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Polycyclic Aromatic Hydrocarbons (PAHs) In Surface Water and Their Toxicological Effects in Some Creeks of South East Rivers State (Niger Delta) Nigeria.

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Abstract: *The concentrations and toxicological effects of polycyclic aromatic hydrocarbons (PAHS) in some creeks of Niger Delta (Nigeria) were assessed taking into cognizance the industrial concentrations of the Delta and the toxic effects of these pollutants believed to be discharged into the creeks from industrial operations. The Eleme and Okrika creeks were sampled out for the analyses. Water sample from these creeks were collected and extracted for PAHs using liquid-liquid partition with dichloromethane. The purified hydrocarbons extract were analyzed for hydrocarbon concentrations using Gas chromatography equipped with flame ionization detection. Results obtained from the studies showed that the concentrations of PAHs ranged between 0.008 and 0.249mg/l. From the results, it was observed that the concentrations of the pollutants were higher than the USEPA recommended limits of between 0.20 and 400ppb for drinking water. Some of the PAHs recorded were those that are toxic even at low concentrations and they were prominent near the point source. The paper therefore concludes that the consumption of any aquatic habitat from these creeks be suspended forthwith as well as the use of the creeks for domestic purposes pending when a proper remediation exercise is carried out.*
Keywords: *hydrocarbon, toxic effect, creeks, surface water, dichloro methane, concentration*

I. Introduction

The name polycyclic aromatic hydrocarbons (PAHs) commonly refers to a large class of organic compounds containing two or more fused aromatic rings, although in a broad sense, non-fused ring systems should be included. Polycyclic aromatic hydrocarbons (PAHs) also are a group of approximately 10,000 organic compounds that have received global attention due to their toxic, mutagenic and carcinogenic properties (Baran *et al.*, 2003; Gomes and Azevedo, 2003; Stabenaut *et al.*, 2006). The six PAHs listed as carcinogens are benzo [a] anthracene, benzo [b] flouranthene, benzo [k] flouranthene, benzo [a] pyrene, dibenzo [a,h] anthracene, and indeno (1,2,3-cd) pyrene (Chrysikou *et al.*, 2008).

High prenatal exposure to PAHs is associated with lower IQ and childhood asthma. The Center for Children's Environmental Health reports studies that demonstrate that exposure to PAH pollution during pregnancy is related to adverse birth outcomes including low birth weight, premature delivery, and heart malformations. Cord blood of exposed babies shows DNA damage that has been linked to cancer. Follow-up studies show a higher level of developmental delays at age three, lower scores on IQ tests and increased behaviourial problems at ages six and eight.

Total toxic benzo[a]pyrene equivalent (TEQ^{carc}) of the carcinogenic PAHs in sediments varied from 31.8 to 209.3 $ngTEQ^{carc}\ g^{-1}$. Benzo[a]pyrene and dibenzo[a,h]anthracene contributed 45.36 and 25.31% to total TEQ^{carc}, posing high toxicological risk to the environment (Yuqiang et tal., 2010).

PAHs toxicity is very structurally dependent, with isomers (PAHs with the same formula and number of rings) varying from being nontoxic to being extremely toxic. Thus, highly carcinogenic PAHs may be small or large. One PAH compound, benzo[*a*]pyrene, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette smoke). The EPA has classified seven PAH compounds as probable human carcinogens viz benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-d)pyrene.

PAHs known for their carcinogenic, mutagenic and teratogenic properties are benzo [*a*] anthracene and chrysene, benzo [*b*] fluoranthene, benzo [*j*] fluoranthene, benzo [*k*] fluoranthene, benzo [*a*] pyrene, benzo [*ghi*] perylene, coronene, dibenz (a,h) anthracene ($C_{20}H_{14}$), ideno(1,2,3-d)pyrene ($C_{22}H_{12}$) and ovalene (Luch, 2005).

Permissible levels of some toxic PAHs in drinking water are anthracene-300 ppb, benzo (a) pyrene-0.2 ppb, benzo (b) flouranthene-0.2 ppb, flouranthene-400 ppb and flourene-400 ppb (US EPA, 2007).

Some of the highly toxic PAHs (naphthalene, NaP; acenaphthylene, Acy; acenaphthene, Ace; flourene, Fl; phenanthrene, PhA; anthracene, A; flouranthene, FIA; pyrene, Py; benzo (a) anthracene, BaA; chrysene, Chy; benzo(a) flouranthene, BbFIA; benzo (e) pyrene, BeP; benzo [a] pyrene, BaP; indeno (1,2,3-cd] pyrene, InP; dibenzo [a,h] anthracene, dBahA; benzo (ghi)perylene, B[ghi]p] have been listed as priority pollutants in waste water, soils, sediments, hazardous solid wastes and groundwater (Christensen *et al.*, 1997).

Although most PAHs are anthropogenic, biogenic PAHs such as cadelene, simonellite and retene are derived from higher plants by diagenetic processes (Gomes and Azevedo, 2003; Stabenau et al, 2006). Nwineewii and Ibok (2014) in their study on the bioaccumulation of polycyclic aromatic hydrocarbons in biota from the Niger Delta, Nigeria, discovered that the concentrations of PAHs in penaeus monodon (shrimp) ranged between 0.943mg/kg and 2.347mg/kg (dry wt.).

Sample Location

Samples were collected from seven locations in Eleme Creeks in Eleme Local Government Area of Rivers State. The sample locations were Agbonchia1, Agbonchia 2, Petrochemicals, Dredging, slaughter, Railway and NNPC QTRS. Agbonchia 1 and 2 were upstream locations. Another three sample locations were from Okrika creeks in Okrika Local Government Area of Rivers State. The sample locations from Okrika creeks were Abam, Ogan and Okrika River. Ten sample locations were taken on the whole. Beside the Eleme creeks is a large Petrochemical company called the Eleme Petrochemicals (now Indorama groups). Apart from this company, there are other activities that take place within the creeks environs. This includes fishing, dredging, farming, cow roasting and housing estate etc.

Water sample collection

Water sample for polycyclic hydrocarbon analyses were collected using a broad mouth 500ml glass bottles fitted tightly with aluminium foil to prevent contamination of the samples. Glass bottles were used for the collection of samples since hydrocarbons interact with plastics containers (APHA, 1998). The collected water samples were properly labelled and preserved in cool boxes before taken for analyses.

Determination of PAHs in Surface water

Polycyclic aromatic hydrocarbons were extracted from the surface waters using liquid-liquid partition with dichloromethane. Extracts were further purified to reduce interferences. The empirical purification entailed the use of alumina (neutral activity 1) as an adsorbent. This was introduced in a slurry form with n-hexane into 1-cm glass columns to a depth of about 10cm. Concentrated extracts were dissolved in hexane and subsequently introduced to the wet adsorbent and eluted with this solvent to remove aliphatic hydrocarbons. The second eluant was benzene, which removed the aromatic materials with sufficient purity for capillary GC analysis. The purified aromatics were analyzed by capillary GC using an HP 6890 Series GC system equipped with FID. The column used was a HP-5, 30 m X 0.25 mm X 0.25μm. Hydrogen (10.2psi) was used as carrier gas at 1.5ml/min. The column was kept at 80^{o}C (1 min), 20^{o}C/min 280^{o}C, 2.5^{o}C/min, 300^{o}C (4 min). Temperature of the FID T_{ij} was kept at 325^{o}C.

II. Results And Discussion

From the analyses of the PAHs extracts, a total of sixteen EPA priority polycyclic aromatic hydrocarbons (PAH_s) were quantified in surface water from Eleme and Okrika creeks as shown in Table 1. It was noted that the concentrations of the individual PAHs varied from location to location, and in some locations, they were not detected. Some locations recorded low concentrations while others were high. For those locations where the concentrations were lower, it could be attributed to be distance from the point source occasioned with gradual dilution of the pollutant. The upstream locations were observed to have recorded low concentrations of these pollutants probably due to reduction in the flow of water toward that direction. The high concentrations recorded in some locations could be ascribed to the closeness of such locations to point source. Fig. 1 below presents the graphic view of the concentrations of PAHs from different locations. The sixteen EPA PAHs quantified were acenaphthylene(Any), acenaphthene(Ace), anthracene(Ant), benzo (a) anthracene[B(a)A], benzo (a) pyrene(BaP), benzo (b) fluoranthene[B(b)F], benzo (g,h,i) perylene(BghiP), benzo (k) fluoranthene[B(k)F], chrysene(Chr), dibenzo (a,h) anthracene (DahA), fluoranthene (Flu), fluorine(Fln),ideno (1,2,3–d) pyrene(ideno), naphthalene (Nap), phenanthrene (Phe) and pyrene(Py). The lowest individual concentration of 0.008mg/l (mean of 0.012mg/l) was observed for benzo (b) fluoranthene. The lowest concentration of benzo(b) fluoranthene of 0.008mg/l was recorded at location 4 (DRG) and the highest concentration of 0.020mg/l was obtained at location 3 (PTC). The highest individual concentration of 0.249mg/l (mean of 0.025mg/l) was obtained for acenaphthylene while the lowest concentration of 0.010mg/l was obtained at location 8 (ABM).

TABLE 1: Individual and mean concentrations of PAHs from different locations

PAHs	abbreviation	1	2	3	4	5	6	7	8	9	10	Total	Mean
Acenaphthene	Ace	0.007	BDL	0.021	0.022	0.021	0.021	0.010	0.020		0.025	0.150	0.017
Acenaphthylene	Acy	0.013	0.024	0.020	0.014	0.089	0.024	0.020	0.010	0.014	0.021	0.249	0.025
Anthracene	Ant	BDL	0.011	0.019	0.021	BDL	0.019	0.047	0.014	0.025	0.024	0.180	0.022
Benzo (a)anthracene	B(a)A	0.013	0.011	0.016	0.014	0.014	0.024	0.016	0.020	0.018	0.024	0.168	0.017
Benzo (a) pyrene	Bap	0.012	0.020	0.012	BDL	0.014	0.013	0.017	BDL	0.011	0.013	0.113	0.014
Benzo (b) fluoranthene	B(b)F	BDL	BDL	0.020	0.008	0.008	0.013	0.009	0.018	BDL	0.010	0.085	0.012
Benzo (g,h,i) perylene	Bghip	0.002	0.008	0.016	0.019	0.014	0.012	0.038	BDL	0.005	0.071	0.185	0.021
Benzo (k) fluoranthene	B(k)F	0.010	0.029	0.012	0.045	0.040	BDL	0.012	BDL	0.012	0.023	0.184	0.023
Chrysene	Chr	0.011	0.014	0.034	BDL	0.019	0.027	0.014	BDL	0.014	0.025	0.158	0.020
Dibenzo (a,h) anthracene	DahA	0.012	BDL	0.012	0.018	0.011	0.012	0.020	0.022	0.014	0.046	0.167	0.019
Fluoranthene	Flu	BDL	0.011	0.031	0.022	BDL	0.028	BDL	0.022	0.023	0.026	0.164	0.023
Fluorine	Fln	BDL	0.014	BDL	BDL	0.012	BDL	0.030	0.017	0.027	BDL	0.099	0.019
Ideno (1,2,3 -d) pyrene	Ideno	0.009	0.011	0.021	0.010	0.021	0.027	0.023	0.027	0.024	0.018	0.191	0.019
Naphthalene	Nap	BDL	0.013	0.006	0.017	0.026	0.014	BDL	BDL	0.043	0.012	0.131	0.019
Phenanthrene	Phe	0.005	0.001	0.017	BDL	0.018	BDL	0.011	0.015	0.010	0.031	0.109	0.013
Pyrene	Py	BDL	0.018	0.012	0.011	0.024	0.021	BDL	0.031	BDL	0.018	0.136	0.019

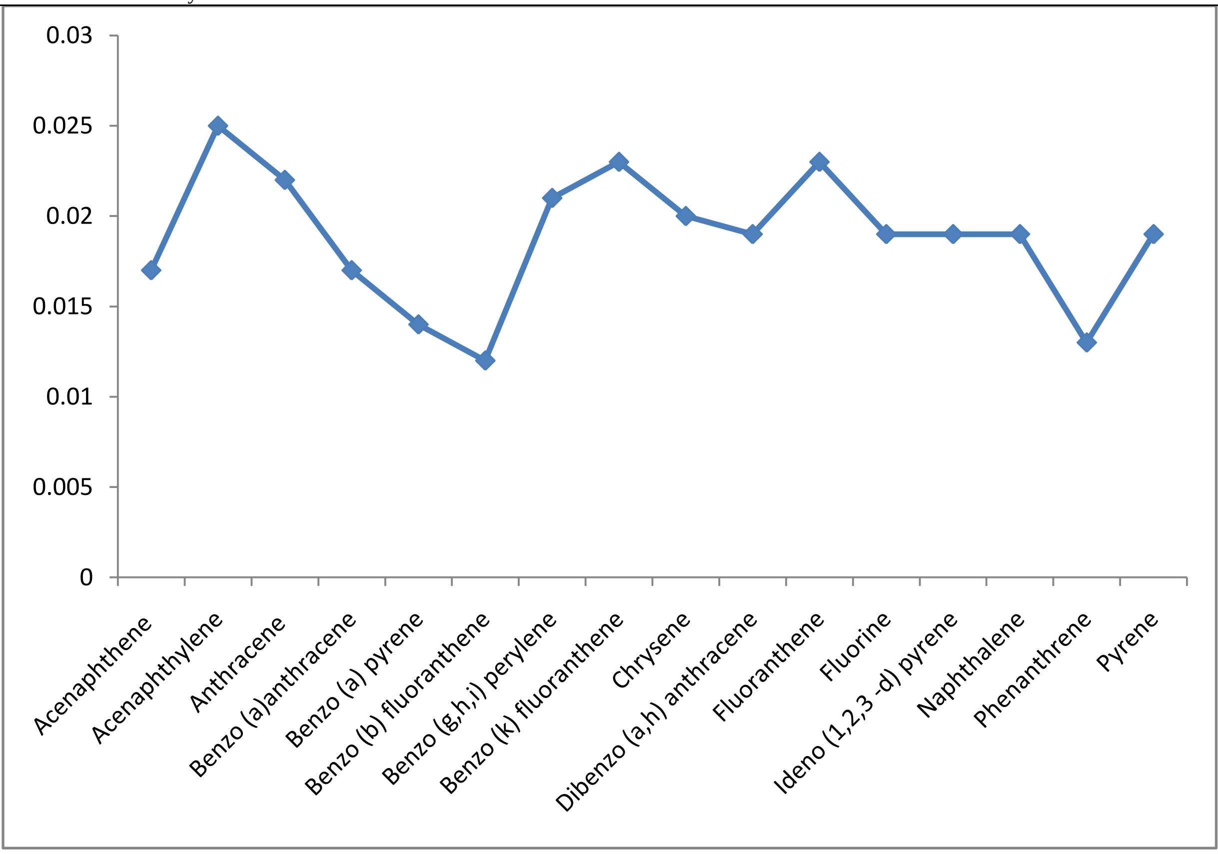

Fig. 1: Graph showing the distributions of PAHs concentrations from various locations

The highest individual concentrations after acenaphthalene were in the order: ideno (1,2,3 – d) pyrene with concentration of 0.191mg/l (mean of 0.019mg/l), benzo (g,h,i) perylene with concentration of 0.185mg/l (mean of 0.021mg/l), benzo (k) fluoranthene with concentration of 0.184mg/l (mean of 0.023), Anthracene with concentration of 0.180mg/l (mean of 0.022mg/l), benzo(a)anthracene 0.168mg/l and mean of 0.017mg/l, dibenzo (a,h) anthracene 0.167mg/l and mean of 0.019mg/l, fluoranthene 0.164mg/l and mean of 0.023mg/l, chrysene 0.158mg/l and mean of 0.020mg/l, acenaphthene 0.150mg/l and mean of 0.017mg/l, pyrene 0.136mg/l and mean of 0.019mg/l, benzo (a) pyrene 0.113mg/l and mean of 0.014mg/l, phenanthrene 0.109mg/l and mean of 0.013mg/l, fluorine 0.099mg/l and mean of 0.019mg/l. Malik et al (2011) in their investigation of the spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in Gunti River (India) revealed that the total concentrations of 16 PAHs in water ranged between 0.06 and 84.21mg/l (average for = n = 4810.33 $\pm$ 1994mg/l. Opuene (2004) in a study on the levels of PAHs in the Taylor creek aquatic ecosystem, Bayelsa State obtained the following mean concentrations for some PAHs viz acenaphthylene 20.5µg/l, phenanthrene 43µg/l, anthracene 109.2µg/l. The concentrations of PAHs obtained in this study were more than permissible levels for drinking water as recommended for some of them anthracene – 300ppb, benzo(a) pyrene-0.2ppb, benzo (b) fluoranthene-0.2ppb, fluoranthene – 400ppb, fluorene-400ppb (USEPA, 2007). Most PAHs in the environment are from incomplete combustion of carbon containing materials such as oil, wood, garbage or coal. Many useful products such as mothballs, blacktop and creosote contain PAHs. In addition to their presence in fossil fuels, they are also formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, and incense (BBC NEWS, 2001). EPA has classified seven PAHs compounds as probable human carcinogens vizbenzo(a)anthracene, benzo (a)pyrene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene, dibenzo (a,h) anthracene, and ideno (1,2,3 –d) Pyrene. PAHs known for their carcinogenic, mutagenic and teratogenic properties are benzo(a)anthracene, chrysene, benzo (b) fluoranthene, benzo (j) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (g,h,i) perlyene, dibenzo (a,h) anthracene and ideno (1,2,3 – d) pyrene (Luch, 2005).

III. Conclusion

The concentration and toxicological effects of polycyclic aromatic hydrocarbons in some creeks of Niger Delta specifically that of Eleme and Okrika were investigated and the results obtained revealed that the concentrations of these pollutants were found to be high compared to the USEPA permissible limits for drinking water. The locations close to the point source were found to record higher concentrations as oppose to those distant away. Since most of these PAHs are poisonous even at low concentrations, it is necessary to curtail the consumptions of aquatic habitat from these creeks at moment and also the use of these creeks for any domestic purpose.

References

[1]. APHA (1992).Standard methods for the Examination of water and waste, 18th Edition. American Public Health Association, American Water Works Association and Water Environmental Fedration (APHA-AWWA-WEF), Published by the American Public Health Association, Washington D.C.
[2]. Baran, S., Olesczuk, P. &Baranowska, E. (2003). Degradation of soil environment in the post flooding area: Content of polycyclic aromatic hydrocarbons (PAHs) and S-Triazine herbicides. Journal of Environmental Health Science and Health 38B (6): 799-812.
[3]. BBC News (2001). Incense link to cancer. http//www.bbc.co.uk/2/hi/health/1467409.stm.
[4]. Chrysikou, L., Germentzis, P., Koaras, A., Manoli, E., Terz, E. &Samera, C. (2008).Distribution of persistent organic pollutants, polycyclic aromatic hydrocarbons and trace elements in soil and vegetation following a large scale landfill fire in Northern Greece.Environment International 34:210-225.
[5]. Christensen, E.R., Li, A., AbRazak, I.A., Rachdworg, P. &Karls, J.F. (1997).Sources of polycyclic aromatic hydrocarbons in sediments of Kinnickinnic River, Wisconsin. Journal of Great Lakes Research 23 (1): 61-73.
[6]. Gomes, A.O. &Azevedo, D.A. (2003). Aliphatic and aromatic hydrocarbons in tropical recent sediments of campus dos Goytacazis, Rj, Brazil. Journal of the Brazilian Clinical Society 14(3): 1-6.
[7]. Luch, A. (2005). The carcinogenic effect of polycyclic aromatic hydrocarbons. London, Imperial College Press.
[8]. Malik, A., Verma, P., Sengh, A.K. &Sengh, K.P. (2011).Distribution of polycyclic aromatic hydrocarbons in water and bed sediments of the Gomti River, India.Environment Monitor Assessment 172 (1-4): 529-545.
[9]. Nwineewii, J.D & Ibok, U.J. (2014). Bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) concentrations in biota from the Niger Delta, South –South, Nigeria 5(3): 31-36.
[10]. Opuene, K. (2004). Water quality levels and impacts of heavy metals and polycyclic aromatic hydrocarbons in the Taylor Creek Aquatic Ecosystem, Bayelsa State, Nigeria.Ph.D Thesis of the University of Nigeria, Nsukka, Nigeria.
[11]. Stabenau, E.K., Giczewski, D.T. &Maillacheru , K.Y. (2006). Uptake and elimination of naphthalene from liver, lung and muscle tissue in the Leopard Frong (RanaPipiens).Journal of Environmental Science and Health 41A: 1449-1461.
[12]. United States Environmental Protection Agency (USEPA, 2007). The national water quality inventory report to congress for the 2002 reporting cycle: A profile. Washington DC.: United States Environmental Protection Agency, 841-843.
[13]. Yuqiang, T., Shuchun, Y., Bin, X., Jianca, D., Xinalong, W., Muhua, F. &Weiping, H. (2010). Polycyclic aromatic hydrocarbons in surface sediments from drinking water sources of Taihu Lake, China: Sources, partitioning and toxicological risk. Journal of Environment Monitoring (12): 2282-2289.