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Seasonal Assessment of Heavy Metals in Water at Effluents Discharge Points into the New Calabar River, Port Harcourt, Southern Nigeria

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Abstract- Water samples were collected at three different effluents discharge points into the New Calabar River. The samples were digested using standard methods. The digests were subsequently examined for heavy metals concentrations using atomic absorption spectrophotometer (AAS). Heavy metals results in the samples showed Ni as the most concentrated metal with a mean value of 2.52±0.055, 1.42±0.01 and 1.275±0.045 mg/L at Iwofe, Jetty, Minipity and Police Post stations respectively, this was followed by the concentration values of Cr, which were 1.72±0.06, 2.17±0.02 and 1.355±0.015 mg/L at the Iwofe Jetty, Minipiti and Police Post sample stations respectively. The least concentrated metal observed in this study was Cd with amean range of 0.03- 0.28 mg/L in the stations. This was followed by the values of Cu from the station which ranged between 0.035 - 1.22 mg/L. The general order of the concentration of metals was Ni>Cr>Fe>Zn>Pb>Cu>Cd. All the metals examined in the water samples except Zn were higher than the WHO maximum standard for drinking water.

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Abstract- Water samples were collected at three different effluents discharge points into the New Calabar River. The samples were digested using standard methods. The digests were subsequently examined for heavy metals concentrations using atomic absorption spectrophotometer (AAS). Heavy metals results in the samples showed Ni as the most concentrated metal with a mean value of 2.52±0.055, 1.42±0.01 and 1.275±0.045 mg/L at Iwofe, Jetty, Minipity and Police Post stations respectively, this was followed by the concentration values of Cr, which were 1.72±0.06, 2.17±0.02 and 1.355±0.015 mg/L at the Iwofe Jetty, Minipiti and Police Post sample stations respectively. The least concentrated metal observed in this study was Cd with amean range of 0.03 - 0.28 mg/L in the stations. This was followed by the values of Cu from the station which ranged between 0.035 - 1.22 mg/L. The general order of the concentration of metals was Ni>Cr>Fe>Zn>Pb>Cu>Cd. All the metals examined in the water samples except Zn were higher than the WHO maximum standard for drinking water. Contamination factor analysis showed that the samples were either severely or excessively polluted by most of the metals. However, Zn and Cu were within the range of contamination in the sampled stations. Pollution load index indicated that the stations ranged from severe pollution to excessive pollution. Contamination degree assessment indicated very high degree of contamination and the modified degree of contamination showed that all the stations were within ultra high degree of contamination. Generally, the result indicated a high degree of water pollution by heavy metals at the discharge point. Therefore caution should be taken to control the sources of these pollutants, which have put this aquatic environment under serious threat.

Keywords: effluents, discharge points, heavy metals, pollution, contamination.

I. Introduction

One of the ways through which water is polluted is by the discharge of effluents or wastewater from industries, homes, runoffs, drifts, precipitation, etc (Al-Zubaidi, 2012).The problem of pollution and waste discharge resulted from urban drift issues and industrial development. The concept and reality of waste production is divers in nature and as such, the wastes so generated can take the form of solids and fluids (liquids and gases). To adequately solve or manage pollution issues, the nature and origin of the pollutant must be ascertained. This will help in the general application of the type of treatment system to be put in place (Abedi and Najafi, 2001).

One of the most commonly found pollutants in effluent discharge are heavy metals. They are known to be toxic and have accumulative tendencies in living organisms. Heavy metals do not easily decompose or undergo biological reactions. They are known to produce negative effects on the environment and are subsequently become part of the food chain. When humans eventually consume these organisms, they become toxic and eventually cause different diseased conditions (Mansourri and Madani, 2016).

Heavy metals are implicated in different health problems such as dwarfism, developmental disorders, cancer, organs destruction and malfunction, nervous system impairment, and in extreme cases, mortality (Iyamaet al., 2014). Exposure or contact with some heavy metals, namely mercury and lead, it even low concentrations can result in self destruction or breakdown of the immune system. Lowered immune system leadsto a combination of diseases like rheumatoid arthritis, kidneys disease andbrain damage which is not reversible. At higher doses, heavy metals can cause irreversible brain damage (Barakat, 2010).

The introduction of high concentrations of heavy metals into aquatic environment leads to grave health and environmental consequences, such as illness, wastewater treatment cost and application of the water for irrigation purposes. In nature, heavy metals are present in trace quantities in most cases. They enter into water bodies through leakage from rocks, fly ash or dust, forest fires, volcanic eruption and foliage from vegetation (Ogoyi *et al*., 2011). The effluent arising from domestic and industrial activities are in most cases discharged into aquatic water bodies such as rivers, streams, estuaries, etc. This action results in the pollution load or burden on that aquatic environment receiving the discharged effluents. Therefore, this study was undertaken to examine the concentrations of some heavy metals at the discharge point along the New Calabar River.

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II. Materials and Methods

Water samples were collected at the different effluent discharge points into the New Calabar at low tide with plastic bottles previously washed plastic bottles. The samples were collected twice each in the different seasons. The water samples were collected at a depth of 20 cm below the water surface. The samples were fixed on site by the addition of two drops of70% concentrated nitric acid and mixed thoroughly after corking it. The samples were transported to the laboratory in an ice pack container and then stored in at a temperature of 4ºC.

In the laboratory, the samples were prepared for analysis, first by digesting them with amixture of mineral acids (Marcus and Edori, 2017) and heated in a steam bath to obtain a clear colour and the content filtered with size 1 Whatmann filter paper.

The filtrates or digest were subjected to metal analysis using atomic absorption spectrophotometer (AAS), model SE-71906 UK. The results obtained were validated by taking three different measurement and further validation by comparing with the values obtained from standard laboratory samples. Mean ± Standard deviations were used to represent the data obtained for the seasons.

The data obtained for the heavy metals were subjected to contamination factor (CF), pollution load index (PLI), degree of contamination (CD) and modified degree of contamination (mCD) analysis. The different formulae used were:

$CF = \frac{Concentration\ \ of\ metal\ in\ measured\ \ sample\ \ (Cm)}{Concentration\ \ \ of\ metal\ at\ backgroud\ \ \ level\ \ (Cb)}$ (Lacatusu, 2000),

$PLI = CFI\ \times CF2\ \times CF3\ \times CF4 \ldots\ldots\ldots\ldots \times CFn)1/n$ (Thomilson *et al*., 1980),

Where $CFI\ \times CF2\ \times CF3\ \times CF4 \ldots\ldots\ldots\ldots \times CFn$ are the individual contamination factors of the different elements to the nth number and 1/n is the nth root of the number of metals measured.

$CD = \sum_{I=1}^{N} CFI$ (Hakanson, 1980)

$\mathrm{mCd} = \frac{1}{N}\sum_{I=1}^{N} CFI$ (Hakanson, 1980)

Where, *N* is the number of elements determined, *CF* is the contamination factor, CD is the contamination degree and mCD is the modified contamination degree.

III. Results and Discussion

The data for the both dry and rainy seasons and the mean values are given in Tables 1-3. It was observed that in both seasons that the concentrations of the heavy metals were more at the Iwofe station than the other station. Also, the results in both dry and rainy season were not statistically different.

The results obtained for copper (Cu) at Iwofe and Minipitistations were higher than the required value for drinking water by WHO, while the values obtained at the police Post station was lower than the WHO standard. The concentration values obtained for Cu in this work is similar to those observed by Marcus and Edori (2016) in two other rivers within the state. Cu, though an essential metal at low concentrations, is known to be toxic at reasonably higher concentrations. Health implications of Cu to humans after high level in take include liver and kidney injury, anaemia, stomach pain, vomiting, headache and vomiting in children (Salem *et al*., 2000).

The concentration values obtained for Pb in the various stations were all higher than the WHO maximum value for drinking water. The findings on Pb in this work corroborates the findings of other authors (Marcus and Eori, 2016; Stanley *et al*., 2017). However, the values obtained for Pb were higher than those observed in another study of effluents from the petrochemical industry discharged into Ekerekana River (Marcus and Edori, 2017) and oily waste water effluents (Wokoma and Edori, 2017) and those obtained by Jenyo-Oni and Oladele, (2016). Lead Pb as a metal is not required by both plants and animals at any concentration. It is considered as a poison or toxicant even at very low concentrations (Edori and Edori, 2012). Pb is associated with different diseased conditions such as blood poisoning and reduced acumen, lesserIQ, neurobehavioral disorder, hearing and speech deformations, growth retardation and irregular behavior in children (Hertz-Picciotto, 2000), while in adults, it causes low sperm count, and induces abortion in women (Flora *et al*., 2007). Other effects of Pb may include brain and kidney impairment, intestinal diseases and distortion in vitamin D production (Apostoli*et al*., 1998).

The values obtained for Zn in the various stations were below the WHO standard. Zn is an essential micronutrient required in both plants and animals at trace level for effective biochemical functions (Meshram *et al*., 2012). The low level of Zn in this work is in agreement with observations made by other authors in similar environments (Olufemi *et al*., 2011; Bhardwaj *et al*., 2017), but quite lower than those observed in surface water in Esi River, Western Niger Delta (Akporido and Onianwa, 2015).Low intake of zinc in pregnant women can result in birth defects.

The values obtained for Cd in the different sampled station were above the recommended WHO levels in drinking water. The values recorded for Cd in this work at the Iwofe Jetty are higher than those observed by Wokhe, (2015) in another Nigerian River, but fall within the range observed by Olufemi *et al*., (2011) in another river in Nigeria. However, the values obtained in the other two stations (Minipiti and Police Post) were within the range observed in other studies elsewhere and Nigeria (Manoj *et al*., 2012; Wokhe, 2015; Ibrahim *et al*., 2016). Cadmium (Cd) is an unwanted metal in both plants and animals. It has not been documented to activate any aspect of plant or animal life, rather it is considered as a pollutant and toxicant to the environment (Banerjee, 2003).Exposure to both short and long term is associated with different organ dysfunctions and diseased conditions such as hypertension, decrease in weight, anaemia, lymphocytosis, increased protein content in urine, emphysema and lung fibrosis (if inhaled), atherosclerosis, stomach and back pains, and marginal neuropathy. Others are cough, pneumonia and general body weakness(Tchounwou *et al*., 2014).

The concentrations of Fe in all the sample stations were higher than the maximum recommended value of 0.03 mg/L by WHO. Iron (Fe) is a very vital metal required by both animals and plants for metabolic functions (Xing and Liu, 2011). Fe is a component of blood, and it is the element that is responsible for the colour of blood. At concentrations greater than 0.03mg/L, it adds taste and colour to water (Iyama *et al*., 2014). The speciation of Fe in water bodies are either in the Fe (II) or Fe (III) states. Fe deficiency leads to anaemic conditions where resistance to diseases is reduced (Banjari *et al*., 2015).

The values observed for Ni in the various stations were all higher than the WHO standard value for drinking water. The values observed for Ni in this study were higher than those observed in Ubeji River (Olufemi *et al*., 2011), Ijana River, Warri (Owamah, 2013) and Lake Asejire (Jenyo-Oni, and Oladele, 2016).Ni as an important element play some role in body metabolism such as activation of enzymes. It is present in both plants and animals. However, at high concentrations, it becomes toxic to consumers (Divrikli *et al*., 2003).

The values obtained for Cr in the water samples from the various stations were higher than the acceptable limit in drinking water. Chromium (Cr) concentrations observed in this work were above the values observed in other work in similar environments (Owamah, 2013; Shakirat and Akinpelu, 2013; Jenyo-Oni, and Oladele, 2016). Chromium (Cr) exist in different oxidations states, of which the most stable are the +3 and +6 oxidation states. It has been found that its toxicity is manifested in humans or animals when consumed as Cr (III), thatis in the +3 oxidation state (Tchounwou *et al*., 2014).

Table 1: Heavy metals concentration at the different effluents discharge points into the New Calabar River in the dry season

Heavy metals (mg/L)	Location		
	Iwofe Jetty	Minipiti	Police Post
Copper (Cu)	1.23 ± 0.03	0.04 ± 0.00	0.27 ±0.01
Lead (Pb)	1.34 ± 0.00	0.64 ± 0.02	0.48 ±0.07
Zinc (Zn)	1.69 ± 0.12	1.33 ± 0.21	0.84 ± 0.10
Cadmium (Cd)	0.25 ± 0.00	0.06 ± 0.00	0.03 ± 0.00
Iron (Fe)	1.44 ± 0.02	1.19 ± 0.03	0.79 ± 0.21
Nickel (Ni)	2.57 ± 0.23	1.43 ± 0.11	1.23 ± 0.08
Chromium (Cr)	1.78 ± 0.13	2.19 ± 0.16	1.34 ± 0.41

Table 2: Heavy metals concentration at the different effluents discharge points into the New Calabar River in the rainy season

Heavy metals (mg/L)	Location		
	Iwofe Jetty	Minipiti	Police Post
Copper (Cu)	1.21± 0.16	0.03 ± 0.00	0.24 ± 0.01
Lead (Pb)	1.25 ± 0.02	0.70 ± 0.02	0.43 ± 0.11
Zinc (Zn)	1.31 ± 0.12	1.29 ± 0.34	0.91 ± 0.24
Cadmium (Cd)	0.31 ± 0.00	0.04 ± 0.01	0.03 ± 0.00
Iron (Fe)	1.32 ± 0.05	1.15 ± 0.25	0.68 ± 0.02
Nickel (Ni)	2.46 ± 0.12	1.41 ± 0.04	1.32 ± 0.21
Chromium (Cr)	1.66 ± 0.48	2.15 ± 0.35	1.37 ± 0.41

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Table 3: Mean concentrations of heavy metals in the two seasons at the effluents discharge points into the New Calabar River

Heavy metals (mg/L)	Location			WHO Standard
	Iwofe Jetty	Minipiti	Police Post	
Copper (Cu)	1.22±0.01	0.035±0.005	0.255±0.015	1.00
Lead (Pb)	1.295±0.045	0.67±0.03	0.455±0.025	0.01
Zinc (Zn)	1.5±0.19	1.31±0.02	0.875±0.035	3.0
Cadmium (Cd)	0.28±0.03	0.05±0.01	0.03±0.00	0.003
Iron (Fe)	1.38±0.06	1.17±0.02	0.735±0.055	0.03
Nickel (Ni)	2.52±0.055	1.42±0.01	1.275±0.045	0.02
Chromium (Cr)	1.72±0.06	2.17±0.02	1.355±0.015	0.05

The result of the contamination index of the heavy metals is shown in Table 4. Based on the intervals of contamination proposed by Lacatusu, (2000), Cu was uncontaminated at the Minipiti sample station, slightly contaminated at the Police Post sample station and slightly polluted at the Iwofe Jetty sample station. Zinc (Zn) showed moderate contamination in all the sampled stations. Cadmium showed very severe pollution at the Police Post station and excessive pollution at Minipiti and Iwofe Jetty stations. The three stations examined showed that the water were excessively polluted with lead (Pb), iron (Fe), nickel (Ni) and chromium (Cr).

The observed values of contamination index in this work were higher than those observed by Marcus and Edori, (2017) at Ekerekana River due to refinery wastewater.

Table 4: Contamination index of heavy metals of water samples at the Effluents discharge points

Heavy metals (mg/L)	Location		
	Iwofe Jetty	Minipiti	Police Post
Copper (Cu)	1.22	0.035	0.255
Lead (Pb)	129.5	67	45.5
Zinc (Zn)	0.5	0.44	0.292
Cadmium (Cd)	93.33	16.67	10
Iron (Fe)	46.0	39.0	24.5
Nickel (Ni)	126.0	71.0	63.75
Chromium (Cr)	34.4	43.4	27.1

The result of pollution load index, degree of contamination and modified degree of contamination is given in Table 5.The results obtained for Pollution load indexproposed by (Thomilson et al., 1980)when analysed based on Lacatusu(2000), incidence of contamination or pollution chart indicated that Iwofe Jetty location was excessively polluted, Minipiti and Police Post stations were severely polluted. In all the sampled stations, using contamination degree assessment, there was a marked observation of very high degree of contamination when the result obtained in these locations were compared with Hakanson (1980) terminologies on contamination levels of water and sediment polluted or contaminated with heavy metals. The modified degree of contamination which was proposed by Hakanson (1980) result showed that all the sampled stations fall within the ultra high degree of contamination.

Table 5: Pollution load index (PLI) and degree of contamination (CD) and modified degree of contamination (mCD) of water samples at the Effluents discharge points

Pollution Description	Iwofe Jetty	Minipiti	Police Post
PLI	20.399	7.981	7.443
CD	430.95	237.565	171.397
mCD	61.429	33.938	24.485

IV. Conclusion

The result obtained from this work is an indication of anthropogenic pollution. The concentrations of the heavy metals in the various drainage outlets showed higher values than those of the standard. Therefore the water is not suitable for consumption. Efforts should be put in place to check all the input sources to make sure that they do not discharge beyond the allowable concentrations of these metals from their effluents, otherwise there is the likely hood of pollution explosion arising from heavy metals.

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