



Polyaromatic Hydrocarbons (PAHs) and Inorganic Chemical Contaminants at Refuse Dumpsites in Awka, South Eastern Nigeria: A Public Health Implication

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Authors' contributions

This work was carried out in collaboration between all authors. Author JKN designed and wrote the entire manuscript including corrections to the reviewers comment and sourced most of the data and literature, author CA in addition to providing some literature on PAHs supervised. Authors EO and FOO during laboratory work while authors TEE and LCN did the sampling and also assisted in sourcing some literature. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

Aim: Is to determine the levels some PAHs and inorganic contaminants in refuse dump soil samples within residential areas in Awka in Anambra State, Nigeria.

Study Design: Ten soil samples (five study samples and five control samples) taken from five major refuse dumpsites in Awka, South Eastern Nigeria were analyzed for the presence of 16 polynuclear aromatic hydrocarbons (PAHs) (organic contaminant) and inorganic contaminants using their respective standard methods.

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Place and Duration of Study: Soil samples were collected from Awka in Anambra State while the analysis was carried out at the Department of Pharmaceutical Chemistry, University of Lagos Nigeria between November 2010 and January 2011.

Methodology: Gas chromatography/mass spectrometry was used for the analysis of 16 specific target compounds which included naphthalene, acenaphthylene, acenaphthene, flourene, phenanthrene, anthracene, flouranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]flouranthene, benzo[k]flouranthene, benzo[a]pyrene, benzo[ghi]perylene, dibenz[a, h]anthracene and indeno[1,2,3-cd]pyrene. Four isotopically labelled polynuclear aromatic hydrocarbons (acenaphthene-d₁₀, phennanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂) were used for internal standardization. Inorganic contaminants were analyzed using their respective standard methods, these include nitrate, nitrites, chloride, hardness, TDS in addition to heavy metals, cation exchange capacity (CEC) etc reported in our previous study.

Results: All 16 PAHs were found in most of the samples and their controls, with highest concentration in sites A, B and C. The range of PAHs in the sites where as follows; site A (14.20 – 710.02mg/kg), site B (Nd-2392.06mg/kg), site C (Nd – 1158.22mg/kg), site D (Nd – 0.92mg/kg) and site E (Nd – 0.84mg/kg). Nitrates were as follows: site A (52.43mg/kg), site B(50.30mg/kg), site C(62.45mg/kg), site D(45.20mg/kg) and site E(38.50mg/kg). These and other examined parameters were present in an amount that can constitute environmental and public health problem.

Conclusion: It is concluded that indiscriminate dumping of refuse within residential areas can accentuate the environmental and public health- problem of the inhabitants.

Keywords: PAH; inorganic contaminant; refuse dumpsite; environmental pollution, public health, South Eastern Nigeria.

1. INTRODUCTION

The municipal status of Awka came into being in 1991 when it became a state capital. The increased government activities, business, private and public institutions have led to increase in population with its attendant environmental and public-health consequences. The study area – Awka, is made of shale and sandstone, referred to as Imo shale, which was deposited under a shallow marine environment. The area is laminated and fissile with bands of clay, sandstone, sandy shale and iron stone. It is covered with lateritic soil with a thickness that averages 1.1m below, which is poorly consolidated whitish – grey sandstone. The underlying dark-grey fissile shale is about 0.32m in thickness; it is observed to be massive, cemented and consolidated. The shale displays polygonal cracks, which developed as a result of water loss in the sediment. The sandstone unit is generally fine to medium in grain size, friable and unconsolidated [1,2]. A common feature in Awka as well as in many Nigerian cities is the high heaps of refuse dumps that emit repulsive odour resulting from decomposing organic and agricultural waste [3]. These heaps act as aesthetic pollutants and as sinks or breeding grounds for disease causing organisms.

The main factor responsible for pollution and other types of environmental deterioration in any community is the combined effect of population, affluence and technology [3,4,5]. A typical refuse dump in Awka consists of organic wastes such as (poultry litter, waste clothing and paper, wood waste and furniture, corn cob and chaff, vegetable residues, left over foods etc), inorganic wastes (glass, discarded battery cells, ceramics, acid wastes), metals (automobile parts, broken pots, stoves, cans, tins, pipes, other waste metallic containers), polymeric materials(plastics, foam, polythene bags, hair weavon etc), electrical and

electronic wastes (refrigerators, damaged phones and accessories, damaged computers and accessories, damaged fans and electric irons, waste bulbs and sockets) and sundry wastes such as pharmaceuticals, paint products and containers etc.

Following favourable weather conditions, physical, chemical and biological factors such as temperature, rain fall, humidity and microbes combine to degrade these wastes. Having reported that heavy metal levels at different depths and infiltration into the soil at these refuse dump sites [6] and heavy-metal levels of farm produce harvested from refuse dump sites in Awka positively correlated with that in the soil samples in the same locations, heavy-metal levels of ground and surface water within the study areas, changes in soil properties and bacterial isolates have also been reported [7]. Presently our interest is on the levels of polynuclear aromatic hydrocarbons (PAHs), nitrate and nitrite levels and other parameters in the soil samples from the refuse dumpsites. The PAHs are a class of compounds composed of two or more aromatic rings. Hundreds of them have been identified and found as complex mixtures [8]. They are generated by incomplete combustion, forest fire and volcanic eruptions [9] or by other anthropogenic sources such as industrial production, transportation and waste incineration [10,11]. They are widespread in the environment and may be due to general use of fossil fuel. The PAHs are classified as environmentally hazardous organic compounds by European Community (EC) and United States Environmental Protection Agency (US EPA), and are included in the priority pollutant list [12]. Several PAHs are known to be potential human carcinogens, some examples include benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene and benzo[g,h,i]perylene [13].

Nitrates are only one of several forms of nitrogen. They are highly mobile in the environment, usually they are released in the form of salt (e.g. sodium nitrate, potassium nitrate or ammonium nitrate), they dissolve in water to liberate free nitrate ions (NO_3^-) [14]. Other sources include agricultural, municipal wastewater or industrial discharges. Nitrates in drinking water have long been considered a health threat for their ability to induce methenoglobinemia, and this health outcome is the basis of the Environmental Protection Agency's maximum contaminant level for nitrates [15]. Usually ground water underlying agricultural areas often have elevated nitrate levels due to runoff of nitrogen fertilizers. Poor sanitation, littered compost heaps, fertilizer application, sewage, abattoir, large organic waste from the market and industrial effluents are major sources of nitrate/nitrite in water sources of a given study area [16]. The aim of this study is to bring to the fore the negative environmental and possible public health problem that may be associated with indiscriminate and unregulated dumping of refuse within residential areas and the result presented can serve as important data for policy makers.

2. MATERIALS AND METHODS

Five (5) major refuse dumpsites at Awka were selected as the sampling points and were labelled as sites A to E (Fig. 1). They are mainly for dumping of domestic and sundry refuse. We coordinated the 5 dump sites with a handheld global positioning system (Garmin Global positioning system, map 765 receiver Garmin Ltd, Olathe, KS) in February of 2007.

We based the coordinates on Minna datum (a local datum that uses the Northern terminal of the Minna base of the Nigerian primary triangulation network), and we also converted them to Universal Transverse Mercator projection systems (Table 1), also reported in our previous study [6]. For consistency across sites, at each site, we collected surface soil samples and

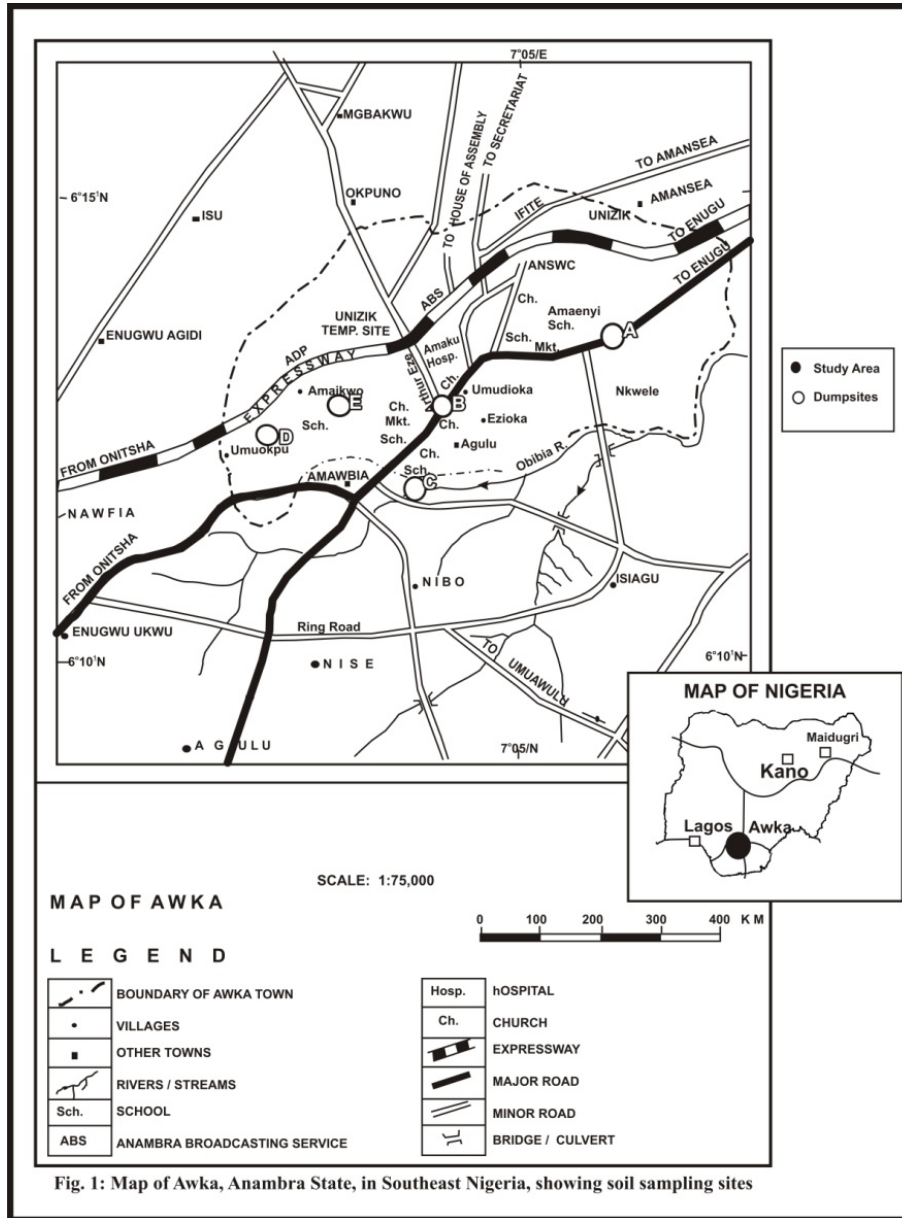


Fig. 1: Map of Awka, Anambra State, in Southeast Nigeria, showing soil sampling sites

control at 30cm depth (control was at between 100 – 120m) away but within a farmland. Table 2 gives the sample information. They were stored in black polythene bags and taken to the laboratory, the temperature of the laboratory was $\pm 29.5^{\circ}\text{C}$ (ambient temperature). We ground up the samples by mixing and dividing them into fine particles that could pass through a 0.5mm sieve. All the soil samples are fine to medium sand in texture.

Table 1. Soil sampling location/sites at Awka

Point (Site)	Location	Latitude ϕ	Longitude λ	Universal tranverse Mercator coordinates (m)	
				Northing	Easting
1(A)	Ring Road Amaenyi	06°13'1 35 ¹¹ .22 ¹¹	07°04'1 50.46 ¹¹	687,646.111	288,485.644
2(B)	Behind Amaku Specialist Hospital	06°13'1 05 ¹¹ .58 ¹¹	07°05'1 18.18 ¹¹	688,559.757	287,636.663
3(C)	Bishop Crowther	06°12'1 00 ¹¹ .90 ¹¹	07°03'1 40.62 ¹¹	685,670.004	285,478.736
4(D)	Prisons Amawbia	06°11'1 54 ¹¹ .42 ¹¹	07°03'1 43.14 ¹¹	685,470.649	285,555.501
5(E)	Kwata (Abattoir/House)	06°12'1 43 ¹¹ .50 ¹¹	07°03'1 31.68 ¹¹	686,949.001	285,208.528

Table 2. Sample information

ID No	Sample description	Analysis method	Extraction method
Site A	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Site B	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Site C	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Site D	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Site E	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Control of site A	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Control of site B	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Control of site C	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Control of site D	Soil Sample	GC/MS-US EPA Method	EPA method 3540
Control of site E	Soil Sample	GC/MS-US EPA Method	EPA method 3540

2.1 Determination of Polyaromatic Hydrocarbons (PAHs)

A PAHs (SRm 647C) standard mixture (NIST, Baltimore, MD) containing naphthalene, acenaphthylene, acenaphthene, flourene, phenanthrene, anthracene, flouranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]flouranthene, benzo[k]flouranthene, benzo[a]pyrene, benzo[ghi]perylene, dibenz[a,h]anthracene and indeno[1,2,3 -cd] pyrene was used in this study. A mixture containing four isotopically labelled PAHs (Chem Service, Westchester, PA) namely acenaphthene-d₁₀, chrysene-d₁₂, phenanthrene-d₁₀ and perylene-d₁₂ was used as an internal standard. The HPLC grade dichloromethane (Fischer Scientific New Jersey) was used for the extraction.

Soxhlet extractions were carried out using a modified form of the US EPA 3540 [17]. The Soxhlet apparatus consisted of a 250mL round bottom flask, condenser and extractor tube, seated in a temperature-controlled heating mantle. 10g portion of the air-dried soil sample was extracted with 100ml of HPLC grade dichloromethane for 16h [18].

2.1.1 Preparation of calibration standards

Five standard solutions each containing 16 target compounds were prepared by diluting the standard mix (1647c mix from NIST) to desired concentrations with dichloromethane. To

these were added 0.5 μ g (volumetric equivalent) of the four internal standards namely acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂. These were transferred to a capped and sealed vial until ready for analysis.

2.1.2 GC/MS Instrumentation and conditions

GC/MS analysis was carried out on a Shimadzu GC/MS QP2010 instrument. The column was HPMS (30m x 0.25 μ m x 0.25mm id). Helium was used as a carrier gas and the column head pressure was maintained at 10psi to give an approximate flow rate of 1mL/min. The injector and transfer line were maintained at 290°C and 250°C respectively. All injection volumes were 1 μ L in the split less mode. The column temperature was initially held at 70°C for 4min, ramped to 300°C at a rate of 10°C/min, the temperature was held at 300°C for 10min. The mass spectrometer was used in electron ionization mode and all spectra were acquired using a mass range of m/z 50 – 400 and automatic gain control (AGC).

2.1.3 Identification and quantification

The PAHs in the samples were identified by a combination of a retention time match and mass spectra match against the calibration standards. Quantification was performed by the method of internal standardization using acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂. Acenaphthene-d₁₀ was used as the internal standard for naphthalene, acenaphthylene, acenaphthene and flourene. Phenanthrene-d₁₀ was used as the internal standard for phenanthrene, anthracene, flouranthene and pyrene. Chrysene-d₁₀ was used for benz[a]anthracene and chrysene. Perylene-d₁₀ was used for the rest of the PAHs. Fig. 2. shows the structure of the 16 priority PAHs. Calibration curves were obtained using a series of standard solution. All 16 calibration curves were linear with correlation coefficients from the regression ranging from 0.999 to 1.000. The relative standard deviations were mostly lesser than 10% as shown in Table 3. Retention time and m/z are shown in Table 4.

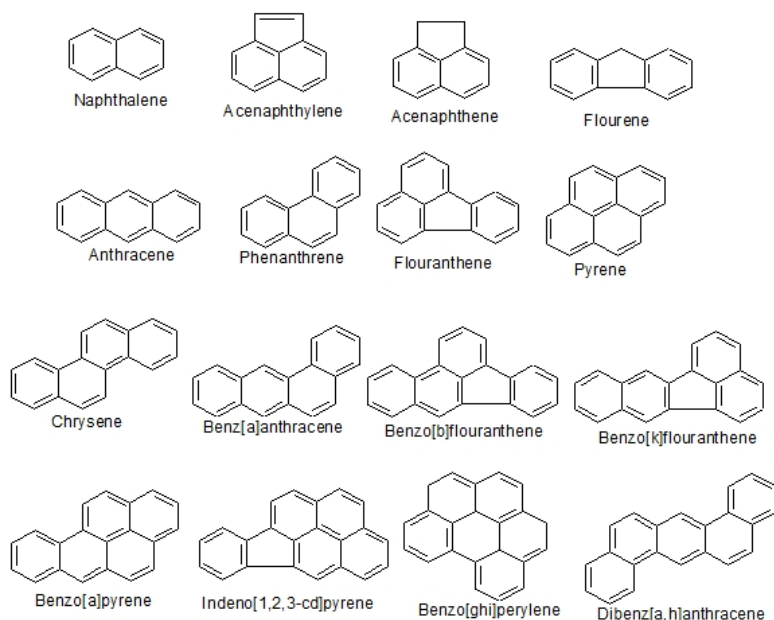


Fig. 2. Chemical structure of 16 priority PAHs

Table 3. Calibration parameters of the PAH compounds

Compound	Linear Range ($\mu\text{g/ml}$)	Slope (10^5)	Intercept (10^5)	Regression coefficient	RSD (%)
Naphthalene	0.125-0.499	5.521	0.145	1.000	6.310
Acenaphthylene	0.125-0.499	6.283	0.132	1.000	4.930
Acenaphthene	0.125-0.498	7.116	0.175	0.999	5.470
Flourene	0.125-0.498	6.357	0.142	0.999	5.040
Phenanthrene	0.125-0.498	6.926	0.155	0.999	5.100
Anthracene	0.125-0.499	7.123	0.121	1.000	3.870
Flouranthene	0.125-0.498	7.596	0.142	0.999	4.150
Pyrene	0.125-0.499	8.151	0.174	1.000	4.940
Benz[a]anthracene	0.125-0.499	6.722	0.108	1.000	3.930
Chrysene	0.125-0.500	5.701	0.116	1.000	4.470
Benzo[b]flouranthene	0.125-0.499	5.985	0.067	1.000	2.500
Benzo[k]flouranthtene	0.125-0.500	7.203	0.061	1.000	2.790
Benzo[a]pyrene	0.125-0.501	5.610	-0.002	1.000	1.260
Benzo[ghi]perylene	0.125-0.501	2.906	-0.059	1.000	5.620
Dibenz[a.h]anthracene	0.125-0.501	4.005	-0.021	1.000	1.510
Indeno[1,2,3 – cd] pyrene	0.125-0.500	3.251	-0.016	1.000	1.230

Table 4. List of retention time and m/z values for the 16 PAHs

Compound	Retention time (min)	m/z
Naphthalene	9.801	128, 115, 102, 87, 75, 63, 51
Acenaphthylene	16.402	152, 126, 98, 87, 76, 63, 50
Acenaphthene	17.274	154, 126, 102, 87, 77, 63, 50
Flourene	19.612	166, 139, 115, 83, 63, 50
Phenanthrene	23.792	178, 152, 126, 111, 99, 89, 76, 63, 50
Anthracene	24.014	178, 152, 126, 89, 76, 63
Flouranthene	29.606	202, 174, 150, 122, 101, 87, 74, 50
Pyrene	30.351	202, 174, 150, 101, 88, 74, 50
Benz[a]anthracene	34.278	228, 200, 150, 113, 88, 63, 50
Chrysene	34.348	228, 202, 176, 150, 113, 101, 63
Benzo[b]flouranthene	36.955	252, 224, 174, 150, 126, 113, 86
Benzo[k]flouranthtene	37.007	252, 224, 198, 150, 126, 74
Benzo[a]pyrene	37.621	252, 225, 161, 126, 74
Benzo[ghi]perylene	40.191	276, 248, 225, 207, 191, 138, 125, 97, 73
Dibenz[a.h]anthracene	40.262	278, 248, 225, 207, 191, 138, 125, 83, 73, 57
Indeno[1,2,3 – cd] pyrene	40.692	276, 248, 225, 207, 191, 138, 111, 97, 73, 57

2.1.4 Determination of other chemical contaminants

200g of each soil sample was added into distilled deionised water; they were stirred and left for 24hrs, then stirred thoroughly before filtering first using cotton wool, then with whatman No.40 filter paper. Filtrates were used for analysis. Nitrate was analyzed using the Brucine Colormetric method [19]. Nitrite was determined according to the gresis method of Montgomery and Dymock [20], while chloride, total hardness, total dissolved solid (TDS) and electrical conductivity (EC) were determined using their respective standard methods [21].

3. RESULTS AND DISCUSSIONS

Degradative processes, such as photolysis, hydrolysis, oxidation and biodegradation, are all involved in the chemical transformation of a compound upon its entry into the environment [22]. Most pollutants are leached into the environment from their source (sink) following favourable conditions of decay and deterioration. The PAHs can be generated as products of incomplete combustion processes such as forest fires [9]. They can also be generated from pyrogenic sources such as waste incineration [11], oxidation (slow burning) processes of organic and inorganic wastes at refuse dumpsites can also release PAHs into the environment [23]. We have reported that indiscriminate dumping of refuse along major roads within residential areas in Awka, Southern Eastern Nigeria, causes aesthetic pollution, emits repulsive odour due to decomposing waste, leads to flooding by blocking drainage channels, releases high concentration of heavy-metals into the soil [6], increases heavy-metal burden of surface and underground water through run-off, infiltration (percolation) and bio-accumulation of metals in agricultural crops [7]. This present study is on polynuclear aromatic hydrocarbons (PAHs) (organic) and other inorganic pollutants that have not been reported in refuse dumpsites of South Eastern Nigeria. A cursory look at the results of our study (Table 5) contained reasonable high values of the 16 priority PAHs with the following ranges: site A (14.20 – 1710.02mg/kg), site B (Nd – 2392.06mg/kg), site C (Nd – 1158.22mg/kg), site D (Nd – 0.92mg/kg) and site E (Nd – 0.84mg/kg). Some PAHs were not detected in some of the soil samples of study (refuse dumps), but were detected in that of the control, and in some cases were not detected in both the sample of study and the control. It was stated by Yun et al [24] that lower molecular mass PAHs with two to four rings tend to have low concentration because they are easily degraded while the high molecular weight PAHs with 5 and 6 rings are more difficult to degrade and therefore more in concentration. This was also evident in the work of Anyakora et al [25]. But in our study both the lower and higher molecular weight PAHs were in higher concentrations especially in sites A, B and C except benzo[ghi]perylene with low concentration in sites A, D and E but with non-detections in sites B and C. Naphthalene was not detected in sites B and E, Acenaphthene was not detected in site C, Anthracene was not detected in sites B and E. Benzo[b]fluoranthene was not detected in site D, Benzo[k]fluoranthene was not detected in site E while Indeno[1,2,3-cd]pyrene was not detected in site D. The low concentrations or non-detection of the 16 priority PAHs in the control samples showed that the PAHs in the refuse dump sites were actually released by the decomposing wastes. The high concentration of the PAHs in sites A, B and C despite the presence of microbial degrading species (Table 6) shows that refuse dump sites are major sources of polynuclear aromatic hydrocarbon and depicts a measure of resistance to microbial degradation by these higher molecular weight PAHs. This study would also suggest that PAHs formed by pyrogenic processes tend to produce higher molecular weight PAHs.

The high levels in sites B and C may be due to absence of *Bacillus sp*, as both *Bacillus* and *Pseudomonas sp* are very good PAHs degraders [26], by utilizing them as source of carbon and energy thereby cleaning the environment. The levels of these PAHs in the refuse soil samples can increase the environmental and public health burden of polynuclear aromatic hydrocarbons, since they are able to enter the groundwater. A previous study by Anyakora et al [27] established a link between the level of groundwater PAHs and level in surrounding sediment. Lower molecular weight PAHs can dissolve in water while higher molecular weight PAHs occur in water by binding to particulate matters in groundwater. They can both percolate and drain into the underground and surface water. The results of our study, especially those of sites A, B and C are higher than those reported recently in water samples in Nigeria's Niger Delta [28,18,29,30].

Table 5. Concentration of 16 PAHs in the soil samples of refuse dump sites in µg/kg

S/No.	Type of PAHs	Site A	Site B	Site C	Site D	Site E
1.	Naphthalene	61.01 (0.02)	Nd (0.01)	122.3 (Nd)	0.01 (0.01)	Nd (0.01)
2.	Acenaphthylene	89.97 (0.05)	39.94 (0.09)	120.20 (0.08)	0.08 (0.09)	0.07 (0.09)
3.	Acenaphthene	29.08 (0.02)	19.70 (0.01)	Nd (0.01)	0.01 (Nd)	0.01 (Nd)
4.	Flourene	63.50 (0.03)	11.86 (0.01)	116.27 (0.02)	0.01 (Nd)	0.10 (Nd)
5.	Phenanthrene	98.94 (0.01)	98.86 (0.08)	99.57 (0.13)	0.02 (Nd)	0.21 (Nd)
6.	Anthracene	124.60 (0.02)	Nd (Nd)	55.73 (0.01)	0.02 (Nd)	Nd (Nd)
7.	Flouranthene	126.01 (0.10)	149.08 (0.03)	109.58 (0.19)	0.17 (0.01)	0.21 (0.01)
8.	Pyrene	313.50 (0.01)	447.59 (0.03)	186.92 (0.21)	0.16 (0.01)	0.20 (0.01)
9.	Benz[a]anthracene	534.20 (0.04)	1036.09 (0.08)	67.85 (0.13)	0.02 (0.07)	0.35 (0.07)
10.	Chrysene	117.31 (0.21)	220.54 (0.03)	14.62 (0.53)	0.92 (0.03)	0.84 (0.03)
11.	Benzo[b]flouranthene	60.24 (0.02)	105.82 (0.04)	15.47 (0.85)	Nd (0.10)	0.22 (0.10)
12.	Benzo[k]flouranthene	307.72 (0.20)	660.53 (0.03)	15.43 (0.14)	0.18 (0.04)	Nd (0.04)
13.	Benzo[a]pyrene	1710.02 (0.11)	2392.06 (0.02)	1158.22 (0.53)	0.75 (0.12)	0.20 (0.12)
14.	Benzo[ghi]perylene	14.20 (Nd)	Nd (Nd)	Nd (0.16)	0.03 (Nd)	0.02 (Nd)
15.	Dibenz[a,h]anthracene	360.24 (Nd)	592.18 (Nd)	132.88 (0.04)	0.03 (Nd)	0.45 (Nd)
16.	Indeno[1,2,3 – cd] pyrene	335.46 (0.01)	376.80 (0.02)	294.63 (0.03)	(Nd) (Nd)	0.11 (Nd)

Nd = not detected, control values in parentheses

Table 6. Bacteria isolates from the dump sites

Bacteria	Site A	Site B	Site C	Site D	Site E
Staphylococcus aureus	Present	Present	Present	Present	Present
Pseudomonas sp.	Present	Present	Present	Present	Present
Streptococcus sp.	Present	Present	Present	Present	Present
Escherichia coli	Present	Present	Present	Present	Present
Bacillus sp.	Present	Absent	Absent	Present	Present
Klebsiella sp.	Present	Absent	Absent	Present	Present
Proteus sp.	Present	Present	Present	Present	Present

Nduka et al. 2008

The PAHs have received considerable attention in recent years because several of them are known to be potential human carcinogens. Examples include benz[a]anthracene, chrysene, benzo[b]flouranthene, benzo[a]perylene and benzo[ghi]perylene [13].

The PAHs are known human carcinogens and have been implicated in various cancers [31,32,33]. They have also been implicated in numerous other toxicological manifestations such as reproductive toxicity, intra-uterine growth retardation and learning and IQ deficit, destruction of oocytes and inflammation of kidney cells [34,35]. Toxicology of PAHs in humans have been carried out in several countries such as Ukraine [36], United States [37], Czech Republic [38], Denmark [39], United Kingdom [40], Poland [41], Germany [42], Sweden [43], and several other countries [44,45,46,47].

Heavy-metal levels and infiltration at refuse dump sites have been reported in our previous work [6,7] as part of inorganic pollutant (Table 7). From the previous study, refuse dumps are major sources of toxic heavy-metals such as lead, arsenic, cadmium, nickel, chromium and manganese (Table 7). Other inorganic chemical pollutants such as nitrates, nitrites, chlorides etc at refuse dumps that have not been reported are presented here alongside PAHs (Table 8). All the refuse dump sites had reasonably high values of nitrates that may be detrimental to health. Nitrates are essential plant nutrient but are harmful to animals and humans. Chronic nitrate toxicity in cow is a form of nitrate poisoning in which clinical signs of the diseases are not observed, but can cause reduction in the rate of weight gain, lowered milk production, depressed appetite and a greater susceptibility to infection [48].

Table 7. Metal levels in mg/kg of soil at different dump sites

	Depth (m)	Pb	Mn	As	Cr	Cd	Ni
Site A	0.00	350 (83.8)	290	620 (Nd)	4.75	2.00	27.00 (Nd)
	1.35	510	280.50	350	4.00	3.00	21.00
Site B	0.00	500 (Nd)	135	30 (Nd)	2.17	2.85	18.95 (Nd)
	1.35	350	160	65	2.50	2.38	31.50
Site C	0.00	620 (Nd)	120	102 (Nd)	2.35	2.66	15.00 (Nd)
	1.35	613.50	105	Nd	2.43	2.57	18.00
Site D	0.00	401 (3.80)	55.70	31.85	2.63	2.80	64.50 (Nd)
	1.35	370	60.55	(Nd)	2.62	1.79	68.35
Site E	0.00	145.30 (Nd)	205	160 (Nd)	3.09	2.14	61.75 (Nd)
	1.35	160.30	136.85	65.90	2.43	3.15	46.50

Nd = Not detected, control values are in parentheses, Nduka et al, 2008

The very fact that nitrates have very high water solubility and mobility in the soil suggests that both surface and underground water can be polluted and hence a route of nitrate entry into food web. Intake of nitrates from drinking water and dietary sources may cause increased exposure to N-nitroso compounds through endogenous nitrosation [49]. In their work, Coss et al. [50], suggested that long-term exposure to nitrates at levels below the maximum contaminant level of 10mg/L is not associated with pancreatic cancer but Niagolova et al. [51], established anthropogenic activity and drinking water supplies as two exposure pathways suggesting that the disease Balkan Endermic Nephropathy (BEN) could result from surface contamination. The work of Turkdogan et al. [52], revealed that traditional foods rich in nitrates and nitrites is significant in the development of endemic upper gastro intestinal (esophageal and gastric) cancers in the Van region of Turkey. We have previously suggested that industrial effluents and decomposition of organic wastes from refuse dumps and food stuff markets as major contributors to the nitrate and nitrite levels of potable water

supply in Warri area of Niger-delta region of Nigeria [16]. Marine invertebrates and fish exposed to nitrates may be smaller in size, have reduced maturity rate and lower reproductive success. In extremely high exposure levels, aquatic invertebrates and fish may die [53]. Our results are all above US EPA maximum contaminant level (US EPA MCL) of 10mg/L and World Health Organisation (WHO) 45mg/L, except site E (Table 8). *Nitrosomonas* and *Nitrobacter species* convert nitrate to nitrite (NO_2^-) which inhibit the function of haemoglobin thereby causing metheglobinemia or blue baby syndrome.

Health problems associated with exposure to nitrates and nitrites which have been reported in Nigeria include mainly incidences among infants and pregnant mothers of cancers and lesion [54]), spontaneous abortion and ectopic pregnancy [55], Malignant lymphomas [56, 57] and soft tissues sarcomas [58]. Pregnant women who drink nitrate contaminated water may be at increased risk of having spontaneous abortion [59] or giving birth to infants with congenital malformations especially of the central nervous system [60]. We have previously believed that in addition to natural concentration, sewage, industrial wastes or intrusion of sea or saline water as only sources of chloride in inland waters, the result of our study shows that refuse dumps are also a major source of chlorides (Table 8). Small concentrations of chloride in drinking water is not harmful to humans and with some adaptation the human body can tolerate water with as much as 200mg/L. High chloride content in process waters may promote pipe corrosion. Infiltration into underground water or into surface water through run-off especially in the rainy season may occur in the study area. Our results (Table 8), shows that refuse dumps can contribute to water hardness evidenced by the presence of sodium, magnesium and potassium reported in our previous study [6], this is because most components of the studied dumpsites have been found to contain high levels of these metals [61]. The same could be said of total dissolved solids (TDS); the primary sources of TDS in receiving waters are agricultural run-offs, leaching of soil, contamination and point source.

Table 8. Inorganic properties of the soil at refuse dumpsites

Sampling points	Nitrate (mg/kg)	Nitrite (mg/kg)	Chloride (mg/kg)	Hardness (mg/kg)	Total dissolved solid(mg/kg)	Electrical conductivity ($\mu\text{S}/\text{cm}$)
Site A	52.43 (4.44)	11.13 (1.93)	212.67 (26.65)	171.33 (51.67)	358.62 (153.92)	1339.00 (242.66)
Site B	50.30 (8.20)	10.28 (4.25)	144.8 (25.56)	224.00 (82.00)	579.00 (190.00)	1690.00 (403)
Site C	62.45 (4.12)	10.15 (0.24)	66.20 (29.86)	135.00 (63.00)	370.00 (230.00)	1490.00 (485)
Site D	45.20 (1.28)	13.21 (1.04)	129.90 (27.60)	155.00 (10.00)	171.10 (57.70)	1212.00 (173.50)
Site E	38.50 (1.20)	10.35 (0.80)	443.00 (27.20)	350.00 (8.00)	127.00 (47.75)	1080.00 (162.00)

Control values are in parentheses

Pollution and a direct relationship exist between total dissolved solid (TDS) and electrical conductivities. Previously we have reported that decomposition and accumulation of material at the dumpsites can modify the soils at the dumpsites as they tend to humus soil (with high organic matter) and therefore high cation exchange capacity (CEC) (Table 9). By this, carbon (iv) oxide (CO_2), methane (CH_4) (under anaerobic condition) and nitrous oxide (N_2O) are generated. These greenhouse gases have profound effect on earth's atmosphere by allowing short-wavelength solar radiation in, but trap much of the outgoing long-wavelength

radiation [62]. This scenario may in part account for urban micro-climate very noticeable in most Nigerian urban centres. The acidity of the top soil at dumpsites and that of control does not vary much, because of high exchangeable cation such as sodium, magnesium, calcium and potassium (Table 9) which are not highly leachable (when leached), they are replaced by hydrogen ion. The percentage pore space of control sample is more than those of test samples; this is in conformity with soil type of the study area [2]. It therefore means that the refuse dump is conferring clayed to loamy properties on the soil and the growth of roots into moist soil is limited by bulk densities ranging from 1.45mg/m³ in clays to 1.85mg/m³ in loamy sand, this agrees with Table 9 and literature [62].

Table 9. Properties of surface soil at the dump sites

	Cation exchange capacity (Cmolc/kg)	Particle density (mg/m³)	Bulk density (mg/m³)	pH	% pore space	% organic matter
Site A	7.66 (3.32)	2.55 (2.65)	1.78 (1.73)	6.61 (6.22)	30.20 (34.72)	2.55 (0.00)
Site B	6.16 (4.04)	2.50 (2.70)	1.88 (1.83)	6.62 (4.45)	24.80 (32.22)	1.72 (0.79)
Site C	5.92 (3.16)	2.60 (2.75)	1.83 (1.73)	6.69 (5.26)	29.62 (37.09)	1.45 (0.00)
Site D	6.56 (4.24)	2.80 (2.55)	1.83 (1.78)	6.68 (6.38)	34.64 (30.20)	2.10 (0.86)
Site E	7.48 (3.04)	2.75 (2.65)	1.68 (1.73)	6.60 (6.65)	38.90 (34.72)	3.07 (0.00)

Control values in parentheses ,Nduka et al, 2008

Although we have stated that the microbial species isolated from the soil at refuse dump sites and as reported in our previous study (Table 6) [7]. They may be using the PAHs as source of carbon and energy, hence cleaning the environment, their public health importance cannot be overlooked. These bacteria have been variously reported in dump site studies. *Escherichia coli* and *Streptococcus sp* have been reported by Ekundayo [63] while *Bacillus sp*, *Escherichia coli*, *Pseudomonas sp* and *Klebsiella sp* have been reported by Cook et al [64] and *Pseudomonas sp* is widely reported to be associated with waste [65]. All the bacteria isolated are known as potential pathogens by Cook et al [64]. Because the dumps are within residential area and Awka has no land fill as is the case with most Nigerian cities, domestic animals and nocturnal insects can serve as vectors of these pathogens. To remediate an already contaminated soil, phytoremediation should be encouraged; this involves planting of flowering plants such as *Ixora* on the contaminated soil. These plants utilize their roots to absorb, translocate and concentrate toxic metals from the soil to the harvestable plant tissues [66]. Polyaromatic hydrocarbons can be remediated by introducing into the soil and encouraging the growth of certain microbes such as *Bacillus sp*, *Pseudomonas sp*, *Klebsiella sp* etc which degrade and utilize organic compound as source of carbon and energy [67]. We conclude that indiscriminate dumping of refuse as it is done in South Eastern Nigeria and in almost all Nigerian cities is a serious public-health issue. We therefore recommend proper and scientific method of refuse disposal especially in and around residential areas.

4. CONCLUSION

We conclude that indiscriminate dumping of refuse within residential areas as it is done in Awka and in all Nigerian cities can release organic and inorganic chemical contaminants into

the environment, act as a sink to disease pathogens, block drainage channels, aesthetically deface the environment and ultimately constitute environmental and public health menace.

COMPETING INTEREST

Authors declare that no competing interest exists.

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