



# The concentration of heavy metals in the sediments of the river nun estuary, around Akassa, Niger Delta, Nigeria

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Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 23<sup>th</sup> April 2022, revised 12<sup>th</sup> October 2022, accepted 19<sup>th</sup> March 2023

## Abstract

Levels of the heavy metals lead (Pb), cadmium (Cd), nickel (Ni), zinc (Zn), and manganese (Mn) were analyzed in the sediments of the River Nun estuary. This was done in order gauge the impact of anthropogenic inputs such as pesticides, fertilizers, oil spillage and other industrial and anthropogenic wastes disposal, especially at the coastal parts of the region on bottom sediments. Three sampling Stations were chosen for the purpose of this research. Station 1 (Buo-Ama Creek) was established close to the entrance of Buo-Ama creek, in the Nun River estuary. Station 2 (Erewei-Kongho) was established along one of the tributaries of the Nun River estuary around Erewei-Kongho. Station 3 was established in Ogbokiri. Soil samples were collected with the aid of a soil auger and a galvanized metal core cylinder from three (3) sampling stations along a transect running from the low intertidal level (LIL), through the mid intertidal level (MIL) to the high intertidal level (HIL). Soil samples were analysed in the laboratory using the method of Atomic Absorption Spectrophotometer (AAS). Means and standard deviations were calculated for all the measured parameters. A one-way ANOVA was employed at the 95% confidence limit to test for differences across stations in the heavy metals. Turkey HSD post HOC test was also employed to separate means and identify where variability and similarities exist. This was aided by the SPSS 20.0 statistical tool kit. The result shows that Pb has the highest concentration, followed by Zn, Ni, Cd, and Mn respectively. The lowest values of all metals were observed at station 2, while the highest concentrations of metals were recorded at sampling stations 1. The results show that the value of Pb was highest in station 1 ( $1.347 \pm 0.001$ ), followed by Station 3 ( $1.24 \pm 0.001$ ). Station 2 had the least mean value of Pb ( $0.884 \pm 0.001$ ). Cd showed similar patterns across the three sampling stations 1, 2 and 3, with the values  $0.068 \pm 0.002$ ,  $0.046 \pm 0.001$ , and  $0.054 \pm 0.002$  respectively. Ni also presented slight difference across the three sampling stations. Concentration of Zn were higher in station 1 and 2 ( $1.265 \pm 0.002$  and  $1.038 \pm 0.002$ ), than in station 3 ( $0.725 \pm 0.001$ ). All metal concentration was however lower than the international permissible limit. The concentrations of Mn were also observed to present a similar pattern across the sampling stations. There is a significant difference ( $P < 0.05$ ) in all heavy metal parameters across all stations. Heavy Metal Concentrations were found to decrease with increasing distance from the river mouth, suggesting that anthropogenic inputs, related to agricultural and domestic discharge into the river, are the major sources of heavy metals in the river sediments. Land based activities therefore have a profound effect on aquatic ecosystem stability and health.

**Keywords:** Heavy Metals, Sediments, River Nun, Estuary, Akassa, Niger Delta, Nigeria.

## Introduction

Heavy metals are metals with high density or high relative atomic weight. They serve useful purposes in our everyday lives and are constituents of both natural and synthetic compounds. They may also result from the activities of oil exploration and exploitation.

However, they are considered a serious threat due to their environmental persistence, toxicity and ability to be incorporated into food chains<sup>1</sup>. They enter these aquatic systems mainly through natural inputs such as weathering and erosion of rocks and anthropogenic sources including urban, industrial and agricultural activities, terrestrial runoff and sewage disposal<sup>2</sup>.

In the aquatic environments, heavy metals are generally attached to particulate matter, and eventually settle down and become incorporated into bottom sediments. Therefore, surface sediments are the most important reservoir or sink of metals and other pollutants in aquatic environments<sup>3</sup>.

Heavy metals in soils and sediments are difficult to migrate due to their long residual time, strong concealment, toxicity, and other characteristics. Consequently, they may be absorbed by crops or fishes through benthos, enter the food chain, or migrate into water and atmosphere, thus threatening the health and reproduction of humans and animals<sup>4,5</sup>. Therefore, the assessment of heavy metal pollution in river sediments and soils has become a urgent and acutely important research topic.

Apart from the obvious exploration and exploitation of oil in the Niger Delta that leads to the aforementioned heavy metal pollutants, other anthropogenic, agricultural and domestic activities that take place in the Niger Delta also leads to the release of harmful substances such as heavy metals into the environment, especially the aquatic environment with dire consequences.

The River Nun with its tributary consists of a rich collection of flora and fauna constituting a unique tropical biodiversity<sup>6</sup>. The river's shoreline, tidal, intertidal and benthic ecosystems is subjected to oil spills resulting from the activities of pipeline vandalism, makeshift crude oil refineries, known locally as Kpo fire and other anthropogenic pollutants. These pollutants in the environment, adversely affects the benthic community in the estuary, resulting to the decline in the population of aquatic organisms including some of the benthic macro invertebrates. Intertidal organisms such as periwinkles and mudskipper are very vulnerable to oil pollution since their habitat are susceptible to coating with oil and may be smothered in the event of heavy oil drifting ashore<sup>6</sup>.

The increasing load of heavy metals cause imbalance in aquatic ecosystems and the biota growing under such habitats accumulate high amounts of heavy metals (Cu, Zn, Cd, Cr, Ni, etc.) which in turn, are being assimilated and transferred within food chains by the process of magnification<sup>7</sup>. Simply put, heavy metals in sediments will result in loss of fauna and health dysfunction in Human. There is a need therefore to monitor heavy metal characteristics in sediments in the River Nun. This will provide a basis for environmental appraisal, protection and remediation.

## Materials and methods

**Description of Study Area:** The River Nun estuary is situated around Akassa Kingdom in Brass Local Government Area of Bayelsa State, Nigeria. The River Nun estuary is connected to several creeks, inlets, and canals, serving as drainages and

navigation routes in the area. The River Nun estuary meets the Atlantic Ocean at the southernmost tip of Nigeria in Bayelsa State in Nigeria. The Brass River estuary is at the Eastern part of the River Nun estuary while the Sangana River estuary is at the Western side and it opens up into the Atlantic Ocean at its southern part (Figure-1).

The Estuary is located on latitude of 40:20" and 40: 17' 'N, longitude of 60:49" and 40:55"E<sup>6</sup>.

**Designation of Sampling Stations: Sampling Station 1 (Near Buo-Ama Creek):** Station 1 (Buo-Ama Creek) was established close to the entrance of Buo-Ama creek in the River Nun estuary. It is located on a latitude of N4<sup>0</sup>20'59.6472" and a longitude of E6<sup>0</sup>2'48.3036". The site was once impacted by the activities of the makeshift crude oil refineries before its abolition. The soil was completely loaded with crude oil, both at the surface and absorbed by the sediments. This station has a mixture of palm and native mangrove vegetation and the soil is sandy at the high intertidal zone, the mid intertidal zone and the low intertidal zone. The intertidal zones of this station have a steep topography. The sediment samples were collected in this station for analysis.

**Sampling station 2 (Erewei- Kongho):** The sampling station termed, station 2 (Erewei- Kongho) was established along one of the tributaries of the Nun River estuary around Erewei-Kongho. As shown by the Global Positioning System (GPS), the coordinates of station 2 are latitude N4<sup>0</sup>20'35.0628" and E6<sup>0</sup>3'0.738". The site was once also highly polluted by crude oil before the abolition of the makeshift oil refinery. The soil was completely loaded with crude oil, both at the surface and absorbed by the sediments. This station also has a mixture of palm and native mangrove vegetation and the soil is sandy at the high intertidal zone, the mid intertidal zone and the low intertidal zone. The intertidal zones of this station have a steep topography. The sediment samples were collected in this station for analysis.

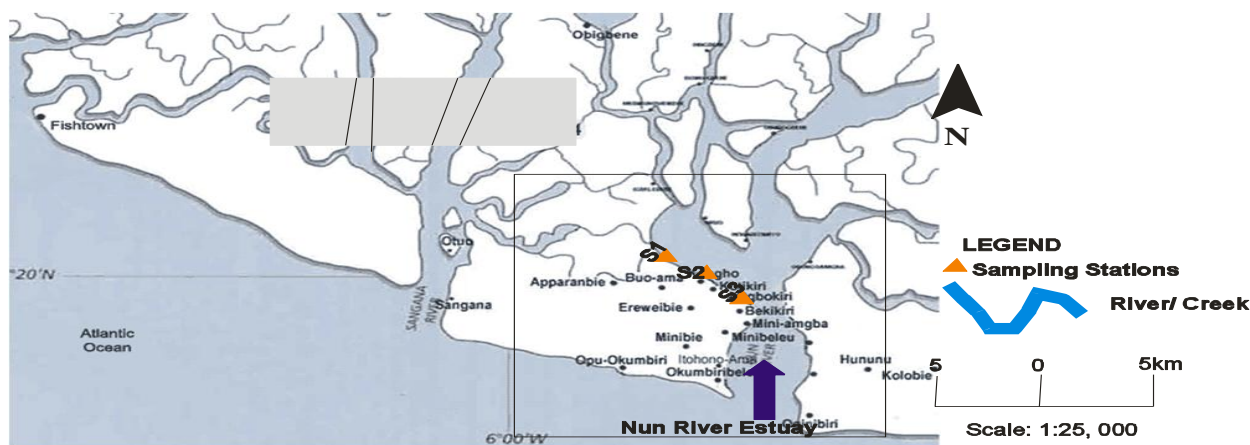


Figure-1: Map showing the Nun River Estuary in Bayelsa State and its tributaries.

**Sampling station 3 (Ogbokiri):** Sampling Station 3 was established in Ogbokiri. This sampling station is situated on a mud flat. It is also located along one of the tributaries of the Nun River estuary, with GPS coordinates of latitude N4<sup>0</sup>19'46.8048" and longitude E6<sup>0</sup>3'49.3596". The site was also polluted by crude oil before the abolition of the makeshift oil refinery. Its mangrove vegetation is dominated by black mangroves and it's a sandy-mould plain, with its sediments loaded with oil pollutants. The sediment samples were also collected for analysis.

**Sample collection:** The soil samples were collected from three (3) sampling stations along a transect running from the low intertidal level (LIL), through the mid intertidal level (MIL) to the high intertidal level (HIL). The soil samples were obtained with the aid of a soil auger and a galvanized metal core cylinder (7.2cm high and 5.8cm internal diameter) by pushing the auger into the soil until it levelled with the soil surface. A section of the soil was then excavated to allow removal of soil auger with intact soil out. The collected samples were kept in appropriately labelled polythene bags. Soil and atmospheric temperatures were also measured *in situ* with mercury in glass thermometer. The samples were then transported to the Central Research Laboratory of the Niger Delta University, Wilberforce Island, Amassoma Bayelsa State, Nigeria, for analysis.

**Laboratory Analysis of Heavy Metals in Sediment Samples:** Sediment samples were brought into the lab and oven dried. 1g each of the air-dried sediments was acid-digested with conc. Nitric Acid and Sulphuric acid in the ratio of 1:3. The digestion continued until the solutions are clear. 20ml of distilled water was added to the digest to dilute the acid in the digest. This was

then filtered into 100ml volumetric flask and made up to the mark with distilled water.

These were transferred into plastic containers and sent to the laboratory for the Atomic Absorption Spectrophotometer (AAS).

**Data Analysis:** Means and standard deviations were calculated for all the measured parameters. A one-way ANOVA was employed at the 95% confidence limit to test for differences across stations in the heavy metals. Turkey HSD post HOC test was also employed to separate means and identify where variability and similarities exist. This was aided by the SPSS 20.0 statistical tool kit

### Results and discussion

**Results:** The results obtained from the analysis of heavy metals in the sediments of the River Nun estuary in the study are given in Table-1 and 2, and Figure-2. Table-1 and 2, and Figure-1 present the concentrations of the heavy metals lead (Pb), cadmium (Cd), nickel (Ni), zinc (Zn), and manganese (Mn) in the sediments along the three tidal levels across the three sampling stations. The concentrations of the five heavy metals analysed fluctuated in wide range, depending on the sampling station and the heavy metal in question.

The mean ( $\pm$ SD) concentrations of the heavy metals analysed across the three sample stations are 0.884 $\pm$ 0.001 - 1.347 $\pm$ 0.001 for lead (Pb), 0.046 $\pm$ 0.001 - 0.068 $\pm$ 0.002 for cadmium (Cd), 0.109 $\pm$ 0.001 - 0.244 $\pm$ 0.001 for nickel (Ni), 0.725 $\pm$ 0.001 - 1.265 $\pm$ 0.002 for zinc (Zn) and 0.027 $\pm$ 0.001 - 0.043 $\pm$ 0.001 for manganese (Mn) along all the tidal levels in all the sampling stations.

**Table-1:** Tidal Heavy metal concentrations in Sediments of the River Nun estuary across the three sampling stations.

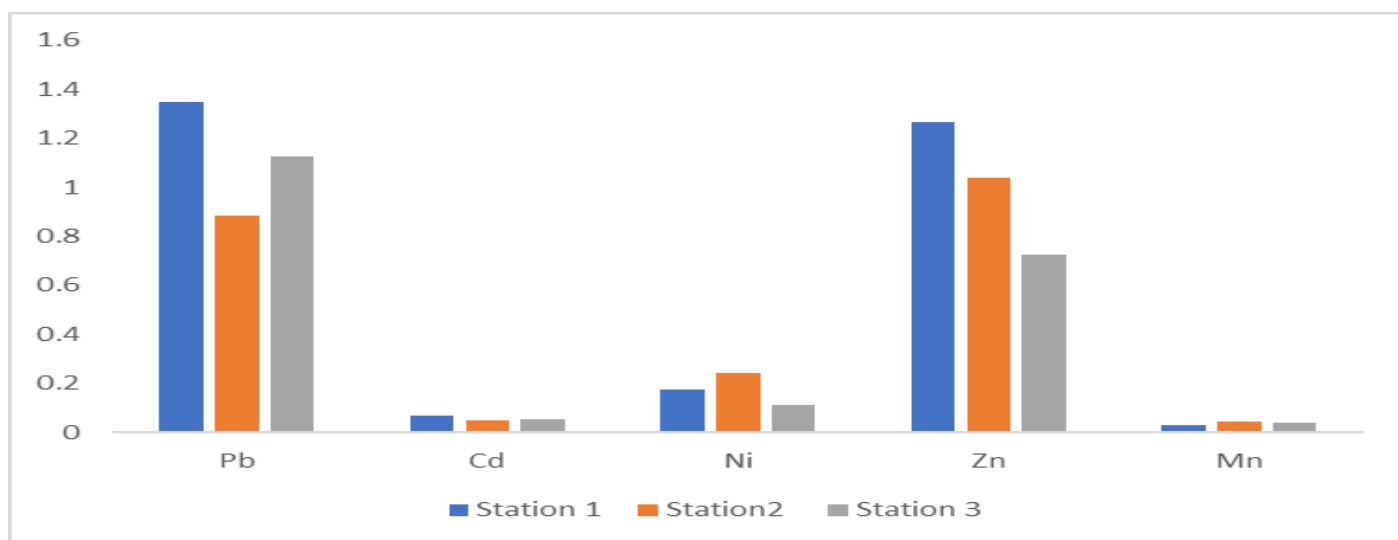
Sampling Stations	Intertidal Levels	Heavy Metal Concentrations (Mg/kg)				
		Pb	Cd	Ni	Zn	Mn
Station 1	LIT	1.346	0.068	0.172	1.264	0.026
	MIL	1.348	0.067	0.174	1.267	0.028
	HIL	1.347	0.070	0.173	1.265	0.027
Station 2	LIL	0.883	0.045	0.245	1.038	0.042
	MIL	0.885	0.047	0.243	1.040	0.044
	HIL	0.884	0.046	0.244	1.037	0.043
Station 3	LIL	1.123	0.052	0.109	0.724	0.036
	MIL	1.125	0.054	0.110	0.726	0.038
	HIL	1.124	0.055	0.108	0.725	0.038

Key: LIL: Low intertidal level, MIL: Mid intertidal level, HIL: High intertidal level.

**Table-2:** Mean concentrations of Heavy Metals in the Sediments of the River Nun.

Heavy Metal (Mg/kg)	Sampling Station		
	Station 1	Station 2	Station 3
Pb	*1.347 <sup>a</sup> ±0.001	0.884 <sup>b</sup> ±0.001	1.124 <sup>c</sup> ±0.001
Cd	0.068 <sup>a</sup> ±0.002	0.046 <sup>b</sup> ±0.001	0.054 <sup>c</sup> ±0.002
Ni	0.173 <sup>a</sup> ±0.001	0.244 <sup>b</sup> ±0.001	0.109 <sup>c</sup> ±0.001
Zn	1.265 <sup>a</sup> ±0.002	1.038 <sup>b</sup> ±0.002	0.725 <sup>c</sup> ±0.001
Mn	0.027 <sup>a</sup> ±0.001	0.043 <sup>b</sup> ±0.001	0.037 <sup>c</sup> ±0.001

Mean±SD = Standard Deviation. Means with same superscript on the same row are not significantly different (P=0.05).



**Figure-2:** Heavy Metals in the Sediments of the River Nun Estuary.

**Table-3:** International permissible limits for heavy metals in water and sediments.

	Cd	Zn	Pb	Cu	Cr	References
Water (mg/l)	0.01	5	0.05	-	0.05	8
	0.001-0.05	0.005-0.05	2-20	0.05-0.15	0.1-0.5	9
	0.001-0.05	-	-	-	-	10
	-	-	10	-	0.05	11
	-	-	-	-	50	12
Sediment (mg/kg)	0.05	-	0.2	-	0.1	13
	0.05	-	0.2	-	-	14
	0.03-0.3	-	0.3	-	-	15
	0.03-0.3	50-300	2-20	20	0.5	9

**Discussion:** The increasing order of concentration of these metals in sediments is as follows: Pb > Zn > Ni > Cd > Mn. Generally, most of the metals show a similar concentration pattern along the study stations. However, there is a significant difference ( $P < 0.05$ ) in all the metal concentrations in all the sample stations. All the metals show a high availability in sediments in all the study stations. The preponderance of these metals can be explained by their mode of availability in nature.

Pb displayed the highest concentration in sediments in this study. The high concentration of Pb may be due to the fact that it is a very soft metal and is used in pipes, drains, and soldering materials for many years. Furthermore, millions of homes built before 1940 still contain Pb (e.g., in painted surfaces) and Akassa contains a plethora of houses built by colonialist around that era. It may also be as a result of Pb used for batteries, cable coverings, plumbing and fuel additives. Other uses are as paint pigments and in PVC plastics, x-ray shielding, crystal glass production, and pesticides. These activities and objects are indeed present in the study area.

The high Zn presence may be due to the manufacture of galvanized iron, bronze, white paint, rubber, glazes, enamel glass, paper, as a wood preservative ( $ZnCl_2$ , fungicidal action), petrochemicals, and fertilizers and in steam generation power plants<sup>16</sup>. Also, some zinc is released into the environment by natural processes, but most comes from activities of people like mining, steel production, coal burning, and burning of waste. Furthermore, most of the zinc in soil stays bound to soil particles as the metal has a low geo-mobility and remain bound for extended periods. Moderately increased zinc concentrations in water also stem from the release of zinc from drainage pipes due to corrosion. Also, abandoned metal parts and effluents from industrial and commercial activities such as fishing (nets, hooks, etc) shipping, timber processing, outboard engine boats, domestic activities (such as building materials, solid wastes), run offs, tidal and wave actions may influence the levels of metals in aquatic ecosystems.

Metal contents were found decreasing with the increasing distance from the river mouth. The lowest values of all metals were observed at station 2. This can be explained by the fact that this station has less anthropogenic activities when compared to the other stations. However, the highest concentrations of metals were recorded at sampling stations 1 and 3, which are severely impacted upon by the makeshift illegal artisanal crude oil refineries prevalent in the vicinity. Heavy metals in the sediments of the River Nun estuary obtained in this current study compares with that obtained from previous studies. The concentration of Pb ranged from  $0.884 \pm 0.001$  to  $1.347 \pm 0.001$ , which when compared to the result reported by Obokoro<sup>17</sup> in a similar study in the River Nun estuary was significantly higher, as he reported the concentration of Pb to be  $0.001 \pm 0.001$  to  $0.02 \pm 0.002$ , but is significantly lower than the value of  $7.00 \pm 10.04$  during the dry season and  $6.42 \pm 9.03$  during the wet season, recorded by Chukwujindu *et al.*<sup>18</sup> in a similar study in Ase River, Niger Delta, Nigeria.

Also, Cd reported mean values ranging from  $0.046 \pm 0.001$  to  $0.068 \pm 0.002$ . Ni has values ranging from  $0.109 \pm 0.001$  to  $0.244 \pm 0.001$ , Zn has values ranging from  $0.725 \pm 0.001$  to  $1.265 \pm 0.002$  and Mn reported mean values ranging from  $0.027 \pm 0.001$  to  $0.043 \pm 0.001$  across all the sampling stations, which are respectively significantly higher than those reported by Obokoro<sup>17</sup>, but were lower than the values reported by Chukwujindu *et al.*<sup>18</sup>. However, the results obtained in the current study are significantly lower than those reported by Chukwujindu *et al.*<sup>18</sup>. The results obtained were in conformity with those recorded by Ideriah *et al.*<sup>19</sup> in a similar study conducted along the Abonnema shoreline, Nigerian. Furthermore, the mean concentration of Pb, Ni and Cd exceeded the background values (average shale) as proposed by Turekian and Wedepohl<sup>20</sup>. The mean concentration of Zn and Mn were less than average shale values.

## Conclusion

This study x-rayed the presence of selected heavy metals in sediments of the River Nun around the Akassa axis of the river. This was undertaken to gauge the amount of these metals in sediments and by implication, the threat it possess to both aquatic organisms and man in the food chain. Three sample stations were selected and samples taken at different tidal levels in the study stations. Result from the study reveals that the concentrations of the heavy metals across sample stations followed this trend: Pb > Zn > Ni > Cd > Mn. It was also observed that metal concentrations reduced in the stations as the distance of the station was far removed from the shore. There were significant differences in heavy metal concentration between all study stations. The concentration of metals was higher than the findings of some similar studies and also lower than the findings of others.

It can be concluded that land based activities near river catchments greatly affect heavy metal levels of receiving water bodies. Although the sediment in the River Nun estuary is mildly contaminated with heavy metals especially Pb, Cd, Ni, Zn and Mn, care should be taken to prevent further contamination as the erroneous believe that sediments is the ultimate inexhaustible sink for heavy metals in the aquatic system may result in dire environmental and health consequences to man.

## Acknowledgement

We hereby thank the Laboratory Technologist in the Department of Chemical Sciences, Niger Delta University, Amassoma, Bayelsa State, Nigeria, for the use of their facility and conduct of analysis.

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