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Assessment of heavy metals concentrations in the upper reaches of Bonny River, Niger delta, Nigeria

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ABSTRACT

Heavy metals concentrations (Lead, Nickel and Cadmium) in different media of the Upper Reaches of the Bonny River, Niger Delta, Nigeria, were sampled and analyzed. Samples of surface water, sediment and swimming crab (*Callinectes amnicola*) were collected from three different stations from January to June. Heavy metals in the different media were analyzed using Atomic Absorption Spectrophotometer (API-RP 45). The laboratory analysis results showed that the concentration of the selected heavy metals in the various media had values ranging between: *Callinectes amnicola*; Lead 0.10-1.5mg/l, Nickel 0.20-0.90mg/l and Cadmium <0.01mg/l. In Sediments; Lead 0.22-0.50mg/l, Nickel 0.30-0.83 and Cadmium <0.01mg/l. Surface water results showed; Lead<0.01-0.09mg/l, Nickel 0.10-0.50mg/l and Cadmium <0.01mg/l. Seasonal variations were also observed in heavy metals concentration. Lead had high concentrations during the wet season as compared to the dry season in *Callinectes amnicola*, sediment and surface water. Nickel had values high in *Callinectes amnicola* and sediments during the dry season and Cadmium had values <0.01 across seasons. Lead had high Bioaccumulation Factor across rainy and dry seasons, Nickel had low Bioaccumulation Factor and Cadmium had values with Bioaccumulation Factor of 1 which implies that Cd had no influences across seasons.

Keywords: Heavy metals, *C. amnicola*, Sediment, Surface water and Bonny River

INTRODUCTION

Pollution is a global threat to every living organism on earth as well as their existence (Abdel-Baki *et al.*, 2013). Water pollution has become a global concern in recent years. This is as a result of the increased level of domestic and industrial waste materials

dumped into the rivers and other aquatic bodies (Miebaka, 2017).

Heavy metals are naturally occurring elements of the earth's crust which cannot be destroyed. Sources of heavy metals in the aquatic ecosystem include geogenic, industrial, agricultural, pharmaceutical,

domestic effluents and atmospheric sources (Tchounwou *et al.*, 2012). Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Jaishankar *et al.*, 2014).

The toxicity effects of heavy metals on aquatic organisms can be directly or indirectly lethal and can impact on the population, ecosystem, the individual and humans. Heavy metals toxicity causes skeletal deformities in fish, improper growth functions, embryo and fry development, reduction in growth and finally increased level of mortality (Lenntech, 2012).

The upper Bonny estuary is an aquatic resource located in the Niger Delta, Southern Nigeria. It is an estuarine creek that receives sewage, domestic, municipal and industrial wastes discharged by coastline and urban dwellers as well as industries located around the Trans-Amadi Industrial layout in Port Harcourt city, Nigeria (Miebaka, 2014). This study is therefore carried out to determine the levels of heavy metals in the following media; water, sediment and biota (swimming crab) of the upper reaches of the Bonny River at the three different sample stations.

MATERIALS AND METHODS

Sampling was carried out once a month for six months (January-June 2018) based on the Bonny river tide table. The sampling stations were at least 1,000 meters apart along the upper reaches of the Bonny River. The sampling locations were geo-referenced and purposely selected to cover areas of the

river receiving effluents and wastes from different anthropogenic activities of the area; Okrika Jetty {Station 1: N4°73'70.04 and E7°09'56.93, Okpoka Creek in Abuloma {Stations 2: N4°78'02.43 and E7°06'66.12} and Trans-Amadi slaughter in Azuabie {Stations 3: N4°81'49.9 and E7°04'63.4}). Figure 1 shows map of the study area with the various sampling stations.

The upper Bonny estuary is an aquatic resource of immense fisheries and socio-economic importance. This section of the river is utilized by residents for artisanal fishing, while various water related activities such as commercial water transportation, industrial/manufacturing activities and oil and gas logistics operations are equally deployed either within or on the shores of this section of Bonny river. This scenario of the river hosting numerous anthropogenic activities results in wastes and effluents that pollute the river constantly.

A composite sampling technique was used in the three sample stations along the creek. The sediments were collected using an 'Ekman grab' sampler, while the surface water samples were collected in pre-cleaned high-density Schott glass bottles and the swimming crabs were collected from the local fishermen and stored in an ice pack to maintain the freshness and later transported to the laboratory. The different sampled media of Bonny river for which heavy metals (Lead, Nickel and Cadmium) were analyzed using standard laboratory procedures include surface water, sediment and biota - *Callinectes amnicola* (Plates 1 to 4).

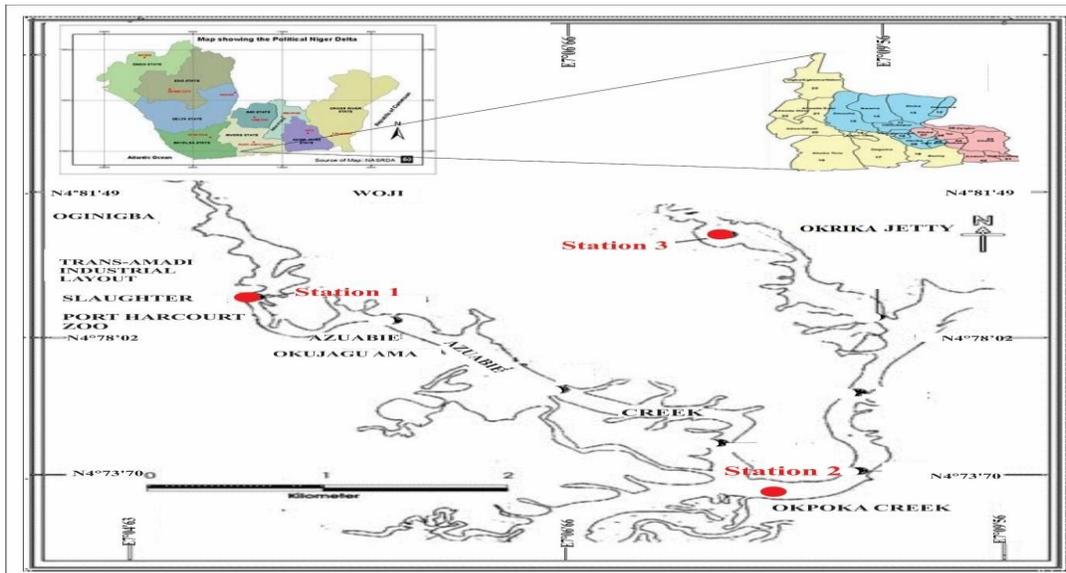


Fig. 1. Map showing the study Area along the Azuabie Creek in Rivers state



Plate 1: *Callinectes amnicola*



Plate 2: Station 1 (Okrika Jetty)



Plate 3: Station 2 (Okpoka Creek)



Plate 4: Photo of Station 3 (Trans-Amadi Slaughter)

A comparative analysis of the levels of these three metals in water, sediment and selected biota was carried out to determine the extent of heavy metal concentrations in them using the Atomic Absorption Spectrophotometric Machine (API-RP 45). Also the Bioaccumulation Factor (BAF) was determined; $BAF = \text{Concentration of metals in fishes (mg/L)} / \text{Concentration of metals in sediments}$.

RESULTS

Physico-chemical Parameters

The physico-chemical parameters like Temperature, pH, Salinity, Total suspended solids and Dissolved oxygen were taken.

Temperature: The temperatures recorded for maximum and minimum values were $28.7 \pm 0.17^{\circ}\text{C}$ and $27.0 \pm 0.17^{\circ}\text{C}$ during the dry season and $28 \pm 0.17^{\circ}\text{C}$ and $26.9 \pm 0.17^{\circ}\text{C}$ during the wet season respectively. There was no significant difference observed between the maximum and minimum values recorded in both the dry and wet season ($P > 0.05$).

pH: The pH value was maximum 7.1 ± 0.07 and minimum 6.64 ± 0.07 during the dry season and 7.0 ± 0.05 and 6.7 ± 0.05 during the wet season respectively. There were no significant differences observed between the maximum values observed during the dry and wet season ($P > 0.05$), but there was significant differences observed between the

minimum values recorded during the dry and wet season ($P < 0.05$).

Salinity: Salinity recorded maximum and minimum values of 145 ± 0.40 ppt and 61.7 ± 0.40 ppt during the dry season and recorded the maximum and minimum values of 147 ± 0.40 ppt and 60.3 ± 0.40 ppt during the wet season respectively. There were significant differences observed between the maximum values recorded during the dry and wet season ($P < 0.05$), but there was no significant difference observed between the minimum values recorded during dry and wet season.

Total suspended solids (TSS): TSS recorded maximum and minimum values of 267 ± 0.03 mg/L and 176 ± 0.03 mg/L during the dry season and recorded the maximum and minimum values at 237.7 ± 0.64 mg/L and 148 ± 0.64 mg/L during the wet season respectively. There were significant differences observed between the maximum and minimum values recorded in both the wet and dry season ($P < 0.05$).

Dissolved oxygen (DO): DO recorded maximum and minimum values during the dry season of 4.23 ± 0.17 mg/L and 3.2 ± 0.17 mg/L respectively, while the maximum and minimum values recorded during the wet season was 3.0 ± 0.10 mg/L and 2.53 ± 0.10 mg/L respectively. There were significant differences observed between the maximum and minimum values recorded in both the wet and dry season ($P < 0.05$).

Table 1: Physico-Chemical Parameters Variations between the months of January to June

Parameters	Dry season			Wet season			FEPA (mg/l)
	Max (mg/l)	Min (mg/l)	S.E(±)	Max (mg/l)	Min (mg/l)	S.E(±)	
pH	7.1 ^a	6.64 ^b	0.07	7.0 ^a	6.7 ^a	0.05	6-9
Temperature	28.7 ^a	27.0 ^a	0.17	28 ^a	26.9 ^a	0.17	<40°C
Salinity	147.7 ^b	61.3 ^a	0.40	145.3 ^a	60.7 ^a	0.40	-
TSS (Total Suspended Solids)	237 ^a	148 ^b	0.03	267.7 ^b	176 ^a	0.64	30
DO (Dissolved Oxygen)	4.23 ^a	3.2 ^a	0.17	3.0 ^b	2.53 ^b	0.10	-

*Along the rows, seasons with the same superscripts show no significant difference while stations with different superscript show significant difference

Variations In Heavy Metals Across The Various Media

Table 2 and Figure 2 show the variations of the heavy metals across the different media sampled between the months of January to June. The results obtained for water, sediments and biota are discussed as follows:

Biota (*Callinectes amnicola*)

In *C.amnicola*, the maximum and minimum values of Pb were at 0.34 ± 0.03 and 0.17 ± 0.03 during the dry season, while the maximum and minimum values observed during the wet season were 0.74 ± 0.27 and 0.22 ± 0.27 respectively, there was significance between the maximum and minimum values observed during the dry and wet season ($P < 0.05$). The maximum and minimum values of Ni recorded during the dry season was 0.54 ± 0.03 and 0.31 ± 0.03 respectively, while the maximum and minimum values observed during the wet season were 0.38 ± 0.02 and 0.24 ± 0.02 respectively, there was significant difference

between the maximum and minimum values observed during the dry and wet season ($P < 0.05$). Cd recorded the same values across seasons at < 0.01 and there was no significant difference across wet and dry season ($P > 0.05$).

Sediment

Sediment recorded the maximum and minimum value of Pb at 0.35 ± 0.01 and 0.21 ± 0.01 during the dry season, while the maximum and minimum values recorded during the wet season were 0.50 ± 0.25 and 0.37 ± 0.25 , there was significance between the maximum and minimum values observed during the dry and wet season ($P < 0.05$). The maximum and minimum values of Ni recorded during the dry season was 0.64 ± 0.02 and 0.31 ± 0.02 respectively, while the maximum and minimum values observed during the wet season were 0.55 ± 0.25 and 0.28 ± 0.25 respectively, there was significant difference between the maximum values observed during the dry and wet season ($P < 0.05$), but there was no significant difference between

the minimum values observed during the dry and wet season ($P>0.05$). Cd recorded the same values across seasons at <0.01 , there was no significant difference across wet and dry season ($P>0.05$).

Surface water

Surface water observed the maximum and minimum value of Pb at 0.29 ± 0.03 and 0.14 ± 0.03 during the dry season, while the maximum and minimum values recorded during the wet season were 0.47 ± 0.10 and 0.15 ± 0.10 , there was significance between the maximum values observed during the dry and wet season ($P<0.05$), but there was no significant difference between the

minimum values observed during the dry and wet season ($P>0.05$) The maximum and minimum values of Ni recorded during the dry season was 0.31 ± 0.03 and 0.21 ± 0.03 respectively, while the maximum and minimum values recorded during the wet season were 0.30 ± 0.02 and 0.15 ± 0.02 respectively, there was no significant difference between the maximum values observed across the months ($P>0.05$), but there was significant difference between the minimum values observed across the months ($P<0.05$). Cd also recorded the same values for all the months (<0.01) and there was no significant difference across wet and dry season ($P>0.05$).

Table 2: Variations of the Heavy Metals for the Month January to June

Media	Metals	Dry season			Wet Season			(FEPA) mg/l
		Max (mg/l)	Min (mg/l)	SE	Max (mg/l)	Min (mg/l)	SE	
<i>C. amnicola</i>	Pb	0.34 ^b	0.17 ^b	0.03	0.74 ^a	0.22 ^a	0.27	<1
	Ni	0.54 ^a	0.31 ^a	0.03	0.38 ^b	0.24 ^b	0.02	<1
	Cd	<0.01 ^a	<0.01 ^a	0.01	<0.01 ^a	<0.01 ^a	0.01	<1
Sediment	Pb	0.35 ^b	0.21 ^b	0.01	0.50 ^a	0.37 ^a	0.07	<1
	Ni	0.64 ^a	0.31 ^a	0.02	0.55 ^b	0.28 ^a	0.25	<1
	Cd	<0.01 ^a	<0.01 ^a	0.03	<0.01 ^a	<0.01 ^a	0.01	<1
Surface water	Pb	0.29 ^b	0.14 ^a	0.03	0.47 ^a	0.15 ^a	0.10	<1
	Ni	0.31 ^a	0.21 ^a	0.03	0.30 ^a	0.15 ^b	0.02	<1
	Cd	<0.01 ^a	<0.01 ^a	0.01	<0.01 ^a	<0.01 ^a	0.01	<1

**Along the rows, seasons with the same superscripts show no significant difference while stations with different superscript show significant difference*

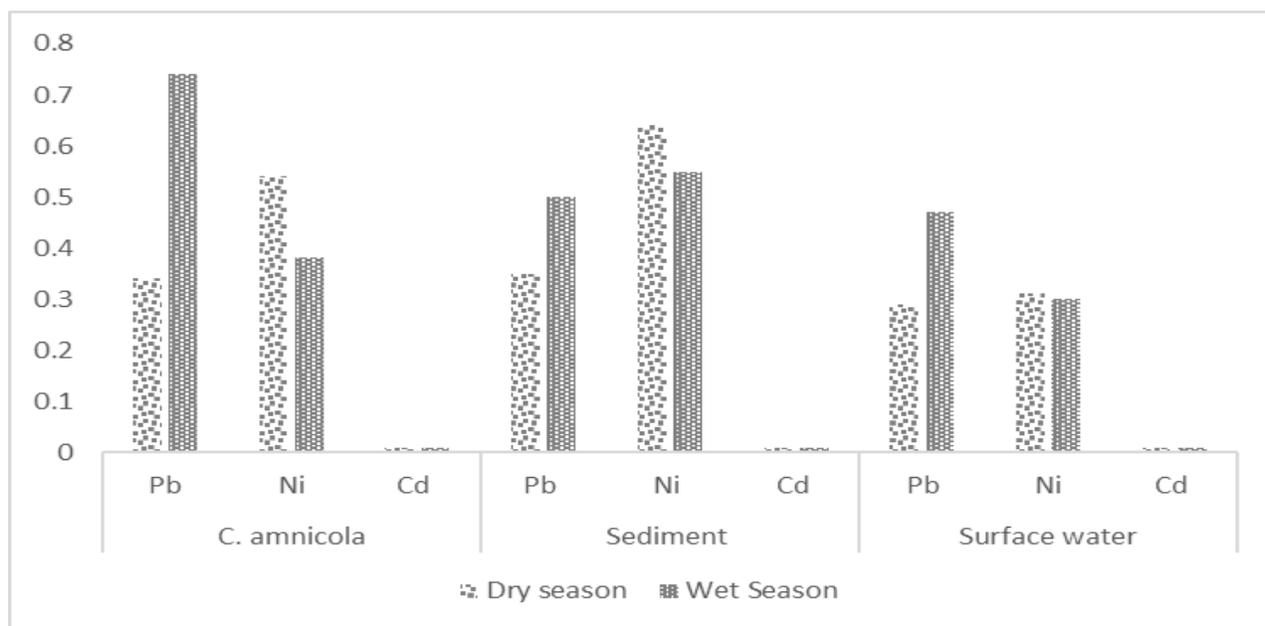


Fig. 2. Seasonal Variations of the Heavy Metals from January to June

Variations in Bioaccumulation Factor

Table 4.15 shows the Bioaccumulation Factor for each metal across wet and dry season. Pb had a higher bioaccumulation during the dry season at 1.65 than during the wet season at 1.53. Both seasons had a BAF >1, which implies that Pb is an accumulator across both seasons. Ni was more bio-

accumulated in the dry season (0.94) and least during the wet season (0.77). Both seasons had a BAF <1, which implies that Ni is an excluder across seasons. The BAF in Cd was the same value across seasons, BAF= 1 and this implies that Cd had no influences across seasons.

Table 3: Showing Seasonal Variations in Bioaccumulation Factor

METAL	DRY SEASON	WET SEASON
	BAF	BAF
Pb	1.65	1.53
Ni	0.94	0.77
Cd	1	1

*BAF = Bioaccumulation factor

DISCUSSION

There was an observed variation in the upper reaches of the Bonny River throughout the duration of this study. The study showed that the pH values for the different media were within the recommended range of DPR (2002) for both seasons, which indicates that it is within the acceptable regulatory limits. Although the pH was observed highest in the dry season at values ranging between 6.64 and 7.1 and lowest in the wet season at values ranging between 6.7 and 7.0., the low pH is linked to increased solubility and toxicity of heavy metals in water (Calvalho *et al.*, 2004). The variations observed in this study is in conformity with the works of Erema and Miebaka (2013) who reported similar pH values during the dry season and lowest values during the wet season in Azuabie creek. This could be attributed to an increase in the photosynthetic activities of aquatic plants, which could be a cause of such variations (Hart and Zabbey, 2005). The temperature values were highest in the dry season at values ranging between 27.0°C and 28.7°C and the lowest in the wet season at values ranging between 26.9°C and 28°C. This result agrees with Dibia (2006) with a range of 25°C to 27°C and Hart and Zabbey (2005) of 27 to 28°C from some creeks of the Niger Delta. A slight seasonal variation was observed in temperature and a similar trend was observed in the works of Abowei (2010) who reported dry and wet season values of 26.49°C and 28.09°C respectively. According to Alabaster and Lloyd (1980), temperature of natural inland waters in the tropics varies between 25-30°C. Salinity was observed highest in the dry season at values ranging between 61.7 and 147.3 ppt and the lowest in the wet season at values ranging between 60.3 and 145.7ppt. The salinity was within the acceptable range of FAO (1986) for water quality management. TSS had the

highest value during the dry season at values ranging from 176 to 267 mg/l and the lowest during the wet season at values ranging from 148 to 237.7 mg/l. These values exceed the standard acceptable limits of FEPA (2003). This could be attributed to physical, geological and biological processes around the sample station (Ekweozor *et al.*, 2017). It could also be as a result of effluents from the sample sites which has led to an increase in the suspended solids. A higher dissolved oxygen value was observed during the dry season ranging between 3.2 to 4.23 mg/l and the lowest values during the wet season at values ranging from 2.53 to 3.0 mg/l. High dissolved oxygen could be attributed to the turbulent effect of excessive rains for which the Niger Delta is known for (Nghah *et al.*, 2017). Calvalho *et al.*, (2004) reported that low dissolved oxygen increases toxicity of heavy metals. Generally, physico-chemical parameters were observed to be highest during the dry season as compared to the wet season.

According to Bakarat *et al.*, (2012), metals enter into the water via oxidation-reduction reactions, adsorption-desorption reaction, sedimentation resuspension and degrading organisms. In *C. amnicola*, Pb recorded the maximum value during the wet season at 0.74mg/l and the minimum value during the dry season at 0.17mg/l. The mean values were lower than the recommended limits of WHO/FEPA (2003) in shell fish. This could be attributed to the differences in the sizes, ages and sampling periods of *C. amnicola* (Idodo-Umeh (2010)). The mean value of Nickel recorded across the different media had maximum value of 0.54 mg/l during the dry season and the minimum value of 0.24mg/l during the wet season. The values were within the recommended limits of FEPA (2003). However, Cadmium values were the same across seasons at 0.01mg/l. The low value of Cadmium in both seasons

in *C. amnicola* was less than what was reported by Davies *et al.*, (2006) in Periwinkle (*Tympanotonus fuscatus var rudula*) from Elechi Creek, Niger Delta. According to Adeyeye (2011) difference in metal concentration in fish could be attributed to the size of the fish species, while Idodo-Umeh (2010) said bigger fishes accumulate high metal concentrations than smaller ones.

According to Gupta *et al.*, (2009) sediments are sinks for metals and other pollutants of the marine ecosystem. From this study, the Pb value in the sediment was higher in the wet season at 0.50mg/l and lower during the dry season at 0.21 mg/l. The results indicated low concentrations when compared with DPR (2002) and were within recommended limits. Belin, *et al.* (2013) states that when there is high pH absorption of metals is promoted while low pH stops metal retention by sediment. The Ni value in the sediment was higher (0.64mg/l) during the dry season and the lowest during the wet season (0.31mg/l). Asalolu and Olaofe (2004) also confirm high Ni value in sediments during the dry seasons than in water. Cd recorded the same values across seasons at 0.01mg/l. Low levels of cadmium is in line with previous works done in the Niger Delta (Vincent-Akpu *et al.*, 2014; Otitoju and Otitoju, 2013; Ideriah *et al.*, 2012). The Pb, Ni and Cd values recorded for surface water was the least when compared to that of the sediment and the fauna during both seasons. According to Chindah and Braide (2003), the low values when compared with the other media could be attributed to the high volume of water that dilutes and also the adequate flushing of the system. This also agrees with Barakat *et al.*, (2012), who reported that the metal concentrations found in water do not

indicate the relative contributions of pollution because most of the metals are trapped, precipitated, settled and stored as pollutants in the sediments and has also bio-accumulated in the aquatic organisms.

Bio-contamination factor results of heavy metals revealed in this study shows that there was bioaccumulation in the three media but at a low rate. Bioaccumulation Factor value of Pb was highest during the dry season at 1.65 and was least during the wet season at 1.53. The study indicated that sediment accumulated more heavy metals than water. This is in line with works of Besada *et al.*, (2001), Chindah and Braide (2003) and Eja *et al.*, (2003). In most cases sediment is the main sink of metals, with more than 99% of the sum amount of metals present in the aquatic system (Odiete, 1999). The value did not agree with what was reported by Moslen and Miebaka (2017) in *Tympanotonus fuscatus var rudula* obtained from the upper reaches of the Bonny estuary (Cd=0.02 and Pb=0.01). However, low BAF could be attributed to assimilation and excretion rate of heavy metals in the organism examined Moslen and Miebaka (2017). Bioaccumulation Factor value of Ni was highest during the dry season at 0.94 and least during the wet season at 0.77 and this implies that Ni is an excluder across seasons, having a BAF<1.

CONCLUSION

The study established that heavy metal concentrations within the sampled media of the different sections of Bonny River across the months of the area (rainy and dry) are within acceptable limits, despite the serious effluents discharges into it. This result may not be unconnected with the high dilution effect of the river as the sections sampled

are subject to tidal influence. However, the result of this study can be used as bench mark/baseline to compare subsequent monitoring activities of heavy metal concentrations within this section of the river. Thus, the study is quite significant as a useful monitoring tool for future assessment studies of the river heavy metal concentrations.

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