



Poisonous Metal Levels in Sediment and Selected Biota in Coastal Waters of Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author FDS designed, supervised the research, wrote the introductory section, author MCO wrote the first draft and was involved in laboratory and statistical analysis of data. Authors OO and POO were involved in field sampling and managed the analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

Sediment and biota samples were collected biannually from the Bonny/New Calabar River Estuary in Niger Delta, Nigeria and analysed for poisonous metals of interest to the International Atomic Energy Agency (Pb, Cd, and Hg) using atomic absorption spectrophotometer A-500 and Direct Mercury analyser (DMA-80). Results for biota showed that Cd ranged from 0.003 to 0.558 ± 0.01mg/kg, Hg ranged from 0.014 ± 0.004 to 0.021± 0.010 mg/kg, Sediment: Cd ranged from 0.022 ± 0.001 – 0.82 ± 0.0002 mg/kg; Hg 0.010 ± 0.005 to 0.027 ± 0.009 mg/kg. Lead was below the detection limit of the instrument both in biota and sediment. The concentrations of the respective poisonous metals were within the permissible limit of the World health organization. The study showed high concentration of Cd in Crayfish compared to other seafood. The bioaccumulation factor showed higher level of Hg compared Cd while the Analysis of variance for the three stations did not show any significant variation among the three stations. Regular monitoring and comparison of level of contamination with regulatory bodies are advocated to prevent the concentration of the metal contaminants from getting to an alarming level.

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1. INTRODUCTION

Nigeria's coastline of approximately 853 Km borders the Atlantic ocean and is situated between (latitude 4°10' - 6°20' N and longitude 2°45' - 8°35'). These waters fall within the Guinea Current large Ecosystem (GCLME), a shared resource by all the coastal west African countries. The area is said to be one of the world's most productive marine ecosystems on account of its rich fishery resources oil and gas reserves, minerals and marine biodiversity.

Consequently, it provides several goods and services for the electronic development of the area and the general wellbeing of its inhabitants. Despite its natural endowment, the coastal zone is home to most of the poor which earn their livelihood from the resources found there. Unfortunately, as a result of over exploitation, environmental degradation population increase and pollution economic dislocation is said to be widespread.

In addition, the coastal area has suffered debilitating environmental but most especially from the oil industries, manufacturing and municipal discharges [1]. The increased discharge of contaminants in the receiving water has triggered undesirable effects on the coastal waters making it imperative to carry out monitoring programmes [2]. This is more so in developing countries where environmental protection laws are either weak or unenforced.

As a result, these waters have been reported to contain elevated levels of several toxic and hazardous substances including heavy metals [3]. It is further realized that a knowledge of the distribution of these pollutants in water and sediment plays a major role in detecting their sources [4].

Therefore, sediment and biota can be used to monitor heavy metal pollution and serve as bio-indicators of water quality respectively [5]. The major sources of poisonous metal pollution in Nigeria waters include: mining, petroleum exploration, agricultural waste disposal, pesticide application and metal-containing fertilizers among others.

With regards to mercury, its levels have increased significantly in the biosphere over the last few decades necessitating the action to reduce its introduction and limit human exposure.

Although information/data on metal profile in sediment and biota are relatively few, available figures indicate that their levels are appreciable in both biota and sediment.

In the Lagos Lagoon for example, Fodake [6], reported levels of 0.10-0.40 ppm in whole minced fish from the Lagos Lagoon. Kakulu and Osibanj [7], found Hg levels in the neighbourhood of 10 mg/kg in fish from the Niger Delta.

Researchers such as Onojake et al. [8], reported that the concentrations of some heavy metals in some seafood (Oyster, Mullet and Crab) in the Bonny/New Calabar River Estuary, have the following ranges: Zn (0.24 - 1.28 mg/kg), Pb (0.23 - 0.30 mg/kg), Cd (0.05 - 0.09 mg/kg), Co (0.20 - 0.28 mg/kg), Cr (1.17 - 2.62 mg/kg), Cu (0.45- 4.89 mg/kg), Fe (23.50 - 35.75 mg/kg) and Ni (0.06 - 0.25 mg/kg). The rank profile of the heavy metals in the seafood investigated according to their mean values were Fe>Cu>Cr>Zn>Pb>Co>Ni>Cd. A separate study carried out by Babatunde et al. [9] on the concentrations of heavy metals like Ca, Mg, K, Zn, Pb, Cd, Co, Cr, Cu, Fe, Ni and Na in the sediment, seawater, fish and crab of the Bonny/New Calabar River Estuary observed the order of magnitude of accumulation of metals in fish from water was Co>Cr>Ni>Mg>Zn>Pb>K>Na>Ca>Cu>Cd>Fe and in crab the accumulation of metals was in the order of magnitude Ni>Pb>Co>Cd>Cu>Mg>K>Cr>Na>Fe>Zn>Ca. The order of magnitude of metal accumulation in fish from sediment was in the sequence Zn>Co>Pb>Ni>Cr>Na>Fe>Mg>K>Ca>Cu>Cd while the pattern in crab was Fe>Ni>Pb>Na>Cu>Zn>Co>Cd>Mg>K>Cr>Ca.

Similarly, values of metals recorded in other Nigerian water bodies indicates low metal concentrations Cu>Cr>Pb>Cd [10]. In the sediment, Cu had 0.13 mg/kg while Pb, Cr and Cd gave values of 0.992, 0.305 and 0.000 mg/kg respectively. In the biota the catfish, *clarias gariepinus* showed values as high as Pb (1.832 mg/kg), Cr (1.33 mg/kg) while Cd was not detected.

However, all the metal values in fish were found to be below the permissible levels. The concentration factor of the metal in the liver and gills indicated that Pb (1.832 mg/Kg) was recorded in the gills and Cr (1.33mg/kg) was observed in the liver of the catfish.

The aim of this article is to evaluate the concentration of some poisonous metals such as cadmium, lead and mercury in sediment and biota of the Bonny/New Calabar River Estuary and establish the pollution level of the Estuary.

2. MATERIALS AND METHODS

2.1 Description of the Study Area

The study area stretched from the lower reach of Bonny River at Bonny town by the Peterside community to Choba town in the upper reach of the New Calabar River (Fig. 1). The entire stretch from the Bonny to Choba is largely influenced by tidal cycles, about 20 km, and lies between longitude 7°00" to 7°15"E and latitude 4°25" to 4°45"N. The tidal amplitude is generally high and above 2m at the Bonny terminal jetty. However, the water level increases and decreases depending on the lunar cycle. The fan-shaped Niger Delta, which is the third-largest in the world after the Mississippi (USA) and Pantanal (South-West Brazil), lies between latitudes 4° and 6° north of the equator and longitudes 5° and 9° east of the Greenwich Meridian. The predominant coastal vegetation of the Bonny river which results from tidal influence - is the mangrove, whose main species are the red and white mangroves and which form more than nineteen percent (19%) of the saline swamps [11]. The white mangroves occur in scattered formation among the red mangroves and thrive in less water-logged places. The Bonny river system is characterized by the interaction of an estuarine and highly saline seawater located seaward of the river mouth (typical of the Niger Delta coastal region), and influenced by tide- and wind-driven surface currents. The coastal areas of Bonny River play host to many fishing settlements while the river itself is a major navigational channel for oil vessels, countless outboard engine boats, maritime and oil-related activities.

2.2 Sample Collection and Data Analysis

Grab bottom sediment and biota samples were collected bi-annually. The samples were transported to the Laboratory and stored frozen. The samples were later oven-dried to a constant weight at 105°C, ground to powder and then sieved through a 650 µm stainless sieve. Ten (10) grams of the sieved sediment was weighed into an acid-washed plastic polythene bottle and digested in a 100 ml solution of conc. HNO₃ and

HCl acids (1:1 ratio). The mixture was vigorously shaken in a mechanical shaker and then filtered through Whatman filter paper No 42 as reported in Onojake et al. [8]. All acid used were of analytical grade quality and control was assured by the use of procedural blanks and spikes. All samples were run in triplicates and the relative standard deviation for the triplicate analysis was less than 10%. Standard solutions of the metals were prepared from their 1000 ppm stock solutions for calibration.

The concentrations of the metals (Pb and Cd) were determined using a Varian Atomic Absorption Spectrophotometer (Spectra AA - 500). As part of Quality assurance/ Quality control measure in the laboratory, a certified reference material (CRM) was analysed along with the samples (Sediment and biota) while the variation in comparison with certified values and the standard deviation noted. The calibration curve showed a high level of dependency of the AAS with established value of 0.999 for Pb and Cd.

Analysis of Hg does not require any sample preparation is required as Direct Mercury analyser (DMA-80) was used. The samples were weighed on the sample boat and placed on the tray. The operating principle of the instrument was based on sample thermal decomposition and atomic adsorption detection.

Metal concentrations in biota were compared using multiple bar charts Fig. 2.

3. RESULTS AND DISCUSSION

3.1 Heavy metals in Biota and Sediment

The world health organisation consider Cd, Pb and Hg as major environmental pollutants that are harmful to health. Pollution with these poisonous metals, if allowed to continue unabated will affect sources of food in the foreseeable future [12]. The results for the Bonny/New Calabar River Estuary samples for Cd, Pb and Hg values from three representative sampling stations 1, 2 and 3 are presented in Table 1. The table of results showed that Pb was below detectable limits by AAS. Generally, the concentration of Cd and Hg in the biota samples which includes crayfish, croaker, catfish, mullet, prawn and sardine has the following values: Cd ranged from 0.003 – 0.558 mg/kg; Hg ranged from 0.014 – 0.021 mg/kg. The concentrations of Cd and Hg are within the permissible level of 0.5

mg/kg for Cd and 0.3 mg/kg for Hg [12]. Cd has been found at elevated levels in seafood such as crustacean and shellfish especially in association with Zn. The main source of Cd in food and water is contaminated water used for irrigation purposes [12]. However, reports from past research showed that sources of direct pollution due to man's activities can have an effect on the level of Hg found fish in estuaries and coastal areas. Natural geological contamination of

individual lakes, oceans and estuaries can be due to underlying mineral deposits containing mercury which may leach into the water and sediment under natural circumstances. Nonetheless, mercury and its related compounds that enter the marine environments can be absorbed through biological or chemical processes and be accumulated by aquatic organisms [12].

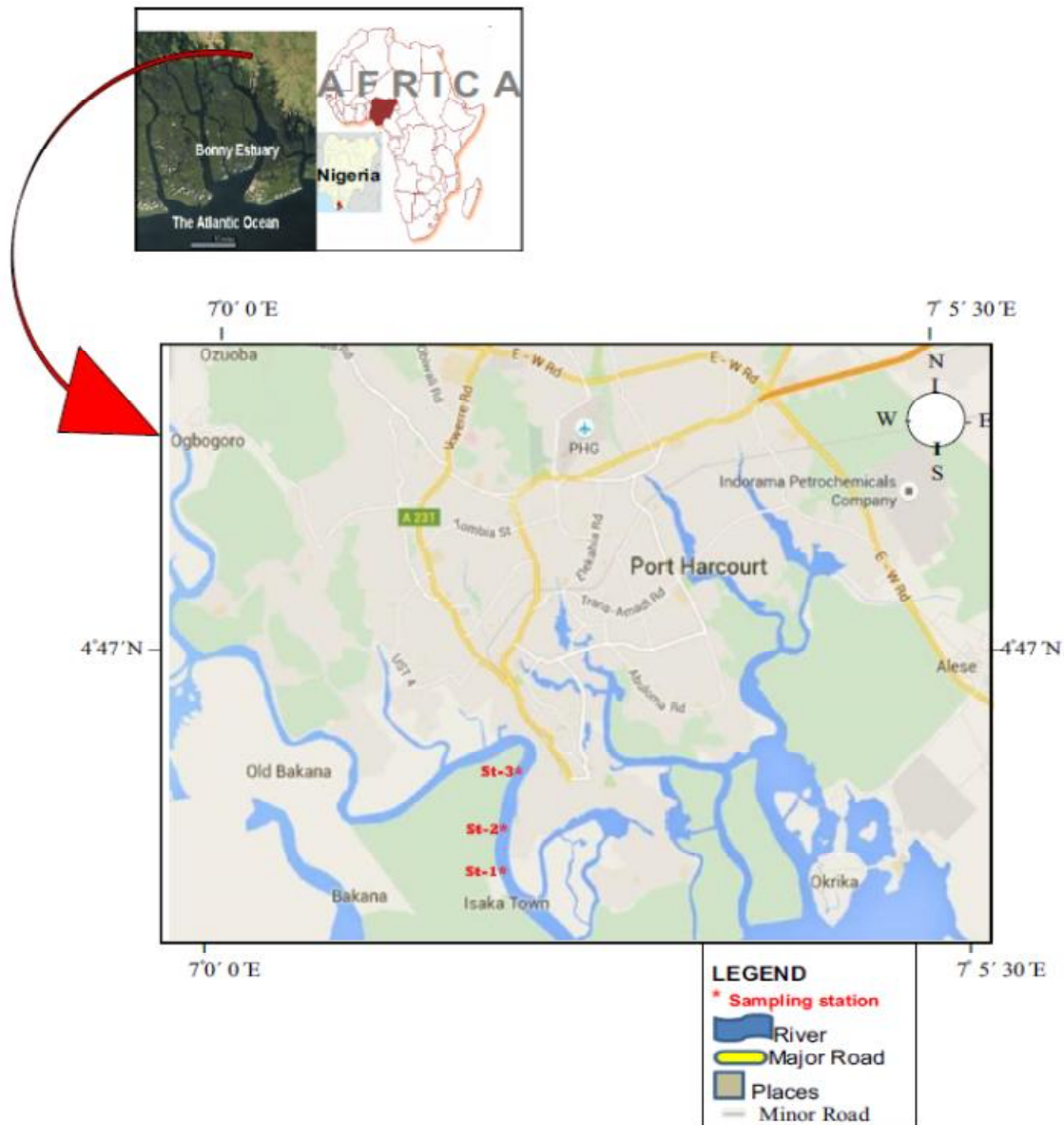


Fig. 1. Map of the study area showing the three sample collection stations

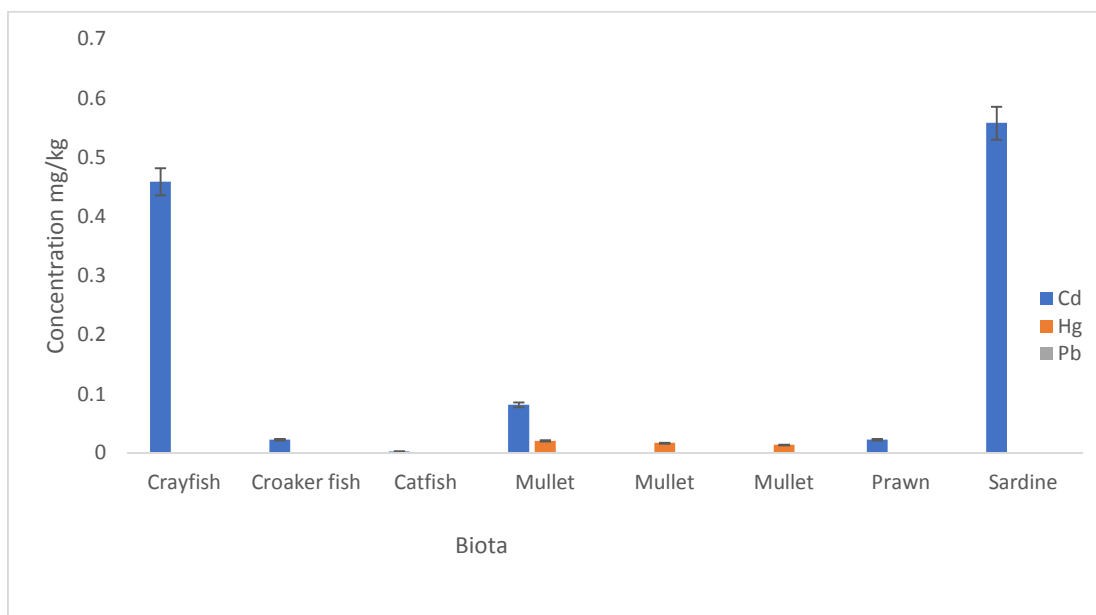


Fig. 2. Comparison of poisonous metals in different biota

Table 1. Results of the Poisonous metals for biota of the bonny/new calabar River Estuary

BIOTA (mg/kg)	Cd	Hg	Pb
Crayfish	0.459 ± 0.0020	NA	ND ± 0.0004
Croaker fish	0.023 ± 0.0042	NA	ND ± 0.0014
Catfish	0.003 ± 0.0046	NA	ND ± 0.0004
Mullet	0.082 ± 0.0035	0.021 ± 0.010	ND ± 0.0001
Mullet	NA	0.017 ± 0.007	NA
Mullet	NA	0.014 ± 0.004	NA
Prawn	0.023 ± 0.0045	NA	ND ± 0.0002
Sardine	0.558 ± 0.0057	NA	ND ± 0.0001

NB: NA = NOT ANALYZED; ND = NOT DETECTED

The obtained values of the concentration of poisonous metals in sediment are Cd: 0.022 – 0.100 mg/kg; Hg 0.010 – 0.027 mg/kg (Table 1). The mean concentrations of Cd was higher in station 3 and least in station 2 with values of 0.100 and 0.022 mg/kg. The concentration of mercury was highest in station 1 and lowest in station 2 with values of 0.027 and 0.010 mg/kg. Pb was below detectable limit of the AAS. The mean concentration of poisonous metals in sediment for the three stations are ranked in the following order Cd>Hg>Pb. Mean level of Cd and Hg were higher in sediments compared to biota except for Cd in crayfish with Cd level of 0.459 ± 0.0020 mg/kg (Table 1). The assertion corroborates with most of the research findings of other workers that sediments customarily serve as sink for many pollutants including heavy metals [13]. Consequently, sediments contaminated by heavy metals constitute a threat

to the health of aquatic organisms [14,15]. The trend of metals in order of ranking in sediment is Cd > Hg > Pb.

3.2 Statistical Analysis of Variance

Results of Cd and Hg for three stations were subjected to single-factor analysis of variance (ANOVA) using Microsoft Excel software. The results are shown in Table 2. The result of the single-factor ANOVA indicates that the sample stations did not show any significant effect on the variations in the group of means for the two poisonous metals. The results showed that between-sample mean square is less than the within-sample mean square. The analysis revealed that the value for (F= 2.4343 < Fcrit = 7.70). The effect of interaction of the metals and the stations were not too significant comparing the difference between F and Fcrit [16,17]. This

Table 2. Results of the poisonous metals for sediment of the bonny/new calabar River Estuary

SEDIMENT(mg/kg)	Cd	Hg	Pb
ST1	0.55 ± 0.0014	0.027 ± 0.009	N/D ± 0.0019
ST2	0.14 ± 0.0060	0.010 ± 0.005	N/D ± 0.0008
ST3	0.82 ± 0.0002	0.015 ± 0.008	N/D ± 0.0026

ST1; ST2 AND ST3= STATION 1, 2 AND 3

Table 3. Single factor ANOVA for Cd and Hg for the sediment samples

SUMMARY						
Groups	Count	Sum	Average	Variance		
Cd	3	0.164	0.054666667	0.001641333		
Hg	3	0.052	0.017333333	7.63333E-05		

ANOVA						
Source of variation	SS	df	MS	F	P-value	F crit
Between Groups	0.002091	1	0.002090667	2.434310111	0.19372251	7.708647
Within Groups	0.003435	4	0.000858833			
Total	0.005526	5				

DF degrees of freedom, F Factor mean square, SS sum of square, MS mean square (P 0.05)

showed that the poisonous metals under investigation were immobile in the estuary/river despite the fact that a lot of activities are going on in the study area.

4. CONCLUSION

The levels of poisonous metals in biota and sediment analysed showed that all metals were below the permissible limit stipulated by the WHO. The concentrations of the metals were higher in sediments compared to biota which is a confirmation of the assertion that sediments customarily serve as sink for many pollutants including heavy metals. Pb was below the detection limit of the instrument (AAS). The calculated bioaccumulation factor (BF) suggested higher bioaccumulation rate for Hg than Cd. The one-way ANOVA for the poisonous metals did not show any statistical difference for the three stations. It is necessary for industrial effluent discharges and activities that introduce metal contaminants to be monitored to ensure that the critical limits are not exceeded.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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