Assessment of Heavy Metals Concentrations in Sediments at Drainage Discharge Points into the New Calabar River, Rivers State, Nigeria

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Abstract: **Sediment samples were collected from three points along the New Calabar River where effluents were discharged from drainage. The samples were collected in the months of July, August and September, 2019. The sediments were prepared for heavy metals analysis using standard laboratory techniques. The filtrate obtained after digestion of the samples were analyzed for heavy metals concentrations using atomic absorption spectrophotometry. The result showed monthly and special variations of heavy metals concentrations. The mean monthly concentrations for the heavy metals showed that the metals were more abundant in the sediment in September, then August and was least in July. Stations variation in concentrations were in the order of Iwofe Jetty > Minipiti > Police Post. The mean concentrations of the metals showed that iron (Fe) > manganese (Mn) > chromium (Cr) > nickel (Ni) > copper (Cu) > lead (Pb) > Cadmium (Cd). The mean values for the metals were 177.1103±12.624, 47.946±1.125, 3.102±0.196, 0.216±0.025, 4.537±0.427, 4.156±0.329 and 2.298±0.221 mg/Kg for Fe, Mn, Pb, Cd, Ni, Cr and Cu respectively. All the metals examined were found to be lower than the world average value in shale and limit values in sediment set by DPR, USEPA and EU. The observed concentrations of the examined metals presently do not pose any threat to the environment except that of Cd whose values in some of the stations in the examined months were within the range of world average value in shale. From the foregoing or findings, it is recommended that proper monitoring of the type of effluents discharged into the drainage and subsequently transported to the river be put under surveillance to prevent upsurge of heavy metals increase in the river.**

Keywords: **Heavy metals, Sediment, New Calabar River, Pollution, Drainage points, human activities**

I. INTRODUCTION

The indiscriminate discharge of industrial as well as domestic waste water into the aquatic environment has posed a serious problem resulting in the gross water pollution (Dibofori-Orji and Marcus, 2012). The entry of contaminants into the environment due to human and natural activities is one of the most important issues facing today activities and communities. Due to the industrial and economic growth and the production of a variety of compounds and chemicals followed by increased consumption, some unwanted pollutants, which may cause serious problems and risks for the environment and for man itself, are discharged into the environment (Maitera et al., 2011; Ahmed and Ahmaruzzaman 2016). Heavy, metals are of high priority pollutant to the river because of their relatively high toxic effect and accumulation in the environment. The pollution of aquatic animals by heavy metals and successive uptake in the aquatic food chain possess high hazard to human population (Obaroh *et al*., 2015).

Heavy metal accumulation in the environment has been attracting increasing attention from both researchers and policy makers because of their toxicity and persistence in the environment and subsequent accumulation in aquatic habitat (Brunner *et al*., 2008). Heavy metals could be found in water at trace level, in a long period of time. Heavy metals such as Pd, Cd, and Cr are micro pollutant and of special interest as they have both health and environmental significance (Galas-Gorcher, 1991).

Sediment play a major role in determining the pollution pattern of aquatic system. It acts as both carrier and sink for contaminant, reflecting the history of pollution and providing a record of catchment input into aquatic ecosystem (Egborge, 1991). Sediment is a combination of numerous constituents of inorganic components and organic remains of which heavy metals are part of their composition, which are discharged into the environment (Venktesha *et al*., 2012). Since, sediment as any particulate matter that can be transported by fluid flow and which eventually is deposited as a layer of soil particles on the bed or bottom of a body of water or other liquid, the metals are non-biodegradable and once discharge into water bodies. They can either be adsorbed on particles or accumulated in aquatic organisms (Guan *et al*., 2014).

Heavy metals pollution may increase the susceptibility of aquatic animals to various diseases by interfering with the normal functioning of their immune, reproductivity and developmental processes. Sediment is a naturally occurring material,that are broken down by processes of weathering and erosion, and is subsequently transported by the action of wind, water in ice by the force of gravity acting on the particles for example, sand and silt can be carried in suspension in river water and on reaching the sea bed deposited by sedimentation and if buried, may eventually become sandstone and siltstone (Sedimentary rocks) (Forstner, 1983).

II. MATERIALS AND METHODS

Sediments were collected at three different points where drainage effluents are being discharged into the New Calabar River. Hand held plastic trowel was used to collect the sediments. The sediments were collected at different points within the discharge area and aggregated together to form a representative sample. The samples were moved to the laboratory in plastic cellophane bags. In the laboratory, the sediments were allowed to freely dry under ambient air conditions. The weights of the sampled sediments were examined at weekly intervals for three weeks to know when constant weight has been established. On the third week, when no recorded weight difference was observed, the samples were transferred to an oven for further heating to remove all forms of residual water.

Thereafter, the sediment samples were powdered with a ceramic mortar and pestle with care not to crush stones of hard objects and sieved with a 2 mm mesh to obtain fine particle of the sediment samples. Prior to powdering the samples, leaves of plants and small sticks were removed. Then a known weight of 2 g of fine powdered sediment was transferred to ceramic containers to which a mixed acid solution of HNO_3, HCl and H_2SO_4 in the ratio of 5:3:2 was added and then heated over steam bath (digestion process).

When the mixed solution of the acid and sediment became clear, 10 ml of deionized water was added and heated for a while to obtain a clear colour. Thereafter, the content of the digested sample was filtered into sample bottles using Whatman size 2 filter paper to obtain the digest. The ensued digest was made up to 50 ml mark with deionized water.

The complete digests were sent to the Jaros Base Laboratory, where the concentrations of the individual heavy metals were determined.

The statistical mean values obtained after all the monthly values were obtained were further subjected to different pollution and ecological assessment evaluation to determine the level of contamination and human influence on the input of heavy metals into the river from the drainage discharge points.

III. RESULTS AND DISCUSSION

The monthly and stations values of the concentrations of the different heavy metals examined are given in Tables 1-5 and Figure 1. The concentrations of heavy metals in sediments of any aquatic media has one major negative consequence on the environment. This is because the possibility of resuspension of the metals back to the water medium at any time when the equilibrium position of the surface water-sediment is disturbed. When such situation take place, the concentrations of the individual metals increases in the water phase.

In all the months and stations examined, iron (Fe) was the most abundant metal. The concentrations of Fe varied from 131.638±15.46 - 206.382±15.24 mg/Kg between the period of July to September and a mean value of 159.267±28.459, 186.526±14.888 and 185.538±12.481 mg/Kg for July, August and September respectively and 201.087±3.744, 163.891±24.085 and166.354±14.348 at Iwofe jetty, Minipiti and Police Post stations respectively. In all the period of examination, the Iwofe station had the highest concentrations of Fe as compared to other stations.

The concentrations of Fe observed in this work is lower than the observed values of Fe in surface sediments alongside the Cross River waterway in Cross River State, Nigeria (Akpan and Thompson, 2013) and the values observed in Andoni River estuaries, Rivers State, Nigeria (Kpee *et al*., 2019), but slightly lower than the values of Fe observed in parts of the New Calabar River, Rivers State, Nigeria (Nwineewii *et al*., 2018). Although, Fe is the most abundant metal naturally, yet its presence in aquatic sediment as in this case might be related to anthropogenic effects from both household and industrial input sources which were drained into the immediate vicinity where the samples were obtained. Monthly variations were observed within the period. These variations probably arose from the content or compositions of the effluents from the discharged sources.

The concentrations of manganese (Mn) within the period of analysis varied from 43.573±5.90 -51.897±6.33 mg/Kg. The mean values for each of the months were 49.478±2.078,47.551±2.892 and 46.808±2.459 mg/Kg for July, August and September respectively. The stations mean values were 48.963±2.304, 50.042±0.264 and 44.833±1.424 mg/Kg for Iwofe Jetty, Minipiti and Police Post stations. In all the months the analyses were conducted, the Minipiti station had the highest concentrations of Mn in the sediment except that of July.

The observed concentrations of Mn in the sediments in the present work are higher than the values recorded in Sediments of River Gongola in Adamawa State, Nigeria (Maitera, *et al*., 2011) and also higher than the values of Mn observed in the sediments of Bonny River, River State, Nigeria (Bubu *et al*., 2018). However, the values from the present research work is lower than those observed in sediment from the Cross River, Cross River State, Nigeria (Akpan and Thompson, 2013), but within the range of values observed in shoreline dregs in Lagos Badagry axis, Lagos, Southwestern Nigeria (Ayodele *et al*., 2019).

The concentrations of Pb in this work varied from 2.894±1.10 - 3.71±1.02 mg/Kg with the months under examination. Monthly mean values showed that July was 2.825±0.182 mg/Kg, August was 3.256±0.322 mg/Kg and September was 3.224±0.297 mg/Kg. Mean station values were 2.990±0.070,3.453±0.317 and 2.863±0.203 mg/Kg for Iwofe Jetty, Minipiti and Polic Post stations respectively. Pb concentrations was highest at the Minipiti station in the month of August but lowest at the Iwofe Jetty station in the month of July.

The concentrations of Pb in the present work when compared with other research findings showed that the values were higher than the values observed in Sediments of Ikpoba River, Edo State, Nigeria (Imiuwa *et al*., 2014), also higher than those of Otitoju and Otitoju (2013) in sediments from selected Niger Delta rivers and creeks, but within the range of values observed in sediment samples from the Bonny river, Rivers State, Nigeria (Bubu *et al*., 2017) and by far lower than the values observed in sediments from beach area in Lagos, Nigeria (Ayodele *et al*., 2019).

The concentrations of Cd within the period (months) of analysis varied from 0.031±0.00 - 0.412±0.06 mg/Kg. The monthly mean values were 0.182±0.142 0.228±0.147 and 0.239±0.121 mg/Kg for July, August and September respectively and stations values were 0.372±0.033, 0.227±0.072 and 0.050±0.015 mg/Kg for Iwofe Jetty, Minipiti and Police Post Stations respectively. The highest value of Cd was observed at the Iwofe Jetty station in August and the lowest value observed at the Police Post station in July.

The values of Cd reported in the present work disagreed with the observation of Aladesanmi *et al*. (2016), in sediments from Yah Stream, Osun state, Nigeria, where Cd was not detected and higher than those of Otene and Alfred-Ockiya (2019), in sediments from Elechi Creek, Port Harcourt, Rivers State, Nigeria, but falls within the range of values observed in Alaro River, Nigeria (Ipeaiyeda and Onianwa, 2018). However, the values of this work were within the range or either lower or higher than the values observed in River Gongola, Adamawa State, Nigeria (Maitera *et al*., 2011).

The concentrations of Ni observed in the sediments at the drainage discharge point varied from 3.521±2.03 - 5.605±0.93 mg/Kg. The mean values observed in the months of analysis were 5.076±0.380, 4.502±0.625 and 4.032±0.434 mg/Kg for July, August and September respectively. Stations mean values were 5.190±0.439, 4.133±0.570 and 4.287±0.318 mg/Kg at Iwofe jetty, Minipiti and Police Post Stations. The lowest value was observed at the Minipiti station in September, while the highest value was observed at the Iwofe Jetty in July.

The present work values observed for Ni were lower than the values observed in Alaro River, Nigeria, where the mean concentration value was 7.74 ± 0.97 mg/Kg, but higher than those of Aladesanmi *et al*. (2016), in Yah Stream sediments, Osun State, Nigeria and those of Imiuwa *et al*. (2014), in Ikpo River, Edo State, Nigeria. However, the observed values from this work falls within the range of values observed in beach sediments in Lagos, Nigeria (Ayodele *et al*., 2019).

The concentration values of Cr observed within the experimental period varied from 2.711±1.13 - 6.811±0.45 mg/Kg. The monthly mean values for July, August and September were 3.792±0.926, 4.589±1.600 and 4.088±0.962 respectively, while the stations mean variations were 5.705±0.796, 2.937±0.168 and 3.827±0.103 mg/Kg for Iwofe Jetty, Minipiti and Police Post stations respectively. The lowest value of Cr within the period of analysis was observed at the Minipiti station in the month of July, while the highest value was observed at the Iwofe Jetty station in August.

The observed concentrations of Cr in the present study were higher than the values obtained in sediments from River Ekulu in Enugu, Nigeria (Adaikpoh *et al*., 2005) and those of Imiuwa *et al*. (2014), in Ikpo River, Edo State, Nigeria, but falls within the range of values observed in sediments from three different rivers (Igbede, Ojo and Ojora Rivers) in Lagos, Nigeria. However, these values were lower than those of Akpan and Thompson (2013) in Cross River channel, Cross River State, Nigeria.

The concentrations of Cu within the period of sampling varied from 0.998±0.48 - 4.012±1.68 mg/Kg. The concentrations variation within the months were 2.480±0.809, 2.427±1.500 and 1.987±1.073 mg/Kg for July, August and September respectively, while stations variation in concentrations were 3.702±0.226, 1.374±0.332 and 1.818±0.236 mg/Kg for Iwofe Jetty, Minipiti and Police post stations respectively. The least concentration (0.998±0.48 mg/Kg) was observed at the Minipiti station in the month of September, while the highest concentration (4.012±1.68 mg/Kg) was observed at the Iwofe Jetty station in August.

The concentrations of Cu in the present work were lower than the values observed in sediments from Lagos Beach, Lagos Nigeria (Ayodele *et al*., 2019) and also those of Ipeaiyeda and Onianwa (2019), in Alaro River, Nigeria, that is subjected to industrial effluents. However, these values were higher than those of Izuchukwu *et al*., (2017), in Onitsha axis of the River Niger, Nigeria, those of Ideriah *et al*. (2012), in sediments from the shorelines of Sombreiro and Abonnema River, Rivers State, Nigeria and those of Bubu *et al*. (2017), in Bonny River, Rivers State, Nigeria.

Table 1: Concentrations of heavy metals in July in sediments at effluents discharge points into the New Calabar River

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	Minipiti	Police Post
Fe	198.427±10.38	131.638±15.46	147.742±13.83
Mn	51.897±6.33	49.714± 8.21	46.824±5.24
Pb	2.894±1.10	3.006±0.73	2.576±0.88
Cd	0.372±0.01	0.142±0.03	0.031±0.00
Ni	5.605±0.93	4.894±1.05	4.728±2.01
Cr	4.972±1.22	2.711±1.13	3.694±1.28
Cu	3.617±1.32	1.806±0.54	2.016±0.56

Table 2: Concentrations of heavy metals in August in sediments at effluents discharge points into the New Calabar River

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	Minipiti	Police Post
Fe	206.382±15.24	170.535±12.43	182.66±18.06
Mn	48.721±8.14	50.360±9.12	43.573±5.90
Pb	3.058±0.87	3.71±1.02	3.001±1.42
Cd	0.412±0.06	0.221±0.01	0.051±0.00
Ni	5.381±1.36	3.985±2.01	4.141±1.36
Cr	6.811±0.45	3.112±0.98	3.843±1.35
Cu	4.012±1.68	1.318±0.67	1.952±0.43

Table 3: Concentrations of heavy metals in September in sediments at effluents discharge points into the New Calabar River

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	Minipiti	Police Post
Fe	198.452±21.32	189.502±15.09	168.66±28.42
Mn	46.27±6.32	50.053±5.23	44.102±4.36
Pb	3.017±1.13	3.643±1.21	3.011±0.74
Cd	0.332±0.04	0.318±0.11	0.068±0.01
Ni	4.583±1.49	3.521±2.03	3.992±1.58
Cr	5.331±2.32	2.987±1.86	3.945±1.64
Cu	3.478±1.82	0.998±0.48	1.486±1.002

Table 4: Mean concentrations of heavy metals in the different months of analysis

Heavy Metals (mg/Kg)	Months			
	July	August	September	
Fe	159.267±28.459	186.526±14.888	185.538±12.481	177.1103±12.624
Mn	49.478±2.078	47.551±2.892	46.808±2.459	47.946±1.125
Pb	2.825±0.182	3.256±0.322	3.224±0.297	3.102±0.196
Cd	0.182±0.142	0.228±0.147	0.239±0.121	0.216±0.025
Ni	5.076±0.380	4.502±0.625	4.032±0.434	4.537±0.427
Cr	3.792±0.926	4.589±1.600	4.088±0.962	4.156±0.329
Cu	2.480±0.809	2.427±1.500	1.987±1.073	2.298±0.221

Table 5: Mean concentrations of heavy metal in the different stations during the period of analysis

Heavy Metals (mg/Kg)	Stations		
	Iwofe Jetty	Minipiti	Police Post
Fe	201.087±3.744	163.891±24.085	166.354±14.348
Mn	48.963±2.304	50.042±0.264	44.833±1.424
Pb	2.990±0.070	3.453±0.317	2.863±0.203
Cd	0.372±0.033	0.227±0.072	0.050±0.015
Ni	5.190±0.439	4.133±0.570	4.287±0.318
Cr	5.705±0.796	2.937±0.168	3.827±0.103
Cu	3.702±0.226	1.374±0.332	1.818±0.236

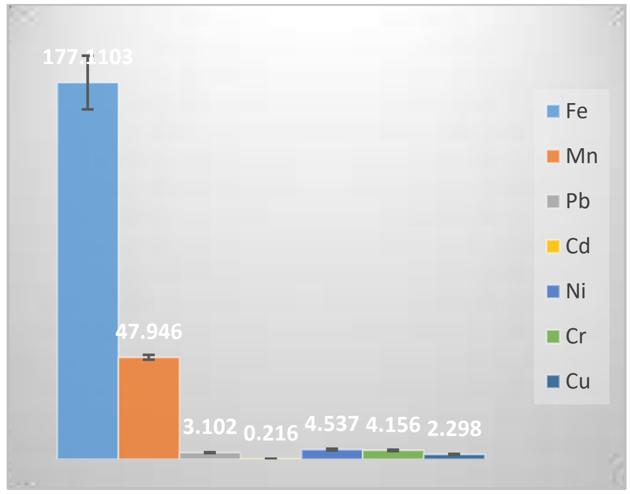

Figure 1: Men concentrations of heavy metals at the sample positions (Discharge points)

Table 6: Permissible Limits of heavy metals in sediment by national and International Organizations

Heavy Metals (mg/Kg)	World Average Shale Value	DPR Value	USEPA
Fe	47, 500	38,000	25
Mn	850	850	-
Pb	20	85	40
Cd	0.3	0.8	-
Ni	68	35	20
Cr	90	100	25
Cu	45	36	25

Sources of heavy metals from the present work may not be unconnected with chemical leaking of rock layer, which are washed off during current flow (especially the Iwofe Jetty station), wastewater effluents from homes and industries whose effluents are directly fixed to the drainage system, runoffs from adjoining lands, pesticides, refining operations from both legal and illegal positions within the area and other unidentifiable sources due to anthropogenic activities that might not be regular. This observation is in agreement with the observations of Chakravarty and Patgiri, (2009), in sediments of the Dikrong River, India. The concentrations of heavy metals that any sediment can carry or release to the environment is a function of the redox condition of the water, the amount of organic matter present and acido-basic condition of the sediment (Carr and Neary, 2008). Sediments overburdened with heavy metals load, will eventually release them back to the surface water and in turn, be a source of heavy metals pollution (Sharma and Dubey, 2005).

IV. CONCLUSION

The concentrations of the examine heavy metals in the sediments from the drainage discharge points at the point of discharge were low when compared to set limits. Therefore, they showed no sign of pollution, but rather contamination. However, the level of Cd was close to the average value in shale, thus showing signs of danger in the near future if allowed to continue. Other metals, despite being at low concentrations should be checked or monitored constantly to avoid sudden rise in their concentrations. This could be achieved through effective policing of the sources of effluents into the drainage system.

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