Assessment of heavy metal pollution in the sediment of the middle reaches of River Orashi, Southeastern Nigeria

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Abstract:

Analysis was carried out on sediment contamination by heavy metals of the middle reaches of River Orashi. Heavy metals, namely Cd, Cr, Fe, Zn and Pb were examined from the river sediments collected from Odieke, Odiobor, Mbiama, Akinima, Oshiobele, on a monthly basis, for a period of 12 months to capture rainy and dry seasons. After preparation, samples were analyzed using Flame Atomic Absorption Spectrometry. Cadmium was not detectable at all sampling stations. The average concentration of heavy metals ranged between 0.326 ± 1.13 and 2.334 ± 8.08. Average heavy metal concentrations of River Orashi sediment compared with the USEPA sediment standard, Average Shale values, and other world standards were lower than the benchmarks recommended. Assessment of the status of pollution by indices EF, Igeo, CF, DOC, PLI and NMI showed that the sediments of the middle reaches of River Orashi had low level of contamination. PLI calculated showed that Odiobor was the most polluted with heavy metals while Odieke was the least polluted, but classified the whole sediments of the middle reaches of River Orashi as unpolluted with heavy metals. Correlation coefficients showed the presence of natural and anthropogenic sources of the heavy metals.

Keywords: sediment, heavy metal, pollution, contamination, seasons

Introduction:

Erosion of bedrock and soils leads to accumulation of sediments of past or on-going natural and anthropogenic processes and components. Data from sediments can provide information on the impact of distant human activity on the wider ecosystem. Erosion of bedrock and soils leads to accumulation of sediments of past or on-going natural and anthropogenic processes and components (Astatkie, et al., 2021; Tijani & Onodera, 2009).

The composition of sediment sequences provides the best information of recent environmental changes. Data from sediments can provide information on the impact of distant human activity on the wider ecosystem. The composition of sediment sequences provides the best natural archives of recent environmental changes.

It is important to carry out sediment analysis in evaluating qualities of total ecosystem of a body of water in addition to water sample analysis because it reflects the long-term quality situation independent of the current inputs and it is the ultimate sink of contaminants in the aquatic system (Davies & Abowei, 2009). Heavy metals occur and accumulate in upper sediment in aquatic environment and become toxic to sediment-dwelling organisms and fish, resulting in death, reduced growth, or in impaired reproduction and lower species diversity (Praveena et al., 2007). Trace elements also occur naturally in rock forming minerals and ore minerals; hence they can reach the environment from natural processes (Akinmosin, et al., 2009; Huu, et al., 2010).

The occurrence of metals in aquatic environment in excess of natural background loads has become a problem of increasing concern (Fagbote & Olanipekun, 2010). Heavy metals in environment may accumulate to toxic levels without visible signs. This may occur naturally from normal geological phenomenon such as ore formation, weathering of rocks and leaching or due to increased population, urbanization, industrial activities, agricultural practices, exploration and exploitation of natural resources (Saeed, et al., 2014; Ololade, et al., 2008).

Seiyaboh et al. (2016) assessed physicochemical quality of River Orashi in Eastern Niger Delta of Nigeria. They found that there were mild anthropogenic activities around the Orashi river. Seiyaboh and Kolawole (2017) carried out research on diversity and levels of bacteriological contamination in Orashi River, Mbiama. They found that the bacteria density exceeded the Standard Organization of Nigeria and World Health Organization/Food and Agricultural Organization allowable limit for potable water. The bacteria isolates identified include Pseudomonas, Proteus, Micrococcus, Shigella,Salmonella, Enterobacter species, Staphylococcus aureus and E. coli. Odoemelam et al. (2019) carried out assessment of heavy metals of Orashi River at the Engenni axis, Rivers State, Nigeria. It was observed that the levels of most of the metals were lower than WHO and SON standards for drinking water. Verla et al. (2019) worked on chemometric assessment of Orashi river after confluence with Oguta Lake. It was found that in both water and sediments, Cd was the highest contaminant, and water revealed pollution load index higher than sediment. Akachukwu et al. (2020) studied quality of Orashi River at four oil producing communities in Nigeria. Their research showed that sediment samples were unpolluted in terms of Total Petroleum Hydrocarbon. Most of the heavy metals had values that were lower than the Sediment Quality Guidelines.

Materials and Method:

Study Area

River Orashi, situated between latitudes 50º 45″ and 60º 35″ N and longitudes 40º 50″and 50º 15″ E, is a river of the lower Niger River basin and a tributary of the Oguta Lake in Imo state, Nigeria. Over the years, the Orashi river system is being subjected to various degrees of anthropogenic activities and environmental degradation (Verla et al., 2019). It started from the rocks in Ezeama community of Dikenafi through several towns including Urualla, Akokwa, Okija, Orsu, Ukpor, Ihiala, Uli, Oguta, Osemotor in Imo State, Omoku, Obiakpo, Ebocha, Ukodu, Okarki, Mbiama in Rivers State, and Epie in Bayelsa State as shown. The river forms tributaries along its flow, from Imo through Anambra, Rivers to Bayelsa, before emptying onto the Altlantic (Enetimi & Ebiotu, 2017).

It provides livelihoods for majority of people in this region. In spite of the numerous values and functions performed by Orashi River, the structure and proper functioning of the river system has been subjected to various human activities, some of which are capable of inducing stress to a large extent (Enetimi & Ebiotu, 2017). Hence, the major reason of this research study is to evaluate the impact of anthropogenic transformation of the middle reaches of Orashi River.

The Orashi river system is known primarily to support local artisanal fishery industry and also facilitates the transportation of goods and human beings from one area to another in canoes and motorized river crafts both in rainy and dry season (Enetimi & Ebiotu, 2017). Thus constituting an essential communication route between various communities within and out-side the Ahoada West local government area. Several communities located along bank of Orashi River often use the place as an avenue for disposal of domestic waste carelessly into the river without treatment. The river also receives run-off discharges from companies and chronic oil spills from pipelines crossing the river at different points including some from local fabricated illegal crude oil distilleries, locally known as kpo-fire

The area covered by the river has a tropical humid hot climate with two major seasons, rainy season (between March and October) and the dry season (between November and March)

Description of sampling sites

Sampling station 1: Located at the water front of Odieke Ugbobi, before the meander loop as shown in Figure 1. The water current was normal and controlled by the deep meander up well. Human activity was minimal in a way that does not affect water quality negatively. Usual human activities include washing, fishing and recreation.

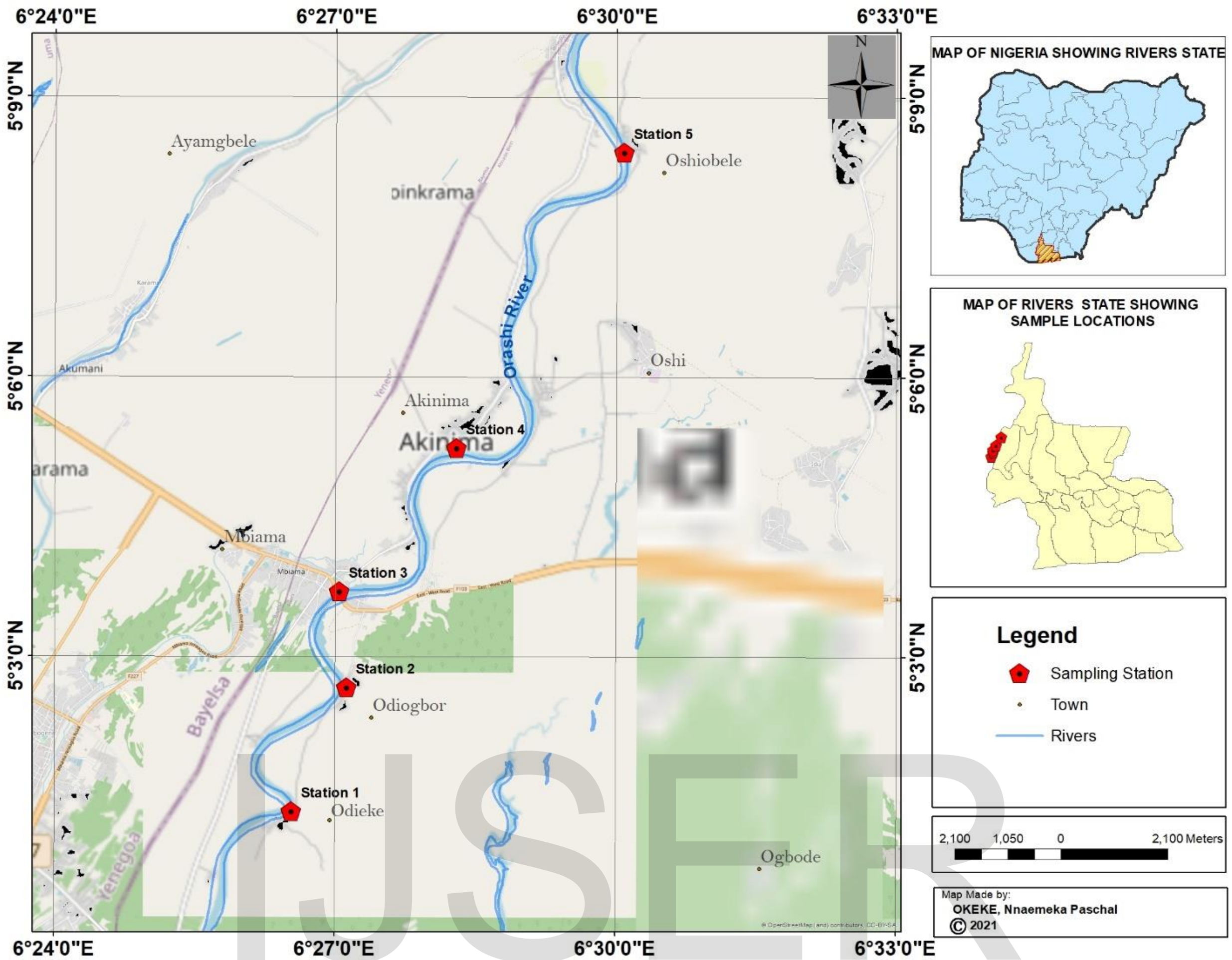

Figure 1: Map of Niger Delta showing the middle riches of Orashi River

Sampling station 2: Situated at Odiobhor water front just a little bit upstream after the community (Figure 1). This was an area with high human activities such as sand dredging, bunkering, illegal artisanal crude oil refineries and waste dump area.

Sampling station 3: This site is close to Mbiama East/West road bridge crossing the Orashi river (Figure 1). Anthropogenic activities were much higher at this site. Lots of dredging activities take place here. It was near the site where illegal refined crude oil products were landed and sold to marketers.

Sampling station 4: This is located upstream of Akinima, Ahoada West L.G.A headquarters (Figure 1). The area has shallow and strait water course. It is one of the major fishing communities in the area, where serious fishing activity and trading is done. Anthropogenic activity was very high upstream about 2 kilometers away, illegal bunkering and crude oil theft was obvious around this point. Oil pipelines creeks cross this section of the river and vandals often damage pipes and steal crude oil which they used for illegal refinery. After which, the waste is dumped into the Orashi river to pollute the water.

Sampling station 5: This sample point is located between Oshiobele and Joinkrama community (Figure 1). This section is the shallowest, widest and fast flowing water current amongst all the area. It is quiet with less anthropogenic activity. Much fishing is done in this section than other areas.

Sample Collection:

Sample was collected every month from October 2018 to September 2019. The upper 10 cm of surface sediment samples was collected with Ekman grab randomly and composited as one sample at each sampled point. Then all the sediment samples were packed in an ice cool box kept at 18 ^{0}C, and transported to the laboratory until further procedure.

Preparation of samples

The procedures involve oven drying of sediment at a specific temperature and time for trace metals. The oven drying sediment for trace metals were placed in clean sheet of paper in the oven and dried at 103^{0}C temperature for 24 hours. The dried samples were crushed with a mortar and sieved through a 2 mm mesh screen was stored in plastic container for analysis.

Determination of heavy metals in sediment

Heavy metal determination in sediment samples used the flame GBC-908 PBMT model of the Flame Atomic Absorption Spectrophotometer (FAAS) (ASTM, 1981; IITA, 1979)

The dried sediment sample at room temperature was homogenized by grinding and sieving the sample through a 2mm mesh sieve. Then exactly 5 gramme (5g) of the prepared sample was transferred and contained into a 100 ml glass beaker, while a mixture of 2 ml concentrated nitric acid (HNO_3), 10 ml of concentrated hydrochloric acid (HCL) and about 20 ml of distilled water was added and properly mixed.

The sample mixture was digested on a corning PC-351 model hot plate water bath at medium to low heat temperature until about 5 ml concentrated extract was left (or with sample concentration tending towards near dryness) afterwards, the content of the beaker was left to cool for about 30 minutes (30 min).

The cooled sample solution was filtered and quantitatively transferred into a 50ml standard volumetric flask for test of metals. The test metals were determined using the GBC-908 PBMT model of the Flame Atomic Absorption Spectrophotometer (FAAS). Each sample was individually aspirated during analysis.

The total metal concentrations were reported in units of ppm (parts per million), mg (milligramme) per kg (killogramme) of sediment and calculated as:

Total metal concentration = (DxRxV)/W

Where: D = serial dilution,

R = concentration reading (PPM or mg/l)

V = final volume of acid during digestion (ml).

W = dry weight of sediment sample (g)

Pollution Indices

Enrichment Factor (EF)

The natural and anthropogenic impacted with heavy metal can be calculated using the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels (Huu, et al., 2010). Pollution can be measured as the amount of the sample metal enrichment above the concentration present in the reference station or material (Abrahim & Parker, 2008; Mediola, et al., 2008)

The EF method normalizes the measured heavy metal content with respect to a samples reference such as Fe, Al or Zn (Mendiola, et al., 2008)

The EF of a heavy metal in sediment can be calculated with the following formula (Huu et al., 2010; Muzerengi, 2017; Malsiu, et al., 2020):

$$EF = [C_{metal}/C_{reference}]/[B_{metal}/B_{reference}]$$

where C_{metal} and $C_{reference}$ are the concentrations of heavy metal in the examined environment and in reference environment and B_{metal} and $B_{reference}$ are the concentrations of the reference element in the examined environment and the reference environment. Average shale concentration will be used as reference as given by Turekian & Wedepohl (1961). Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure, and to assess the degree of anthropogenic influence. Five contamination categories are recognized on the basis of the enrichment factor as follows (Fagbote & Olanipekun, 2010; Sutherland, 2000):

- EF < 2 is deficiency to minimal enrichment
- EF 2 – 5 is moderate enrichment
- EF 5 – 20 is significant enrichment
- EF 20 – 40 is very high enrichment
- EF > 40 is extremely high enrichment

As the EF values increase, the contributions of the anthropogenic origins also increase

(Sutherland, 2000).

Index of Geo Accumulation (Igeo)

Index of Geo-accumulation (Igeo) has been used widely to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environment (Tijani, et al., 2009). The Igeo of a metal in sediment can be calculated with formula: (Astatkie, et al., 2021; Guan et al., 2018; Mediola et al., 2008; Asaah & Abimbola, 2005):

Igeo = Log2[Cmetal/1.5Cmetal(background)]

Where Cmetal is the concentration of the heavy metal in the enriched sample and Cmetal(background) is the concentration of the metal in the unpolluted sample or control. Average shale concentration was used as control as given by Turekian and Wedepohl (1961). The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the sediment (Mediola, et al., 2008). The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows (Singh, et al., 2017):

- Igeo <0 = means unpolluted
- 0<=Igeo<1 means unpolluted to moderately polluted
- 1<=Igeo<2 means moderately polluted
- 2<=Igeo<3 means moderately to strongly polluted
- 3<=Igeo<4 means strongly polluted
- 4<=Igeo<5 means strongly to very strongly polluted
- Igeo>=5 means very strongly polluted.

Metal contamination factor (CF)

Contamination factor can be calculated by comparing the mean of trace metal concentration with average shale concentration (Turekian & Wedepohl, 1961; Odoemelam, et al., 2019), which is used as global standard reference for unpolluted sediment (Singh, et al., 2017).

CF for each metal was determined by the following equation (Hakanson, 1980; Graca, et al., 2002; Bubu, et al., 2017; Astatkie, et al., 2021):

$$\text{Contamination Factor (CF)} = \frac{\text{Mean metal concentration at contaminated site}}{\text{Metal average shale concentrations}}$$

CF < 1 in class 1 with low CF

1 <= CF < 3 in class 2 with moderate CF

3 <= CF < 6 under class 3 with considerable CF

CF >= 6 in class 4 with very high CF

Degree of Contamination (DOC)

The Degree of Contamination is the sum of all CF values of a particular sampling site (Perumal et al., 2021):

$$DOC = \sum_{i=1}^{i=n} CF$$

DOC in sediments can be classified as follows (Ahdy & Khaled, (2009):

DOC < 6 follows the class 1 which shows low DOC.

6 <= DOC < 12 follows the class 2 which shows moderate DOC

12 <= DOC< 24 follows the class 3 which shows considerable DOC

DOC >= 24 follows the class 4 which shows very high DOC.

Modified Degree of Contamination (mDOC)

The mDOC is the sum of all CF values of a particular sampling site to the number of elements analyzed (Perumal et al, 2021).

$$mDOC = \frac{\left(\sum_{i=1}^{i=n} CF\right)}{n}$$

mDOC in sediments can be classified as follows (Ahdy & Khaled, (2009):

mDOC < 1.5 follows the class 1 which shows nil to very low contamination level.

1.5 <= mDOC < 2 follows the class 2 which shows low contamination level.

2 <= mDOC< 4 follows the class 3 which shows moderate contamination level.

4 <= mDOC< 8 follows the class 4 which shows high contamination level.

8 <= mDOC< 16 follows the class 5 which shows very high contamination level.

16 <= mDOC< 32 follows the class 6 which shows extremely high contamination level.

mDOC >= 32 follows the class 7 which shows ultra-high contamination level.

Pollution Load Index (PLI)

The pollution load index (PLI) of a specific station was assessed using the equation (Tomlinson et al., 1980):

$$PLI = n\sqrt{(CF1 \times CF2 \times CF3 \times \ldots CFn)},$$

where CF is the contamination factor and n is the number of parameters.

The PLI for a single site is the n^{th} root of n number of parameters multiplying the factors (CF values) together (Singh et al., 2017).

PLI is rated as follows (Jorfi, et al., 2017):

PLI= 0 (background concentration);

0 < PLI <= 1 (Unpolluted);

1 < PLI <= 2 (Moderately to unpolluted);

2 < PLI <= 3 (Moderately polluted);

3 < PLI <= 4 (Moderately to highly polluted);

4 < PLI <= 5 (Highly polluted);

PLI > 5 (Very highly polluted)

Nemerow Multi-Factor Index (NMI)

The Nemerow multi-factor index was calculated using the following equation (Nemerow, 1991):

$$NMI = \sqrt[2]{\frac{(CF_{i\,\max})^2 + (CF_{iave})^2}{2}}, CF_i = C_i / B_i$$

where CF_i is the ratio between the measured concentration (C_i) and background value (B_i) of the heavy metal *I (*Average shale concentration was used as background value (Turekian & Wedepohl, 1961); CF_{imax} and CF_{iave} represent the maximum contamination and average of contamination factors, respectively, *NMI* is the nemerow multi-factor index.

NMI can be used to assess the status of comprehensive pollution caused by all the heavy metals in the sediments, because different heavy metals may have impacts in the same station (Fang et al., 2019)

NMI values are categorized as follows (Yan, et al., 2016):

PI < 1 is considered unpolluted;

1 ≤ PI < 2.5 is considered lowly polluted;

2.5 ≤ PI < 7 is considered moderately polluted;

PI ≥ 7 is considered highly polluted.

Correlation Coefficient

Correlation coefficient is a numerical measure of some type of correlation, meaning a statistical relationship between two variables (Singh, et al., 2017):

Correlation coefficient assume values in the range from −1 to +1 and classified as follows:

Correlation value = 1 means perfect positive correlation

Correlation value = > 0.8 means strong relationship

Correlation value from 0.5 - 0.7 means moderate correlation

Correlation value from 0.1 - 0.4 means weak correlation

Correlation value of 0 means no correlation

Correlation value of -1 means perfect negative correlation

Results and Discussion:

Table 1: Range, mean and standard deviation of Heavy Metals in sediment in different stations in the middle reaches of Orashi river (2018-2019)

Parameter	**Odieke**	**Odiobor**	**Mbiama**	**Akinima**	**Oshiobele**
Cd (mg/kg)	0.001-0.001	0.001-0.001	0.001-0.001	0.001-0.001	0.001-0.001
	0.001±0.0	0.001±0.0	0.001±0.0	0.001±0.0	0.001±0.0
Cr (mg/kg)	0.001-3.9	0.001-28	0.001-18.7	0.001-10.4	0.001-10.6
	0.326±1.13	2.334±8.08	1.559±5.4	0.868±3.0	0.884±3.06
Fe (mg/kg)	10.855-24.637	13.272-27.843	12.861-74.546	7.338-24.902	3.488-27.824
	18.02±4.32	21.08±5.28	24.01±16.72	17.89±6.01	20.07±7.57
Zn (mg/kg)	5.375-22.2	5.418-36.3	4.209-44.4	6.596-19.6	11.608-30.8
	9.83±4.58	12.07±8.12	15.35±9.91	12.99±3.78	14.61±5.38
Pb (mg/kg)	0.001-16.5	0.001-26.6	0.001-18.8	0.001-19.3	0.001-9.6
	1.376±4.76	2.218±7.68	1.568±5.43	1.609±5.57	0.801±2.77

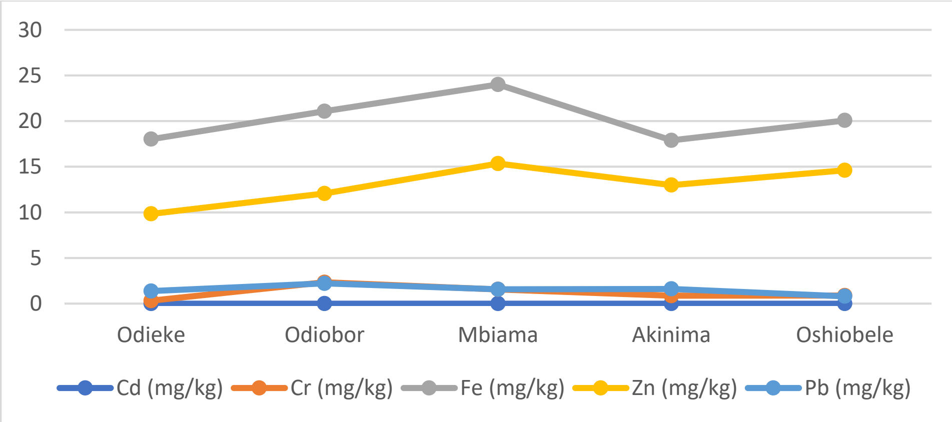

Figure 2: Average concentration of Heavy Metals in sediment in different stations in the middle reaches of Orashi river (2018-2019)

Table 2: Monthly range, mean and standard deviation of heavy metals in sediments of Orashi River (October 2018 – September 2019)

Parameter	**Cd (mg/kg)**	**Cr (mg/kg)**	**Fe (mg/kg)**	**Zn (mg/kg)**	**Pb (mg/kg)**
Month					
	<0.001 - <0.001	<0.001 - <0.001	18.665-27.599	7.918-13.146	<0.001 -<0.001
Oct	0±0	0±0	24.08±3.28	11.17±2.15	0±0
	<0.001 - <0.001	<0.001 - <0.001	12.861-24.482	7.973-14.709	<0.001 -<0.001
Nov	0±0	0±0	17.53±4.44	11.89±2.82	0±0
	<0.001 - <0.001	<0.001 - <0.001	15.431-24.978	7.056-16.473	<0.001 -<0.001
Dec	0±0	0±0	21.75±3.87	11.02±3.91	0±0
	<0.001 - <0.001	<0.001 - <0.001	21.735-27.824	9.309-16.683	<0.001 -<0.001
Jan	0±0	0±0	25.35±2.54	12.74±3.2	0±0
	<0.001 - <0.001	<0.001 - <0.001	24.39-27.843	10.491-14.346	<0.001 -<0.001
Feb	0±0	0±0	25.91±1.75	12.28±1.5	0±0
	<0.001 - <0.001	<0.001 - <0.001	21.721-27.341	10.49-18.864	<0.001 -<0.001
Mar	0±0	0±0	24.11±2.35	13.19±3.42	0±0
	<0.001 - <0.001	<0.001 - <0.001	12.967-24.58	10.474-17.744	<0.001 -<0.001
Apr	0±0	0±0	19.27±4.28	14±3.27	0±0

	<0.001 - <0.001	<0.001 - <0.001	12.346-18.899	5.375-13.128	<0.001 -<0.001
May	0±0	0±0	16.75±2.82	9.74±3.44	0±0
	<0.001 - <0.001	<0.001 - <0.001	12.854-19.835	5.418-12.819	<0.001 -<0.001
Jun	0±0	0±0	17.03±2.81	9.29±3.67	0±0
	<0.001 - <0.001	<0.001 - <0.001	10.688-18.855	6.728-17.809	<0.001 -<0.001
Jul	0±0	0±0	15.88±3.33	11.9±4.02	0±0
	<0.001 - <0.001	<0.001 - <0.001	12.325-13.622	4.209-11.624	<0.001 -<0.001
Aug	0±0	0±0	13.04±0.61	7.77±2.87	0±0
	<0.001 - <0.001	3.9-28	10.855-74.546	19.6-44.4	9.6-26.6
Sep	0±0	14.32±9.28	21.89±29.6	30.66±10.18	18.16±6.1

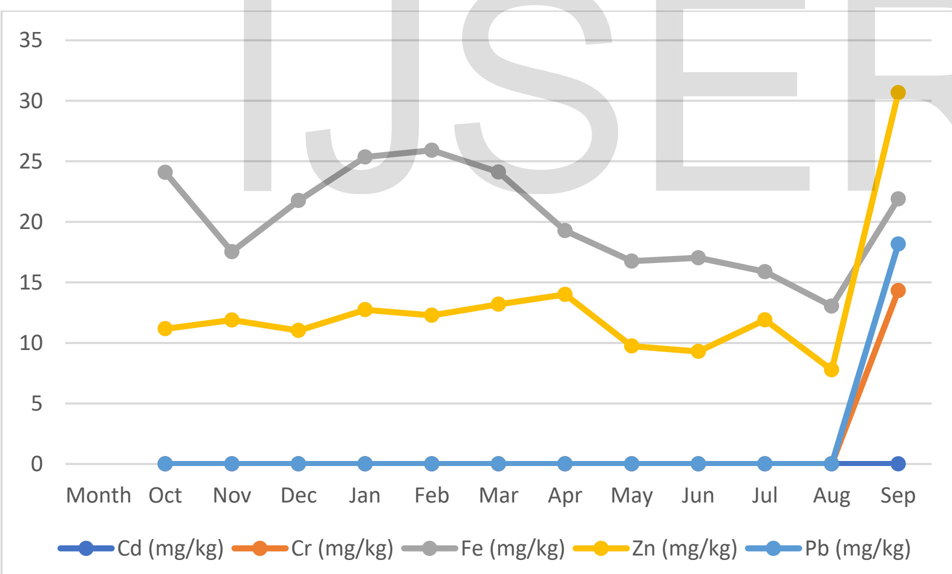

Figure 3: Mean values of heavy metals in sediments of Orashi River (October 2018 – September 2019)

Table 3: Seasonal variation of heavy metals of sediments of Orashi river (2018-2019) (Range, mean and standard deviation)

Parameter	**Rainy Season**	**Dry Season**	**Wet Season**	**Dry Season**

Cd (mg/kg)	0.001-0.001	0.001-0.001	0.001-0.001	0.001-0.001
	0.001±0.0	0.001±0.0	0.001±0.0	0.001±0.0
Cr (mg/kg)	0.001-28	0.001-0.001	0.001-28	0.001-0.001
	2.05±6.00	0.001±0.0	2.05±6.00	0.001±0.0
Fe (mg/kg)	10.688-74.546	12.861-27.843	10.688-74.546	12.861-27.843
	21.06±14.2	22.9±4.2	21.06±14.2	22.9±4.2
Zn (mg/kg)	4.209-44.4	7.056-18.864	4.209-44.4	7.056-18.864
	13.5±8.6	12.2±2.91	13.5±8.6	12.2±2.91
Pb (mg/kg)	0.001-26.6	0.001-0.001	0.001-26.6	0.001-0.001
	2.60±6.78	0.001±0.0	2.60±6.78	0.001±0.0

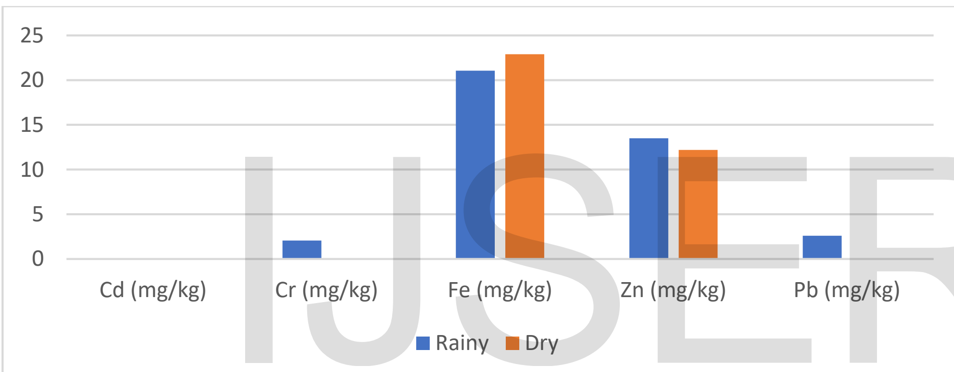

Figure 4: Seasonal variation of heavy metals of sediments of Orashi river (2018-2019)

Table 4: Average Heavy metal concentration of River Orashi sediment compared with USEPA sediment standards, Average Shale Values, Toxicity Reference Values and World River System values (WRS).

Heavy Metals	**Sediment of River Orashi (Rainy season) (mg/kg)**	**Sediment of River Orashi (Dry season) (mg/kg)**	**USEPA Sediment Standards (USEPA, 1999)**	**Average Shale Values (Turekian and Wedepohl, 1961) (Singh et al., 2017)**	**Toxicity Reference Values (Singh et al., 2017)**	**World River System (Singh et al., 2017)**
Cd	0.001±0.0	0.001±0.0	0.99	0.30	0.60	Nil
Cr	2.05±6.00	0.001±0.0	43.4	90	26	100

Fe	21.06±14.20	22.90±4.20		47,200		
Zn	13.5±8.60	12.20±2.91	121	95	110	350
Pb	2.60±6.78	0.001±0.0	35.8	20	31	Nil

Table 5: Heavy Metal Enrichment Factor (EF), Geoaccumulation Factor (Igeo)

Heavy Metals	**Cd (mg/kg)**	**Cr (mg/kg)**	**Fe (mg/kg)**	**Zn (mg/kg)**	**Pb (mg/kg)**	**Cd (mg/kg)**	**Cr (mg/kg)**	**Fe (mg/kg)**	**Zn (mg/kg)**	**Pb (mg/kg)**
Season	**Rainy Season**					**Dry Season**				
Average Conc. of metal in the environmment	0.001	0.001	22.9	12.2	0.001	0.001	2.05	21.06	13.5	2.6
Average Shale Concentration (Turekian and Wedepoh (1961) - Reference), Singh et al (2017))	0.3	90	47,200	95	20	0.3	90	47,200	95	20
Enrichment Factor (EF)	0.00	0.00	1.00	264.69	0.00	0.00	51.05	1.00	318.49	291.36
Geoaccumulation Index (Igeo)	-8.97	-17.04	-11.61	-3.56	-14.89	-8.97	-5.21	-11.70	-3.40	-3.52

Table 6: Heavy Metal Contamination Factor (CF), Degree of Contamination (DOC), modified Degree of Contamination (mDOC), Pollution Load Index (PLI), Nemerrow Multi-Factor Index (NMI)

Heavy Metals	**Average Shale Concentration (Turekian and Wedepoh (1961) - Reference), Singh et al (2017))**	**Sampling Sites**									
		Odieke (mg/kg)	**Odieke (CF)**	**Odiobor (mg/kg)**	**Odiobor (CF)**	**Mbiama (mg/kg)**	**Mbiama (CF)**	**Akinima (mg/kg)**	**Akinima (CF)**	**Oshiobele (mg/kg)**	**Oshiobele (CF)**
Cd	0.30	0.0010	0.0033	0.0010	0.0033	0.0010	0.0033	0.0010	0.0033	0.0010	0.0033
Cr	90.00	0.3260	0.0036	2.3340	0.0259	1.5590	0.0173	0.8680	0.0096	0.8840	0.0098
Fe	42200.00	18.0200	0.0004	21.0800	0.0005	24.0100	0.0006	17.8900	0.0004	20.0700	0.0005
Zn	95.00	9.8300	0.1035	12.0700	0.1271	15.3500	0.1616	12.9900	0.1367	14.6100	0.1538
Pb	20.00	1.3760	0.0688	2.2180	0.1109	1.5680	0.0784	1.6090	0.0805	0.8010	0.0401
DOC			0.1797		0.2677		0.2612		0.2306		0.2075
mDOC			0.0359		0.0535		0.0522		0.0461		0.0415
PLI			0.008		0.014		0.013		0.011		0.01
Av. CF			0.0359		0.0535		0.0522		0.0461		0.0415

NMI			0.0775		0.0975		0.1201		0.1020		0.1126

Correlation Analysis:

	Cd	*Cr*	*Fe*	*Zn*	*Pb*
Cd	1				
Cr	#DIV/0!	1			
Fe	#DIV/0!	0.652181	1		
Zn	#DIV/0!	0.304598	0.676147	1	
Pb	#DIV/0!	0.720033	0.194923	-0.27927	1

The range, mean and standard deviation of the concentrations of Heavy Metals in sediment in different stations in the middle reaches of Orashi river (2018-2019) is shown in Table 1, Table 2, Table 3, and illustrated in Figure 2, Figure 3, Figure 4.

Cadmium was not detectable at all sampling stations and throughout the twelve months of sampling. This shows that the sources of Cd were missing in the environment. These sources include natural sources, such as underlying bedrock, and anthropogenic input such as mining operations.

The lowest average value of Cr was 0.326 ± 1.13 recorded at Odieke, followed by 0.884 ± 3.06 mg/kg at Oshiobele, 0.868 ± 3.0 mg/kg at Akinima, 1.559 ± 5.4 mg/kg at Mbiama, and the highest was 2.334 ± 8.08 recorded at Odiobor. In the month of September which is the rainy season, there was a spike in the value of Cr. The source of this input is probably anthropogenic. Average heavy metal concentration of River Orashi sediment compared with USEPA sediment standards, Average Shale Values, Toxicity Reference Values and World River System values (WRS) is shown in Table 4. The highest average concentration of 2.05 ± 6.00 mg/kg of Cr obtained in the rainy season at the middle reaches of Orashi River was lower than 43.4 mg/kg benchmark recommended by United State Environment Protection Agency (USEPA), 9.0 mg/kg recommended by Average Shale Value (ASV), 26.0 mg/kg recommended Toxicity Reference Value (TRV) and 100 mg.kg recommended by World River System (WRS) (Singh et al., 2017). However the level of Cr in the sediment of Orashi river may increase considerably in future due to increase in population and activities at Orashi River middle reaches. Chromium may go into the aquatic body through the small-scale tanneries, mining sites, natural origins, etc. (Singh et al., 2017).

The minimum average concentration of Fe was 17.89 ± 6.01 mg/kg at Akinima sampling station, followed by 18.02 ± 4.32 mg/kg at Odieke, 20.07 ± 7.57 mg/kg at Osiobele, 21.08 ± 5.28 mg/kg at Odiobor, and the maximum was 24.01 ± 16.72 mg/kg recorded at Mbiama. There are no significant differences between average concentrations Fe in the dry season and the rainy. The highest average was In the month of February in the dry season and the lowest was 10.85 ± 74.54 mg/kg in the rainy season. The highest average concentration of 24.01 ± 16.72 mg/kg of Fe at the middle reaches of Orashi River was lower than 47,200 mg/kg recommended by Average Shale Value (ASV) (Singh, et al., 2017). This is in agreement with an earlier research carried out on sediment quality of Orashi River at Four Oil Producing Communities of Nigeria (Akachukwu et al., 2020), where the value of Fe reported was lower than the value recommended by Sediment Quality Guideline (SQG).

Average concentrations of zinc (Zn) were 9.83 ± 4.58 mg/kg measured at Odieke, 12.07 ± 8.12 mg/kg at Odiobolor sampling station, 12.99 ± 3.78 mg/kg at Akinima, 14.61 ± 5.38 mg/kg at Oshiobele, and 15.35 ± 9.91 mg/kg at Mbiama. Seasonal variation of the concentrations of Zn was monitored over a period of 12 months as shown in Table 3 and illustrated in Figure 4. The highest average of 30.66 ± 10.18 mg/kg was recorded in the month of September (rainy season) and the lowest was 9.29±3.67 mg/kg (rainy season). The highest average concentration of 15.35±9.91 mg/kg of Zn at the middle reaches of Orashi River was lower than 121 mg/kg benchmark recommended by United State Environment Protection Agency (USEPA), 95 mg/kg recommended by Average Shale Value (ASV), 110 mg/kg recommended Toxicity Reference Value (TRV) and 350 mg/kg recommended by World River System (WRS) (Singh et al., 2017). It will be necessary to monitor the concentration of Zn at the middle reaches Orashi river due to increase in all the villages at the middle reaches of the river. The main sources of Zn are smelting, fertilizers, and pesticides used in agriculture, soil erosion due to rainfall, fossil fuel, and land construction activities (Singh et al., 2017) Zinc occurs naturally in the earth's crust and It is often associated with the ores of other metals. In the aquatic environment, it will combine with suspended materials before finally accumulating in the sediment.

The Concentration of Pb was measured at five sampling stations in this research for a period of twelve months. The lowest average concentration of Pb was 0.801 ± 2.77 mg/kg at Oshiobele sampling station, followed by 1.376 ± 4.76 mg/kg at Odieke, 1.568 ± 5.43 mg/kg at Mbiama, 1.609 ± 5.57 mg/kg at Akinima, and the highest was 2.218 ± 7.68 mg/kg recorded at Odiobor. There was a sudden increase in the concentration of Pb in the month of September. The highest average concentration of 2.218 ± 7.68 mg/kg of Zn at the middle reaches of Orashi River was lower than 35.8 mg/kg benchmark recommended by United State Environment Protection Agency (USEPA), 20 mg/kg recommended by Average Shale Value (ASV), and 31 mg/kg recommended Toxicity Reference Value (TRV) (Singh et al., 2017). It will be necessary to monitor the concentration of Pb at the middle reaches Orashi river due to increase population in all the villages at the middle reaches of the river. (Singh et al., 2017). This is in agreement with earlier research carried out on sediment quality of Orashi River at four oil producing communities of Nigeria (Akachukwu, et al., 2020), where the value of Pb reported was lower than the value recommended by Sediment Quality Guideline (SQG).

Enrichment Factor (EF)

The Enrichment Factor (EF) of the heavy metals at the five sampling locations is shown in Table 5. The EF value of Cd is 0.00 in both rainy season and dry season. This indicates that the sediments in the study area was deficient in Cd. Cr had EF of 0.00 in the rainy season indicating no enrichment in the sediments and 51.05 indicating extremely high enrichment in the sediments. Zn had extremely high enrichment in both rainy and dry seasons. Pb had no enrichment in the rainy season but had extremely high enrichment in the dry season. Some of the EF values calculated are extremely high and did not show consistency. EF is the minimum factor by which the weight percent of mineral in an orebody is greater than the average occurrence of that mineral in the Earth's crust. The assumption of enrichment factor as pollution detection tool inherits many theoretical shortcomings. The EFs calculation is strongly influenced by the natural variable composition of the reference material, biogeochemical processes and physico-chemical alteration of elements in crust materials (Seng-Chee & Norhayati, 2017). Another shortcoming of EFs approach in assessing the level of anthropogenic sources to environment is EFs did not take into account the natural variation of element concentration in environmental samples in relation to biogeochemical and localized lithogenic processes (Reimann & Caritat, 2005). Therefore, enrichment factor should be used carefully as pollution detection tool.

Geo-accumulation index (Igeo)

Table 5 shows the Geo-accumulation Index (Igeo) of the heavy metals at the middle reaches of Orashi River. Cr had the lowest Igeo index of -17.04 in the rainy season while Pb had the highest Igeo of -3.52 in the dry season. Igeo index values of all the metals in the rainy and dry season were below zero. This indicates the sediments of the sampling stations were unpolluted. However, it has been reported that Igeo failed to various degrees to indicate the intensity of pollution (Karbassi, et al., 2008; Yahaya, et al., 2012)

Contamination factor (CF)

Contamination Factor (CF) of the metals at the sampling locations are shown in Table 6. At Odieke, Fe had the lowest CF of 0.0004 while Zn had the highest CF of 0.1035. Fe had the lowest CF of 0.0005 and Zn had the highest CF of 0.1271 at Odiobor. At Mbiama, Fe had the lowest CF of 0.0006 while Zn had the highest CF of 0.1616. At Akinima, Fe had the lowest CF of 0.0004 and Zn had the highest CF of 0.1367. Fe had the lowest CF of 0.0005 while Zn had the highest CF of 0.1538 at Oshiobele. At all the sampling Fe had the CF. The highest CF recorded during this research was 0.1616. This was recorded for Zn at Mbiama. This implies that CF of the heavy metals at the middle reaches of Orashi River was in Class 1 which means low level of contamination.

Degree of Contamination (DOC)

The highest Degree of Contamination (DOC) of 0.2677 recorded at Odiobor, followed by 0.2612 at Mbiama, 0.2306 at Akinima, 0.2075 at Oshiobele, and lowest of 0.1797 was recorded at Odieke as shown in Table 6. DOC of the sediments of the middle reaches of Orashi River with heavy metals falls in Class 1, indicating the sediments have low level of contamination.

Modified Degree of Contamination (mDOC)

The modified Degree of Contamination (mDOC) ranged between 0.0359 at Odieke to 0.0535 at Odiobor as shown in Table 6. mDOC of the sediments of the middle reaches of Orashi River falls in Class 1, indicating the sediments had very low level of contamination

Pollution Load Index (PLI)

The Pollution Load Index (PLI) of the sediments of the middle reaches of Orashi River is presented in Table 6. The lowest PLI value of the sediments was 0.008 and the highest was 0.014. The PLI values in increasing order at the sampling locations was Odieke < Oshiobele < Akinima < Mbiama < Odiobor. The highest PLI was less than 1, indicating that the sediments of the middle reaches of Orashi River were unpolluted with the heavy metals tested in this research.

Nemerow Multi-Factor Index (NMI)

NMI values in this research are shown in Table 6. The highest value (0.1201) was at Mbiama, followed by Oshiobele (0.1126), Akinima (0.1020), Odiobor (0.0975), and the lowest value (0.0775) was at Odieke. NMI can be used to assess the status of comprehensive pollution caused by all the heavy metals in the sediments, because different heavy metals may have impacts in the same station (Shen Fang et al., 2019). NMI values calculated in this research were less than 1, therefor, sediments of the middle reaches of Orashi River were considered unpolluted.

Correlation coefficient

Heavy metals in the sediment of the middle reaches of Orashi River have different levels of positive correlation with each other at a significant level of $P < 0.05$, as shown in Table 7. Positive relationship between heavy metals demonstrates a characteristic natural origin. Fe and Cr (0.652), Zn and Fe (0.676), Pb and Cr (0.720) have moderate positive correlation. Zn and Cr (0.305), Pb and Fe (0.195) and Pb and Zn (0.279) have weak positive correlation. Weak correlation between Zn and Cr, Pb and Fe, and Pb and Zn indicates these metals are not controlled by any single element, but rather it is controlled by a combination of geochemical support and associations.

Conclusion:

Average heavy metal concentration of River Orashi sediments in the rainy and dry seasons were below the benchmark recommended by USEPA sediment standards, Average Shale Values, Toxicity Reference Values and World River System values (WRS). Assessment of the status of pollution by the pollution indices namely Enrichment Factor, Geo-accumulation Index, Contamination Factor, Degree of Contamination, Pollution Load Index, and Nemerow Multifactor Index showed that the sediments of the middle reached of Orashi River had low level of contamination. The Degree of Contamination showed that Odobor was the most contaminated with heavy metals while Odieke was the least contaminated. Pollution Load Index calculated showed that Odiobor was the most polluted with heavy metals, probably due to very high human activity such dredging, bunkering and waste dump, while Odieke was the least polluted, but classified the whole sediments of the middle reaches of Orashi River as unpolluted with heavy metals.

Correlation coefficient of the heavy metals showed the presence of natural and anthropogenic sources of heavy metals.

Assessment of the present status of heavy metals pollution of the sediments of the middle reaches of Orashi River at five communities showed values that were lower than the international recommendations, and using the pollution indices, demonstrated the sediments were unpolluted with heavy metals. However, this might alter very soon, with the increasing population load at the communities. During the research, it was observed that a large area along the stretch of Orashi River was undergoing gradual disintegration and degradation, following the use of illegal method of crude oil refinery and pipeline destruction in order to obtain petroleum products, coupled with sand dredging operations and other illegal activities going on in the area. Other related human activity that was causing problem in the area was the introduction of locally designed and fabricated fishing devices and the use of obnoxious fishing methods.

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