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Sediment Hydrocarbon Pollution across Oligohaline and Polyhaline Deltaic Environment of Nigeria.

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Abstract

Sediments are a vital component of the marine ecological systems. They are habitat to diverse marine coral reefs, benthic and meso-benthic, organisms, marine mammals and aquatic flora and fauna and numerous aquatic biotas. Spills from hydrocarbon exploration and illicit artisanal refineries in the Niger Delta adversely impact sediment quality, marine life and humans. This study adopted the causal-comparative and longitudinal designs to evaluate seasonal (dry and wet/rainy) levels of petroleum-based pollutants in the bottom sediments of the contiguous oligohaline and polyhaline Lower Orashi and Sombriero River Systems, Nigeria. The study area was segmented into 10 grids/sampling sites, where from sediment samples were collected into decontaminated zip lock bags, sealed and appropriately labeled according to sample stations, and placed in ice-parks cooler for preservation of the oxidation states. Standard laboratory methods were adopted for physico-chemical parameters, PAHs and BTEX analysis. FAAS and GC-FID were used to determine heavy metals, total hydrocarbon content, PAHs and BTEX respectively. The findings show that Dry Cd(dry) = 10.8 and Cd(wet) = 48.8, indicating low to very high anthropogenic contamination by the Contamination Factor (Cf) and Degree of Contamination(Cd). Locational Cd(dry) and Cd(wet): ranges in the order: TZ2>OR3>OR4>TZ1>OR1>SR3>SR4>OR2>SR1>SR2 and SR3>TZ1>OR2>SR4>OR4>SR2>OR1>SR1>TZ2>OR3 respectively. Individual metal Cf ranges: Cd>Cr>Zn>Fe>Cu>Pb>K>Na. Significant seasonal variation exists in Zn, Fe, K, and Cr only between the sediment at $p<0.05$. However, no significant seasonal variation exists in the petroleum-based pollutants in sediment except BTEX and Cr. The study revealed elevated levels of trace ecotoxic sediment xenobiotics in the study area with likelihood of gastrointestinal, cardiovascular, neurological and organ related illnesses to predisposed populations. Enforcement of mining environmental standards, global best practices, efficient and remediation and sustainable monitoring is needed in the Niger Delta region amongst others. Keywords: Lower Orashi, Sombriero, Sediment, Degree of Contamination and demersal.

Introduction.

Globaly River sediments are a significant component of the marine ecological systems. Marine sediment houses vital organisms and ecologies including coral reefs, meso-bentic/benthic biotas, crustaceans, marine mammals, aquatic flora and fauna. Sediments are habitats to many ecologies and diverse species due to its position and complex composition. It is critical in shaping the characteristics of the euphotic zone that regulates marine photosynthesis to both fauna and floral organisms. Bottom sediments enable the ability of marine ecosystem to sustain lives, support biodiversity, provide related ecosystem services to man and play critical roles in climate change mitigation for the past 4.5 million years.

Decades of hydrocarbon exploration has left unremediated episodes of crude oil and condensate spills and gas flares/vents that release millions of barrels of crude and related petroleum-based pollutants, through direct discharges and atmospheric deposition into the marine environment. Geochemically, hydrocarbons oozing from reservoir faults add to the total sediment pollution load. Recent artisanal refinery activities in the Niger Delta exacerbate the situation (Otiasah, Ezekwe & Lawal, 2020; Otiasah, Ezekwe and Chukwu-Okeah, 2021). Otiasah, Ezekwe and Lawal (2020) further reported 487 crude oil spills of 34,008.66BBLS and 73 gas leaks of unquantified MMfsc/d of flared/vented gas incidences in nine years (2008 to 2017) in the five local government areas (Ahoada West, Abua/Odual, Asari - Toru, Akuku - Toru & Degema) that make up the study area. Ezekwe, Otiasah, Raimi and Iyingala (2022) implicated urban erosion washing terrestrial pollutants into the marine environment, the final receptor of legacy and fresh/recent marine ecotoxins; which makes sediment highly sensitive to aquatic lives (Nwaichi & Uzazobona, 2011; Otiasah, Ezekwe, Babatunde & Otiasah, 2023). It was further observed that these ecotoxins become dense by their affinity to marine particulates and by a downward vertical travel get deposited in the sediments with adverse implication to sediment quality, aquatic lives and related livelihoods of the riparian populations (Otiasah, Ezekwe & Lawal, 2020; Otiasah, Ezekwe, Otiasah, Raimi & Iyingala, 2022; Otiasah, Ezekwe, Babatunde & Otiasah, 2023).

Migration, depletion or extinction of certain rare and protected aquatic species in River water could also be an outcome in the affected area. For instance, it was documented that popular crustaceans like shrimps, lobsters, aquatic mollusks (both univalves/gastropods and bi-valves) like periwinkle and numerous oysters are diminishing due to impaired fawning occasioned by sediment hydrocarbon pollution. ***Opulo***, a nocturnal moonlight seasonal freshwater fatty/protein crustacean indigenous to the Soku people have become extinct for over 20 years due to the effect of hydrocarbon-based ecotoxins in the sediments of Soku oilfield (Otiasah, Ezekwe & Lawal, 2020; Otiasah, Ezekwe & Chukwu-Okeah, 2021). Aquatic gastropods (snail, periwinkle, abalone and conchs) and bivalves (clams, oysters, cockles, mussels and scallops) oftentimes bury themselves in sediment as a means of adaptation from predators and trapping of planktons for food (Otiasah, Ezekwe & Lawal, 2020). These sessile filter-feeders bioaccumulate ecotoxins in their sensitive body parts, subcutaneous exoskeletons and transport them along the delicate food web when eaten by predators. Species migrations and extinctions of sediment resources equally negatively affects livelihoods, shrinks the local economy and reduces quality of lives in the affected populations (Igwe, Ezekwe & Otiasah, 2016; Otiasah, Ezekwe & Lawal, 2020; Otiasah, Ezekwe and Chukwu-Okeah, 2021). Polluted sediment causes death of plankton community and various aquatic species, mosses, particularly the benthic community with adverse implications on marine energy profile, transportation and optimum functioning of the fragile food chain and interrelated symbiotic interactions. (Ezekwe, Oshionya & Demua, 2018; Otiasah, Ezekwe, Babatunde & Otiasah, 2023). Sediment resuspension reintroduce heavy metals, soluble phosphates and other xenobiotics to the surface water column wherefrom it reenters the water gradient easily as secondary pollution (Onwubguta-Enyi, Zabbey & Erondu, 2008; Otiasah, Ezekwe, Babatunde & Otiasah, 2023). According to IPCC (2023), fish migration, deaths or extinction affect the carbon footprint of marine waters and exacerbates global climate change.

The Lower Orashi and Sombriero River system is host to ten (10) crude oil and gas fields, a gas plant, four crude oil transportation trunk lines and other hydrocarbon exploration, production, liquefaction and transportation assets. According to the Niger Delta Development Commission (2006) and IUCN-NDP (2013), the populations in the study area are rural fishermen, farmers, hunters, petty traders on marine resources and artisans who depend entirely on the resources of the surrounding Rivers and wetlands for their daily sustenance. Contamination of their River sediment holds grievous existential consequence to them. Consequently, this study undertook a critical scientific comparison of sediments from sections of the Lower Orashi and Sombriero Rivers, Nigeria with the Contamination Factor **(C_f)** and Degree of Contamination (**C_d**) to determine the marine sediment pollutant load and provide bases for sediment monitoring.

MATERIALS AND METHODS

The Lower fringes of the Orashi and Sombriero River estuary covering territories of Ahoada West, Abua/Odual, Degema, Akuku-Toru and Asari-Toru Local Government Areas of Rivers State, Nigeria (Figure 1 below) is the study area showing the sampling points . It is a freshwater and saline mangrove wetland of coastal vegetation dominated by economic trees (*pentaclethramacrophylla, chrysophyllumalbidum and irvingiagabonenesis*), rain forest, tidal and semi tidal flat mud characteristics 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 that shape the entire flow pattern of the area. The area is predominantly a 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 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, thatch making, hunting, palm oil production, timber logging, canoe-carving and wine tapping, artisans, petty trades, local sand and hydrocarbon mining and gas reserves of the tertiary Niger Delta (Reigers et al., 1996 in Nduka, Obumselu & Umedum, 2012; IUCN-NDP, 2013). The study area is of freshwater and marine forest ecology with fresh and saline water on the Orashi and Sombriero respectively. The Orashi River, particularly from Mbiama to Hulk is fresh water while the Sombriero River from Degema, beheading the Orashi River (Transition Zone) to Ebemaboko is saline water, intertidal and waterlogged mud flatlands with rich flora, fauna and complex strata of diverse trees.

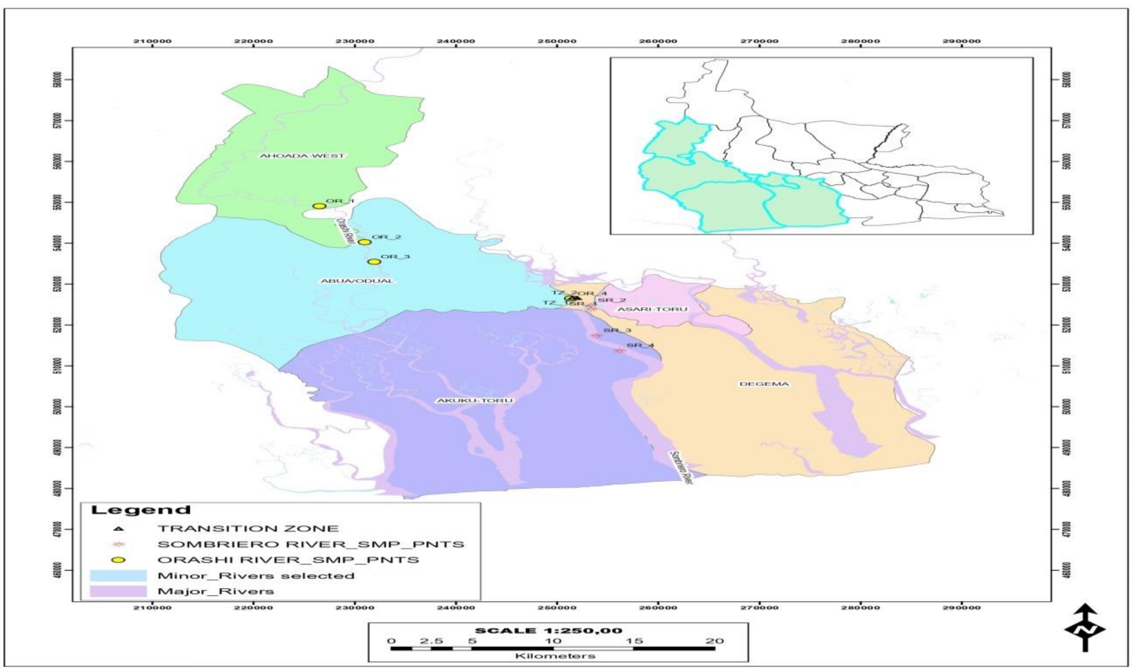

Figure 1. Sampling Points across the Study Area

Research Design

Descriptive and inferential statistics designs were adopted for this study. Sediment data for the study were obtained directly from the field sampling and analysis of sediment for petroleum-based pollutants (Heavy metals – H/M, Polycyclic Aromatic Hydrocarbon – PAHs and BTEX). The transition zone is under the dual influence of the less oligohaline Orashi freshwater River and polyhaline brackish waters of the Sombriero River. The data obtained in this study was analyzed with descriptive, inferential and comparative (the One Sample t-test) statistics.

Table 1. Sampling Sites and their GPS Positions

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”

Sample and Sampling Techniques

The study area was divided into ten (10) grids and sediment samples were collected from each grid. The sampling sites stretch from the Lower section of Orashi and Sombriero Rivers. Mbiama water front to Hulk (Agada)/Degema which is in the transitional zone between the two River systems, and, from there down through the Sombriero to the mouth of the Atlantic Ocean receiver were the specific areas of sampling. Sampling was done in two seasons (dry and wet/rainy).

Standard Operating Procedure (Laboratory/Analytical) Procedures)

The Contamination Factor (C_f) and Degree of Contamination (C_d) standards were used for sediment quality determination while a combination of saponification, extraction with n-hexane, clean-up on Sep-Pak silica cartridges and gas chromatograph-mass spectrometry analysis were adopted to measure PAHs concentrations. Flame atomic Absorption Spectrophotometer and ASTM-D3651 were used to determine heavy metal and total hydrocarbon content concentrations (THC). BTEX measurement in sediment was obtained using methods prescribed in Mohammed, El-Hashemy., Hazim and Ali (2018) and Amit, Anurag, Lall, Ajay and Raj (2018), using Gas Chromatography with Flame Ionization (GC-FID) (Shimadzu GC – 17A, Noisiel, France ®).

Heavy Metals (Cr, Cu, Pb, Fe, Cd, Zn & Ni) APHA 3111-B (AAS): To determine the concentrations of heavy metals, the PinAAcle 500 Flame Atomic Absorption Spectrometer (AAS) described in API-IA 3111B and ASTM D3651 was used. It involved direct aspiration of the sample into air/acetylene or nitrous oxide/acetylene flame generated by a hollow cathode lamp at specific wavelength applicable only to the metal under analysis. Standards and blanks were prepared and applied for calibration for any metal analyzed before samples were aspirated. Respective concentrations at specific absorbance were equally shown on the data system monitor for need of printout at less than 0.001mg/l detection limit.

Results and Discussions

Tables 2 - 6 present the results of sediment qualities, Contamination Factors (C_f-values), Degrees of Contamination (C_d) and Summary/Comparison of Degrees of Contamination from sections of the Orashi and Sombriero Rivers for the dry and wet/rainy seasons of the study respectively. Specifically, sediments from sections of Orashi and Sombriero Rivers of the study area were compared with established preindustrial reference values.

Table 2. Results of Sediment Quality from Different Sections of Orashi and Sombriero Rivers for Dry Season.

Parameters (mg/L)	PHAs	BTEX	Cadmium	Chromium	Lead	Copper	Zinc	Iron	Sodium	Potassium	Mean
SR1	**0.014**	**0.052**	**0.008**	**0.116**	**0.001**	**0.009**	**0.53**	**0.247**	**0.042**	**0.402**	**0.138**
SR2	0.001	0.002	<0.001	0.005	<0.001	<0.001	0.002	0.008	0.002	0.014	0.004
SR3	0.40	0.46	0.72	0.57	0.87	0.63	1.56	1.33	1.07	1.73	0.934
SR4	4.70	3.62	11.66	7.02	2.66	3.89	19.40	7.20	11.39	5.00	7.654
OR1	8.07	1.18	1.44	6.35	<0.001	5.90	6.28	10.20	13.62	1.43	5.447
OR2	0.87	2.20	2.21	0.99	0.89	1.72	5.06	4.49	3.10	2.28	2.381
OR3	4.85	14.35	2.28	22.33	2.78	0.72	29.57	23.27	23.10	22.11	14.536
OR4	365.75	5,497.7	395.66	4,217.0	860.51	1,339.9	8,073.7	7,691.5	7,847.6	2,883.1	3,917.24

Table 3. Results of Sediment quality from the different sections of Orashi and Sombriero Rivers for the wet/rainy season.

Parameters (mg/L)	SR1	SR2	SR3	SR4	OR1	OR2	OR3	OR4	TZ1	TZ2	Mean
PAHs	<0.001	<0.001	5.866	12.958	<0.001	2.252	0.192	0.044	0.033	0.118	2.147
BTEX	<0.001	<0.001	0.182	0.370	<0.001	0.070	0.007	0.002	0.001	0.049	0.068
Cadmium	<0.001	0.07	0.54	0.09	<0.001	0.45	<0.001	<0.001	0.40	<0.001	0.156
Chromium	5.18	<0.001	5.12	<0.001	<0.001	<0.001	<0.001	8.05	7.52	1.04	2.692
Lead	<0.001	<0.001	8.93	<0.001	15.14	3.35	4.60	<0.001	1.58	1.90	3.550
Copper	<0.001	0.24	2.82	<0.001	<0.001	4.13	<0.001	3.17	0.59	<0.001	1.096
Zinc	11.59	5.39	12.72	13.56	0.76	0.85	<0.001	13.11	12.56	18.18	8.872
Iron	4541.7	4053.6	6273.5	2402.1	2428.8	7826.7	588.84	7429.1	5690.6	1648.7	4288.364
S odium	41.76	19.56	64.05	15.34	7.11	4.97	5.98	102.20	26.03	12.43	29.943
Potassium	431.18	464.54	447.70	486.10	15.34	27.03	19.66	494.00	458.65	54.03	289.823

Polycyclic Aromatic Hydrocarbon (PAHs): From tables 2 and 3, concentration of PAHs in the different bottom sediment sources of the study area ranges from 0.001 – 0.402mg/L. Lowest PAHs concentrations of <0.001 is observed at sampling locations OR1, while sampling location TZ2 with a value of 0.402mg/L has the highest observed concentration of PAHs. PAHs study mean is 0.138mg/L. Ecological means are Orashi River = 0.078mg/L. Sombriero River = 0.048mg/L and Transition Zone = 0.222mg/L respectively. Both individual values and their means show that only the bottom sediment of OR1 at 0.001mg/L is safe within the WHO allowable limit of 0.002mg/L, and suitable for benthic fishes and species**.** Bottom sediments from the Sombriero ecological zone at a mean of 0.048mg/L are less polluted with PAHs compared to sediment of Orashi at 0.078mg/L, which in turn is less contaminated than sediments of the Transition zone at 0.222mg/L. However, both ecological and overall study means are above the WHO desirable limit for PAHs toxicity. The above situations reveal that bottom sediments of the entire study area, particularly at TZ2, OR4 and SR4 are unsuitable with respect to heavy metal aquatic sediment quality.

BTEX (mg/L) in Sediment: Concentrations of BTEX in the different bottom sediment sources of the study ranged between 0.001 - 0.014mg/L. Four locations (SR1, SR3, OR1 and OR2) had the least value of <0.001 while station TZ2, with a BTEX concentration of 0.014mg/L is the highest. Ecological means are Orashi River = 0.003mg/L. Sombriero River = 0.002mg/L and Transition Zone = 0.008mg/L respectively. The WHO permissible concentration level for BTEX in sediments of marine ecologies is B= 0.005mg/L, T= 1mg/L, E= 0.7mg/L, and $X_{[1-4]}$ =10mg/L. The results show that BTEX is only within the allowable limit in the bottom sediment of Sombriero River whereas the bottom sediments of the Orashi River and Transition Zone are above the WHO value of 0.002mg/L. We find that BTEX concentrations are sensitive and possibly suppressed by River salinity as the oligohaline Orashi River environment recorded higher BTEX values compared to the polyhaline Sombriero River even with the same anthropogenic activities.

Heavy Metals (Pb, Zn, Mn, Fe, Cr, K, Mg, Ca, Na & Cd, mg/L) in Sediment: The W.H.O permissible limits for the respective heavy metals are:- Zn = 1.0mg/L, Pb = 0.01mg/L, Cr = ≤0.05mg/L, Mn = 0.05mg/L, Fe = 0.3mg/L, K = 0.01mg/L, Mg = 0.2mg/L, Ca = 1.0mg/L, Na = 30-60mg/L and Cd = 0.005mg/L respectively. The concentrations of the heavy metals in the sediments and their ecologic and human implications are as follows;

Cadmium: Cadmium concentrations in the sediment of the study area ranged from 0.40 – 1.734mg/L. SR1 at 0.40mg/L is the lowest while TZ2 at 1.73mg/L is the highest. All individual sampling stations have Cadmium values above the WHO concentration level of <0.005mg/L, hence suffers from cadmium ecotoxicity and not suitable for aquatic sediment quality.

Chromium: Concentration of Chromium in the bottom sediments ranged from 2.66-19.40mg/L. The least and highest concentrations of 2.66mg/L and 19.40mg/L is at OR1 and OR3 respectively. Chromium concentration in all stations are above the WHO permissible limit of <0.005mg/L. The bottom sediment of the study area suffers from Chromium ecotoxicity.

Lead: Lead concentration in the sediment ranged between <0.001-13.62mg/L, with OR1 having the least value of <0.001mg/L and TZ1 highest at 13.62mg/L. Lead abundance in the sediments of all sampling locations are above the WHO healthy threshold value of <0.001 except OR1. The bottom sediment of the study area suffers from Lead ecotoxicity.

Copper: The relative abundance of Copper in the bottom sediments ranged between 0.87mg/L-5.06mg/L. SR1 have the lowest value of 0.87mg/L while OR3 with a value of 5.06mg/L is the highest. All sampling stations have a copper concentration above the WHO healthy level of 0.03mg/L; indicative of Copper ecotoxicity.

Zinc: Zinc concentration in the sediment ranged between 0.72-29.57mg/L. The least concentration of 0.72mg/L is at OR1 while the highest of 29.57mg/L is at OR3. Again, all sampling locations have zinc concentration above the River water WHO permissible limit of 1.0mg/L except OR1, hence suffer from Zinc ecotoxicity.

Means of the heavy metals: The respective seasonal means of the individual heavy metals in the sediment from sections of the Orashi and Sombriero Rivers systems are presented thus; The mean for the various heavy metals as revealed by the study are as follows:- Zn = 0.01mg/L, Pb = 0.01mg/L, Cr = 0.01mg/L, Mn = 0.361mg/L, Fe = 0.596mg/L, K = 0.62.266mg/L, Mg = 0.86.81mg/L, Ca = 1.70.761mg/L, Na = 1601.399mg/L and Cd = 0.068mg/L respectively. The ecological means for Orashi River are as follows:- Zn = 0.01mg/L, Pb = 0.01mg/L, Cr = 0.01mg/L, Mn = 0.361mg/L, Fe = 0.623mg/L, K = 19.321mg/L, Mg = 30.950mg/L, Ca = 21.192mg/L, Na = 163.097mg/L and Cd = 0.052mg/L respectively. The ecological means for Sombriero River are as follows:- Zn = 0.01mg/L, Pb = 0.01mg/L, Cr = 0.01mg/L, Mn = 0.579mg/L, Fe = 0.644mg/L, K = 91.046mg/L, Mg = 127.248mg/L, Ca = 103.412mg/L, Na = 580.75mg/L and Cd = 0.085mg/L respectively. The ecological means for Transition Zone River are as follows:- Zn = 0.01mg/L, Pb = 0.01mg/L, Cr = 0.01mg/L, Mn = 0.323mg/L, Fe = 0.452mg/L, K = 90.615mg/L, Mg = 117.66mg/L, Ca = 104.60mg/L, Na = 6518.90mg/L and Cd = 0.065mg/L respectively. The W.H.O permissible standard limits for the different heavy metals are:- Zn = 1.0mg/L, Pb = 0.01mg/L, Cr = ≤0.05mg/L, Mn = 0.05mg/L, Fe = 0.3mg/L, K = 0.01mg/L, Mg = 0.2mg/L, Ca = 1.0mg/L, Na = 30-60mg/L and Cd = 0.005mg/L. The findings equally show that concentrations of heavy metals in the bottom sediment from sections of the

Orashi and Sombriero Rivers systems differ significantly in terms of individual metal and sampling locations.

Sediment Quality Standards Determinations: [Contamination Factor (C_f) and Degree of Contamination (C_d)]. Hakanson (1980) defined Contamination Factor (Cf) as a ratio between observed concentration of any given metal (pollutant) in sediment of a given water body and the pre-industrial reference value for the metal or pollutant. Contamination Factor (Cf) is the quantification of the extent of contamination in relation to the average crustal composition of a given metal (pollutant) or the measured background values from geologically similar uncontaminated area (Hakanson, 1980; Milena et al, 2020). Cf = Metal Conc in Sediment/Background Value of Metal (Hakanson, 1980).

Flowing from this, Milena et al (2020) stated that the extent or Degree of Contamination is the summation of all the contamination factors. The Degree of Contamination is an indication of the degree of overall contamination in all the sampled sites of sediment which is the sum of the Contamination Factor of each metal (Cf^i), expressed as; $C_d = \Sigma Cf^i$. Where, Cf^I is the measured metal concentration (C_i), divided by the pre-industrial/background concentration value of the substance. It is expressed as: $Cf^i = C_i / C_n i$.

C_f and C_d of Dry Seasons Sediments of Orashi and Sombriero Rivers

Table 4 and 5 represent the Contamination Factors and Degrees of Contamination for the dry and wet season sediments. The total Degree of Contamination (C_d) for the sediments of the selected 10 sites for the dry and wet/rainy seasons from the Orashi and Sombriero Rivers = 10.8 and 48.8 respectively. Locational $C_{d(dry)}$ and $C_{d(wet)}$ ranges: TZ2>OR3>OR4>TZ1>OR1>SR3>SR4>OR2>SR1>SR2 and SR3>TZ1>OR2>SR4>OR4>SR2>OR1>SR1>TZ2>OR3. Individual cumulative metal C_f load ranges: Cd>Cr>Zn>Fe>Cu>Pb>K>Na; thus; C_d >32, C_d>24 is far higher than the limits prescribed in both Hakanson (1980) and Harikuma, Prajitha and Silpa (2010). It is therefore concluded that the dry and wet/rainy season sediments of the Lower Orashi and Sombriero River systems are highly and very highly contaminated with environmental stressors of anthropogenic origin respectively.

Table 4. Contamination Factors (C_f-values) and Degree of Contamination (C_d) of Sediments of 10 Sites of Orashi and Sombriero Rivers [$C_f = (C_i / C_0^i)$]; ($C_d = \Sigma Cf^i$) for Dry Season

SUB	SR1	SR2	SR3	SR4	OR1	OR2	OR3	OR4	TZ1	TZ2
Contamination Factors (Cf)										
Cd	1.82	2.091	2.273	2.591	3.955	2.864	7.091	6.045	4.864	7.864
Cr	0.052	0.040	1.130	0.078	0.030	0.043	0.220	0.08	0.127	0.1
Pb	1.135	0.020	0.024	0.106	0.00	0.098	0.105	0.17	0.23	0.024
Cu	0.022	0.056	0.057	0.025	0.023	0.044	0.130	0.115	0.08	0.058
Zn	0.040	0.120	0.019	0.186	0.023	0.006	0.250	0.194	0.193	0.184
Fe	0.014	0.208	0.015	0.160	0.033	0.051	0.306	0.291	0.30	0.11
Na	0.001	0.002	0.001	0.011	0.005	0.001	0.021	0.020	0.016	0.002
K	0.003	0.007	0.007	0.022	0.003	0.007	0.005	0.025	0.025	0.004
$C_d = \Sigma Cf^i$	**3.047**	**2.544**	**3.526**	**3.179**	**4.039**	**3.114**	**8.128**	**6.940**	**5.835**	**8.346**

Background reference values (BRV) used: *PAHs = NA; BTEX = NA; Cadmium (Cd) = 0.22; Chromium (Cr) = 90; Lead (Pb) = 60; Copper (Cu) = 39; Zinc (Zn) =120; Iron (Fe) = 26,400; Sodium (Na) 9,600=; Potassium (K) = 26,600.*

Table 5. Contamination Factors (C_f-values) and Degree of Contamination (C_d) for Wet/Rainy Season of Sediments of 10 Sites of Orashi and Sombriero Rivers [$C_f = (C_i / C_0^i)$]; ($C_d = \Sigma Cf^i$)

SUB	SR1	SR2	SR3	SR4	OR1	OR2	OR3	OR4	TZ1	TZ2
Contamination Factors (Cf)										
Cd	0.005	0.318	2.455	0.410	0.005	2.045	0.005	0.005	1.818	0.005
Cr	0.058	0.000	0.057	0.000	0.000	0.000	0.000	0.089	0.084	0.012
Pb	0.000	0.000	0.149	0.000	0.252	0.056	0.077	0.000	0.026	0.032
Cu	0.000	0.006	0.072	0.000	0.000	0.106	0.000	0.081	0.015	0.000
Zn	0.097	0.045	0.106	0.113	0.006	0.007	0.000	0.109	0.105	0.151
Fe	0.172	0.154	0.238	0.091	0.092	0.296	0.022	0.281	0.216	0.062
Na	0.004	0.002	0.007	0.002	0.001	0.001	0.001	0.011	0.003	0.001
K	0.016	0.017	0.017	0.018	0.001	0.001	0.001	0.019	0.017	0.002
$C_D = \Sigma Cf^i$	**0.352**	**0.542**	**3.101**	**0.634**	**0.357**	**2.512**	**0.106**	**0.595**	**2.284**	**0.265**

Background reference values (BRV) adopted: *PAHs = NA; BTEX = NA; Cadmium (Cd) = 0.22; Chromium (Cr) = 90; Lead (Pb) = 60; Copper (Cu) = 39; Zinc (Zn) =120; Iron (Fe) = 26,400; Sodium (Na) 9,600=; Potassium (K) = 26,600.*

CF and CD of Wet/Rainy Seasons Sediments of Orashi and Sombriero Rivers

Table 6 shows the comparison of degree of contamination for both seasons.

From Table 4 and 5 respectively, the degree of contamination **C_d (dry) season** for the sediments of each the selected 10 sites from the Orashi and Sombriero Rivers are: SR1 = 0.352, SR2 = 0.542, SR3 = 3.101, SR4 = 0.634, OR1 = 0.357, OR2 = 2.512, OR3 = 0.106, OR4 = 0.595, TZ1 = 2.284 and TZ2 = 0.265 = 10.8, whereas **C_d wet season** = SR1 + SR2 + SR3 + SR4 + OR1 + OR2 + OR3 + OR4 + TZ1 + TZ2, which is 3.047 + 2.544 + 3.526 + 3.179 + 4.039 + 3.114 + 8.128 + 6.940 + 5.835 + 8.346 = **48.7.** Locational **C_d (dry)** ranges: TZ2>OR3>OR4>TZ1>OR1>SR3>SR4>OR2>SR1>SR2. **C_d wet season** = SR1 + SR2 + SR3 + SR4 + OR1 + OR2 + OR3 + OR4 + TZ1 + TZ2 which implies 3.047 + 2.544 + 3.526 + 3.179 + 4.039 + 3.114 + 8.128 + 6.940 + 5.835 + 8.346 = **48.7.** Individual cumulative C_f metal load ranges thus: Cd>Cr>Zn>Fe>Cu>Pb>K>Na. Thus, C_d >32, C_d>24 is far higher than the limits prescribed in both Hakanson (1980) and Harikuma, Prajitha & Silpa (2010).

Table 6. Summary/Comparison of Degree of Contamination of substance in Orashi and Sombriero Rivers for Dry and Wet/Rainy Seasons

Site	SR1	SR2	SR3	SR4	OR1	OR2	OR3	OR4	TZ1	TZ2	Mean
Dry Season	3.047	2.544	3.526	3.179	4.039	3.114	8.128	6.940	5.835	8.346	**4.88**
Wet Season	0.352	0.542	3.101	0.634	0.357	2.512	0.106	0.595	2.284	0.265	**1.07**
Total	**3.40**	**3.09**	**6.63**	**3.81**	**4.40**	**5.62**	**8.23**	**7.54**	**8.12**	**8.61**	**5.95**

Comparison of individual locational seasonal pollutant's effect by their total shows that TZ2, OR3, TZ1, OR4 & SR3 falls within $6=C_d<12$. This indicates moderate contamination, whereas $\mathbf{C_d}$ for sample locations (SR1, SR2, SR4, OR1 & OR2) <6, hence of low anthropogenic contamination according to Harikuma, Prajitha & Silpa (2010). However, only TZ2, OR3, TZ1 & SR3 values fall within $8\leq C_d<16$, also indicating moderate contamination. The rest locations (SR1, SR2, SR4, OR1, OR2) fall within Cd<8, and are of low anthropogenic contamination according to Hakanson (1980). It is therefore conclude that the dry and wet season sediments of the Lower Orashi and Sombriero Rivers systems ranges from low, moderate and very high contamination by petroleum-based environmental stressors of anthropogenic origin respectively. The difference between the dry and wet/rainy season contaminations could be due to additional pollutants input from terrestrial urban runoff occasioned by the heavy rains. Moreover, terrestrial pollutants from urban runoff and atmospheric depositions, regardless of their lipohyitic, lighter density but with affinity to marine particulates characteristics may have fastly settled down into the bottom sediments of the study area.

Clinton, Ugwemorubong and Horsfall (2009) carried out a Spectrophotometric analysis of total hydrocarbons in some aquatic media in a crude oil polluted mangrove wetland in the Niger Delta, which revealed that high temperature and microbial activities were catalytic of higher rate of biodegradation over time. The study equally revealed consistent higher values of THC in the sediments compared to the surface water as proof that aquatic sediments are greater sink than water and biota. Similarly, in a Buck Scientific Atomic Absorption Spectrophotometric investigation of heavy metals concentrations (Mn, Fe, Zn, Cu, Ni, Cd, Co, Cr & Pb) in four selected Rivers (Bakassi, Calabar, Great Kwa & Qua-Iboe) and three canals (Ogini, Olomoro & Ughelli) of Niger Delta, it was found that sediment quality below sustainably effective range low (ERL), with enrichment factor < 1. Metal inputs were mainly from natural sources. This confirms the position of many studies that natural biological processes of the environment alone cannot elevate heavy metal concentrations to levels above the environments' carrying capacity. It is consistent with the point that anthropogenic inputs of pollutants are the greatest sources of environmental pollution that endangers its sustainability. In the absence of anthropogenic inputs, concentrations of heavy metals in the sediment are usually at levels healthy to sustain aquatic lives, and therefore with no likelihood of adverse health impact to human populations in the world.

Also, in a seasonal Atomic Absorption Spectrophotometry and Microwave Digestion and ICP-AES analysis of the distribution of THC and heavy metals (Cr, Cd, V, Pb, Zn & Cu) in sediments and mollusk (periwinkle – *tympanotamus fuscatus*) of three salinity classified ecological zones (Oligohaline, Mesohaline & Polyhaline) of the Lower Bonny and Upper Calabar contiguous River estuary, Niger Delta, Nigeria; higher sediment THC concentrations were observed for the dry season as against the wet season in all zones, THC was in the order of: Upper > Middle> Lower in zonal distribution, whereas the concentration of the metals (Cr, Cd, & Pb) recorded higher values in the wet season compared to the dry season except for V, Zn, & Cu; and was in the order: Upper ≥ Lower ≥ Middle ≥ between zones (Chindah et al, 2009). Ismail and Salah (2012) analyzed heavy metals in the waters and fish (*Tilapia Sp*) of the Tasik Mutiara Punhong, to identify and quantify their source and prevalence in the lake respectively. It was observed that the fractional mobility of Cd in sediment made it more prone to poisoning food chain whereas Zinc exhibits proactive effect compared to Cadmium and Lead. Also, pH, hardness and alkalinity influences Copper (Cu) prevalence and toxicity, together with geochemical characteristics of bottom sediment influencing metal prevalence and renders water aesthetics offensive to sight in the marine environment.

Therefore, this study is consistent with (Clinton, Ugwemorubong and Horsfall, 2009) to the extent that THC concentrations are higher in the sediments compared to the surface water and aquatic sediments. The study equally agrees with (Chindah et al, 2009) in terms of higher sediment THC levels in the dry season compared to the wet season. There was convergence to the effect that the polyhaline Sombriero River ecology has higher concentration of trace elements than oligohaline Orashi River. It agrees with (Diete-Spiff & Kpee, 2022) that anthropogenic activities and terrestrial sources are implicated major sources of marine sediment pollution than geochemical inputs. It is consistent with the point that anthropogenic inputs of pollutants are the greatest sources of environmental pollution that endangers sediment quality sustainability. It equally differs with Ismail and Salah (2012) to the effect that geochemical inputs other than anthropogenic sources pollutes sediment quality.

Conclusion

The study concluded that the bottom sediment of OR1 values for polycyclic aromatic hydrocarbon (PAHs) was within the WHO/USEPA allowable limit suitable for benthic aquatic fishes and species; while all the individual values and mean values were above the WHO/USEPA permissible, hence unsuitable for aquatic sediment quality. The bottom sediment levels of BTEX were within the allowable limit only in the sediment of Sombriero River, whereas the bottom sediments of the Orashi River and Transition Zone exceeded the WHO limits. Furthermore, concentrations of heavy metals in the bottom sediments from the Orashi and Sombriero Rivers differ significantly in terms of individual metals and sampling locations; though the concentration levels of most of the metals (Cd, Cr, Pb, Cu & Zn) were above the WHO/USEPA limits, therefore not suitable for aquatic sediment quality. The degree of contamination (C_d) for the dry season showed that the sediments of Orashi and Sombriero River systems are moderately contaminated with petrogenic stressors of anthropogenic origin while very highly contaminated in the wet season. Cadmium (Cd) contributed the highest sediment pollution load.

This study assessed petroleum-based pollutants in sediment in the Lower Orashi and Sombriero River systems in Rivers State, Niger Delta of Nigeria. Most of the heavy metals, physicochemical and biological parameters evaluated were higher than institutional permissible limits, including analysis for PAHs and BTEX, and thus implicated in the bottom sediments pollution. Though, the concentrations of heavy metals in the bottom sediments of the two River systems differ significantly in terms of individual metals and sampling locations, the concentration levels of most of them were above the WHO limits, and thus not suitable for marine ecological sediment quality and aquatic species health. Sequel to the findings, the study infers that the marine sediment in the Lower Orashi and Sombriero River systems are polluted with petroleum-based pollutants (H/M, PAHs, PCBs) of anthropogenic origin when compared with sediment standard quality established by the Degree of Contamination (C_d) and Contamination Factor (C_f). Decontamination, elimination of illicit artisanal refineries and periodic monitoring of the two River sediments is necessary.

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