Fate, Distribution and Sources of Polycyclic Aromatic Hydrocarbons (PAHs) in Contaminated Soils in Parts of Calabar Metropolis, South Eastern Nigeria

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ABSTRACT: The paper is aimed at the investigation of polycyclic aromatic hydrocarbons (PAHs) in contaminated soils collected at depths of 15 to 100cm from two spilled sites in the vicinity of a leaking pipeline (Calabar, Nigeria). The soils were prepared in the laboratory using standard procedure and were analyzed for sixteen priority PAHs using Gas Chromatography – Mass Spectrophotometer (GC - MS).The concentration of total PAHs (TPAHs) in the contaminated soils ranged from 4.28 to 29.77mg/Kg and decreased with depth. These levels are higher than values obtained from rural and semi urban soils but lower than values obtained from soils in the vicinity of some petroleum handling facilities in part of the study area. Generally the soils were relatively enriched with medium- and lower-molecular-weight PAHs. Phenanthrene/Anthracene, Fluoranthene/Pyrene, Fluorantine/Fluorantine+Pyrene and Benzo(A)Anthracene/Chrysene ratios and the relative abundance of PAHs according to the number of rings were used to access the sources of PAHs. In addition, the main mechanism of PAHs transport in the study area was proposed. © JASEM

Introduction: Polycyclic aromatic hydrocarbons (PAH) are widely distributed in the environment, and some are carcinogenic to human beings even at very low concentrations (Franco, 2008; Sabate et al., 2006 ;Petterson, 1989). Benzo[a]pyrene, one of the PAH has received considerable attention due to its carcinogenic and mutagenic properties (Lorenzi et al., 2010; Santodonato et al., 1981). PAHs are derived from natural or petrogenic sources (including geogenic, forest fires and volcanic activities) and anthropogenic or pyrogenic sources (including oil leakages, oil spills and combustion of fossil fuels). The pyrogenic sources are mainly associated with higher-molecular-weight PAHs while the petrogenic sources are commonly associated with lower-molecular weight PAHs (Neff et al., 2003). PAHs are among the list of USEPA priority pollutants. Studies (Bruce, 1993; Clark and Sim, 1998, Zhang et al., 2006, 2007; Riccardi et al., 2008) have shown that oil leakage and spillage from petroleum storage facilities have the potential to impact soil and vulnerable shallow groundwater system. In the study area fuel spills and leakages, bush fires and refuse combustion or burning are sources through which polycyclic aromatic hydrocarbons (PAHs) are released into the environment. The release of the PAHs could take the form of major oil spillages or minor leakages of petrol from fuel storage tanks and pipelines, mechanic worksops and petrol stations (Nganje et al 2012 ,2007a).

The polycyclic aromatic hydrocarbons (PAHs) are usually persistent in the subsurface environment i.e. they may be present long after the contamination or pollution incidence and cannot be removed from the subsurface within a reasonable time period by pump and treat technique (Travis and Dotty, 1990). The persistence of PAHs in the environment is mainly caused by their slow dissolution and slow diffusion kinetics (Grathwohl, 2001; Totsche, 2004). Low aqueous solubility's of PAHs and high octanol-water partition coefficients (Ko_W) often result in their accumulation in soils and sediment to levels several orders of magnitude above aqueous concentrations (Grathwohl, 2001). Extensive studies on the sources, occurrence, transport, and fate of PAHs in natural environments have been documented in some countries including China (Li et al, 2008; Zhang et al., 2007, 2008; Zhu et al 2004a,b; Chen et al., 2004; Zhou and Maskaoui, 2003; Mai et al., 2003); Hongkong (Zhang et al., 2006); Taiwan (Fang et al.,2006, 2004); USA(Neff et al., 2003), Germany (Manz et al., 2001), Ireland (Charlesworth et al., 2002); Russia and Spain (Savinov et al.,2003; Nada et al., 2000); and France (Cachot et al. , 2006). Unfortunately, such studies are scarce in developing countries such as Nigeria where environmental issues are given secondary considerations to economic issues.

Reported cases of PAHs contamination in soil, sediment and water (surface and groundwater), in the study area have been documented by Nganje et al., (2012, 2007a, b) and Ibe et al., (2012, 2013). The

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two major oil spills documented in the study area in December 1999 and October 2000 were due to leaking pipes which convey refined petroleum products between the Nigerian National Petroleum Company (NNPC) jetty and the Depot. Unfortunately, minor leakages are anticipated since these pipes had been installed more than twenty five years ago whereas, pipes are susceptible to leakage just after 10 to 15 years of installation (Barber et al 1990). The first spilled site (site 1) is closer to the NNPC Jetty and the second spilled site (site2) is between Ekorinm and the NNPC depot in Calabar metropolis. Ekorinim and its environs have undergone rapid urbanization and economic development in the last two decades and is now considered as one of the most populated residential areas in Calabar. In view of the known carcinogenic properties of several PAHs, persistence in the environment, increasing health hazards, and the lack of published soil guideline values for PAHs in the study area and in Nigeria, it is imperative to evaluate the fate of PAHs in soils from the spilled fuel. Hence, the aim of this study is to investigate the levels of PAHs in the soil at various depths within the vicinity of the leaking pipeline. This will contribute to the existing data and provide basis for planning of future monitoring of PAHs in the area of study.

MATERIAL AND METHODS

Fourteen soil samples were collected within the vicinity of the leaking pipeline between the months of August and November 2000 at depths of,15cm, 30cm, 45cm, 60cm, 75cm, 90cm and 100cm.The soil samples were collected using manual/motorized soil auger and were wrapped with aluminum foil which were cleaned with toluene and transported to the laboratory. Each of the spilled sites was investigated in the same manner. Safety precautions considered during soil sampling included the wearing of disposable gloves, and boots that could be de-contaminated. In the laboratory, soil samples were air-dried in ambient air in a fume cupboard before disaggregation using a mortar and a pestle. The soil samples were then sieved to size fraction of less than 2mm and were sealed in plastic bags, labeled and stored in the refrigerator at 4ºC prior to analysis. 15g of each soil sample wee extracted by accelerated solvent extractor (ASE C 300) Dionex Sunnyvale. The soil extracts were prepared and analysed by gas chromatography coupled to mass spectrometry (HP5890/HP5972) auto sampler HP 7673 and software HPG1304C at the hydrogeochemistry laboratory, University of Tubingen (Germany), for the USEPA, 16 priority PAHs: (naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ace), fluorene (Fln), Phenanthrene (Phe), anthracene(Ant), Fluoranthene(Flu), Pyrene(Py), (B(a)A)chrysene(Chr), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthe

(B(k)F), benzo(a) pyrene (Bap), dibenzo (a, h) anthracene (DahA), Ideno (1,2,3-d) pyrene (ideno) and benzo (g,h, I) perylene (Bghip). Details of sample preparation, extraction, GC program and analyses are contained in Nganje et al., (2007a,b and 2012). Quality control and accuracy were evaluated by analyzing several standards (covering a range of concentrations), field replicates and splits, and by addition of standards to unknown samples to assess for matrix effects.

RESULTS AND DISCUSSION

Concentrations of TPAHs in soil: The sum of concentration of PAHs decreased with depth at the spilled sites (Fig.1) with ranges from 4.28 to 24.87mg/Kg (site 1) and 6.76 to 29.77mg/Kg(site 2). These trends reflect PAHs enrichment in soil at a depth of 15cm which is the primary absorptive surface (Dzomback and Luthy, 1984). The PAHs enrichment at depth of 15cm is similar to results of previous studies by Nganje et al., (2007a) in part of the study area. PAHs accumulate in the surface soil by adsorption because of their persistence and affinity for soil organic matter (Means et al.,1980).

The observed variability in the composition of the PAHs with depths at the spilled sites could also be attributed to the different transport mechanisms at the different sites. Areas where leaching is the predominant process the concentration of lower-molecular-weight PAHs ($\leq$ 4 ring PAHs) increased to a larger extent compared to sites where bioturbation is predominant (Pichler et al.,1996). Transport of five and heavier rings PAHs to the subsurface are probably with dissolved organic matter or colloids.

Generally, the results also showed that the soil samples, irrespective of the depths and site, had total PAH concentration less than the Dutch Intervention limit for total PAHs of 40 mg/kg from landscaping residential area (VROM, 2000; Tim O'Hare Associates, 2002). Also, concentration of benzo[a]pyrene at the various depths and sites were less than 1mg/Kg and below the range of 1.08 – 1.32mg/Kg for UK generic assessment criteria (GAC) for residential land use (Nathanial et al, 2007). Values for benzo[a]pyrene above these ranges are considered to be a potential risk in the environment for human health. Thus, the values obtained in the present study revealed that the environment within the study area is safe with regards to benzo[a]pyrene concentration.

The results from the present study were compared with total PAH concentrations in soils in part of the study area (Table 1), The present study showed relatively higher total PAH concentrations than values reported by Nganje et al (2007b) and Ibe et al (2013) in the vicinities of petrol station, kerosene tank, rural and semi-urban soils, but less than values

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reported Nganje et al (2007a) for soils around airport fuel dump site. Comparison with studies from other countries of the world for soils from urbanization, agricultural and industrial activities (Table 1), the values of TPAHs obtained from this study were lower than values reported in the vicinities of oil refineries in Belgium, United Kingdom, Slovakia and Australia but higher than values reported for soils contaminated by other human activities in Ghana,

Korea, China, France and Spain. Although soil total PAH concentrations reported in the present study are yet to attain polluted status, the potential environmental implications should not be overlooked since PAHs are known to constitute human health risk (Franco et al., 2008). Hence regular checks or monitoring of spilled sites are highly recommended around residential quarters and sources of drinking water.
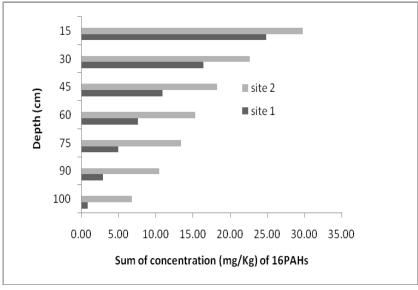

Fig 1.Distribution of sum of concentrations of PAHs with depth

Table 1. TPAHs concentrations (mg/Kg) in soils in part of the study area and other countries

TPAHs	Countries	Soil depth (cm)	Sources	Reference
0.34 - 18	Nigeria	0 - 30	Vicinity of Petrol station	Nganje et al. (2007a)
60.65	Nigeria	0 - 30	Near Fuel dump site	Nganje et al. (2007b)
3.14	Nigeria	0 - 30	Vicinty of kerosene tank	Nganje et al. (2007b)
334.45	Nigeria	0 - 30	Near petrol station and mechanic workshop	Ibe et al. (2012)
16- 25	Nigeria	0-30	Tank farm distribution facility	Nganje et al. (2012)
5.64 - 17,47	Nigeria	0 - 30	Rural soils	Ibe et al .(2013)
14.65 - 15.33	Nigeria		Semi urban soils	Ibe et al .(2013)
0.1	Ghana	ND	Periurban agricultural soils	Wilcke (2000)
300	Belgium	ND	Vicinity of an oil refinery	Bakker et al. (2000)
0.53	China	0 - 20	Vicinity of industrial activities	Xing et al.(2006)
0.45 - 5.65	France	ND	Near Industrial area	Motelay-Massei et al. (2004)
10.2	Germany	ND	Vicinity of industrial activities	Wilcke et al. (1997
1.00 - 1.52	Spain	ND	Near chemical industries	Nadal et al. (2004)
6.6 - 1404.16	Uk	0 - 10	Former tar works	Lorenzi et al. (2010)
4.28 - 29.77	Nigeria	15 - 100	Contaminated soils (spilled sites)	Present study

ND = Not determined

Soil individual PAH concentrations: Plot of individual PAH concentrations (Fig 2) showed marked variations in the distributions of individual PAHs and the higher concentrations of most

individual PAHs in site 2 relative to site1. However, higher individual PAH concentrations were observed for higher- molecular- weight PAHs (three to six rings)(Fluoranthene and Pyrene) at site 1 and for

[1]NGANJE, TN; [2]NEJI, PA; [3]IBE, KA; [1]ADAMU, CI, [1]EDET, A

lower-molecular-weight PAHs (Fluorene, Phenanthrene and Pyrene) at site 2 (Figs.2). Specifically, phenanthrene, fluoranthene and pyrene were recovered from the soils in significantly higher concentrations than the rest of the PAHs. It is obvious that lower- molecular- weights PAHs such as naphthalene, acenaphthylene, acenaphthene) may have evaporated from the soil over time due to their high volatility (Wilcke, 2000). The higher concentrations of the lower-molecular- weight PAHs at site 2 compared to site 1 was attributed to the fact that the soil samples at site 2 were collected a few days after the spills had occurred. The low values of lower-molecular-weight PAHs may be attributed to volatilization during sample porcessing/postextraction, solvent evaporation process prior to GC–MS analysis (Lorenzi et al., 2010 ; Dean, 2003). Generally the order of distribution of PAHs is medium-molecular-weight PAHs (e.g. fluoranthene and pyrene) >lower-molecular-weight PAHs (e.g. naphthalene, acenaphthylene, acenaphthene)>high-molecular-weight PAHs. It has been well documented that PAHs recovered from sites that are typical of anthropogenic (pyrogenic) sources tend to have high molecular weights PAHs, as opposed to petrogenic sources which are typically characterised by lower-molecular-weight PAHs (Li et al., 2008). Therefore, it is most likely that the higher concentrations of medium-molecular-weight PAHs at site 1 are indicative of pyrogenic (anthropogenic) input while the higher levels of the lower-molecular weight PAHs (fluorene and phenenathrene > pyrene medium-molecular weight PAHs) at site 2   are indicative of petrogenic sources..

Diagnostic ratios of PAHs can be used to trace the pollution sources (Shen et al,.2009; Matt, 1999; Fang et al., 2004; De Luca et al.,.2004; Budzinski et al.,. 1997;). Commonly used ratios include Phenanthrene/anthracene(phen/Ant), Fluoranthene/pyrene(Flu/Pyr), Fluoranthene/fluorantine plus Pyrene (Flu/Flu +Pyr), benzo(a)anthracene to chrysene (B(A)A/chr). The values obtained for the soil samples at different depths are presented in table 2. Values of Phen/Ant >10, flu/pyr <1, Flu/(FLu+pyr)< 0.5 and B(A)A/chr<1   indicate a petrogenic origin of contaminations (Colombo et al.,1989, Sicre et al. ,1987; De Luca et al.,2004). In the study sites Phen/Ant and Flu/pyr for the soils at all depths excepting soils at 30cm (site 1) are indicative of pyrogenic and petrogenic sources while Flu/Flu +Pyr,B(A)A/chr) ratios showed no defined trend (Table 2). However, values of Phen/Ant and Flu/Flu+pyr are similar to values measured for gasoline and diesel combustion sources (Matt, 199; Fang et al.,2004) for most of the soils (Table 2). Also, the values for B(A)A/Chr ratios at both sites were within the ranges obtained from gasoline and coal combustion sources (Wilcke, 2000).
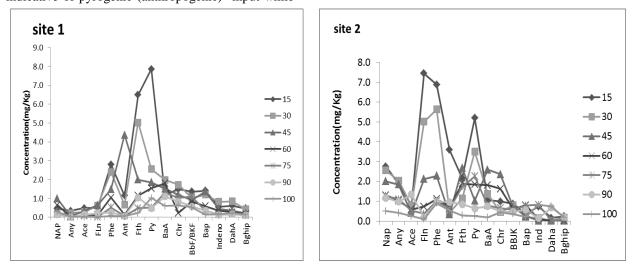

Fig. 2 Individual PAH concentration showing distribution with depth(cm) in soil

[1]NGANJE, TN; [2]NEJI, PA; [3]IBE, KA; [1]ADAMU, CI, [1]EDET, A

Table 2: Summary of diagnostic indicators in soil with depth(cm)

	Depth (cm)	Phen/Ant		Flu/Pyr		Flu/Flu+Pyr		BA(A)/CRY	
Spilled site		1	2	1	2	1	2	1	2
	15	2.43	1-92	0.83	0.42	0.45	0.88	0.79	1.07
	30	3.64	12.82	0.48	0.33	0.66	0.31	1.14	3.07
	45	0.33	6.74	0.94	0.39	0.52	0.53	1.26	1.10
	60	7.11	1.56	0.75	0.98	0.43	0.63	7.87	1.11
	75	7.43	1.63	0.92	0.77	0.48	0.29	1.28	1.20
	90	4.33	1.00	0.33	0.90	0.69	0.54	1.31	1.56
	100	1.33	1.69	0.23	0.86	0.23	0.15	0.94	0.40
Other studies									
Gasoline		3.4 - 8						0.28 – 1.20	
Diesel		7.6 –8.8				65±0.05		0.17 – 0.36	
coal		3				0.74		1.0 – 1.2	
Coke oven		0.79						0.93	
	1 = site 1			2 = site 2					
Sources	Colombo et al., (1989); Sicre et al., (1987): Matt et al., (1999); Fang et al.,(2004): De Luca et al., (2004): Shen et al., (2008)								

The relationship between the concentration of sum of PAHs and the concentration of the dominant PAHs compounds in each sample matrix are shown in Fig.3. The piots show a significant correlation between the concentrations of the sum of PAHs and the dominant PAHs compounds in the soil, thus indicating their common sources.
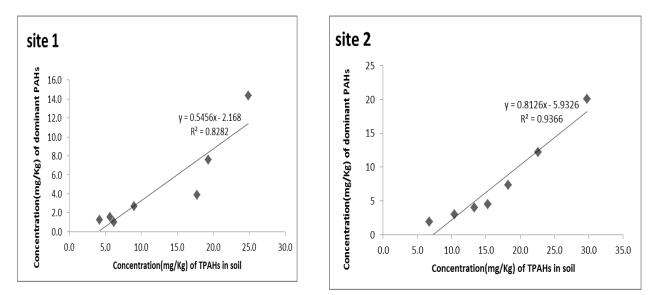

Fig.3 Relationship between sum of concentrations of PAHs and dominant PAHs in soil.

Conclusion: The sum of concentration of PAHs within the vicinity of the leaking pipeline decreased with depth from the spilled sites. Although soil total PAH concentrations reported in the present study are yet to attain polluted status, their potential harmful effects should not be overlooked as PAHs constitute environmental human health risk. The distribution of individual PAHs in soils, the dominance of medium and lower-rmolecular- weights PAHs, and the diagnostic ratios revealed that the PAHs were derived from both petrogenic and pyrogenic sources. The results acquired in this investigation provide additional contribution to the background value for future pollution monitoring in the soils and aquifers of the study area. Due to the toxicity and persistence of PAHs in the environment, remediation of the spilled sites are recommended and also regular checks should be carried out on the pipelines (since they have existed for more than twenty five years) to prevent further oil leakages.

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