EVALUATON OF HEAVY METAL WATER QUALITY POLLUTION OF THE MIDDLE REACHES OF ORASHI RIVER, NIGER DELTA

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ABSTACT
River water is an essential source of water for organisms in and around the river. The study was conducted to investigate river water quality pollution from five stations between October 2017 and September 2019 with the aim of evaluating concentration of heavy metals in the aquatic ecosystem. Cd, Cr, Fe, Zn and Pb were selected. Heavy metals in water samples were determined using an Atomic Absorption Spectrophotometer. Concentration was < 0.001 mg $L^{-1}$for Pb and Cd across all stations. Fe ranged from 1.54 – 4.97 mg L^{-1}, Zn 0.01mg/l – 0.34 mg L^{-1}. Cr was <0.001 in stations 1, 4 and 5, while stations 2 and 3 had their range and mean values to be 0.003 – 0.08 mg L^{-1}. Results were compared with WHO permissible limits and NESREA standard. Concentration of Cd in all stations was less than WHO permissible limit of 0.05 mg L^{-1} and NESREA standard of 0.01 mg L^{-1}. NESREA standard indicates the study area is Cr while WHO indicates stations 2 and 3. All stations were Fe polluted when compared with both standards. Zn and Pb were below both standards indicating that the middle reaches of Orashi River are free of Zn and Pb. To determine the harmful effect of these metals in the study area two indices were selected. These are Contamination Factor (CF) and Pollution Load Index (PLI). The study site is in a low state of Cd and Pb pollution ($1 \leq CF$). Fe was moderately polluted ($1 \leq CF < 3$). Stations 1 and 4 was $1 \leq CF$ suggesting low Cr pollution while Stations 2 and 3 experienced high level of Cr pollution ($CF \leq 6$). Decreasing order of PLI was station 2 > station 3 > station 1 >station 4. It is therefore pertinent for the Ministry of Environment to monitor anthropogenic activities especially at Odiobor and Mbiama.

Key words: aquatic, concentration, compare, elements, river

INTRODUCTION
Activity close to rivers releases elements that have led to stress on the river. The water is polluted with increase in the stress level, which eventually worsen the health status of the environment. Elements that have high density and toxic at low concentrations are known as heavy metals. Both anthropogenic activities and geochemical processes are responsible for heavy metal contamination (Li et al; 2007) which eventually ends in the aquatic ecosystem. Meeting of water quality expectations for streams and rivers is required to protect drinking water resources, recreational activities and to provide good environment for fish and wildlife (Amadi et al;2010).
Heavy metal pollution of the aquatic environment has become a worldwide problem in recent years, since they are indestructible and most of them have toxic effects on organisms. Among environmental pollutants, metals are of particular concern, due to their potential toxic effect and ability to bio accumulate in aquatic ecosystems (Censi et al., 2006). Pollution of these heavy metals in river may cause effects on the ecological balance of the aquatic environment. With the increase in contamination, the aquatic organisms become limited (Ay T et al; 2009). Due to human civilization, the element content in water rises. Such elements are cadmium, lead,

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mercury, zinc and chromium. Unlike chemicals, there are some metals that cannot be converted into compounds with lesser toxicity, and one of its characteristics is loss of biodegradability. Some heavy metals such as copper, iron, chromium and nickel are essential metals since their play an important role in biological systems, whereas cadmium and lead are non-essential metals, as they are toxic, even in trace amounts (Fernandes et al., 2008). For the normal metabolism of the fish, the essential metals must be taken up from water, food or sediment (Canlı and Atlı, 2003). These essential metals can also produce toxic effects when the metal intake is excessively elevated in the water .

The Orashi River is one of the major rivers in the Niger Delta and plays host to several communities along its bank. It therefore serves as a major transportation root for motorized river crafts and canoes, transporting goods and humans from various points. The river serves as a breeding and nursery area for several important commercial fishes, which supports huge artisanal fisheries. Other human activities in the river catchment include artisanal and industrial sand mining (dredging). Recently, there had been incidents of illegal artisanal oil theft and refining (locally called kpofire) in the river catchment, which results in oiling of the environment. The river serves as a source of water for domestic uses of the riparian population.

Presence of some of these toxic metals in rivers is a course for concern. It is therefore pertinent to assess, monitor, and control the release of these metals into the environment through various socio-economic and industrial activities because the quality of the water where aquatic organisms live need to be studied and protected. The objective of the present study was to determine heavy metals pollution in the middle reaches of Orashi River.

MATERIAL AND METHODS

Study area

The study was conducted along the middle reaches of Orashi River and lies between longitude 06^0 26' 32.5" to 06^0 30' 05.^{0}" E and latitude 05^0 26'32.5" to 05^0 08' 24.6" N . The sampling stations were arranged from downstream of the river to the upstream section as follows: OdiekeUgbobi, station 1 (05^o 01'20.4'' N,0 6^o 26' 32.5''E); Odiobor, station 2 (05^o 02' 41.3'' N and 06^o 27'07.6''E); Mbiama, station 3 (05^o 3' 41.8'' N and 06o 27' 02.9'' E); Akinima, station 4 (05o 05' 14.3'' N and 06^o 28' 17.9'' E) and Oshiobele, station 5 (05^o 08' 24.6''N and 06^o 30' 05.^{0}''E).

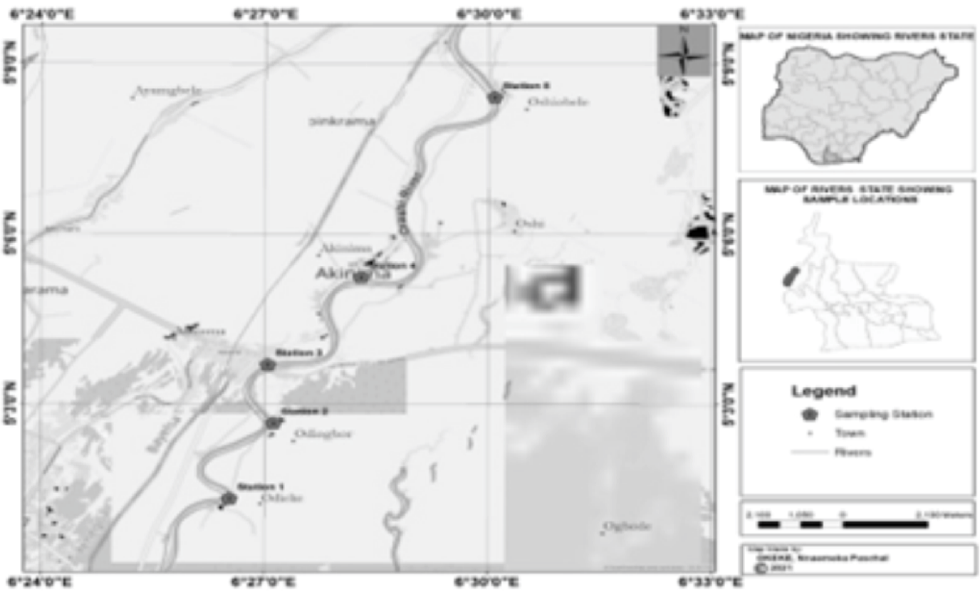

Fig 1: Map of study area

Orashi River is a major flood plain river system on the eastern flank of the lower Niger Delta (NEDECO, 1961). The headwater where Orashi River originated is far up Imo State after Oguta

Lake, and flow towards the southern direction where it joins the Oguta Lake water system. The water from Oguta Lake discharges into Orashi River both in dry and wet seasons and serves as the second main source of the Orashi. The hydrology of Orashi River is strongly influence by seasonal flooding. The water from Orashi River drains in one directional flow into the sea through the St Bartholomew and St Barbara rivers into the Atlantic Ocean.

Quality Control Assurance

Standard field methods were used for sample collection at every point with the appropriate equipment/materials. Plastic containers and glassware used for samples were soaked in nitric acid for period not less than twelve hours. The containers were washed with detergent (teepol) and rinse with clean tap water and concluded with de-ionized water as stipulated by (Onianwa, 2001). Water collected was preserved with the appropriate preservatives before being stored in ice-packed cool box in accordance with (APHA, 2005). All equipments (in-situ meters) were calibrated with the appropriate reagent before use.

Surface Water Sample Collection

The samples for trace metals analysis were placed in 150 ml plastic container and treated with concentrated trioxonitrate (V) acid (HNO3) to adjust the pH of the sample to 2.

Determination of Heavy metals in Water

Heavy metals in water samples were determined using an Atomic Absorption Spectrophotometer (AAS) as described in APHA, 1998.3111B and ASTM D3651. Water samples were collected 0.5 m below water surface, in 250 ml pre-cleaned polythene bottles. For trace element analysis, a 200 ml sample was immediately filtered through a What man's0.45 nm glass fibre filter and transferred into an acid-cleaned 250 ml polypropylene bottle, and then acidified with concentrated nitric acid to pH less than 2.0. For the determination of Cd, Cr, Pb, Fe, and Zn in water samples. Air-acetylene flame was used for the analyses, using an Atomic Absorption Spectrophotometer (AAS), Perkin 2280 model. This involved direct aspiration of the sample into an air/acetylene or nitrous oxide/acetylene flame generated by a hollow cathode lamp at a specific wavelength peculiar only to the metals programmed for analysis. For every metal investigated, standards and blanks were prepared and used for calibration before samples were aspirated. Concentrations at a specific absorbance were displayed on the data system monitor for printing. Limit of detection is <0.001 mg/L.

Laboratory (Analytical) Procedures

The analysis for trace metal concentration was carried out by the use of Atomic Absorption Spectrophotometer (AAS Unican, 969). Total hydrocarbon concentration, exchangeable cations and anions were measured by the use of flame photometer and UV/visible spectrometer (Unican Helios Gamma, UVG: 073201 and Spectronic 21D).The trace metals Cadmium, Chromium, Lead, Iron and Zinc.

Analysis of heavy metals

All data collected were subjected to statistical analysis using Analysis of variance (ANOVA) to determine their variations at stations.

Pollution assessment

Contamination Factor (CF)

The contamination factor (CF) was used to determine contamination of heavy metals in water samples (Graça et al., 2002; Zemełka,2019). Contamination factor (CF) was calculated by Eq. (1)

$CF = C_{sample/Cbackground}$ (1)

C_{sample} = mean metal content in water sample,

$C_{background}$ = mean natural background value of the metal.
The natural background sample was collected from station 5 with minimal anthropogenic activities. The area is assumed to be free from the known anthropogenic source of heavy metals. Ratio of the measured concentration to the natural abundance of a given metal had been proposed as the index CF. Contamination factor is categorized into four classes for monitoring the pollution of a single metal over a period of time (Ali et al.,2016; Shen F, et al; (2019): low degree (CF < 1),moderate degree (1 ≤CF < 3), considerable degree (3 ≤ CF < 6), and very high degree (CF ≤ 6).

Pollution Load Index

Pollution Load Index (PLI) is used to assess the water quality. PLI of the combined approaches of the heavy metals was calculated according to Islam et al., (2017). The PLI is the nth root of the multiplications of the contamination factor of the target heavy metals (CF).

PLI = (CF1 × CF2 × CF3 × . . . × CFn) 1/n (2)

CF1 = concentration of first metal

CF2 = concentration of second metal

CFn = concentration of metal nth

n = total number of studied heavy metals in the sample.

PLI = 0 means excellence; PLI = 1 suggests the presence of only a baseline level of pollutants and PLI > 1 indicates progressive deterioration of the site and estuarine quality (Tomlinson et al.,1980). The PLI evaluated the overall toxicity status of the sample and its contribution to the contribution of the five metals.

RESULTS

Results from Table 1 indicate heavy metals recorded a < 0.001 mg L−1for Pb and Cd across all stations. Bothe metals were below the WHO permissible limit and the NESREA (Table 2).

Table 1: Variation in range, mean, and standard deviation of heavy metals of surface water in different stations in the middle reaches of Orashi River

Parameter	**Odieke (Stn_1)**	**Odiobor (Stn_2)**	**Mbiama (Stn_3)**	**Akinima (Stn_4)**	**Oshiobele (Stn_5)**	**NESREA Standard**
Cd	<0.001	<0.001	<0.001	<0.001	<0.001	
(mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001	0.01
Cr	<0.001	0.003-0.08	0.032-0.062	<0.001	<0.001	
(mg L^{-1})	0.001±0.00	0.009±0.02	0.007±0.017	0.001±0.00	0.001±0.0	0.5
Fe	3.135-3.816	2.483-4.749	3.257-3.981	2.205-4.966	1.542-3.528	
(mg L^{-1})	3.53±0.18	3.52±0.39	3.58±0.25	3.55±0.49	2.9±0.47	0.5
Zn	0.01-0.238	0.028-0.32	0.009-0.322	0.003-0.24	0.008-0.338	
(mg L^{-1})	0.08±0.07	0.09±0.08	0.07±0.07	0.07±0.07	0.06±0.07	0.2
Pb	<0.001	<0.001	<0.001	<0.001	<0.001	
(mg L^{-1})	<0.001	<0.001	<0.001	<0.001	<0.001	-

Table 2: Standards for heavy metals

Heavy metal	WHO permissible limit (mg L^{-1})	NESREA standard (mg L^{-1})
Cd	0.05	0.01
Cr	0.003	0.50
Fe	0.30	0.50
Zn	3.00	0.20
Pb	0.01	-

Chromium (Cr) had <0.001 in stations 1, 4 and 5, while stations 2 and 3 had their range and mean values to be 0.003 – 0.08 mg L^{-1}. Stations 1,4 and 5 recorded low Cr values when compared with

WHO permissible limit of 0.003mg L^{-1} while stations 2 and 3 were higher. The mean values of all stations were below the NESREA standard of 0.5 mg L^{-1}.
Fe ranged from 1.54 – 4.97 mg L^{-1} (Table 1) and was above both the WHO permissible limit and NESREA standard of 0.30 mg L^{-1} and 0.5 mg L^{-1} respectively (Table 2) from the mean in all stations. Zn ranged from 0.01mg/l – 0.34 mg L^{-1}. The mean concentration of Zn was below the WHO permissible limit of 3.00 mg L^{-1} and NESREA standard of 0.2 mg L^{-1} (Table 2) in all stations.

Table 3: Estimates of contamination level (CF) in Middle reaches of Orashi River

Station	Cd	Fe	Cr	Zn	Pb
OdiekeUgbobi (station 1)	1	1.22	1	1.33	1
Odiobor (station 2)	1	1.21	9	1.50	1
Mbiama (station 3)	1	1.23	7	1.12	1
Akinima (station 4)	1	1.22	1	1	1

DISCUSSION

The concentration of Cadmium (Cd) in all the study sites was<0.001.The value obtained in the study was less than the World Health Organization (WHO) permissible limit of 0.05 mg L^{-1} and the National Environmental Standards and Regulations Enforcement Agency (NESREA) standard of 0.01 mg L^{-1}. This suggests that the study area is free of Cd pollution. Cd is homogeneously distributed in the earth crust at an average concentration of between 0.15 to 0.2mg/kg (Hiatt and Huff, 1975). Its concentration in pure fresh water is generally less than 0.001 mg L^{-1}which agrees with Fleischer et al.,(1974) but disagrees with Wangboje and Ikhuabe (2015) who recorded a range of 0.00-0.14 mg L^{-1} in their study of heavy metal content in fish and water from River Niger at Agenebode, Edo State, Nigeria.

Chromium (Cr) concentration in this study ranged from <0.001-0.08mg L^{-1} (Table 1). As recorded by Batayneh (2012), surface water range is from 0.004 to 0.007mg/L.This value suggested that only station 2 is polluted with Cr. The standard NESREA value is 0.5 mg L^{-1} while WHO permissible limit is 0.003 mg L^{-1}. The NESREA standard indicates the study area is Cr free since all the sites are below the concentration of 0.5 mg L^{-1}. According to the WHO the concentration of Cr in the water, indicates that the water is Cr polluted in stations 2 and 3 because the mean concentration is higher than the WHO value of 0.009±0.02 and 0.007±0.017 respectively. This could be due to the serious anthropogenic activities in these areas. Station 2 was observed to have some much human activities such as sand dredging, bunkering, illegal artisanal crude oil refineries (kpo – fire) and waste dump area. Station 3 experienced more serious anthropogenic activities. There were lots of dredging activities in the area coupled with the landing and sale of illegal refined crude oil products in.
In this findings, Iron (Fe) varied between 1.54 – 4.97 mg L^{-1} (Table 1). Fe presence in water is due to the use of iron coagulants or the corrosion of steel and cast iron pipes during water supply and from mineral industries (WHO, 2006). WHO permissible limit for Fe is 0.30 mg L^{-1}, while the NESREA standard is 0.5 mg L^{-1}. The concentration of Fe in all water samples were found above these standards which implies that the middle reaches of Orashi River was Fe polluted.

The element Zinc (Zn) is always present in all igneous rocks. It is an essential micronutrients. The concentration of Zn as determined in the middle reaches of Orashi River was in the range 0.01mg/l – 0.34 mg L^{-1} (Table 1). The ranges of Zn investigated in all stations of the river were within the permissible limits of 3.00 mg L^{-1} set by World Health Organization (Table 2). Mean concentrations in all stations were also below WHO permissible limits. This suggests that the middle reaches of Oradhi River are not Zn polluted by the WHO standard. The NESREA limit is contrary to that of WHO if the range is to be considered because all stations recorded a maximum value above the NESREA standard of 0.2 mg L−1. When the mean concentrations of the different stations were compared to the NESREA standard all stations were below NESREA standard. This indicates that the study area is not Zn polluted. Concentration of lead (Pb) in all study stations were below the WHO standard. This indicates that the middle reaches of Orashi River are free of lead.

Concentration of heavy metals alone does not provide enough information on potential toxicity and mobility of contaminants or the possible harmful effects on the environment. Different chemicals can inactivate and promote synergistic effects. CF and PLI were used to determine the potentially harmful effect of heavy metals in the environment (Table 3) because these indices provide basis for assessing the effects of contaminants compared to the values concerning each index (Moore et al., 2011).

The CF of Cd and Pb in all stations was 1. This indicates the river water is in a low state of Cd and Pb pollution ($1 \leq CF$). Fe was between 1.21 and 1.23 indicating that the water is moderately polluted ($1 \leq CF < 3$). CF of Cr in stations 1 and 4 was ($1 \leq CF$) suggesting low pollution level. Stations 2 and 3 experienced high level of pollution ($CF \leq 6$) because the CF values were 9 and 7 were respectively. Zn in all stations was ($1 \leq CF < 3$) indicating that the river is moderately polluted.

The PLI values for each station show the decreasing order of contamination: station 2 > station 3 > station 1 >station 4. Stations 1 and 4 PLI value were less than 1 suggesting zero pollution of the stations. Stations 2 and 3 PLI values were more than 1 (PLI > 1) suggesting pollution from anthropogenic sources in the areas. This indicates progressive deterioration of the area and river quality (Tomlinson et al.,1980).

CONCLUSION

Concentration of Cd suggests that the study area is free of Cd pollution. The CF value indicates all stations were in a low state of Cd and Pb pollution ($1 \leq CF$). Chromium (Cr) concentration in this study ranged from <0.001-0.08 mg L−1. The NESREA standard indicates the study area is Cr free. WHO concentration of Cr in the water, indicates that the water is Cr polluted in stations 2 and 3. CF of stations 2 and 3 experienced high level of pollution ($CF \leq 6$).Concentration of Fe in all water samples were found above these standards which implies that the middle reaches of Orashi river was Fe polluted. CF value of Fe was ($1 \leq CF < 3$) in all stations indicating moderate pollution. The middle reaches of Oradhi River is not Zn polluted by the WHO and NESREA standards. Zn in all stations was ($1 \leq CF < 3$) indicating that the river is moderately polluted. Stations 2 and 3 PLI values were more than 1 (PLI >1) indicating progressive deterioration of the river quality due to anthropogenic activities. The results from the study suggested that the middle reaches of Orashi River are moderately polluted especially in Odiobor and Mbiama axis. It is therefore pertinent for the ministry of environment to monitored anthropogenic activities, most especially in Odiobor and Mbiama.

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