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Organic matter and trace metals levels in sediment of bonny river and creeks around Okrika in Rivers State, Nigeria

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Analysis was carried out on the sediment of Bonny River and creeks around Okrika in order to determine the concentrations of organic matter, lead, nickel, vanadium and cadmium as well as their probable sources and diagenesis. Samples for trace metal analysis were prepared by acid digestion and analysed by atomic absorption spectrophotometry. Organic matter content was determined by the method of Walkey and Black. Mean concentrations (µg/g, dry wt) of trace metals were: Pb(23.22 ± 13.43), Ni (57.19 ± 16.93), V (0.06 ± 0.05), Cd (0.24 ± 0.32) while organic matter (% dry wt) were: TOC(1.14 ± 0.40) and TOM(1.990 ± 0.70) and revealed anthropogenic trace metal enrichment. The large standard deviations indicate temporal and spatial variations due largely to anthropogenic waste input. There was a weak association for Pb/organic matter (/r/=0.58, p<0.01) in the wet season suggesting a common source, most likely from land-derived wastes brought in by runoff water.

Key words: Organic matter, trace metals, anthropogenic enrichment, Bonny River.

INTRODUCTION

Trace metals in sediments can play a major role in the pollution scheme of a river system. Sediments are repositories for physical debris and sink for chemical contaminants. They can therefore be used to detect pollutants that escape water analysis and also provide information about the critical sites of the river system. River sediments are a major potential sink for hydrophobic pollutants in the aquatic environment (Kreina et al., 2003; Schorer, 1997). The organic matter content of river sediment has been shown to be an important factor in determining the extent of sorption (Calmano and Fôrstner, 1996). It has been assumed that the efficacy of inorganic exchange sites of clay and its associated organic matter are responsible for the amount and behaviour of the sorbed substances (Karickhoff and Brown, 1978). Bonny River is a recipient of effluent/wastewater from the Port Harcourt Refining Company (PHRC). The company discharges directly into Ekerekana creek, one of the creeks associated with Bonny River. From this discharge outfall, the waste spreads into other creeks and down Bonny River. The studied area is a riverine and intertidal wetland on the north bank of Bonny River, about 35 miles (56 km) upstream from the Bight of Benin in the Eastern Niger

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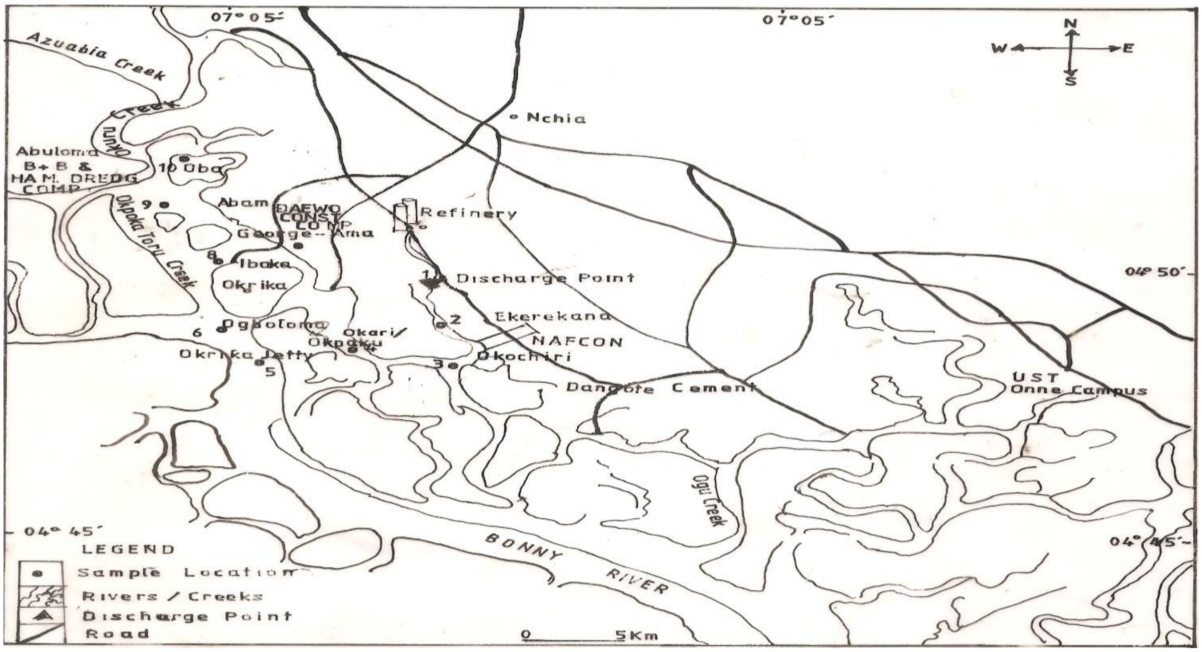

Figure 1. Map of Bonny River and Creeks around Okrika showing sampling locations.

Delta of Nigeria. This area like most parts of the Niger Delta has suffered extensive environmental degradation due to oil exploration and exploitation. The oil industry has attracted many other industries and economic activities and urban population leading to a considerable volume of waste production. Unfortunately the wastes are discharged indiscriminately. Direct and indirect discharge of wastes including domestic, refinery and other kinds of industrial wastes and from land-derived sources, could have great impact on the quality of water in Bonny River and its associated creeks. Many municipal and industrial wastes are rich in trace toxic metals (Yusuf et al., 2003). Rainfall in the coastal belt of the Niger Delta usually starts from March, reaching the peak between June/August and ending in November. During the rains, runoff water collects a lot of wastes from diffuse non-point sources from far and wide into the aquatic system.

Oil prospecting activities and sewage are considered the major sources of organic pollution that can adversely affect fish and other aquatic life principally through dissolved oxygen (DO) depletion, when it occurs in the aquatic system at concentrations higher than normal. Apart from depleting DO, decomposition brings about hazardous consequences on the aquatic life (Saad and Badr, 2012). Organic pollution causes various changes in the chemical and physical properties of water such as pH, turbidity, sedimentation rates, organic matter content, decomposition products, nutrient salt supply and other biologically active materials. This paper therefore examines organic matter, lead, nickel, vanadium and cadmium contents of sediment of Bonny River and creeks around Okrika in Rivers State, and evaluates their sources and seasonal diagenesis.

MATERIALS AND METHODS

Sample collection

Sampling was carried out from 10 designated locations in the creeks and rivers as shown in Figure 1. Surface sediment samples were collected at low tide by the grab method using Eckman grab sampler from 3 to 4 points at each location (APHA, 1975). This was done at two-monthly intervals between December 2008 and October, 2009, covering dry and rainy seasons of the year. The samples for trace metals were put in polythene bags previously washed in dilute HCl while those for organic matter were put in aluminium foils and stored in the laboratory by freezing (APHA, 1975).

Sample treatment and analysis

Sediment samples were allowed to thaw and air-dried at ambient temperature. They were sieved through 0.5 mm sieve and 2 g samples were digested using 25 ml 1:3:1 mixture of $HClO_4$, HNO_3 and H_2SO_4 acids in water bath. To the digest, 10 ml deionized water was added and decanted into 50 ml standard flask and after rinsing, the solution was made up to the mark with deionized water. Buck Scientific atomic absorption spectrophotometer model 200A and air-acetylene flame were used for trace metal analyses. Accuracy of the method was checked using a standard sediment sample PACS-2. For each batch of elemental analysis, an intra-run Quality Assurance Standard (1 mgl^{-1}, Multi-Element Standard Solution, Fisher Scientific) was analysed to check for reading deviation and accuracy of every 10 samples (Cantillo and Calder, 1990). For organic carbon, 1 g dried, sieved sediment was weighed into

Table 1. Results of recovery analysis using standard sediment material (PACS-2).

Value type	Lead	Nickel	Vanadium	Cadmium
Certified value	90.70	183.00	39.50	364.00
Measured value	86.30 ± 4.40	174.00 ± 9.00	37.40 ± 2.10	340.00 ± 24.00
Recovery (%)	94.38	95.08	94.68	93.41

Table 2. Average bimonthly (n=6) concentrations of trace metals (µg/g, dw) and organic matter (%, dw) in sediment of Bonny River and creeks around Okrika.

S/N	Parameter	Sampling locations										Ov.mean±SD
		PRE	EKC	OKC	OOC	OBR	OGR	GAC	IBC	OTR	OAC	
1	Lead	4.21	2.17	33.82	19.06	37.44	26.85	11.69	27.81	29.03	40.10	23.22 ± 13.43
2	Nickel	51.87	46.47	62.41	86.58	44.03	46.75	31.51	81.00	58.19	63.13	57.19 ± 16.93
3	Vanadium	0.02	0.07	0.02	0.01	0.15	0.07	0.13	0.03	0.02	0.08	0.06 ± 0.05
4	Cadmium	0.04	0.44	0.20	0.06	1.01	0.09	0.02	0.02	0.25	0.17	0.24 ± 0.32
5	TOC (%)	0.48	0.75	1.43	1.01	1.40	1.20	0.97	0.80	1.54	1.77	1.14 ± 0.40
6	TOM (%)	0.83	1.23	2.47	1.74	2.42	2.07	1.68	1.39	2.65	3.073	1.99 ± 0.70

PRDC - Port Harcourt Refinery Discharge Channel, PRE - Port Harcourt Refinery Effluent/Wastewater Outfall, EKC - Ekerekana Creek, OKC - Okochiri Creek, OOC - Okari/Okpaku creek, OBR - Okrika/Bonny River, OGR - Ogoloma River, GAC - George Ama Creek, IBC- Ibaka Creek, OTR - Okpoka-Toru or Okpoka River, OAC - Oba Ama Creek, OV. mean - Overall mean, dw -dry wt.

250 ml conical flask and digested with 10 ml 0.5 M $K_2Cr_2O_7$ and 20 ml conc H_2SO_4, for 30 min (Walkey and Black, 1934). 100 ml deionized water and 3 drops of Ferroin indicator were added and titrated with 0.25 M $FeSO_4$ solution. Organic matter was obtained by multiplying organic carbon values by 1.724.

RESULTS AND DISCUSSION

Results of the recovery analysis as shown in Table 1 were in the range of 93.41 to 95.08%, for all the trace metals which shows good recovery and accuracy. The average concentrations of trace metals and organic matter in the sediment are presented in Table 2. The mean values of trace metals (µg/g, dry weight) and organic matter (%) in the year were: Pb (23.22 ± 13.43), Ni (57.19 ± 16.93), V (0.06 ± 0.05), Cd (0.24 ± 0.32), TOC (1.14 ± 0.40) and TOM (1.99 ± 0.70). The detection limits (µg/g) for all the trace metals are as follows: lead (0.005), nickel (0.002), vanadium (0.002) and cadmium (0.002). As shown in Table 2, the levels of nickel and lead were appreciably high when compared with the other two metals. Lead showed average bimonthly concentrations (n=6) of 2.17 to 40.10 and overall mean of 23.22 ± 13.42, while average bimonthly concentrations of nickel were; 31.51 to 86.57 and overall mean was 57.19 ± 16.92. Their occurrences at appreciable levels in most samples suggest widespread contamination arising from many diffuse non-point sources other than refinery effluent waste water. Vanadium and cadmium were very low with mean values of 0.06 and 0.24 µg/g, dry wt, respectively. Organic matter was also very low 0.48 to 1.77%. Generally, all the analytes occurred at low levels and this is attributable to high self purification capacity. Rivers are “open” systems with continual renewal of water, and therefore have high capacity for self-purification due to oxygen diffusion at the surface, together with dilution, which enables the water to assimilate polluting discharges. Consequently, in the sediment, all trace metals investigated recorded low concentrations.

The mean seasonal levels of the metals and organic matter are given in Table 3. Both the metals and organic matter had higher values in the wet season except nickel, but the seasonal levels were only significant ($p<0.05$) for lead and TOM. The absence of significant seasonal differences ($p>0.05$) in the concentrations of trace metals except lead and TOM, may be explained as resulting from high flushing and dilution rates during the rains as well as “solution effect” which according to Welcome (1986) and King and Nkata (1991), a process whereby ions bound in previous semi-dry land by decaying macrophytes get dissolved as water levels increased with inundation of fringing swamps and riparian zones.

Table 4 shows the levels of trace metals (ppm, dry weight) in sediment compared with Netherlands’s class limits. The average percentage organic matter is about 3.32%, much below the 10% maximum stipulated for the use of this table. It is clear that all metal levels fall within Classes 1 and 2 which are within acceptable levels inspite of heavy waste loadings from human and sundry sources. However, there is concern with regards to nickel which falls within Class 2, the slightly polluted class.

Table 3. Mean seasonal concentrations of trace metals (µg/g, dw) and organic matter (%, dw) in sediment of Bonny River and creeks around Okrika.

S/N	Metals	Dry season	Wet season
1	Lead	(0.075 - 69.525) 19.472 ± 19.146	(0.069 - 67.356) 29.965 ± 22.074
2	Nickel	(0.075 - 105.775) 60.027 ± 27.827	(0.500 - 102.525) 54.360 ± 29.992
3	Vanadium	(BDL - 0.275) 0.117 ± 0.052	(BDL - 0.875) 0.331 ± 0.226
4	Cadmium	(BDL - 0.863) 0.247±0.305	(BDL - 0.650) 0.512 ± 0.699
5	TOC (%)	(0.341 - 2.141) 1.048 ± 0.418	(0.040 - 3.202) 1.189 ± 0.691
6	TOM (%)	(0.588 - 3.691) 1.747 ± 0.739	(0.641 - 5.520) 2.095 ± 1.142

dw - dry wt.

Table 4. Levels of trace metals (µg/g, dw) in sediment of Bonny River and creeks around Okrika compared with Netherlands's class limits for sediments with organic matter content less than 10%.

Metal	Class limits in Netherlands				
	Bonny River and Okrika Creek sediment	Class 1	Class 2	Class 3	Class 4
Lead	23.22	<530	-	-	>530
Nickel	57.19	<35	35 - <90	45 - < 210	>210
Vanadium	0.06	-	-	-	-
Cadmium	0.13	<2	2 - <7.50	7.50 - > 12	>12

Notes: Class 1 = Excellent; Class 2 = Acceptable; Class 3 = slightly polluted; Class 4 = polluted. Source: EWA (2005).

Matrices of correlation coefficient /r/ in sediment given in Tables 5a and b showed low levels of association between the metals and signify both seasonal and spatial variations. Only the pairs of Pb/TOC and Pb/TOM showed any reasonable association ($p<0.01$) in the wet season. The correlation between TOC, TOM and Pb in the wet season suggests that an important source of lead in the water is organic loading by runoff water. The spatial and seasonal variations leading to lack of associations in the metal-metal correlation matrices could only be ascribed to substantial anthropogenic input of metals into the water from direct waste discharge from domestic and industrial sources and many diffuse non-point sources.

Nickel values determined in the present study compares well with values reported for Iko river sediment in Akwa Ibom State (Benson and Etesin, 2008), but higher than those of Lagos lagoon (Okoye et al., 1991). The levels of lead, nickel and cadmium were all higher than those previously obtained in Niger Delta and Lagos Lagoon. Apart from direct discharge of industrial and domestic wastes, the immense volume of storm water runoff and river waters entering the Bonny River and creeks around Okrika could transport metals originating from wastes discharge on land and in small streams, especially during the rains, thus resulting in the higher levels obtained for most of the metals in the sediment in the wet season.

Conclusion

The sediments of Bonny River and creeks around Okrika

Table 5. Correlation matrices of trace metals and organic matter in sediment of Bonny River and creeks around Okrika for (a) dry season and (b) wet season.

Metal	Pb	NI	V	Cd	TOC	TOM
			(A)			
Lead	1					
Nickel	-0.20297	1				
Vanadium	0.294878*	-0.35906**	1			
Cadmium	0.258518	-0.21362*	-0.07992	1		
TOC	0.504208	-0.07938**	0.027149	0.12231	1	
TOM	0.472626	0.001751**	0.030523	-0.11363	0.936481**	1
			(B)			
Lead	1					
Nickel	-0.19358	1				
Vanadium	0.285027	-0.48197**	1	.		
Cadmium	a.	a.	a.	a.	.	.
TOC	0.569866**	-0.10655	0.054137	.a	1	
TOM	0.581137**	-0.04885	0.036772	.a	0.961787**	1

are enriched with trace metals mainly due to direct input of industrial and domestic wastes and indirect input via tributary rivers and runoff waters. Anthropogenic metal inputs are the major sources of trace metals in the sediment. However, rapid sedimentation appeared to have played major role in accumulation of nickel in the bottom sediment.

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