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Physicochemical Characteristics and Concentrations of Heavy Metals (Fe, Zn, Cr, Pb) in Sediments of Two Jetties in Okirika, Nigeria.

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Abstract: *Numerous activities take place around jetties and some of these may impact negatively on the aquatic environment. There is thus the need for a study of the levels of the physico-chemical characteristics of the sediments around jetties from which aquatic invertebrates feed on. Sediment samples from two jetties (local and industrial) in Okirika, Rivers State, Nigeria were sampled for six months (February – July, 2014). Standard methods, including acid digestion, toluene extraction and spectrophotometric methods were employed in the determination of the levels of the parameters. Fe and Cr levels, in both jetties, were higher than national and international standards of (1.0 mgkg^{-1}) and (0.05mgkg^{-1}) respectively. On the other hand, Zn levels in both jetties were within the permissible limits (50 – 300mgkg^{-1}). Pb levels measured in the local were below the notable limits (<0.01), whereas in the Industrial jetty, the levels were higher than the standard (0.05 mgkg^{-1}). Mean levels of other parameters were as follows: Local – pH (6.02±0.47), Electrical conductivity (187.20±66.86µScm^{-1}), organic matter (24.78±9.22%) and THC (238.15±144.45mgkg^{-1}). Industrial – pH (5.97±0.37), Electrical Conductivity (212.68±26.94 µScm^{-1}), Organic matter (29.78±6.43%) and THC (568.73±370.82mgkg^{-1}). Possible sources of contaminants in the sediments have been highlighted in the study. Although little variations in the concentrations of the pollutants across the study areas were obtained, these were attributed to anthropogenic contributions. The study recommends continuous assessment of the jetties in order to achieve good sediment quality which is an important indication of water quality and contaminant free aquatic organisms for safe human health.*

I. Introduction

Jetties are found in many coastal regions around the world, especially at water fronts where ships, boats, canoes and other marine transport facilities are docked for the transportation of humans, goods and services across water bodies to cities that are not accessible by road transport. In Nigeria, there are a number of coastal states such as Rivers, Bayelsa, Delta, Akwa Ibom, Lagos and Cross River. The mode of transportation in riverine communities in such coastal states is by marine transport. At the banks of the rivers, jetties are constructed using wood or blocks and cement, to enable commuters embark and disembark the boats.

In Rivers State, there are as well, jetties for local transport and industrial services such as Eagle cement, Abonnema Wharf, Marine base, Refinery, Aker base, Nembe waterside and Okirika waterside.At Okirika waterside (the local jetty), commuters shuttle between Okirika and other riverine communities in Rivers State. As they embark and/or disembark at the jetty, they discard empty cans, sachets and polyethylene bags and bottles of drinks into the river, thereby introducing hydrocarbon components into the aquatic system. Furthermore, during the fueling of marine vessels, some wastes of oil and diesel are discharged into the river and these also contribute to the hydrocarbon load in the system. Maintenance services which may involve welding and re-painting of worn out parts, runoff from nearby automobile garages, indiscriminate discharge of effluents and bunkering activities around the jetties - all introduce contaminants into the river. At the Refinery (the industrial) jetty, in addition to the various activities that take place at the local jetty , components of heavy duty equipment as well as huge quantities of petroleum products are routinely transported.Often times as these substances get into the river, they finally settle into the sediment which acts as a sink for contaminants in aquatic systems (Adams *et al*., 1992; Burton and Scott., 1992; Mucha *et al*., 2003).

Since water and sediments are commonly used as indicators for determining water quality and the effects of pollution on the aquatic ecosystem, the presence of pollutants in the ecosystem poses serious health hazard to the aquatic organisms and humans. For instance, heavy metals are not biodegradable; they can either be adsorbed onto sediment or accumulated by fishes and other aquatic organisms to a toxic level. They then enter the food chain where they are eventually consumed by humans (Yu *et al*., 2000). In addition, important macro-nutrients are continuously interchanged between sediment and overlying water (Abowei and Sikoki, 2005). Since humans depend largely on the aquatic ecosystem, a regular study of changes in the ecosystem is imperative.

Several researches have been conducted in water and sediment in Bonny and Ase rivers as well as in Elechi and Amadi-ama creeks of the Niger Delta region of Nigeria (Chindah *et al.*, 2004; Davies *et al*., 2006; Obunwo *et al*., 2006 ;Chukwjindu *et al*., 2007; Chindah *et al*., 2009; Abagwa and Okpokwasili, 2011 and Otene and Iorchor, 2013). However, records of studies conducted on sediments in jetties of the region are scanty. For this reason, this study aims at establishing the effect of human activities such as loading and offloading of goods and services and anchorage of marine transport facilities on the extent of pollution of the sediment by investigating the physicochemical characteristics as well as levels of some heavy metals (Fe, Zn, Pb and Cr) in the sediments of Refinery and Okirika Waterside jetties in Okirika, Rivers State, Nigeria.

II. Methodology

Sediment samples were randomly collected; during low tide, by scooping with plastic containers into polythene bags. The samples were air dried at room temperature for three (3) weeks after which they were ground and sieved through a 2mm mesh size sieve, into finely ground particle size.

The measurements of levels of pH, Electrical conductivity, Total organic matter and Total hydrocarbon concentration (THC) in the sediments were carried out using standard methods (APHA, 2003). Concentrations of Fe, Cr, Pb and Zn were determined using the Bulk Scientific atomic absorption spectrophotometer (model: Aceusys 211) after acid digestion of the sediment samples with aqua- regia.

III. Results And Discussion

Table 1: Monthly Data of Physicochemical characteristics of Industrial (Refinery) jetty.

Parameter	Feb	March	April	May	June	July	Mean	SD
pH	6.1	6.1	5.1	6.1	6.4	6.3	6.02	0.47
EC(µS/cm)	22.1	23.1	23.5	22.3	16.56	19.53	21.18	2.65
OM (%)	32	34	28	28.2	19.6	25.2	27.83	5.1
THC(mg/kg)	204.12	521.18	238.24	152.95	121.8	190.59	238.15	144.45
Fe(mg/kg)	13700	21000	13500	49550	47600	48050	32233.3	17926.4
Cr(mg/kg)	17.5	15.1	14.7	31.8	25.7	25.7	21.75	6.99
Pb(mg/kg)	5.5	4.7	3.4	4.8	6.3	5.1	4.97	0.96
Zn(mg/kg)	90.8	137	109	115	82.5	101	105.88	19.28

Table 2: Monthly Data of Physicochemical characteristics of Local (Okirika waterside) jetty

Parameter	Feb	March	April	May	June	July	Mean	SD
pH	5.4	5.8	6.2	5.8	6.2	6.4	5.97	0.37
EC(µS/cm)	10.1	12.13	25.7	24.6	23	16.56	18.68	6.69
OM (%)	19	13	32	30.2	30.8	17.2	23.7	8.25
THC(mg/kg)	715.3	570	1210	194.71	241.18	481.2	568.73	370.82
Fe(mg/kg)	8370	9750	23700	24030	21980	9540	16228.3	7723.08
Cr(mg/kg)	9.4	11.6	29.1	30.9	24.3	10.1	19.23	9.98
Pb(mg/kg)	13.5	19.5	32	18.7	10.7	9.3	17.28	8.31
Zn(mg/kg)	241	256	591	88	74.6	64.2	219.13	201.1

The monthly data of the physicochemical characteristics of the sediment samples of the two jetties are presented in Tables 1 – 2. A comparison of the mean data of the characteristics from the jetties with national and international standards is presented in Table 3.

The mean pH values of the sediments of Industrial (Refinery) jetty (5.97±0.37) and the local (Okirika Waterside) jetty (6.02± 0.47) did not differ markedly and reflected acidic characteristics. Electrical conductivity values were generally low but higher in the dry season than in the wet season (Tables 1 and 2). The low Electrical conductivity values at both jetties, however, did not reflect the marine nature of the environment. On the other hand, mean Total hydrocarbon concentrations (568.73±370.82mgkg-[1] for Refinery and 238.15±144.45mgkg-[1] for Okirika waterside) exceeded permissible limits (200mgkg-[1]) (WHO, 1996). This observation is indicative of high hydrocarbon load in the jetties, with a significantly higher concentration in the sediments of the industrial ($p<0.05$) jetty.

Table 3: Comparison of mean levels of parameters in sediments of the jetties.

Parameter	Refinery	Okirika Waterside	WHO	SON
pH	5.97	6.02	6.5 - 8.5	6.5 - 8.5
EC (µS/cm)	212.68	187.2	100	100
Organic matter (%)	29.78	24.78	-	-
THC (mg/kg)	568.73	238.15	200	200
Fe (mg/kg)	32233.3	16228.3	1.0	1.0
Cr (mg/kg)	21.75	19.23	0.05	0.05
Pb (mg/kg)	17.28	4.97	0.05	0.05
Zn (mg/kg)	219.43	105.88	50 - 300	50 - 300

Metal concentrations in the sediments were higher in the industrial jetty than in the local jetty. For example, Fe concentrations were 32233.33±17926.40mgkg^{-1} and 16228.33±7723.08mgkg^{-1} for the industrial and local jetties respectively. Similarly, Pb levels were higher in industrial (17.28±8.31mgkg^{-1}) than in the local (4.97±0.96mgkg^{-1}). Although these values far exceed WHO standards (Table 3), Fe and Pb concentrations were markedly and significantly higher in the industrial jetty than in the local jetty and this trend may be as a result of the anchoring of a larger number of unserviceable barges within the vicinity of the industrial than at the local.
This high metal load at the industrial may bioaccumulate in fish and other aquatic macroorganisms which feed on the sediments and eventually enter the food chain.

Table 5a: Correlation matrix of Industrial (Refinery) jetty

	pH	EC	OM	THC	Fe	Cr	Pb	Zn
pH	1.00	-0.51	0.80	0.02	0.47	0.22	0.00	-0.03
EC	-0.51	1.00	-0.90	0.59	-0.71	-0.53	0.74	0.67
OM	0.80	-0.90	1.00	-0.43	0.74	0.53	-0.43	-0.46
THC	0.02	0.59	-0.43	1.00	-0.83	-0.81	0.73	0.94
Fe	0.47	-0.71	0.74	-0.83	1.00	0.93	-0.58	-0.82
Cr	0.22	-0.53	0.53	-0.81	0.93	1.00	-0.50	-0.78
Pb	0.00	0.74	-0.43	0.73	-0.58	-0.50	1.00	0.90
Zn	-0.03	0.67	-0.46	0.94	-0.82	-0.78	0.90	1.00

Table 5b: Correlation matrix of Local (Okrika waterside) jetty

	pH	EC	OM	THC	Fe	Cr	Pb	Zn
pH	1.00	-0.39	0.54	-0.13	-0.39	-0.44	0.89	-0.25
EC	-0.39	1.00	0.30	-0.49	0.96	0.94	-0.28	-0.13
OM	0.54	0.30	1.00	-0.70	0.15	0.10	0.46	-0.49
THC	-0.13	-0.49	-0.70	1.00	-0.46	-0.41	-0.35	-0.35
Fe	-0.39	0.96	0.15	-0.46	1.00	0.99	-0.23	-0.12
Cr	-0.44	0.94	0.10	-0.41	0.99	1.00	-0.31	-0.03
Pb	0.89	-0.28	0.46	-0.35	-0.23	-0.31	1	-0.59
Zn	-0.25	-0.13	-0.49	-0.35	-0.12	-0.03	-0.59	1.00

On the basis of the correlation matrices (Table 5) of the chemical characteristics of the sediments in the two jetties, a strong correlation existed between Iron (Fe) and Organic Matter (OM) content in the industrial jetty. This trend was not observed in the local jetty and may thus be related to the volume of organic products discharged at the industrial jetty. Lalonde *et al*, (2012) had noted that the association between OM and Fe was formed primarily through co-precipitation and/or direct chelation in order to promote the preservation of the Organic Matter in the sediment.

IV. Conclusion

As a result of high human activities around jetties compared with other areas of the coastal region, there is need for regular monitoring of the water bodies.

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