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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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.

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, oetacane, cyclohexane), aromatics (Naphlhwenw, Phenathrine, Benzene & Pyrene), asphaltenes (phenols, fatty acids, ketones, esters and porphyrms) and resins (pyradines, quinolones, carbozoles, sulphoxides and amides) (Ite & Sempe, 2012; Al-Hashem, 2017). PAHs are mostly soluble in fats and therefore easily bioaccummlate 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]fluorine (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 (FI/Py), benz(a) anthracene/chrysene (BaA/Ch), phenanthrene/(phenanthrene + anthracene) Ph/(Ph + An) and indenol $[1, 2, 3 – cd]$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 Clarais garrienpious*) 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.
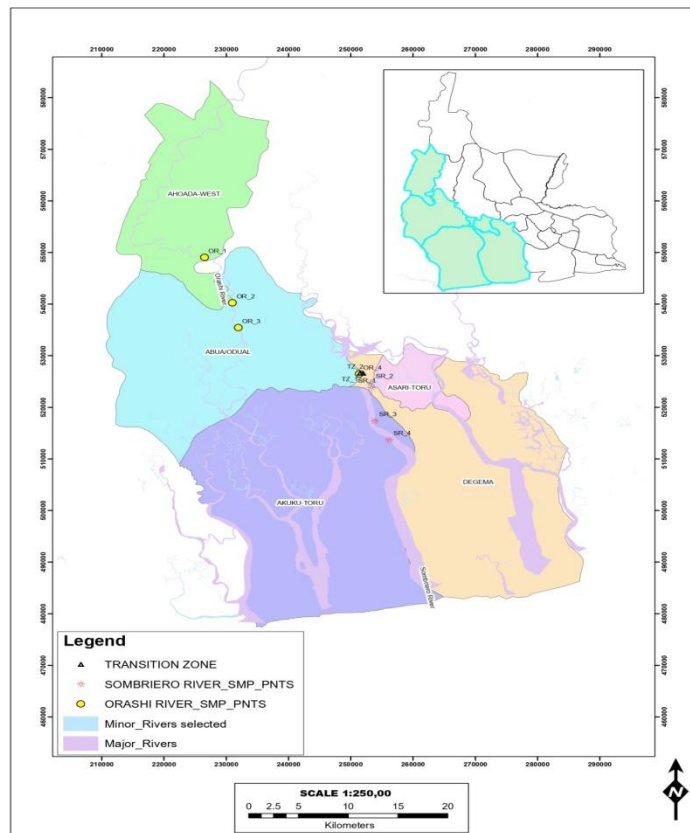
The Lower Orashi and Sombriero River systems host many petroleum hydrocarbon exploration, production and transportation assets including ten (10) crude oil and gas fields, gas plants and many crude oil delivery trunk lines. The Niger Delta Development Commission (2006) and IUCN-NDP (2013) documented 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, chrysophyllumalbidum and irvingiagabonenesis*), 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 low-lying 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 ≤ 7meters 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 parchment 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	Sampling Sites	Designation	GPS
1	Ozuochi	OR1	E006º 32 02.0" N04º57 45.5"
2	Emesu	OR2	E006º 34 29.9" N04º53 03.1"
3	Ogbema Corridor	OR3	E006º 36 07.0" N04º48 44.3"
4	Ogonokom	OR4	E006º 45 06.0" N04º 45.33.0"
5	Hulk-Transition Zone	TZ1	E006º 45 31.4" N04º45 46.7"
6	Atala-Degema Waterfront	TZ2	E006º 45 51.4" N04º45 40.4"
7	Opulogoloboko	SR1	E006º 45 34.1" N04º44 08.3"
8	Idama Flow Station	SR2	E006º 46 34.7" N04º44 38 3"
9	Minjidukiri	SR3	E006º 46 52.5" N04º40 36.9"
10	Ebemaboko	SR4	E006º 48 08.0" N04º38 38.7"

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

SN	PAHs COMPD, ppm	OR1	OR2	OR3	SR1	SR2	SR3	TZ1	TZ2	MEAN	USEPA/WHO /ASTDR STNDRD
1	Naphthalene	0.80	0.10	0.52	0.66	0.66	0.37	0.85	0.04	0.50	0.02
2	Acenaphthylene	0.10	0.41	0.04	0.34	1.32	3.62	0.63	0.71	0.90	0.004
3	Acenanphthene	0.01	0.33	0.08	0.34	0.36	0.36	0.17	0.04	0.21	0.06
4	Fluorene	0.06	0.24	ND	0.11	0.32	3.82	0.67	ND	0.57	3.0
5	Phenanthrene	0.72	0.18	ND	ND	0.49	0.19	ND	0.58	0.27	0.02

6	Anthracene	0.12	0.03	ND	ND	0.30	ND	0.05	ND	0.06	0.1
7	Fluoranthene	0.80	0.01	0.19	0.02	0.02	0.04	0.01	0.01	0.14	0.4
8	Pyrene	0.90	0.06	0.27	0.03	0.01	0.01	0.01	0.89	0.27	0.2
9	Chrysene	ND	0.02	0.02	0.02	0.01	0.02	0.01	0.44	0.07	0.001
10	Benz(a) anthracene	ND	0.01	0.05	0.04	0.50	9.29	0.02	0.50	1.30	0.001
11	Benzo(b) fluoranthene	0.12	0.01	0.03	0.01	0.01	0.02	0.02	0.11	0.04	0.1
12	Benzo(k) fluoranthene	0.70	0.01	0.03	0.02	0.01	0.04	0.02	0.29	0.06	0.01
13	Benzo(a) pyrene	0.10	0.01	0.31	0.02	0.02	0.52	0.02	0.47	0.18	0.2
14	Indeno(1,2,3-cd) pyrene	ND	ND	0.10	0.01	0.01	0.31	0.40	1.30	0.27	0.1
15	Dibenz(a,h) pyrene	0.02	0.02	0.03	0.01	0.06	3.72	0.20	ND	0.51	0.0003
16	Benzo(g,h,i) perylene	0.01	0.01	0.28	0.02	0.01	0.71	0.01	0.33	0.17	0.01

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 COMPD, ppm	OR1	OR2	OR3	SR1	SR2	SR3	TZ1	TZ2	MEAN	USEPA/WHO/ASTDR 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	Acenanphthene	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	N D	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±0.14ppb, 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 ± 3.04ppb, 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 genotoxical 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 ± 2.36ppb. 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 ± 1.14ppm 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 ± 0.38ppm are above recommended toxicological threshold of 0.01ppm, 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 ortho-and-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±1.04ppm, above the WHO/USEPA TVL of 0.2ppm. 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 ecotoxity 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 symetrical 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 0.07ppm, above allowable TVL of 0.001ppm. 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±0.05ppm, implying that sediment abundance is less than that of surface water. However, all are above the TVL of 0.001ppm. 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±206µg/l above the TVL of

0.001ppm. 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 formular $C_{20}H_{12}$ 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±0.04mg/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; ACGIH-Worldwide, 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 0.3mg/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±0.302mg/l, while Anyakorah et al and Olayinka et al, 2018 documented concentrations ranging from <0.00088±0.505mg/l around the Lagos waters. The findings of this study for B[b]f at 0.1±0.04mg/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 $C_{20}H_{12}$ having five fused rings (ACGIH-Worldwide, 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±0.16ppm which is above permissive TVL of 0.01ppm. 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 photoxic (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±600°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±0.02ppm, 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±0.11ppm 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±0.04ppm above the WHO/USEPA TVL of 0.1ppm. 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 & 0.652ppm) 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 ∑PAHs concentration ranging from 14.3-163mg/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±3.029ppm) 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±5616µg kg^{-1} and 642±21595616µg 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;)

Dba 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±29.23ppm/ 225.84µg/kg, North Central 0.11±9.47ppm/1.09 µg/kg, Southwest 0.94±14.55ppm and Niger Delta 2.28±22.88ppm). Dba was amongst the highest pollutant contributors (> 0.2ppm) 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±0.14ppm, exceeding the WHO/USEPA permissible level of 0.0003ppm. 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±0.04ppm, above the WHO/USEPA TVL of 0.1ppm. 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.

References

Almeida R., Mucha A.P., Teixeira C., Burdalo A.A & Almeida C.M., (2013). Biodegration of Petroleum Hydrocarbons in Estuarine Sediment Metal Influence. Biodegr. 24(1): 111-123.

Amaize E (2001) Crises from the Creeks. Saturday Vanguard Newspapers (www.vanguardngr.com) March 17.pp.

American Conference of Governmental Industrial Hygienists-HSDB (2013). Documentation of the TLVs and BEIs with Other World Wide Occupational Exposure Values. 7th Ed. CD-ROM Cincinnati, OH 45240-1634 2013.

Anifowose B (2008). Assessing the Impact of Oil and Gas Transport on Nigerian Environment. U21 Postgraduate Conference Proceedings1, University of Birmingham, UK. http:/www.eia.doe.gov/cab/index.html.pds.

Anyakora, C & Coker, H (2007) Assessment of Polynuclear Aromatic Hydrocarbon Content in Four Species of Fish in the Niger Delta by Gas Chromatography/ Mass spectrometry. African Journal of Biotechnology 6(6),737-743, March, 2007. ISSN 1684-5315. Academic Journals. http://www.academicjournals.org/AJB.

Anyakora, Ch, Coker, H & Arbabi, M (2010) Application of Polynuclear Aromatic Hydrocarbons in Chemical Fingerprinting. The Niger Delta Case Study. Iranian Journal of Environrulutal Health Science Engineering. 2011,1- 75-84.

Anyakora, G & Coker, H. (2006). 'Determination of Polynuclear Aromatic Hydrocarbons (PAHs) in Selected Water Bodies in the Niger-Delta. A.J. Biotechnology.

Anyakora, G; Ogbeche, A.; Palmemr, F., Coker, H.; Ukpo, G & Ogah C (2005). GC/MC Analysis of Polynuclear Aromatic Hydrocarbons in Sediments Samples from Niger-Delta Region Chemosphere.

Anyokora, C. A, Ogbche, K. A., Palmer, P., Cekerh, Ukpog & Ogha C (2004). A Screen for Benzo (a) Pyrene a Carvinogen, in the Water Samples from the Niger Delta Reigion, Nigeria J. Hosp. Med.

APHA (2012) Standard Methods for the Examination of Water and Waste Water, 22nd ed. American Public Health Association, Washington DC, USA.

Arokoyu, S.B & Umeuduji, J.E (eds): Perspectives of the Human Environment, Amaethyst and Colleagues Publishers, Port Harcourt.

Aspects of Aquatic Pollution in Nigeria (2011). Research Journal of Environmental and Earth Sciences 3(6): 673-693, 2011. Maxwell Scientific Organization 2011. ISSN: 2041-0492.

ASTM (American Standard of Testing Materials) (2003). Test Method for Oil in Water Analysis. Annual Book of ASTM Standards, ASTM International U.S.A.

Aweto, A (2002). Outline Geography of Urhoboland. Urhobo Historical Society, http;// www.waado.org/Geography/UrhoboGeography-Aweto.htm.

Baxter, C.S & Warshawsky, D (2012). Polycyclic Aromatic Hydrocarbons and Azaaromatic Compounds. Patty's Toxicology, 6th ed (1999-2016). New York, NY: John Wiley & Sons, Inc, 17 August, 2012.

Benka-Coker, M. O & Olumagin, A (1996). "Effects of Waste Drilling fluid on Bacterial Isolates from a Mangrove Swamp Oilfield Location in the Niger Delta of Nigeria," Bioresoarce Technology,55(3). 175-179, 1996.

Bicnews (2005). Bioremediation: Natures's Way to a Cleaner Environment. Malaysian Biotechnology Information Center [Matric] (www.bic.org.my).

Bobmanuel, P.G (2012). Acute Toxicity Tests of Different Concentrations of Diesel Fuel On Mudskipper, periopthalmus koelreuteri (pallas 1770): (Gobiidae) joomal of human ecology 39 (2) : 171-174.

Boehm, A.B, Ismail, N.S, Sassoubre, L.M & Andruszkiew, E.A (2017) Oceans in Peat: Graud Challenges in Applied Water Quality Research for the 21st Century.

Broecker, W.S (1981). Geochemical Tracer and Ocean Circulation in Evolution of Physical Oceanography; B.A. Warren and C. Wunsch, eds. Cambridge, MA: MIT Press, 1981.

Buzcu-Guven, B & Harriss, R (2012). "Extent, Impacts and Remedies of Global Gas Flaring and Venting," Carbon Management, 3 (1). 95-108.

Campbell, L. G. .M (2004). World Bank Group. Oil, and D. Chemicals: A Voluntary Standard for Global Gas Flaring and Venting Reduction, 29555, World Bank Group, Oil, Gas, Mining and Chemicals Dept., Washington, D.C.

Chisholm, H (1911) Chrysene Encyclopaedia Britannica. 6 (11th ed). Cambridge University Press. P. 319.

Christen, K. (2004) "Environmental Impacts of Gas Flaring, Venting and Uptake," Environmental Science & Technology, 38 (24). 480A-480A.

Daniel-Kahn. L A & Sotosnon Amabaeaye (2002) "The Impact of Accidental Oil Spill on Cultivated and Natural Vegetation in a Wetland Area of Niger Delta, Nigeria," Ambio, 31(5).441-442,2002.

David, L (2002), Sense and None-Sense-.The Environmental Impact Of Exploration and Marine Organisms Offshore Cape Breton: Submission to the Public Review Comission, Cape Breton Island, Nova Scotia, for the Sierra Club Canada, Sierra Club Website http://www.sierraclub.ca/.

Defois, C., Ratel, J., Denis, S., Batut, B., Beugnot, R., Peyretaillade, E., Engel, E & Peyret, P (2017) Environmental Pollutant Benzo[a] Pyrene Impacts the Volatile Metabolome and Transcriptome of the Human Gut Microbiota. Front Microbiol. 2017 Aug 15;8:1562. Doi: 10.3389/fcicb.2017.01562. PMID:28861070; PMCID: PMC5559432

DHHS/National Toxicology Program (2016). Report on Carcinogens, Fourteenth Edition: Polycyclic Aromatic Hydrocarbons .Hazardous Sustances Data Bank (HSDB). https://ntp.niehs.nlh.gov/pubhealth/roc/index-html.

Doust, H (1990) "Petroleum Geology of the Niger Delta," Geological Society, London, Specurl Publications.50 (1).365-365. 1990.

Doyle, A. B., Pappworth, S. S. R & Caudle, D. D (2008) "Drilling and Production Discharges in the Marine Environment" Environmental Technology in the Oil Industry, S. Orsuzullk, ed., pp. 155-1 87: Springer Netherlands.

Ekpo B.O., Oyo-Ita O. E., Oros, D.R & Simoneit B. R. T (2012) Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Surface Sediments from Cross River Estuary S.E. Niger Delta Environ. Monit. Assess., 184(2): 1037- 1047.

Ekpoh, I & Obia, A (2010) "The Role of Gas Flaring in the Rapid Corrosion of Zinc Roots in the Niger Delta Region of Nigeria," The Environmentalist 30(4). 347-352. Endib Vol. 34.

Ekundayo, E. O & Obuekwe, C (2001) Effects of an Oil Spill on Soil Physico-chemical Properties of a spill Site in a Typical udipsamment of the Niger Delta Basin of Nigeria. Environment mentoring and assessment.

Ekuri, P & Eze, E. S (1999) "Teaching Environmental Pollution in Primary/ Secondary Schools" Workshop Paper on the Orientation Workshop for Teachers on the Implementation of the National Environmental Education Curricula at Ogoja, Cross-River State, Nigeria, 2001.

Emuedo, O., Anoliefo, G. O & Emuedo, C (2014). Oil Pollution and Water Quality in the Niger Delta: Implications for the Sustainability of the Mangrove Ecosystem. Global Journal of Human – Social Sciences Bio-Geography, Geo-Sciences, Environmental Disaster Management. 14 1.0, 2012. GJHSS – B Classification code 960305, 700401.

Eweje, G. (2006) Environmental Costs and Responsibilities Resulting from Oil Exploitation in Developing Countries: The Case of the Niger Delta of Nigeria, Journal of Business Ethics, 69 (1). 27-56, 2006.

Ezekwe I. C & Utong I. C (2015) Ecological Risk Levels from Hydrocarbons and Metal Concentrations in the Sediments of an Oil Polluted Coastal River in Andoni, Eastern Niger Delta of Nigeria. A Paper Prepared for Presentation at the 2015 International Conference of Water Resources and Environment, July 25th-28th, Beijing China.

Ezekwe I. C., Odu N. N & Onyedikam, L (2014) Heavy Metals and Polycyclic Aromatic Hydrocarbons in Water from Drilling Waste Polluted Freshwater Swamp in the Mgbede Oil Field of South-South, Nigeria. Journal of Bioremediation and Biodegradation 5: 258. doi: 10.4172/2155-6199.1000258.

Ezekwe, I. C., Ezekwe, A. S & Endoro, O. P (2013) Biological Contaminants in the River Nun and Environmental Ethics of River Side Communities in the Niger Delta: The case of Anassoma, Bayelsa, Nigeria.

FAO/WHO (1999) Expert Committee on Food Additives, Summary and Conclusions, 53rd Meeting, Rome.

FEPA (1991) Guidelines and Standards for Environmental Pollution Control in Nigerian. Federal Environmental Protection Agency (FEPA) Nigeria.

Field Guide to the Commercial Marine Resources of the Gulf of Guinea. FAO Regional Office for Africa. 222pp.

Gbadebo, A.M, Taiwo, A.M & Ola, O. B (2009) Effects of Crude Oil on Clarias Garipinue, A Typical Marine Fish. American Journal of Environmental Science.

Georgewill, O.A. (2012) "Crude Oil: Sweet and Sour - Effort at Mitigating the Toxic Effects''. An Inaugural Lecture Series 93, University of Port Harcourt, Port Harcourt.

Guo, J, Li, Z., Rana-Singhe, P., Bonina, S., Hasseini, S., Carcoran, M. B., Smalley, Coln., Rockne, K.J, Sturchio, N.C., Giesy, J. P &Li, A (2016) Spatial and Temparal Trends of Polyhalogenated Carbazoles in Sediments of Upper Great Lakes: Insights into their Origin. Environmental Science and Technology 2017. Doi: 10.1021/acs. est6bo6128. Acs Publications.

Hazardous Substances Data Bank (HSDB) (2016). [1,2,3-cd] pyrene. Product Number: 48499, Version 5.5 (Revision Date 05/27/2016). https://www.sigmaaldrich.com/safety-center.html. Acceseed February 7, 2021.

HHS/ATSDR, Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs) p.8 PB/95/264370 (1995). https://www.atsdr,cdc.gov/toxprofiles/index.asp. *Acessed 18 July, 2022*.

Holdway, D. A (2002) The Acute and Chronic Effects of Wastes Associated with offshore Oil and Gas Production on Temperate and Tropical Marine Ecological Processes, Marine Pollution bulletin, 44(3). 185-203.

Howard I. C., Gabriel U. U & Horsfall, M (2009) Evaluation of Total Hydrocarbon Levels in some Aquatic Media in an Oil Polluted Mangrove, Wetland in the Niger Delta. Applied Ecology and Environmental research 7(2): 111 – 120.

IARC Monograph (2010) Some Non-Heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures. Volume 92 and Volume Sup 7: Overall Evaluations of Carcinogeneity: An Updating of IARC Monographs Volumes 1-42, 1987; page 440. ISBN 92-832-1411-0.

Ibigani, C.H; Ugwemarubong, G.U & Horsefall, M (2009) Evaluation of Total Hydrocarbon Levels in Some Aquatic Media in an Oil Polluted Mangrove Weff and in the Niger Delta.

Applied Ecology and Environmental Research 7(2): 111-120. ISSN 1589 1623, Peukaia Bt. Budapest, Hungary.

ICES (2008) Report of the Working Group on Biological Effects of Contaminants (WGBEC); 31 March – 4 April, Sete, France; ICES; Sete, France, 2008.

Institute of Pollution Studies- IPS (1996) Environmental Impact Assessment Report on Soku Gas Plant, Rivers State University of Science and Technology, Rivers State, Nigeria.

International Agency for Research on Cancer (IARC) (1987). Monograph on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. https://monographs.iarc.fr/ENG/Classification/index.php, p. S7 58 (1987).

International Agency for Research on Cancer (IARC) of the World Health Organization (2006 and 2015) *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. IARC MONOGRAPHS,* Volumes 1-121. Last updated April 18, 2018. Accessed 20/04/18 and available from http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf.

International Maritime Organization, (IMO) (2000). Guidance on Assessment of Sediment Quality, Global Investigation Pollution in the Marine Environment (GIPME).IOC-UNEP-IMO London. Pub no.439/00.

International Union for the Conservation of Nature and Natural Resources (2013). A Report by the Independent IUCN-Niger Delta Panel (IUCN-NDP), (July 2013) to the Shell Petroleum Development Company Limited of Nigeria (SPDC): Soku Biophysical Report on Sustainable Remediation and Rehabilitation of Biodiversity and Habitat of Oil Spill Sites in the Niger Delta. IUCN, Gland, Switzerland. 978-2-8317-1617-6. www.iucn.org.

International Union of Pure & Applied Chemistry (2014) Nomenclature of Organic Chemistry: IUPAC Recommendations and Preferred Names 2013. The Royal Soceity of Chemistry p. 206. Doi:10.1039/9781849733069. ISBN 978-0-85404-182-4.

Ite, A. B & K. T. Semple (2012) Biodegradation of Petroleum Hydrocarbons in Contaminated Soils, "Microbial Biotechnology: Energy and Environment, It Arora, ed., pp. 250.278.

Ite, A. B & U. J. Ibok (2013) "Gas Flaring and Venting Associated with Petroleum Exploration and Production in the Nigeria's Niger Delta," American. Journal of Environmental Protection, 1 (4). 70- 77.

Ite, A. E., Ibok U. I, Ite, M. U & Petters, S. W (2013) Petroleum Exploration and Production: Past and Present Environmental Issues in the Nigeria's Niger Delta." *American Journal of*

Environmental Protection 1.4 (2013): 78-90.http://pubs.sciepub.com/env/1/4/2/, accessed 05/06/2018.

IUCN/CEESP (2006) Niger Delta Natural Resources Damage Assessment and Restoration Project, Phase 1 Scoping Report. May 31, 2006 Report from the IUCN commission on Environment, Economic and Social policy, 14pp.

Iwuchukwu, J. J. I (2006). Environmental Hazard Management: Principles and Procedure, Owerri, Nigeria.

Joint FAO/WHO Expert Committee on Food Additives (JECFA) (2010). Journal as Environmental Pollution 172 (2013)235-242.02697491/52012, Elsevier http //dx.org110.1016/j.envpol.2012.09.014. Journal of Bioremediation and Biodegradation 5: 258. doi:10.4172/2155-6199.1000258.

Kadafa, A. A (2012) Oil Exploration and Spillage in Niger Delta of Nigeria. Civil and Environmental Research. ISSN 2222-1719 (paper) ISSN 2222-2863. Vol. 2, No. 3, 2012.

Kamalu, M & Wokocha, E. C. C (2011). Land Resource Inventory and Ecological Vulnerability: Assessment of Onne Area in Rivers State. Nigeria, Research Journal of Environmental and Earth Sciences, 3(5).438-447.

Keddy, P.A (2010) Wetland Ecology: Principles and Conservation (2nd edition) Cambridge University Press, UK Cambridge 497-511.

Kharaka, Y. K & N. S. Dorsey, (2005) "Environmental Issue of Petroleum Exploration and Production: Introduction," Environmental Geosciences, 12 (2). 61-63.

Kharaka, Y. K., and J, K. Otton, (2003) "Environmental Impacts of Petroleum Production: Initial Results from Time Osage-Skiatook Petroleum Environmental Research Rites, Osage County, Oklahoma," Water Resources Investigations Report 03-42611.

Larranaga, M.D; Lewis, R.J & Lewis, R.A (2016). Hazardous Substances Data Bank (HSDB). Hawley's Condensed Chemical Dictionary, 16th Edition. John Wiley & Sons, Inc. Hoboken NJ 2016.; p. 755.

Lewis, R.J S (ed) (2004). Hazardous Substances Databank. Sax's Dangerous Properties of Industrial Materials. 11th Edition. Wiley-Interscience, Wiley & Sons, Inc. Hoboken, NJ. 2004., p. 2079
.
Mbukwa, E.A., Msagati, T. A .M & Mamba, B. B (2012). Supported Liquid-Membrane-Liquid-Chromatography-Mass-Spectrometry Analysis of Cyanobacterial Toxins in Fresh Water Systems. Phys Chem Earth 50: 84-91.

Meff, J . M (1987). Biological Effects of Oil in the Marine Environment. Chem. Eng. Progr.

Merck Index, 14th edition

Michael Harsfall & Ayebaemi, S. I (2013). Principles of Environmental Pollution, Toxicology and Waste Management. Oyome Research Publications, II Orogbum Crescent, GRA Phase II, Port Harcourt.

Moore, J. W. & Ramamoorthy, S. (1984). Polycyclic Aromatic Hydrocarbon. In: Organic Chemicals in Natural Naters: Applied Monitoring and Impact Assessment. Springer-Verlag, New York, USA.

National Toxicology Program (NTP) (1992). Institute of Environmental Health Sciences, National Institute of Health (NTP). 1992 National Toxicology Program Chemical Repository Database. Research Triangle Park, North Carolina, USA.

Ndubuisi, A. L & Asia, I. O (2007). "Environmental Pollution in Oil Producing Area of the Niger Delta Basin, Nigeria". Empirical Assessment of Trends and People's Perception. Environmental Research Journal, (1 — 4): 18 —26.

Nduka J. K & |Orisakwe O. E (2011). Assessment of Pollution Profile of Selected Surface Water in the Niger Delta Region of Nigeria. The Lambert Academic Publishers, Germany.

Nduka J. K & Orisakwe O. E (2010). Precipitation Chemical and Occurrence of Acid Rain over the Oil-Producing Niger Delta Region of Nigeria. The Scientific World Journal.

Nduka J. K. C, Orisakwe O. E, Ezenweke, Chendo M. N, Ezeabasili (2008). Acid Rain Phenomenon in Niger Delta Region of Nigeria. Economic, Biodiversity and Public Health Concern. The Scientific World Journal.

Nduka, K J, Obumselu, O. F & Umedum, L. N (2012). Crude Oil and Fractional Spillages Resulting from Exploration and Exploitation in Niger Delta Region of Nigeria: A Review about the Environmental and Public Health Impact. Crude Oil Exploration in the World. Prof. Mohammed Younes (Ed). ISBN: 978-953-51-0379-0, In Tech. Available From http://www.intechopen.com/books/crude-oil-exploration-in-the-world/environmental-impact-of-crude-oil-exploration-and-in-niger-delta-region-of-nigeria-a-review.

Nieva-Cano M. J, Rubio-Barrisos & Santos-Deigado M. J (2001). Determination of PAH in Food Samples by HPLC with Flourimetric Detection following Sonication Extraction without Sample Clean-up.

Niger Delta Petroleum Systems, Nigeria (2000) " Petroleum Systems of South Atlantic Margins. AAPG Memoir 73, M. R. Mello and B. J. Katz, eds., pp.213-231: Association of Petroleum Geologists (AAPO), 2000.

NOAA; CAMEO Chemicals. Dadabase of Hazardous Materials. Dibenzo(a,h) pyrene (189-64-0). National Ocean Atmos Admin, Off Resp Rest, NOAA Ocean Serv. Available from Sept 12, 2016, https://cameochemicals.noaa.gov/.

Nwilo, P. C & Badejo, O. T (2006) "Impacts and Management of Oil Spill Pollution along the Nigerian Coastal Areas," Administering Marine Spaces: International Issues '119.

Nwilo, P. C & Badejo, O.T. (2007). Comps, Impacts and Management of Oil Spill Pollution along the Nigerian Coastal Areas. http: //fig.net/pub/figpub/pub36/chapters/chapter8 .pdf. Accessed 20th May, 2015.

Obafemi A. A (2004). Pollution and the Human Environment in Bellgam, W. I, Arokoyu, S.B and Umeuduji, J.E (eds): Perspectives of the Human Environment, Amaethyst and Colleagues Publishers, Port Harcourt.

Obanya, E. E; Omoarukhe, A; Amaeze, N. H & Okoroafor, CU (2019). Polycyclic Aromatic Hydrocarbons in Ologe Lagoon and Effects of Benz[b] fluorouthene in African Catfish. J. Health Pollut. 2019. Jun 4, 9(2.2): 190605. doi:10.5696. 2156-9614-9.22. 190605. PMID:31259081: PMCID. PMC6555255.

Obire, O. Tamuno, D. C & Wemedo, S. A (2003). Physic-Chemical Quality of Elechi Creek in Port-Harcourt, Nigeria. Journal of Applied Science and Environmental Management.

Odokuma, L. O & Okpokwasili, G. C (2004). Seasonal Ecology of Hydrocarbon-Utilizing Microbes in the Surface Waters of a River. Environ. Monit. Assess. 27 (3): 175-191.

Ogri, O. R (2001). "A Review of the Nigerian Petroleum Industry and the Associated Environmental Problems," The Environmentalist, 21(1) 11-21.

Ojaveer, E (2017) Receut Dynamics of the Environment and Biota. Ecosystems and Living Research of the Baltic Sea; Springer, pp 209-236.

Okoro D & Ikolo A. O (2005). Compositional Pattern and Sources of Polynuclear Aromatic Hydrocarbons in Water and Sediment Samples of Ogunu Creek of the Warri River Proc. 28th Annual Int. Conf. Chem. Soc. Nigeria.

Olaire A. A, Altenburgerr, Kuster E & Brack W (2005). Chemical and Ecotoxixological Assessment of Polycyclic Aromatic Hydrocargon Contaminated Sediments of the Niger Delta, Southern Nigeria Science Total Environment.

Ologunorisa, T. E., (2001) "A Review of the Effects of Gas flaring on the Niger Delta Environment," International Journal of Sustainable Development & World Ecology, 8(3), 249-255.

Onojake, M.C, Sikoki, F.D, Omokheyeke,O & Akpiri, R.U (2015). Surface Water Characteristics and Trace Metal Level of the Bonny/New Calabar River Estuary, Niger Delta, Nigeria. Applied Water Science, Crossmark, Springer. July 09, 2015. Doi.10.1007/5/3201-015-0306-y.

Onuoha, F.C. (2008). Oil Pipeline Sabotage in Nigeria: Dimensions, Actors and Implications for National Security. African Security Reviews, 17 (3), 4-9.

Onwugbuta, J; Zabbey, N & Erondi, E. S (2008). Water Quality of Bodo Creek in the Lower Niger Delta Basin.

Orisakwe O.E, Njan A.A, Afonne O.J, Akumka D.D, Orish V.N and Udemezue O.O (2004). Investigation into the Nephrotoxicity of Nigerian Bonny Llight Crude Oil in Albino Rats. Int. J. Environ. Res. Public Health.

Oyefolu, K. O & Awobajo, O. A (1980) "Environmental Aspects of the Petroleum Industry in the Niger Delta: Problems and Solutions at pages 146-148.

Oyegun C.U (1997). The Human Environment, Its Form and Process, Paragraphics, Port Harcourt.

Oyegun C.U (2003). Essential of Social and Environmental Research, University of Port Harcourt Press, Port Harcourt.

Oyegun C.U (2004). Water Resources in W.I. Bell-Gam, S. B Arokoyu and J.E. Umeuduji (eds):

Persaud, D., Jaagumagi, R., & Hayton, A. (1993). Guidelines for the Protection and Management of Aquatic Sediments in Ontario. Standards Development Branch and Environmental Monitoring and Reporting Branch. Ontario Ministry of Environment and Energy. Toronto, Canada. Retrieved from https://atrium.lib.uoguelph.ca/xmlui/bitstream/handle/10214/15546/OME_guide_aquatic _sed93.pdf?sequence=1&isAllowed=y.

Pohanish, R.P (2012). Sitting's Handbook of Toxic and Hazardous Chemicals Carcinogens 6th Edition, Volume 1:A-K, Volume 2: L-Z. William Andrew, Waltham, MA 2012, p. 1494.

Reijers T.J.A, Petters S.W & Nwajide C.S (1996). The Niger Delta Basin in Selected Chapters in Geology Sedimentary Geology and Stratigraphy in Nigeria SPDC, Nigeria.

Rohit, S., Raghvendra, K., Suresh, C. S., Nadhir, A., Krishna, KS., Rajendra, PM., Anuj, KA., Hiep, VL & Benh, TP (2020). Analysis of Water Pollution Using Different

Physicochemical Parameters: A Study of Yamuna River. Front. Environ. Sci., 11 December, 2020. https://doi.org/10.3389/fenvs.2020.581591.

S86|TATTOOINK | Regulated Tattoo Ink Ingredients as per EU Regulation 2020/2081 | A List of Regulated Ingredients for Tattoo Ink and Permanent Make Up. Appendix 13 added to the Commission Regulation (EU) 2020/2081, 14 December 2020 Amending Annex XVII of REACH (https://eur-lex.europa.eu/eli/reg/2020/2081/oj)Doi:10.5281/zenodo.5710243. https://ec.europa.eu/jrc/en/news/how-safe-are-our-tattoos-and-permanent-makeup.

Said, T. O; El-Moselhy, K. M; Rashad, A. A. M & Shreadah, M. A (2008). Organochlorine Contaminants in Water, Sediment and Fish of Lake Burullus, Egyptian Mediterranean Sea. Bulletin of Environmental Contamination and Toxicology, 81(2): 136-146.

Scheren, P. A., A. C. Ibe, F. J. Janssen, and A. M. Lemmens, (2002). "Environmental Pollution in the Gulf of Guinea-a regional approach," Marine Pollution Bulletin. 44 (7). 633-641.

Seasonal Variations in Some Physio-Chemical Parameters of the Bonny Estuary, Niger Delta. Technical Paper No59. Nigerian Institute for Oceanography and Marine Research, Lagos. ISBN-978-2345-058 July, 1990.

Seleye-Fubara, D., Nwosu. S. O & Yellowere (2005). Soft Tissue Sarcomas in the Niger Delta Region of Nigeria [A referral hospital study]. Niger .J. med.

Sericano, S.L (2000) The Mussel Watch Appproched Its Applicability to Gobal Chemical Contamoination Monitoring Programme. International Journal of Environment and Pollution 13 (1-6) Doi:10.1504/IJEP 2000.002323

Sociey of Environmental Toxicology and Chemistry, (SETAC) (1997). Technical Issue Paper: Ecological Risk Assessment. Pensacola, FL, USA: SETAC. 4p.

Sonne, C (2010). Health Effects from Long-Range Transported Contaminants in Arctic Top Predators: An Integrated Review Based on Studies of Polar Bears and Relevant Model Species. Environ.Int. 2010, 36, 461-491.

Sruthy, S & Rosemary, E. V (2016). Microplastic Pollution in Vembanad Lake, Kerala, India: The First Report of Microplastics in Lakes and Estuarine Sediments in India. Environmental Pollution, 222, 315-322.

The Chemical & Products Databasee (2018). A Resource for Exposure-Relevant Data on Chemicals in Consumer Products, Scientific Data. 5, Article number: 180125. Doi:10:1038/sdata.2018.125.

The Impact of Oil Production on the Biota of the Niger Delta in the Petroleum Industry and the Environment of the Niger Delta, II – Proceedings of 1979 Seminar (NNPC, Lagos), 87 at 93;

The Tell Magazine, No. 44, November, 2, 1998, 10-15.

The Thisday Newspaper of Saturday, October 24, 1998, 6 & 12.

The Weekend Concord of Saturday October 24, 1998, 2, 3& 6.

Ugochukwu, C. N. C (2008). "Sustainable Environmental Management in the Niger Delta Region of Nigeria: Effects of Hydrocarbon Pollution in Local Economy. pp. 12-18, 192 – 208, 75 – 92.

United Environmental Programme (UNEP) (2011). Environmental assessment of Ogoni land. United Nation Environment Programme (UNEP), Nairobi.

United Nations Development Programme (UNDP). Niger Delta Human Development. http:hdr.unde.org/en/reports/nationareports/Africa.

United States Environmental Protection Agency – USEPA (2003). Development of National Bioaccumulation Factors Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health. https://www.epa.gov/waterscience/criteria/humanhealth/method/index.html. Acessed 30th March, 2024.

United States Environmental Protection Agency – USEPA (2006a). Standard Operating Procedures Routine Analysis of PCBs in Water and Soil/Sediment Samples by GC/ECD. Bethesda, MD: Scientific Engineering Response and Analytical Services. https://elu-in.org/download/ert/180l-r20.pdf. Accessed 30th March, 2024.

USEPA (2009). National Primary Drinking Water Regulation. https://www.epa.gov/ground-water-and-drinking-water/TABLE-REGULATED-DRINKING-WATER-CONTAMINANTS. Accessed 30th March, 2024.

USEPA (2009): Toxics Release Inventory (TRI) Program Fact Sheet. 2009 9/20/2009 [cited 2010-1/19]; Available from: http://www.epa.gov/triinter/triprogram/tri_program_fact_sheet.htm.

USEPA (1980) Guidelines and Methodology Used in the Preparation of Health Effect Assessment Chapters of the Consent Decree Water Quality Criteria. *Federal Register / VoL 45, No. 231 / Fridak. November 28, 1980 / Notices; 45 Fed. Reg. 79347 1980. Appendix C of Federal Registry notice announcing availability of water quality criteria documents (45 FR 79347).* https://www.epa.gov/wqc/guidelines-and-methodology-used-preparation-health-effect-

assessment-chapters-consent-decree accessed June 2, 2018, Pdf version from https://www.epa.gov/sites/production/files/2015-10/documents/45fedreg7.pdf.

USEPA (1991, 2016) Risk Assessment for Toxic Air Pollutants: A Citizen's Guide. Originally published as EPA 450/3-90-024.

USEPA (1992). Framework for Ecological Risk Assessment. EPA/630/R-92/001. Risk Assessment Forum Washington, DC.

USEPA (1996). Proposed Guidelines for Ecological Risk Assessment. Federal Register 61: 47552-47631.96.

USEPA (1999a): Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition. Compendium Method TO-15: Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS); Center for Environmental Research Information, Office of Research and Development U.S. Environmental Protection Agency, Cincinnati, OH 45268, January 1999, EPA/625/R-96/010b. Accessed 08/07/18 and available from https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-15r.pdf.

USEPA (1999b) Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition: Compendium Method TO-2: Method for the Determination of Volatile Organic Compounds (VOCs) in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS), Office of Research and Development National, Risk Management Research Laboratory, Center for Environmental Research Information, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268, January, 1999, EPA/625/R-96/010b;https://www3.epa.gov/ttnamti1/files/ambient/airtox/tocomp99.pdf, accessed 09/05/18.

USEPA (1999c) Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air - Second Edition: Compendium Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC), Center for Environmental Research Information, Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268,January 1999, EPA/625/R-96/010b; https://www3.epa.gov/ttnamti1/files/ambient/airtox/to-11ar.pdf, accessed 11/07/18.

USEPA (2000). Hudson River PCBs Reassessment RI/FS Phases 3 Report. Feasibility Study. US Environmental Protection Agency and US Army Corps of Engineers. https://www.epa.gov/hudson/back to clearwater's PCB page.

USEPA (2003). Procedures for the derivation of equilibrium partitioning sediment bench marks (ESBs) for the protection of benthic organisms: PAH mixtures. EPA600-R-02-013.USEPA Office of "Research and Development, Washington, D.C.

USEPA (2005). Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal mixtures (cadmium, copper, lead, nickel, silver and zinc). EPA.600-R-02-011.

USEPA (2014a)Dose-Response Assessment for Assessing Health Risks Associated With Exposure to Hazardous Air Pollutants: *Table 1:Prioritized Chronic Dose-Response Values for Screening Risk Assessments (5/9/2014).* https://www.epa.gov/sites/production/files/2014- 05/documents/table1.pdf, accessed March 12, 2018.

USEPA (2014b)Dose-Response Assessment for Assessing Health Risks Associated With Exposure to Hazardous Air Pollutants: *Table 2: Acute Dose-Response Values for Screening Risk Assessments (9/18/2014).* https://www.epa.gov/sites/production/files/2014-05/documents/table2.pdf, accessed April 28, 2018.

USEPA (2015): Technical Support Document, EPA's 2011 National-scale Air Toxics Assessment, 2011 NATA TSD, Office of Air Quality, Planning, and Standards, Research Triangle Park North Carolina 27711; Appendix H, Exhibit H-1: Toxicity Values Used in the 2011 NATA, August 13, 2015; Final Report Final Report Prepared for U.S. Environmental Protection Agency Research Triangle Park, NC, STI-915110-6315, pp. H-1 – H-7. Accessed 08/06/18 and available from https://www.epa.gov/sites/production/files/2015-12/documents/2011-nata-tsd.pdf.

USEPA (2016). Integrated Risk Information System (IRIS). Summary on Benz(A)anthracene (56-55-3). https://www.epa.gov/iris/. *Accessed 25th June, 2022.*

USEPA (2017a) Initial List of Hazardous Air Pollutants with Modifications. Accessed March 13, 2018 and available from https://www.epa.gov/haps/initial-list-hazardous-air-pollutants-modifications.

USEPA (2017b)Urban Air Toxic Pollutants. Accessed 27/03/2018 and available fromhttps://www.epa.gov/urban-air-toxics/urban-air-toxic-pollutants.

USEPA (2017c) Integrated Urban Air Toxic Strategies**.** Accessed 27/03/2018 and available fromhttps://www.epa.gov/urban-air-toxics/integrated-urban-air-toxics-strategy.

USEPA (2017d) Dose-Response Assessment for Assessing Health Risks Associated With Exposure to Hazardous Air Pollutants: *Risk Assessment for Carcinogenic Effects*. https://www.epa.gov/fera/risk-assessment-carcinogenic-effects, accessed June 14, 2018.

USEPA (2017e) Dose-Response Assessment for Assessing Health Risks Associated with Exposure to Hazardous Air Pollutants: *Risk Assessment for Other (noncarcinogenic) Effects*. https://www.epa.gov/fera/risk-assessment-other-effects, accessed April 13, 2018.

USEPA-HSDB (2016). Estimation Program Interface (EPI) Suite. Ver. 4.11. Nov, 2012. https:www2.epa.gov/tsca-screening-tools. *Accessed 14th August, 2022*.

Vanguard News January 4th, 2010. www.vanguardngr.com/2010/10/45980. Accessed 10th August 2015.

Varol, M (2020). Use of Water Quality Index as Multivariate Statistical Methods for the Evaluation of Water Quality of a Stream Affected by Multiple Stressors. Environmental Pollution, 266, 115417. https://doi.org/10.1016/j.envpol.2020.115417.

WHO & FAO (2011). Codex Alimentarius Commission: Strategic Plan 2008-2013. https://www.fao.org/docrep/010/a1384e/a1384e00. Accessed 27th March, 2022.

WHO Guidelines for Drinking Water Quality (2006). Retrieved from http://www.who.ind/about/license/copyright)_form/en/index.html Accessed on 27th July, 2016.

WHO Guidelines for Drinking Water Quality (2010). 4th Edition. Retrieved from http://www.who.ind/ Accessed on 27th July, 2016.

Wilson V.S & Blanc, G. A (1999/2000). Petroleum pollution. Rev. toxicol.

Wisconsin Department of Natural Resources (2003). Consensus-Based Sediment Quality Quidelines: Recommendations for Use & Application. December 2003 Interim Guidance RR-088. Retrieved from https://dnr.wi.gov/doclink/rr/RR088.pdf.

World Health Oganisation (WHO) (2017). Evolution of WHO Air Quality Guidelines: Past, Present and Future. Copenhagen: WHO Regional Office for Europe; 2017. World Health Organization Regional Office for Europe UN City, Marmorvej 51, DK-2100 Copenhagen Ø, Denmark. Accessed 29/02/18 and available from http://www.euro.who.int/__data/assets/pdf_file/0019/331660/Evolution-air-quality.pdf

World Health Organisation (WHO) (2016). Ambient (Outdoor) Air Quality and Health. Fact Sheet. Updated September 2016. Accessed 29/03/18 and available from http://www.who.int/mediacentre/factsheets/fs313/en.

World Health Organisation (WHO) International Agency for Research on Cancer (IARC) (2006 and 2015): *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans– Preamble. IARC MONOGRAPHS, VOLUMES 1–121*. Lyon, France. Amended January,

2006 and updated September, 2015. Accessed 22/05/2018 and available from http://monographs.iarc.fr/ENG/Preamble/CurrentPreamble.pdf

Zabbey, N (2002). An Ecological Survey of Benthic Microinvertebrates of Woji Creek Off the Bony River System, Rivers State. MSc Thesis, University of Port Harcourt; Nigeria.