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Concentrations and Health Risk Assessment of Polycyclic Aromatic Hydrocarbons in Soils of an Urban Environment in the Niger Delta, Nigeria

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Abstract

The concentrations and compositional patterns of the United States Environmental Protection Agency (US EPA) 16 priority polycyclic aromatic hydrocarbons (PAHs) were determined in surface soils of an urban environment in the Niger Delta of Nigeria with a view to providing information on the sources, extent of contamination and human health risks of PAHs in these soils. The analyses were performed by means of gas chromatography-mass spectrometry (GC-MS) after extraction of the soils with hexane/dichloromethane and clean-up of the extracts. The concentration of $\sum$16 PAHs in the urban soils ranged from 188 to 684 μg kg^{-1}, while the $\sum PAH_{7c}$ (carcinogenic PAHs) ranged from 28.5 and 571 μg kg^{-1}. The estimated carcinogenic and mutagenic potency factors for these sites ranged from 2.34 to 197 and 9.66 to 195 μg kg^{-1} respectively. The composition of PAHs in these soils follows the order: 5-rings > 4-rings > 3-rings > 6-rings > 2-rings, and higher molecular weight PAHs accounted for a significant proportion of the $\sum$16 PAH concentration in this study. The results indicated that there is a high potential risk of cancer development as a result of exposure of PAHs via ingestion, dermal contact and inhalation. The diagnostic ratios indicate that the PAHs in these soils originated mainly from pyrogenic processes, such as combustion of petroleum, fossil fuels and biomass such as woods, charcoal straw and grasses. The results of this study provided information on the concentrations and compositional patterns of PAHs, which is useful in understanding the effects, sources, fate and transport of PAHs in soils, as well as environmental quality management and environmental forensic studies.

Keywords: Polycyclic aromatic hydrocarbons, Soil contamination, Source apportionment, Urban soils

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of pervasive hydrophobic organic compounds that consist of two or more fused aromatic rings in a linear, angular or cluster arrangement. PAHs in the environment originate mainly from anthropogenic sources which include heat-induced decomposition of organic matter (e.g. coal, petroleum and wood), industrial operations and power plants that use fossil fuels, smelting, garbage incineration, and vehicle engines powered by gasoline or diesel fuel[1,2]. Other sources include natural processes such as forest fires and volcanic eruptions, soil seeps, ancient sediment erosion and early diagenesis. Many of the PAHs exhibit deleterious effects on the respiratory, immunological, neurological and reproductive systems of humans[3]. The presence of PAHs in the environment is of great concern because of their persistence, carcinogenic, mutagenic and genotoxic properties, and long-range transportation and deposition capabilities. The mobility of PAHs in soil matrices is relatively low due to their low aqueous solubilities and high organic carbon (C)-water (Koc) partition coefficient. However, the mobility, bioavailability and degradation of PAHs the environment can be enhanced by the presence of water-dispersible naturally occurring colloids[4].

The accumulation of PAHs in surface soils is controlled by atmospheric deposition. However, losses due to volatilization, biodegradation and mixing/burial to depth do occur. Higher concentrations of PAHs have been observed in urban soils near point sources and those with high organic matter contents[5,6], and the close proximity of these soils to humans may increase the probability of human exposure to these pollutants via inhalation, ingestion or dermal contact[3,7]. PAHs tend to accumulate in soil owing to the fact that they are sparingly soluble, readily adsorbed by soil particles and difficult to degrade.

Urban areas and cities have now become the geographic focus of resource distribution, consumption and chemical emissions due to the fact that most industrial and economic activities are concentrated in urban areas. Besides, 50% of the world's 6.9 billion population now live in urban centers[8]. Therefore, contamination of urban soils has serious consequences on the health of humans and the surrounding ecosystem. Thus, knowledge of the mechanisms and distribution of contaminants in urban environments is crucial in order to delineate areas where contaminants have exceeded threshold limits, and for developing strategies for site remediation and management of urban environmental quality[8], as well as source identification and evaluation of the health risks associated with PAHs[9].

A number of studies have reported the concentrations of PAHs in urban soils of developed countries[3,5,6,10]. However, for Nigeria, only a few studies have documented the concentrations and profiles of PAHs in soils[11-13]. The aim of the present study was to determine the concentrations of PAHs in urban soils with a view to providing information on the profiles, sources and human health risks associated with the levels of PAHs in these soils.

Results and Discussion

The results for the determination of $\sum$16 PAHs in the urban soils are presented in Table 1. The concentrations of $\sum$16 PAHs in these soils ranged between 188 μg kg^{-1} and 684 μg kg^{-1}. The highest concentration of $\sum$16 PAHs was observed in site 8 while the lowest concentration was found in site 21. Analysis of variance indicated that the concentrations and compositions of

Table 1. Concentrations (μg kg^{-1}) of polycyclic aromatic hydrocarbons in urban soils.

PAHs	Acronyms	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Acenaphthylene	Acy	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	44.9	<LOQ	<LOQ	<LOQ	140	<LOQ	<LOQ	44.7	<LOQ	88.6	<LOQ
Acenapthene	Ace	<LOQ	<LOQ	<LOQ	38.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	102	8.0	<LOQ	<LOQ	58.5	<LOQ	<LOQ
Fluorene	Flu	<LOQ	<LOQ	<LOQ	21.9	54.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	51.6	<LOQ	<LOQ	<LOQ	<LOQ	31.5	<LOQ	103.0	<LOQ	<LOQ
Phenanthrene	Phen	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	38.7	<LOQ	21.2
Anthracene	Ant	51.8	33.4	6.7	40.8	107	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	36.2	<LOQ	46.2	<LOQ	<LOQ	67.1	<LOQ	28.5	<LOQ	13.4
Fluoranthene	Flt	<LOQ	28.1	25.3	9.9	32.0	<LOQ	<LOQ	31.8	<LOQ	<LOQ	<LOQ	<LOQ	42.4	<LOQ	<LOQ	12.9	<LOQ	14.1	42.2	102.1	35.0
Pyrene	Pry	25.9	24.2	5.4	42.6	32.5	32.5	<LOQ	28.7	38.7	<LOQ	59.8	<LOQ	<LOQ	<LOQ	88.8	31.3	47.2	36.7	8.3	9.1	53.0
Benzo[*a*]anthrancene	B*a*A	51.3	6.6	<LOQ	27.3	45.7	45.7	25.0	52.6	72.2	<LOQ	28.5	<LOQ	90.9	29.8	28.6	82.8	<LOQ	18.8	<LOQ	9.7	<LOQ
Chrysene	Chry	27.8	8.7	<LOQ	33.5	39.8	39.8	<LOQ	60.4	<LOQ	<LOQ	35.6	<LOQ	35.6	111	35.6	21.3	<LOQ	7.7	28.4	19.1	<LOQ
Benzo[*b*]fluoranthene	B*b*F	42.2	45.5	33.2	27.0	8.5	8.5	200	220	28.1	71.9	<LOQ	<LOQ	23.9	200	74.0	35.5	55.7	57.8	<LOQ	7.4	<LOQ
Benzo[*k*]fluoranthene	B*k*F	140	5.2	5.5	34.4	38.2	38.2	40.6	58.8	29.2	8.0	255	44.1	59.4	26.3	<LOQ	28.5	9.5	15.6	7.3	60.8	<LOQ
Benzo[a]pyrene	B*a*P	96.9	7.2	28.4	30.8	5.7	5.7	96.1	106	9.1	8.1	<LOQ	36.8	26.8	30.1	<LOD	37.0	60.4	45.5	28.2	<LOQ	28.5
Indeno[*1,2,3-cd*]pyrene	IndP	47.7	39.8	36.0	35.1	39.9	39.9	50.8	45.1	18.9	18.0	<LOQ	25.2	<LOQ	54.2	<LOQ	<LOQ	<LOQ	77.7	<LOQ	<LOQ	<LOQ
Dahenz[*a,h*]anthracene	D*ah*A	23.9	12.6	31.2	129	10.8	10.8	22.7	28.1	96.3	180	<LOQ	39.0	<LOQ	8.5	<LOQ	<LOQ	<LOQ	31.1	29.9	<LOQ	<LOQ
Benzo[*g.h,i*]perylene	B*ghi*P	15.6	22.3	49.5	26.0	68.8	68.8	7.4	52.6	38.7	37.1	<LOQ	44.9	46.1	10.7	<LOQ	<LOQ	36.4	57.4	<LOQ	<LOQ	37.1
$\sum$16PAHs		523	234	221	497	484	290	443	684	325	323	423	278	331	517	468	257	308	407	373	297	188
$\sum$3-ringed PAHs		51.8	33.4	6.7	101	162						44.9	87.8	5.8	46.2	241	8.0	98.6		170	88.6	34.6
$\sum$4-ringed PAHs		105	67.4	30.7	113	150	118	17.2	174	111		124		169	141	153	148	47.2	77.3	78.9	140	88
$\sum$5-ringed PAHs		303	70.5	98.3	222	63.2	63.2	359	413	156	268	255	119	110	265	74	101	126	150	65.4	68.2	28.5
$\sum$6-ringed PAHs		63.3	87.3	85.5	61.1	109	109	58.2	97.7	57.6	55.1		70.9	46.1	64.9			36.4	135			37.1
$\sum PAH_{7c}$		430	126	134.3	317	189	189	436	571	254	286	319	145	237	460	138	205	126	254	93.8	97.0	28.5
TOC		1.2	0.8	1.3	0.6	0.7	1.1	2.1	2.3	0.9	0.8	0.6	1.3	1.5	1.7	0.7	0.6	1.1	1.2	1.3	0.8	0.9
pH		5.1	6.1	4.7	7.1	5.7	4.7	5.3	5.5	6.1	6.5	6.8	7.4	5.6	5.2	4.8	4.9	6.1	6.4	5.3	6.4	7.5

TOC = Total organic carbon; LOQ = Limit of quantification

Table 2. A comparison of the concentrations of PAHs in soils of the area studied with those from other regions of the world.

Location	Soil type	Concentration ranged (µg kg^{-1})	Reference
Nigeria	Urban soils	188-684	This study
Estonia	Rural, urban and industrial soils	50-22,200	15
China (Hong Kong)	Rural and urban soils	30-170	16
Switzerland	Pasture grassland and urban soils	50-600	17
Germany (Rhine River)	Alluvial soils	20-3600	18
China (Beijing)	Rural and suburban soils	20-3900	19
China (Huanghuai plain)	Agricultural soils	15.7-1247.6	2
United States of America (Miami, Florida)	Urban soils	251-2364	3
Korea (An-san city)	Industrial soils	109.93-178.92	20
Nigeria (Niger Delta)	Soil vicinity oil installation	24-120	13
Spain (Sevilla)	Agriculture and urban soils	89.5-4004.2	6
Nigeria (Niger Delta)	Urban soils	182-433	11
India (Jalandhar, Punjab)	Road side soils	4040-16380	21
Mexico	Industrial soils	7-1384	22
India (Kuruksheta)	Urban Roadside soils	16.1-2538.0	23
Nigeria (Lagos)	Mangrove fresh soil	65.5-188.0	24
United Kingdom	Urban soil	2700 ± 500	25
Japan	Urban soil	1300 ± 800	26
China (Beijing)	Urban soil	467-5470	27
China (Songhua River Basin)	Alluvial soil	30.1-870	28
China (Shanghai)	Urban soil	83.3-7220	29
China (Hangzhou)	Urban soil	180.77-1981	30
United Kingdom (Greater London)	Urban soil	4000-67000	31
China (Dagang oil field)	Industrial soil	103.6-5878	32
Slovakia (Bratislava)	Urban soil and playgrounds	4500-12151	33
North Pacific Ocean (Midway Atoll)	Urban soil	3.55-3200	34
Nigeria (Niger Delta)	Floodplain soil	812-10700	35

$\sum$16 PAHs varied significantly ($p < 0.05$) between the various sites. Malizewkwa-Kordybach[14] has classified the contamination levels into four categories based on the $\sum$PAH concentrations. Soils with $\sum$16 PAHs concentrations less than 200 µg kg^{-1} are not contaminated, between 200-600 µg kg^{-1} are weakly contaminated, from 600-1000 µg kg^{-1} are contaminated and greater than 1000 µg kg^{-1} are considered heavily contaminated. Based on this classification, the majority of the investigated sites fall within the weakly contaminated category. A comparison of the concentrations of $\sum$16 PAHs obtained in this study with the levels reported for urban soils in the literature is presented in Table 2. The concentrations of $\sum$16 PAHs in the investigated soils corresponds to the levels observed in dust and gutter sediment samples (165.1-1012 µg kg^{-1}) collected in the study area[36]. Although, this is a continuation of our previous works[36], but the present study focused more on the distribution, and sources of PAHs in the urban soil in order to provide a complete picture of the risk of exposure to PAHs in other environmental matrices within the urban setting. The concentrations of $\sum$16 PAHs in these soils were below the target value set for soil $\sum$PAH (1000 µg kg^{-1}) by the Dutch Government[37]. The concentrations of $\sum$16 PAHs found in the sites sampled were lower than the concentrations of PAHs found in urban soils in the literature (Table 2), but were comparable to concentrations found in rural and agricultural soils. The concentrations of $\sum$16 PAHs found in these sites were comparable to PAH concentrations reported for urban soils in the Niger Delta[11]. In this study, there was no significant correlation between $\sum$16 PAHs concentration and TOC ($R^2 = 0.0667$). The presence of poor correlation between the $\sum$PAHs and TOC has been reported in the literature[2,16,35,38]. However, some studies have reported good correlation between PAH concentrations and TOC in highly contaminated soils[39,40]. The lack of significant correlation between PAHs and soil physicochemical parameters is related to the continuous input of recent contamination or the presence of different sources[2,41]. Nevertheless, the volatility and chemical structure i.e. ringwise distribution patterns are influenced by several environmental factors including temperature, daily radiation and/or humidity and the total organic contents in the soil environments.

Generally, lower molecular weight (LMW) PAHs (2- and 3-ringed compounds) were not detected in most of the sites as compared with the heavier PAHs, presumably due to their high volatility and lower K_{ow} values (less hydrophobic). The lower molecular weight PAHs are mainly in the gaseous form and capable of under-

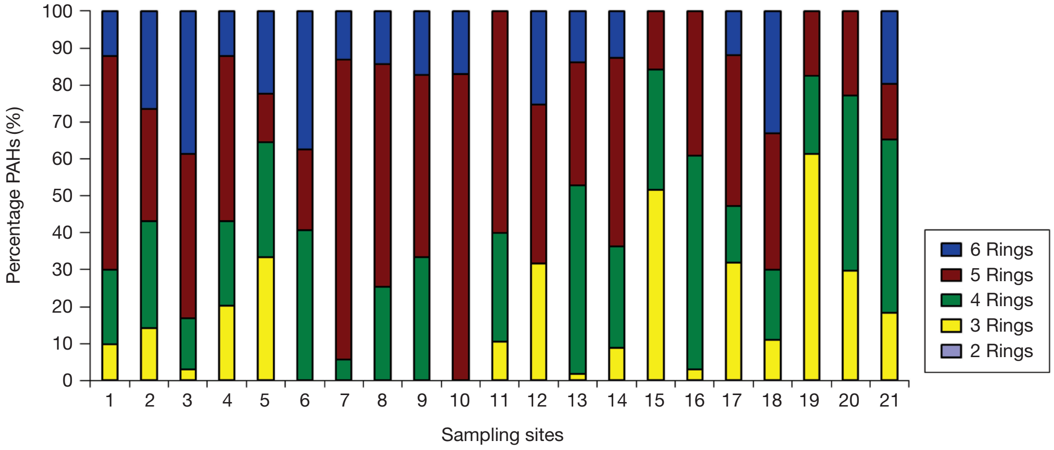

Figure 1. Percentage composition of PAHs in soils of sites.

going long-range transportation to more remote areas from the emission sources, while the higher molecular weight (HMW) PAHs are associated with air-borne particulates that undergo 'single hop' transportation properties thereby restricting the accumulation of HMW PAHs to soils close to the emission sources[42-44]. Soil bacteria utilize LMW PAHs as an energy source during biodegradation rather than the HMW PAHs, which may also account for the low concentrations of LMW PAHs in our sites[45].

On the contrary, the less volatile PAHs, dibenz[*a,h*]anthracene, benzo[*g,h,i*]perylene and indeno[*1,2,3-cd*]pyrene were not detected in 33%, 24% and 38% of these sites respectively. Morrillo *et al.*[6] have observed similar distribution patterns in urban soils.

The ringwise distribution patterns of PAHs in these soils followed the order: 5-ring > 4-ring > 3-ring > 6-ring > 2-ring (Figure 1). The HMW PAHs (4-6-rings) account for higher proportions of the $\sum$16 PAHs concentrations compared with the LMW PAHs (2- and 3-rings) for the reasons stated.

In this study, the 2-ringed PAH, naphthalene, was not detected in any of the sites. The 3-ringed PAH concentrations in these sites ranged from 5.8 to 241 μg kg^{-1}. The highest concentration of 3-ring PAH compounds was observed at site 15. The 3-ringed PAHs constituted 1.8 to 61.3% of the $\sum$16 PAHs. Anthracene was the dominant 3-ring PAH compound in these soils in terms of concentration and frequency of occurrence. The occurrence frequency of 3-ringed PAH compounds followed the order anthracene > fluorene > acenaphthene = acenaphthylene > phenanthrene. The concentrations of the individual 3-ringed PAHs were not greater than 140 μg kg^{-1}.

The concentrations of $\sum$4-ringed PAHs ranged between 17.2 and 169 μg kg^{-1}. The highest concentration of $\sum$4-ring PAHs was found in site 13. Four ringed PAHs were detected in 19 of the 21 sites, and constituted 5.6 to 57.6% of $\sum$16 PAH in these sites. The four-ringed PAHs constituted significant proportions of the $\sum$16 PAHs in sites 13 (51%), 16 (58%), 20 (47%) and 21 (47%). Pyrene was the most abundant 4-ring PAH in these soil samples. The distribution pattern of the 4-ringed PAHs followed the order: pyrene > benzo[*a*]anthracene > chrysene > fluorene. The concentrations of the individual 4-ringed PAH compounds were not greater than 111 μg kg^{-1}.

The 5-ringed PAHs: benzo[*b*]fluoranthene (B*b*F), benzo[*k*]fluoranthene (B*k*F), benzo[*a*]pyrene (B*a*P) and dibenz[*a,h*]anthracene (D*ah*A), were detected in 14 to 19 of the 21 sites investigated and the $\sum$5-ring PAH concentrations ranged from 29 to 413 μg kg^{-1}. The 5-ringed PAHs constituted significant proportions of the $\sum$16 PAHs (13-83%). Higher concentrations of 5-ringed PAHs were observed in sites 1, 4, 7, 8, 10, 11 and 14. The 5-ringed compounds were the dominant PAHs in these soils in terms of frequency of occurrence. The occurrence frequency of the 5-ringed PAHs follows the order: B*k*F > B*a*P > B*b*F > D*ah*A. The concentrations of B*b*F, B*k*F, B*a*P and D*ah*A in these soil samples were in the range of 7.4 to 220, 5.2 to 255, 5.7 to 106 and 8.5 to 180 μg kg^{-1}, respectively. On an individual basis, these 5-ringed PAH compounds contributed approximately 1.2 to 60.1% of the $\sum$16 PAHs in these soils.

The concentrations of the 6-ringed PAH compounds ranged from 36 to 135 μg kg^{-1}. The highest concentration of $\sum$6-ringed PAHs was found in site 18, and no 6-ringed PAH compound was detected in sites 11, 15, 16, 19 and 20. The 6-ringed PAHs constituted 11.8 to 38.7% of the $\sum$16 PAHs of these soils. Benzo[*ghi*]perylene (B*ghi*P) was the dominant 6-ringed PAH com-

Table 3. B*a*P$_{\text{TEQ}}$ and B*a*P$_{\text{MEQ}}$ concentrations (μg kg^{-1}) for soils.

Sites	B*a*A	Chry	B*b*F	B*k*F	B*a*P	IndP	D*ah*A	B*a*P$_{\text{TEQ}}$	B*a*A	Chry	B*b*F	B*k*F	B*a*P	IndP	D*ah*A	B*a*P$_{\text{MEQ}}$
1	5.13	0.03	4.22	1.40	96.9	4.77	23.9	136	4.21	0.47	10.55	15.4	96.9	14.8	6.93	149
2	0.66	0.01	4.55	0.05	7.20	3.98	12.6	29.1	0.54	0.15	11.38	0.57	7.20	12.3	3.65	35.8
3	ND	ND	3.32	0.06	28.4	3.60	31.2	66.6	ND	ND	8.30	0.61	28.4	11.2	9.05	57.5
4	2.73	0.03	2.70	0.34	30.8	3.51	129	169	2.24	0.57	6.75	3.78	30.8	10.9	37.5	92.5
5	4.57	0.04	0.85	0.38	5.70	3.99	10.8	26.3	3.75	0.68	2.13	4.20	5.70	12.4	3.13	31.9
6	4.57	0.04	0.85	0.38	5.70	3.99	10.8	26.3	3.75	0.68	2.13	4.20	5.70	12.4	3.13	31.9
7	2.50	ND	20.0	0.41	96.1	5.08	22.7	147	2.05	ND	50.1	4.47	96.1	15.8	6.58	175
8	5.26	0.06	22.0	0.59	106	4.51	28.1	166	4.31	1.03	55.0	6.47	106	14.0	8.15	195
9	7.22	ND	2.81	0.29	9.1	1.89	96.3	118	5.92	ND	7.03	3.21	9.10	5.86	27.9	59
10	ND	ND	7.19	0.08	8.10	1.80	180	197	ND	ND	18.0	0.88	8.10	5.58	52.2	84.7
11	2.85	0.04	ND	2.55	ND	ND	ND	5.43	2.34	0.61	ND	28.0	ND	ND	ND	30.9
12	ND	ND	ND	0.44	36.8	2.52	39.0	78.8	ND	ND	ND	4.85	36.8	7.81	11.3	60.8
13	9.09	0.04	2.39	0.59	26.8	ND	ND	38.9	7.45	0.61	5.98	6.53	26.8	ND	ND	47.4
14	2.98	0.11	20.0	0.26	30.1	5.42	8.50	67.4	2.44	1.89	50.0	2.89	30.1	16.8	2.47	107
15	2.86	0.04	7.40	ND	ND	ND	ND	10.3	2.35	0.61	18.5	ND	ND	ND	ND	21.5
16	8.28	0.02	3.55	0.29	37.0	ND	ND	49.1	6.79	0.36	8.88	3.14	37.0	ND	ND	56.2
17	ND	ND	5.57	0.10	60.4	ND	ND	66.1	ND	ND	13.9	1.05	60.4	ND	ND	75.4
18	1.88	0.01	5.78	0.16	45.5	7.77	31.1	92.2	1.54	0.13	14.4	1.72	45.5	24.1	9.02	96.4
19	ND	0.03	ND	0.07	28.2	ND	29.9	58.2	ND	0.48	ND	0.80	28.2	ND	8.67	38.2
20	0.97	0.02	0.74	0.61	ND	ND	ND	2.34	0.80	0.32	1.85	6.69	ND	ND	ND	9.66
21	ND	ND	ND	ND	28.5	ND	ND	28.5	ND	ND	ND	ND	28.5	ND	ND	28.5

pound in terms of occurrence frequency. The concentrations of indeno[*1,2,3-cd*]pyrene (IndP) and B*ghi*P in these soil samples ranged from 18 to 78 μg kg^{-1} and from 7.4 to 69 μg kg^{-1} respectively.

In this study, the summation of the 7 carcinogenic PAHs ($\sum$PAH$_{7c}$) (B*a*A + Chry + B*b*F + B*k*F + B*a*P + IndP + D*ah*A) ranged from 29 to 571 μg kg^{-1}, which constituted 15 to 98% of the $\sum$16 PAHs concentrations in some of these sites.

Assessment of Carcinogenic Potential Risk

B*a*P$_{\text{TEQ}}$ is directly linked to carcinogenicity while B*a*P$_{\text{MEQ}}$ (mutagenicity) may not be directly linked to carcinogenicity[46,47] but may be linked to other non-cancerous adverse health effects including pulmonary diseases, birth defects, impotency, low IQ, etc.[48,49]. The B*a*P$_{\text{TEQ}}$ and B*a*P$_{\text{MEQ}}$ values calculated for $\sum$PAH$_{7c}$ are presented in Table 3. The B*a*P$_{\text{TEQ}}$ and B*a*P$_{\text{MEQ}}$ ranged from 2.34 to 197 μg kg^{-1} and 9.66 to 195 μg kg^{-1} respectively. B*a*P and D*ah*A had a significant impact on the B*a*P$_{\text{TEQ}}$ values while B*a*P$_{\text{MEQ}}$ (mutagenic activity) was dominated by B*a*P, IndP and D*ah*A. In this study, sites 1, 4, 7, 8, 9 and 10 had B*a*P$_{\text{TEQ}}$ values greater than 100 μg kg^{-1} which indicated that these sites have higher carcinogenic potency than the other sites. The values of B*a*P$_{\text{TEQ}}$ obtained in this study are comparable to those reported for agricultural soils of Huang-huai plain, China[2] and for soils of a natural reserve located in front of a plant for the production of cement in Italy[50] but they were higher than B*a*P$_{\text{TEQ}}$ (27.75 μg kg^{-1}) reported for Beijing, Nanjing, Tianjin and surrounding areas in China[51,52]. However, higher B*a*P$_{\text{TEQ}}$ and B*a*P$_{\text{MEQ}}$ concentrations were reported by Olawoyin *et al.*[53] for Niger Delta soils. In this study, the B*a*P$_{\text{TEQ}}$ in 67% of the soil samples were more than the Dutch target value (33 μg kg^{-1})[37].

Incremental Lifetime Cancer Risk via Ingestion, Dermal Contact and Inhalation of Soil

The ILCR is a valuable tool for assessing the potential risk of cancer induction in humans exposed to environmental toxicants[53,54]. The estimated ILCR values are shown in Table 4. The ILCR levels via soil ingestion, dermal contact and inhalation ranged from 2.25×10^{-5} to 1.90×10^{-3}, 8.19×10^{-6} to 6.91×10^{-4}, and 2.12×10^{-13} to 5.70×10^{-12} respectively for a child and 1.41×10^{-5} to 1.19×10^{-3}, 7.28×10^{-6} to 6.14×10^{-4}, and 1.06×10^{-12} to 2.85×10^{-11} respectively for an adult. The observed inhalation cancer risks for PAHs were 10^8 and 10^7 times lower than the corresponding cancer risks via ingestion and dermal contact respectively. This may be a consequence of a lack of evaluation of air samples[28]. However, the total cancer risk ranged from 3.07×10^{-5} to 2.59×10^{-3} and 2.13×10^{-5} to 1.80×10^{-3} for a child and an adult respectively. The ILCR values obtained indicated that children residing in the vicinity of sites 1, 4, 7, 8, 9, 10, 12 and 18 and adults at sites 1, 4, 7, 8, 9 and 10 are at greater risk than those living close to the other sites. The values for the ILCR obtained showed that the soils in the study area fall into the low to moderate cancer risk category[55].

Table 4. Potential carcinogenic risk due to exposure to PAHs in soil.

	Child				Adult			
	$ILCR_{ing}$	$ILCR_{inh}$	$ILCR_{derm}$	Total cancer risk	$ILCR_{ing}$	$ILCR_{inh}$	$ILCR_{derm}$	Total cancer risk
1	1.31×10^{-3}	4.03×10^{-12}	4.78×10^{-4}	1.79×10^{-3}	8.20×10^{-4}	2.02×10^{-11}	4.25×10^{-4}	1.25×10^{-3}
2	2.80×10^{-4}	8.18×10^{-13}	1.02×10^{-4}	3.82×10^{-4}	1.75×10^{-4}	4.09×10^{-12}	9.06×10^{-5}	2.65×10^{-4}
3	6.42×10^{-4}	1.86×10^{-12}	2.33×10^{-4}	8.75×10^{-4}	4.00×10^{-4}	9.30×10^{-12}	2.08×10^{-4}	6.08×10^{-4}
4	1.63×10^{-3}	4.91×10^{-12}	5.94×10^{-4}	2.23×10^{-3}	1.02×10^{-3}	2.46×10^{-11}	5.28×10^{-4}	1.55×10^{-3}
5	2.54×10^{-4}	8.28×10^{-13}	9.23×10^{-5}	3.46×10^{-4}	1.58×10^{-4}	4.14×10^{-12}	8.21×10^{-5}	2.40×10^{-4}
6	2.54×10^{-4}	8.28×10^{-13}	9.23×10^{-5}	3.46×10^{-4}	1.58×10^{-4}	4.14×10^{-12}	8.21×10^{-5}	2.40×10^{-4}
7	1.41×10^{-3}	4.06×10^{-12}	5.14×10^{-4}	1.93×10^{-3}	8.83×10^{-4}	2.03×10^{-11}	4.58×10^{-4}	1.34×10^{-3}
8	1.60×10^{-3}	4.65×10^{-12}	5.83×10^{-4}	2.19×10^{-3}	1.00×10^{-3}	2.33×10^{-11}	5.19×10^{-4}	1.52×10^{-3}
9	1.13×10^{-3}	3.43×10^{-12}	4.12×10^{-4}	1.55×10^{-3}	7.07×10^{-4}	1.72×10^{-11}	3.67×10^{-4}	1.07×10^{-3}
10	1.90×10^{-3}	5.70×10^{-12}	6.91×10^{-4}	2.59×10^{-3}	1.19×10^{-3}	2.85×10^{-11}	6.14×10^{-4}	1.80×10^{-3}
11	5.23×10^{-5}	7.63×10^{-13}	1.90×10^{-5}	7.14×10^{-5}	3.27×10^{-5}	3.81×10^{-12}	1.69×10^{-5}	4.96×10^{-5}
12	7.59×10^{-4}	2.30×10^{-12}	2.76×10^{-4}	1.03×10^{-3}	4.74×10^{-4}	1.15×10^{-11}	2.46×10^{-4}	7.19×10^{-4}
13	3.75×10^{-4}	1.19×10^{-12}	1.36×10^{-4}	5.11×10^{-4}	2.34×10^{-4}	5.93×10^{-12}	1.21×10^{-4}	3.55×10^{-4}
14	6.49×10^{-4}	1.90×10^{-12}	2.36×10^{-4}	8.85×10^{-4}	4.05×10^{-4}	9.52×10^{-12}	2.10×10^{-4}	6.15×10^{-4}
15	9.92×10^{-5}	2.83×10^{-13}	3.61×10^{-5}	1.35×10^{-4}	6.19×10^{-5}	1.41×10^{-12}	3.21×10^{-5}	9.40×10^{-5}
16	4.73×10^{-4}	1.38×10^{-12}	1.72×10^{-4}	6.46×10^{-4}	2.96×10^{-4}	6.91×10^{-12}	1.53×10^{-4}	4.49×10^{-4}
17	6.37×10^{-4}	1.78×10^{-12}	2.31×10^{-4}	8.68×10^{-4}	3.97×10^{-4}	8.91×10^{-12}	2.06×10^{-4}	6.03×10^{-4}
18	8.88×10^{-4}	2.57×10^{-12}	3.23×10^{-4}	1.21×10^{-3}	5.55×10^{-4}	1.28×10^{-11}	2.87×10^{-4}	8.42×10^{-4}
19	5.61×10^{-4}	1.65×10^{-12}	2.04×10^{-4}	7.65×10^{-4}	3.50×10^{-4}	8.23×10^{-12}	1.81×10^{-4}	5.32×10^{-4}
20	2.25×10^{-5}	2.12×10^{-13}	8.19×10^{-6}	3.07×10^{-5}	1.41×10^{-5}	1.06×10^{-12}	7.28×10^{-6}	2.13×10^{-5}
21	2.75×10^{-4}	7.59×10^{-13}	9.99×10^{-5}	3.74×10^{-4}	1.71×10^{-4}	3.79×10^{-12}	8.88×10^{-5}	2.60×10^{-4}

The total cancer risk values obtained in this study are comparable to the total cancer risks reported for exposed to dust-bound PAHs in Pakistan[56,57].

Children are the most susceptible group to contaminants in soils due to high physical contact with soil and dusts during peer play time and also because of the smaller body weight[53]. Once PAHs are ingested, they act more in their systems and interfere with organ development and proper functioning of the central nervous system[53]. The cancer risk via inhalation for adults was higher than for the child scenario and this could be due to the longer exposure duration (ED) for adults. The results obtained for the assessment of cancer risk in this study are comparable to those of previous studies on the health risk from PAH exposure to soils from the Niger Delta of Nigeria[53], contaminated soils from Hong Kong[28] and soils from metropolitan areas in China[44,58].

The total cancer risk values obtained in the sites investigated here for both the children and adult cases were greater than the acceptable risk of 10^{-6} (one chance in a million population)[59] which signifies a high potential human carcinogenic risk in the study area.

Source Apportionment by Diagnostic Ratios of PAHs

Source apportionment of PAHs in the environment is essential for the assessment of environmental and human risks. Petrogenic and pyrogenic sources are by far the most important sources of PAH input into the environment. Petrogenic input can occur due to oil spillage or human discharge of petroleum products and road construction materials, while pyrogenic sources include fossil fuel combustion, forest fires, and shrub and grass fires[24,27]. The isomeric ratios such as Flt/(Flt + Pyr), Ant/(Ant + Phen), Phen/Ant, LMW/HMW, B*a*A/(B*a*A+ Chry), and IndP/(IndP + B*ghi*P) have been used in the literature for source apportionment[1,27,35,36,57,60-63]. Although these compositional parameters are usable for source distinction, they are not definitive since there are many limitations[1]. In this study, the LMW/HMW ratio ranged from 0.02 to 1.06 (Table 5) indicating that the soils had a major input of pyrogenic PAHs. Besides the ratio, LMW/HMW, the Flt/(Flt + Pyr) ratios in these sites were in the range of 0.19 to 1.0 (Table 5). When the ratio of Flt/(Flt + Pyr) is <0.4, between 0.4 and 0.5 and >0.5 is indicative of petroleum leaks, petroleum combustion and coal/biomass/combustion, respectively[2,60,61]. Based on these ratios, sites 4, 16 and 17 had inputs from petrogenic sources while the other sites had input from pyrogenic sources such as combustion of petroleum and biomass. For the B*a*A/(B*a*A+ Chry) ratios, values less than 0.20 imply a petroleum origin, from 0.20 to 0.35, either petroleum or/and above 0.35 of combustion origin[60,64]. The B*a*A/(B*a*A + Chry) ratios of the examined sites were in the range of 0.21 to 1 (Table 5) indicating that the sources of PAHs in

Table 5. Diagnostic ratios of PAHs in urban soils

Site	LMW/ HMW	Ant/ (Ant + Phe)	B*a*A/ (B*a*A + Chy)	Flt/ (Flt + Pyr)	IndP/ (IndP + B*ghi*P)	ΣCOMB/ Σ16PAHs	PAH(4)/ PAH(5 + 6)	Total index
1	0.11	–	0.65	–	0.75	0.86	0.29	4.8
2	0.17	–	0.43	0.54	0.64	0.8	0.42	4.8
3	0.03	–	–	0.83	0.42	0.83	0.17	2.9
4	0.26	–	0.45	0.19	0.57	0.54	0.4	3.9
5	0.5	–	0.53	0.5	0.37	0.64	0.87	4.6
6	–	–	0.53	–	0.37	0.96	0.68	3.4
7	–	–	0.47	0.53	6.46	0.95	0.04	16.6
8	–	–	1	–	0.87	0.96	0.34	6.7
9	–	–	1	–	0.33	0.72	0.52	5.7
10		–	–	–	0.33	0.44	–	0.7
11	0.12	–	0.44	–	–	0.9	0.48	2.2
12	0.46	–	–	–	0.36	0.54	–	0.7
13	0.02	–	0.72	1	–	0.98	1.08	6.1
14	0.1	–	0.21	–	0.84	0.89	0.43	2.7
15	1.06	–	0.45	–	–	0.49	2.07	2.3
16	0.03	–	0.8	0.29	–	0.97	4.78	4.7
17	0.12	–	0.71	0.28	0.58	0.68	0.29	5.4
18	0.43	–	0.34	0.92	–	0.81	0.27	4.0
19	0.57	0.44	–	0.84	–	0.31	1.21	6.5
20	0.43	–	0.34	0.92	–	0.7	2.05	4.0
21	0.23	0.86	–	0.4	–	0.82	1.34	9.6

these soils are from combustion sources. An IndP/(IndP + B*ghi*P) ratio <0.2 indicates a possible petrogenic origin while a liquid fossil fuel (automotive and crude oil) origin would yield a ratio of 0.2 to 0.5, while a ratio >0.5 is due to local grass and wood combustion[60,61,65]. The IndP/(IndP + B*ghi*P) ratio values of our sites are in the range of 0.33 to 0.87 (Table 5) indicating that combustion of fossil fuels and biomass are the sources of PAHs in these urban soils. The ratios of the sum of the major combustion specific compounds such as Flt, Pyr, B*a*A, Chry, B*b*F, B*k*F, B*a*P, IndP and B*ghi*P relative to the total of the US EPA 16 PAHs, ($\sum$COMB/$\sum$16 PAHs), provide useful information on the relationship between the origins of the PAHs and combustion of typical organics[66]. The values of the ratio $\sum$COMB/$\sum$16 PAHs in our sites ranged from 0.31 to 0.98 (Table 9) with an average value of 0.74. The values of $\sum$COMB/$\sum$16 PAHs in sites 4, 5, 10, 12, 15 and 19 showed a predominance of petroleum/petrogenic sources over combustion sources while the values obtained in the other 15 sites indicated the dominance of combustion over petrogenic sources and the relative importance of gasoline, diesel or oil combustion, as well as traffic sources. The ratio of PAH(4)/PAH(5 + 6) could be used to ascertain the transportation behaviour of PAHs. For instance, a high ratio of PAH(4)/PAH(5 + 6) suggests long distance transportation while a lower ratio suggests that the PAHs originate from emissions of local sources[67,68]. The ratios of PAH(4)/PAH(5 + 6) obtained in this study ranged from 0.0 to 4.78 (Table 5) with the majority of the investigated sites having a value less than 0.9. This suggests that the PAHs in soils of Warri and its environs originated from emissions from local sources. However, the values for sites 15, 16 and 20 indicated that the PAHs in these sites originated from emissions from distant sources. The total index Barreca *et al.*[69] was also evaluated as the sum of single indices (discussed earlier) normalized for the limit value (low temperature sources-high temperature sources) reported in the literature[60].

$$\text{Total Index} = \frac{\text{Ant/(Ant + Phen)}}{0.1} + \frac{\text{Flt/(Flt + Pyr)}}{0.4} + \frac{\text{B}a\text{A/(B}a\text{A + Chry)}}{0.2} + \frac{\text{IndP/(IndP + B}ghi\text{P)}}{0.5}$$

PAHs associated with high temperature processes (combustion) have a total index that is greater than 4, while PAHs originating from low temperature processes (petroleum products) have a total index that is less than 4. In this study, the total index values ranged between 0.7 and 16.6 with the majority of the sites having total index values greater than 4. The total index values confirm the fact that PAHs contamination of these sites originated from both high and low temperature combustion processes.

Principal Component Analysis

The principal component analysis (PCA) is a value tool to represent total variability of data with minimum number of factors. PCA was performed on the 16 individual PAHs and 21 soil samples to identify the possible sources of PAHs contamination. In this study, three components (Factors) were extracted representing 78.97% of the total variance (Supplemental Material 1). Factor 1 one contributed 32% to the total variance, and had significant positive loadings in Acy, Ace and Pyr with negative bipolar loadings in D*ah*A, IndP and B*ghi*P. Factor 2 contributed 25.48% of the variance and was heavily weighted by Flu, Phen and Ant. The compounds in Factors 1 and 2 are typical representation of low temperature processes such as wood combustion[2,70]. The Ace is indicative of oil exploitation[71]. Therefore Factors 1 & 2 represents sources including natural gas, wood, charcoal, straw and biomass combustion. Component 3 contributed 20.49% of the total variance which consist of Chry, B*b*F, B*a*P and IndP which are indicator of diesel combustion and characteristic emissions from traffic sources[2,28]. Thus biomass combustion and traffic emissions are the dominant sources of PAHs in these urban soils.

Conclusions

The concentrations of polycyclic aromatic hydrocarbons found in these soils fit into the weakly contaminated range, and 4-6-ringed PAHs accounted for a higher proportion of the $\sum 16$ PAHs. The carcinogenic PAHs (PAH_{7c}) constituted 15 to 98% of the $\sum 16$ PAHs in these soils. The results indicate that there is a high potential risk of cancer development as a result of human exposure to PAHs in these soils. The diagnostic ratios indicated that the sources of PAHs in these soils were mainly pyrogenic, originating from a combination of fossil fuel, petroleum and biomass combustion. The results obtained from this study provide useful information for developing strategies for risk and urban environmental quality management.

Materials and Methods

Reagents and Chemicals

N-hexane and dichloromethane were of HPLC-grade (Merck, Darmstadt, Germany). The standard mixture of the US EPA 16 priority PAHs was purchased from Supelco Inc., Bellefonte, PA, USA. Sodium sulfate, alumina and silica gel were obtained from BDH (Poole, United Kingdom), helium gas (99.99%) purity was obtained from Air Liquide (Lagos, Nigeria). The isotopically labelled PAHs were obtained from Cambridge Isotope Laboratories Inc., Tewksbury, MA, USA.

Description of the Study Area

The city of Warri, Nigeria, and its environs (Supplemental Material 2), hosts the Warri Refinery and Petrochemical Company (WRPC), Nigerian Gas Company (NGC) and Delta Steel Company (DSC). Other industries found in these areas include those rendering services to the oil and gas sector, and food processing companies[72]. The positions of the sampling locations are displayed in Supplemental Material 3. A detailed description of the geology, vegetation, climatic conditions and soil types of the study area can be found elsewhere[72-75]. Briefly, the area has a typical tropical climate, with well-defined rainy and dry seasons. The dry season occurs from November to April while the rainy season occurs between May and October. The average annual rainfall is 2500 mm. The minimum air temperature is 18°C, while the maximum is 35°C. Warri occupies a low-lying area with height generally less than 6 m above sea level. The area is drained by the Warri River and its network of tributaries and creeks, emptying into the sea. The drainage pattern is dendritic with tributaries branching without any preferred orientation[72,74,75].

Sampling

Nigerian regulation does not require any kind of permission before sampling urban soils for environmental studies. Besides, the study does not involve the use of animals or human or cover protected areas or involved endanger species. Therefore, no permission is required in this case. A total of 21 soil samples were collected from different locations within Warri and its environs at a depth of 0-15 cm. It was difficult to categorise the sampling locations according to land use patterns because of the mixed land use in the city. For example, samples collected in the vicinity of the refinery may be classified as industrial but this zone is now surrounded by residential apartments. Soil samples were collected in areas with high human activity, such as, industries, car and truck parks, roadsides, commercial areas, and high traffic and residential zones. At each sampling site, 3 to 4 samples were collected and mixed together to form composite sample for each site. The soil samples were labelled and stored in an ice chest prior to being transported back to the laboratory. Thereafter, all the soil samples were dried, sieved to < 2 mm after removing stones and residual roots, and stored at −4°C until analysis.

Sample Extraction and Clean-up

Five grams of each soil sample was extracted with hexane and dichloromethane (1 : 1, v/v) in an accelerated solvent extractor (ASE 200, Dionex, Sunnyvale, CA, USA). The extraction cells were filled with the solvents, pressurized to 14 MPa, and heated to 120°C for 5 min. The pressure and temperature were held constant for the extraction time of 5 min and the cells were rinsed with cold solvents and purged with argon for 2.5 min. The static extraction and purge steps were combined[76,77]. The extracts were evaporated to 1 mL with a rotary evaporator and purified by solid phase extraction with 2 g of aluminium oxide (5% deactivated, upper part) and 2 g of silica gel (5% deactivated, lower part). The PAHs were subsequently eluted with 15 mL of hexane, 5 mL of hexane : dichloromethane (9 : 1, v/v) and 20 mL of hexane : dichloromethane (4 : 1, v/v). Before extraction, a range of surrogate PAHs (isotopically labelled PAHs, namely, naphthalene-d_8, acenaphthene-d_{10}, anthracene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were spiked into selected soil samples for monitoring the efficiency of extraction and clean-up procedures. The extracts were reduced to 1 mL under a gentle stream of nitrogen gas prior to gas chromatographic analysis.

Gas Chromatographic Analysis

The individual PAHs were quantified by means of gas chromatography-mass spectrometry (Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass selective detector, Agilent, Palo Alto, CA, USA). The separation of the analytes was effected on a DB5 capillary column (cross-linked phenyl methyl siloxane) (0.25 μm film thickness, 0.25 mm × 30 m) (J&W, USA). The carrier gas was helium (99.999%) with a linear flow rate of 1 mL/min. The initial temperature was 70 °C, held for 1 min, then increased to 260°C at a rate of 10°C/min, and finally increased to 300°C at a rate of 5°C/min. Splitless injections were used with an injection volume of 0.1 μL. The mass spectrometer was operated in selected ion mode.

Quality Control/Assurance and Statistical Analysis

All data were subjected to strict quality assurance and control procedures. For every five samples, a method blank (solvent and glassware) and a matrix spike (working standards spiked into pre-extracted soil) was analysed together with the samples, and two sample duplicates were processed for the entire extraction, clean-up and analysis procedure. The spike recoveries for the individual PAH compounds ranged from 65.4 to 103% while the recoveries for the surrogate PAH compounds ranged from 69.7 to 98.5%. The r^2 values for the calibration lines ranged from 0.9995 to 0.9999. The limits of detection for PAHs were determined by replicating the analysis of cleaned samples ($n = 4$) that were spiked with known amount of 1.0 ng and taking three and ten folds of the standard deviation as the limit of detection (LOD and limit of quantification (LOQ) respectively. The limits of detection for the PAH compounds were in the range of 0.03 to 0.2 $\mu g\,kg^{-1}$ while the limits of quantification (LOQs) ranged from 0.1 to 0.6 $\mu g\,kg^{-1}$. The PAHs were quantified by using external calibration method, and the calibration was performed by injections of standard solution of the mixed PAHs standard at 6 calibration levels. Analysis of variance (ANOVA) was used to determine whether the concentrations of PAHs varied significantly among the various sites. The statistical analyses were performed with SPSS version 15.1. The sources of PAHs in these soils were evaluated by using the different isomeric ratios.

Assessment of Health Risk from PAH Exposure

PAHs occur as mixtures and the risk to human health from various PAH exposures can be evaluated by comparing the toxicity or carcinogenic potency of the individual PAH compounds relative to benzo[*a*]pyrene (B*a*P). The B*a*P toxic equivalency factor (BaP_{TEF}) and B*a*P mutagenic equivalency factor (BaP_{MEF}) have been adopted by several researchers to evaluate the risk of PAHs in foods, dust, soil and sediments[78-82]. The B*a*P carcinogenic equivalency quotient (BaP_{TEQ}) for the mixture of PAHs was evaluated by using the formula:

$$BaP_{TEQ} = \sum C_i \times BaP_{TEF} \quad (1)$$

where BaP_{TEF} is the carcinogenic potency relative to B*a*P and C_i is the concentration of the individual PAH compound.

The B*a*P mutagenic equivalency quotient (BaP_{MEQ}) for the mixture of PAHs was evaluated from the formula:

$$BaP_{MEQ} = \sum C_i \times BaP_{MEF} \quad (2)$$

where BaP_{MEF} is the mutagenic potency relative to B*a*P and C_i is the concentration of the individual PAH compound.

The B*a*P carcinogenic (BaP_{TEF}) and B*a*P mutagenic (BaP_{MEF}) equivalency factors for the seven carcinogenic PAHs assessed in this work are provided in Supplemental Material 4.

Incremental Lifetime Cancer Risk

Exposure risk assessment was carried out by applying the USEPA standard methods assuming three major routes of exposure, namely, ingestion, dermal absorption and inhalation of vapour or dust - IDI[83]. The total carcinogenic risk was calculated by summation of the individual risks through each route of exposure. Evaluation of the incremental lifetime cancer risk (ILCR) in terms of IDI was carried out by using the parameters in Supplemental Material 4 and equations 3-5[4,84].

$$\mathrm{ILCR_{ing}} = \frac{\mathrm{C_{soil} \times IngR \times EF \times ED \times CF \times SFO}}{\mathrm{BW \times AT}} \tag{3}$$

where $\mathrm{ILCR_{ing}}$ is the incremental lifetime cancer risk via ingestion of soil particles, $\mathrm{C_{soil}}$ is the concentration of the pollutant in soil (mg/kg), IngR is the ingestion rate of soil (mg/day), EF is the exposure frequency (days/year), ED is the exposure duration (years), BW is the average body weight (kg), AT is the averaging time (days), CF is the conversion factor (1×10^{-6} kg/mg) and SFO is the oral slope factor $(\mathrm{mg/kg/day})^{-1}$ (see Supplemental Material 4).

$$\mathrm{ILCR_{derm}} = \frac{\mathrm{C_{soil} \times SA \times AF_{soil} \times ABS \times EF \times ED \times CF \times SFO \times GIABS}}{\mathrm{BW \times AT}} \tag{4}$$

Here $\mathrm{ILCR_{derm}}$ is the incremental lifetime cancer risk via dermal contact of soil particles, SA is the surface area of the skin that contacts soil ($\mathrm{cm^2}$/day), AF is the skin adherence factor for soil ($\mathrm{mg/cm^2}$), ABS is the dermal absorption factor (chemical specific) and GIABS is the gastrointestinal absorption factor.

$$\mathrm{ILCR_{inh}} = \frac{\mathrm{C_{soil} \times EF \times ET \times ED \times IUR}}{\mathrm{PEF \times AT^{*}}} \tag{5}$$

where $\mathrm{ILCR_{inh}}$ is the incremental lifetime cancer risk via inhalation of soil particles, ET is the exposure time (h/day), IUR is the inhalation unit risk $(\mu\mathrm{g/m^3})^{-1}$ (see Supplemental Material 4), AT is the averaging time (h) and PEF is the particle emission factor (1.36×10^9 $\mathrm{m^3}$/kg). PEF gives an indication of the inhalation of pollutants that are adsorbed to respirable particles ($\mathrm{PM_{10}}$), and it gives the relationship between the concentration of a pollutant in soil and that of respirable particles in the air, due to fugitive dust emissions from contaminated soils[85]. The parameters for estimating human cancer risk are listed in (Supplemental Material 5). Qualitative descriptions of lifetime cancer risks are provided in (Supplemental Material 6).

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