

**Assessment of occupational exposure to Polycyclic Aromatic Hydrocarbons via  
involuntary ingestion of soil from contaminated soils in Lagos, Nigeria**

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**Abstract**

Soils from twelve sites in Lagos area, Nigeria impacted by anthropogenic activities were extracted by ultrasonication and analysed for the concentration of 16 priority polycyclic aromatic hydrocarbons (PAHs) by gas chromatograph-mass spectrometer (GC-MS). The concentration of the sum of PAHs ranged from 0.2 to 254µg/g at these sites. The sum benzo[a]pyrene-equivalent dose (BaP<sub>eq</sub>) at the sites ranged from 0.0 (K, forest soil) to 16.7 µg/g (C, the lubricating oil depot soil). Mean daily intake (MDI) for the composite soils

samples when compared that of food revealed that some of the individual PAH in samples from sites A (Dump site), C (Depot and loading point for used for black oil), F (Dump site), G (petroleum depot), H (Roadside ) and L (Car park ) exceeded the recommended the recommended MDI threshold for food, indicating some risk associated with activities on these sites based on this ingestion estimate exceeded value.  $8.2 \times 10^{-6}$ ,  $7.1 \times 10^{-7}$ ,  $1.2 \times 10^{-4}$ ,  $4.9 \times 10^{-7}$ ,  $7.3 \times 10^{-7}$ ,  $1.4 \times 10^{-5}$ ,  $7.9 \times 10^{-5}$ ,  $4.6 \times 10^{-6}$ ,  $3.4 \times 10^{-7}$ ,  $2.4 \times 10^{-7}$ ,  $2.2 \times 10^{-7}$  and  $1.1 \times 10^{-4}$  estimated theoretical cancer risk (ER) for an adult with a body weight of 70 kg working on sites were composite soil samples A, B, C, D, E, F, G, H, I, J, K and L respectively were sampled. The ER from occupational exposure to surface soil based on oral ingestion for some were higher than the target risk of  $1 \times 10^{-6}$  for normal exposure but were all less than the  $1 \times 10^{-4}$  for extreme exposure for most of the sites except for site C and L. The differences in concentration and risk were related to the different activities (e.g. handling of petroleum products, open burning, bush burning) undertaken at these locations. However, it should be noted here that the resultant risk could be overestimated, since these calculations were based on an exhaustive extraction technique which may be different from uptake by the human guts (bioavailability study).

**Key words:** Polycyclic aromatic hydrocarbons; PAHs; Risk assessment; soils; Anthropogenic activities.

## **Introduction**

Polycyclic aromatic hydrocarbons (PAHs) are compounds known for their carcinogenic and mutagenic properties hence potentially hazardous to human health. They are ubiquitous environmental contaminants present in many urban soils. Parent PAHs are unsubstituted compounds, but other substituted forms (e.g. alkyl PAHs) also exist with varying chemical structures.<sup>[1]</sup> These are mainly derived from pyrogenic and petrogenic sources. The United States Environmental Protection Agency (USEPA) has identified 16 unsubstituted PAHs as priority PAHs. Industrial activities (e.g. incomplete burning of petroleum products, coal and garbage), use of internal combustion engines, barbequing of foodstuffs and burning tobacco can lead to the formation of PAHs.<sup>[2][3]</sup> Many urban waste sites are a concentrated source of PAHs on a local scale.

Humans are exposed to PAHs by direct inhalation of contaminated air and dusts, ingestion of contaminated food, hand-to-mouth activities and through direct dermal contact with contaminated media or soils.<sup>[3]</sup> High concentrations of PAHs in soil are significantly associated with the correspondingly high concentrations in air and household and urban street dusts.<sup>[4][5]</sup> The concentration of PAHs in soil is therefore a good indicator of the degree of environmental pollution by various human activities.<sup>[6]</sup>

There are concerns over high levels of exposure to PAHs amongst people living or working in the vicinity of urban waste sites.<sup>[7][8]</sup> The cancer potential for PAHs has been measured for selected soils/sediments and used as an indicator in health risk assessments. Estimated theoretically, cancer risk is defined as the number of additional cases of cancer in a population due to exposure to a toxic substance during a lifetime of exposure. Another health risk measure for these substances is the  $BaP_{eq}$  derived from the toxic equivalent factor (TEF) used for estimating the carcinogenic potency of PAH.<sup>[8][9]</sup> Benzo[a]pyrene (BaP) is the best characterized, most potent carcinogenic PAH compounds and is the only PAH for which its

toxicological potency factor is labelled. <sup>[10][11]</sup> TEF is a term used to express the toxicities of other PAHs determined in relation to BaP. The TEF for calculating BaP<sub>eq</sub> and determining potential health risks for PAHs with the characteristic “bay-K region”; a structural distinction that defers carcinogenic properties to BaP and the other carcinogenic PAHs has been developed by United States Environment Protection Agency (USEPA),<sup>[11]</sup> Another method for the estimation of risk is ER, which is based on a reasonable maximum exposure to PAHs. Davoli, et al. <sup>[12]</sup> assessed the health risks for people living near landfills, based on a population exposure to dioxins, furans and PAHs and their results showed that cancer risk derived were largely below the values accepted from agencies such as World Health Organisation (WHO) and USEPA. The exposure route for PAHs from soil to man includes dermal, inhalation and ingestion. However Zhong, et al.<sup>[13]</sup> found the ingestion was the primary route of exposure. Soil ingestion can occur by the inadvertent ingestion of soil on hands or food items, mouthing of objects, or through intentional ingestion of soil. The health risks associated with ingestion of toxic chemicals can be estimated. <sup>[14]</sup>

Lagos, situated on the south-western coast of Nigeria, is one of the largest and most densely populated cities in Africa. <sup>[15]</sup> Approximately 60% of Nigeria’s industrial and commercial activities are situated here. <sup>[16]</sup> In view of this, several workers have measured pollution in the city caused by trace metals and priority PAHs. <sup>[15][17]</sup> but not their risk assessment. We undertook a study to measure concentrations of (16) priority USEPA in 12 composite soils collected in Lagos at sites with different anthropogenic activities. We used these data to estimate the occupational health risks associated with people working on these sites.

## **Materials and methods**

### ***Sampling***

Composite samples of surface soils (depth 0-10 cm) were obtained in Lagos, Nigeria from locations with different anthropogenic activities (Table 1).

### ***Physico-chemical analysis of soils***

Particle size distribution of soils (A to L) was determined by a wet sieving and sedimentation technique.<sup>[14] [18]</sup> The pH of soil was determined after adding 0.01 mol/L CaCl<sub>2</sub> (10 mL) to 5 g of soil. Total organic carbon and Total Organic matter were determined by the Walkley-Black titrimetric method.<sup>[7]</sup> Oil and grease were determined gravimetrically after ultrasonic extraction (acetone: *n*-hexane, 50:50 v/v).<sup>[19]</sup> The concentration of analyte in blanks was subtracted from field samples.

### ***Chemicals and Standards***

A standard mixture of 16 USEPA priority PAHs and 2 alkyl PAHs (2000 µg/mL) was obtained from Supelco (Bellefonte, PA, USA). It contained naphthalene (NAP), 1-methylnaphthalene (1-MNAP), 2-methylnaphthalene (2-MNAP), acenaphthylene (ACY), acenaphthene (ACP), 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). The deuterated internal standard solution mixture (2000 µg/mL in dichloromethane) contained d<sub>10</sub>-acenaphthene, d<sub>8</sub>-naphthalene, d<sub>10</sub>-phenanthrene, d<sub>12</sub>-chrysene, d<sub>12</sub>-perylene and d<sub>4</sub>-1,4-dichlorobenzene (Supelco). The certified reference materials, CRM 172-100G and CRM115-100G for USEPA PAHs were used for method validation were from Supelco Analytical (Bellefonte, USA). All solvents were of HPLC grade or better and purchased from Fisher Scientific Ltd. (Loughborough, UK).

### ***Extraction and clean-up of PAHs in soil***

PAHs from soil and CRM172 (0.5-5 g) were extracted ultrasonically using three sequential extractions (10 mL, 3 mL and 2 mL) of acetone:*n*-hexane (1:1 v/v) <sup>[20]</sup>. The combined extract was spiked with internal standard solution (25 µL of 10µg/mL) and concentrated under nitrogen to 500 µL. The concentrated extract was cleaned-up using preconditioned solid-phase extraction (SPE) cartridges (200 mg C<sub>18</sub>, Bond Elute, in 5 mL cartridge). The cartridges were pre-conditioned with dichloromethane (DCM), methanol, methanol:water (1:1 v/v), water, acetone:*n*-hexane mixture:water ((1:1):1 v/v) and finally acetone:*n*-hexane (1:1 v/v) sequentially. The extract was then loaded and eluted with DCM:*n*-hexane (1:1 v/v, 5 mL) at a flow rate of 1mL/min. Eluates were evaporated to dryness under nitrogen and reconstituted in *n*-hexane (1 mL). Care was taken so that the cartridge did not dry during the conditioning and loading of the sample extract. <sup>[21][22]</sup> A sample series was made up of CRM, six standards for calibration and use of r<sup>2</sup> value is used for assessing linearity and one standard that has been treated similarly to the samples (recovery determination).

### ***Analysis of PAHs***

All working standard solutions were prepared daily in *n*-hexane. An Agilent GC/MS (6890N GC) equipped with split/splitless injector, fitted with a HP-5MS UI capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness) was 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 mins), raised to 150°C (30°C/min), then raised to 238°C (2°C/min), 272°C (3 °C/min) and to 300°C (70°C/min and held for 2.73 mins). Helium was used as a carrier gas at a constant flow rate of 1 mL/min. Mass spectra was acquired using electron ionization (EI) at 70 eV.

Identification and analysis of PAHs in soils were carried out by confirmation of retention time, abundance of quantification/confirmation ions compared to authentic standards. All the identified compounds quantified using selective ion monitoring (SIM). For quality control, procedural recoveries for certified reference material were quantified using the response factors related to the respective internal standards based on six-point calibration curve for individual compounds.

### ***Health risk analysis***

Health-risk posed by the exposure of 16 USEPA priority PAHs is based on carcinogenic potency relative to BaP<sup>[23]</sup>. The TEFs developed by Nisbet and LaGoy<sup>[24]</sup> were used in this study because, they were suggested to be a better set of indicators by Xia et al<sup>[25]</sup> and Boström, et al.<sup>[26]</sup> BaP<sub>eq</sub> dose was calculated as follows:

$$\text{BaP}_{\text{eq}} (\mu\text{g/g}) = \text{TEF} \times \text{concentration} (\mu\text{g/g})^{[10]}$$

$$\sum \text{BaP}_{\text{eq}} (\mu\text{g/g}) = \sum(\text{TEF} \times \text{concentration} (\mu\text{g/g}))$$

The estimated dose ingested daily (D) is another risk assessment approach based on an estimation of PAHs consumed due to involuntary consumption of soils. <sup>[12]</sup> Here D of PAH ingested was estimated as

$$D (\mu\text{g/kg/day}) = [\text{EC} \times \text{SIR}]/\text{BW} \quad \text{based on daily exposure}$$

Where BW= body weight of adult (70 kg) <sup>[27] [28]</sup>

SIR = soil ingestion rate for adult (0.10 g/day), <sup>[27]</sup> EC = exposure concentration of PAHs

( $\mu\text{g/g}$ ). The annual daily exposure dose ( $D_a$ ) also called the average life time daily exposure or estimated exposure dose and is calculated from D by introducing the **EF (exposure frequency)** value.

$$D_a (\mu\text{gkg}^{-1}\text{day}^{-1}) = [\text{EC} \times \text{SIR} \times \text{EF}]/\text{BW} \quad [27] [29]$$

EF was estimated for workers on these sites based on as 246 days a year and 52 weeks. This was arrived at after considering 15 public holidays and 2 weekend days in a week when workers usually do not go to work. 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. It was assumed that a person will work for 40 years (25-65 years of age) at these sites.

The estimated theoretical cancer risk (ER) from exposure to contaminants was calculated by multiplying the estimated exposure dose (base on B (a)P eq concentration) by the cancer slope factor (CSF) for a suspected or known carcinogenic substance. <sup>[29]</sup> Ohio Department of Health, <sup>[29]</sup> Fromberg, et al. <sup>[30]</sup> and Ding, et al. <sup>[31]</sup> estimated the cancer risk using the B(a)P eq concentration to calculate  $D_a$  and then multiplied it by the Cancer Slope Factor of 7.3 ( $\text{mgkg}^{-1}\text{day}^{-1}$ )<sup>-1</sup>.



$$ER = CSF \times \text{Dose (mg/kg/day)}^{[29]}$$

$$CSF = (7.3 \text{ (mgkg}^{-1}\text{day}^{-1})^{-1})^{[29] [32]}$$

ER of  $1 \times 10^{-5}$ , for example, refers to one additional case of cancer per one hundred thousand individuals.<sup>[29]</sup> An ER of less than  $1 \times 10^{-6}$  population exposure is typically considered as negligible under normal exposure while  $1 \times 10^{-4}$ , is considered as an extreme exposure.<sup>[33,34]</sup>

## **Results and discussion**

### ***Concentration and type of PAHs in soils***

The extraction and GC-MS method used was able to separate all of the standard PAHs. The calibration curves were linear and gave good regression ( $r^2$ ) values of 0.98 or higher for all the individual PAHs. The physico-chemical properties of the soils are given Table 2. Tables 3, show the concentrations of PAHs found in soil samples collected from sites with anthropogenic activities.

The sum concentration of the measurable PAHs in the different soils ranged from 0.2-254 $\mu\text{g/g}$  and is as shown in Table 3. These concentrations are similar to those reported by other studies undertaken at related field sites elsewhere in the world (Table 4). Wang, et al.<sup>[45]</sup> reported that the PAHs concentration in surface dusts from various sources varied greatly and was attributed to the anthropogenic activities undertaken in the areas. In this study, the site with the highest concentration of sum PAH was found at the fuel depot on Coconut Lagos (site G). Here sampling took place where the transfer of petroleum products between tanks to kegs took place. A stench of petroleum was evident during sampling. Based on the concentrations of the sum PAHs (Table 3) the order of variation was: Coconut fuel depot (G)

> black oil depot Orile (C) > mechanics workshop Lagos (L) > large dump site in Akoka (F) > small dump site in Onike (A) > a road side near a dump site (H) > fuel depot area Apapa (E) > trailer park Ibafo (I) > farm land in Lagos (B) > a road side (D) > car park Akoka (J) > forest soil (K). PAHs are known to be constituents of petroleum and its product,<sup>[45] [46] [47]</sup> is probably the reason why locations G, C and L had higher concentrations compared to the other sites. The activities at these sites were such that a lot of petroleum related products like engine oil, kerosene, and gasoline were used and spilt to the bare floor. At the mechanics workshop, where soil L was sampled, during servicing of cars, engine oil was spilled on the bare soil as there was no structured way of disposing the used oil.

Sample C was a composite sample from a used oil depot where these dirty oil (black in colour) was stored, often in leaky drums. Sample E though sourced from a location similar to G in appearance, where petroleum products were used and handled, the total PAHs was low. This may be explained by the fact that this place is sparingly used for this purpose because it was an illegal location for sales and buying of petroleum products located outside the depot. Samples A and F are both dump sites samples. The dump site where sample F was sourced is an older and bigger dump site. The sum PAHs concentration values for these dump sites were 11.9 $\mu\text{g/g}$  and 21.4 $\mu\text{g/g}$  respectively. These values were higher than the values for sum PAHs concentration of 4.3  $\mu\text{g/g}$ , 5.9  $\mu\text{g/g}$  and 2.5  $\mu\text{g/g}$  found by Nduka, et al.<sup>[48]</sup> for other dump sites. In another study of illegal waste dumps and its surroundings, values that ranged from 21-59  $\mu\text{g/g}$  were recorded for sum PAHs.<sup>[49]</sup> The method of waste reduction on the dump sites in this study was open burning. The two vehicle park samples (J and I) had sum PAHs of 0.2  $\mu\text{g/g}$  and 0.7  $\mu\text{g/g}$  respectively. The difference in total PAHs may be due to the type of vehicular activities. At site J, the vehicular activities were made up of small vehicles usually fuelled with gasoline unlike site I where the vehicular activities involved bigger sized vehicles like trailers and lorries usually fuelled with diesel. Emissions from diesel engines are

more visible than emissions from petrol engines this due to the nature of combustion in diesel engines due to the high amount particulate emissions from a diesel engine<sup>[50]</sup> and PAHs because of their strong affinity for organic carbon in particulate matter are known to preferentially adsorb onto particulates which finally accumulate in the sediments or soils.<sup>[51]</sup><sup>[52]</sup> Pohjola, et al.<sup>[53]</sup> found large differences in content of 14 individual PAHs in diesel and gasoline exhaust sample extracts studied, showing higher concentration of 14 PAHs and BaP in diesel than in gasoline extracts. The values we obtained are similar to previous studies (Table 4). Sample H and D were both road soil samples but showed a wide variation in total PAHs concentration. Sample D sourced from a main road had lower concentration of total PAHs compared to H. This may be explained by its proximity to a dump site where open burning is employed as a garbage reduction technique.

The sum concentration for the 2-3 ring PAHs in the samples were generally higher compared to the sums of concentration of the 4, 5 and 6 ringed PAHs (higher sum of 4-6 ring PAHs indicates a pyrogenic source)<sup>[54]</sup> except for samples B, H, F, L (Table 3). These showed the dominance of petrogenic contribution (since petrogenic PAHs are usually dominated by lower ringed systems)<sup>[46] [55]</sup> as source for all the samples except for samples B, H, F and L (where pyrogenic PAHs dominated). The petrogenic source can be traced to the activities on these sites. The 4 and 5 ringed PAHs (pyrogenic PAHs) which dominated sample B can be traced to the type of farming practice currently practiced 'bush burning' before tilling the soil for planting. Fires and smokes, from burning of vegetation in agricultural process, and bushfires releases of large amount of PAHs into the environment.<sup>[4] [56] [57]</sup> Roadside soil (H) which was predominated by pyrogenic PAHs may be due to combustion from exhaust of vehicles plying on the road<sup>[55]</sup> and its proximity to a dump site. The predominance of pyrogenic PAHs in sample F may be due to garbage open burning. Sample A, from a dump site where open burning was also employed, had it dominant PAHs as being petrolytic. This

may be due to the type of waste on this site since it was a dump site for a mechanics workshop where some oils and car parts were disposed.

### ***Classification of soil samples base on level of contamination***

The 0.2-254  $\mu\text{g/g}$  range for sum PAHs found in this study, shows that anthropogenic activities contributed to PAHs present in the soils sampled since the 0.00-0.01  $\mu\text{g/g}$  range typical of endogenous sum PAHs in soil ( resulting from plant synthesis and natural fires) was exceeded as suggested by Edward<sup>[58]</sup> Wilcke<sup>[59]</sup> Abbas and Barck.<sup>[60]</sup>

Maliszewska-Kordybach, et al.<sup>[61]</sup> and Yang, et al.<sup>[8]</sup> classified contamination levels in soils based on sum PAHs. Heavily contaminated were soils with sum PAHs greater than 1.00  $\mu\text{g/g}$ , contaminated soils between 0.60-1.00  $\mu\text{g/g}$ , weakly contaminated soils between 0.60-0.20  $\mu\text{g/g}$  and not contaminated soils below 0.20  $\mu\text{g/g}$ . Based on their classification, results (Table 3) showed that soils from sites A, C, F, G, H, L were heavily contaminated, E and I were contaminated and B, D, J and K were weakly contaminated.

Since there is no official soil standard for PAHs in soil and sediment in Nigeria, the standard the 'New Dutch List' was used in the study. The 'New Dutch List' has a target value of 1.0  $\mu\text{g/g}$  and an intervention value of 40.0 $\mu\text{g/g}$  for the sum of 10 PAHs (summation of the amount of NAP, PHE, ANT, FLA, BaA, CHR, BkF, BaP, IcP and BgP) (sum PAHs<sub>10</sub>).<sup>[55]</sup><sup>[62]</sup> The target value indicates the benchmark for quality on the long-term. At the target value, compounds and/or elements are known or assumed not to affect the natural properties of the soil while the intervention value is the maximum tolerable concentration above which remediation is required and if exceeded, entails serious potential risk to biota and the functional properties of the soil.<sup>[53]</sup> Soil/sediment values in the 'New Dutch List' are

expressed as the concentration in a standard soil (10% organic matter and 25% clay). No soil correction value is required to correct soils with organic matter content of up to 10%.<sup>[64]</sup> <sup>[65]</sup> Hence, the Dutch limit values were applied without any correction in the assessment of soil A to L because none of the soil organic matter content exceeded 10% as shown in Table 2. The Sum PAHs<sub>10</sub> in soils from sites A, C, F, G, H and L already classified as heavily contaminated sites in this study exceeded the 1.0 µg/g 'New Dutch List' target value pose a serious risk. However, only C, G and L exceeded the 'New Dutch List intervention level (40 µg/g) (Table3). Since the intervention value is the maximum tolerable concentration above which remediation is required,<sup>[63]</sup> remediation is required for sites C, G, L. The soil samples E, I, K, J, B and D already classified as contaminated and weekly contaminated in this study, were within the target value of the 'New Dutch List' for sum PAHs<sub>10</sub>.

#### *BaP<sub>eq</sub> of soils from different anthropogenic Sites in Lagos area.*

TEF value of each PAH was used to determine BaP<sub>eq</sub>. The sum BaP<sub>eq</sub> dose for each soil was calculated using the concentrations of PAHs found in the sample (Table 5) and the result is as shown in Table 5. The sum BaP<sub>eq</sub> in the soils at the six sites ( A,C, F, G, H and L), classified as 'highly contaminated' had higher values compared to the other samples. Sum BaP<sub>eq</sub> dose of 0.892 µg/g was calculated for the roadside soil of Shanghai, China,<sup>[66]</sup> 1.009 µg/g in the traffic soil from Delhi India, 0.048 µg/g rural soil from Delhi, India,<sup>[67]</sup> 0.650 µg/g, for surface soils of Agra, India<sup>[68]</sup> and 0.124 µg/g for soil from Tarragona, Spain.<sup>[69]</sup> In our study, values of 0.655 and 0.069µg/g were calculated for road soils. The sum BaP<sub>eq</sub> dose at different sampling sites in Lagos ranged from 0.033 (K, Forest soil) to 16.709 µg/g (C, the lubricating oil depot soil). Sum BaP<sub>eq</sub> dose order for samples studied was C > G > L > F > A

> H > E > D > B > I > J > K. There was a difference in this order compared to the order for sum PAH concentrations (G > C > L > F > A > H > E > I > B > D > J > K). The soil with the highest concentration of PAHs in this study G (25.39  $\mu\text{g/g}$ ) did not have the highest sum BaP<sub>eq</sub>. Sample C from where black oil was handled had the highest value for sum BaP<sub>eq</sub>.

***Estimate risk of PAHs due to involuntary consumption of soils from different anthropogenic sites.***

The potential health risk from soil can be assessed by determining the concentration of each individual PAH if 0.1g of dust was ingested by an adult of BW (70kg) (Known as the average daily intake also called estimated mean daily intake (MDI)) and comparing the values with the MDI of food as given by Lorenzi, et al. <sup>[14]</sup> Soil ingestion rate for involuntary ingestion of soil by adult has been set as 0.1g/day. <sup>[7][11]</sup> MDI of individual PAH ingested from the soils from the sites of anthropogenic activities were calculated. The values obtained were compared with the MDI of food (Table 6). In this study, a comparison of PAH MDIs for the composite soils samples and food was carried out and the result showed that all individual PAHs in samples B, D, E, F, H, I, J and K were less than the oral MDI oral for food. However, some individual PAHs in samples A, C, G, and L exceeded the recommended MDI value (Table 6), indicating some risk associated with activities on these sites based on this estimate.

Da was estimated the base on the sum PAH concentration in Table 3 and the result is as shown in Table 6. To calculate ER,  $D_{a(\text{BaP}_{\text{eq}})}$  which is Da generated based on Sum BaP<sub>eq</sub> was

used and the results are given in Table 6. PAHs of sampled sites would be associated with a  $8.2 \times 10^{-6}$ ,  $7.1 \times 10^{-7}$ ,  $1.2 \times 10^{-4}$ ,  $4.9 \times 10^{-7}$ ,  $7.3 \times 10^{-7}$ ,  $1.4 \times 10^{-5}$ ,  $7.9 \times 10^{-5}$ ,  $4.6 \times 10^{-6}$ ,  $3.4 \times 10^{-7}$ ,  $2.4 \times 10^{-7}$ ,  $2.2 \times 10^{-7}$  and  $1.1 \times 10^{-4}$ , ER for an adult with a body weight of 70 kg working on sites were composite soil samples A, B, C, D, E, F, G, H, I, J, K and L respectively were sampled. The ER from occupational exposure to surface soil based on oral ingestion for some were higher than the target risk of  $1 \times 10^{-6}$  for normal exposure but were all less than the  $1 \times 10^{-4}$  for extreme exposure for most of the sites except for two sites C and L. However, the resultant risk may have been overestimated, since these calculations were based on exhaustive extraction techniques which may be different from uptake by the human gut (bioavailability studies). Bioavailable PAHs from soils in other studies have been found to vary between 10- 60% for soil containing Sum PAHs between 10-300  $\mu\text{g/g}$ ,<sup>[70]</sup> 0.1-1.4%<sup>[71]</sup> 1-3% in aged crude oil contaminated soil<sup>[72]</sup> and 0.5-2% gastro-intestinal solubility.<sup>[73]</sup> It should be noted that the cancer risks estimated in this study are not consistent with those found in epidemiological studies. For example, Diggs, et al.<sup>[74]</sup> in their review pointed out that though laboratory studies pointed towards the likelihood of PAHs causing gastric cancer, epidemiological studies presented contrary evidence. For this reason, whether the high cancer risks estimated from this study was due to the over estimation, the risk should be further estimated based on the PAHs bioavailability or bioaccessibility study. Therefore, the high value of estimated cancer for the exposure group in this study requires further confirmation.

## **Conclusion**

This study was undertaken to assess potential health risks from PAHs in soils impacted by different anthropogenic activities in the Lagos region. The USEPA 16 priority PAHs were analysed and their concentrations quantified.

The results indicated that:

1. Soils from sites A, C, F, G, H and L were classified as heavily contaminated sites in this study. However, only C, G and L exceeded the 'New Dutch List' intervention concentration of 40.0  $\mu\text{g/g}$ .
2. The sum  $\text{BaP}_{\text{eq}}$  at different sampling sites in this study ranged from 0.0  $\mu\text{g/g}$  (K,) to 16.7  $\mu\text{g/g}$  (C, lubricating oil depot soil). The soils classified as heavily contaminated (A, C, F, G, H and L) still had a higher total  $\text{BaP}_{\text{eq}}$  compared with other soils.
3. MDI for soil samples was calculated and compared with that of food. Some of the individual PAHs in sample A, C, F, G, H and L exceeded the recommended MDI value for food, indicating some risk associated with activities on these sites based on this ingestion estimate.
4. The overall cancer risk from exposure to surface soil based on oral ingestion is not above health guidelines of 1 in 10,000 except for composite soil samples C and L.

However, it should be noted here that the resultant risk could be overestimated, since these calculations were based on exhaustive extraction techniques (ultrasonication) which may be different from uptake by the human gut (bioavailability studies).

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**Table1.** Co-ordinate and anthropogenic activities undertaken at each sampling site.

Sample Identifier	Co-ordinates	Location in Lagos and its environment sampled
A	N 06 30' 42.11" E 003 23' 15.5 "	Dump site near Onike canal on Mainland
B	N 06 34' 44. 7" E 003 24' 57.2 "	Farm in Lagos
C	N 06 30' 56.31" E 003 23' 58.5"	Depot and loading point for used for black oil Iganmu/Orile, Apapa
D	N 04 30' 46.7" E 003 29' 21.3 "	Busy roadside Akoka, Mainland
E	N 06 27' 31.0" E 003 21' 36.2"	Premium motor spirit andkKerosene depot, Apapa
F	N 06 30' 51.7" E 003 23' 32.4 "	Dump site in Akoka, Mainland

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G	N 06 26' 26.25" E 003 19' 49.5"	Premium motor spirit, kerosene depot coconut Island (petroleum product depot)
H	N 06 30' 40.1" E 009 20' 21.9 "	Roadside in Lagos
I	N 06 43' 44.4" E 003 24' 57.2 "	Trailer park/mechanics workshop, Ibafo, Obafemi Owode
J	N 05 30' 44.0" E 003 23' 23.1 "	Car park, Akoka
K	Outside Lagos	Control site (forest soil) outside Lagos
L	N 06 30' 42.1" E 003 23' 15.3 "	Mechanics workshop, Mainland

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**Table2.** Physico chemical properties of composite soils from different sampling sites in Lagos area, Nigeria.

Sample ID	Grain particles size analysis				Physico-chemical properties				Location
	Gravel (%)	Sand (%)	Clay (%)	Silt (%)	<sup>a</sup> TOC (%)	Soil organic matter (%)	pH	Oil and grease (%)	
A	8.30	50.20	21.10	20.40	3.57	6.14	8.10	1.86	Dump site near Onike canal
B	2.90	55.90	15.36	25.36	1.37	2.36	7.90	0.40	A farm in Lagos
C	28.52	66.50	4.92	0.06	1.73	2.98	8.00	4.92	Depot and loading point for used oil (black oil), Iganmu, Orile
D	6.67	88.48	4.81	0.04	1.61	2.77	8.10	0.18	Busy road side Akoka
E	13.79	74.67	11.54	6.37	2.23	3.84	7.30	1.41	Premium motor spirit and kerosine depot, Apapa
F	1.77	71.63	4.00	24.60	2.77	4.76	8.10	2.29	dumpsite in Akoka
G	4.99	84.73	10.20	0.08	2.40	4.13	7.10	3.96	Premium motor spirit and kerosine depot, Coconut
H	16.86	71.17	09.34	2.63	0.49	0.84	7.77	0.13	Road, Lagos
I	0.31	71.17	12.00	16.52	1.84	3.16	8.60	9.35	Trailer park mechanics workshop Ibafo
J	5.85	80.78	13.30	0.07	0.36	0.62	7.70	0.18	Car park Akoka
K	1.25	49.71	20.03	29.01	4.50	7.74	6.80	0.18	Control (forest soil) outside Lagos
L	8.00	50.50	22.10	19.40	3.60	6.19	8.10	1.92	Mechanics workshop in Onike

Total organic carbon--TOC

**Table 3.** Concentration ( $\mu\text{g/g}$ ) of sixteen priority PAHs found in the twelve composite soil samples collected in the Lagos area, Nigeria.

Soil sample		A	B	C	D	E	F	G	H	I	J	K	L
No of rings	PAHs	Dump site	Farm land	Black oil depot	Road side (busy)	Fuel Depot Apapa area	Dump site Akoka	Fuel depot coconut	Road side near dump site	Trailer Park Ibafo	Car park Akoka	Forest soil	Mechanics workshop
2-3 rings	NAP	6.5	0.1	0.7	0.1	0.1	0.7	1.1	0.2	0.3	0.1	0.1	2.3
	ACY	0.1	0.0	2.5	0.0	0.0	0.0	8.4	0.1	0.0	0.0	0.0	3.8
	ACP	0.1	0.0	0.1	0.0	0.0	0.0	0.6	0.1	0.0	0.0	0.0	0.1
	FLR	0.1	0.0	0.8	0.0	0.1	0.1	1.9	0.0	0.0	0.0	0.0	0.7
	PHE	1.0	0.0	18.0	0.0	0.1	0.2	86.2	0.4	0.1	0.0	0.0	17.1
	ANT	0.9	0.0	2.9	0.0	0.0	0.0	84.8	0.1	0.1	0.0	0.0	3.9
Sum		8.7	0.2	25.0	0.2	0.3	1.1	182.9	1.0	0.5	0.1	0.1	27.9
4 rings	FLT	0.1	0.0	4.0	0.0	0.0	0.1	2.6	0.3	0.0	0.0	0.0	5.7
	PYR	0.2	0.0	10.7	0.0	0.0	0.1	44.8	0.2	0.0	0.0	0.0	6.9
	BaA	0.2	0.0	6.8	0.0	0.0	2.5	2.1	0.2	0.0	0.0	0.0	7.1
	CHR	0.3	0.0	20.1	0.1	0.1	15.1	11.2	0.4	0.0	0.0	0.0	4.0



Sum		0.8	0.1	41.7	0.1	0.2	17.7	60.7	1.2	0.1	0.0	0.0	23.6
5 rings	BbF	0.0	0.1	8.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	7.5
	BkF	0.0	0.1	10.3	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	10.2
	BaP	0.9	0.0	3.3	0.0	0.0	1.2	0.0	0.1	0.0	0.0	0.0	1.3
	DaH	0.2	0.1	10.0	0.0	0.1	0.4	10.0	0.3	0.0	0.0	0.0	11.0
	BgP	1.1	0.0	0.3	0.0	0.0	0.9	0.2	0.0	0.0	0.0	0.0	0.2
Sum		2.3	0.2	32.0	0.1	0.2	2.5	10.3	1.3	0.1	0.1	0.1	30.2
6 rings	IcP	0.0	0.0	5.8	0.0	0.1	0.1	0.0	0.7	0.0	0.0	0.0	4.7
	Sum PAHs	11.9	0.5	104	0.4	0.7	21.4	254	4.1	0.7	0.2	0.2	86.4
	Sum PAHs <sub>10</sub>	11.1	0.3	72.2	0.3	0.4	20.8	188	2.9	0.6	0.2	0.2	56.4
	Target val	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Interv val	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0

Where 0.0 is  $\leq 0.03 \mu\text{g/g}$  for ACY,  $\leq 0.04 \mu\text{g/g}$  for FLR,  $\leq 0.02 \mu\text{g/g}$  for PHE,  $\leq 0.03 \mu\text{g/g}$  for ANT,  $\leq 0.04 \mu\text{g/g}$  for FLT,  $\leq 0.03 \mu\text{g/g}$  for PYR,  $\leq 0.01 \mu\text{g/g}$  for BaA,  $\leq 0.01 \mu\text{g/g}$  for CHR,  $\leq 0.02 \mu\text{g/g}$  for BbF,  $\leq 0.02 \mu\text{g/g}$  for BkF,  $\leq 0.02 \mu\text{g/g}$  for BaP,  $\leq 0.04 \mu\text{g/g}$  for DaH,  $\leq 0.01 \mu\text{g/g}$  for BgP,  $\leq 0.01 \mu\text{g/g}$  for IcP.

Sum PAHs<sub>10</sub> - Sum of 10 PAHs = sum of NAP, PHE, ANT, FLT, BaA, CHR, BkF, BaP, IcP and BgP.

Target val – The ‘New Dutch List’ target value for the sum of 10 PAHs = sum of NAP, PHE, ANT, FLT, BaA, CHR, BkF, BaP, IcP and BgP.

Interv val - The ‘New Dutch List’ intervention value for the sum of 10 PAHs = sum of NAP, PHE, ANT, FLT, BaA, CHR, BkF, BaP, IcP and BgP.

**Table 4.** Concentration of PAHs for different sites affected by anthropogenic activities measured in other studies.

<b>Location</b>	<b>Concentration (ng/g dw<sup>a</sup>)</b>	<b>Number of PAHs analysed</b>	<b>Source</b>	<b>Reference</b>
Linz (Austria)	1,450	18	Industrial area	Weiss, et al. <sup>[35]</sup>
West Macedonia (Greece)	55.2–495	16	Lignite-fired power plants Oil-shale thermal treatment	Stalikas, et al. <sup>[36]</sup>
Kohtla-Järve (Estonia)	12,390 ± 9,810	16	industry, power station and traffic	Trapido <sup>[37]</sup>
Tallinn (Estonia)	2,200 ± 1,396	12	Urban soils	Trapido <sup>[37]</sup>
Harjumaa (Estonia)	232 ± 153	12	Rural soil	Trapido <sup>[37]</sup>
Zelzate (Belgium)	300,000	7	50 m from an oil refinery	Bakker, et al. <sup>[38]</sup>
Zelzate (Belgium)	3,000–14,000	7	1.3–4.2 km from an oil refinery	Bakker, et al. <sup>[38]</sup>
Ilawa Glowna (Poland)	383.7	14	Control	Malawska and Wilkomirski <sup>[39]</sup>
New Orleans (United States)	3,731	16	Urban soils	Mielke, et al. <sup>[40]</sup>
Five cities (Tallinn, Helsinki, Vilnius, Chicago and London)	1,092	16	Urban soils	Saltiène, et al. <sup>[41]</sup>
Novi Sad (Serbia and Montenegro)	47,870	16	Oil refinery (after Kosovo war)	Skrbic and Miljevic <sup>[42]</sup>
Novi Sad (Serbia and Montenegro)	4,650	16	Oil refinery (after Kosovo war)	Skrbic and Miljevic <sup>[42]</sup>
Tokushima (Japan)	610.6	13	Urban soils	Yang, et al. <sup>[43]</sup>
Five sites in Korea	49.4	16	Control soil	Kim, et al. <sup>[44]</sup>

**Table 5.** BaP<sub>eq</sub> (µg/g) and Sum BaP<sub>eq</sub> (µg/g) for the PAHs in found in the twelve soil samples collected in Lagos region, Nigeria.

	TEFvalues	A	B	C	D	E	F	G	H	I	J	K	L
NAP	0.001	0.007	0.000	0.001	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.000	0.002
ACY	0.001	0.000	0.000	0.003	0.000	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.004
ACP	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000
FLR	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.001
PHE	0.001	0.001	0.000	0.018	0.000	0.000	0.000	0.086	0.000	0.000	0.000	0.000	0.017
ANT	0.01	0.009	0.000	0.029	0.000	0.000	0.000	0.848	0.001	0.001	0.000	0.000	0.040
FLT	0.001	0.000	0.000	0.004	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.006
PYR	0.001	0.000	0.000	0.011	0.000	0.000	0.000	0.045	0.000	0.000	0.000	0.000	0.007
BaA	0.1	0.022	0.001	0.684	0.001	0.004	0.250	0.205	0.023	0.001	0.000	0.000	0.705
CHR	0.01	0.003	0.000	0.201	0.001	0.001	0.151	0.112	0.004	0.000	0.000	0.000	0.040
BbF	0.1	0.002	0.006	0.804	0.003	0.003	0.002	0.000	0.038	0.002	0.002	0.002	0.745
BkF	0.1	0.003	0.007	1.032	0.003	0.004	0.003	0.000	0.049	0.002	0.002	0.002	1.020
BaP	1	0.903	0.018	3.297	0.008	0.008	1.184	0.000	0.143	0.012	0.006	0.004	1.295
DaH	1	0.209	0.068	10.043	0.050	0.077	0.425	10.049	0.330	0.029	0.024	0.023	10.993
BgP	0.01	0.011	0.000	0.003	0.000	0.000	0.009	0.003	0.000	0.000	0.000	0.000	0.002
IcP	0.1	0.003	0.001	0.579	0.004	0.007	0.009	0.000	0.066	0.001	0.001	0.001	0.466

Sum													
BaP <sub>eq</sub>	1.174	0.101	16.709	0.069	0.103	2.034	11.363	0.655	0.048	0.036	0.033	15.343	

A BaP<sub>eq</sub> of 0.00 µg/g, means that the concentration of a particular PAHs in table 1, is equal to 0.00 µg/g of BaP in terms of toxicity.

**Table 6.** MDI (µg/day) D<sub>a</sub> (µg/kg/day), D<sub>a(BaP<sub>eq</sub>)</sub> (µg/kg/day) and ER of composite soils from different sampling sites in the Lagos area, Nigeria.

	A	B	C	D	E	F	G	H	I	J	K	L	<sup>a</sup> Oral MDI food
NAP	0.65	0.01	0.07	0.01	0.01	0.07	0.11	0.02	0.03	0.01	0.01	0.23	7
ACY	0.01	0.00	0.25	0.00	0.00	0.00	<b>0.84</b>	0.01	0.00	0.00	0.00	0.38	0.14
ACP	0.01	0.00	0.01	0.00	0.00	0.00	0.06	0.01	0.00	0.00	0.00	0.01	0.98
FLR	0.01	0.00	0.08	0.00	0.01	0.01	0.19	0.00	0.00	0.00	0.00	0.07	0.59
PHE	0.10	0.00	<b>1.80</b>	0.00	0.01	0.02	<b>8.62</b>	0.04	0.01	0.00	0.00	<b>1.71</b>	1.54
ANT	<b>0.09</b>	0.00	<b>0.29</b>	0.00	0.00	0.00	<b>8.48</b>	0.01	0.01	0.00	0.00	<b>0.39</b>	0.08
FLT	0.01	0.00	0.40	0.00	0.00	0.01	0.26	0.03	0.00	0.00	0.00	<b>0.57</b>	0.35
PYR	0.02	0.00	<b>1.07</b>	0.00	0.00	0.01	<b>4.48</b>	0.02	0.00	0.00	0.00	<b>0.69</b>	0.35
BaA	0.02	0.00	<b>0.68</b>	0.00	0.00	0.25	0.21	0.02	0.00	0.00	0.00	<b>0.71</b>	0.06(0.05) <sup>b</sup>

CHR	0.03	0.00	<b>2.01</b>	0.01	0.01	<b>1.51</b>	<b>1.12</b>	0.04	0.00	0.00	0.00	<b>0.40</b>	0.11
BbF	0.00	0.01	<b>0.80</b>	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	<b>0.75</b>	0.11
BkF	0.00	0.01	<b>1.03</b>	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	<b>1.02</b>	0.09
BaP	0.09	0.00	<b>0.33</b>	0.00	0.00	0.12	0.00	0.01	0.00	0.00	0.00	<b>0.13</b>	0.11
DaH	0.02	0.01	1.00	0.00	0.01	0.04	<b>1.00</b>	0.03	0.00	0.00	0.00	<b>1.10</b>	0.1
BgP	<b>0.11</b>	0.00	0.03	0.00	0.00	<b>0.09</b>	0.02	0.00	0.00	0.00	0.00	0.02	0.04
IcP	0.00	0.00	<b>0.58</b>	0.00	0.01	0.01	0.00	<b>0.07</b>	0.00	0.00	0.00	<b>0.47</b>	0.06
sum PAHs MDI	1.19	0.05	10.44	0.04	0.07	2.14	25.39	0.41	0.07	0.02	0.02	8.64	
D <sub>a</sub>	2.0 x10 <sup>-4</sup>	2.1 x10 <sup>-4</sup>	4.8 x10 <sup>-4</sup>	4.2 x10 <sup>-4</sup>	6.7 x10 <sup>-4</sup>	6.6 x10 <sup>-4</sup>	3.9 x10 <sup>-3</sup>	1.1 x10 <sup>-2</sup>	2.1 x10 <sup>-2</sup>	2.4 x10 <sup>-1</sup>	1.0 x10 <sup>-1</sup>	8.3 x10 <sup>-2</sup>	
D <sub>a(BaPeq)</sub>	1.1 x10 <sup>-3</sup>	9.7 x10 <sup>-5</sup>	1.6 x10 <sup>-2</sup>	6.7 x10 <sup>-5</sup>	1.0 x10 <sup>-4</sup>	1.9 x10 <sup>-3</sup>	1.1 x10 <sup>-2</sup>	6.3 x10 <sup>-4</sup>	4.6 x10 <sup>-5</sup>	3.4 x10 <sup>-5</sup>	3.1 x10 <sup>-5</sup>	1.5 x10 <sup>-2</sup>	
ER	8.2 x10 <sup>-6</sup>	7.1 x 10 <sup>-7</sup>	1.2 x 10 <sup>-4</sup>	4.9 x 10 <sup>-7</sup>	7.3 x 10 <sup>-7</sup>	1.4 x 10 <sup>-5</sup>	7.9 x 10 <sup>-5</sup>	4.6 x 10 <sup>-6</sup>	3.4 x 10 <sup>-7</sup>	2.4 x 10 <sup>-7</sup>	2.2 x 10 <sup>-7</sup>	1.1 x 10 <sup>-4</sup>	

<sup>a</sup>Oral mean daily intake threshold for PAHs in food (oral MDI) in Nathaniel et al.<sup>[59]</sup> cited by Lorenzi et al.<sup>[11]</sup>, <sup>b</sup>alternative measure of oral MDI

<sup>[34]</sup>. A value of 0.00 µg/g for individual PAH, means that the concentration MDI of that PAH is equal or less than 0.004 µg/g. D<sub>a</sub> value of 0.00

µg/g ≤ 0.0039 µg/g. Bold figures show data that exceeded the limits.

