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Assessment of Heavy Metal Status of Orashi River Along the Engenni Axis, Rivers State of Nigeria

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Abstract *In order to assess the status of heavy metal contamination in Orashi River, water samples were collected from Orashi River bimonthly at different stations. The samples were analyzed for the concentrations of manganese (Mn), mercury (Hg), cadmium (Cd), lead (Pb), copper (Cu), nickel (Ni), iron (Fe), chromium (Cr) and zinc (Zn) ions using atomic absorption spectrophotometry (AAS). It was observed that the mean concentrations of the metal ions varied in the order: Ni >Fe > Mn > Cu > Zn > Cr > Pb > Cd > Hg. The levels of all the heavy metal ions were lower than WHO and SON standards for drinking water except Ni. There were both spatial and monthly variations in the metal ions concentrations. Calculated contamination factors indicated that the river was at various levels of contamination by the heavy metals except Ni that was observed at pollution level. Pollution index analysis showed slight level of contamination with the heavy metals. Contamination degree and modified contamination degree analysis showed very low degrees of contamination. Findings from this study portend that the Orashi River is at the threshold of contamination if pollution load to the river is not controlled.*

Key Words: *Heavy metals, surface water, Orashi River, contamination, Engenni axis*

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1.0 Introduction

The significance of rivers to the ecological and economic development of the society cannot be overemphasized. Nevertheless, water obtained from rivers are reasonably susceptible to pollution because they are obviously exposed; simply reachable for substantial uses for agriculture, industries, and public and private practices (Li *et al*., 2016). Water pollution arises after a body of water is undesirably affected owing to the introduction of huge quantities of chemical constituents into the water, rendering it unhealthy for proposed use. There are two ways by which the hydrosphere is polluted. These sources will either be point source and nonpoint source pollution. Most pollution problems arise from unidentifiable sources (nonpoint sources) and these are responsible for major part of contaminants present in the aquatic hydrosphere (Maitera *et al*., 2011).

In general, human quest for development has led to serious social changes in the form of industrial growth, population growth in cities (a consequence of urban drift) and increased technological advancements in recent years. These have led to a sharp increase in the release of contaminants such as heavy metals in the environment (Liu *et al*., 2009). Some of the heavy metals (Hg, Cd, Cr, and Pb) are known to be very toxic even when present in small or trace amounts. These metals enter the environment primarily from anthropogenic activities. Some heavy metals (Cu, Fe, Zn and Mn) are very beneficial as essential elements when present in desirable amounts due to their nutritional importance to both plants and animals. Despite their importance, when they are present in higher than required proportion, they pose serious toxicological effects on both humans and the environment (Alsaffar *et al*., 2016). The toxic effects of certain heavy metals e.g. Hg are normally produced when their characteristics are changed through combination with some organic compounds in the formation of complexes (Akbulut and Tuncer, 2011).

Different projects for monitoring the environment have been put in place in many developed countries of the world. Despite these projects, the developing countries seem to lag behind in attending to increasing issues of environmental decay and deterioration arising from different human interferences with the environment. The search for life up-keep and maintenance requires influencing the natural ecosystem. This is done through exploration and exploitation of mineral resources, invasion of natural wildlife through fetching of wood for fuel, cutting of timber for building, food provision through agricultural activities, manufacturing processes and other industrial and domestic activities. These activities are accompanied with the release of toxic chemicals such as heavy metals into water bodies, which when allowed to continue will lead to accumulation (Biney *et al*., 1991). The Orashi River is not left out in all these. This study was designed to examine levels of some heavy metals in Orashi River, along Engeni axis of Rivers State of Nigeria.

2.0 Materials and Methods

2.1 Study area

The Orashi River (also Urashi or Ulasi) takes off as a stream from the rocks in Urashi in Dikenafai, Ideato South LGA of Imo State of Nigeria. It traverses many communities in Imo and Rivers States to enter the Atlantic Ocean. In Engenni, Ahoada West Local Government Area of Rivers State, the river passes through all the communities except Edagberi. The river serves as all-purpose river for drinking, washing and many other domestic purposes to the communities surrounding it. The Orashi River is situated between latitudes 50º 45″ and 60º 35″ N and longitudes 40º 50″and 50º 15″ E (Seiyaboh *et al*., 2016a). It is one of the most important rivers in the Easter Niger Delta. The area is prone to flood during the rainy season and subject to sedimentary depositions which varies depending on the nature and size of the flood (Seiyaboh *et al*., 2016b). The Engenni area under investigation is subjected naturally to wet (from April to October) and dry (November to March) seasons. The rural dwellers are artisanal farmers and fishermen and also engage in petty trading. There is also marine transportation with outboard engine and recently the outburst of artisanal refining of crude oil, which has occasioned incessant spills and discharges of petroleum products.

2.2 Collection of surface water samples

The surface water samples were collected with plastic water bottles of 1L capacity at a depth of 30 cm. The samples were collected bimonthly from four designated stations. The samples from each station were collected in triplicates. Prior to sampling, the bottles were rinsed with water from the sample points and immediately after collection, three drops of concentrated nitric acid were added and the container was adequately corked. The stations where samples were collected and their geographic positions were Odawu (4º 107.3′ N, 6º30′ 6.6″ E), Mbiama (5º3′ 39.2″ N, 6º 26′ 58.7″ E), Okarki (5º9′ 5.2″ N, 6º25′ 47.6″ E) and Okparaki (4º59′ 10.1″ N, 6º27′ 2.5″ E).

2.3 Analysis of heavy metals in surface water

The concentrations of the heavy metals in the water samples were determined with atomic absorption spectrophotometer (AAS) Model SG 71906), UK. The concentration of each metal was determined from the water sample directly without previous treatment of the water samples.

2.4 Determination of contamination factor, pollution index, contamination degree and modified contamination degree

The contamination factor (CF) and pollution index (PI) were determined using the formula proposed by Lacatusu, (2000) and interpreted based on the chart or table provided to describe the different intervals of contamination or pollution of water. The contamination degree (CD) and modified contamination degree (mCD) of the water samples were calculated using the formulae proposed by Hakanson (1980), which describe contamination of heavy metals on the basis of combined effects or contributions of each of the individual metals examined in any research work or environmental monitoring. The obtained figures or data were then explained on the basis of a chart provided to explain the extent of the combined effects of the metals (Hakanson, 1980).

$$CF = C_m/C_b \quad (1)$$

$$\text{PI} = \text{n}\sqrt{C_{F1}\ \text{x}\ CF_3\ \text{x}\ \ldots\ \text{x}CF_n} \quad (2)$$

$$\text{CD} = \sum_{i=1}^{n} CF \quad (3)$$

$$\text{mCD} = \frac{1}{N}\sum_{i=1}^{N} CF \quad (4)$$

where C_m is metal concentration in polluted water, C_b is background value or maximum recommended value of the metal in water, N is the number of elements examined, *I* = *i*th element or pollutant.

2.5 Statistical analysis

The data obtained were analyzed using analysis of variance (ANOVA) and Duncan's multiple range test.

3.0 Results and Discussions

Levels of heavy metals determined in water samples from Orashi River are presented in Table 1 while the mean monthly concentrations of heavy metals during the months of analysis are presented in Table 2. The concentrations of the metals examined showed that Mn ranged from 0.006 ± 0.00 - 0.225 ± 0.02 mg/L while the mean monthly concentrations ranged from 0.008 ± 0.00 - 0.293 ± 0.12. These values were lower than the standard set by WHO and SON except for Ni. This shows that the Orashi River was not contaminated with respect to Mn at the time of this study. This observation is in agreement with the findings of other authors in similar environments (Iyama *et al*., 2014; Iyama *et al*., 2019) in Sombreiro River Ahoada, Rivers State and Sagbama Creek, Bayelsa State, Nigeria. Manganese does not occur in the elemental form naturally, but exists in combination with other substances (Nádaská *et al*., 2010). The sources of Mn in Orashi River may include anthropogenic activities such as sewage discharges and oil prospecting.

The concentration of Hg in Orashi River ranged from nd – 0.001±0.00 mg/L while mean monthly levels ranged from nd - 0.002±0.00 mg/L. The values were lower than the WHO requirement of 0.006 mg/L for domestic water consumption. The results for Hg in the present study is higher than those reported by Iyama *et al*., (2019) in Sagbama Creeks, where values were not detected, but lower than the values observed in surface water across the rural-urban boundary of the Wen-Rui Tang River, China (Qu *et al*., 2018).

Cadmium levels in the water samples from Orashi River did not vary spatially among the stations except in Station 2 where the value of 0.004±0.00 mg/L was observed. In the rest of the stations, the value of 0.001±0.00 mg/L was observed. Mean monthly concentrations observed ranged from 0.001±0.00 - 0.006±0.00 mg/L. All the observed concentrations of Cd, except for Station 2 and December mean were lower than the WHO and SON limits for drinking water. The values reported for Cd in the present study were lower than those reported for Bodo Creek, Niger Delta in Nigeria (Abu and Nwokoma, 2016) and River Gongola in Adamawa State, Nigeria (Maitera *et al*., 2011).

The concentration of Pb ranged from 0.003±0.00 – 0.004±0.01 mg/L while the mean monthly concentration varied from 0.002 ± 0.00 to 0.007 ± 0.00 mg/L. The values were lower than the WHO and SON requirements for drinking water. The concentrations of Pb observed in the present study were lower than the values obtained in surface water from Soku oil Field, Rivers State of Nigeria (Olu *et al*., 2019), River Gongola in Adamawa State, Nigeria (Maitera *et al*., 2011) and Wen-Rui Tang River, China (Qu *et al*., 2018), but were either lower or within the range of values observed in surface water of Nun River around Gbarantoru and Tombia Towns, Bayelsa State, Nigeria (Aghoghovwia *et al*., 2018).

The levels of Cu observed in the present study ranged from 0.039 ± 0.01 - 0.087 ± 0.03 mg/L while the mean monthly concentration ranged from 0.014 ± 0.01 - 0.344 ± 0.11 mg/L. These values were lower than the 1.0 mg/L SON standard or 0.5 – 2.0 mg/L WHO limit for drinking water. The observed concentrations of Cu in the present study were lower than the values reported by Okegye and Gajere (2015) in surface water around Udege Mbeki Mining District, North-Central Nigeria, and those of Aliyu *et al*., (2015) in surface water sources within Kaduna City, Nigeria, but within the range of values observed in surface water of major rivers in Penang, Malaysia (Alsaffar *et al*., 2016).

Nickel was the most abundant element in the surface water of Orashi River at the time of this study. The concentration of Ni ranged from 0.158 ± 0.01 - 0.221 ± 0.03 mg/L but the mean monthly level varied from 0.140 ± 0.11 to 0.236 ± 0.12 mg/L. The observed concentrations of Ni were all higher than the recommended values by WHO and SON. The concentrations of Ni reported in the present study were higher than the values previously reported for similar water bodies in Nigeria (Okegye and Gajere, 2015; Aghoghovwia *et al*., 2018). However, the values corroborate with those of Radulescu *et al*.

(2015) for surface water from different salt lakes in Romania.

Iron concentration in Orashi River ranged from 0.034 ± 0.01- 0.306 ± 0.01 mg/L during the period of study while the mean monthly concentration varied from 0.091 ± 0.00 - 0.184 ± 0.12 mg/L. All the observed concentrations were below the recommended value for domestic water usage by WHO and SON. The concentrations reported for Fe in this study were lower than the values reported for Bodo Creek in Niger Delta (Abu and Nwokoma, 2016) and surface water sources within Kaduna metropolis (Aliyu *et al*., 2015), but within the range of values reported for River Nun in Bayelsa State of Nigeria (Aghoghovwia *et al.,* 2018) and surface water bodies (lakes) in Nagpur City, India (Puri *et al*., 2015).

The values recorded for Cr ranged from 0.007± 0.00 to 0.016 ± 0.00 mg/L and mean monthly concentrations were within the range of 0.002 ± 0.00 - 0.021 ± 0.01 mg/L. These values were lower than the WHO and SON standards for drinking water.

The surface water contents of Cr observed in this study were either higher or within the same range of values observed in surface water near oil installations in Gbarantoru and Tombia in Bayelsa State, Nigeria (Aghoghovwia *et al.,* 2018), but lower than those reported for River Gongola in Adamawa State, Nigeria (Maitera *et al*., (2011) and surface water sources in Kaduna metropolis, Nigeria (Aliyu *et al*., 2015).

The concentrations of Zn observed in the stations ranged from 0.023 ± 0.01 - 0.088 ± 0.02 mg/L while the mean monthly levels ranged from 0.011 ± 0.00 - 0.076 ± 0.02 mg/L. Zinc concentrations observed were lower than the standards recommended by WHO and SON for drinking water.

Table 1. Concentration of heavy metals in water samples from Orashi River at the different stations

Heavy Metals (mg/L)	Stations				WHO Std	SON Std
	1	2	3	4		
Mn	0.022 ± 0.02	0.010 ± 0.01	0.225 ± 0.02	0.006 ± 0.00	0.4	0.2
Hg	0.001 ± 0.00	0.001 ± 0.00	nd	Nd	0.006	0.006
Cd	0.001± 0.00	0.004 ± 0.00	0.00 1± 0.00	0.001 ± 0.00	0.003-0.03	0.003
Pb	0.004 ± 0.00	0.003 ± 0.00	0.003 ± 0.00	0.003 ± 0.00	0.01	0.01
Cu	0.087 ± 0.03	0.039 ± 0.01	0.053 ± 0.01	0.046 ± 0.02	0.5-2.0	1.0
Ni	0.195± 0.01	0.221± 0.03	0.194 ± 0.02	0.158 ± 0.01	0.01-0.02	0.02
Fe	0.229 ± 0.01	0.306 ± 0.01	0.034±0.01	0.042±0.01	0.3	0.3
Cr	0.007 ± 0.00	0.016 ± 0.00	0.008 ± 0.00	0.008 ± 0.00	0.05	0.05
Zn	0.026 ± 0.01	0.023 ± 0.01	0.023 ± 0.01	0.025 ± 0.01	1.0-5.0	5.0

Table 2: Mean bi-monthly concentrations of heavy metals in water samples from Orashi River

	Months					
Metals (mg/L)	December	February	April	June	August	October
Mn	0.008 ± 0.00	0.013 ± 0.00	0.293 ± 0.12	0.014 ± 0.01	0.082 ± 0.03	0.020 ± 0.00
Hg	Nd	Nd	0.001 ± 0.00	0.001 ± 0.00	0.002 ± 0.00	0.001 ± 0.00
Cd	0.006 ± 0.00	0.001 ± 0.00	0.002 ± 0.00	0.001 ± 0.00	0.001 ± 0.00	0.001 ± 0.00
Pb	0.007 ± 0.00	0.002 ± 0.00	0.002 ± 0.00	0.003 ± 0.00	0.003 ± 0.00	0.005 ± 0.00
Cu	0.014 ± 0.01	0.055 ± 0.01	0.344 ± 0.11	0.042 ± 0.02	0.037 ± 0.01	0.042 ± 0.02
Ni	0.140 ± 0.11	0.209 ± 0.04	0.236 ± 0.12	0.201 ± 0.01	0.188 ± 0.13	0.194 ± 0.03
Fe	0.091 ± 0.00	0.184 ± 0.12	0.141 ± 0.00	0.165 ± 0.01	0.169 ± 0.11	0.145 ± 0.13
Cr	0.002 ± 0.00	0.009 ± 0.00	0.021 ± 0.01	0.007 ± 0.00	0.009 ± 0.00	0.017 ± 0.00
Zn	0.011 ± 0.00	0.028 ± 0.00	0.076 ± 0.02	0.026 ± 0.01	0.036 ± 0.01	0.037 ± 0.02

The levels of Zn observed in the Orashi River were slightly lower than those reported for Sagbama Creek in Bayelsa State, Nigeria (Iyama et al., 2019) but very much lower than the values reported for surface waters of Wen-Rui Tang River in China (Qu *et al*., 2018) and Bomu and Oginigba Rivers in Rivers State of Nigeria (Marcus and Edori, 2016).

3.1 Contamination factor of surface water of Orashi River

The contamination factor of the individual heavy metals is given in Tables 3. The values of contamination factor for Mn ranged from 0.12 – 4.50. These values indicate contamination levels from slight contamination (0.10-0.25) to severe pollution (4.1-8.0). The values obtained showed that stations 2 and 4 were slightly contaminated with Mn, station 1 was moderately contaminated while station 3 was severely polluted. Mercury was not detected in statins 3 and 4, indicating that these locations were not contaminated with Hg at the time of this study. On the other hand, stations 1 and 2 had a CF of 0.17 each which indicate that these locations were very slightly contaminated.

Table 3: Contamination factors of heavy metals from different sampling stations in Orashi River

Heavy metals	Stations 1	2	3	4
Mn	0.44	0.20	4.50	0.12
Hg	0.17	0.17	-	-
Cd	0.33	1.33	-	0.33
Pb	0.40	0.30	0.30	0.30
Cu	0.04	0.02	0.03	0.02
Ni	2.79	3.16	2.77	2.26
Fe	0.76	1.02	0.11	0.14
Cr	0.14	0.32	0.16	0.16
Zn	0.01	0.03	0.01	0.01

The contamination factor values showed that stations 1 and 4 were moderately contaminated while station 2 was slightly polluted with Cd. However, Cd was not detected in station 3. The values obtained for Pb in the contamination factor assessment ranged from 0.30 – 0.40. These values indicate that the river was moderately contaminated with Pb. The contamination factor obtained for Cu in this study ranged from 0.02 – 0.04. These values indicate that the Orashi River was not contaminated with Cu as at the time of this study. Nickel had contamination factors ranging from 2.27 – 3.16. The values indicate moderate pollution of the water with Ni. The values recorded for Fe in the contamination factor evaluation of Orashi River ranged from 0.11 – 1.02. Stations 3 and 4 were slightly contaminated and station 1 was severely contaminated while station 2 was slightly polluted. Contamination factor values for Cr in the present study ranged from 0.14 – 0.32. The result showed that stations 1, 3 and 4 were slightly contaminated while station 2 was moderately contaminated. Zinc had contamination factors ranging from 0.01- 0.03 which indicate that the Orashi River was not contaminated with respect to Zn.

3.2 Pollution index, contamination degree and modified contamination degree of surface water from Orashi River

The values of pollution index, contamination degree and modified contamination degree are presented in Table 4. The pollution index of the Orashi River ranged from 0.136 – 0.271 which indicate that the river is at the threshold of contamination by the metals investigated. The pollution index values obtained in the present study were lower than the values reported for surface water of Bonny River estuary (Onojake *et al*., 2015) and New Calabar River where pollution indices ranged from 7.44 – 20.399 indicating very severe pollution to excessive pollution by heavy metals (Edori and Kpee, 2018).

The contamination degree of the heavy metals obtained from the surface waters of Orashi River ranged from 3.341-7.878. These values indicate that the river was at a very low stage of contamination. This observation is at variance with the observation of Edori and Kpee (2018) with respect to New Calabar River, where values reported for contamination degree indicate very high degree of contamination with heavy metals.

Table 4. Pollution index, contamination degree and modified contamination degree of water samples from Orashi River

Index	Stations 1	2	3	4
PI	0.265	0.271	0.202	0.136
CD	5.075	6.543	7.878	3.341
mCD	0.564	0.727	0.875	0.371

The modified contamination degree ranged from 0.371-0.875. These values also indicate very low degree of contamination of Orashi River with heavy metals.

4.0 Conclusion

Findings from this study show that there were both spatial and seasonal variations in the concentrations of heavy metals investigated. However, the variations did not follow a specific pattern. The low level of the examined heavy metals may have resulted from the constant flow of the Orashi River, thus not supporting accumulation. The study concludes that the Orashi River was not highly contaminated or polluted by the indicated heavy metals at the time of the investigation. However, drinking of water from Orashi River over one's lifetime is not advisable for obvious accumulation of heavy metals at concentrations that might be detrimental to health.

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