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HYDROCARBON POLLUTION AND POTENTIAL ECOLOGICAL RISK OF HEAVY METALS IN THE SEDIMENTS OF THE OTURUBA CREEK, NIGER DELTA, NIGERIA

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Abstract

This study aimed at examining the impact of oil pollution from artisanal oil refineries on the Oturuba river ecosystem using active river bottom sediment. Specific objectives included to determine the level of hydrocarbons and trace metals (Pb, Cd, Zn, Cu, Ni, V and Mg) in the sediments and to relate this with general ecosystem health. The study found elevated concentrations of both hydrocarbons and heavy metals in the range above most sediment quality guidelines exceeding the respective Threshold Effects Level and Probable Effects. Level guideline values and occurring at levels where impairment to biological communities is certain and where toxicity levels can lead to negative impacts on benthic animals or infaunal communities. Heavy metal geochemical accumulation index and potential ecological risk analysis also returned anomalously high concentrations in the range of very highly polluted sediment environments with very high ecological risk indices, thereby ranking the Oturuba Creek as one of the most polluted coastal river systems in the world.

Keywords: sediment pollution; trace metals; artisanal refining; estuaries; Andoni River

INTRODUCTION

The survival of coastal rivers and estuaries which are among the most sensitive and biologically productive habitats on earth is currently being threatened by human activities including oil production. Coastal rivers are dynamic ecosystems with spatial and temporal fluctuations in reach and constituents. Concentrations of organic and inorganic constituents in coastal river systems, especially metals and hydrocarbons are mediated by biogeochemical forcings such as sediment composition and texture, sediment-water redox reactions, pH, temperature, salinity, nutrients and oxygen availability, microbial populations, competition, transportation dynamics and anthropogenic perturbations (Förstner and Salomons, 1981; Whitehead, 2013). These anthropogenic disturbances and naturally induced biogeochemical stressors may impose suboptimal conditions leading to physiological adaptations or forced migration by resident species. For instance, oil pollution in coastal river systems through oil-induced oxygen-deficiency, toxicity, asphyxiation, coating or smothering, which affects gas exchange, thermo-reactions and osmoregulation, can threaten the life-support processes in a river ecosystem by imposing hypoxic conditions thereby affecting community resilience and population dynamics (Luoma et al., 1997; Mendelssohn et al., 2012; Whitehead, 2013).

Sediments are sinks for contaminants in river ecosystems and their physico-chemical properties and response to the chemical dynamics of the hydrological system may enhance subsequent contamination to the ecosystem components to which they are linked. Significant contamination of sediments may lead to species and biodiversity losses (Markovic, 2003; Luoma, 1990) and deleterious food chain reactions from benthic communities to upper trophic levels (Burton, 2002) either through direct adverse impacts on bottom fauna or by becoming long-term sources of toxic substances to the environment. They can also impact wildlife and humans through the consumption of food or water or by direct bodily contact. Of critical importance, is that these impacts may be present even though the overlying water meets water quality criteria (USEPA, 1992) thereby underscoring the importance of sediment quality analysis in monitoring ecosystem integrity.

River bottom or deposited channel materials represent the closest approximation of sediment provenance, movement and deposition, however directly linking sediment chemistry data to observed adverse biological effects on organisms is problematic (USEPA, 2005), hence, a few screening guidelines, indices or benchmarks (below which toxic effects are not expected to occur and above which toxic effects are usually expected) relate chemical concentrations in sediments to their "potential for biological effects" (Bay et al., 2012).

Buchman (2008) presented sediment screening levels based on Threshold Effects Level (TEL), Effects Range-Low (ERL), and Probable Effects Level (PEL) for evaluating sediment quality. TELs define chemical sediment concentration benchmarks where toxic effects are scarcely observed in key indicator organisms while PELs on the other hand define concentrations which when exceeded can cause observable detrimental effects on organisms. ERL thresholds are statistical derivations of the10th percentile concentration of chemicals in samples identified as toxic occurring between the TEL levels and the PEL benchmark. Also heavy metals in sediments have been used successfully in calculating pre-industrial and anthropogenic pollution sources and ecological risks in sediments (Håkanson, 1980, 1988; Forstner, 1989; Singh et al., 2003; Li et al., 2012) and more recently in the analysis of groundwater contamination in industrial areas (Bhutiani, 2017).

These benchmarks which have been previously tested and accepted have been applied in this study to measure the impact of artisanal oil refining activities on the ecosystem health of the Oturuba Creek where illegal crude oil refining activities has been ongoing since 2010 and where ambient ecosystem destruction and reduction in fish catch has been observed. This study therefore attempts to show the latent and manifest ecological impacts of hydrocarbon and heavy metal concentrations in sediments of the Oturuba Creek, hence similar ecological systems. It also aims to show the relationships and spatio-temporal spread of heavy metals and hydrocarbons in the Oturuba Creek.

STUDY AREA

Oil was first discovered in commercial quantities in 1956 in Nigeria in the freshwater swamps of the Niger Delta, around Oloibiri, currently in the Bayelsa State of Nigeria. Since then the Niger Delta environment and its eco-systems have been adversely impacted and altered by oil and gas exploration and exploitation. This has triggered a conflict of interest and sometimes armed conflicts between production/facilities host communities on the one hand and the federal government and oil companies on the other. This has led to wanton pipeline vandalism, oil theft, illegal bunkering and illegal refining (using make- shift refineries) of probably stolen crude oil, and consequent oil spills into, and damage to the environment. When oil is spilled, it is washed into water bodies (as in the study area) via surface run off and may persist (bio-accumulate and bio-transform) in the media it attaches to for a very long period of time. About 50% of spilled oil evaporates, others migrate and stray away via the action of wind and tidal waves, others emulsify, while a percentage of it, unnoticeably, sinks to the bottom of the river bed and permeates into bottom sediments (USEPA, 1999).

The Oturuba Creek is a tributary of the Andoni River -a major river which drains the eastern part of the Niger Delta of Nigeria. The creek (Fig. 1) has an approximate length of about 3.66km and width of about 100m, and average depth of about 3.7 metres. The river stretch starts from the Egwede area and drains into the Andoni River in the inter-tidal mud flat mangrove ecosystem terrain characteristic of the eastern Niger Delta coastline. It is a low-lying terrain (< 5 m asl) and consists of about 3-5 m of soft mud with high organic matter content. The Oturuba
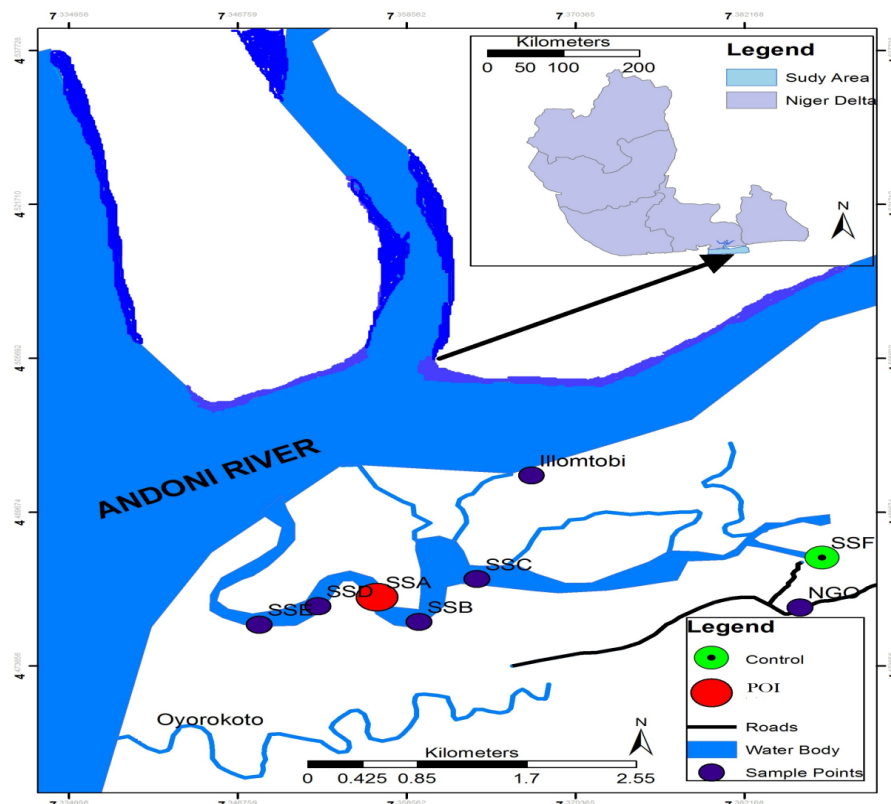

Fig. 1 Location of the study area and the sample sites (SS)

Creek is a permanently saline sheltered river system tied to the tropical deltaic tide influenced Andoni River system with its characteristic silty muds, acidic sediments (pH: 4.09 –5.04), high water temperatures (26.2–32.4°C), deep waters (17 fathoms) and wide water salinity ranges (8–21ppt) (Ssentongo, Ukpe and Ajayi, 1986; Ansa et al., 2007; Ansa and Francis, 2007; Ezekwe and Edoghotu, 2015). The study area also falls within the transitional zone of the Aw and Af climate types of the Koppen's climatic classification scheme. It is thus characterized by long hours of day light, high temperatures of about 27°C and high rainfall (≥ 1,800mm).

MATERIALS AND METHODS

Sample sites

Sediment samples were collected from six sample sites after an initial reconnaissance of the study area. The geographical location of each sampling point (Fig. 1) was recorded using handheld GPS equipment (Garmin 76) and described in Table 1.

Table 1 Sampling Sites

Sampling Site	Latitude	Longitude	Site Description
1. SSE	4° 28′ 40.675″N	7° 20′ 53.685″E	First point upstream near the mouth of the Oturuba Creek (about 1 km from POI) close to the Andoni River.
2. SSD	4° 28′ 38.963″N	7° 21′ 13.654″E	About 500 m upstream from point of impact (POI).
3. SSA	4° 28′ 50.945″N	7° 21′ 23.353″E	Point of Impact (POI) where raw waste from the crude oil refining process, refined products and sludge are discharged into the creek
4. SSB	4° 28′ 42.95″7N	7° 21′ 37.046″E	About 500 m downstream
5. SSC	4° 28′ 50.374″N	7° 21′ 53.592″E	About 1 km downstream
6. SSF	4° 29′ 05.78″N	7° 23′ 15.43″E	About 3.7 km downstream (Control; un-impacted area.

Visual observation of site1 conditions showed that the site had relatively buoyant biomass; which can be attributed to its location, almost at the point where the Oturuba Creek joined the Andoni River and therefore receives fresh and relatively uncontaminated water from the larger Andoni River system. Oil sheen was only observed on the surface of the water during ebb tides. Site 2 had oil sheens on the surface of the river with mud flats on both sides of the river showing signs of heavy oil-staining. It was also characterised by scanty and unhealthy looking fauna and flora especially mangroves plants and crabs. Site 3 or the point of impact (POI) was characterized by greasy and muddy surfaces with darkened soils and scorched vegetation. The site was bereft of visible biological activity as no marine organisms were spotted in the vicinity during the fieldwork. Oil sheen and slicks were seen floating freely on the surface of the creek; while site 4 had oil sheen on the surface of the water, especially during low tide. Mangrove plants were sparse with a few marine fauna such as juvenile periwinkle, crabs, mudskipper, etc. in the mangrove mud. The mud had oil stains as in the point of impact but no direct inlet of spilled oil into the water body was observed. This immediate downstream sampling site from the POI was the most impacted section of the creek after site 3. At site 5, mangrove plant species were densely populated and there where sightings of crabs, mudskipper, periwinkles and birds. The mud and surface water showed very little sign of pollution. At site 6, which served as the control site for this study, the mangrove vegetation was dense and green with an abundance of bio-activity (crabs, periwinkles, mudskippers, birds, reptiles and other aquatic invertebrates). The mangrove mud flats and water did not show any visible sign of contamination.

Sample collection and analysis

River bottom sediments were collected from the 6 designated locations in the Oturuba Creek following methods outlined by Marcus et al. (2013). Sediment samples were collected by the grab method in triplicates at low tide in June 2013 (rainy season) and November 2013 (dry season) (APHA, 1998). Samples for hydrocarbon analysis were stored in sterilized bottles, while the samples for the analysis of trace metals were stored in polythene bags previously washed in diluted HCl while those for organic matter analysis were collected in aluminium foils. Samples were stored in polyethelyne sealed and stored in ice packed plastic coolers (below 4°C) thereafter, transported to the laboratory and analyzed within 2 days.

The sediment samples were allowed to thaw and were air-dried at ambient temperature ground and sieved through a 0.5 mm mesh. Later, 2 g of each sample was digested using 25 ml 1:3:1 mixture of $HClO_4$, HNO_3 and H_2SO_4 acids in a water bath. 10 ml deionized water was added to the digest and decanted into 50 ml standard flask and made up to mark with deionized water after rinsing. The Buck Scientific Atomic Absorption Spectrophotometer Model 200A and air-acetylene flame were used for trace metal analyses with quality assurance checked with standard sediment sample PACS-2 using an intra-run Quality Assurance Standard (1 mg/l, Multi-Element Standard Solution, Fisher Scientific) after every 10 samples (Cantillo and Calder, 1990).

The Walkley-Black wet chemistry "reference" procedure for the determination of Total Organic Carbon as described in Schumacher (2002) and applied by Marcus

and Ekpete (2014) was used in analysing total organic carbon (TOC) in this study. 1 g of dried, sieved sediment was put into 250 ml conical flask and digested with 10 ml 0.5 M $K_2Cr_2O_7$ and 20 ml concentrated H_2SO_4, swirled and allowed to cool. To overcome the concern for incomplete digestion of organic matter, the sample and extraction solutions were gently boiled at 150 ºC for 30 minutes and allowed to cool (Walkley and Black, 1934; Tiessen and Moir, 1993). When cool (after 20–30 minutes), 100 ml de-ionized water was added for dilution and 3 or 4 drops of 'Ferroin' indicator was added and titrated with 0.4 N FeSO₄ solution (NSW EH, 2015). Results of TOC were reported as percentage and later converted to dry weight (Table 1) by multiplying total organic matter content (%) by sediment bulk density (1.61 gcm^{-3}) and depth (20 cm) of sampling (Pluske et al., 2016).

Samples for hydrocarbon analysis was weighed to obtain wet weight, and then sun-dried and then grounded to powdery form and sieved with a 1.0mm sieve. The sieved samples were stored in well-labelled smaller plastic containers with cover, from where samples were withdrawn for analysis. 5g each of dry powdery samples were weighed out and placed in 250ml beakers. To this was added 30ml of xylene; the beaker was then swirled/shaken for about 5 minutes and allowed to settle, the mixture was later filtered into a clean 100ml standard flask through a Whatmann filter paper that contains about 2g of Anhydrus Sodium Sulphate on a cotton wool. This was done three times and was later made up to the 100ml mark with xylene. The absorbance of the filtrate was measured at 340nm using Hach DR 2800 Spectrophotometer. The corresponding concentrations of Total Hydrocarbon (THC) content were then obtained from the calibration curve and calculated on dry weight basis. Same procedure was applied to the analysis for Total Petroleum Hydrocarbon (TPH), although, after the extraction, the filtrate was treated with silica gel to remove non-petroleum hydrocarbons and re-filtered. The readings were obtained in the same manner with that of THC and the final value calculated as usual (Howard et al., 2009). Calibration of the spectrophotometer (HACH DR 2800) was carried out before each analysis using diluents of a stock solution of 1ml of crude oil in 100ml of xylene at 340nm in line with ASTM (2003) and Howard et al. (2009).

Environmental Impact and Ecological Risk Assessment Methods

Environmental impacts of oil contamination and potential ecological risks were calculated by analysing the relationships, differences and similarities between contaminant concentrations in sample sites. Contaminant concentrations in sediments were further compared with sediment quality guidelines including; the National Ocean and Atmospheric Administration of the USA (NOAA) and the Dutch government intervention values (Verbruggen, 2004) for the protection of ecosystems using the apparent effects threshold (AET), the effects range low (ERL), effects range medium (ERM), the threshold effects and probable effects level (TEL/PEL) (IMO, 2000) and maximum permissible concentrations (MPCs).

Potential Ecological Risk Index (PERI), a diagnostic tool suggested by Håkanson (1980, 1988) for the analysis of contamination in lakes and coastal systems was used to calculate an ecological risk index for the Oturuba river ecosystem. PERI is formed by three basic modules: Degree of contamination (C_D); toxic-response factor (Tr^i); and potential ecological risk factor (Er^i).

The first module of PERI corresponds to the estimate of the degree of contamination (C_D). The C_D is expressed by the sum of the contamination factor of each metal (C_f^i) as:

$$C_D = \sum C_f^i$$

where, C_f^i, is the mean metal concentration (C^i), divided by the pre-industrial concentration of the substance (C_0^i):

$$C_f^i = C^i / C_0^i$$

According to Håkanson (1980, 1988), the potential ecological risk index (PERI) is defined by:

$$RI = \sum Er^i$$

$$Er^i = Tr^i * C_f^i$$

where; RI is calculated as the sum of all risk factors for heavy metals in sediments; Er^i is the monomial potential ecological risk factor; TR^i is the dimensionless derived toxic-response factor for a given substance (e.g., Cu = 5, Pb = 5, Ni = 5, Zn = 1, Cd = 30), which mainly reflects the heavy metal toxicity level and the degree of environment sensitivity to pollution from a particular heavy metal (Jiao et al., 2015).

C_f^i, C_0^i, and C_n^i are the contamination factor, the concentration of metals in the sediment and the background reference level, respectively. International background values for metals in sediments (shale) include 0.22 mg/kg for Cd, 39 mg/kg for Cu, 68 mg/kg for Ni, 120 mg/kg for Zn, 0.85 mg/kg for Mn (Rodrigues et al., 2006) and 60 mg/kg for Pb (Li et al., 2012).

Håkanson (1980) also proposed the following values to be used in the interpretation of ecological risks in sediments:

  – RI <150, low ecological risk for the sediment;
  – 150≤ RI <300, moderate ecological risk for the sediment;
  – 300≤ RI <600, considerable ecological risk for the sediment;
  – RI ≥600, very high ecological risk for the sediment.

In order to assess the intensity of metal contamination in the sediments of the Oturuba Creek, the geochemical accumulation index was calculated using the equation proposed by Singh et al. (2003) to quantify metal accumulation in the sediments, and represent their contamination degree. This index is expressed as follows:

$$I_{geo} = \log_2 C_n / 1.5 B_n$$

where I_{geo} is the geochemical accumulation index; C_n is the total concentration of metal n in the silt/clay fraction;

Bn is the geochemical background value of element n and 1.5 is a correction factor due to lithogenic effects. The I$_{geo}$ classification entails seven grades (0 to 6) of pollution, ranging from no pollution (0) to very high pollution (Forstner, 1989).

RESULTS AND DISCUSSION

Heavy metals, organic matter and hydrocarbons in the sediments

The results of the analysis of sampled sediments are presented in Figure 2. Organic matter concentration ranged between 201 (mg/kg) and 2782.1(mg/kg) with both lowest and highest concentrations occurring in the wet season. Highest concentrations occurred 500m downstream (Site 4) from the point of impact in both seasons.

Concentrations of copper in the sediment ranged between 4.78 – 83.5 mg/kg with highest and lowest concentrations occurring in site 4 and 6 in the dry season respectively. Concentrations also followed the same pattern in the wet season (6.24 mg/kg – 50.02 mg/kg) although with slightly lower concentrations in site 4. Concentrations of copper (4.78 – 83.5 mg/kg) in sediments were above the Dutch maximum permissible concentrations (73 mg/kg) in site 4 in the dry season. Copper concentrations were also above the TEL (18.7 mg/kg) in 7 out of 12 cases and above the ERL (34 mg/kg) in three cases while nickel exceeded TEL limits (15.9 mg/kg) in 7 cases out of 12 in all seasons. Concentrations of zinc ranged between 199.53 and 1007.8 mg/kg, lowest and highest concentrations occurred at site 1 and 6 respectively. The concentrations of zinc were higher in the dry season for all sites apart from site 6 and also above TEL, ERL and PEL guidelines in all seasons.

While lead concentrations (123.3 – 327.5 mg/kg) were above TEL, PEL and ERL in all cases except for PEL in the dry season in site 6 cadmium concentrations (38.1 – 259 mg/kg) were above all the standards in all seasons. For vanadium (1.21 – 5.24 mg/kg) and manganese

(42.71 – 959.4 mg/kg) the only available guideline is the AET (57 and 260 mg/kg respectively). While all the sampling sites were below maximum specified limits for vanadium, manganese exceeded standards in sites 3, 4 and 5 in the dry season and all sampling sites apart from site 6 in the wet season.

Total petroleum hydrocarbons (TPH) in sediments ranged from 3997.9 (mg/kg) dry weight at the POI to 1546 (mg/kg) at site 6 in the dry season. Concentrations in the wet season followed a similar trend with ranges between 5118.5 mg/kg at site 3 and 1727.5 mg/kg in site 6. Total hydrocarbon (THC) concentrations ranged between 5133.6 mg/kg in site 3 and 2151.2 mg/kg in site 6 in the dry season. There was however a slight difference in trend as the POI had a total concentration of 6118.5 (mg/kg) with lowest concentrations (2272.5 mg/kg) downstream in site 5.

Potential ecological impacts of heavy metals and hydrocarbons in the sediments

Species that are intolerant to metal contamination can be adversely affected in a number of ways from heavy metal pollution of marine sediments. Impacts on reproduction and growth can impair the survival of individuals, and affect populations and communities. For instance, copper can be acutely toxic to microalgae at levels between 190mg/kg and 300 mg/kg (Markovic, 2003). In this study, copper occurred between maximum contaminant limits and the low level effects range where biological activities can be impaired. Also, recruitment can also be affected by metal contamination in clams (*Macoma bathilica*) (Langston, 1990; Markovic, 2003). Concentrations of zinc in this study occurred far above these toxic levels. Negative impacts related to metal contamination do not necessarily result from direct toxicity but contaminant-related changes to phytoplankton communities may have serious consequences for higher trophic levels. A change in the phytoplankton community structure can lead to a reduction in preferred prey species,
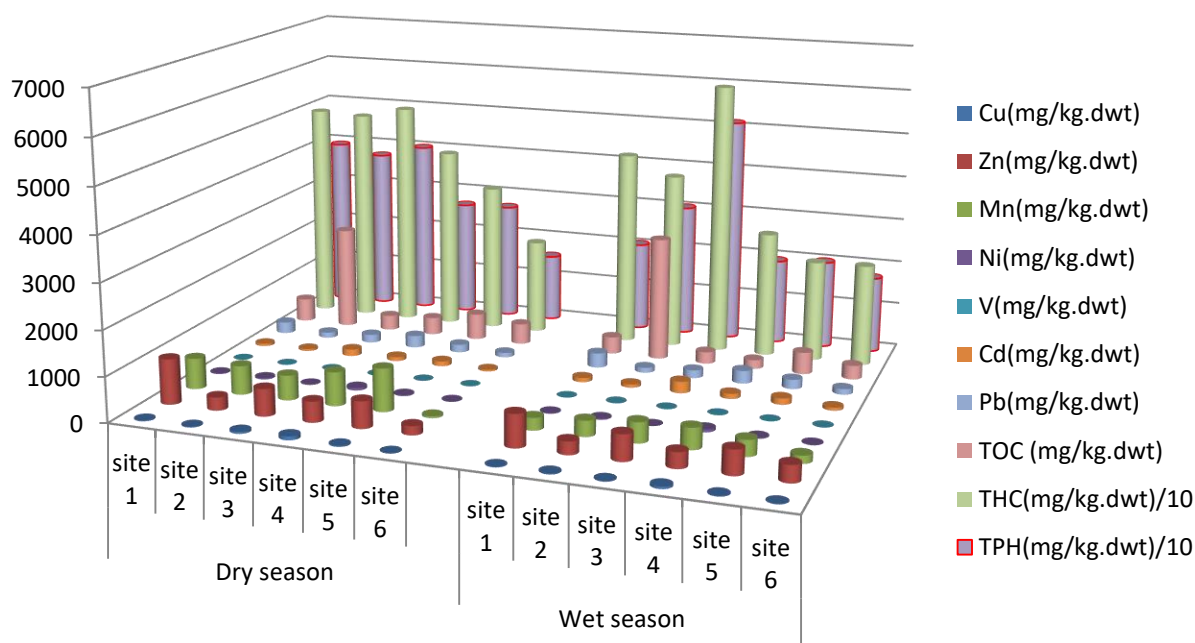

Fig. 2 Hydrocarbons, Heavy metals and TOC in the Oturuba Creek

Table 2 Marine Sediment Quality Guidelines (Modified from NOAA, 2008 and Bay et al., 2012)

Mg/kg	Intervention Dutch Guidelines			Consensus Sediment Guidelines			
	Intervention values	MPC	TEL	ERL	PEL	ERM	AET
P$_A$H$_S$	40		1.684	4.022	16.77	44.8	
Mineral oil	1100	5000					
Cu	190	73	18.7	34	108	270	390 Microtop larvae
Zn	720	620	124	150	271	410	410 Infaunal community impacts
Mn							260 Neanthes
Ni	210	44	15.9	20.9	42.8	51.6	110 Echinoderm larva; Bioassay Larvae
V							57 Neanthes
Cd	12	0.68	0.68	1.2	4.21	9.6	3.0 Neanthes
Pb	530	530	30.2	46.7	112	218	400 Bivalve

and ultimately the loss of higher trophic species in those communities. It is possible that the indirect effects triggered by the loss of sensitive species have a much more significant impact on marine communities than indicated by toxicity tests with an individual species (Langston, 1990; Markovic, 2003). All the trace elements in the bottom-sediment samples from this study also exceeded the respective TEL and PEL. According to USEPA (1998), these values are in the range where toxic effects can occur to benthic organisms.

These results suggest that heavy metal and hydrocarbon levels in the study area are at concentrations high enough to impair biological communities and are likely to cause toxicity levels that will lead to negative impacts on infaunal communities (Table 2) including *Leptocheirus* amphipods bivalves, neanthes worms, echinoderm and Oyster larvae (ADEC, 2011). According to Capuzzo (1985), retention of hydrocarbons in lipophilic cellular compartments may result in disruptions in membrane functions or alterations in energetic processes and impairment of an organism's adaptive capacity within its natural habitat. Capacity for metabolism of lipophilic compounds may influence the disposition or removal of aromatic hydrocarbons by marine organisms.

Relationships, spatial and temporal variations of contaminants in the sediments

Organic matter in the study area tended to have a negative relationship with both total hydrocarbon and heavy metal concentrations without showing much variation in both seasons. This is at variance with the findings of Jamil et al. (2014) and the reason for this difference may be a result of pH, salinity and grain size differences (Du Laing, 2009) which were not measured in this study. Heavy metal concentrations increased progressively in both upstream and downstream directions in the dry seasons but tilted downstream in the wet season. THC concentration characteristics in the sampled sites also revealed profound between site variations. This could be indicative of the irregular pattern in waste discharges and spills and the power of tidal influence in redistributing contaminants in the creek's ecosystem.

A correlation matrix can indicate associations and relationships among metals and their sedimentary environments (Table 2-4). High correlation coefficients between different metals in a matrix could mean that they

have common sources, mutual dependence and identical behaviour during transportation and probably deposition. The absence of strong correlations among metals on the other hand may be indicative that the concentrations of these metals are not controlled by a single factor, but may be a pointer to a combination of geochemical support phases and the effects of the mixed association and interactions among the metals (Veerasingam et al., 2012).

Table 2 Proximity Matrix of sampling sites for heavy metals

Correlation between vectors of values in the dry season						
	SSA	SSB	SSC	SSD	SSE	SSF
SSA	1					
SSB	.916	1				
SSC	.934	.985	1			
SSD	.863	.981	.985	1		
SSE	.973	.847	.864	.774	1	
SSF	.739	.493	.475	.343	.828	1
Correlation between vectors of values in wet season						
	SSA	SSB	SSC	SSD	SSE	SSF
SSA	1					
SSB	.923	1				
SSC	.938	.984	1			
SSD	.857	.967	.979	1		
SSE	.974	.858	.873	.776	1	
SSF	.754	.526	.504	.362	.837	1

Distances and similarities between sites were calculated using the Pearson correlation statistics. Results (Table 2) for heavy metals revealed a high level of similarity among sites, although site SSF (background) was least similar to SSB, SSC and SSD in both seasons. The reason for dissimilarities is obvious; however, the similarity between sites SSF (background) and site SSA (POI) is not readily explainable. It may be posited that the tidal nature of the environment may be redistributing contaminants within the marine environment. Results for TOC, THC and TPH (Fig. 3 and Table 3) also show a high level of similarity among sites.

Table 3 Proximity Matrix of sampling sites for TPH, THC and TOC

Correlation between vectors of values in the dry season						
	SSA	SSB	SSC	SSD	SSE	SSF
SSA	1					
SSB	.988	1				
SSC	1.000	.986	1			
SSD	1.000	.992	.999	1		
SSE	1.000	.986	1.000	.999	1	
SSF	.998	.996	.997	.999	.997	1
Correlation between vectors of values in wet season						
	SSA	SSB	SSC	SSD	SSE	SSF
SSA	1					
SSB	.987	1				
SSC	.999	.979	1			
SSD	.996	.997	.992	1		
SSE	.915	.968	.897	.946	1	
SSF	. 996	.997	.990	1.000	.946	1

Since the above analysis did not show very distinct relationships, the data was subjected to further multivariate statistical analysis using the Pearson's correlation to test for relationship between contaminants. Results (Table 4) of this analysis (strong – medium correlations verged in red) however revealed very weak relationships among the contaminants; however, only cupper and manganese; vanadium and THC; TPH and TOC had any form of significant strong relationship. Subjecting the data to further query by principal component analysis (PCA) using the varimax analysis with Kaiser Normalization rotation method (Table 5); three components were realized accounting for 80.56% of observed variation in the dataset. Principal component one (29.528%) has a strong relationship between TPH and TOC with a moderate association with zinc, cadmium and manganese. This factor is most likely an indication of pollution from uncooked crude oil spilled during transportation and pre-

cooking (refining) operations in the study area. The indicated petroliferous heavy metals have been identified (Marcus and Ekpete, 2014) as key components of crude oil from th is part of the Niger Delta.

Factor two which accounts for 26.71% of variance indicates a strong affinity between vanadium and THC. Vanadium is a major constituent of nearly all coal and petroleum crude oils. The most prominent anthropogenic source of vanadium in the environment is the combustion of fossil fuels, particularly residual fuel oils, which also constitute the single largest overall release of vanadium to the atmosphere. While the levels of vanadium in residual fuel oil usually vary by source, concentrations of 1–1,400 ppm have been reported (ATSDR, 2012). The third factor loaded 24.322% and has affinity for copper, lead and nickel. While urban sewage contains substantial amounts of copper, nickel is ubiquitous in the environment while lead is the most abundant heavy metals occurring in nature. This may therefore indicate mobilisation from natural sources and long distance pollution drifted from upstream sources in the Port Harcourt-Eleme-Onne industrial axis located northwest of the study area.

Table 5 Rotated component matrix of variables

	Component		
	1	2	3
Cu	.042	-.082	**.887**
Zn	**.645**	-.461	.095
Mn	**.506**	.137	.656
Ni	-.311	.060	**.908**
V	.240	**.938**	.100
Cd	**.613**	-.391	-.127
Pb	.185	.612	**.587**
THC (x 0.001)	-.013	**.957**	-.040
TPH (x 0.001)	**.921**	.197	.085
TOC (%)	**.931**	.262	-.042
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization			

Table 4 Pearson's correlation matrix of contaminants

	Cu	Zn	Mn	Ni	V	Cd	Pb	THC (x 0.001)	TPH (x 0.001)	TOC (%)
Cu	1									
Zn	-.014	1								
Mn	**.763****	.219	1							
Ni	**.509***	**.407**	.398	1						
V	-.014	-.184	.070	.268	1					
Cd	.074	.229	-.233	.117	-.279	1				
Pb	**.458**	**.592***	**.450**	.262	-.390	.168	1			
THC (x 0.001)	-.174	.395	.029	.063	**.923****	-.372	**.498***	1		
TPH (x 0.001)	.130	**.459**	-.191	**.424**	**.415**	**.443**	.167	.172	1	
TOC (%)	.038	.386	-.278	**.448**	**.436**	**.531***	-.086	.190	**.913****	1

** Correlation is significant at the 0.01 level (1-tailed)

 * Correlation is significant at the 0.05 level (1-tailed)

Potential ecological risk of heavy metals in the sediments

Calculated contamination factors for the various metals are Cu: 0.652, Zn: 205.73, Mn: 560.34, Ni: 0.321, Cd: 472.5 and Pb: 3.28, while international toxicity factors for Cd: 30, Ni, Cu, Pb and Zn include 30, 5, 5, 5 and 1 respectively (Li et al., 2012) while toxicity values for Mn and V are not available. Therefore, the degree of contamination (C_D) for the Oturuba Creek system for the analyzed metals is 1,242.82.

Calculated Er^i for metals include 3.26, 205.73, 1.605,14,175 and 16.4 for Cu, Zn, Ni, Cd and Pb respectively; giving a total value of 14,401.995, with Cd contributing more than 98% of ecological risks followed by Zn with 14.43%. Going by the recommendations of Håkanson (1980), the calculated Er^i for the study area is over 700% beyond the baseline for very high ecological risk metal concentrations. Li et al. (2012) in a study of heavy metal contamination in sediments from a coastal industrial basin in Northeast China concluded that the area "is one of the most polluted of the world's impacted coastal systems". However, evidence from this study shows worse but similar sediment quality situation. Therefore, the Oturuba Creek can be declared to be one of the most polluted coastal rivers in the world.

Index of geoaccumulation (I_{geo})

In order to assess the intensity of metal contamination in the sediments of the Oturuba Creek, the geochemical accumulation index was calculated as proposed by Singh et al. (2003) to quantify metal accumulation in the sediments, and represent their contamination degree. The I_{geo} classification entails seven grades (0 to 6) of pollution, ranging from no pollution (0) to very high pollution (Forstner, 1989).

Table 6 I_{geo} classes, range and sediment quality (Singh et al., 2003)

I_{geo} class	I_{geo} range	Sediment Quality
0	<0	Background concentrations
1	0-1	Unpolluted
2	1-2	Polluted to unpolluted
3	2-3	Moderately polluted
4	3-4	Moderately to Highly polluted
5	4-5	Highly polluted
6	>5	Very highly polluted

Calculation of the geochemical metal accumulation index for the Oturuba river system returned 269.4 for Cu, 2628 for Zn, 11.35 for Mn, 453.9 for Ni, 2.211 for Cd and 685.8 for Pb. This result therefore places metal concentrations in the study area in the range of very highly polluted sediment environment with only cadmium occurring in moderately polluted status (Table 6).

CONCLUSIONS

The Oturuba river system is a sink for wastes and spills from the artisanal refining, transportation and handling of probably stolen petroleum. These activities have led to elevated levels of heavy metals and hydrocarbon contaminants in sediments of the river. All the sampled sites in the creek had hydrocarbon concentrations that where above limits for total PAHs in terms of ERL, ERM, TEL, PEL, AET and the Dutch intervention values for the protection of ecosystems. However, only the POI (SSA) exceeded the Dutch maximum permissible concentrations (MPCs) for mineral oils in both season. The results of this study suggest that levels of hydrocarbons are at concentrations high enough to impair biological communities and are likely to cause toxicity levels that will lead to negative impacts on infaunal communities.

Also, all the trace elements in the bottom-sediment samples from this study (except vanadium) exceeded the respective TEL and/or PEL guideline values, which are range where toxic effects occur to benthic organisms (USEPA, 1998). Heavy metal geochemical accumulation index analysis also returned anomalously high metal concentrations in the range of very highly polluted sediment environment with only cadmium occurring in the moderately polluted status.

Heavy metal pollution in the Oturuba Creek has some variability from other river systems in the Niger Delta region. While concentrations of copper and nickel in the study area is similar to those found in the sediments of the Benin River, zinc, vanadium and lead concentrations were far above those found in the same river (Akporido and Ipeaiyeda, 2014) and in the Orogodo River in Agbor Delta State (Issa et al., 2011) all in the far northwester flank of the Niger Delta. Metal concentrations from this study were also very much higher than those found in the Bonny River system around Okrika (Marcus et al., 2013) located not more than twenty kilometres northwest of the study area, while manganese concentrations in the Oturuba system were very much above those found in the sediments of the Taylor Creek system in Bayelsa Nigeria (Okafor and Opuene, 2007).These not only shows that the Oturuba Creek is heavily polluted but that heavy metal pollution of river sediments may be more related to local anthropogenic inputs than terrigenous sources.

Hydrocarbon concentrations found in the sediments of the Oturuba Creek were below figures found by Akporido and Ipeaiyeda (2014) in the sediments of the Benin River. Also, TPH concentrations found in this study were far above that found in the Qua Iboe River mangrove ecosystem (Benson and Essien, 2009). This may simply be related to the intensity of oil spill-causing activity in the study area.

The potential ecological risk factor (Er^i) for metals calculated for this study showed that Cd contributed more than 98% of ecological risks followed by Zn with 14.43%. Going by the recommendations of Håkanson (1980), the calculated Er^i for the study area is beyond the baseline for very high ecological risk metal concentrations, thereby ranking the Oturuba Creek as one of the most polluted coastal river ecosystems in the world; thereby not only endangering the ecosystem and threatening the livelihoods of the nearly one million people who live along the coastline and depend on the marine environment for sustenance but also the life of those who consume fish from these contaminated rivers. Urgent steps must therefore be taken to stop all illegal and artisanal refining activities in the Andoni River areas of Nigeria.

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