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Determination of the levels of heavy metals in water and sediment of new Calabar River, Rivers State, Nigeria

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Abstract
The research evaluated the concentrations of heavy metals in surface water and sediment of the New Calabar River. Water and sediment samples were collected from different locations based on effluent characteristics. The samples were treated with standard procedures and methods and were analyzed for heavy metals concentrations in both water and sediments. The analysis was performed using atomic absorption spectrophotometer (AAS). The results obtained for the heavy metals analysis were in the order Zn (4.72 ± 1.59 mg/l) > Cr (3.87 ± 0.96 mg/l) > Pb (3.39 ± 0.83 mg/l) > Cu (3.34 ± 1.45 mg/l) > Ni (2.65 ± 1.38 mg/l) > Cd (0.85 ± 0.74 mg/l) >As (0.09 ± 0.11 mg/l) > Ba (0.06 ± 0.06 mg/l) for water samples. The concentration of heavy metals in the water samples of the river were above the WHO and NESREA guideline except Ba. The results of the heavy metals levels in sediment samples of the river were in the order Zn (14.380±3.402mg/kg) > Cr (7.951±0.010 mg/kg) > Cu (7.294±1.650mg/kg) > Ni (6.751±1.550mg/kg) > Pb (6.607±1.671 mg/kg) > Cd (2.495±1.750 mg/kg) > Ba (1.855±1.656 mg/kg) > As (1.595± 1.311 mg/kg). There was pronounced pollution by heavy metals in surface water of New Calabar River. Hence, adequate measures should be adopted to halt and prevent further degradation of the river.

Keywords: heavy metals, pollution, water, sediment, environment, aquatic ecosystm

Introduction

The quality of drinking water is an important factor of the wellbeing of an organism. There is a need to ensure that the water is clean and pure to avert health implications that arise from the consumption of polluted and contaminated water (Okumgba & Ozabor, 2014) [28].

The industrialization, urbanization and the development of rural areas had caused a steady growth and persistent increase in the contamination of water bodies through the activities of man.

Two groups of chemical pollutants have a lasting effect on the natural balance in the aquatic system. The first group comprises plant nutrients such as nitrate, phosphate, and sulphate, which are not directly harmful to plants and animals in water but may add unpleasant odour or taste to it. This can significantly upset the ecosystem. Water pollution resulting from the afore-mentioned group result from over-enrichment that promotes unrestricted growth of aquatic plant biomass. This eventually lead to oxygen depletion arising from decay of plants and the death of fishes thus leading to foul smell and taste of the resulting water.

The second consists of environmentally refractory chemical species such as heavy metals, radionuclide, chlorinated hydrocarbons and polycyclic aromatics, as well as sulphur and nitrogen oxides which can form acids in rainwater. This group can have direct toxic effects on the ecosystem. They also produce long-term, less obvious effects but are environmentally significant. In the aquatic system, they tend to bio-accumulate in the bottom sediments and become concentrated by the biota and they can get to humans causing acute and chronic ailments.

Sediment is the most vital reservoir or sink of metals and other pollutants in aquatic organisms and the pollutants in the sediment are absorbed by plants and animals (Ekpete, 2019) [11].

Heavy metals are present in effluents discharged from homes and industries. They act as essential nutrients for flora and fauna when present at low concentrations, thus regarded as micronutrients. They also play key roles in the regulation of metabolism and growth. For example, Iron is a component of haemoglobin that aids in the transportation of oxygen. However, some of them are hazardous, while others exhibit toxicity when their concentration exceeds the acceptable permissible limit. Studies have shown that long term exposure of organisms and humans to low concentrations of these metals can lead to chronic diseases. The forms in which metal pollutants exist in water discharged, determine their release into the aquatic ecosystem. This study evaluated the concentrations of some heavy metals such as Ba, As, Cu, Cd, Cr, Ni, Zn, Pb present in the water and sediment of the New Calabar River.

Materials and Methods

Study Area

The study area is the New Calabar River, located in the coastal zone of the Niger Delta in Nigeria, between 7°60' east longitude and 5°45' north latitude, directly flowing into the Atlantic Ocean. Riverbank operation such as logging, forestry, and dredging can cause large-scale river pollution. The New Calabar Rivers passes through Aluu in Ikwerre Local Government Area to Bakana in Degema Local Government Area of Rivers State and linked to the ocean (Nwineewii & Unochukwu, 2018) [27]. Three sampling points were identified downstream: Ogbakiri (S1), Minipiti (S2) and Eagle Cement (S3). These locations were chosen based on accessibility, slightly different wastes, low tide zone, and economic activities on their territories.

Table 1: Geographic coordinates of the Sample Locations along New Calabar River

Sample Location	Geographic Coordinates
Ogbakiri Station	4º47’47.2” N, 6º54’46.1” E
Minipiti Station	4º48’37.4” N, 6º55’43.7” E
Eagle Cement Station	4º48’55.9” N, 6º56’38.2” E

Sampling and Analysis

Water sampling bottles were washed with nitric acid and sampling water. The water sample was collected in a 1L capacity plastic bottles and 5 ml of concentrated nitric acid was added to prevent further oxidation and degradation of the aqueous solution. 2cm^3 of top sediments were collected from each site and wrapped in polythene bags. Samples were transported in labelled containers, plastic bags, glass bottles, kept in an ice chest and transported to the laboratory, where they were stored in a refrigerator at 4°C until the analysis was completed.

The Preparation of water samples for heavy metal analysis was done by solvent extraction, also known as liquid-liquid extraction. It is the most ideal method for brackish water because the metal matrix in the solution is very strong, so it is difficult to recover the metal using the usual acid digestion process.

The extraction procedure followed procedure earlier adopted by Kpee (2012) [20]. 1 g of ammonium pyrrolidine dithiocarbamate (APDC) was dissolved in 100 ml of distilled water. The water was transferred to a 250 ml beaker with a replaceable standard stopper. A few drops of 2M HNO_3 acid was added to the beaker until the pH was adjusted to 2.5. This was measured with a pH meter.

2.5 ml of APDC solution and 10 ml of 2% methyl isobutyl ketone (MIBK) aqueous solution was added to a beaker with a stopper, and the contents of the flask was vigorously stirred for one minute. The two layers was separated, and the organic layer was transferred to a 25ml volumetric flask. 5ml of deionized water was added to raise the organic layer to the top of the 25ml volumetric flask. This procedure was used in other experiments; blanks and standard solutions of heavy metals were also prepared.

Sediment samples from different Stations were air-dried for 10 days at room temperature, disaggregated and sieved. The sieved sample was then homogenized in a porcelain mortar and mixed again. The sediment sample was digested and analysed according to an earlier method adopted by Kpee, (2012) [20]. A weighed mass of 2g of the air-dried homogeneous sediment was placed in a 50 ml volumetric flask, and 3 ml concentrated Nitric (HNO_3), 1 ml perchloric acid ($HClO_4$) of 60% concentration, and 1 ml tetraoxosulphate (VI) acid (H_2SO_4) was added and heated on a hot plate to near dryness. The contents of each flask were diluted to the mark with 10 ml of distilled water, and then filtered through Whatman #1 filter paper, and the filtrate was analysed. The concentrations of heavy metals such as Ba, As, Ni, Zn, Cd, Pb, Cr and Cu in sediments, water samples, blanks and standard metal solutions were analysed using a Solar Thermal Elemental Atomic Absorption Spectrophotometer (Model SN.SG710960) with an air-acetylene flame.

Statistical tool for Analysis of Results

The raw data was subjected to descriptive statistical analysis like One-way Analysis of Variance (ANOVA).

Results and Discussion

Results of the heavy metals present in water sample is presented in Table 2 and sediment sample is presented in Table 3.

Table 2: Concentrations (Mean ± S. D) of Heavy Metals (mg/l) in the Water Sample

Heavy metals	Stations			Mean± SD	WHO (2012)	NESREA
	Ogbakiri	Minipiti	Eagle Cement			
Ba	0.0064±0.015	0.042±0.001	0.125±0.010	0.058±0.061	2.0	-
As	0.007±0.002	0.039±0.007	0.217±0.005	0.088±0.113	0.001	0.1
Cu	1.695±0.003	3.891±0.004	4.421±0.005	3.336±1.446	1.0	1.0
Cd	0.004±0.001	1.164±0.010	1.375±0.006	0.848±0.738	0.005	0.003
Ni	1.169±0.006	2.892±0.107	3.897±0.017	2.653±1.380	0.02	0.02
Zn	3.152±0.004	6.325±0.004	4.695±0.010	4.724±1.586	5.0	3.0
Pb	2.718±0.013	3.138±0.007	4.317±0.006	3.391±0.830	0.05	0.01
Cr	2.891±0.006	4.817±0.011	3.914±0.004	3.874±0.963	0.5	0.05

Table 3: Concentrations (Mean ± S.D) of Heavy metals (mg/kg) in the Sediment Samples

Heavy metals	Stations			Mean ± SD
	Ogbakiri	Minipiti	Eagle Cement	
Ba	0.074±0.004	2.1423±0.001	3.348±0.010	1.855±1.656
As	0.159±0.007	1.897±0.011	2.729±0.004	1.595±1.311
Cu	5.428±0.008	8.562±0.005	7.891±0.006	7.294±1.650
Cd	0.842±0.001	2.315±0.005	4.327±0.001	2.495±1.750
Ni	6.392±0.050	5.413±0.013	08.449±0.004	6.751±1.550
Zn	11.628±0.006	13.329±0.003	18.184±0.004	14.380±3.402
Pb	4.810±0.007	6.897±0.008	8.113±0.003	6.607±1.671
Cr	6.911±0.004	9.33±0.004	7.61±0.080	7.951±0.010

The concentrations of heavy metals in water and sediment samples of the river varied from station to station with the average concentration of heavy metals in water samples in the order Zn >Cr > Pb > Cu > Ni > Cd > As > Ba and Zn > Cr > Cu > Ni > Pb > Cd > Ba > As in sediment sample of the river.

Table 2 showed that the Barium (Ba) concentrations in the analysed water samples ranged from 0.0064 ± 0.00 to 0.125 ± 0.01 mg/l, with Ogbakiri station as the least and Eagle cement as the highest while Ba concentrations in sediment samples ranged from 0.074 ± 0.004 mg/kg to 3.348 ± 0.010 mg/kg, with the highest level at Eagle cement Station and the lowest Ba level at Ogbakiri station (Table 3). All values and the mean concentration of 0.058+0.061 mg/l in water samples were below the allowable value of 2.0 mg/l recommended by the World Health Organisation for drinking water. The barium concentration in groundwater in the Netherlands was measured at 60 locations; the average and maximum concentrations were 0.23 and 2.5 mg/L, respectively (Van Duijvenbdered, 1989) [36], which was much higher than the values obtained from the study. Result of a one-way ANOVA showed $p<0.05$. This indicated that there was a significant difference in concentrations of Ba in all stations. The mean value of 1.855±1.656 mg/kg (Table 3) gotten from the study was at variance with that reported by Uche *et al*. (2016) and Buru, (2013). Values of 403 mg/kg and 402±63.47 mg/kg were reported by the duo. The concentrations of Ba in the river could be attributed to anthropogenic activities that involve indiscriminate dumping of wastes such as plastics, rubber, electronics, textiles, rodenticides, cosmetic product, and pharmaceutical items into waterbody or soil that is subsequently washed into the river.

From Table 2 and 3, the range of arsenic concentrations was 0.007 ± 0.00 to 0.1254 ± 0.009 mg/l in water samples and 0.159±0.007 mg/kg to 2.729±0.004 mg/kg in sediment samples of the river. The mean arsenic concentrations in the water sample of the river was 0.088±0.113 mg/l, and higher than the WHO and NESREA values of 0.001 and 0.1 mg/l respectively for drinking water. Table 3 revealed the mean levels of arsenic in sediment obtained to be 1.595±1.311 mg/kg. The mean concentration obtained from water samples of the river was lower than the mean value of 0.1±0.01 mg/l reported in the investigation of the Nta-Nwogba Creek by Nweke & Ekpete (2003) [21]. The result of the one-way ANOVA conducted revealed $p<0.05$, indicating a significant difference in the levels of arsenic in the stations sampled. The result obtained for sediment was consistent with value of 1.175±0.086-1.129 mg/kg obtained in the study of sediment quality of Orashi River (Akachukwu *et al*., 2011). However, the study result was in sharp contrast to results of 0.25-0.72 mg/kg and 0.14-0.17mg/kg obtained by Kpee and Nwineewii, (2011) in the study of heavy metal concentration of sediments of Andoni River and Leizou *et al*., (2015) [23] in the investigation of speciation of some heavy metals in sediment of the Pennington River of Delta state. High levels of arsenic could be from natural bottom sediments or industrial and agricultural pollutants, especially those pollutants containing arsenic, fertilizers or herbicides that are washed into water bodies. Drinking arsenic-rich water can cause skin problems, including skin cancer, lung, bladder, and kidney cancer, and possibly other internal tumors; peripheral vascular disease and high blood pressure (Hopenhayn, 2006) [15].

Copper is an essential element for the growth of animals and plants; in humans, it contributes to the production of hemoglobin in the blood; copper in plants promotes seed production, disease resistance and water regulation. The copper concentrations in the water samples ranged from 1.695 ± 0.003 to 4.421 ± 0.005 mg/l (Table 2). The mean concentration in the river was 3.336±1.446 mg/l. The result of one-way ANOVA revealed $p<0.05$, indicating a significant difference in the levels of copper in the different stations with Eagle cement station being the highest and Ogbakiri, the lowest. The values from the study were all above the WHO and NESREA permissible limit of 1.0 mg/l. The result obtained from the study was in contrast to that reported by Osa-Iguehide *et al*., (2016) [29] and Ishaq *et al*., (2012) [18] and in a study to determine the heavy metals concentrations in surface water of Ikpoba River in Edo State and River Benue, in Benue State. In both study, copper concentrations of 0.022-0.042 mg/l and 0.056±0.04 mg/l were reported. The copper levels in sediment obtained from the study was consistent with the reported values in the assessment of the link between industrial activities and pollution status of Asa River (Adekola & Eletta, 2009). The values from the study were lower than the mean concentration obtained in sediment samples of Kalabari Creek (Kpee & Ekpete, 2014) [21]. It was however, higher than that reported by Osakwe & Peretiemo-Clark (2008) [30] in the evaluation of heavy metals in sediment of River Ethiope. Copper can enter into the soil through wares of vehicular parts which in turn is washed off into water bodies. High concentration of copper can cause anemia, liver and kidney damage, stomach and intestinal irritation. In addition, copper is indirectly related to neurological diseases such as Alzheimer's disease, Wilson disease, and prion disease (Desai and Kaler, 2008; Huster, 2010) [8, 16].

Cadmium is a toxic metal and has no metabolic benefits to humans or aquatic organisms. The range of cadmium concentrations in water samples at different stations of the New Calabar River was 0.004 ± 0.00 to 1.375 ± 0.006 mg/l (Table 2) while in sediment samples, the levels ranged from 0.842 ± 0.001 mg/kg to 4.327 ± 0.001 mg/kg (Table 3). The highest concentrations for water and sediment samples was at Eagle cement station and the lowest at Ogbakiri station. The mean concentration of cadmium was 0.848±0.738 mg/l which is higher than the World Health Organisation recommended limit of 0.005 mg/l for drinking water. The result of a one-way ANOVA showed $p<0.05$, indicating a significant difference between the concentrations of the cadmium in all three stations. The mean concentration of water samples obtained from this study was below the mean concentration of 1.48 mg/l reported by Goje *et al*. (2017) [14] in the assessment of heavy metal concentrations of River Gongola in Adamawa State. However, it was higher than 0.052±0.02 mg/l reported by Ishaq *et al*. (2012) [18] in the study of pollution level of River Benue in Makurdi Metropolis and 0.251±0.00 obtained by Edori *et al*. (2019) [9] in the study to determine the heavy metal levels in Elelenwo Creek of River State. The mean concentration of cadmium in sediment samples of the river was 2.495±1.750 mg/kg which was consistent with value of 0.948±0.07 to 3.120±0.131 mg/kg reported by Akachuwu *et al*. (2020). However, the result was at variance with that reported from other work. Edori *et al*. (2020) [10] reported mean value of 0.216±0.025 mg/kg in the study of sediment samples from three other locations of New Calabar River. Quyang *et al*. (2001) [31] analysed heavy metals in sediments from Cedar and Ortega River Sub-basin of the lower St. John's River Basin in North-Eastern Florida and reported value of 0.07-3.83 ppm which was slightly lower than value obtained from this research. Akan *et al*. (2010) also reported higher cadmium levels of 7.34-64.0 mg/kg in sediment samples of the Ngada River in Borno State. High levels of cadmium is attributed to industries involved in the manufacture of batteries, paints and plastics. High levels of cadmium in water can cause kidney disease, lung damage, and bone fragility (Bernard, 2008) [6].

The concentration of Ni in the surface water of New Calabar River ranged from 1.169 ± 0.007-3.897 ± 0.184 mg/l while that of sediment ranged from 5.413±0.013 - 8.449±0.004 mg/kg (Table 2). The mean concentration of nickel in water was 2.653±1.380 mg/l, which was higher than the World Health Organisation standard and NESREA requirement of 0.015mg/l and 0.02mg/l for drinking water respectively. The result of a one-way ANOVA showed $p<0.05$, indicating a significant difference in the mean concentrations of the various sampling stations. The result obtained for water samples in the study was higher than the mean value of 0.04 mg/l reported by Emoyan *et al*. (2006) [12] in the evaluation of levels of metals in surface water of River Ijan in Warri. Wogu and Okaka (2011) [38] also reported a higher mean value of 0.0328 mg/l in the study to determine the heavy metals concentrations in surface water of Warri River. The result obtained for sediment was below 20.90±10.47 mg/kg reported by Kpee & Ekpete (2014) [21] in the evaluation of heavy metal levels of sediment sample of Kalabari Creek. The result was, however, higher than values reported in separate studiy carried out on sediment sample of New Calabar River (Nwineewii & Unochukwu, 2018; Edori *et al*., 2020) [27, 10]. Nickel is released into the water body through wastes discharged by industries involved in the production of batteries, dyes and catalysts and also ceramic companies. Nickel has been shown to produce free radicals, hence, it is also involved in carcinogenesis (Agel *et al*., 2019; Valko *et al*., 2005) [34].

The concentrations of zinc in the surface water of New Calabar River ranged from 3.152±0.004 to 6.325±004 mg/L while the levels of zinc (Zn) obtained in the sediment samples ranged from 11.628 ± 0.006 mg/kg to 18.184 ± 0.004 mg/kg (Table 3). The mean concentration of zinc in water samples of the river was 4.724±1.586 mg/l, which was higher than the World Health Organisation and NESREA permissible limit (Table 2). The result of this study was lower than the mean value of 6.59 mg/l reported by Wegwu and Akaniwor (2006) [37] on the heavy metal profile of the same River. However, result from the study was higher than value of 0.0787±0.02 mg/l reported by Ishaq *et al*. (2012) [18] for surface water of River Benue and 0.39-0.41mg/l reported by Ikhuoriah & Oronsaye (2016) [17] in surface water of Ossiomo River in Edo State. The average value of zinc in the sediments of the New Calabar River was 14.380±3.402 mg/kg, which is slightly below the recommended limit of 50.0mg/kg for sediment set by the World Health Organisation. The result from the study was lower than the value of 37.25-110.00 mg/kg reported by Aghoghovwia *et al*. (2015) [2] in sediment samples of Warri River. Nwineewii and Unochukwu (2018) [27] also reported lower zinc (Zn) level of 5.49±0.005 mg/kg in sediment sample of same New Calabar River. The result of a one-way ANOVA revealed $p<0.05$ indicating a significant difference in the concentrations of Zinc in all stations. However, high zinc levels can cause health problems such as stomach cramps, skin irritation, vomiting, nausea, and anaemia (ATSDR, 2005; Valko *et al*., 2006) [35].

Lead does not play any biological role in animals. The Lead concentrations of water samples of New Calabar River at different stations ranged from 2.718 ± 0.013 to 4.317 ± 0.06 mg/l (Table 2), while it was 4.810±0.007 mg/kg to 8.113±0.003 mg/kg in sediment (Table 3). The result of a one-way ANOVA revealed $p<0.05$, indicating a significant difference in the concentrations of lead (Pb) in the stations sampled with Eagle cement Station recording the highest and Ogbakiri Station, the lowest. The mean concentration obtained from the study was 3.391±0.830 mg/l, and higher than the WHO and NESREA limit of 0.05 and 0.01 mg/l respectively. The results of the study was at variance with value of 0.11±0.01 mg/l reported by Nweke and Ekpete (2003) [26] in an investigation carried out to ascertain the level of heavy metals in Nta-Nwogba Creek and 0.0001 mg/l reported by Wogu & Okaka (2011) [38] in the study to determine the heavy metals concentrations in surface water of Warri River. The mean concentration of lead in sediment was 6.607±1.671 mg/kg which was in contrast to values from other studies. Aghoghowvia *et al*. (2015) reported 6.88-55.25 mg/kg in sediment sample of Warri River while Osakwe and Peretiemo-Clark (2008) [30] reported 0.27-0.72 mg/kg in sediments of Ethiope River.

Like Cadmium, Lead compounds are found in urban and industrial waste and are discharged into surface water along with wastewater. Gas stations and high traffic are other sources of lead as vehicles and boats all make use of gasoline. This could be attributed to the reason why Minipiti station had the highest level of lead concentration due to its location. Plants with high concentrations of lead will accelerate the production of reactive oxygen (ROS), leading to damage to the lipid membrane, which ultimately lead to damage to the chlorophyll and photosynthesis process and inhibits the growth of all plants (Najeeb *et al*., 2014) [25].

Chromium (Cr) is an essential micronutrient required by animals and plants for metabolism and help insulin molecule in glucose transport in cells for metabolism and glycolysis. Chromium concentration at different sampling stations ranged from 2.891±0.181 to 4.817±0.29 mg/l, with an average of 3.874±0.963 mg/l, which was higher than the World Health Organisation value of 0.5 mg/l for drinking water (Table 2). The mean value obtained from this study was at variance with those of other researches. Goje *et al*. (2017) [14] obtained a mean value of 1.09 mg/l in surface water of River Gongola in Adamawa State. Onojake *et al*. (2017) also had chromium concentrations of 0.925-1.49mg/l in the study of surface water characteristics of the Bonny/New Calabar River Estuary in Rivers State. The chromium (Cr) concentration in sediment sample of New Calabar River ranged from 6.911±0.004 to 9.33±0.004 mg/kg (Table 3). The mean concentration of chromium was below the allowable limit of 100.0 mg/kg set by World Health Organisation. The result obtained from this study was lower than 28.87-45.14 mg/kg reported by Akan *et al*. (2010) in the determination of the heavy metals levels in sediments from River Ngada in Maiduguri. However, Edori *et al*. (2020) [10] reported lower value of 3.102±0.196mg/kg of chromium in sediments of New Calabar River.

It was also observed that all the stations were seriously polluted with chromium. Chromium may come from man-made sources, such as wastewater from leather production, wood preservatives and pigments in printing and dyeing industry, sewage discharge, fertilizers and run-off into the waterbody. High levels of chromium in drinking water could be detrimental to human health.

Conclusion

Result from the study showed pronounced pollution by heavy metals in surface water of New Calabar River. It was also observed that the concentrations of most metals increased in concentration from station 1 to 3. This revealed that the major source of pollution in the area is anthropogenic considering the fact that the concentration of the metals increased based on the commercial activities in the stations. There is a significant increase in levels of most heavy metals above the World Health Organisation and NESREA standards. The Continuous pollution of water bodies can lead to high risk of metal poisoning, which may ultimately affect the biota, distort the food web and ultimately cause the death of plants and animals and as a result the following recommendations were suggested;

Local fishermen should be enlightened on the dangerous effect on the use of chemicals in fishing has on aquatic environment. Finally, the government must put in place measures that will guide against upsurge of illegal refineries in the area.

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