

ENVIRONMENTAL AND PUBLIC HEALTH IMPLICATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS POLLUTION IN SURFACE WATERS AND SEDIMENTS OF LOWER ORASHI AND SOMBRIERO RIVER SYSTEMS OF NIGER DELTA; NIGERIA

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DOI: 10.5281/zenodo.14794188

Abstract

River waters and sediments of the marine ecological systems are habitats to diverse species and biodiversity for their position and complexities as major recipient of pollutants from natural and anthropogenic sources. Polycyclic Aromatic Hydrocarbons (PAHs) account for the abiotic synthesis of materials resulting in carbon-based pollutions in the natural environment at elevated concentrations. These ecotoxic stressors are oftentimes bequeathed as legacies with increasing potencies and reactivity in surface waters and bottom sediments of the marine environment. Crude oil spills from hydrocarbon exploration and illicit artisanal refineries have become major cause of marine ecological pollutions affecting aquatic life and humans in the Niger Delta. Descriptive and comparative statistics designs were adopted in this study to evaluate the environmental and public health implications of seasonal (dry and wet/rainy) levels of marine ecological bioavailability and characteristics of PAHs in the waters and bottom sediments of the contiguous saline differentiated coastal deltaic Lower Orashi and Sombriero River Systems, Rivers State, Nigeria; to determine the extent of PAHs pollution. The study area was segmented into 10 sites, where water and sediment samples were collected into decontaminated plastic bottles and zip lock bags, sealed and appropriately labeled sample stations-wise, stored in ice-parks cooler for preservation of their oxidation states. Standard laboratory methods were adopted for analysis of physico-chemical parameters. Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used for the sequencing/speciation of PAHs. The study findings show that 15 of 16 IARC priority PAHs exceeded the WHO/USEPA tolerant values (TLV) in the study media except Fluorine. Significant variation exists in the PAHs among the surface waters and sediments at $p < 0.05$. This shows that the marine media are contaminated with PAHs, hence unsuitable for pelagic and benthic aquatic demersals/species, thus, predisposing the riparian population to possible health risks associated with PAHs exposure. Articulation of efficient and sustainable multi-stakeholder environmental decontamination/remediation and mitigation of the study area and Niger Delta urgently recommended.

Keywords: Lower Orashi, Sombriero, PAHs, Pelagic and Benthic

Introduction

Sediments are unconsolidated grains of materials from organic matters or pre-existing rocks particles transported through erosion (wind, ice or water) and deposited by accretion over geologic years. Polycyclic Aromatic

Hydrocarbons (PAHs) are organic hydrocarbon compounds comprising only carbon and hydrogen with multiple aromatic rings and delocalized electrons. PAHs are produced by the pyrolysis or incomplete combustion of organic matters such as crude oil in marine biomass, urban landfills, incinerators, engines, and petroleum products, with naturally uncharged and non-polar molecules (Horsfall & Spiff, 2013). According to Al-Hashem (2017), PAHs are a combination of numerous organic compounds consisting two or more aromatic rings of carbon and hydrogen environmentally ubiquitous, including marine waters, benthos, bottom sediments, aquatic biota and exoplanets. PAHs in the marine waters are mostly compounds having complex structures, whose valence forms dictate different ecotoxicological reactivity, such as saturates (pentane, hexadecane, octadecane, cyclohexane), aromatics (Naphthalene, Phenanthrene, Benzene & Pyrene), asphaltenes (phenols, fatty acids, ketones, esters and porphyrins) and resins (pyradines, quinolones, carbozoles, sulphoxides and amides) (Ite & Sempe, 2012; Al-Hashem, 2017). PAHs are mostly soluble in fats and therefore easily bioaccumulate along the food chain, particularly in the tissues and cells of man as synergists and or causative agent as ecotoxins for various carcinogenic, mutagenic and genotoxic diseases (Anyakora, Coker & Arbabi, 2010). Unlike Benzenes, PAHs carry no heteroatoms or sub-constituents. Examples include anthracene, phenanthrene, tetracene, chrysene, triphenylene, pyrene, pentacene, benzo[a]pyrene, corannulene, benzo[ghi]perylene, coronene, ovalene and benzo[c]fluoranthene (Anyakora, Coker & Arbabi, 2010).

Guo, Li, Ranasngbe, Bonina, Hosseini, Corcoran, Smalley, Rockne, Sturchio, Geisy and Li (2016) documented that sources of polycyclic aromatic hydrocarbons, polyhalogenated hydrocarbons, organohalogens, carbazoles and their derivatives in marine waters and sediments are basically from background geochemical, atmospheric and direct discharges of anthropogenic origins. PAHs are classified into three basic groups according to their sources, viz: - diagenetic, pyrogenic and petrogenic (Mazeas & Budzinski, 2001; Wang et al., 2004; Anyakora & Coker, 2006; in Anyakora, Coker & Arbabi, 2010).

Introduction of PAHs and their derivatives into Nigeria's Niger Delta aquatic environment is mainly through oil spill, gas flares and pyrolysis activities which pollute the environment, poses great danger to ecological sustainability and human health (Kampa & Castanas, 2008). PAHs are highly toxic and hyper reactive to marine organisms and man and make up a minimum of 5% of total anthropogenic pollutants in marine ecosystem (Killister & Brack, 2005; Guo et al., 2016). Horsfall and Spiff (2013) observed that marine debris such as floatables from urban runoff trap persistent organic pollutants like PAHs, PCBs and DDT in the Rivers. Impact of PAHs in the marine environment have been receiving local and global attention including classification of the sixteen priority PAHs (phenanthrene/anthracene (Ph/An), fluoranthene/pyrene (Fl/Py), benz(a)anthracene/chrysene (BaA/Ch), phenanthrene/(phenanthrene + anthracene) Ph/(Ph + An) and indeno[1,2,3-cd]pyrene + benzo[ghi]perylene) according to their ecotoxicity and public health impact and the setting up of the Inter-Agency Committee for Research on Cancer (IARC), due to the carcinogenic, mutagenic and genotoxic

characteristics (USEPA – IRIS, 1992; USPA, 2000b; Ite & Sempe, 2012). Anyakora and Coker (2007) assessed IARC PAHs -16 in four fishes (*Parachana obsura*, *Pseudolithus elongates*, *Lizza dumerilii* and *Claris garriempious*) in fresh and brackish River estuaries in the Niger Delta; by Gas Chromatography and Gas Spectrometry and documented that PAHs-5 & 6 were consistently higher in the waters owing to their densities and persistence without established trend in the two River systems. Similarly, the rate of absorption of all PAHs-16 was observed in the two River systems, indicative of PAHs pollution predominance in the River waters of Niger Delta in Nigeria.

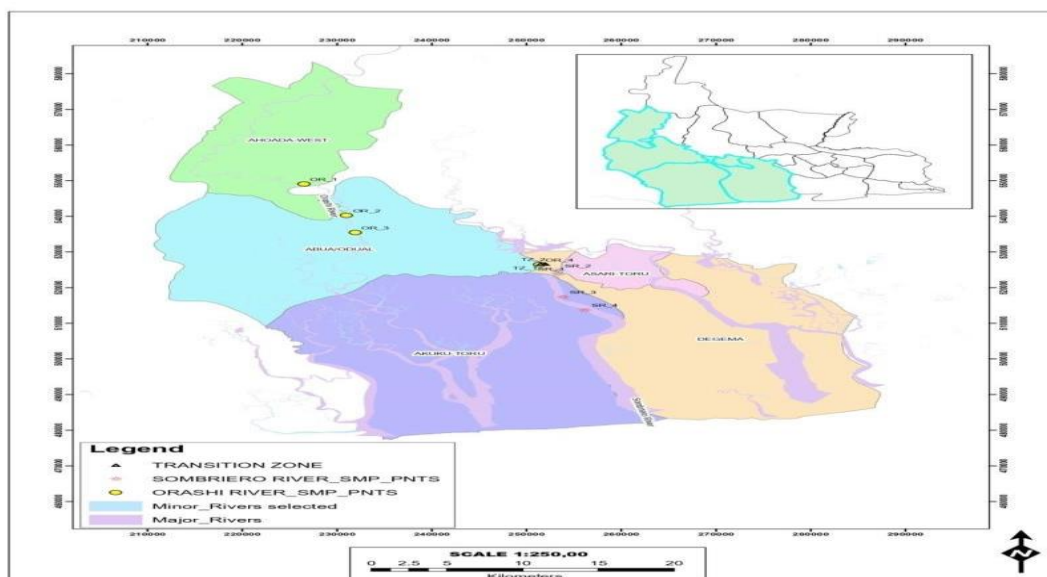
The Lower Orashi and Sombriero River systems host many petroleum hydrocarbon exploration, production and transportation assets including ten (10) crude oil and gas fields, gas plants and many crude oil delivery trunk lines. The Niger Delta Development Commission (2006) and IUCNNDP (2013) documented that rural fishermen, farmers, river sand miners, hunters, petty traders on marine resources and artisans constitute the riparian populations whose right and sustainable livelihoods depend entirely on the resources of the surrounding marine ecology and wetlands. Georgewill (2012) reported that inhabitants of the Niger Delta become exposed to PAHs toxicity from their surrounding waters and mangrove vegetation as a result of frequent crude oil spilling into the waters, sediments and mangrove wetlands, causing a wide range of adverse public health impacts including pregnancy miscarriages, secondary pollution and human mortalities, as was the case in Asitubo Gbanraun, Bayelsa State in 1997. Ezekwe, Otiasah, Raimi and Asomeji (2022) documented that Emago-Kugbo community, Odual district; Abua-Odual Local Government Area of Rivers State recorded the Nigeria's first operational crude oil spill involving 4,928 barrels in May 31, 1960 from a Shell Petroleum Development Limited (SPDC) failed valve. Otiasah, Ezekwe, Lawal and Otiasah (2020) relying on a 2018 record of the National Oil Spill Detection and Response Agency (NOSDRA) documented 34 million barrels of oil spills and unspecified cubic feet of gas flares/vents in the study environment. Contamination of their River waters and sediment portends existential threat to the livelihoods, economy, health and survival of the riparian populations. Consequently, this study critically evaluated the environmental and public health implications of seasonal (dry and wet/rainy) levels of marine ecological bioavailability and characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) in the waters and bottom sediments of the coastal Lower Orashi and Sombriero River Systems, Rivers State, Nigeria. It determined the extent of PAHs pollution. It equally provided bases for remedial actions for the surface waters and sediments, species conservation, public health advisory and monitoring.

Materials and Methods

According to Otiasah, Otiasah and Ohanunu (2024) the Lower Orashi and Sombriero River estuaries covering territories of Ahoada West, Abua/Odual, Degema, Akuku-Toru and Asari-Toru Local Government Areas of Rivers State, Nigeria (Figure 1) constituted the study area. It is a freshwater and saline mangrove wetland of coastal lowland rain forest vegetation dominated by economic trees (*pentaclethramacrophylla*,

chrysophyllum albidum and *irvingia gabonensis*), of tidal and semi tidal flat mud characteristic of the Niger Delta (Abam & Okagbue, 1997; Oyegun, 1997, Niger Delta Development Commission in Lawal, Arokoyu & Udeh, 2015). The Orashi, Sombriero, Santh Batholomew and Santa Barbara are the major Rivers shaping the entire flow pattern of the area. It is predominantly humid tropical climate with long annual rainy season spanning March - October, a shorter dry season between November -February, and two characteristic South-West Monsoon wind and North East trade wind. The monsoon is dominant during the rainy season while the trade wind dictates activities during the dry season. It is of a lowlying plain of fresh unconsolidated fluvial sediments of Quaternary Age, characterized by layered heterogeneous sediment structure of alternating sands, silts and clay, of the Benin, Agbada and Akata Formations (Abam & Okagbue, 1997). The soil is majorly Entisols and Inceptisols occasionally mixed with Alfisols and elevated ≤ 7 meters above mean sea level (Awosika, 1995; Aweto, 2002). Most of its freshwater between 100 – 200m in the Benin Formation is 2000m thick; consolidated at near bottom depth, having sprouting shallow water aquifer (Ekundayo & Obuekwe, 2001). The area is characterized by subsistence farming on the parchments of lands, fishing, weaving, hunting, palm oil production, timber logging, canoe-carving and wine tapping, artisans, petty trades, hydrocarbon mining and gas reserves of the tertiary Niger Delta (Reigers et al., 1996 In Nduka, Obumselu & Umedum, 2012; IUCN-NDP, 2013). The Orashi River, from Mbiama to Hulk is fresh water while the Sombriero River from Degema beheading the Orashi River (Transition Zone) to Ebemaboko is saline water. Both Rivers are intertidal and waterlogged mud flatlands with complex strata of diverse flora/trees and rich fauna.

Figure 1: Sampling Points across the Study Area



Sample and Sampling Technique

A total of ten (10) sampling sites were selected for this study. Water and marine sediment samples were collected in all ten sites. The sampling sites stretch from the Lower section of Orashi and Sombriero Rivers. Mbiama water front through the Sombriero River down to the mouth of the Atlantic Ocean were the specific areas of sampling. Hulk (Agada)/Degema is in the Transitional Zone between the two River systems. Water and sediment data for the study were obtained directly from the field sampling and analysis of water and sediment for PAHs in the laboratory. Standard laboratory methods were adopted for physico-chemical parameters of water while Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used for the sequencing/speciation of PAHs. The data obtained in this study were then analyzed with descriptive and comparative statistics

Table 1. Sampling Sites and their GPS Coordinates

S/No

2	Emesu	OR2	E006° 34 29.9" N04°53 03.1"
3	Ogbema Corridor	OR3	E006° 36 07.0" N04°48 44.3"
4	Ogonokom	OR4	E006° 45 06.0" N04° 45.33.0"
5	Hulk-Transition Zone	TZ1	E006° 45 31.4" N04°45 46.7"
6	Atala-Degema Waterfront	TZ2	E006° 45 51.4" N04°45 40.4"
7	Opulogoloboko	SR1	E006° 45 34.1" N04°44 08.3"
8	Idama Flow Station	SR2	E006° 46 34.7" N04°44 38 3"
9	Minjidukiri	SR3	E006° 46 52.5" N04°40 36.9"
10	Ebemaboko	SR4	E006° 48 08.0" N04°38 38.7"
1	Sampling Sites	Designation	GPS
	Ozuochi		
	OR1		E006° 32 02.0" N04°57 45.5"

Tables 2 and 3 present the results of speciation chemistry for surface water and bottom sediment from sections of the Orashi and Sombriero Rivers for the study respectively.

Table 2. Results of Speciation Chemistry of PAHs in Surface Water Samples of the Study Area S PAHs
COMP, O OR OR SR SR SR TZ TZ MEA USEPA/WHO N ppm R1 2 3 1 2 3 1 2 N /ASTDR

STNDRD

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1	Naphthalene	0.8	0.1	0.5	0.6	0.6	0.3	0.8	0.0	0.50	0.02		
0	0	2	6	6	7	5	4						
2	Acenaphthylene		0.1	0.4	0.0	0.3	1.3	3.6	0.6	0.7	0.90	0.004	
				0	1	4	4	2	2	3	1		
3	Acenanphthene		0.0	0.3	0.0	0.3	0.3	0.3	0.1	0.0	0.21	0.06	
1	3	8	4	6	6	7	4						
4	Fluorene	0.0	0.2	ND	0.1	0.3	3.8	0.6	N	0.57	3.0		
				6	4		1	2	2	7	D		
5	Phenanthrene	0.7	0.1	ND	N	0.4	0.1	N	0.5	0.27	0.02		
2	8	D	9	9	D	8							
6	Anthracene	0.1	0.0	ND	N	0.3	ND	0.0	N	0.06	0.1		
				2	3		D	0		5	D		
7	Fluoranthene	0.8	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.14	0.4		
				0	1	9	2	2	4	1	1		
8	Pyrene	0.9	0.0	0.2	0.0	0.0	0.0	0.0	0.8	0.27	0.2		
				0	6	7	3	1	1	1	9		
9	Chrysene	N	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.07	0.001		
				D	2	2	2	1	2	1	4		
10	Benz(a) N	0.0	0.0	0.0	0.5	9.2	0.0	0.5	1.30	0.001	anthracene	D 1 5 4 0 9 2 0	
11	Benzo(b)	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.04	0.1	fluoranthene	2 1 3 1 1 2 2 1	
12	Benzo(k)	0.7	0.0	0.0	0.0	0.0	0.0	0.2	0.06	0.01	fluoranthene	0 1 3 2 1 4 2 9	
13	Benzo(a) pyrene		0.1	0.0	0.3	0.0	0.0	0.5	0.0	0.4	0.18	0.2	
				0	1	1	2	2	2	2	7		
14	Indeno(1,2,3-cd)	N	ND	0.1	0.0	0.0	0.3	0.4	1.3	0.27	0.1	pyrene	D 0 1 1 1 0 0
15	Dibenz(a,h)	0.0	0.0	0.0	0.0	0.0	3.7	0.2	N	0.51	0.0003	pyrene	2 2 3 1 6 2 0 D
16	Benzo(g,h,i)	0.0	0.0	0.2	0.0	0.0	0.7	0.0	0.3	0.17	0.01	perylene	1 1 8 2 1 1 1 3

USEPA = United States Environmental Protection Agency| WHO = World Health Organization | ASTDR = Agency for Toxic Substances and Disease Registry.

Table 3. Result of Speciation Chemistry for PAHs in Bottom Sediment Samples of the Study Area.

SN	PAHs	OR1	OR2	OR3	SR1	SR2	SR3	TZ1	TZ2	MEAN	USEPA/WHO/ASTDR	COMP, ppm
	STNDRD											
1	Naphthalene		0.03	0.03	0.03	0.51	0.16	0.25	0.11	0.06	0.10	0.02
2	Acenaphthylene		2.99	2.44	0.58	2.46	0.31	9.55	2.00	4.55	2.45	0.004

3	Acenaphthene	6.49	0.70	2.48	1.62	0.20	5.58	0.48	1.35	1.89	0.06
4	Fluorene	1.31	3.71	ND	1.91	0.17	2.66	1.60	ND	1.14	3.0
5	Phenanthrene	2.08	0.54	0.21	0.48	0.28	4.35	0.94	0.20	0.91	0.02
6	Anthracene	0.22	0.17	0.01	0.28	0.03	1.35	1.75	0.03	0.38	0.1
7	Fluoranthene	0.35	ND	0.06	0.27	0.03	ND	1.07	0.13	0.19	0.4
8	Pyrene	0.19	ND	0.18	0.09	0.02	ND	0.76	7.07	0.83	0.2
9	Chrysene	ND	0.32	ND	0.08	0.01	0.07	0.04	0.01	0.05	0.001
10	Benz(a)anthracene	ND	0.02	0.03	0.06	0.01	0.14	0.08	0.02	0.04	0.001
11	Benzo(b)fluoranthene	ND	0.93	ND	0.03	0.02	0.06	0.26	ND	0.13	0.1
12	Benzo(k)fluoranthene	ND	0.88	ND	0.03	0.01	0.10	0.25	ND	0.13	0.01
13	Benzo(a)pyrene	ND	ND	ND	ND	0.01	ND	0.11	ND	0.01	0.2
14	Indeno(1,2,3-cd)pyrene	0.04	0.01	0.05	0.05	0.07	0.06	0.06	0.01	0.04	0.1
15	Dibenz(a,h)pyrene	0.05	0.06	0.08	0.28	0.07	0.49	0.07	ND	0.11	0.0003
16	Benzo(g,h,i)perylene	ND	0.01	0.02	0.11	0.02	0.09	0.05	0.02	0.03	0.01

USEPA = United States Environmental Protection Agency | WHO = World Health Organization | ASTDR = Agency for Toxic Substances and Disease Registry.

Discussion

PAHs in the Environmental Media (Water & Sediment).

Tables 2 and 3 show the locational ranges and mean ecological abundance of the 16 priority PAHs across the study media.

Naphthalene: The Occupational Safety and Health Administration - OSHA (2005) and the Agency for Toxic Substances and Disease Registry – ATSDR (2005), documented irritation of the nose and throat, headache, fatigue, confusion, tremor, nausea and vomiting could also result from elevated exposure. USEPA (2000) classified naphthalene as a group C possible human carcinogen. Morbidity in children and adults and hyperplasia has been reported due to misuse of mothballs and accidental exposure to naphthalene (USEPA, 2000; Brent et al, 2017). Oxidative stress causative of methemoglobinemia, hemoglobin oxidation, visible heinz bodies and

hemolysis of the red blood cells (rbc) due to high exposure to naphthalene were also reported (USEPA, 2000; Brent et al, 2017).

From tables 2 and 3, the mean value of naphthalene in the environmental media (water and bottom sediment) is 0.50 ± 0.14 ppb, far in excess of the 0.02ppb allowable by WHO/USEPA/ATSDR. It is therefore safe to conclude that the riparian populations of Orashi and Sombriero Rivers are possibly predisposed to any or all of the enumerated ailments. The study agrees with (OEHHA (2009) that the occurrence of naphthalene in the environmental media of the study area is from anthropogenic sources and with (USEPA, 2000; Goldfrank, Flomenbaum & Lewin, 2002; Brent et al, 2017) that documented naphthalene occurrence beyond standard prescribed threshold in marine ecologies.

Acenaphthylene: Acenaphthylene occurrence in all sample locations and mean value in the environmental media is 0.90 ± 3.04 ppb, in excess of the 0.0004ppb allowable by

WHO/USEPA/ATSDR and that of the American Conference of Governmental Industrial Hygienists and Beis thresholds for chemical substances, physical agents and biological exposure indices. This predisposes the riparian populations of Orashi and Sombriero Rivers to various forms of cancer, mutagenic and genotoxic ailments. Pregnant women have the likelihood to suffer endocrine dysfunctions, hence heightened preterm delivery risks. Other public health issues the population are exposed to include fatal skin irritation, skin corrosion and serious eye irritation/damage, respiratory/tract irritation, dizziness, suffocation, vomiting and target human organs dysfunction (Singh, et al, 2008; Shimada, 2015).

Acenaphthene: Acenaphthene is a PAH of the arenes dynasty found mostly in coal tar, cigarette smoke, automobile exhaust smokes, wood preservatives and cyclization of α -ethylnaphthalene with a molecular formula $C_{12}H_{10}$ (USEPA, 2000; Greene, 2009; John, 2018). The mean value of Acenaphthylene in the environmental media is 0.21 ± 2.36 ppb. This is far above the WHO/USEPA/ATSDR allowable threshold of 0.06ppb, indicative that populations of the lower fringes of the contiguous Orashi and Sombriero River systems are predisposed to acenaphthene exposure from consumption of pelagic and benthic biota, and are likely to suffer breath shortages, dizziness, vomiting, methemoglobinemia, photomutagenic dermatological cells destruction, and tumors of the skin, gastrointestinal tract, liver, lung and mammary glands depending on the ingestion pathway (Klein, 2014; Purcaro & Conte, 2016; Ifegwu & Anyakora, 2016). This could worsen in those ingesting more of benthic biota like aquatic mollusks, crustaceans, mammals and resources

Phenanthrene: Mean phenanthrene quantitative abundance in the environmental media is 0.27 ± 1.14 ppm above the toxicological TVL of 0.02ppm. This indicates populations in the Lower Orashi and Sombriero Rivers systems are exposed to phenanthrene ingestion are likely to irritation of the skin, nose and throat, dermatitis, bronchitis, cough, dyspnea, neoplasm of the respiratory tract and kidney, and respiratory irritation (NTP, 1992). This study agrees Prashant and Kamini (2019) that reported elevated phenanthrene occurrence in a study of microbial

degradation of aromatic pollutants from the terrestrial environments in pharmaceuticals and personal care products, waste management and treatment technology.

Anthracene: Anthracene with a molecular formula $C_{14}H_{10}$ is also called paranaphthalene or green oil, is the simplest solid tricyclic PAHs. All locational ecoabundance and mean anthracene stoichiometric availability in the environmental media at 0.06 ± 0.38 ppm are above recommended toxicological threshold of 0.01 ppm, which indicates that populations in the study area are exposed to anthracene ingestion and likely to suffer significant lung damage, headaches, nausea, appetite loss, sluggishness and dizziness. Skin, eye and dermal tissue irritations/burns and destruction of the gastrointestinal tract, hematopoietic and lymphoid systems are other human impacts. Jianwang et al (2012) interrogated PAHs in water, sediment, soil and plants of the Aojiang River Waterway in Wenzhou, China in 2012. The study found elevated concentration levels of anthracene in the environmental media amongst other USEPA prioritized PAHs. This study is thus in agreement with (Jianwang et al, 2012) on elevated anthracene bioavailability in the marine ecology.

Pyrene: Pyrene is colorless but occasionally yellow crystal-like solid PAHs, with flat four orthoand-peri-fused fused benzene rings (IUPAC, 1998; Zhang et al, 2012; Yan, Jiang, Li & Shi, 2014). The abundance of pyrene in the study media ranges 0.27 ± 1.04 ppm, above the WHO/USEPA TVL of 0.2 ppm. Pyrene bioavailability is more in the sediment compared to the surface water which is consistent with literatures. This implies that populations in the study corridor are exposed to pyrene pollution and therefore likely to suffer one or more of the adverse human effects enumerated. In a study of accelerated removal of pyrene and benzo(a) pyrene contamination in freshwater sediments with amendment of cyanobacteria-derived organic matters, Yan et al (2014) found pyrene responsible for the resultant ecotoxicity with concomitant effects on organisms of the ecosystem. Elevated pyrene concentration was implicated in a study of warburg-like metabolic reprogramming dependent on N-1 associated with cell survival induced by high concentrations of environmental carcinogen benzo (a) pyrene (Hardonniere, Saunier, Lamarie et al, 2016). This study is therefore in agreement with (Yan, Jiang, Li & Shi, 2014; Hardonniere et al, 2016; Umar et al, 2021).

Chrysene: Chrysene is a white crystalline solid PAH having symmetrical four ortho-and-peri-fused benzene rings (IUPAC, 2014; Vaidya et al, 2018). Chrysene mostly occurs naturally in the atmosphere in particulate form with small percentage found in sediment/soil and surface/ground water as micro solids due to its affinity with marine suspended solids (Linda, 2005). Chrysene stoichiometric abundance in the study media is 0.07 ppm, above allowable TVL of 0.001 ppm. Chrysene is a semivolatile organic compound (SVOC) ecologically low in bioavailability but a persistent carcinogen whose exposure causes liver tumor, malignant lymphomas, skin saromas, liver and lung cancers, skin, eye irritations, and reproductive damages (Encyclopedia of Toxicology, 2014; Vaidya et al, 2018). Ifegwu and Anyakorah (2016) assessed the metabolism of 3-hydroxychrysene in liver microsomes isolated from arochlor 1254 in laboratory rodents where elevated chrysene was identified for

molecular dysfunction. This predisposes the riparian population of the study area to the likelihood of suffering irritation of the skin and eyes; molecular dysfunction, and reproductive damages amongst others. This study is therefore in consonance with (Ifegwu & Anyakorah, 2016; Vaidya et al, 2018) who recorded elevated chrysene and other priority polynucleated hydrocarbons in marine ecologies in the Niger Delta.

Benz[a]anthracene: Locational and mean benzo(a) anthracene abundance in the study media from tables 3 and 4 is 1.30 ± 0.05 ppm, implying that sediment abundance is less than that of surface water. However, all are above the TVL of 0.001 ppm. It is therefore our deduction that populations in the study area are predisposed to benzo(a) anthracene with likelihood to suffer from one/combination of benzo(a) anthracene induced ailments, particularly through water and fish consumption. Levels of PAHs in the environmental media (surface waters, sediments and shrimps) of Estero de Urias estuary, Mexico and their toxicological effects were interrogated seasonally. It was reported that elevated benzo[a]anthracene levels and implicated exogastrulation and reduction in the rate of growth together with DNA and protein distortions in a monitoring study of incidence and spatial distribution of PAHs in the Buffalo River estuary in the Eastern Cape Province of South Africa, PAHs were not detected in some cases of the water samples whereas it was elevated in the sediment in most of the sites. Total PAHs concentrations ranged 14.91 ± 206 µg/l above the TVL of

0.001 ppm. Concentrations of benzo(a) anthracene was higher in sediment than water samples, and poses higher carcinogenic and mutagenic risk, particularly in the sediments (Adeniji, Okoh & Okoh, 2019). This study is therefore in agreement with Foday, Henry, Jose and Armando (2012) and Adeniji, Okoh & Okoh (2019) on elevated of benzo(a)anthracene marine ecological bioavailability above the USEPA/WHO/ ATSDR TVL levels, except that benzo(a) anthracene concentration in this study is more in water samples than sediments, thus negating that of Adeniji, Okoh and Okoh (2019) and many literatures. This could be due to the fact that oil pollutions in the environment are fresh and mostly driven away into the Atlantic Ocean by water current without enough density, having not accumulated particulates for vertical downward travel into the bottom sediment. It could also be attributed to the low water ions and attenuations in the Niger Delta that accounts for the negligibly low sediment mean. Furthermore, sediment cyanobacteria and invasive flora species like water hyacinth in the coastal environment of the study area, particularly along the oligohaline Orashi River, the mixed Transition zone and some parts of the polyhaline Sombriero River, with their purification/degradability capabilities/characteristics may have metabolized and degraded the benzo[a]anthracene in the sediments of the study area in the dry season without dilution effect.

Benzo[b]fluoranthene: Benzo[b]fluoranthene - B[b]f is an ortho-and-peri-fused colorless or yellow fluffy powdery, needle shaped solid PAH having a chemical formula $C_{20}H_{12}$ with a characteristic four benzene rings surrounding five acephenanthrylene rings from incomplete combustion of fossil fuels, petroleum products, coals, coke, asphalt and smokes of cigarette, tobacco, wood, bush burning, oven emissions and source gases from

unengineered incinerators and geochemical seepages from background crustal faults; establishing great affinity with atmospheric, surface and ground water and sediment particulates (NTP, 1992; Farhadian et al, 2012; Obanya et al, 2019; Adeniji, Okoh & Okoh, 2019; ACGIH-Worldwide, 2020).

The concentration of B[b]f for the environmental media in the present study ranges from $0.1 \pm 0.04 \text{ mg/l}$ above allowable TVL, hence poses adverse health challenge to the exposed population within the study area. B[b] f is both a probable human carcinogen and mutagen (EFSA, 2005; IARC, 2010; Obanya et al, 2019). Irritations, redness of the throat and bronchial tubes and burns of the eye, skin and nose could result from b[b] f exposure in the short term. However, when combined with sunlight the irritation and burn could be severe (Pohanish, 2012; ACGIHWorldwide, 2020). B[b]f exposure was reported to cause lung, liver and skin cancers (Olayinka, Adewusi et al, 2018). PAHs in Ologe Lagoon and effects of b[b]f in Africa catfish was investigated by Obanya et al (2019). It found b[b]f concentration above TVL of 0.3 mg/l . Anyakorah, et al (2004), Anyakorah and Coker (2007), Nwineewii and Marcus (2015), Asagbara et al (2015), Adebayo et al (2012), Olayinka et al (2018), Adeniji, Okoh and Okoh (2019) documented various PAHs limit in the Niger Delta and regional marine ecosystem ranging from $0.00195 \pm 0.302 \text{ mg/l}$, while Anyakorah et al and Olayinka et al, 2018 documented concentrations ranging from $<0.00088 \pm 0.505 \text{ mg/l}$ around the Lagos waters. The findings of this study for B[b]f at $0.1 \pm 0.04 \text{ mg/l}$ fall within the reported cases in the Niger Delta and Africa. This study is consilient with (Olayinka et al, 2018; Obanya et al, 2019; Adeniji, Okoh & Okoh, 2019) as to B[b]f pollution in the marine ecological systems and consequential health challenges to populations of the Niger Delta.

Benzo[k]fluoranthene: Benzo[k]fluoranthene is a colorless (occasionally pale yellow) solid and low water soluble PAHs with molecular formula $\text{C}_{20}\text{H}_{12}$ having five fused rings (ACGIHWorldwide, 2020). Pyrogenic, petrogenic, biological and anthropogenic sources account for Bkf environmental bioavailability, fate and diffusion (Olayinka et al, 2018; Obanya et al, 2019).

Bkf levels in the study media ranged from $0.06 \pm 0.16 \text{ ppm}$ which is above permissive TVL of 0.01 ppm . This is indicative that populations in the study area exposed to Bkf toxicity with likelihood of adverse impact such as inhibition of human metabolism and causes lung adenomas/cancer, liver hepatomas/hematomas and adenomas; various tumors and squamous-cell carcinoma and sarcoma (Ding, Lu & Liang, 2014; EFSA, 2015). Bkf causes mutagenic strain in fish (salmonella tyhimurium) and study animals is implicated, but not phototoxic (Ding, Lu & Liang, 2014). Fibroblast, DNA damage, potent inducement of human genetic disruptions and changes in both physiological and histopathological behavior of aquatic organisms are observed impacts of Bkf toxicity (Ren et al, 2012; Zavala et al, 2014). Lower fish ethosxyresorufin-o (EROD) and metallothioneins (mt) with increased superoxide dismutase (SOD) and malodialdehyde (MDA) synthesis responses exacerbating oxidative stress in fish is a documented consequence of Bkf toxicity in combination with heavy metals. It is also reported to cause major malformation and death of certain fishes like the Zebrafish (Ding, Lu & Liang, 2014). Other human impacts

of Bkf toxicity include adverse embryo biotransformation and development due to changes in hydrocarbon receptor routes (Barranco et al, 2016).

Consequently, the study agrees with others that have reported elevated concentrations of PAHs, particularly Bkf in surface waters, sediments and aquatic biota of the Niger Delta and global marine ecosystems such as (Olayinka et al, 2018; Obanya, Omoarukhe, Amaeze & Okoroafor, 2019).

Benzo[a] pyrene: Benzo[a] pyrene is one of the heavy molecular PAHs with formula $C_{20}H_{12}$. Its environmental entry and transportation is from incomplete combustion of organic matters at temperatures from $300\pm 600^{\circ}C$; and pyrogenic, petrogenic, biological and anthropogenic sources (Choi, Kim, Kim, Kemp & Sancer, 2015; Obanya et al, 2019). Bap diol expoxide genetically reduces tumor development (Zavala et al, 2014). Exposure pathways include direct absorption and inhalation from the atmosphere through inhalation, cigarette/tobacco smoking and skin contact; and ingestion of contaminated water and food/fish (Mao, Smerdon, Roberts & Wyrick, 2016).

Bap is ecotoxic and impacts public health as (IARC Group 1) human genotoxic and tumorigenic carcinogen (Adebali et al, 2017; ACGIH-Worldwide, 2020).

The mean Bap bioabundance in the study media is 0.18 ± 0.02 ppm, above the permissible TVL threshold of 0.02ppm. Bap is within TVL in the sediment but above in the surface waters, implying that Bap abundance in the study media are mostly recent unsedimented pyrogenic and anthropogenic atmospheric depositions suspended in the water column from artisanal refinery fumes and soot as opposed to background petrogenicity or biologic sources. The study is indicative that consumption of crustaceans and other benthic organisms by populations of the study area will not predispose them to Bap induced ailments, whereas ingestion of water and pelagic fishes and their products poses the likelihood of adverse pyrogenicity impact from Bap toxicity. Oyetunde and Francis (2022) reported the existence of [Bap] in concentrations above TVL in studies in the Niger Delta, Nigeria. In a prevalence of benzo[a] pyrene [Bap] in the surface waters and sediments of a flow station and its environs in the Niger Delta, Nigeria; Ibigoni and Nduka (2014) documented [Bap] values of 1.15 ± 0.11 ppm in Sombriero River. Pyrogenic sources (crude spills and condensate leaks) were the reported sources. This study therefore agrees with (Ibigoni & Nduka, 2014; Oyetunde & Francis, 2022) as to the documented pyrogenic and anthropogenic sources of Bap ecoabundance to the extent that water Bap is higher above TVL but disagrees with the contrasting sediment Bap bioabundance levels in the Niger Delta marine ecological systems.

Indeno [1,2,3-cd]pyrene: Indeno [1,2,3-cd]pyrene, mostly applied for scientific researches and auto maintenance, auto fluids (power steering, brake, injector cleaners, gas treatments, leak stoppers etc), additives and absorption of extreme solar radiation produces hazardous oxides of carbon and acrid smokes of carcinomutagenic and genotoxic potency and may cause explosion of containers when thermally decomposed (Egr, 2016; Sigmaaldrich, 2016; Salat, Williams, Chiu, Eickmeyer, Kimpe, Blais & Crump 2021).

The media mean concentrations of indeno [1,2,3-cd] pyrene ranged from 0.27 ± 0.04 ppm above the WHO/USEPA TVL of 0.1 ppm. This reveals that only IP levels in water is above the WHO/USEPA allowable limits, revealing that IP bioavailability is more concentrated in the waters than sediment samples. It further shows that the marine ecological waters and sediments of the study area is polluted by indeno [1,2,3-cd] pyrene and pose health challenges to aquatic lives and the riparian populations of the Lower Orashi and Sombriero River systems, particularly if prolonged. Different studies have documented PAHs concentrations including indeno [1,2,3-cd] pyrene contamination, sources, transport and associated human health risks in Nigeria and global marine environment (Adeniji et al, 2019; Uzochukwu et al, 2022; Okedere et al, 2022). Elevated mean IP concentrations (0.353 & 0.652 ppm) were observed in the water samples of Egbe dam, Ekiti State, Nigeria; by Ibigbami et al (2020). Human health risks assessment of legacy PAHs and economic implications of the prolonged effluent receiving sediments of Nwaenebo River, Enugu State, Nigeria; were interrogated by Uzochukwu, Nnameka, Chika and Obiora (2022). The sediments were found polluted with Σ PAHs concentration ranging from 14.3-163 mg/l. Also, PAHs occurrence in the environment of Nigeria was found above WHO/USEPA/EU in a meta review by Okedere and Elehinafe; 2019; Olayinka, Abidemi and Ibigbami (2022). Bayowa and Agbozu (2016) also observed high seasonal values for the 16 IARC/USEPA priority PAHs (4.18 ± 3.029 ppm) for dry/wet season in Warri city, Nigeria. The 5ringed benzo[a] pyrene was reported the most abundant of all 16 priority PAHs. Similarly, Yendry, Oyebayo, Guilherme and Paulo (2019) observed high total PAHs values ($489 \pm 5616 \mu\text{g kg}^{-1}$ and $642 \pm 21595616 \mu\text{g kg}^{-1}$) for soil and sediment. Indeno [1,2,3-cd] pyrene was documented with the highest occurrence in the soil. Consequently, this study agrees with (Ibigbami et al, 2020; Uzochukwu et al, 2022) which documented Indeno [1,2,3-cd] pyrene pollution in the River waters and bottom sediments, posing consequential adverse human health impact to the riparian populations of the study area. Benzo[a,h] pyrene diol epoxide metabolites (Bpde) attaches itself to human and animal DNAs and causes mutations and cancer of the skin lungs, liver, colon, associated renal failures and covalent DNA moieties (Knafla & Phillipps, 2006; USEPA, 2016;) Dbp was detected above safe dose levels posing carcinomutagenic risks by Isioma, Ozekeke and Ezemonye (2017) in an examination of human health risk assessment of PAHs in tissues of smoked fishes (*Scomber scombrus*, *Clarias gariepinus*, *Ethmalosa fimbriata*) from markets of Southern Nigeria. Orisakwe, Igweze, Okolo and Udowelle (2015) reported above safe human health permissible values of the 16 priority PAHs in regions of Nigeria ranging from (Southeast 0.24 ± 29.23 ppm/ $225.84 \mu\text{g/kg}$, North Central 0.11 ± 9.47 ppm/ $1.09 \mu\text{g/kg}$, Southwest 0.94 ± 14.55 ppm and Niger Delta 2.28 ± 22.88 ppm). Dbp was amongst the highest pollutant contributors (> 0.2 ppm) in selected seafood (prawn, periwinkle, crab and oyster) by Onajeke, Nwokonkwo and Osakwe (2020) in an assessment of human health risk of PAHs from the Niger Delta.

The mean concentrations of DBA in the study is 0.51 ± 0.14 ppm, exceeding the WHO/USEPA permissible level of 0.0003 ppm. This implies the waters, sediments and their products are not safe for consumption for populations along the study corridor. The study further revealed that the Lower Orashi and Sombriero sediments are more polluted compared to the surface waters. It is therefore safe to infer that this study shares concordance in terms of higher values of DBA and sources (petroleum and anthropogenic sources) of PAHs with (Orisakwe et al, 2015; Isioma, Ozekeke & Ezemonye, 2017; Onajeke, Nwokonkwo & Osakwe, 2020).

Benzo[g,h,i] perylene or benzo ghi or B[ghi]p is a white crystalline solid ortho-and-peri-fused heavy molecular PAH with a molecular formula $C_{22}H_{12}$, ubiquitous, sharing similar sources, fate and transport with previous PAHs, and used for the manufacture of dyes, plastics, pesticides, explosives, drugs, permanent inks of marker pens, bile acids, artificial cholesterol and medical steroids (USEPA, 2016; HHS/ATSDR, 2016).

The mean b[ghi]p abundance in the media is 0.17 ± 0.04 ppm, above the WHO/USEPA TVL of 0.1 ppm. B[ghi]p abundance in surface water is unsafe whereas it is within safe levels in the sediments. This is consistent with most of the heavy molecular PAHs of the study and signifies that the PAHs of the study are mostly recent light unsedimented/unsettled atmospheric depositions of soot from artisanal refineries (locally called kpo-fire) and other pyrogenic/anthropogenic sources. The finding further corroborates the lipophilic fingerprint of PAHs preponderance in literature. The lack of affinity of PAHs to water particulates coupled with their water insolubility slows their vertical downward travel for bottom sedimentation. The above implies b[ghi]p surface water pollution predisposes the riparian populations of the study area to b[ghi]p induced ailments through consumption of waters and pelagic fishes than benthic fishes and crustaceans. The study therefore finds support in (Ito et al, 2015; Isioma, Ozekeke & Ezemonye, 2017; Onajeke, Nwokonkwo & Osakwe, 2020) who reported elevated bioabundance and ecotoxicity of the IARC 16 priority PAHs in Nigeria and global marine environments.

In summary, the speciation chemistry study shows that 15 of the 16 IARC priority PAHs were above the WHO/USEPA permissive TLV in the environmental media (water and sediment). Fluoranthene is within permissible TVL. Indeno [1,2,3] pyrene and benzo[g,h,i] concentrations are above TVL only in the water but not in the sediment samples of the study. It shows that riparian populations within the Lower Orashi and Sombriero River systems are predisposed to health risks associated with exposure of PAHs.

Conclusion

This study evaluated the environmental and public health implications of seasonal (dry and wet/rainy) levels of marine ecological bioavailability and characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) in the waters and bottom sediments of the contiguous saline differentiated coastal deltaic Lower Orashi and Sombriero River Systems, Rivers State; Nigeria. PAHs's chemical speciation showed 15 of the 16 IARC priority PAHs exceeded their respective WHO/USEPA permissive tolerant values. Fluorine is within allowable thresholds. Furthermore, all the 16 IARC priority PAHs showed similar seasonal characteristics in terms of their stoichiometric abundance

in the study media. Consequently, the study concluded that the waters and bottom sediments, and indeed the marine ecologies of the Lower Orashi and Sombriero River Systems, Rivers State, and by extension the Niger Delta are polluted with the 16 IARC priority PAHs unsuitable for ecological life and public health. Ingestion of the surface waters and or consumption of both benthic/pelagic fishes and aquatic species expose the riparian population within the study area to adverse health risks associated with PAHs environmental prevalence with the likelihood of suffering one or multiple ailments arising from PAHs pollution. However, long term bioaccumulation of Fluorine could prove detrimental. Effective decontamination, remediation and monitoring of PAHs in the marine media (surface waters and bottom sediments) of the Lower Orashi and Sombriero River Systems, Rivers State, and indeed the Niger Delta; Nigeria is recommended.

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