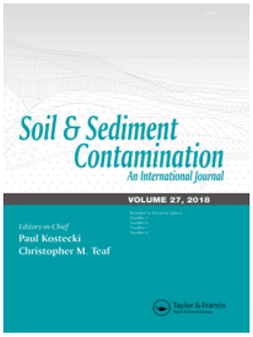

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Bioaccessibility-Based Risk Assessment of PAHs in Soils from Sites of Different Anthropogenic Activities in Lagos, Nigeria Using the Fed Organic Estimation Human Simulation Test Method

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ABSTRACT

The aim of this study was to carry out a bioaccessibility-based risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soils from sites of different anthropogenic activities in Lagos, Nigeria. Using an *in vitro* gastrointestinal model—Fed Organic Estimation Human Simulation Test method (FORESHT), the concentration of bioaccessible 16 priority US Environmental Protection Agency (USEPA) PAHs in soils were determined. Total concentration of 16 priority USEPA PAHs was also determined. The concentration range was 702–253,922 ng g^{-1} and 92–760 ng g^{-1} for total and bioaccessible PAHs, respectively. For persons involved with activities at these sites no health risks were observed, based on bioaccessibility values of PAHs. Mean daily intake of PAHs from these soils were below the oral mean daily intake threshold for PAHs in food. Also, overall estimated theoretical cancer risk (2.5×10^{-09}, 6.5×10^{-07}, 5.5×10^{-10}, 2.7×10^{-09}, 6.5×10^{-10}, 9.5×10^{-10}, 2.0×10^{-09}, and 4.1×10^{-07} for the eight sites based on their bioaccessible concentration) for exposure to PAHs in surface soils were below the health guidelines for extreme (1×10^{-04}) and normal (1×10^{-06}) exposures.

KEYWORDS

Bioaccessibility; fed organic estimation human simulation test method; polycyclic aromatic hydrocarbons; risk assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in the environment. Human activities such as refining of petroleum, burning of fossil fuels, oil spills and open incineration of waste among others have contributed significantly to the PAHs concentrations in the environment. PAHs are semivolatile, hydrophobic organic compounds covering a wide range of molecular weights. Hence they can be deposited onto soil, plant surfaces, and water bodies (Abdel-Shafy and Mansour, 2016; Lawal and Fantke, 2017; Li *et al.*, 2009). Soil PAHs, when taken up by plants roots bioaccumulate. Plant PAHs are transferred to other organisms by ingestion; often reaching concentrations that can cause toxicological effects (e.g., cellular mutations)

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(Manoli *et al.*, 2004). Human exposure to PAHs occurs via various routes such as ingestion of contaminated food, inhalation of contaminated air and dusts, or dermal contact with contaminated media (Hussein *et al.*, 2016; Kim *et al.*, 2009; Oomen *et al.*, 2003; USEPA, 2008a; USEPA, 2008b). Concentration of PAHs in soils are significantly associated with their corresponding concentrations in air, household and urban street dusts which have far reaching agricultural, environmental and human health effects. The concentration of PAHs in soil is a good indicator of the overall degree of environmental pollution (Adetunde *et al.*, 2014). Therefore, contaminant levels in soils are of concern to regulatory agencies in most countries.

Exposure to the "total" concentration of a chemical (estimated using exhaustive extraction procedures such as ultrasonication or Soxhlet) in soil is often used as the basis of risk assessments, e.g., the overall estimated theoretical cancer risk (ER), mean dietary intake (MDI), or benzo(a)pyrene equivalence dose (BaP_{eq}). This approach, however, can lead to overestimation of any risk, since only a fraction of the total concentration of the chemical is absorbed into the systemic circulation (Adetunde *et al.*, 2014; Gomez-Eyles *et al.*, 2010; Turkall *et al.*, 2009). The most important factor in predicting or assessing the health risk of lipophilic organic chemicals, such as PAHs, is the bioavailable and bioaccessible fractions (Tao *et al.*, 2009).

There have been attempts to measure both the bioavailability and bioaccessibility of pollutants using *in vivo* procedures, but these have limitations because of ethical issues, disparities between human and animal absorption systems (Intawongse and Dean, 2006). *In vitro* assessment may overcome some of these limitations. The Fed Organic Estimation Human Simulation Test (FOREShT) a standardized *in vitro* bioaccessibility test for organic pollutants in soils was developed by members of Bioaccessibility Research Group Europe (BARGE) as a follow-on from the Unified Barge Method used for inorganic contaminants (Cave *et al.*, 2010).

Knowledge of the bioavailability/bioaccessibility of a pollutant is important for risk assessments especially in risk based clean-up when a level of remediation is to be determined (Liptak and Lombardo, 1996; Zia *et al.*, 2011). The degree of any risk-based clean-up of a contaminant in the environment increases with its decreasing bioavailability. That is the limiting values are high if the contaminant is not bioassessable and low limits are used if the contaminant is bioaccessible (Rostami and Juhasz, 2001; Wan-ling *et al.*, 2011; Zia *et al.*, 2011).

Lagos, the fastest growing city in Nigeria, is one of the largest and most densely populated city in Africa. It is situated on the South-Western Coast of Nigeria and approximately 60% of Nigeria's industrial and commercial activities are situated here (Ajibola *et al.*, 2012; MoELS, 2010). Thus the land of Lagos over the years has been put to many uses including industrial. The increasing population of Lagos state has also led to an increase in the demand for land and to meet this demand reclamation of swamps, former industrial sites and dumpsites are on the rise. Hence, the need for site-specific risk assessment of such sites. Bioaccessibility is highly site and source-specific, insufficient data usually make it difficult to adequately define a value that differs from the default approach of 100%. A site-specific assessment of bioaccessibility can be undertaken to carry out risk assessment (Hansen *et al.*, 2007).

In Nigeria information on the concentration and distribution pattern of PAHs in soils within the country is lacking. This information is important for regulators in order to make valid hazard and risk assessments. We undertook a study to assess occupational exposure to PAHs via involuntary ingestion of soil from different sites around the city of Lagos (Adetunde *et al.*, 2014). Assessment was based on the total 16 PAHs on the USEPA's priority list. The aim of this follow-on study was to measure the bioaccessible PAHs at these

locations and use it to evaluate the risk associated with bioaccessible PAHs present. This preliminary information will be beneficial to Nigerian agencies who are tasked with undertaking environmental health assessments.

Material and methods

Sampling

Six subsamples of surface soil (collected at a depth 0–10 cm) were obtained from eight locations (A–H) associated with different anthropogenic activities in Lagos, Nigeria (Figure 1). Samples were collected during April, 2011 corresponding to the rainy season with ambient temperatures ranging typically between 18°C and 30°C. A composite sample for analysis from each site was made by thoroughly mixing the subsamples followed by sieving (2 mm mesh size). The eight soil samples were classified as A = dark grey sandy/clayey, B = dark grey sandy/clayey, C = dark brown sandy/silty, D = dark brown sandy/ silty, E = oily black sandy/clayey, F = sandy/gravel, G = grey sandy/silty, and H = dark black oily sandy/clayey types.

Chemicals and standards

A mixture of 16 USEPA PAHs (all 2,000 μg mL^{-1}) was obtained from Supelco (Bellefonte, PA, USA). The components of the mixture were naphthalene (NAP), 1-methylnaphthalene (1-MNAP), 2-methylnaphthalene (2-MNAP), acenaphthylene (ACY), acenaphthene (ACP),

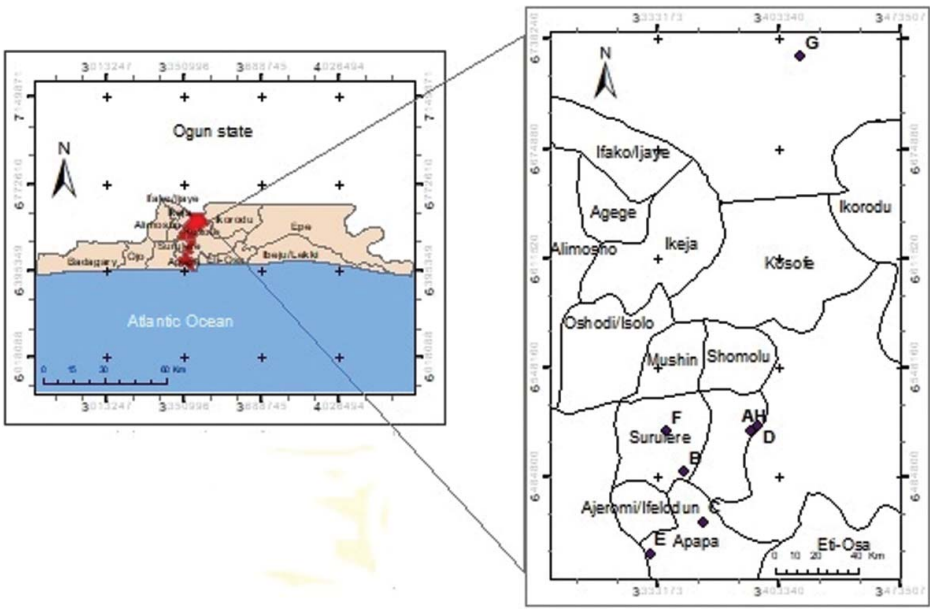

Figure 1. Map of soil sampling locations in Lagos, Nigeria. Key to locations: A = Dump site near Onike canal, Mainland area; B = Depot/loading point for black oil, Iganmu/Orile, Apapa; C = Motor spirit/kerosene depot, Apapa; D = Dump site, Akoka, Mainland area; E = Motor spirit/kerosene depot, Coconut Island; F = Roadside, central Lagos; G = Trailer park/mechanics workshop, Ibafo, Obafemi Owode; and H = Mechanics workshop, Mainland area.

fluorene (FLR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcP), dibenzo[a,h]anthracene (DaH), and benzo[g,h,i]perylene (BgP). Deuterated PAHs were used as internal standards. The deuterated internal standard solution (all 2,000 μg mL^{-1} in dichloromethane) contained d_{10}-acenaphthene, d_8-naphthalene, d_{10}-phenanthrene, d_{12}-chrysene, d_{12}-perylene, and d_4-1,4-dichlorobenzene (Supelco). The certified reference material CRM 172-100G for USEPA PAHs used for method validation was from Supelco. HPLC grade solvents were purchased from Fisher Scientific Ltd. (Loughborough, UK). Gut enzymes (α-amylase (activity: 1,000–3,000 units/mg protein), pepsin (activity: 2,500 units/mg protein), pepsin from porcine gastric mucosa (activity: 3,200–4,500 units/mg protein, pancreatin and lipase), and reagents for the bioaccessibility study where from Supelco Ltd. and Fisher Scientific Ltd.

Extraction, clean-up, and analysis of PAHs

Extraction, clean up and analysis of PAHs were carried out as in Adetunde *et al.* (2014). Briefly PAHs from 0.5 to 5 g soil and the CRM 172-100G (1 g) were extracted ultrasonically using three sequential extractions of acetone: *n*-hexane (1:1 v/v). The combined extract (25 mL) was spiked with internal standard solution (25 μL of 10 mg mL^{-1}) and concentrated under nitrogen to 500 μL. C_{18} Bond Elut (200 mg, 5 mL) cartridges were used for clean-up. Cartridges were preconditioned, concentrated extracts were loaded on them and eluted with dichloromethane: *n*-hexane (1:1 v/v, 5 mL) at a flow rate of 1 mL min^{-1}. Eluates were evaporated to dryness under nitrogen and reconstituted in *n*-hexane (1 mL). Working standard solutions were prepared daily in *n*-hexane. An Agilent GC/MS (6890N GC) equipped with split/splitless injector, with a HP-5MS UI capillary column (30 m long, 0.25 mm i.d. $\times$ 0.25 μm film thickness) connected to a mass selective detector (Agilent 5975) was used to separate and quantify the PAHs. Samples were injected (2 μL) in the splitless mode at an injection temperature of 290°C. The column oven was held at 50°C (3.2 min), raised to 150°C (30°C min^{-1}), then raised to 238°C (2°C min^{-1}), 272°C (3°C min^{-1}), and to 300°C (70°C min^{-1} and held for 2.73 min). Helium was used as carrier gas at a constant flow rate (1 mL min^{-1}). Mass spectra were acquired using electron ionization (EI) at 70 eV. Identification of PAHs was by confirmation of retention time and abundance of quantification/confirmation ions compared to authentic standards. Compounds were quantified using selective ion monitoring (SIM). The analytical samples series comprised the CRM, one standard treated similarly to the samples (to determine recoveries), a blank and six standards for calibration (Marce and Borrull, 2000; Oluseyi *et al.*, 2011; Silva *et al.*, 2011). Internal standard calibration using the response factors of individual PAHs related to the respective internal standards based on six-point calibration curve were used to quantify individual compounds in the soils.

Measurement of bioaccessible PAHs

The extraction of bioaccessible PAHs present in soil samples was undertaken by using the FOREhST method developed by BARGE (Cave *et al.*, 2010; Lorenzi *et al.*, 2012) with modifications at the clean-up step. The procedure involved three stages and was carried at 37°C utilizing an end-to-end rotator to simulate human bowel movements. At the first stage, gastrointestinal fluids namely saliva (pH: 6.8 $\pm$ 0.5), gastric (pH: 1.3 $\pm$ 0.5), duodenal (pH: 8.1 $\pm$ 0.2), and bile fluids (pH: 8.2 $\pm$ 0.2) were simulated using gut enzymes, mucin salts, and urea. At the second

stage gastrointestinal fluids were used to extract the bioaccessible PAHs. Test soil sample (0.3 g), food (organic cream porridge, from HiPP UK Ltd., Newbury, UK), water, and oil (sunflower oil, from ASDA Stores Ltd., Leeds, UK) were placed in amber bottles and extracted by adding gastrointestinal fluids one by one. To simulate the mouth, saliva was put in the food mixture for 5 min. Gastric phase was simulated by adding gastric juice to the mixture from mouth phase and allowing it to rotate for 2 h. The intestinal phase was simulated by adding duodenal and bile fluids to derived gastric phase mixture. The intestinal phase was left to mix for 2 h. Fluid ratio for saliva: gastric:duodenal:bile was 1:2:2:1 *v/v/v/v* in at the end of the test. Saponification is the last step which is an extra isolation stage that helps to facilitate the complete extraction of PAHs from the complex food and enzymatic juice mixture. The resultant mixture was centrifuged at 3,000 rpm for 5 min. An aliquot (1 mL) of supernatant was removed into a heat resistant glass vial for saponification (3 mL of KOH (5.6 M) in methanol for 1 h at 100°C).

Extraction and quantification of bioaccessible PAHs was carried out after extracts were left to cool. The extracts were diluted with water (6 mL) and cleaned-up on a preonditioned C_{18} Bond Elut SPE cartridge (200 mg, 5 mL). The elution was performed by dichloromethane (5 mL). Eluents were concentrated to dryness under nitrogen, then reconstituted in *n*-hexane (500 μL). Concentration of the bioaccessible PAHs was measured using the GC/MS-SIM method as described above. Extractions were carried out in triplicate. A blank extraction was also carried out. Spiked blanks were used for recovery studies of PAHs in the bioaccessibility study.

Risk assessment

Health-risk posed by exposure to PAHs was determined using the quantified bioaccessible PAHs. Carcinogenic potency of PAHs relative to BaP was calculated as given by Tsai *et al.* (2001) using the toxic equivalency factors (TEFs) developed by Nisbet and LaGoy (1992). Xia *et al.* (2010) and Boström *et al.* (2002) sugguested these TEF were better risk indicators. BaP_{eq} dose was calculated as follows:

BaP_{eq} dose ($\mu g\ g^{-1}$) = TEF × concentration ($\mu g\ g^{-1}$) (Huang *et al.*, 2005), Sum BaP_{eq} dose ($\mu g\ g^{-1}$) = $\sum$(TEF × concentration ($\mu g\ g^{-1}$).

Mean daily intake (MDI) concentrations, annual daily exposure dose (D_a) and estimated theoretical cancer risk (ER) from exposure to contaminants were calculated as in Adetunde *et al.* (2014), Davoli *et al.* (2010), and Lorenzi *et al.* (2011) but bioaccessible PAHs fractions were used in this calculations since it is this fraction that causes the actual risk.

Briefly, D ($\mu g\ kg^{-1}\ day^{-1}$) = [EC × SIR]/BW based on daily exposure and MDI is like D but without BW taken into account. Where BW = body weight of adult (70 kg) (ATSDR, 2005; USEPA, 2011), SIR = soil ingestion rate for adult (0.10 g day^{-1}) (ATSDR, 2005), EC = exposure concentration of PAHs ($\mu g\ g^{-1}$). The annual daily exposure dose (D_a) also called the average life time daily exposure or estimated exposure dose and is calculated from D.

D_a was estimated for workers on these sites based on 246 work days a year. This was arrived at by considering 52 weeks in a year. The 15 days of public holidays per year in Nigeria and 2 weekend days (Saturday and Sunday) a week when workers usually do not go to work were also considered. The nature of work undertaken at these sites is unstructured so leave from work was not considered in this assumption. Working hours were taken as 8 h day^{-1}. It was assumed that a person will work for 40 years (25–65 years of age) at these sites. The default value for bioaccessibility and bioavailability in calculation of D_a is one when the study on availability or accessibility study is not carried out. A value of one assumes that all of the PAHs to which the workers on

site are orally exposed to solubilizes in the guts (bioaccessibility) or is absorbed from the guts (bioavailability) (ATSDR, 2005) but since bioaccessibility was carried the default value of one was not used. AF = bioaccessibility factor, was used in calculating D_a.

The estimated theoretical cancer risk (ER) from exposure to contaminants was calculated by multiplying the estimated exposure dose by the cancer slope factor (CSF) for a suspected or known carcinogenic substance (ODH, 2011). Where ER = CSF × estimated exposure dose (mg $kg^{-1}day^{-1}$) and CSF = (7.3 (mg $kg^{-1}day^{-1})^{-1}$) (Nyarko *et al.*, 2011; ODH, 2011).

Results and discussion

Concentration of PAHs in soil

The sum of concentrations of the PAHs in the different soils ranged between 702 and 253,922 ng g^{-1}. Heavily contaminated soils are defined as those where the total concentration of PAHs is > 1,000 ng g^{-1}, contaminated soils 600–1,000 ng g^{-1}, weakly contaminated soils 200–600 ng g^{-1} and noncontaminated < 200 ng g^{-1} (Maliszewska-Kordybach, 2005). Using these definitions, soil from sites A, B, D, E, F, and H were classified as heavily contaminated, and sites C and G as contaminated (Table 1). The very high concentrations of PAHs (~254,000 ng g^{-1}) found at site E were associated with its long time use as a kerosene and petrol loading station.

Analytical performance of FORESh T procedure for bioaccessibility test

In order to test the effectiveness C_{18} Bond Elut SPE cartridges in extracting the PAHs from the saponified extract, recovery experiments were carried out. The standard USEPA PAHs mixture was spiked into the diluted saponifcation medium (such that each of the individual USEPA PAHs had a concentration of 5,000 ng mL^{-1}), applied to the SPE cartridge and then

Table 1. Concentration (total, ng g^{-1}) of 16 USEPA priority PAHs found in soil samples collected from the Lagos region, Nigeria.

Location	A	B	C	D	E	F	G	H
PAHs								
NAP	6,531	675	105	733	1,070	161	308	2,274
ACY	79.4	2,540	25.3	47.0	8,353	108	2.9	3,843
ACP	51.1	130	43.1	31.4	640	125	4.3	122
FLR	142	750	58.4	67.6	1,855	40.9	22.6	652
PHE	962	17,970	83.5	181.7	86,179	408	107	17,078
ANT	935	2900	4.8	34.08	84,837	111	56.1	3,945
FLT	63	4020	13.7	54.2	2,585	320	28.7	5,663
PYR	242	10,700	30.7	50.7	44,834	246	23.2	6,927
BaA	216	6,840	36.0	2500	2,054	232	7.4	7,053
CHR	320	20,110	77.9	15119	11,217	353	35.2	3,982
BbF	21.0	8,040	28.8	20.5	0	381	17.8	7,453
BkF	28.5	10,320	35.1	28.9	0	492	23.0	10,202
BaP	903	3,300	8.2	1,184	0	143	12.3	1,295
DaH	209	10,040	76.6	425	10,049	330	28.5	10,993
IcP	34.4	5,790	68.7	87.5	0	657	10.4	4,655
BgP	1,113	320	6.1	870	249	0	1.3	236
Sum PAHs	11,850	104,445	702	21,435	253,922	4,108	689	86,373

*Where 0 values correspond to: ≤0.03 μg g^{-1} for ACY, ≤0.04 μg g^{-1} for FLR, ≤0.02 μg g^{-1} for PHE, ≤0.03 μg g^{-1} for ANT, ≤0.04 μg g^{-1} for FLT, ≤0.03μg g^{-1} for PYR, ≤0.01 μg g^{-1} for BaA, ≤0.01 μg g^{-1}, for CHR, ≤0.0 2μg g^{-1}, for BbF, ≤0.02 μg g^{-1}, for BkF, ≤0.02 μg g^{-1}, for BaP, ≤0.04 μg g^{-1} for DaH, ≤0.01 μg g^{-1} for IcP, and ≤0.01 μg g^{-1} for BgP. For abbreviations of individual PAHs see Materials and methods section.

eluted with dichloromethane (5 mL). The results are shown in Figure 2. As expected lower recoveries were found for the more volatile compounds (i.e., naphthalene, acenaphthylene, acenaphthene, and fluorene) in this multistep clean-up method; as has been observed by other workers using the FORESHT procedure (Lorenzi *et al.*, 2012). Generally, this overall analytical method was considered acceptable; typically with accuracy (% recoveries between 70% and 130%) and precision (relative standard deviation < 30%) in accordance with USEPA criteria for the quality control and validation of analytical methods (USEPA, 1992).

Bioaccessibility of PAHs in soils

Bioaccessibility (using the *in vitro* FORESHT model) was assessed by measuring the orally accessible PAHs to the human gut due to the potentially involuntary consumption of soil by workers at the eight test sites. Many of the USEPA priority PAHs were not bioaccessible from the soil. The concentration of the bioaccessible priority USEPA PAHs that were measured is shown in Table 2. The bioaccessible fraction expressed as a percentage of the total concentration found is also given in the table. Naphthalene was the most bioaccessible of 16 USEPA PAHs present for all the soil samples. Total bioaccessible priority USEPA PAHs for the soils studied ranged between 0.1% and 41.2% of the total amount (total amount of PAHs in this study was between 689 and 104,445 ng g^{-1}). In other studies, bioaccessible PAHs varied between 10% and 60% for soils containing between 10,000 and 300,000 ng g^{-1} total PAHs (Cave *et al.*, 2010), 0.1%–1.4% (Van de Wiele *et al.*, 2004) and 1%–3% in aged crude oil contaminated soil (Kogel-Knabner *et al.*, 2000). Our study, like others (Tao *et al.*, 2009; Cave *et al.*, 2010), showed that only a small fraction of PAHs present in soil is bioaccessible to humans.

Estimation of risk based on bioaccessible PAHs

Bioavailability/bioaccessibility is site dependent and source-specific. Since insufficient data have been available on bioaccessibility, the default approach of risk assessment is 100% (total

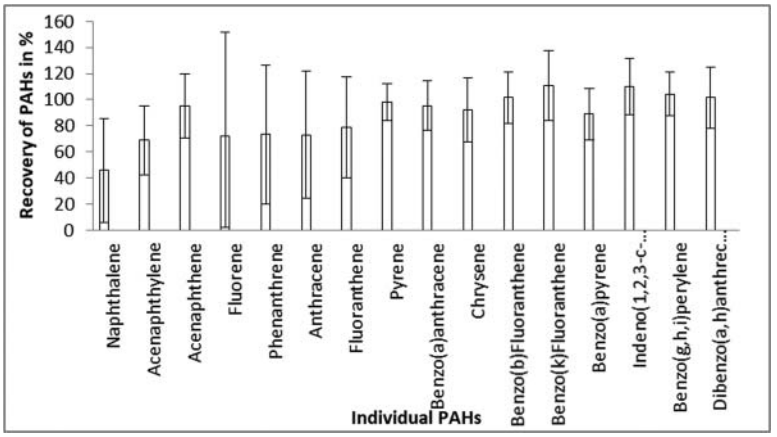

Figure 2. Percentage recovery ($n = 4$) of the 16 USEPA priority PAHs spiked (5,000 ng/mL) into the FORESHT saponification extract (1 mL) and subsequently extracted on a C18 Bond Elut solid-phase extraction cartridge and analyzed by the definitive GC/MS method.

Table 2. Concentration (ng g^{-1}) and percentage* of the bioaccessible priority USEPA PAHs found in eight contaminated soil samples ($n = 3$) collected in the Lagos area, Nigeria.

	Soil sample								
Compound	A	B	C	D	E	F	G	H	LOD
NAP	299 ± 2.3 (5%)	92.7 ± 9.15 (14%)	90.5 ± 34.5 (87%)	327 ± 24.6 (45%)	316 ± 132 (30%)	100 ± 34.5 (62%)	267 ± 34.5 (87%)	171 ± 8.0 (8%)	11.6
ANT	17.6 ± 4.0 (2%)	29.7 ± 1.2 (1%)	nd	28.5 ± 9.8 (25%)	40.1 ± 10.0 (0.1%)	28.5± 5.4 (26%)	17.0 ± 34.5 (30%)	26.2 ± 9.0 (0.7%)	1.6
BaP	nd	549 ± 3.0 (17%)	nd	nd	nd	nd	nd	273 ± 1.56 (21%)	11.4
DaH	nd	88.6 ± 55.2 (0.9%)	nd	nd	nd	nd	nd	nd	20.0
BgP	194 ± 6.4 (17%)	nd	nd	nd	nd	nd	nd	101 ± 2.8 (43%)	18.8
Sum bioaccessible PAH	511 ± 4.2 (4.3%)	760 ± 23.0 (0.7%)	91.5 ± 35.0 (12.9%)	356 ± 15.0 (1.7%)	356 ± 100 (0.1%)	129 ± 12.9 (3.1%)	284 ± 30.0 (41.2%)	570 ± 18.0 (0.9%)	

*Percentage = Concentration of bioaccessible PAH/Total concentration PAH in soil × 100, LOD = limit of detection, nd = not detected. For abbreviations of individual PAHs see Materials and methods section.

concentration of PAHs) in calculations. However, for comprehensive work (e.g., remediation, allotments among others) a site-specific assessment of bioaccessibility is required for accurate risk assessment (Hansen *et al.*, 2007). Sites in this study classified as contaminated or heavily contaminated by PAHs were assessed for the risk posed based on their degree of bioaccessibility.

BaP_{eq} of soils based on the bioaccessibility study

Sum BaP_{eq} dose at different sampling sites in Lagos, Nigeria was between 0.03 (forest soil) and 16.79 $\mu g\ g^{-1}$ (petroleum product handling site) (Adetunde *et al.*, 2014). A sum BaP_{eq} dose of 0.048 $\mu g\ g^{-1}$ was found for rural soil from Delhi, India (Agarwal, 2009), 0.892 $\mu g\ g^{-1}$ for road-side soil in Shanghai, China (Jiang *et al.*, 2009), 1.009 $\mu g\ g^{-1}$ for traffic dust in Delhi India, 0.650 $\mu g\ g^{-1}$ for surface soils in Agra, India (Masih and Taneja, 2006), and 0.124 $\mu g\ g^{-1}$ for soil from Tarragona, Spain (Nadal *et al.*, 2004). The dose values found in this study for sites with similar activities were lower than those reported by other workers. This may have been as a consequence of the approach used. Previous studies used the traditional risk assessment approach which makes use of the total concentration PAHs present in the matrices (usually derived from exhaustive extraction techniques). The sum BaP_{eq} dose calculations in our study were, based on the bioaccessible PAH(s) concentration derived from the FOREShT method, because this is the fraction that poses a health risk. The sum BaP_{eq} dose ranged from zero (sites C, F, and G) to 0.637 $\mu g\ g^{-1}$ (site B). The sites were ordered C, F, G < D, E (0.001 $\mu g\ g^{-1}$) < A (0.002 $\mu g\ g^{-1}$) < H (0.275 $\mu g\ g^{-1}$) < B for the test sites (Table 3).

Mean dietary intake of PAHs based on the bioaccessibility study

Lorenzi *et al.* (2011) estimated risk by comparing the MDI for soil with the oral mean daily intake threshold for PAHs in food (oral MDI). In our study, a comparison of MDI for the soils (based on the concentration of bioaccessible PAHs) with oral MDI for PAHs in food was also undertaken (Table 3). The results showed that all the PAHs in composite samples

Table 3. Bioaccessibility data for test soils and associated MDI (mg day^{-1}), $Da_{(BaPeq)}$ (mg kg^{-1} day^{-1}), and ER based on bioaccessible PAHs, BaP_{eq} dose ($\mu g\ g^{-1}$).

MDI	A	B	C	D	E	F	G	H	[a]Oral MDI food
NAP	0.030	0.009	0.009	0.033	0.032	0.010	0.027	0.017	7
ACY	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.14
ACP	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.98
FLR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.59
PHE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.54
ANT	0.002	0.003	0.000	0.003	0.004	0.003	0.002	0.003	0.08
FLT	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.35
PYR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.35
BaA	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.06 (0.05)[b]
CHR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.11
BbF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.11
BkF	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.09
BaP	0.000	0.055	0.000	0.000	0.000	0.000	0.000	0.027	0.11
DaH	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.1
BgP	0.019	0.000	0.000	0.000	0.000	0.000	0.000	0.010	0.04
IcP	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.06
MDI of sum bioaccessible PAHs	0.051	0.076	0.009	0.036	0.036	0.013	0.028	0.057	
Sum BaP_{eq} dose	0.002	0.637	0.000	0.001	0.001	0.000	0.000	0.275	
$Da_{(BaPeq)}$ sum bioaccessible PAHs	3.39×10^{-07}	8.83×10^{-05}	7.5×10^{-08}	3.67×10^{-07}	8.96×10^{-08}	1.3×10^{-07}	2.7×10^{-07}	5.59×10^{-05}	
ER based on bioaccessible PAHs	2.5×10^{-09}	6.5×10^{-07}	5.5×10^{-10}	2.7×10^{-09}	6.5×10^{-10}	9.5×10^{-10}	2.0×10^{-09}	4.1×10^{-07}	

[a]Oral mean daily intake threshold for PAHs in food (oral MDI) (Nathaniel et al. 2009: cited by Lorenzi et al. 2011); [b]Alternative measure of oral MDI (Falco et al. 2003). A value of 0.000 $\mu g\ g^{-1}$ MDI for individual PAH, means that the concentration of the bioaccessible PAH less than or equal to the LOD value in Table 3. Benzo(a)pyrene equivalence dose (BaP_{eq}), mean daily intake (MDI), annual daily exposure dose base on benzo(a)pyrene equivalence dose $Da_{(BaPeq)}$. For abbreviations of individual PAHs see Materials and methods section.

were less than the oral MDI for PAHs in food. This indicates that was no risk associated with activities on these sites, based on the MDI risk assessment approach.

Cancer estimate of PAHs based on the bioaccessibility data

The ER results given in Table 3 were based on the bioaccessible PAHs. In this study, the estimated total annual daily intake of PAHs will be associated with an ER of 2.5×10^{-09}, 6.5×10^{-07}, 5.5×10^{-10}, 2.7×10^{-09}, 6.5×10^{-10}, 9.5×10^{-10}, 2.0×10^{-09}, and 4.1×10^{-07} for soils A–H, respectively; being based on a 70 kg adult, exposed at work for 40 years (aged between 25 and 65 years). The overall estimated theoretical cancer risks from occupational exposure to surface soil based on bioaccessible oral ingestion were all lower than both the target risk of 1×10^{-06} for normal exposure and the 1×10^{-04} for extreme exposure all the test sites. The total ER combining the childhood (5 years) and adult (40 years) exposure periods was 2.3×10^{-05} based on sum PAHs (ODH, 2011). ER values for an adult working at the on these sites were between 7.3×10^{-07} and 1.2×10^{-04} according to Adetunde *et al.* (2014). However, these values were based on the concentration of total 16 priority PAHs in soil. Using the concentrations of bioaccessible PAHs, the fraction that causes the actual harm, the risk associated with sites in this study where lower (between 4.1×10^{-07} and 9.5×10^{-10} as shown in Table 3).

Conclusion

This study assessed potential health risk associated with the bioassessable PAHs of soils impacted by different anthropogenic activities in the Lagos region of Nigeria. Concentrations of the 16 priority USEPA PAHs were measured and FOREShT an *in vitro* gastrointestinal model was used to extract the bioaccessible PAHs in soils for quantification. Results indicated that though soils from sites were classified as heavily contaminated or contaminated, based on their total concentration of PAHs, only a percentage (0.7%–41.2%) was bioaccessible for uptake by humans. MDI results showed that no risk was associated with the bioaccessible fraction of PAHs. The overall cancer risk from exposure to surface soil based on oral ingestion was not above the approved health guidelines of 1 in 10,000 for extreme exposures. The concentration of bioaccessible PAHs found in our study was used to carry out a risk assessment of some soils in the Lagos region of Nigeria. This type of approach should now always be used by regulatory agencies when undertaking any comprehensive risk assessment of any contaminated land. It must be noted, however, that values derived by this approach only provide a theoretical estimate of risk. Since the actual risk of cancer is unknown and it could be as low as zero. PAHs are lipophilic and can accumulate in the body, care should be exercised at all times to ensure minimal exposure from all routes to these to these potentially harmful substances.

References

Abdel-Shafy, H. I., and Mansour, S. M. 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Petrol.* **25**, 107–123. doi:10.1016/j.ejpe.2015.03.011.

Adetunde, O. T., Mills, G. A., Olayinka, K. O., and Alo, B. I. 2014. Assessment of occupational exposure to polycyclic aromatic hydrocarbons via involuntary ingestion of soil from contaminated soils in Lagos, Nigeria. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **49**, 1661–1671.doi:10.1080/10934529.2014.951223.

Agarwal, T. 2009. Concentration level, pattern and toxic potential of PAHs in traffic soil of Delhi, India. J. Hazard. Mater. 171, 894–900.

Ajibola, M. O., Adewale, B. A., and Ijasan, K. C. 2012. Effects of urbanisation on Lagos Wetlands. *Intern. J. Buss. Soc. Sci.* **3**, 310–318.

ATSDR. 2005. Public health assessment guidance manual Appendix G: calculating exposure doses (2005 Update). In: Registry Aftsad, editor. USA, ATSDR.

Boström, C. E., Gerde, P., Hanberg, A., Jernström, B., Johansson, C., Kyrklund, T., Rannug, A., Törnqvist, M., Victorin, K., and Westerholm, R. 2002. Cancer Risk Assessment, Indicators, and Guidelines for Polycyclic Aromatic Hydrocarbons in the Ambient Air Environ. Health Perspect. 1101, 451–488.

Cave, M. R., Wragg, J., Harrison, I., Vane, C. H., Wiele, T. V., and Groeve E. D. 2010. Comparison of batch mode and dynamic physiologically based bioaccessibility tests for PAHs in soil samples. *Environ. Sci. Technol.* **44**, 2654–2660. doi:10.1021/es903258v.

Gomez-Eyles, J. L., Collins, C. D., and Hodson, M. E. 2010. Relative proportions of polycyclic aromatic hydrocarbons differ between accumulation bioassays and chemical methods to predict bioavailability. *Environ. Pollut.* **158**, 278–284. doi:10.1016/j.envpol.2009.07.012.

Hansen, J. B., Oomen, A., Edelgaard, I., and Gron, C. 2007. Oral bioaccessiblity and leaching: Tests for soil risk assessment. *Engin. Life Sci.* **7**, 170–176.doi:10.1002/elsc.200620174.

Intawongse, M., and Dean, J. R. 2006. Uptake of heavy metals by vegetable plants grown on contaminated soil and their bioavailability in the human gastrointestinal tract. *Food Addit. Contamin.* **23**, 36–48. doi:10.1080/02652030500387554.

Jiang, Y. F., Wang, X.T., Wang, F., Jia, Y., Wu, M. H., Sheng, G. Y., and Fu, J. M. 2009. Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China. Chemosphere, 75, 1112–1118.

Kim, D. W., Kim, S. K., and Lee, D. S. 2009. Relationship of pyrogenic polycyclic aromatic hydrocarbons contamination among environmental solid media. *J. Environ. Monit.* **11**, 1244–1252. doi:10.1039/b900620f.

Kogel-Knabner, I., Totsche, K. U., and Raber, B. J. 2000. Desorption of polycyclic aromatic hydrocarbons from soil in the presence of dissolved organic effect of solution composition and aging. *J. Environ. Qual.* **29**, 906–916.

Lawal, A. T., and Fantke, P. 2017. Polycyclic aromatic hydrocarbons. A review. *Cogent Environ. Sci.* 3, 1–89. doi:10.1080/23311843.2017.1339841. doi:10.1080/23311843.2017.1339841.

Liptak, J. F., and Lombardo, G. 1996. The development of chemical-specific, risk-based soil cleanup guidelines results in timely and cost-effective remediation. *J. Soil Contam.* **5**, 1–12. doi:10.1080/15320389609383514.

Lorenzi, D., Entwistle, J. A., Cave, M., and Dean, J. R. 2011. Determination of polycyclic aromatic hydrocarbons in urban street dust: Implications for human health. *Chemosphere* **83**, 970–977. doi:10.1016/j.chemosphere.2011.02.020.

Lorenzi, D., Entwistle, J., Cave, M., Wragg, J., and Dean, J. R. 2012. The application of an in vitro gastrointestinal extraction to assess the oral bioaccessibility of polycyclic aromatic hydrocarbons in soils from a former industrial site. *Anal. Chim. Acta* **735**, 54–61. doi:10.1016/j.aca.2012.05.030.

Maliszewska-Kordybach, B. 2005. Dissipation of polycyclic aromatic hydrocarbons in freshly contaminated soils—The effect of soil physicochemical properties and ageing. *Water Air Soil Pollut.* **168**, 113–128. doi:10.1007/s11270-005-0940-3.

Manoli, E., Kouras, A., and Samara, C. 2004. Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. *Chemosphere* **56**, 867–878. doi:10.1016/j.chemosphere.2004.03.013.

Marce, R. M., and Borrull, F. 2000. Solid-phase extraction of polycyclic aromatic compounds. *J. Chromatogr.* **885**, 273–290. doi:10.1016/S0021-9673(00)00428-3.

Masih, A. and Taneja, A. 2006. Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi-arid region of India. Chemosphere 65, 449–456.

MoELS. 2010. State of the Environment Report. In: Lagos: Ministry of the Environment, Lagos State.

Nadal, M., Schuhmacher, M., and Domingo, J. L. 2004. Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. Environ. Pollut. 132, 1–11.

Nisbet, I. C. T., and Lagoy, P. K. 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

Nyarko, E., Botwe, B. O., and Klubi, E. 2011. Polycyclic aromatic hydrocarbons (PAHs) levels in two commercially important fish species from the coastal waters of Ghana and their carcinogenic health risks. West African J. of App. Ecol. 19, 53–66.

ODH. 2011. Evaluation of Ohio EPA soil sampling in support of the Clyde and Eastern Sandusky County childhood cancer investigation. Clyde Sandusky County, Ohio. Ohio Department of Health, US Ohio. p. 32.

Oluseyi, T., Olayinka, K., Alo, B., and Smith, R. M. 2011. Improved analytical extraction and clean-up techniques for the determination of PAHs in contaminated soil samples. *Intern. J. Environ. Resour.* **5**, 681–690.

Oomen, A. G., Rompelberg, C. J. M., Bruil, M. A., Dobbe, C. J. G., Pereboom, D. P. K. H., and Sips, A. J. A. M. 2003. Development of an in vitro digestion model for estimating the bioaccessibility of soil contaminants. *Arch. Environ. Contaminat. Toxicol.* **44**, 281–287. doi:10.1007/s00244-002-1278-0.

Rostami, I., and Juhasz, A. 2011. Assessment of persistent organic pollutant (POP) bioavailability and bioaccessibility for human health exposure assessment: A Critical Review. *Crit. Rev. Environ. Sci. Technol.* **41**, 623–656.doi:10.1080/10643380903044178.

Silva, B. O., Adetunde, O. T., Oluseyi, T. O., Olayinka, K. O., and Alo, B. I. 2011. Comparison of some extraction methods and clean-up procedures for the 16 priority US EPA PAHs. *J. Sci. Res. Develop.* **13**, 129–143.

Tao, Y., Zhang, S., Wang, Z., and Christie, P. 2009. Predicting bioavailability of PAHs in field-contaminated soils by passive sampling with triolein embedded cellulose acetate membranes. *Environ. Pollut.* **157**, 545–551. doi:10.1016/j.envpol.2008.09.030.

Tsai, P. J., Shieh, H. Y., Lee, W. J., and Lai, S. O. 2001. Health-risk assessment for workers exposed to polycyclic aromatic hydrocarbons (PAHs) in a carbon black manufacturing industry. *Sci. Total Environ.* **278**, 137–150. doi:10.1016/S0048-9697(01)00643-X.

Turkall, R. M., Skowronski, G. A., and Abdel-Rahman, M. S. 2009. Effects of soil matrix and aging on the dermal bioavailability of polycyclic aromatic hydrocarbons in the soil. *Intern. J. Soil, Sediment Water.* **2**, 1–9.

USEPA. 1992. Guidance for methods development and methods valiation for the Resource Conservation and Recovery Act (RCRA) programme. In: *methods TOoRCaRsOmoE-aa, editor. 2014*, pp. 32. Washington, D.C., US Environmental Protection Agency.

USEPA. 2008a. *Child-specific exposure factors handbook. EPA/600/R-06/096F.*

USEPA. 2008b. Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Lead in Soil In: Agency USEP, editor, USA.

Van de Wiele, T. R., Verstraete, W., and Siciliano, S. D. 2004. Polycyclic aromatic hydrocarbon release from a soil matrix in the in vitro gastrointestinal tract. *J. Environ. Qual.* **33**, 1343–1353. doi:10.2134/jeq2004.1343.

Wan-ling, H., Xiao-li, L., Jia-li, S., Xiao, Y., and Ji-liang, Z. 2011. Effects of cadmium pollution in soil on cadmium accumulation of cabbage and its biological effects on human intestinal cells line. *Procedia Eng.* **18**, 157–161. doi:10.1016/j.proeng.2011.11.025.

Xia, Z., Duan, X., Qiu, W., Liu, D., Wang, B., Tao, S., Jiang, Q., Lu, B., Song, Y., and Hu, X. 2010. Health risk assessment on dietary exposure to polycyclic aromatic hydrocarbons (PAHs) in Taiwan, China. *Sci. Total Environ.* **408**, 5331–5337.

Zia, M. H., Codling, E. E., Scheckel, K. G., and Chaney, R. L. 2011. In vitro and in vivo approaches for the measurement of oral bioavailability of lead (Pb) in contaminated soils: A review. *Environ. Pollut.* **159**, 2320–2327. doi:10.1016/j.envpol.2011.04.043.