Heavy metal levels in water and sediment of Warri River, Niger Delta, Nigeria

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Abstract: ***Over the years, anthropogenic activities are increasing in Warri River including oil and gas exploration, dredging and waste disposal. Indigenous people use the river water as sources of drinking and for fishing. This study thus, determined concentration of Fe, Cu, Zn, Ni, Pb, Cd and Cr in water and sediment from the Warri River. The results obtained show that the levels of all the metals have appreciated in comparison to the baseline studies of 1994. The concentration of Pb, Cd and Cu in water exceeded regulatory limits for safe water to support the health of fish and for safe drinking. This implies that the Warri River is continually being polluted with effluents from anthropogenic sources. There is therefore the need to control discharge of pollutants in order to forestall dwindling of the river resources besides ensuring the beneficial use of river especially by the local communities that depend on it for fish and water.***

Keywords: dredging, effluents, heavy metals,crude oil exploration, untreated Wastes, pollutants.

1. Introduction

Heavy metal refers to metallic chemical element that has a relatively high density. Most heavy metals are toxic even at low concentrations. Heavy metals are dangerous because they tend to bio-accumulate. The source of trace metals in aquatic environment could be either fromnatural or anthropogenic source[1]. Natural source may include volcanic activity, continental weathering and forest fires, while anthropogenic sources may include industrial effluents, urban storm, water runoff, leaching of metals from garbage and solid dump, metal input from rural area.

In the Niger Delta, heavy metal pollution could be linked to crude oil exploration and other industrial activities. Oil exploration activities that could result in heavy metal pollution are drilling activities and disposal of drilling mud. Drilling muds are known to contain heavy metal [2, 3]. But the many shallow anatomizing canals is a major obstacle to drilling activities. Hence, the oil industry typically carries out dredging to create navigable accesses to drilling locations. The resultant mangrove spoils containing pyrite are typically dumped at the banks of the newly dredged canals. Weathering of the dredged spoils often result in the leaching of acidic and heavy metal laden effluents [4 – 6]. A major steel manufacturing company is also located in the Niger Delta [7]. Municipal solid wastes including scrap metals are also freely dumped in Nigerian environment including the aquatic ecosystem.

Egborge[8] described heavy metals as inorganic elements essential for plant growth in traces or very minute quantities, toxic and poisonous in relatively higher concentration, biologically undergradable but easily assimilable and bio-accumulated in the protoplasm of aquatic organisms. According to the author, Mercury (Hg) and Cadmium (Cd) blacklisted in the European Economic Community (EEC) directive on discharge of dangerous substance into the aquatic environment, have been implicated in the death of millions of organisms resulting from accidental chemical discharges into the aquatic system, which are absorbed by fish. This study assessed the heavy metal concentration of the surface water and sediment of Warri River, an areas that is exposed to oil exploration activities, water disposal and receives effluent from industrial activities including a steel manufacturing plant.

2. Materials and Methods

2.1 Study Area

The study area was Warri River (Fig. 1) in Delta State, Nigeria. Its source is around Utagba Uno and runs in a Southwest direction passing between Oviorie and Ovu-inland and southwards at Odiete through Agbarho to Otokutu and Ugbolokposo[8].

On the banks of Warri River are a number of industries, markets, sawmills, etc. These includes, the refinery, Warri ports, Main Warri Market, New Ultra modern market at Udubridge, Steel Complex, and oil producing companies.Samples were collected from nine (9) locations, Sampling Points A-I. Seven of them were point of effluent discharge/recipient, while two were collected at distant locations up and downstream, which served as control.

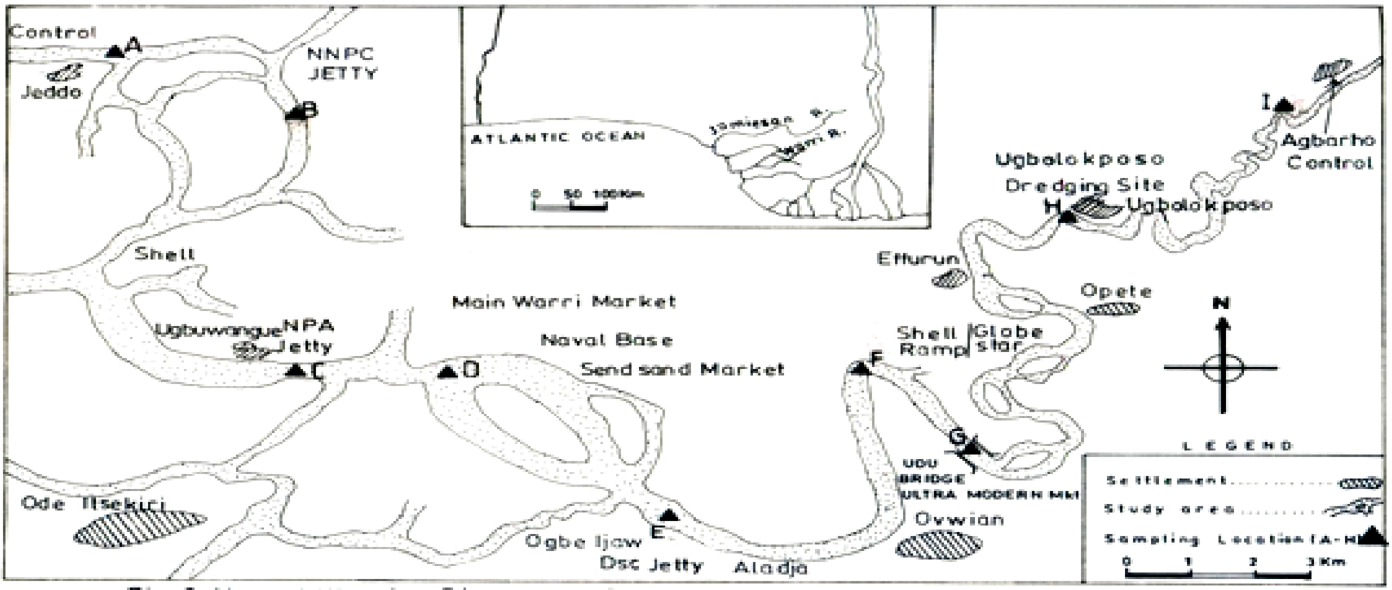

Fig 2 Map of Warri River showing the Sampling Locations
SOURCE:- ADAPTED FROM NIGERIA PORTS, WARRI 2005

2.2 Sampling Techniques

Water samples were collected monthly, while sediment were collected quarterly between September 2005 and August 2007. Plastic containers for metals analysis were washed with hot soapy water and rinse [9]. They were soaked for 4 hours in 14% HNO_3 (to prevent adsorption of metals into walls of the bottle), then rinsed thoroughly with de-ionized water. The bottles were air dried and stored until time for sample collection. Water samples along the Warri River within the sampling sites were collected in triplicate in 2litre capacity plastic bottles with screw caps at 30cm depth and stored before taken to laboratory for analysis. Sediment samples were collected from the waterbed with the aid of Eckman grab into plastic bag [10]. The top 30.0 cm of each grab sample and stored in clean polythene bag for metal analysis. They were labeled carefully and kept in cooler of ice blocks. The sediment samples were later transferred into a freezer to halt biological and chemical transformation in the samples. They were later air-dried at room temperature and preserved for further analysis.

2.3 Analytical Technique

Water samples collected from respective locations were not subjected to further treatment. They were aspirated directly in the flames of the Varian Tectron B atomic absorption spectrophotometer (AAS). But pollutant effluent water obtained at point of discharge from respective locations was digested before reading off in the AAS.

Sediment samples were air dried at 40 ^oC and ground to powder. The powder was passed through 2mm diameter sieve to remove ungrounded materials. 2.5g of sediment was taken and 10ml of nitric/perchloric acid mixture (ratio 2:1 by volume) was added before digestion. It was heated at 150^oC until a clear solution was obtained. 10ml of distilled water was added to digest samples thus preventing formation of complex compounds before filtration. The filtrates were diluted with distilled water to 50ml and the samples taken in a bottle and stored in refrigerator pending analysis. A Parkin Einmer A Analyst 400 (model) Atomic absorption spectrophotometer was used for the analysis of the heavy metals.

2.4 Statistical Analysis

Statistical Analysis was carried out using SPSS version 17 (SPSS Inc. Chicago). Descriptive statistics and analysis of variance was carried followed by Duncan Multiple Range Tests (α=0.05).

3. Results and Discussion

Heavy Metals in Sediments of the Warri River

Results showed that heavy metal values in water are comparatively lower than corresponding values in the sediment, an observation reported by Oguzie[11]. In the sediment, the highest mean concentration of Fe (6782.5 mg/kg), Cu (22.50 mg/kg) and Pb (55.25 mg/kg) were recorded at the steel company while the highest concentration of Cr (8.43 mg/kg), Ni (6.83 mg/kg), Zn (110.00 mg/kg) and Cd (0.72 mg/kg) were obtained at Ugbolokposo dredging site. The levels of Cr, Ni, Zn and Cd in sediments at Ugbolokposo may not be unconnected with the incessant sand dredging and filling operations in the location at the time of sampling [12]. The physical process of dredging according to Sly [13] and Oguzie[11] could help to release pore solutions (rich in heavy metals) in the sediment. Similar reason might be responsible for higher values of Fe, Cu and Pb at the steel company where occasional dredging is done to allow for shipment of raw materials and rolled products in and out of the Jetty, besides iron casting, rolling, milling and finishing operations of the steel company. All heavy metals in sediment differed significantly ($P < 0.05$) between the sampling locations (Table 2). Sediment samples taken at locations F (oil industry facility) and G (Udu bridge) ranked second and third in value of Pb (46.75 and 41.00 mg/kg) respectively. This might suggest the predominance of Pb compounds associated with gasoline and fumes from vehicular traffic, which characterize the locations. Largerweff and Specht [14] reported the burning of gasoline and fossil fuels as source of Pb in urban aerosols and roadside dust, which get flushed, into the aquatic environment through flood run-off and atmospheric precipitation.

Table 1: Mean Concentration of heavy metals μg l^{-1} in Warri River water at sampled locations in the study area

LOCATIONS	Fe	Cu	Pb	Cr	Ni	Zn	Cd
A	300.00a ±0.003	3.42ab ±0.000	34.67b ±0.000	195.92bcde ±0.007	24.83ab ±0.000	39.00c ±0.000	28.25a ±0.000
B	700.00d ±0.001	17.58c ±0.000	76.00e ±0.000	235.17e ±0.001	39.33abc ±0.000	50.17d ±0.000	63.00f ±0.000
C	450.00bc ±0.029	16.42c ±0.000	31.83b ±0.000	208.67de ±0.001	57.75c ±0.000	18.00b ±0.000	47.58c ±0.000
D	400.00abc ±0.010	15.33c ±0.000	84.83f ±0.000	235.17e ±0.000	17.25a ±0.000	4.67a ±0.000	54.75de ±0.000
E	500.00c ±0.008	6.25b ±0.000	64.67d ±0.000	197.00cde ±0.001	40.83bc ±0.000	17.50b ±0.000	56.83ef ±0.000
F	330.00ab ±0.047	1.50a ±0.000	28.67a ±0.000	152.33bcd ±0.004	21.33ab ±0.000	5.83a ±0.000	47.75cd ±0.000
G	470.00bc ±0.027	5.17b ±0.000	68.42d ±0.000	180.58bc ±0.001	23.17ab ±0.000	9.08a ±0.000	52.83cde ±0.000
H	490.00c ±0.031	0.75a ±0.000	39.92c ±0.000	139.92b ±0.003	26.75ab ±0.000	3.25a ±0.000	46.75c ±0.000
I	370.00 ±0.001	0.75a ±0.000	27.25a ±0.000	69.25a ±0.001	20.58ab ±0.000	2.08a ±0.000	37.17b ±0.000

(Means in the same column with the same letters are not significantly different (P> 0.05)

* Locations with highest concentration of a particular metal

Table 2: Mean concentration of heavy metals ($mgkg^{-1}$) dry weight in sediment from Warri River at sampled locations

Locations	Heavy Metals						
	Fe	Cu	Pb	Cr	Ni	Zn	Cd
A	687.50a ±14.58	2.13a ±0.04	6.88a ±0.19	1.00a ±0.02	1.00a ±0.02	37.25a ±2.46	0.10ab ±0.00
B	726.38ab ±6.21	2.10a ±0.01	8.10ab ±0.01	1.10a ±0.03	1.05a ±0.58	60.50b ±0.83	0.13b ±0.00
C	746.43abc ±4.34	3.50ab ±0.06	10.45b ±0.83	2.03b ±0.02	0.98a ±0.02	68.65c ±1.07	0.08a ±0.00
D	826.35bcd ±12.34	5.48b ±0.13	33.00d ±4.33	2.90c ±0.03	4.78d ±0.04	87.50d ±1.38	0.11ab ±0.00
E	6782.50g* 80.44	22.50e* ±3.17	55.25g* ±3.46	6.28ef ±0.19	6.10e ±0.02	108.00e ±7.78	0.18c ±0.00
F	890.75d ±7.71	16.75d ±0.46	46.75f ±3.79	4.53d ±0.00	3.98bc ±0.08	89.15d ±5.57	0.18c ±0.00
G	864.00cd ±17.05	16.38d ±0.12	41.00e ±1.67	6.80ef ±2.23	3.50b ±0.06	88.25d ±6.46	0.70e ±0.00
H	4687.50f ±5.31	17.25d ±4.15	38.50e ±3.5	8.43f* ±0.06	6.83f* ±0.14	110.00e* ±4.46	0.72e* ±0.00
I	1032.50e ±17.12	10.50c ±0.83	22.00c ±1.67	6.08e ±0.03	4.20c ±0.15	90.50d ±2.58	0.56d ±0.00

(Means in the same column with the same letters are not significantly different ($p > 0.05$) * zone with highest concentration of a particular metal.

Heavy Metals in Water (of Warri River)

All heavy metals analyzed in the study differed significantly ($P<0.05$) between locations. The summary of the result also showed that the levels of all the metals have appreciated when compared to the base line studies of 1994[8]. The range of iron values of Egborge [8] base line studies reported (0.00001 – 0.0004 μgl^{-1}) were lower than those recorded in the present study (300.00 – 700.00 μgl^{-1}) (Table 2). The highest mean value of Fe was reported at the Jetty while the least was obtained at Agbarho. The copper level obtained in this study (0.75 – 17.58 μgl^{-1}) were higher than those in the 1994 baseline ($0.0092x10^{-3}$ μgl^{-1}) but also lower than (1000 μgl^{-1}) allowable limit by [15, 16] for safe drinking water.

The concentration of lead (Pb) detected in baseline studies ($0.002x10^{-3}$ μgl^{-1}) showed that the value in the present study (27.25-84.83 μgl^{-1}) were also very high. The values were higher than stipulated (50 μgl^{-1}) specified limit for safe drinking water [15, 16] at most locations (Jetty, main Warri market, steel plant and oil servicing facility). The 1994 baseline study recorded that there was no trace of Cr in water, whereas the present study recorded values with the range of 169.25 – 235.17 μgl^{-1}. The concentration of Cr in this study, were higher than the documented permissible limit 50 μgl^{-1} for safe drinking water [15, 16].

Levels of zinc ranged between 3.25 and 50.17 μgl^{-1}, which were also higher than 1994 studies (0.002×10^{-3} – 0.006 x 10-3 μgl^{-1}), but were lower than 5000 μgl^{-1} specified EEC [16]; WHO [15] for safe drinking water. The 1994 baseline had lower values of Cd (0.0008×10^{-3} μgl^{-1}) compared to those of this study (28.25 – 63.00 μgl^{-1}). Cadmium also exceeded the stipulated permissible limit 0.0005×10^{-3} μgl^{-1}) for safe drinking water [15, 16]. The result of this study, shows that the levels of heavy metals in the water (Warri River) had not only enormously appreciated but also exceeded stipulated permissible/allowable limit in four heavy metals (lead, chromium, nickel and Cadmium) documented by EEC [16] and WHO [15] respectively. This is due probably to the various anthropogenic activities post industrialization era in the Warri River environment till date.

4. CONCLUSION

Highlights from the study showed that the level of pollutants in effluents discharged by identified sources (Jetty, market, steel plant, oil industry facility, Udu bridge/market and Ugbolokposo dredging site) exceeded desired/allowable limits for heavy metals. However, the ability of the river to purify itself has been demonstrated by fairly lower values in water, compared to those recorded for sediment. Reasons could be because water analysis only indicates a short-term condition; several workers have advocated the use of fish and invertebrates, which produce relatively stable concentrations. To avoid further deterioration of water quality and aquatic resources of the Warri River, it is expedient to place the river under surveillance in view of the local community (especially the poor) who depend on the river for food fish and drinking.

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