Comparative Evaluation of Heavy Metal Concentration in Water and Sediment, Choba Segment of New Calabar River, Port Harcourt, Nigeria

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DOI: 10.56201/ijaes.v8.no3.2022.pg29.36

Abstract
The heavy metal concentration in water and sediment, Choba segment of New Calabar River, Port Harcourt was investigated between February and April, 2020. Samples collected from the three locations were analysed in the laboratory for heavy metals using Atomic Absorption Spectrophotometer (AAS) following standard method of APHA. The mean values of heavy metal in water (mg/l) were: Cr (2.29±1.29), Ni (2.32±0.28), Pb (2.46±0.38), Cd (0.04±0.02), Fe (52.18±7.26) while that of sediment were: Cr (7.18±0.43), Ni (5.57±0.29), Pb (8.09±0.39), Cd(0.30±0.15), Fe (123.64±5.17). The heavy metal values showed variations across the stations at P<0.05. The order of concentration of heavy metal in water was: Fe>Pb>Ni>Cr>Cd while that of sediment is Fe>Pb>Cr>Ni > Cd with heavy metal concentration in sediment higher than that of water while Fe and Cd concentrations were highest and lowest in both water and sediment respectively. All the heavy metals in water except Ni exceeded the permissible limits of World Health Organisation (WHO), Federal Environmental Protection Agency (FEPA) while that of sediment were below the permissible limits except Fe. It was concluded from the results that Choba segment of the New Calabar River is under stress since the heavy metals apart from Nickel (Ni) present were above the permissible limit. This implies that the quality of the water is unsafe for use especially for domestic purpose if untreated owing to the on-going anthropogenic activities in the area. Therefore, regulatory standards for discharges from anthropogenic activities should be strictly controlled.

Keywords: *Evaluation, Heavy Metals Concentration, Water, Sediment, New Calabar River, Port Harcourt*

Introduction

Pollution of the aquatic environment by heavy metals due to anthropogenic activities has been a serious source of concern to government regulatory agencies, environmentalists and the general public (Otene and Alfred – Ockiya, 2019, Otene and Ukwe,2018). Otene and lorchor, (2019) opined that it is impossible for man to do without use of metals which therefore led to the inundation of the environment with excesses of these metals either biologically essential or non-essential. Contemporarily, most technologically industrialized areas or nations of the world are located on the banks of rivers making the aquatic

environment to be particularly at risk from the metallic contaminants since it causes continuous deterioration of water quality and its biotic resource (Otene and Nnadi, 2019, Otene and Nnadi,2020).
Contaminants when released into the aquatic systems generally show a large propensity to bind to suspended matter and thus through sedimentation accumulate in aquatic sediments (Saygi and Yigit, 2012).

It has been observed and reported that metals play essential role in the functions of living organisms (including man and other aquatic organisms) by constituting a nutritional requirement and fulfilling physiological roles. However, their concentration beyond limits in the environment is problematic (Jane, 2003). The non-essential ones called heavy metals such as Nickel (Ni) mercury (Hg), cadmium (Cd), lead (Pb)and chromium (Cr) etc are known to be toxic at any concentration. Gastrointestinal (GI) disorder, diarrhoea, stomatitis, hemoglobinuria causing a rust-red colour to stool, ataxia, paralysis, vomiting and convulsion etc are known to be the associated signs with these heavy metals (MCcluggage, 1991).

It is based on the negative impacts of heavy metals and the significant roles played by Choba segment of the New Calabar Rivers that this study became necessary. The study is therefore aimed at comparing the concentration of heavy metals in water and sediment to monitor and regulate the influx of contaminants and toxicants into the aquatic system resulting from anthropogenic activities in the area.

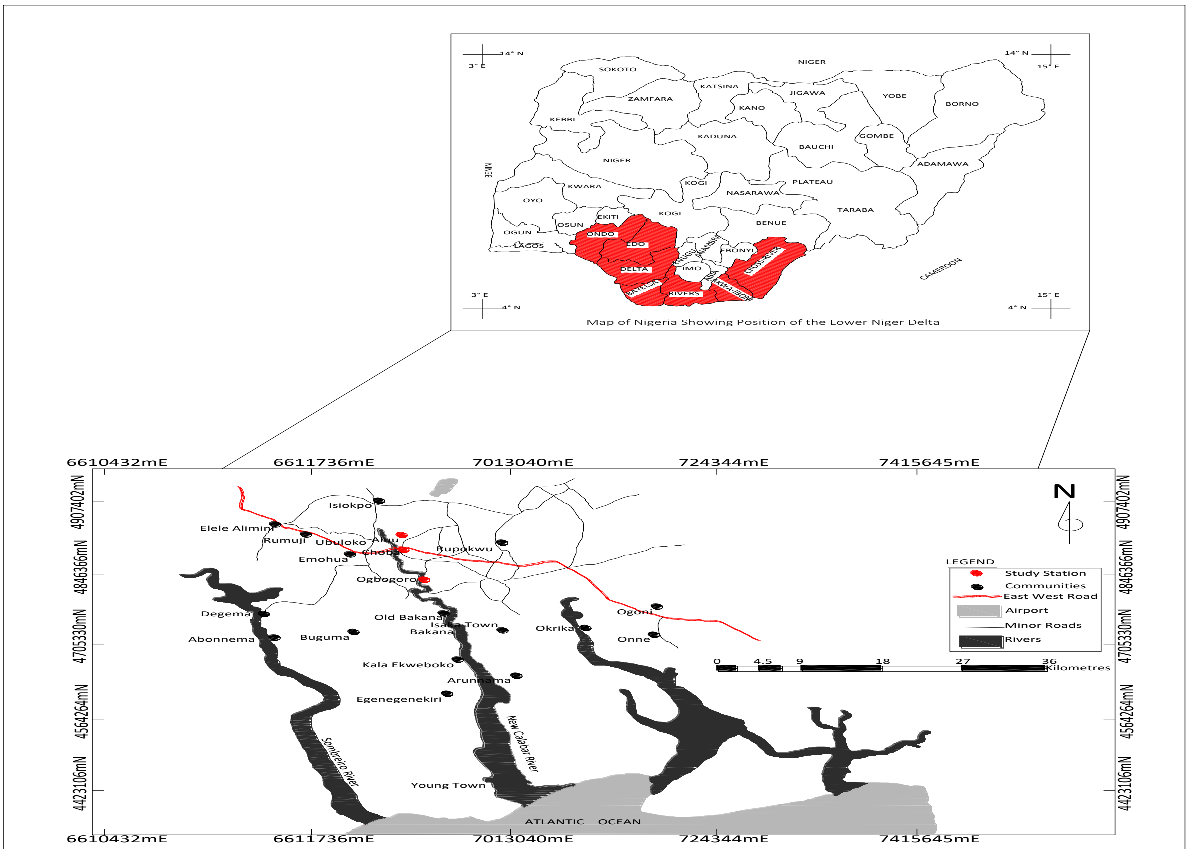
Materials and Methods.

Study area.

The new Calabar river course lies between longitude 7^0 6^0 E and latitude 5^0 45’ N in the coastal area of Niger Delta, a tributary of the Bonny estuary which empties into the Atlantic Ocean (Nkoli, *et al*, 2017) (Fig.1). With respect to the numerous anthropogenic activities in the area, the river is considered to have received quantum of effluents of industrial and domestic origin. This water body provides the inhabitants of the area with numerous services ranging from provision of sea food, water for domestic use, source of irrigation, wate for cooling system for the companies and source of transport.

Sample Collection and Analysis

Sediment and water samples were collected from three locations on Monthly basis between February and April, 2020 using Eckman grab and plastic bottles, respectively, packed in ice-boxes and carried to the laboratory and stored at 40^c for further analysis. Sediment samples were air-dried, ground with a porcelain mortar and pestle then passed through mesh sieve of O.5mm then digested with 30ml agua – regia ($HCL:HN0_3$,3:1) on a hot plate and thermo staled at 150^{OC}. About 10ml of concentrated peraloric acid ($HC10_3$) was added for digestion after 2hrs for 30 minutes. Water samples were concentrated in a sandy ovun at 80^{0C} until the volume reached 50ml after which 4ml concentrated sulphuric acid (Merck 98%) was added and digested by digest dahi apparatus for 3 minutes. About 10ml hydrogen peroxide (Merck, 30%) was added and heated until oxidation was competed. After cooling, filtrate of both samples were analysed for the heavy metals, Cr, Ni, pb, Cd and Fe by Atomic Absorption Spectrophotometer (Raleigh WFX 320) following standard method adopted from APHA (1998).



Data Analysis

The data obtained were subjected to descriptive and inferential statistics such as mean, standard deviation, Analysis of Variance (ANOVA), Duncan Multiple Range Test (DMRT) for separation of means and significant difference at $P<0.05$ using the SPSS software version 23.

Results

Table 1 showed the spatial overall mean values and the ranges of heavy metals of water and sediment. The mean values of the heavy metals, Cr, Ni, Pb, Cd and Fe in mg/l and mg/g for water and sediment were respectively 2.29 ± 0.29, 2.32 ± 0.28, 2.46 ± 0.38, 0.04 ± 0.02, and 52.18 ± 7.26 for water and 7.18 ± 0.43, 5.57 ± 0.29, $8.09 + 0.29$, 0.300 ± 0.15 and 123.64 ± 5.17 for sediment. All the heavy metal concentrations in the sediment were consistently higher than that of water with values varying from station to station. Also, all the heavy metals except Ni present in water exceeded the permissible limit unlike in sediment where only Fe exceeded the permissible limits of FEPA and WHO.

Table 1: Spatial and Overall Mean Values of Heavy Metals in Water and Sediment of New Calabar River

Stn/Hm	Cr		Ni		Pb		Cd		Fe	
	A	B	A	B	A	B	A	B	A	B
1	2.23± 0.19[b]	7.15± 0.53[a]	2.09± 0.17[b]	5.54± 0.56[a]	2.39± 0.35[a]	7.76± 0.24[b]	0.038± 0.02[a]	0.10± 0.0	53.7±3. 08[a]	126.81± 4.76[a]
2	2.45± 0.36[a]	7.41± 0.56[a]	2.48± 0.18[a]	5.60± 0.13[a]	2.44± 0.32[a]	7.93± 0.06[b]	0.06±0 .03[a]	0.40± 0.10	53.49±1 0.49[a]	125.34± 4.63[a]
3	2.17± 0.33[b]	6.99± 0.01[a]	2.55± 0.57[a]	5.57± 0.10[a]	2.55± 0.57[a]	8.58± 0.08[a]	0.04±0 .02[a]	0.25± 0.20	49.34±8 .57[b]	118.79± 2.84[b]
Mean	2.29± 0.29	7.18± 0.43	2.32± 0.28	5.57± 0.29	2.46± 0.38	8.09± 0.39	0.04±0 .02	0.300 ±0.15	52.18±7 .26	123.64± 5.17
Range	1.98- 2.75	6.55- 7.88	1.89- 2.80	7.56- 8.67	1.98- 3.12	7.56- 8.67	0.02- 0.08	0.10- 0.40	41.45- 65.55	115.58- 130.47
FEPA, (2003), WHO, (2011)	0.05	26	0.02	16	0.05	31	0.01	0.60	0.3	<2
Remark/Status	Poor/ high	Good/ low	Good/ low	Good/ low	Poor/ high	Good/ low	Poor/ high	Good/ low	Poor/ high	Poor/ high

Key:A=Water, B=Sediment, Stn=Station, Hm=Heavy metals
Mean values with difference in superscript across the column shows significant difference statistically at p<0.05.

The order/hierarchy of accumulation of heavy metals in water was Fe > Pb > Ni > Cr > Cd while that of sediment was Fe > Ob > Cr > Ni > Cd with Fe and Cd being the highest and the lowest metals respectively in both media. Cd did not exhibit significant difference in both media across the stations unlike the other metals at $P < 0.05$. From Table 2, the concentration of the heavy metals studied except Fe were slightly above the recommended limits of MPI/WHO, WPC and CMC for natural waters.
Temporally, the concentration of heavy metals in both media fluctuates with Fe having the highest value throughout the period (Fig.2 and 3).

Table 2: Acceptable level (mg/l) of Heavy Metals in Natural Waters (Water Guideline)

Heavy Metal	Cd	Cr	Pb	Ni	Fe
Maximum Permissible Limit (MPL	0.003	0.05	0.01	NA	NA
Threshold Concentration for aquatic life TC	0.01	0.05	0.10	NA	NA
Bureau of Indian Standards BIS	0.01	0.05	0.05	NA	NA
World Average of trace element in unpolluted rivers (WA)	0.001	NA	0.04	NA	NA
Turkish Standard,2006) (TSE-266)	0.005	0.05	0.01	2.0	NA
Water Pollution Control (WPCL,2004)	0.003	0.02	0.01	0.02	NA
Annonymous Criterion of the Irrigation Water (CIW,1997)	0.01	0.10	5.0	0.20	NA
World Health Organisation (WHO,2006)	0.01	0.05	0.05	2.00	NA

European Community (EC)Water Guideline	5	50	10	2.00	NA
Environmental Protection Agency (EPA)	0.01	0.05	0.05	1.30	NA
Fresh Water Quality Criteria					
Criterion Maximum Concentration (CMC) (USEPA,2006)	0.002	0.016	0.07	NA	**NA**
Criterion Continous Concentration (CCC) (USEPA,2006)	0.0003	0.011	0.003	NA	**NA**

NA=Not

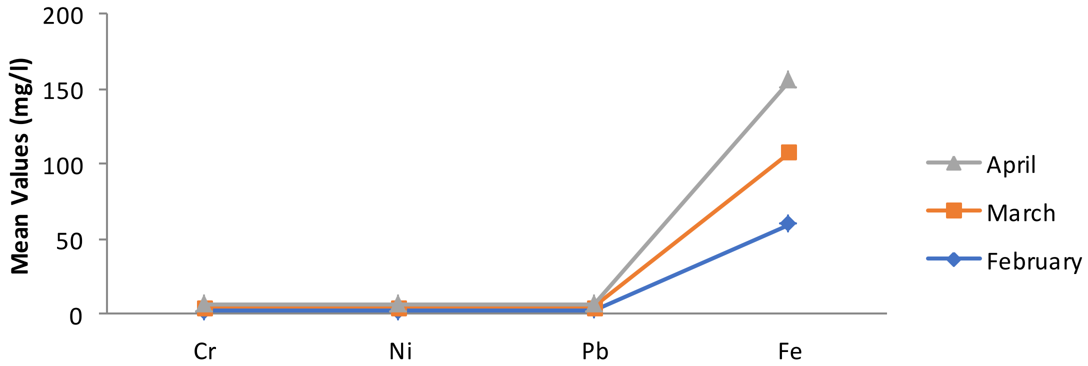


Fig. 2: Monthly Mean Values of Some Heavy Metals in Water in the Study Area

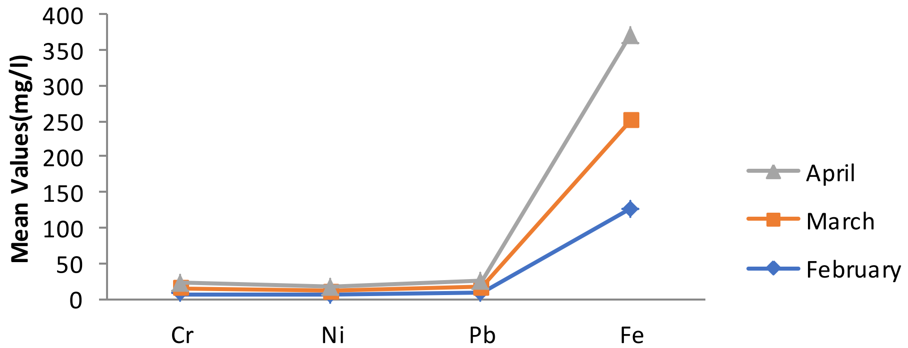


Fig.3: Monthly Mean Values of Some Heavy Metals in Sediment in the Study Area

Discussion

Heavy metals are usually released into an environment by different anthropogenic activities such as mining, agricultural, industrial and even nuclear activities. The higher mean values of heavy metals in sediment than water in this study is in line with the assertion that sediment is a sink and a reservoir of contaminants (Otene and Ockiya, 2019, Otene and Iorchor,2019, Maitera *et al*.,2011). This observation is also in line with the finding of Davies *et al*., (2009) in Elechi creek where virtually all the metals studied were higher in sediment than water. This observation could also be attributed to the fact that sediments are considered to be the bedrock of inhabiting or accommodating heavy metals and pollutants. This value is also in line with the values reported by Eleta (2007) in Asa River and Joseph *et al*., (2012) in Lake Chad, Baga, North Eastern Nigeria but contrary to the finding of Odigie and Adejumo (2018) where low concentration of heavy metals were reported across the stations and months which was linked to low degree of anthropogenic activities in the areas.

The spatial variation and fluctuation in heavy metal concentrations across the stations could be attributed to difference in anthropogenic activities in the respective stations. Also, the observed variation/fluctuation in monthly values of heavy metals could be linked to variation in climatic and other environmental factors such as physicochemical parameters, dilution factor due to rainfall/surface runoff (Davies *et al*.,2009).

The observed higher concentration of heavy metals such as Cr, Pb, Cd and Fe above the permissible limits of WHO (1993, 2006,2011), WPCL (2004), CCC (USEPA, 2006) and CMC (USEPA, 2006) is in tandem with the findings of Joseph *et al.,* (2012), and Maitera *et al* (2011) in Gongola River Adamawa State where toxic metals such as Cr, Pb and Cd were consistently present in water above the permissible limit. This is also in line with the finding of Esam *et al.,* (2015) who reported higher concentrations of Cd, Fe, Pb and Ni and Pb and Ni above the permissible limit of WHO (2011) and NOAA (2009) for sediment in Jeddah Coast, Red Sea in Saudi Arabia. The presence of these metals in water above the permissible limits implies that consuming or drinking untreated water from this river is unhealthy and may pose high risk of infection. When large quantities of pollutants are released, there may be an immediate impact as measured by large-scale sudden mortalities of aquatic organisms, e.g. fish kills resulting from contamination of waterways with agricultural pesticides (Austin, 1999). Zeitoun *et al*.,(2014) also opined that reduction in ecosystem productivity, loss of biological diversity, alteration of habitats and contamination of aquatic biota are among the most important effects of these pollutants.It was also observed that apart from Fe which was though considered to be an essential nutrient, all other heavy metals (Cr, Pb,Ni and Cd) present in the sediment were within the permissible limit of WHO (2011) and FEPA (2011). According to Hamed, (1998) and Nguyena *et al* (2005) higher accumulation of metals in sediment than water is owing to the fact that sediment acts as reservoirs for all containments and dead organic matter descending from the ecosystem above.

Conclusion and Recommendation

It could be concluded from the results that Choba segment of the New Calabar River is under stress/threat since the heavy metals studied apart from Nickel (Ni) are present above the permissible limit. Also, the sediment contains only Fe above the permissible limit while other metals were within the limit. This implies that the quality of the water is unsafe for use (especially for drinking and other domestic purposes) if untreated owing to the on-going anthropogenic activities in the area. Therefore, regulatory standards for discharges from human activities and industries should be strictly controlled/monitored. Serious efforts should be intensified so as to ensure that such anthropogenic activities identified around the river be reduced or eradicated completely especially the illegal bunkering.

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