ASSESSMENT OF HEAVY METALS CONTAMINATION IN SEDIMENT OF OBII STREAM, UFUMA, ANAMBRA STATE, NIGERIA

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Abstract

This research work was conducted to assess the levels of heavy metal (Cd, Pb, Ni, Cu, Zn, and Fe) concentrations in sediment of Obii stream, Enugwu-Abo Ufuma in Orumba North; Anambra State. Sediment pollution assessment was undertaken using geoaccumulation index (I_{geo}), pollution Load Index (PLI), contamination factor (Cf) and ecological factor (Er). The contamination factor (mg/kg) in dry and rainy season respectively showed Cd: (0.520, 0.207); Pb: (0.026, 0.000); Ni: (0.009, 0.002); Cu: (0.004, 0.000); Zn: (0.126, 0.020); and Fe: (0.001, 0.000) while the ecological factor (mg/kg) in dry season and rainy season respectively showed Cd:(1.040, 0.415); Pb: (0.132, 0.001); Ni: (0.046, 0.010); Cu: (0.023, 0.004) and Zn: (0.126, 0.020).The mean geoaccumulation indices (I_{geo}) suggested that the magnitude of heavy metals pollution of the sediment followed the order Cd > Zn >Pb > Ni > Cu > Fe in dry season and Cd > Zn >Ni >Cu > Fe > Pb during the rainy season. The pollution load index (PLI) calculated for all the heavy metals during the dry and rainy seasons were 0.00006 mg/kg and 0.00545 mg/kg respectively.I_{geo} for the analyzed metals suggested that sediment from this stream ranged from unpolluted to moderately polluted degree of pollution.

1.0: INTRODUCTION

Due to chemical and geological conditions, heavy metals in sediments can exist in different forms: soluble, exchangeable, bound to organic matter, sorbed in Mn and/or Fe oxides, as a component of carbonates, phosphates, sulphurs, or other secondary minerals, or bound to silicates (residual) (Devesa-Rey et al., 2010).Contaminated sediments expose worms, crustaceans and insects (benthic organism) to hazardous concentrations of toxic chemicals and this in most cases kills them. Benthic organisms take up these contaminants in the sediments in a process called bioaccumulation. When higher animals feed on these contaminated organisms, the toxins are taken into their bodies, moving up the food chain in increasing concentrations in a process called biomagnifications (Abida et al.,2009). Contaminated sediment can be resuspended especially when a process such as dredging disrupts the water movement and when this happens, almost all the aquatic organisms will be directly exposed to the toxic contaminant. Metal-mobility in the ‘’sediment- water phase’’ can be determined by the following factors: decomposition-resuspension; sorption-adsorption and complexation-decomplexation and all these processes are governed by pH, salinity and redox condition (Ruiz, 2001, Utete et al., 2013). Metal occurs in different complexes in both the water and sediment phase. Heavy metals in unpolluted sediment are mainly bound to silicates and primary minerals and such species are relatively immobile and usually not available to living organisms. But in some polluted sediments, heavy metal are more mobile and bound to sediment; hence the reason most metal discharged in a river are found in the bottom sediment (Utete et al.,2013). This study therefore evaluates the heavy metals contamination in sediment of Obii stream using geoaccumulation index (I_{geo}), pollution Load Index (PLI), contamination factor (Cf) and ecological factor (Er).

1.1. Significance of Study

This research showed the effect of the dry and rainy season on the metal concentrations of Cu, Fe, Zn, Cd, Ni, and Pb. It gives information on the extent of pollution of the stream. It also showed which fish parts bioaccumulate the highest concentrations of heavy metal

2.0 MATERIALS AND METHOD

2.1 Study area

Obii stream is located at Ufuma, Orumba North, Anambra State, Nigeria (latitude 6d 3' 40N-6d 7' 40N and longitude 7d 11'E- 7d 15'40E). The coordinates of the three sampling stations (1,2,3) are 6d 6'47.055N, 7d 13'37.077E, 6d 6'24.784N, 7d 13' 4.526E, and 6d 6' 3.54N, 7d 12' 34.716E respectively. The climate in the area is tropical with two major seasons; the wet (April – September) and dry (October – March) seasons. Rainfall is biomodal, peaking usually in June and again in August. Domestic and agricultural activities such as fishing, bathing, washing are carried out in the stream.

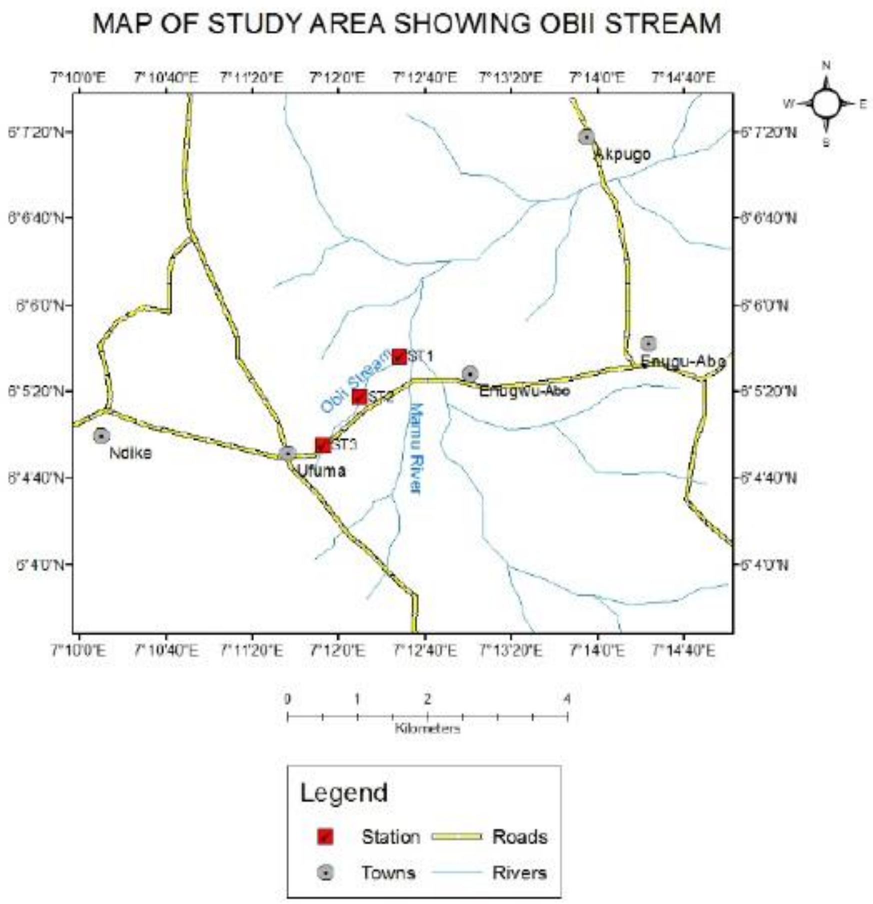

Figure 1: Map of Obii stream showing the different sampling stations

2.2: Sampling and sample treatment

At each station, sediment samples were collected at the depth of about 0.305m at six different points randomly for six months. The sediment collected was stored in metal free plastic bowel that had been thoroughly washed and sun-dried. The bowels were properly labeled to indicate their sampling points. The sediment samples were first air – dried and later placed in porcelain oven- dried crucibles and at a temperature of 105^0C for 24 hours to remove moisture. The dried samples were then ground into a homogenous mixture with the help of a porcelain mortar and pestle and sieved through 2mm mesh screen to remove coarse materials. Each of the finely dried sediment (2.0g) was kept in an air tight plastic bottle prior to digestion.

The finely homogeneous sediment samples (2.0 g) were digested using a mixture of nitric acid and hydrochloric acid in the ratio of 3:2 in a silica beaker and refluxed in a hot sand bath for 1 hour. After refluxing, the resultant solutions were transferred to an evaporating dish where they were heated gently on a hot plate and left to evaporate to near dryness. They were leached with $5cm^3$ of 20% nitric acid and the undigested portion of the sediments filtered off using acid washed filter paper. The filtrate was put in a volumetric flask and made up to $100cm^3$ with distilled water. All the digested samples were stored in plastic bottles with plastic cover and labeled appropriately. They were later used for the determination of the concentrations of heavy metals.

Heavy metal analysis of the digested sediment sample was conducted using Agilent FS240AA Atomic Absorption Spectrophometer (AAS) according to the method of APHA (1995).
Working principle: The digested sample was aspirated into the flame and atomized when the AAS's light beam was directed through the flame into the monochromator, and onto the detector that measures the amount of light absorbed by the atomized element in the flame. Since metals have their own characteristic absorption wavelength, a source lamp composed of that element is used, making the method relatively free from spectral or radiational interferences. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample.
Include the method or technique you used to determine the concentration of the metals. If it was AAS, explain how you did it.

2.3: Statistical Analysis

Analysis of variance (ANOVA) was used to evaluate the difference between sites. **A hypothesis test was stated to ascertain the significant difference in the observed value compared with WHO and NESREA standard. Differences were considered significant at $P<0.05$ and insignificant at $P > 0.05$.** The mean concentrations between groups were compared using Post hoc test (LSD). T –test was used to compare each parameter with standards (NESREA, 2011; WHO, 2011) using Microsoft Office Excel 2007.

2.4. Sediment quality assessment

Contamination factor (Cf), Ecological risk factor (Er), Pollution load index (PLI), and geoaccumulation index were powerful tool used for the evaluation of the sediment contamination.

2.4.1. Contamination factor (Cf)

The contamination factor (Cf) evaluates soil contamination. (Hakanson 1980) suggested this factor and it was modified by (Loska et al., 2004). They enable an assessment of soil contamination through reference of the concentrations in the surface layer of bottom sediments to the geochemical background values as reference value.

The calculation of Cf is according to equation:

$$Cf = \frac{Cm}{Cn} \qquad 2.1$$

Where Cm is the mean concentration of metals from sample sites and Cn is the geochemical background value (reference value) of individual metals. The geochemical background values for Zn, Cu, Ni, Pb, Cd, and Fe in soil (mg/kg) are 95, 70, 75, 20, 0.3, and 47,200 respectively (Liao and Chao, 2004;Eze et al., 2018).This factor assesses the degree of pollution and takes value: Cf <1 low contamination factor, 1≤ Cf ≤ 3 moderate contamination factor, 3 ≤ Cf ≤6 considerable contamination factor and Cf > 6 is very high pollution.

2.4.2. Pollution load index (PLI)

The Pollution Load Index is given by (Tomlinson et al., 1980) as

$$PLI = \sqrt[n]{Cf_1.Cf_2.Cf_3 \ldots Cf_n} \qquad 2.2$$

In this formula, $Cf_1$to Cf_n indicates the contamination factors calculated for the first soils sample to the n^{th} one. PLI value close to one indicates heavy metal loads near the background levels, while values above one indicate soil pollution (Liu et al., 2005)

2.4.3. Geoaccumulation index (I_{geo})

This index defines the ratio of the concentration of heavy metals in soil to background of metal levels in soil or in corresponding soils. The concentration of metal in background is multiplied by constant 1.5. This constant is used because of possible variations in background values for a given metal in the environment as well as detects very small anthropogenic influence (Dolezalova et al., 2015). The calculation of geoaccumulation index is described by the following equation;

$$I_{geo} = \log2 (Cn/1.5Bn) \qquad 2.3$$

Cn is the measured concentration of the element in soil. Bn is the value of geochemical background. The index of geoaccumulation consists of sevengrades, whereby the highest grade (Loska et al., 2004) reflects 100- fold enrichment above background values. The I_{geo} was classified into six categories. $I_{geo} < 0$ (practically unpolluted, $I_{geo} = 0$), $0 \leq I_{geo} < 1$ (unpolluted to moderately polluted, $I_{geo} =1$), $1 \leq I_{geo} <2$ (moderately polluted, $I_{geo} =2$), $2\leq I_{geo} <3$ (moderately to strongly polluted, $I_{geo} =3$), $3 \leq I_{geo} < 4$ (strongly polluted, $I_{geo} =4$), $4 \leq I_{geo} <5$ (strongly to extremely polluted, $I_{geo} = 5$) and $I_{geo} > 5$ (extremely polluted, $I_{geo} = 6$)

2.4.4. Ecological risk factor (Er)

An ecological risk factor to quantitatively express the potential ecological risk of a given contaminant also suggested by (Hakanson, 1980) is

$$Er = Tr.Cf \qquad 2.4$$

Where Tr is the toxic – response factor for a given substances and Cf is the contamination factor. The toxic response factors for Zn, Cu, Ni, Pb, Cd, and Fe in soil are 1, 5, 5, 5, 30, nil respectively (Hakanson, 1980).

The following terminologies are used to describe the risk factor: Er < 40, low potential ecological risk; 40 ≤ Er <80, moderate potential ecological risk; 80 ≤ Er < 160, considerable potential ecological risk; 160 ≤ Er <320, high potential ecological risk; and Er ≥ 320, very high ecological risk. Although the risk factor was originally used as a diagnostic tool for the purpose of controlling water pollution, it was successfully used for assessing the quality of sediments and soils in the environment by heavy metals.

3.0: RESULTS AND DISCUSSION

Table 1: Concentration of Cd in sediment for dry and rainy season

Sample	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
	Dry	1	0.192±0.248				
		2	0.155±0.172				
Sediment		3	0.121±0.140				
(mg/kg)		**Mean**	**0.156±0.035**	0.006	0.01	3.00	0.00
	Rainy	1	0.046±0.069				
		2	0.083±0.110				
		3	0.058±0.081				
		Mean	**0.062±0.018**	0.006	0.03	3.00	0.00

Cadmium level in sediment samples ranged from 0.121mg/kg at upstream to 0.192 mg/kg at downstream during the dry season. As the rainy season set in, there was a reduction in the concentration of cadmium in the sediment from 0.046 mg/kg at downstream to 0.083 mg/kg when compared with the dry season sediment concentrations. Obii sediment could be said to be polluted with cadmium since P < 0.05. This was in agreement with the findings (Edward et al., 2013) who reported cadmium levels higher than (WHO, 2011) permitted values for their analysis on water and sediment samples from Odo-Ayo River, Ekiti State.

Table 2: Concentration of Pb in sediment for dry and rainy season

Sample	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
	Dry	1	0.553±0.334				
		2	0.476±0.182				
Sediment		3	0.556±0.512				
(mg/kg)		**Mean**	**0.528±0.045**	0.04	0.00	0.16	0.00
	Rainy	1	0.003±0.006				
		2	0.010±0.018				
		3	BDL				
		Mean	**0.004±0.004**	0.04	0.00	0.16	0.00

BDL = below detection limit

The lead level for the sediment samples ranged from 0.476 mg/kg at midstream to 0.556 mg/kg at upstream during the dry season. As the rainy season set in, the concentration of lead in the sediment decreased drastically when compared with its dry season concentration. This could be because of the rainy season effects in washing off the bioaccumulated metal of the soil. During the rainy season, lead concentration was below its detection in the sediment sample at upstream. The sediment samples for both seasons showed existence of enough evidence to reject the null hypothesis ($P < 0.05$) and conclude that sediment from Obii stream was highly polluted with lead.

Table 3: Concentration of Ni in sediment for dry and rainy season

Sample	**Seasons**	**Stations**	**Mean Conc.**	**WHO**	**P-value**	**NESREA**	**P-value**
	Dry	1	0.590±0.750				
		2	0.622±0.771				
Sediment		3	0.882±1.192				
(mg/kg)		**Mean**	**0.698±0.160**	0.03	0.01	0.07	0.02
	Rainy	1	0.131±0.161				
		2	0.110±0.125				
		3	0.246±0.259				
		Mean	**0.162±0.073**	0.03	0.08	0.07	0.16

The sediment concentrations ranged from 0.590 mg/kg at downstream to 0.882 mg/kg at upstream during the dry season and from 0.110 mg/kg at midstream to 0.246 mg/kg at upstream during the rainy season. The sediment samples showed no significant different from the standard during the rainy season ($P > 0.05$). This implied that the sediment sample was not polluted with Ni during rainy season. However, in the dry season, sediment samples showed a significant different from the control. This implied the sediment was polluted with Ni as dry season set in.

Table 4: Concentration of Cu in sediment for dry and rainy season

Sample	**Seasons**	**Stations**	**Mean Conc.**	**WHO**	**P-value**	**NESREA**	**P-value**
	Dry	1	0.203±0.318				
		2	0.265±0.388				
Sediment		3	0.511±0.774				
(mg/kg)		**Mean**	**0.326±0.162**	0.02	0.08	0.50	0.20
	Rainy	1	0.045±0.040				
		2	0.062±0.059				
		3	0.081±0.041				
		Mean	**0.063±0.018**	0.02	0.05	0.50	0.01

The sediment samples ranged from 0.203 mg/kg at downstream to 0.511 mg/kg at upstream during the dry seasons. However, as the rainy season set in, its concentration in the sediment's samples decreased and ranged from 0.045 mg/kg to 0.081mg/kg. The sediment sample showed no significant different since P>0.05 during the dry season and that implied the sample may not be polluted with Cu.

Table 5: Concentration of Zn in sediment for dry and rainy season

Sample	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
	Dry	1	7.490±11.876				
		2	8.749±13.625				
Sediment		3	19.799±31.926				
(mg/kg)		**Mean**	**12.012±6.772**	0.01	0.09	0.42	0.09
	Rainy	1	3.004±1.949				
		2	0.789±0.448				
		3	2.189±2.515				
		Mean	**1.994± 1.120**	0.01	0.09	0.42	0.13

Obii sediment concentrations ranged from 7.490 mg/kg at downstream to 19.799 mg/kg at upstream during the dry season but as the rainy season set in, the zinc levels in the sediment reduced drastically and ranged from 0.789 mg/kg at midstream to 3.004 mg/kg at downstream. The high concentrations of zinc in the sediment samples could be attributed to the use of chemicals and zinc – based fertilizer by farmers and other human activities. However, comparing with 5 and 6, the sediment samples showed no significant difference since P >0.05. This implied that Obii sediment may not be polluted with Zn in both seasons.

Table 5: Concentration of Fe in sediment for dry and rainy season

Sample	Seasons	Stations	Mean Conc.	WHO	P-value	NESREA	P-value
	Dry	1	65.980±72.171				
		2	94.293±121.274				
Sediment		3	91.973±118.022				
(mg/kg)		**Mean**	**84.082±15.720**	0.03	0.01	0.02	0.01
	Rainy	1	20.944±1.150				
		2	19.622±1.029				
		3	20.596±0.773				
		Mean	**20.387±0.685**	0.03	0.00	0.02	0.00

In dry season, the sediment samples showed high Iron concentrations. The highest was recorded at midstream (94.293 mg/kg) but during the rainy season, its values declined and ranged from 19.622 mg/kg at midstream to 20.944 mg/kg at the downstream. The P- value for both seasons showed that Obii sediment was heavily polluted with Fe.

4.0: Assessment of sediment quality

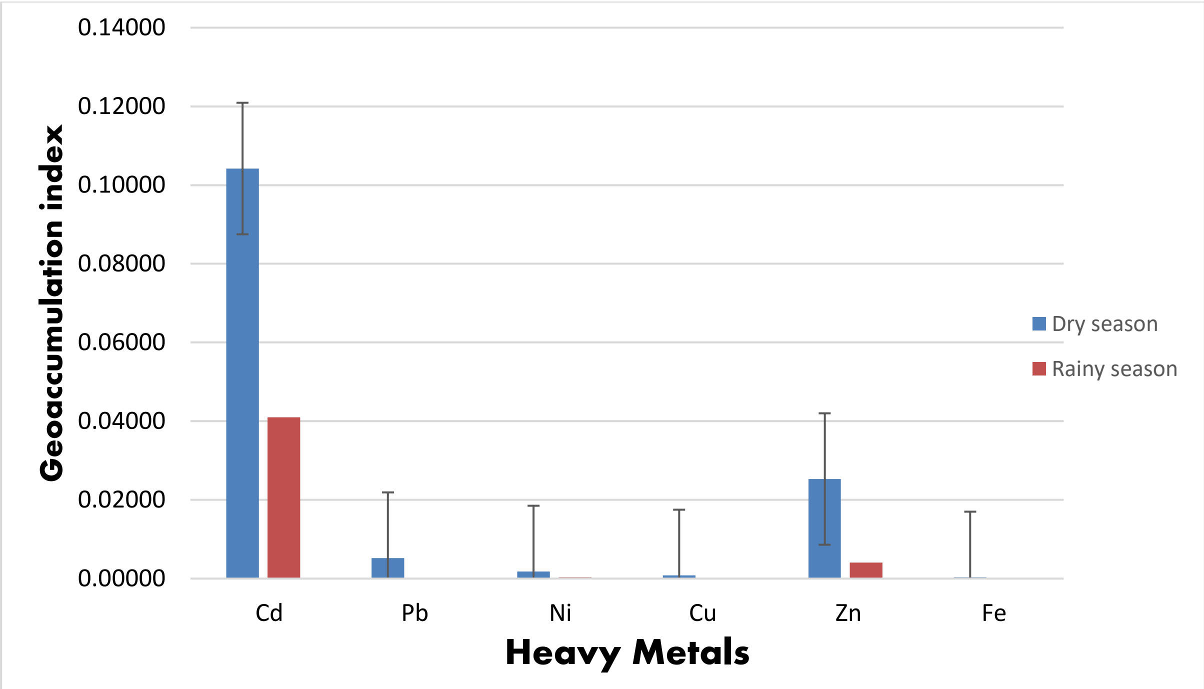

Figure 2 shows bar chart of geoaccumulation (I_{geo}) index of sediment sample from Obii stream against heavy metal in mg/kg

The mean geoaccumulation indices (I_{geo}) suggested that the magnitude of heavy metals pollution of the sediment of Obii stream followed the order Cd > Zn >Pb > Ni > Cu > Fe in dry season and Cd > Zn >Ni >Cu > Fe > Pb during the rainy season. Hence, Cd showed the highest I_{geo} for all the heavy metals in the sediment in both seasons. The I_{geo} calculated showed Obii sediment fell into class 1($0 \leq I_{geo} < 1$) of unpolluted to moderately polluted degree of pollution.

The contamination factor evaluated the soil contamination. The contamination factors of Cd, Pb, Ni, Cu, Zn, and Fe for both seasons showed that Obii sediment were of low contamination since Cf < 1. However, Cd with value 0.5200 mg/kg and 0.2077 mg/kg showed the highest contamination factor during the dry season and rainy season respectively for all the heavy metals while Fe with contamination factor of 0.0017 mg/kg and 0.0004 mg/kg for dry and rainy season respectively showed the lowest value. The ecological risk factor (Er) which quantitatively expresses the potential ecological risk of a given contamination showed that all the metal present in the sediment have low potential ecological risk since Er < 40. The highest ecological risk factor was given by Cd (1.0400 mg/kg) during the dry season. Toxic response for Fe was unknown and so its ecological factor wasn't calculated. The low ecological risk values calculated indicated a low contribution of anthropogenic activity in the region as regard Pb, Ni, Cu, and Zn.

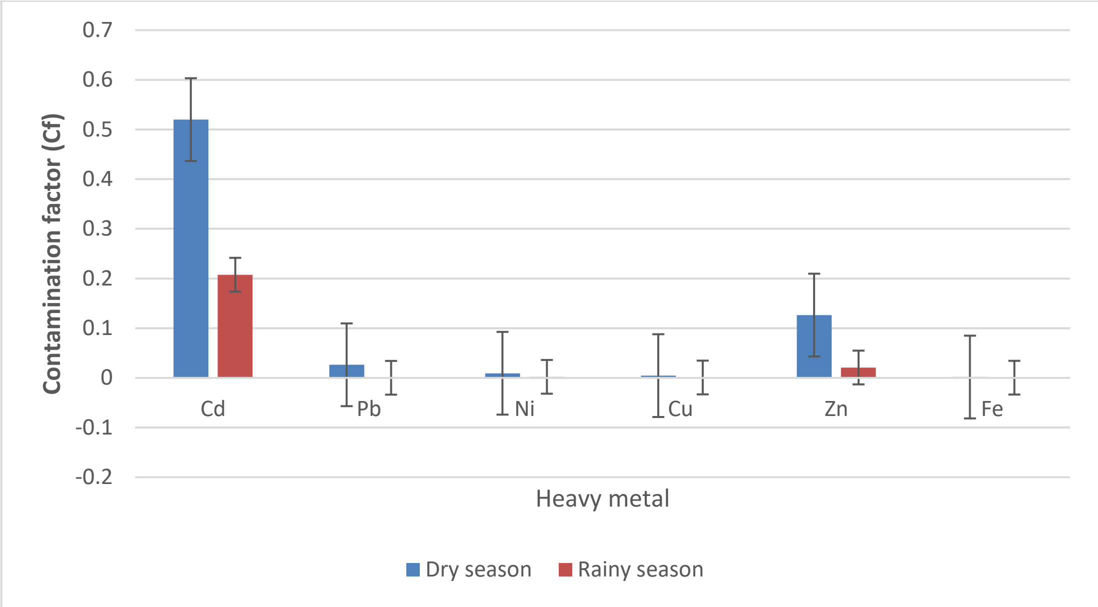

Figure 3 shows bar chart of contamination factor of sediment sample from Obii stream against heavy metal in mg/kg

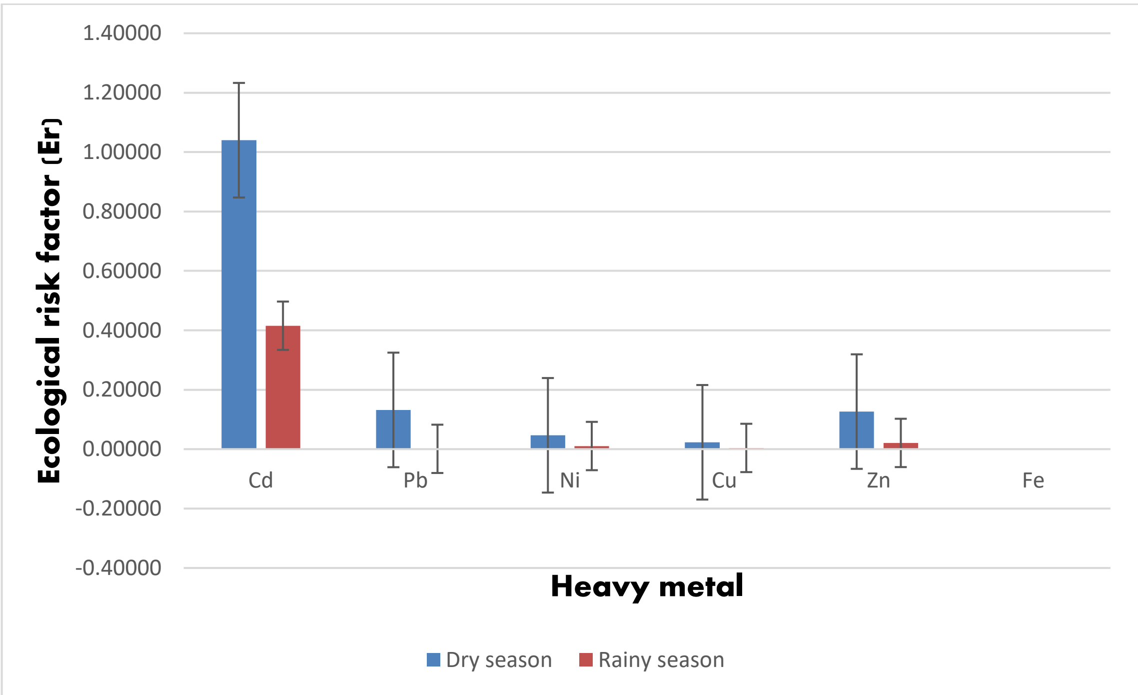

Figure 4 shows bar chart of ecological factor of sediment sample from Obii stream against heavy metal in mg/kg

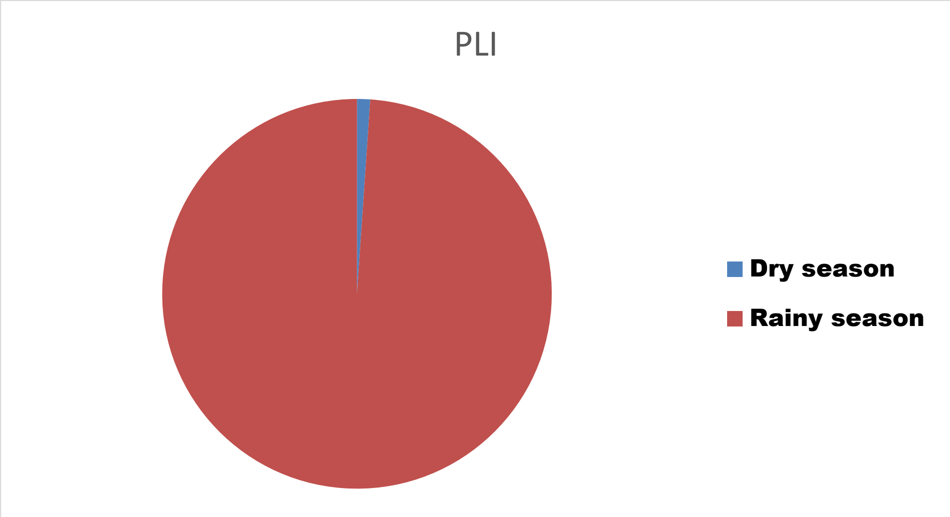

Figure 5 shows pie chart of pollution load index of Obii sediment for both seasons

The pollution load index (PLI) calculated for all the heavy metals during the dry and rainy seasons were 0.00006 mg/kg and 0.00545 mg/kg respectively. PLI values close to one indicate heavy metal loads near the background level while values above one indicates soil pollution (Tomlinson et al., 1980). Lower PLI values were observed in the sediments' samples.

5.0: Conclusion

This work showed Obii sediment contain some levels of Cd, Pb, Fe, Ni, Cu, and Zn. The results indicated that concentrations of Cd, Pb, and Fe in sediment samples were significantly different from their control in both seasons. This implied that the sediment was polluted with Cd, Pb and Fe. However, Obii sediment showed a different trend with Ni, Cu, and Zn. Their P-value was calculated to be above 0.05 and that implied Obii sediment may not be polluted with Ni, Cu, and Zn. The I_{geo} calculated for all the heavy metals showed Obii sediment fell into class 1($0 \leq I_{geo} < 1$) of unpolluted to moderately polluted degree of pollution. In general, ecological risk factor, contamination factor and pollution load index calculated showed Obii sediment were of low contamination.

References

Abida, B., Harikrishna, S., and Irfanulla, K., (2009). Analysis of heavy metals in water, sediments and fish samples of Madivala Lakes of Bangalore, Karnataka. *International Journal of Chemistry Technology Research*, 1: 245-249.

American Public Health Association (APHA), (1985): Standard Methods for Examination of Water and Wastewater, 16th, Edition, United States of America, Baltimore, Maryland.

Devesa-Rey, R., Diaz-Fierros, F., Barral, M.T., (2010): Trace metals in river bed sediments: An assessment of their partitioning and bioavailability by using multivariate exploratory analysis. *Environ. Manage.91*, 2471–2477.

Dolezalova,W.H., Pavlosky,J., and Chovanee, P., (2015). Heavy metal contaminations of urban soils in Ostrava, Czech Republic: Assessment of metal pollution and using principal component analysis. *International Journal of Environmental Research,* 9(2): 683 – 696.

Edward,J.B., Idowu,E.O., Oso, J.A., and Ibidapo,O.R., (2013). Determination of heavy metal concentration in fish samples, sediment and water from Odo-Ayo River; Ekiti State, Nigeria. *International Journal of Environmental Monitory and Analysis,* 1(1):27-33

Eze,O.C., Tukura, B.W.,.Atolaiye,B.O., and Opuluwa,O.D (2018). Index model assessment of heavy metal pollution in soil selected from three irrigated farm sites in FCT Abuja, Nigeria. International Journal of Advance in Scientific Research and Engineering, (4): 93 - 105

Hakanson.L., (1980). *An ecological risk index for aquatic pollution control*. A sedimentological approach, Water Resources. 14,975 – 1001.

Liao,G.O., and Chao,W., (2004). Assessment of heavy metallic ions pollutions for a river near a metal mine. *Journal Mining and Metallurgy,* 13 (1): 86 -90

Liu,W.H., Zhao,J.Z., Ouyang, Z.Y., Soderlund, L., and Liu,G.H., (2005). Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. *Environment International*, 31:805 -812.

Loska,K., Wiechu,D., and Korusa,I., (2004). Metal contamination of farming soils affected by industry. *Environment International*, 30:159 -165.

NESREA (2011). National environmental standard and regulation enforcement agency regulation

Ruiz,F., (2001). Trace metals in estuarine sediments from the South Western Spanish Coast. *Marine Pollution Bulletin,* 42:482-490.

Tomlinson, L.,Wilson, G.,Harris,R., and Jeffery,D.W., (1980). Problems in the assessment of heavy metal levels in estuaries and formation of a pollution index. *Helgol Meeresunters*, 33:566 - 575

Utete,B., Nhiwatiwa,T., Barson,M., and Mabika,N., (2013). Metal correlations and mobility in sediment and water from the Gwebi River in the Upper Manyame Catchment Zimbabwe. *International Journal of Water Science.*

WHO (2011), Guideline for Drinking Water Quality WHO library cataloguing in Publication data. 4th ed: Accessed from http://www.who.int/water sanitation health/....../201119789241548151 annex pdf