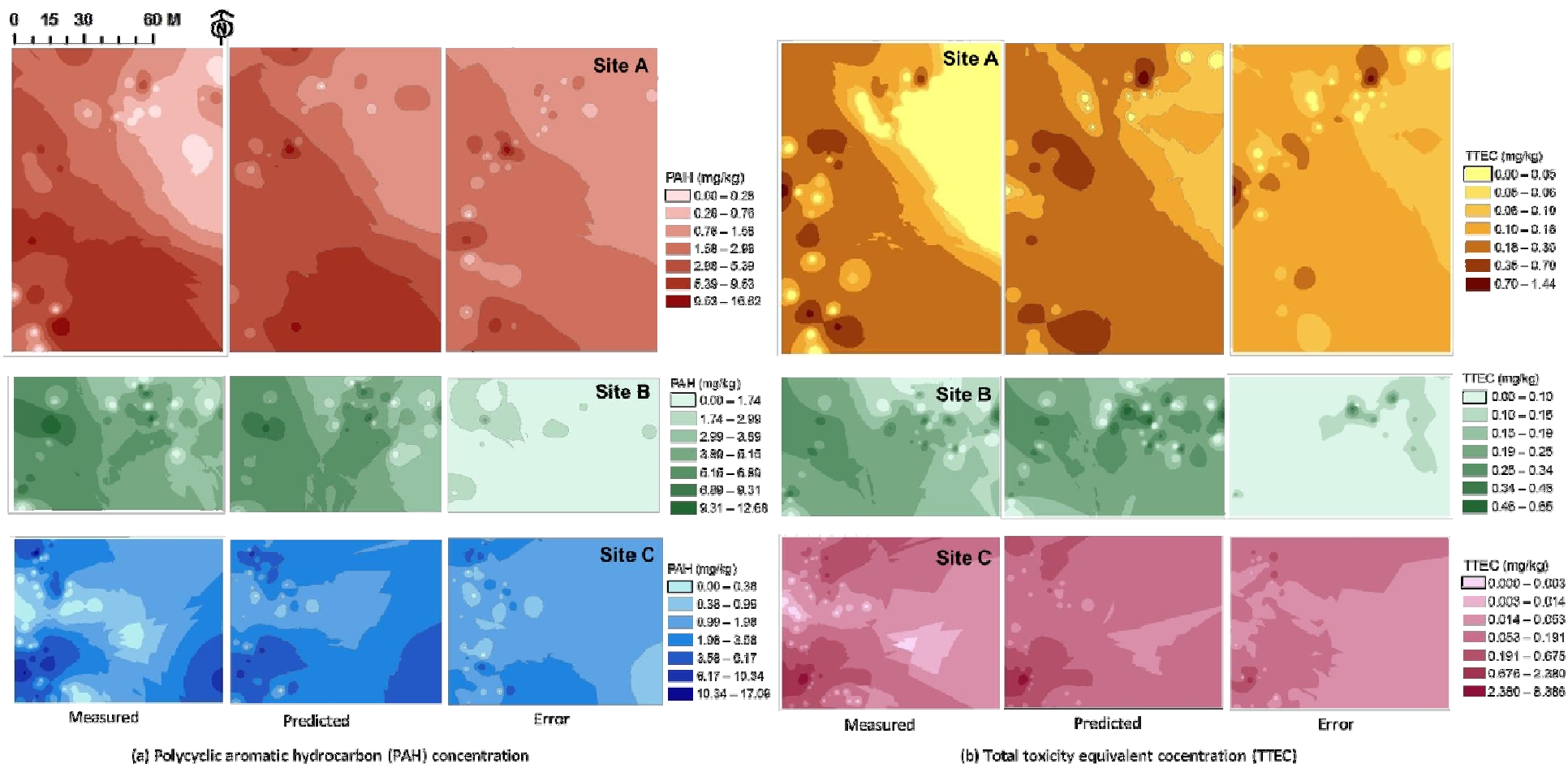


Figure 2: Comparison inverse distance weighting (IDW) soil maps for three petroleum release sites in Ogoniland in the Niger Delta province of Nigeria. The measured maps were drawn using chemical GC–MS soil data as follows: Site A (43 samples); Site B (58 samples), and Site C (36 samples). The predicted maps were drawn using 401 vis-NIR spectral data.

The histogram plot of the error between the two measurement methods for both PAH and TTEC is shown in Figure 3. For PAH measurement, the histogram shows that about 52% of the error for site B with a PAH range of 12.68 mg kg<sup>-1</sup> (see Figure 2) is less than 1 mg kg<sup>-1</sup> in absolute values. Similarly, 49% of the error for site A with a PAH range of 16.62 mg kg<sup>-1</sup> (see Figure 2) and 42% for site C with a PAH range of 17.09 mg kg<sup>-1</sup> are less than 1 mg kg<sup>-1</sup> in absolute values. The frequency of samples with low error is higher for TTEC measurement as compared to PAH measurement (Figure 3). Here, about 63 and 69% of the error are less than 0.2 mg kg<sup>-1</sup> (absolute) for site A and C respectively while 62% are less than 0.1 mg kg<sup>-1</sup> (absolute) for site B. Overall, the frequency of samples with low error is relatively larger than the frequency with high error (Figure 3). The histogram also shows that the error distribution is skewed for both PAH and TTEC measurements particularly in site A and C (Figure 3). The skewness in the negative range is largely attributed to the low concentration of PAH measured at some parts of the sites (Tables are not shown). As a result, PAH concentrations at these parts of the sites have been slightly overestimated by the vis-NIR method. There are also differences due to some cases of underestimation of the PAH as shown by the error distribution in the positive range (Figure 3). Nonetheless, these differences are non-significant ( $p < 0.05$ ) as the analysis of variance (ANOVA) reveals in Table 4. These results underline the potential of vis-NIR spectroscopy for exploring the spatial variability of PAH and assessing the toxicity level of PAH in petroleum release sites.

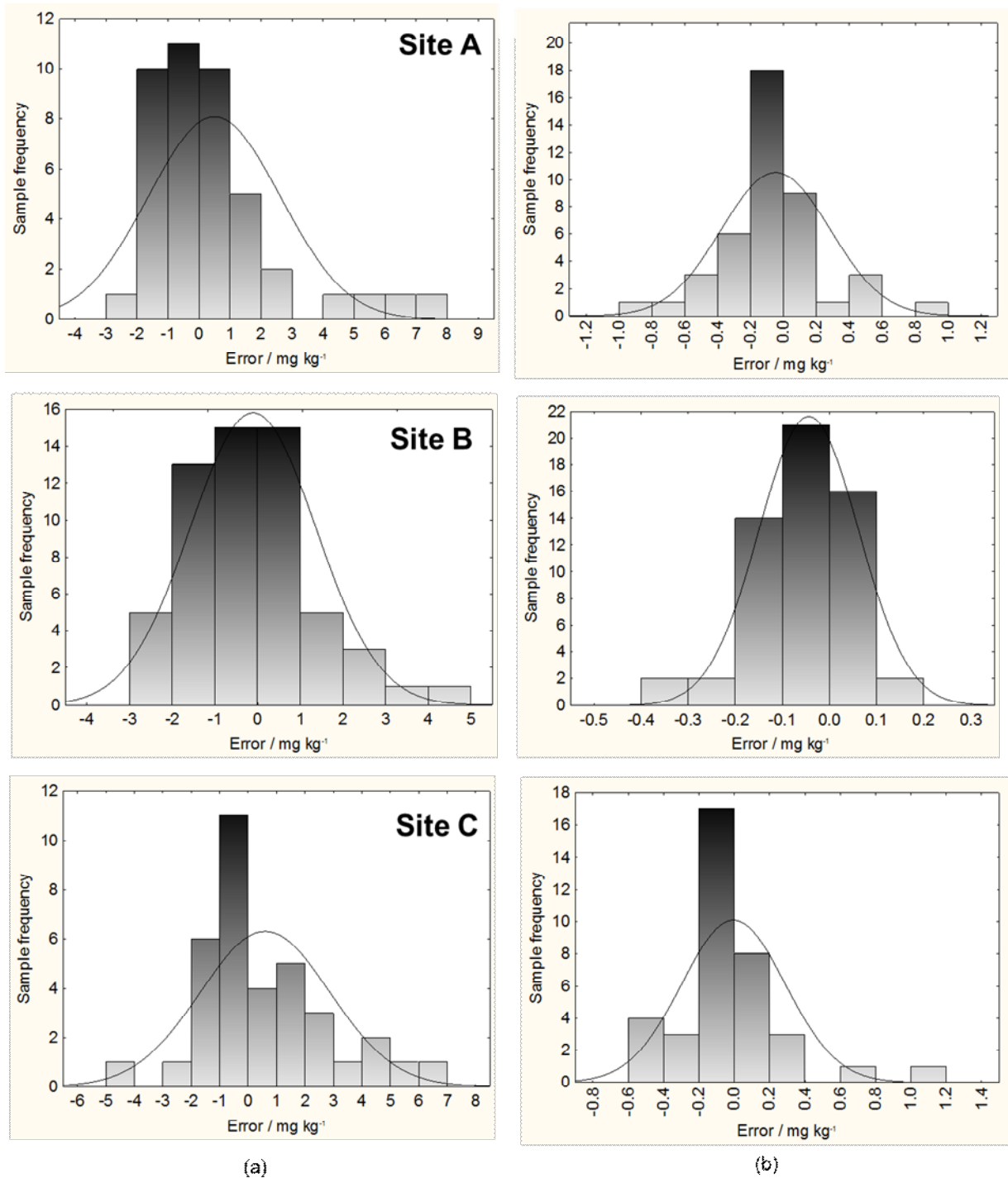


Figure 3: Histogram showing the distribution of error between measured and predicted soil maps of (a) polycyclic aromatic hydrocarbons (PAHs), and (b) total toxicity equivalent concentration (TTEC) of the PAH mixture in three contaminated sites at Ogoniland, Niger Delta province of Nigeria.



Table 4: One-way ANOVA on the analysis of the significance of the difference between measured and predicted soil maps of polycyclic aromatic hydrocarbon (PAH) and total toxicity equivalent concentration (TTEC) in three petroleum release sites in Ogoniland, Niger Delta province of Nigeria.

| Site  | Source of Variation | S.S.    | d.f. | M.S.  | F       | p value | F crit. |
|---|---------------------|---------|------|-------|---------|---------|---------|
| <i>Polycyclic aromatic hydrocarbon (PAH)</i>          |                     |         |      |       |         |         |         |
| Site A  | Between Groups      | 0.05    | 1    | 0.05  | 0.01**  | 0.94    | 3.93    |
|   | Within Groups       | 1060.37 | 118  | 8.99  | -       | -       | -       |
|   | Total               | 1060.42 | 119  | -     | -       | -       | -       |
| Site B  | Between Groups      | 0.07    | 1    | 0.07  | 0.01**  | 0.92    | 3.93    |
|   | Within Groups       | 770.78  | 104  | 7.41  | -       | -       | -       |
|   | Total               | 770.85  | 105  | -     | -       | -       | -       |
| Site C  | Between Groups      | 2.12    | 1    | 2.12  | 0.23**  | 0.63    | 3.93    |
|   | Within Groups       | 1044.76 | 112  | 9.33  | -       | -       | -       |
|   | Total               | 1046.88 | 113  | -     | -       | -       | -       |
| <i>Total toxicity equivalent concentration (TTEC)</i> |                     |         |      |       |         |         |         |
| Site A  | Between Groups      | 0.08    | 1    | 0.08  | 1.38**  | 0.24    | 3.92    |
|   | Within Groups       | 6.58    | 118  | 0.06  |         |         |         |
|   | Total               | 6.66    | 119  |       |         |         |         |
| Site B  | Between Groups      | 0.06    | 1    | 0.06  | 3.15**  | 0.08    | 3.92    |
|   | Within Groups       | 2.41    | 118  | 0.02  |         |         |         |
|   | Total               | 2.47    | 119  |       |         |         |         |
| Site C  | Between Groups      | 0.00    | 1    | 0.001 | 0.001** | 0.97    | 3.92    |
|   | Within Groups       | 123.02  | 118  | 1.04  |         |         |         |
|   | Total               | 123.02  | 119  |       |         |         |         |

S.S., sum of squares; d.f., degrees of freedom; M.S., mean squares

\*\*not significant (p<0.05)

### *Potential management zones and hazard assessment of studied sites using GAC*

The high spatial variability of PAH within the studied sites underscore the importance of management zones in the site-specific management of PAH-contaminated land. Its benefit in resource allocation and conservation during remediation projects cannot be overemphasized. In this study, management zones developed using measured and predicted data are compared in Figure 3. As shown in Figure 3, there is a near-perfect match of the geometry of the management zones between measured and predicted maps. The geometrical area of each zone within each site is summarised in Table 5. As shown in Table 5, most zones determined by vis-NIR method are almost equal in area to those determined by the conventional method. For instance for zone 1 and 2 in site C, their areas measured by vis-NIR method differ by a very small margin (about 1%) from those measured by the conventional method (Table 5). In this study, remarkably small zones were integrated into much larger zones, which in practice, allows for easy management (Halacro et al., 2013). This zones fusion and human cartographical error are partly responsible for differences in area between measured and predicted zones. Remarkably, vis-NIR method produces an equal number of management zones as the conventional method does in the studied sites. This result is remarkable because it leaves the area of the management zones as the main distinguishing feature between the two measurement methods. Other hazard assessment rubrics applicable to petroleum release sites based on GAC can be applied without distinction between the two measurement methods (Table 5). As shown in Table 5, the degree of action for site-specific risk assessment and/or remediation differs among the different zones. These results suggest that vis-NIR method may be used for hazard assessment to inform site-specific risk assessment and/or remediation of petroleum release sites in the Niger Delta province of Nigeria.

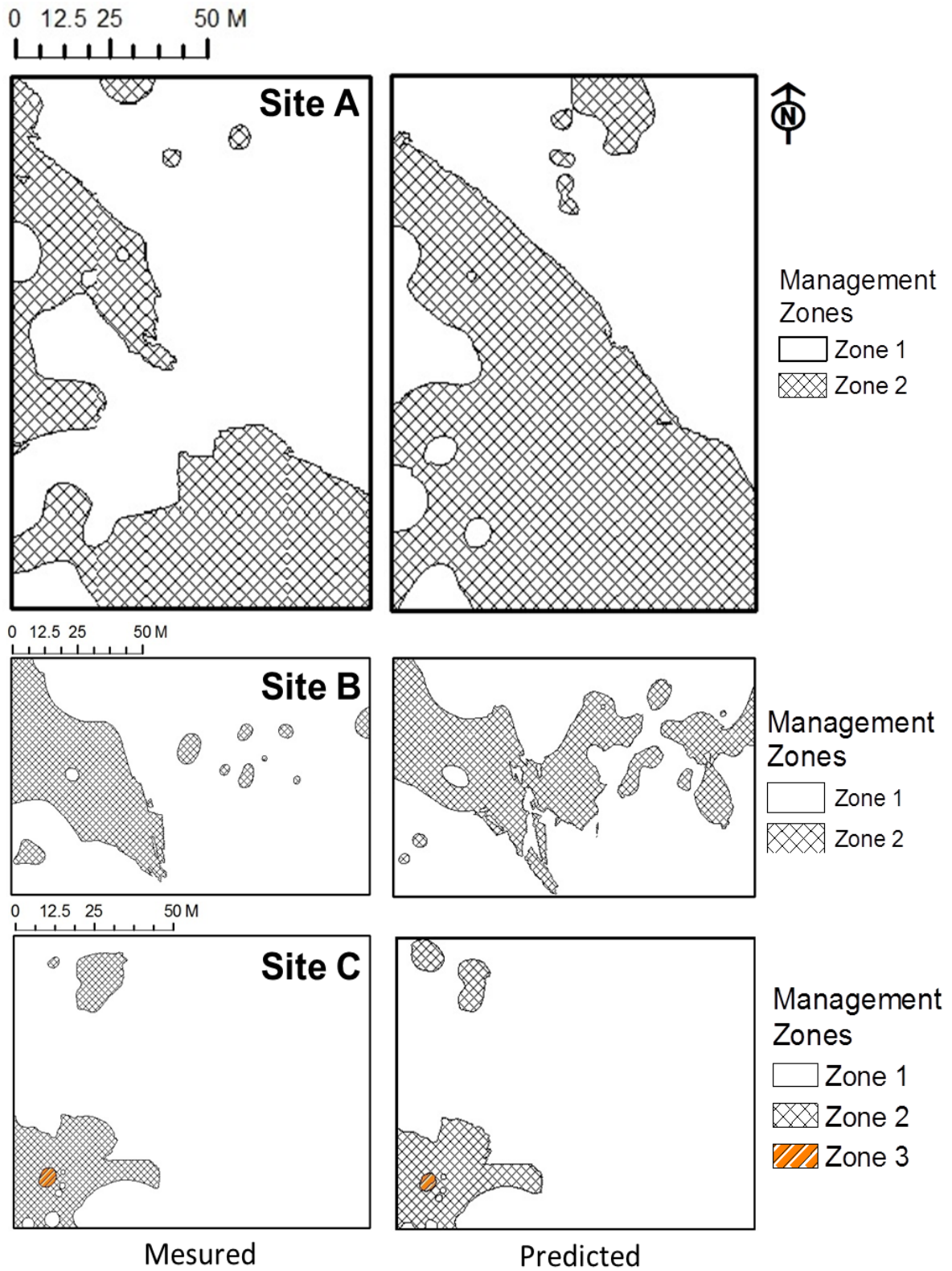


Figure 4: Comparison maps of potential management zones for three petroleum release sites in Ogoniland, Niger Delta province of Nigeria. The degree of action for site-specific risk assessment and/or remediation if any differs among the different zones.

Table 5: Result of hazard assessment of three petroleum release sites in Ogoniland, Niger Delta province of Nigeria, using Generic Assessment Criteria (GAC) established in this study. The areal extent of contamination in the sites as determined by the conventional GC–MS and innovative vis-NIR methods is compared by management zone.

| Site | MGZ | Hazard assessment rubrics     |                              |                               |   |                |
|------|-----|-------------------------------|------------------------------|-------------------------------|---|----------------|
|      |     | GAC<br>(mg kg <sup>-1</sup> ) | Risk impact                  | Action required               | Areal extent of contamination (m <sup>2</sup> ) |                |
|      |     |                               |                              |                               | GC–MS method                                    | Vis-NIR method |
| A    | 1   | < 0.24                        | Insignificant                | None                          | 7778  | 5473           |
|      | 2   | 0.24–2.40                     | Significant and acceptable   | Site-specific risk assessment | 4421  | 6726           |
| B    | 1   | < 0.24                        | Insignificant                | None                          | 9303  | 8001           |
|      | 2   | 0.24–2.40                     | Significant and acceptable   | Site-specific risk assessment | 2650  | 3952           |
| C    | 1   | < 0.24                        | Insignificant                | None                          | 9307  | 9433           |
|      | 2   | 0.24–2.40                     | Significant and acceptable   | Site-specific risk assessment | 1164  | 1043           |
|      | 3   | > 2.40                        | Significant and unacceptable | Site-specific remediation     | 25  | 20             |

GAC, generic assessment criteria; GC–MS, gas chromatography–mass spectrometry; MGZ, management zone; vis-NIR; visible and near-infrared

## **Conclusions**

This study investigated the possibility of using point vis-NIR reflectance spectroscopy for mapping of PAH and the level of toxicity in three petroleum release sites in Ogoniland in the Niger Delta province of Nigeria. Results obtained support the following conclusions. IDW soil maps of PAH and TTEC show high spatial variability of PAH and the toxicity levels across the studied sites with a near-perfect match of high and low concentrations zones between measured and predicted maps. There were non-significant ( $p < 0.05$ ) differences between measured and predicted soil maps of PAH and TTEC of the PAH mixture as the ANOVA revealed. Potential management zones also presented a near-perfect match of high and low risk zones in the studied sites between measured and predicted maps. The degree of action for site-specific risk assessment and/or remediation differs among the different zones. Only one management zone covering some 20 m<sup>2</sup> in site C requires site-specific remediation as the PAH level exceeds the action value of 2.40 mg kg<sup>-1</sup> set out as GAC for studied sites. These results suggest that vis-NIR method may be used for hazard assessment to inform site-specific risk assessment and/or remediation of petroleum release sites in the Niger Delta province of Nigeria. However, it should be emphasized that this study is nowhere close to covering the numerous petroleum release sites up and down the Niger Delta region, and have not covered every likely source of variability in all petroleum release sites in the region. The large expanse of land in the Niger Delta province may indicate large variability in soils, parent materials, colour, and other properties that have to be accounted for in the vis-NIR modelling procedure.

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