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THE EVALUATION OF HEAVY METAL LOAD IN BENTHIC SEDIMENT USING SOME POLLUTION INDICES IN OSSIOMO RIVER, BENIN CITY, NIGERIA.

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Abstract

The sediment-pollution load of any river can be associated with wide range of anthropogenic and natural factors that surround it. A thorough analysis of the nature of sediments is required to identify the natural lithogenic and anthropogenic sources of contaminants. A total of 360 sediment samples were collected with an Eckman grab and 9 heavy metal parameters investigated monthly between March 2015 and August 2016 using standard analytic methods and quality control techniques. The concentrations of Fe, Mn, Zn, Cu, Cr, Cd, Pb, Ni and V, varied individually with a significant difference ($p < 0.05$) and no significant difference ($p > 0.05$) values across the stations with their ranks in this order Fe > Mn > Zn > Cu > Cr > Cd > Pb > Ni > V. Most of the environmental computed heavy metals in this current study were above the national and international unity standards as compared with their standard limits. The Enrichment Factors, Pollution Index (PI) and Nemerow Integrated Pollution Index (NIPI) were used to assess heavy metals contamination in the river bed. All the indices showed varied grades of characterized pollution with EF values >1, PI and NIPI values >3. The sources of pollution were mainly from lithogenic (crustal origin) and anthropogenic activities. The high concentration values of some of the metals in the sediment indicated that more comprehensive investigations are required to be carried out in this study area to ensure long term preservation of aquatic biodiversities and the water course.

Keywords: *Heavy Metals, Enrichment Factor, Pollution Index, Nemerow Index, Lithogenic origin.*

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1. Introduction

Developing countries in the recent years have undergone rapid industrialization revolution, urbanization expansion, massive population growth which has resulted in the increase of land use arrangement and organization. This has been a significant reflection in country like Nigeria which is in the forefront of economic hub of Africa. These factors have directly influenced the aquatic systems and contributed to their deterioration in quality (Kumar and Pratap, 2014).Most of the aquatic watercourses in Nigeria are seen as receptors of wastes. The sediment-pollution load of any river can be associated with wide range of anthropogenic and natural factors that surround it. Agricultural activities; such as farming, fishing and lumbering where different chemicals like pesticides and fertilizers are used, boat transportation, sawmilling activities, domestic activities, local gin and cassava processing, crude oil exploration and processing are notable anthropogenic activities in Ossiomo (Ologbo axis) community.

Effluents and wastes are being released into the water body via these activities and tend to alter the original state of the water chemistry which in turn percolates to benthic region. A thorough analysis of the nature of sediments is required to identify the natural (lithogenic) and anthropogenic sources of contaminants (Begum *et al*., 2009 and Milenkovic *et al*., 2005). Investigation of elements distribution in sediments is also important to understand their behaviour and transport in the fluvial or aquatic environment (Prasad *et al*., 2006). Sediments work as adsorbent pads for elements which can remobilize in due course under changed physical and chemical conditions of the water bodies (Palumbo-Roe *et al*., 2012). However, sediments also act as habitat and major source of nutrients for aquatic organisms (Olubunmi and Olorunsola, 2010). Recent examinations of river beds put more emphasis on the presence of trace elements in sediments because of their persistent, non-degradable nature and potential to enter the food chain (Kumar and Pratap, 2014).

Elements entering the river system become bound to particulate matter, which after settling down become part of the sediments (Suthar *et al*., 2009). Though, elements such as Fe, Zn and Cu are required for the normal functions of the body, at concentrations higher than the required value they can be detrimental to the physiology and health of the living organisms (Kumar and Pratap, 2014). On the other hand, elements like Cd and Pb are toxic even at minute concentrations (Begum *et al*., 2009 and Milenkovic *et al*., 2005, Dan' Azumi and Bichi, 2010, Kar *et al*., 2008, Nair *et al*., 2010 and Nicolau *et al*., 2011). Threats to benthic communities by pollutants are caused by the water-sediment coefficient percolating potentials and bioturbation activities in the sediments by the macro benthic invertebrates. Residential chemicals such as heavy metals can be precursor of benthic organisms' morbidity and bioaccumulation severity. Metal pollution in the aquatic environment is fast becoming a global concern. In the recent years, many researchers around the globe have investigated the distribution of heavy, trace and rare earth in sediments of rivers, lakes and oceans in an attempt to estimate the potential risks associated with metal contaminations (Qian *et al*., 2005 and Zhang *et al*., 2012). Regular environmental monitoring and assessment of aquatic systems for the presence of elements is indispensable to examine possible impacts of developmental projects on their sediment environment (Kumar and Pratap, 2014). Since sediment environment directly influences the physicochemical and ecological dynamics of aquatic resources, a deteriorated sediment quality may severely impact the supports that sustain aquatic life and the surrounding ecosystem, which also includes human beings, dependent on it (Harikumar and Jisha, 2010).

The objectives of this study were to monitor and evaluate the heavy metal pollution load using Enrichment Factor, Pollution Index and Nemerow Integrated Pollution Index in benthic sediment of Ossiomo River, Benin City, Nigeria. To the best of our knowledge, this study is the first in this River to ascertain the trend of Pollution load in this river.

2.0 Materials and Methods

2.1 Study Area

The study covers 5.0873 km stretch of Ossiomo River Ologbo axis, Benin City situated in the South West, Nigeria (Latitude 6° 03'.1'' N - Longitude 5° 40'.3'' E) Fig. 1. Four sampling stations in the river were selected to reflect the upstream and downstream status of the river based on the possible amount of agricultural and other anthropogenic pollution it received.

Station 1: a neutral zone free from agricultural and anthropogenic activities. It lies at Latitude 6° 02'.890'' N and Longitude 5° 39'.599'' E.

Station 2: it is located closed a timber factory and closed to a deck of boats and where human activities are very high. It lies at Latitude 6° 01'.759'' N and Longitude 5° 38'.344'' E.

Station 3: is located closed to local distillers, palm oil farm (PRESCO) and sawmill of Latitude 6° 01'.859'' N and Longitude 5° 36'.870'' E.

Station 4: is located closed to a large cassava farm and sawmill which lies at Latitude 6° 01'.091'' N and Longitude 5° 35'.199'' E.

The river is mostly fed by surface run-off from neighbouring communities of Okuku, Ugbenu, Ovade, Asaboro and Imasabor respectively through streams and rivers. The climate of Ologbo and its neighbourhoods is not steady. Tempo of rainfall occurs in combination with the movement of the Southern-West rainy season wind across the Atlantic Ocean and the programing of this movement varies from year to year (Afangideh *et al*., 2010). There are two separate annual seasons associated with this region: the rainy season which begins in early March and ends in late November, and the dry season which starts from November and ends in March. Rainfall for 2015, ranged from 160.7 – 708.5mm with the lowest recorded in the month of May (158.4mm) and the peak recorded in the month of September (708.5mm). The mean rainfall value was (434.6mm). The principal plants here include; *Pandanus candelabrum*, *Elaeis guineensis*, *Azolla africana*, *Nymphaea lotus*, *Salvinia nymphellula*, *Echinochloa pyramidalis* and *Pistia stratiotes*. Many human activities within and around this river stretch include logging, fishing, boating, watercraft maintenance, discharging of cassava effluent products, saw-milling, transportation, laundering, bathing and swimming, crude oil exploration and processing.

2.2 Physicochemical and heavy metal analysis

The sediment samples were collected with an Eckman grab in accordance with standard procedures described by (APHA, 2005). The samples were air-dried at room temperature, and were further dried in an oven at a temperature of 105° C and then were crumpled to a fine texture in a ceramic mortar, and thereafter sieved mechanically using a 0.5 mm mesh sieve. A total of 28 samples were collected and analyzed monthly from March 2015 – August 2016. The analyzed physicochemical and heavy metals parameters are; pH, electrical conductivity, nitrate, sulphate, chloride, available phosphate, ammonium nitrate, total nitrogen, organic carbon, exchangeable ions, oil and grease (THC), sodium, calcium, magnesium, potassium, clay, silt, sand and heavy metals namely iron, manganese, zinc, copper, chromium, cadmium, lead, nickel, and vanadium, were analyzed according to methods adopted from [APHA, 1998 and Radojevic and Bashkin 1999] using Atomic absorption spectrophotometer model - Solaar 969 Unicam Series.

2.3 Data Analysis

Inter station comparisons were carried out to test for significant differences in the physicochemical conditions using parametric analysis of variance (ANOVA) and Duncan Multiple Range (DMR) test were used to test for significant difference among stations and also to locate site(s) of significant difference. SPSS version 16.0 was used to compute the Ecological Risk Assessment.

2.3 Ecological Indices

This Research work employed different Ecological Indices which were: (i) Enrichment Factors as proposed by Duce *et al*., (1975) which was progressively extended to the study of soils, lake sediments, peat, tailings, and other environmental materials (Reimann and Caritat, 2005) and (ii) Methods of Heavy Metal Assessment; Pollution Index (PI) and Nemerow Integrated Pollution Index (NIPI) as proposed by Caeiro *et al*., (2005) to assess heavy metals contamination.

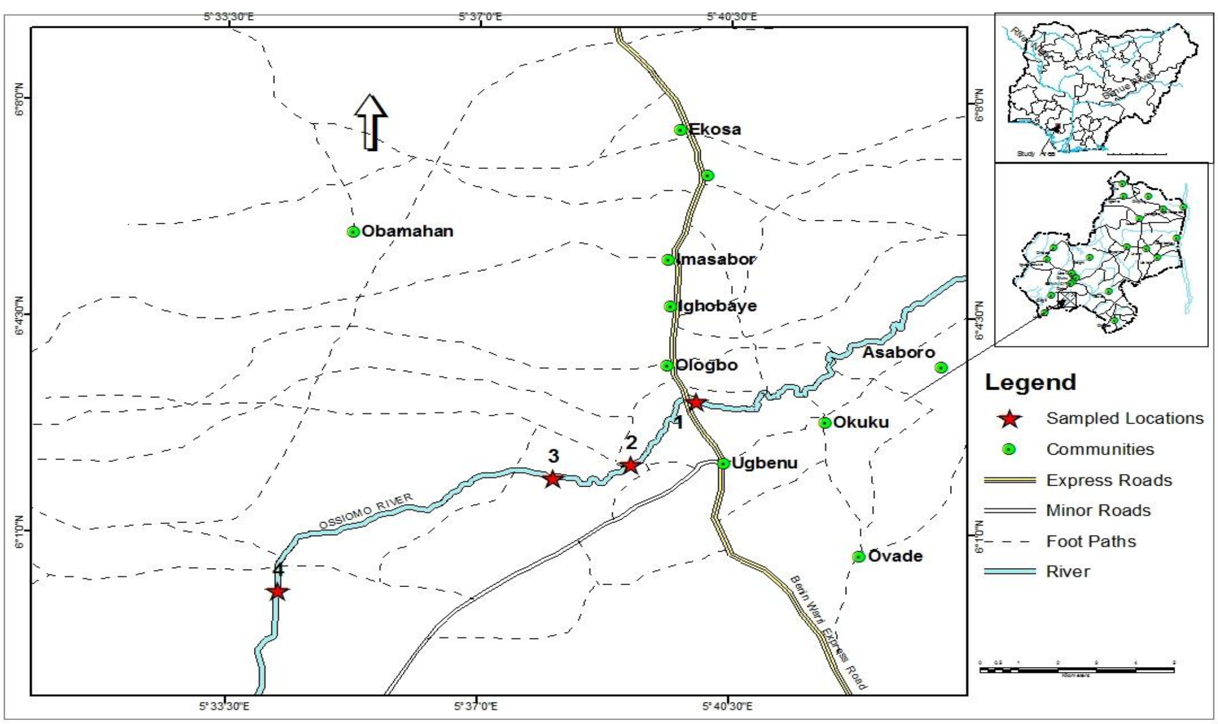

Fig. 1: Map of the study area showing sampling stations

3.0 Results And Discussion

3.1 Heavy Metal Characterization

The computed results of the heavy metal analysis, the mean, the standard deviation, the minimum and the maximum values of the heavy metals are shown in Table 1.These values were placed alongside the World Health Organisation (WHO 1984 and 2003) limit for discharge into sediment and the Nigeria Federal Environmental Protection Agency (FEPA, 1999 and 2003). The concentrations of Fe, Mn, Cu, Cr, Cd, Pb, Ni and V, varied individually with a significant difference ($p<0.05$) across the stations, *a posteriori* DMR test revealed that the difference sourced from the concentrations of each of these parameters at station 2 and 3. Only Zn exhibited no significant difference ($p>0.05$) across the stations. At average, the ranks of the heavy metals concentrations in the sediment were Fe > Mn > Zn > Cu > Cr > Cd > Pb > Ni > V. Figure 2 showed the spatial variations of heavy metals across the stations. It was also noticed that the ranks of the heavy metals showed similar pattern across the stations: Fe > Mn > Zn > Cu > Cr > Cd > Pb > Ni > V.

Table 1: Summary of the Heavy metals Characteristics of Sediment from Ossiomo River collected from designated stations from March 2015 - August 2016

Code	**Units**	Station 1 $\overline{X}$± SD (Min-Max)	Station 2 $\overline{X}$± SD (Min-Max)	Station 3 $\overline{X}$± SD (Min-Max)	Station 4 $\overline{X}$± SD (Min-Max)	WHO/FEPA LIMITS (2003)	FEPA (1991)/ WHO (1984) LIMITS	P-values
Fe	mg/kg	156.49±84.25 (0.49-322.40)	329.14±154.27 (0.95-593.20)	284.00±145.84 (0.76-564.70)	226.80±109.69 (0.32-368.60)	0.030	0.30	P<0.05
Mn	mg/kg	13.33±9.64 (0.06-34.60)	24.50±14.14 (0.07-51.70)	20.92±13.56 (0.09-49.00)	19.08±12.81 (0.06-38.70)	0.030	0.05	P<0.05
Zn	mg/kg	28.38±23.63 (0.13-71.40)	43.63±28.12 (0.38-88.10)	39.17±26.12 (0.20-83.50)	34.92±23.81 (0.11-70.70)	0.0123	3.00	P>0.05
Cu	mg/kg	4.52±3.17 (0.03-11.50)	10.73±6.35 (0.05-21.90)	9.84±5.27 (0.06-17.80)	7.20±4.60 (0.01-13.40)	0.030	1.00	P<0.05
Cr	mg/kg	1.99±2.33 (0.00-6.38)	4.89±4.25 (0.03-13.40)	3.98±3.29 (0.01-10.10)	3.03±2.49 (0.00-6.71)	-	2.00	P<0.0
Cd	mg/kg	1.80±1.74 (0.01-5.60)	5.89±5.92 (0.02-17.40)	5.26±4.74 (0.01-14.80)	3.25±2.60 (0.01-7.38)	0.040	0.003	P<0.05
Pb	mg/kg	1.41±1.33 (0.00-4.27)	6.36±6.14 (0.00-19.50)	4.86±4.71 (0.00-15.20)	3.10±2.79 (0.00-9.46)	0.006	0.01	P<0.05
Ni	mg/kg	1.08±1.01 (0.02-3.29)	2.65±1.97 (0.04-6.78)	2.30±1.49 (0.02-4.80)	1.89±1.42 (0.02-3.56)	-	0.02	P<0.05
V	mg/kg	0.98±0.97 (0.00-3.10)	2.23±1.66 (0.00-5.46)	1.97±1.29 (0.00-4.33)	1.70±1.31 (0.00-3.27)	-	N/A	P<0.05

Most of the parameters were measured in mg/kg; $p<0.05$ – Significant difference; $p>0.05$ –No significant difference. NS: indicates not specified and N/A; indicates not available. FEPA indicates; Federal Ministry of Environment Nigeria/Federal Environmental Protection Agency, WHO; World Health Organisation.

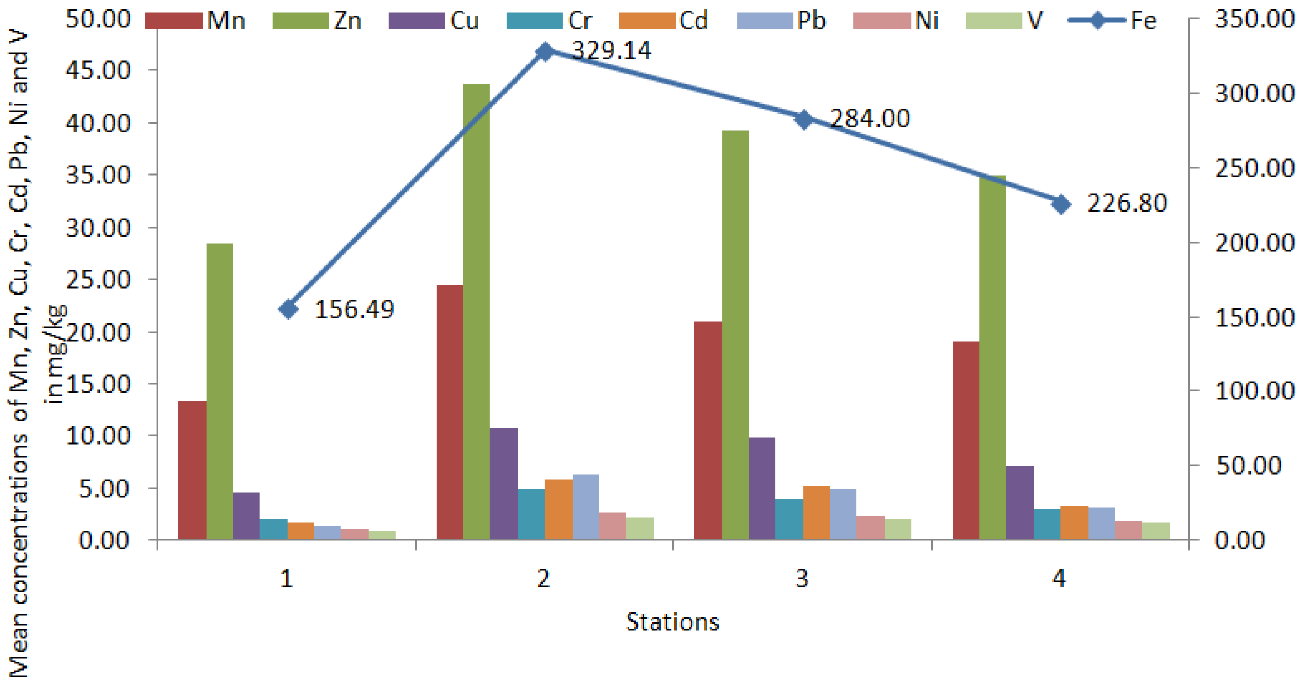

Fig. 2: Spatial variations of the mean concentrations of selected heavy metals across the stations

3.2.The Results of Enrichment Factor (Ef)

The values computed for the EF of all the selected heavy metals in this study were itemised in Table 2. The average EF calculated values ranged from 0.15 to 17.19. These average values indicated that the sediment samples were sourced from anthropogenic and of significant enrichment origin. The significant enrichment origin results of enrichment factor showed that Cd contributed to the enrichment of the sediment and was considered high across the stations. Fig. 3: showed the spatial distribution of selected heavy metals across the stations indicating Cadmium as the major Enrichment Factors.

3.3 The Results of Heavy-Metal Pollution Assessment; Pollution Index (PI), Nemerow Integrated Pollution Index (NIPI)

The computed mean NIPI values in the sediment fluctuated from 2.83 to 46.46, mean values of PI from 2.55 to 41.5 and mean maximum from 2.91 to 48.60 (Table 3). In all, the mean values of the rank of values of the NIPI of the entire selected study element showed a distinct high level of pollution (Zn, Cu, Cr, Cd and Pb), exempting Ni which showed a pace of moderate pollution.

Table 2: The Results of Enrichment Factors (EFs)

ENRICHMENT FACTORS								Class of Enrichment Factors (Efs)			
Stations	Fe	Zn	Cu	Pb	Cr	Cd	Ni	Elements	Enrichment Factor (EF)	Rank	Interpretation
1	232.7	0.16	0.21	0.19	0.04	10.47	0.03	Zn	0.15	<1	Anthropogenic origin
2	232.7	0.14	0.24	0.22	0.06	22.49	0.04	Cu	0.23	<1	Anthropogenic origin
3	232.7	0.13	0.25	0.20	0.06	19.89	0.04	Pb	0.20	<1	Anthropogenic origin
4	232.7	0.15	0.23	0.19	0.05	15.92	0.04	Cr	0.05	<1	Anthropogenic origin
Mean	**232.70**	**0.15**	**0.23**	**0.20**	**0.05**	**17.19**	**0.04**	Cd	17.19	>1	Significant enrichment
								Ni	0.04	<1	Anthropogenic origin

Table 3: The Results of Pollution Index (PI), Nemerow Integrated Pollution Index (NIPI)

		Parameters of importance							Pollution Levels by Yang et al. (2010)		
Stations	Sourced values	Zn	Cu	Cr	Cd	Pb	Ni	Element	NI PI	Ranks of values	*interpretation*
1	PI	0.10	0.14	0.03	7.04	0.12	0.02	Zn	46.5	NIPI > 3	High level of pollution
	Max	71.40	11.50	6.38	5.60	4.27	3.29	Cu	9.97	NIPI > 3	High level of pollution
	NIPI	50.49	8.13	4.51	6.36	3.02	2.33	Cr	5.63	NIPI > 3	High level of pollution
2	PI	0.19	0.34	0.08	31.81	0.31	0.05	Cd	17.5	NIPI > 3	High level of pollution
	Max	88.10	21.90	13.4	17.40	19.50	6.78	Pb	7.92	NIPI > 3	High level of pollution
	NIPI	62.30	15.49	9.48	25.6	13.79	4.79	Ni	2.83	2 < NIPI ≤ 3	Moderate level of pollution
3	PI	0.16	0.31	0.07	24.3	0.25	0.05				
	Max	83.50	17.80	10.1	14.8	15.20	4.80				
	NIPI	59.04	12.59	7.14	20.1	10.75	3.39				
4	PI	0.15	0.23	0.05	15.5	0.19	0.04				

	70.	13.	6.7	7.3	9.4	3.5
Max	70	40	1	8	6	6
	49.	9.4	4.7	12.	6.6	2.5
NIPI	99	8	4	2	9	2
Mean	48.	10.	5.7	16.	7.6	2.9
Maxi.	60	17	9	9	7	1
	41.	8.8	5.1	16.	6.7	2.5
Mean PI	54	4	2	9	4	5
	46.	9.9	5.6	17.	7.9	2.8
MEAN NIPI	46	7	3	5	2	3

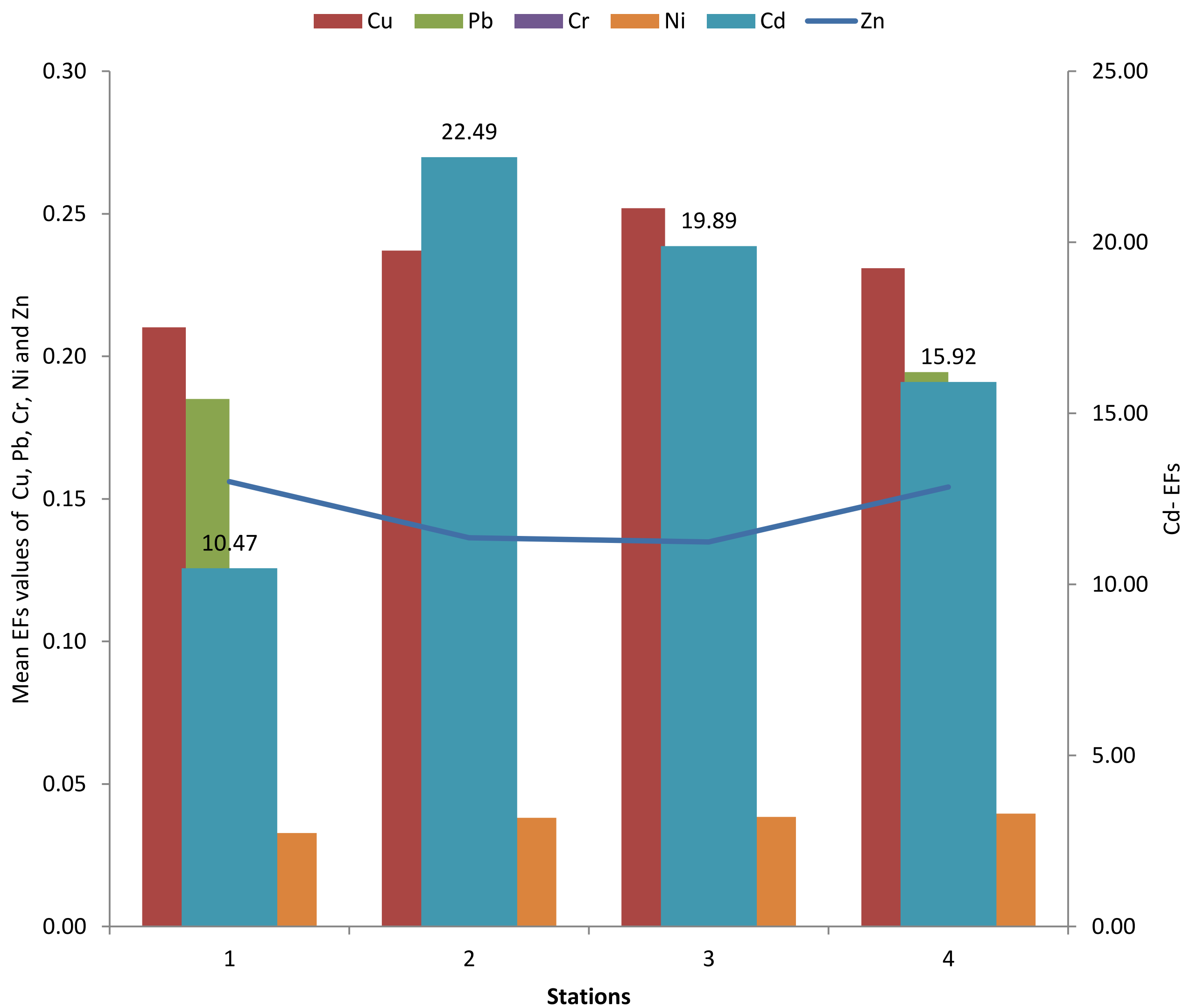

Fig. 3: Spatial distribution of selected heavy metals across the stations indicating Cadmium as the major Enrichment Factors.

4. DISCUSSION

4.1 The Characterization of Heavy Metals Chemistry

The concentrations values of all the heavy metals (iron, manganese, zinc, copper, chromium, cadmium, lead, nickel and vanadium) in this study were far higher than the maximum permissive limits set by World Health Organisation (WHO 1984 and 2003) and the Federal Environmental Protection Agency (FEPA, 1999 and 2003). This is an indication of sediment pollution. The highest concentrations of the heavy metals analyzed in this study were recorded in station 2 and 3; also these stations recorded the highest level of variability. At average, the ranks of the heavy metals concentrations in the sediment were Fe > Mn > Zn > Cu > Cr > Cd > Pb > Ni > V. These variations were attributed to the nature of the anthropogenic activities carried out on the neighbourhood and within the river (Erhunmwunse *et al*., 2013 and Ogbeibu *et al*., 2014). Heavy metals in river bed have been investigated to have negative impacts on humans and other biodiversities. Their sources and likely impacts are different but in some cases similar. The nature of the ranks of the concentrations of the heavy metals iron, manganese, zinc, copper, chromium, cadmium, lead, nickel and vanadium in this current study were higher in stations 2, 3 and 4. Iron has been reported to occur at high concentrations in Nigerian soil or sediment (Adefemi *et al*., 2007, Kakulu *et al*., 1985, and Ogbeibu *et al*., 2014). Chromium reaches water bodies primarily from the discharge of industrial wastes and disposal of products containing the metals (Akan et al. 2010 and Radojevic and Bashkin, 1999). Zinc contents have been associated with high contamination from sewage runoff (Ogbeibu *et al*., 2014 and Turnland, 1998). Copper have been linked to paint, pesticides, weathering of rocks and minerals, and can pose a hazard at concentration of 18.7 mg/kg by which can be bioaccumulated and biomagnified into the food chain (CCREM, 1987). High levels of copper have been implicated in anaemia, liver and kidney damage, stomach and intestinal irritation (Priju and Narayana, 2007). Lead toxicity has been linked with anthropogenic sources which include the use of lead as a petrol additive, runoff from the cities, discharge of improperly treated waste effluents, sewage sludge and the use of pesticides containing lead compounds (Radojevic, and Bashkin, 1999). Nickel and vanadium have been labelled to be linked with the nature of the anthropogenic activities carried out on the within the river axis (Erhunmwunse *et al*., 2013 and Ogbeibu *et al*., 2014 and WHO, 1991 and 1988,) which can be sourced from residues from wastes, land treatment, sewage, sludge, cement factory, processing machineries and in batteries (WHO, 1991 and 1988). The computed results gotten from this study have shown that the high heavy metals pollution load on the river sediment was sourced from intense anthropogenic activities mainly farming and petrochemical complexes.

4.2 Enrichment Factors (EF)

The computed mean EFs values ranged from 0.15 to 17.19. These average values indicated that the sediment samples were sourced from lithogenic and anthropogenic sources of contaminants (Begum *et al*., 2009 and Milenkovic *et al*., 2005). The EF values were interpreted as suggested by (Acevedo-Figueroa *et al*., 2006), where: EF<1 indicates no enrichment; <3 is minor; 3–5 is moderate; 5–10 is moderately severe; 10–25 is severe; 25–50 is very severe; and >50 is extremely severe. The results of the enrichment factor showed that Cd contributed to the enrichment of the sediment and was also high across the stations. Enrichment of Cd and other elements in aquatic beds can affect entire range of biotic spectrum ranging from benthic biota to the organisms higher up the food chains due to their persistence, bio-accumulative and injurious properties (Kumar and Padhy, 2014). In aquatic ecosystems both abiotic and biotic components continuously interact with each other and presence of toxic elements beyond the restoring capacity can severely impact the ecological functioning of the aquatic systems in long term, which in short term may not be visible to us (Kumar and Padhy, 2014). Zhang and Liu, (2002), established the facts that, EF value between 0.5-1.5 indicate the metal is entirely from crustal material or natural processes, whereas EF greater than 1.5 suggests the source is more likely to be anthropogenic. The computed results of the EF in this current study showed that, Zn, Cu, Pb, Cr and Ni enrichment factors status were considered depletion of metals Zsefer *et al*., (1996), while the values of Cd was significantly enriched (Sutherland, 2000) the ecosystem.

4.3 Heavy-Metal Pollution Assessment; Pollution Index (PI) and Nemerow Integrated Pollution Index (NIPI)

The mean PI and NIPI values of the selected heavy metals (Zn, Cu, Cr, Cd and Pb) in this current study varied greatly across the stations. The mean PI values of Zn, Cu, Cr, Cd, Pb and Ni were 41.54, 8.84, 5.12, 16.9, 6.74 and 2.55 respectively. The PI of each metal was classified as non-pollution (PI<1), low level of pollution (1 PI<2), moderate level of pollution (2_PI<3), strong level of pollution (3 PI<5) and very strong level of pollution (PI <5) (Yang et al., 2011). While the NIPI values of Zn, Cu, Cr, Cd, Pb and Ni were 46.46, 9.97, 5.63, 17.5, 7.92, and 2.83 respectively. The NIPI was classified as non-pollution (NIPI ≤ 0.7), warning line of pollution (0.7 < NIPI ≤ 1), low level of pollution (1 < NIPI ≤ 2), moderate level of pollution (2 < NIPI≤3) and high level of pollution (NIPI > 3) (Yang *et al*., 2010). These significant high values indicated that the sediment was highly polluted with Zn, Cu, Cr, Cd and Pb, while Ni was observed to contribute moderately to the pollution of the river sediment. The possible potential pollution sources were from lithogenic (crustal origin) and anthropogenic sources of contaminants (Begum *et al*., 2009 and Milenkovic *et al*., 2005).

5. Conclusion

The use of standard descriptive statistics, multivariate source allotment and various ecological pollution indices to characterise the integrity of Ossiomo River sediment have helped to demystify several possible potential sources of contaminants into the river and how they and their source points. All the characterized heavy metals using descriptive statistics showed high degree of variability (Fe > Mn > Zn > Cu > Cr > Cd > Pb > Ni > V) and they were observed to have surpassed the unity levels of both national and international bodies (FEPA and WHO standards). The various pollution indices Enrichment Factors and Methods of Heavy Metal Assessment; Pollution Index (PI), Nemerow Integrated Pollution Index (NIPI) were used to assessed the heavy metals contamination in the river-sediment bed all showed varied grades of characterized pollution. The sources of pollution were mainly from lithogenic (crustal origin) and anthropogenic. This study underscores the importance of employing a combination of sediment assessment techniques in elucidating sediment pollution impacts from various sources. The high concentration values of some of the metals in the sediment indicated that more comprehensive investigations are required to be carried on in this study area to ensure long term preservation of aquatic biodiversities and the water course.

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References

Acevedo-Figueroa, D., Acevedo-Figueroa, B., Jiménez, C., Rodroguez-Sierrra. (2006). Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environ. Pollut*, **pp**. 336–342.

Adefemi, O.S., Asaolu, S.S., and Olaofe, O. (2007). Assessment of the physicochemical status of water samples from major dams in Ekiti State. Nigeria. *Pak. Nut*. **6**(6): 657 - 659.

Afangideh, A.I., Edet, E.O., Ekanem, E.M. (2008). An analysis of the trend in Annual Rainfall Dynamics for the humid tropics, a case study of calabar, CRS, Nigeria. *Neo-africanists Review*. Vol. II, No 1.

Akan, J.C., Abdulrahman, F.I. and Yusuf, E. (2010). Physical and Chemical Parameters in Abattoir Wastewater Sample. *Pacific Journal of Science and Technology*, **11**(1):640-648.

American Public Health Association (APHA). (2005). Standard Methods for the Examination of Water and Wastewater. 21st ed. American Public Health Association, Washington DC. **pp**. 120.

Ankley, G.T., Lodge, K., Call, D.J., Balcer, M.D., Brooke, L.T., Cook, P,M., McAllister, J.J. (1992). Heavy metal concentrations in surface sediments in a near shore environment, Jurujuba Sound, Southeast Brazil. *Environmental Pollution*, **109**: 1 - 9.

APHA (American Public Health Association), AWWA (American Water Works Association), WPCF (Water Pollution Control Federation). (1998). Standard methods for the examination of water and waste water. 20th ed., Washington, DC. **pp**. 1325.

Begum, A., Ramaiah, M., Harikrishna, Khan, I. and Veena, K. (2009). Heavy Metal Pollution and Chemical Profile of Cauvery River Water. *E-Journal of Chemistry*, **6**, 47-52. http://dx.doi.org/10.1155/2009/154610.

Caeiro, S., Costa, M.H., Ramos, T.B., Fernandes, F., Silveira, N., Coimbra, A., Medeiros, G., Painho, M. (2005). Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach, *Ecol. Indicators*, **5**, 151–169.

Canadian Council of Resource and Environment Ministers, (CCREM). (1987). Canadian Water Quality Guidelines - Water Quality for the Protection of Aquatic Life.

Dan'Azumi, S., and Bichi, M.H. (2010). Industrial Pollution and Heavy Metals Profile of Challawa River in Kanao, Nigeria. *Journal of Applied Sciences in Environmental Sanitation*, **5**, 23-29.

Duce, R.A., Hoffmann, G.L., Zoller, W.H. (1975). Atmospheric trace metals at remote northern and southern Hemisphere sites. *Pollution or natural Science*, **187**: 59–61.

Erhunmwunse, N.O., Dirisu, A.R., and Ogbeibu, A.E. (2013). Managing Eutrophication in Nigeria Inland waters. *Journal of Water Research and Protection (JWARP)*, **5,** 743-746.

Federal Environmental Protection Agency (FEPA). (1999). Guidelines and Standards for environmental pollution control in Nigeria. Decree 58 of 1988, limits not considered to be a cause for toxicological **pp**: 238.

FEPA. (2003). Guidelines and standards for environmental pollution control in Nigeria. Federal Environmental Protection Agency. **pp**: 238.

Harikumar, P.S., and Jisha, T.S. (2010). Distribution Pattern of Trace Metal Pollutants in the Sediments of an Urban Wetland in the Southwest Coast of India. *International Journal of Engineering Science and Technology*, **2**, 840-850.

Kakulu, S.E. (1985). Heavy metals in the Niger Delta: Impact of petroleum industry on the baseline levels. Ph.D. Thesis University of Ibadan, Ibadan.

Kar, D., Sur, P., Mandal, S.K., Saha, T. and Kole, R.K. (2008). Assessment of Heavy Metal Pollution in Surface Water. *International Journal of Environmental Science & Technology*, **5**, 119-124. http://dx.doi.org/10.1007/BF03326004.

Kumar, M., Pratap, K. P. (2014). Distribution, Enrichment and Ecological Risk Assessment of Six Elements in Bed Sediments of a Tropical River, Chottanagpur Plateau: A Spatial and Temporal Appraisal. *Journal of Environmental Protection*, **5**, 1419-1434.

Milenkovic, N., Damjanovic, M., and Ristic, M. (2005). Study of Heavy Metal Pollution in Sediments from the Iron Gate (Danube River), Serbia and Montenegro. *Polish Journal of Environmental Studies*, **14**, 781-787.

Nair, I.V., Singh, K., Arumugam, M., Gangadhar, K. and Clarson, D. (2010).

Trace Metal Quality of Meenachil River at Kottayam, Kerala (India) by Principal Component Analysis. *World Applied Sciences Journal*, **9**, 1100-1107.

Nicolau, R., Galera-Cunha, A., and Lucas, Y. (2006). Transfer of Nutrients and Labile Metals from the Continent to the Sea by a Small Mediterranean River. *Chemosphere*, **63**, **469**-476. http://dx.doi.org/10.1016/j.chemosphere.2005.08.025.

Ogbeibu, A.E, Omoigberale, M.O, Ezenwa, I.M., Eziza, J.O., and Igwe, J.O. (2014). Using Pollution Load Index and Geoaccumulation Index for the Assessment of Heavy Metal Pollution and Sediment Quality of the Benin River, Nigeria. Sciknow Publications Ltd. *Natural Environment*, **2** (1):1-9.

Olubunmi, F.E., and Olorunsola, O.E. (2010). Evaluation of the Status of Heavy Metal Pollution of Sediment of Agbabu Bitumen Deposit Area, Nigeria. *European Journal of Scientific Research*, **41**, 373-382.

Palumbo-Roe, P., Wragg, J., and Banks, V.J. (2012). Lead Mobilisation in the Hyporheic Zone and River Bank Sediments of a Contaminated Stream: Contribution to Diffuse Pollution. *Journal of Soils and Sediments*, **12**, 1633-1640. http://dx.doi.org/10.1007/s11368-012-0552-7.

Prasad, M.B.K., Ramanathan, A.L., Shrivastav, S.K., Anshumali and Saxena, R. (2006). Metal Fractionation Studies in Surfacial and Core Sediments in the Achankovil River Basin in India. *Environmental Monitoring and Assessment*, **121**, 77-102. http://dx.doi.org/10.1007/s10661-005-9108-2.

Priju, C.P., and Narayana, A.C. (2007). Heavy and Trace Metals in Vembanad Lake Sediments. *Int. J Environ. Res*. **1** (4): 280 - 289.

Qian, F., Zhen, F., Ong, C., Jin, S.W., Meng Soo, H., Stainer, D.Y., Lin, S., Peng, J., Wen, Z. (2005). Microarray analysis of Zebrafish cloche mutant using amplified cDNA and identification of potential downstream target genes. ZFIN Publications. *Wiley-liss Inc*. **233**. 1163-1172.

Radojevic, M., Bashkin, V.N. (1999). Practical Environmental Analysis. Royal school of chemistry, Thomas Graham house, science park Cambridge, UK. **pp**. 645.

Reimann, C., and de Caritat, P. (2005). Distinguishing between natural and anthropogenic sources of element in the environment: regional geochemical surveys versus enrichment factors. *Science of the Total Environment*, **337**, 91-107. DOI: 10.1016/j.scitotenv.2004.06.011.

Suthar, S., Nema, A.K., Chabukdhara, M. and Gupta, S.K. (2009). Assessment of Metals in Water and Sediments of Hindon River, India: Impact of Industrial and Urban Discharges. *Journal of Hazardous Materials*, **171**, 1088-1095. http://dx.doi.org/10.1016/j.jhazmat.2009.06.109.

Sutherland, R.A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, **39**: 611–627.

Trocine, R.P., Trefry, J. H., Windsor, J.G., Surma, J.M. (1993). Toxic substances survey for the Indian River Lagoon system. Florida Institute of Technology, Marine and Environmental Chemistry Laboratories.

Turnland, J.R. (1988). Copper nutrition, bioavailability and influence of dietary factors. *J. Am. Dietetic Assoc*, **1**: 303 - 308.

WHO (World Health Organization). (1984). Guidelines for drinking water: health criteria and other supporting information. 1st ed. Geneva. vol 2.

WHO. (1988). Vanadium. In: Environmental health criteria 81. Geneva, Switzerland: World Health.

WHO. (1991). Environmental Health Criteria of Nickel., Genewa, **108**.

World Health Organization WHO. (2003). Chromium , zinc, lead, in drinking – water . Background.

Yang, Z.P., Lu, W.X., Long, Y.Q., and Liu, X.R. (2010). Prediction and precaution of heavy metal pollution trend in urban soils of Changchun City, Urban Environ. *Urban Ecol*, **23**, 1–4.

Yang, Z.P., Lu, W.X., Long, Y.Q., Bao, X.H., and Yang, Q.C. (2011). Assessment of heavy metals contamination in urban topsoil from Changchun City, China. *J. Geochem. Explor*. **108**, 27–38.

Zhang, J., Liu, C.L. (2002). Riverine composition and estuarine geochemistry of particulate metals in China-Weathering features, anthropogenic impact and chemical fluxes. *Estuary Coast Shelf S.* **54**:1051-1070.

Zhang, H., Liu, Y.H., Zhang, Z., Zhang, X., Shaw, S.L., Knipping, E.M., Weber, R.J., Gold, A., Kamens, R.M., Surratt, J.D. (2012). Secondary organic aerosol formation from methacrolein photo - oxidation: Roles of NO_3 level relation humidity and aerosol acidity. *Environ.Chem*, **9**, 247-262.

Zsefer, P., Glasby, G.P., Sefer, K., Pempkowiak, J., Kaliszan, R. (1996). Heavy-metal pollution in superficial sediments from the southern Baltic Sea off Poland. *Journal Environmental Science Health*, Part A: Environmental Science and Engineering and Toxicology, **31**:2723-2754.