ZIBELINE INTERNATIONAL™ PUBLISHING

Geological Behavior (GBR)

DOI: http://doi.org/10.26480/gbr.02.2022.68.75

ISSN: 2521-0890 (Print)
ISSN: 2521-0491 (Online)
CODEN: GBEEB6

CrossMark

RESEARCH ARTICLE

ASSESSMENT OF TEMPORAL VARIATION OF HEAVY METALS IN SEDIMENTS OF WARRI RIVER, SOUTHWESTERN NIGERIA

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ARTICLE DETAILS

Article History:

Received 14 April 2022
Accepted 18 May 2022
Available online 02 June 2022

ABSTRACT

Contaminated sediment poses a serious environmental problem, therefore knowledge of the concentration of heavy metals in stream sediments is very important because of their significance to aquatic life and human health. The concentration of heavy metals (Cd, Pb, Cr, As, Ni, Zn, Fe and Cu), in stream sediments of some parts of Warri River, Southwestern Nigeria were examined during the rainy and dry seasons using Atomic Absorption Spectrophotometer, in order to assess their contamination levels using the environmental contamination indexes; Geoaccumulation Index, Enrichment Factor (EF), and Contamination Factor (CF). For both the rainy and dry seasons, the results revealed average heavy metal concentrations obtained in all samples in the study area in the order As>Cd>Pb>Ni>Cr>Zn>Cu>Fe. The trend in mean Igeo values was as follows: As (-0.66) > Zn (-4.93) > Cu (-5.8) > Fe (-5.31) > Cd (5.76) > Pb (-6.35) > Ni (11.25), showing that River Warri's sediments were not polluted by heavy metals. Cu= Zn (0.08), Cd (0.34), Pb (0.02), As (0.01), and Ni (0.00) were the mean CF values across all measured locations, indicating a low contamination factor. The average EFs for the sediments were As (1.09) > Cd (1.10) > Cu (1.46) > Zn (1.61) > Pb (1.09) > Ni (1.09) > Fe (0.83), showing low enrichment (<2). Evaluation of enrichment factor, geo-accumulation index and contamination factor values showed that the stream sediments of the study area were unpolluted. Heavy metals in the sediments were found to be linked to anthropogenic activities in the study region, according to the results of the hierarchical cluster analysis (HCA). The metal concentrations in the sediment were found to be elevated at some sampled points, it is therefore recommended that annual monitoring of the stream sediments of the study area is undertaken. Also, sustainable practices should be employed in order to conserve the resources of the Warri River.

KEYWORDS

Heavy Metals, Sediments, Warri River and Contamination Indexes

1. INTRODUCTION

The sediments of Warri River are important because they constitute food and an abode for many aquatic organisms. Stream sediments serves as a significant reservoir for heavy metals and other contaminants in aquatic systems, since they can accumulate heavy metals via adsorption and by natural and manmade processes be released into the overlying water, thereby increasing the potential for entering and contaminating the food chain and posing a risk to human health (via consumption) and organisms who dwell at the ecosystems (Izah and Angaye, 2016; Argese and Betticol, 2001; Daskalakis and O'connor, 1995). Contaminated sediment poses a serious environmental problem, therefore an understanding of heavy metal concentrations in stream sediments is very important because of their significance to aquatic life, and hence their use as geo-markers in the aquatic environment for monitoring and identifying potential contamination sources (Iwuoha et al., 2012; Ong and Kamaruzzaman, 2019). Warri River receives industrial and domestic waste from various sources in addition to discharge from drains and as a result of several activities which occurs along its banks. These activities increase the heavy metal load in the sediments of Warri River. Warri and environs have experienced rapid urbanisation and development for some decades. As a result, industrialization and the use of agrochemicals have intensified, general environmental degradation has occurred, and heavy metals have accumulated in the environment.

Because heavy metals are not eliminated from water as a result of self-purification, but are bio-accumulative, do not degrade easily, are soluble and this increases their mobility when released into the environment, they are considered to be serious environmental contaminants (Tavakoly, 2011; Wuana and Okieimen, 2011; Adelekan and Abegunde, 2011). Heavy metals as micronutrients could be essential to humans, however they can also have negative effects when the maximum admissible values are exceeded (Adamu et al., 2014). The occurrence of heavy metals in elevated concentrations constitutes a substantial threat in aquatic ecosystems because of their significance to plant and animal life (Iwuoha et al., 2012). When heavy metals are released into the river, they are usually attached to particulate matter which finally settles and integrates into the underlying stream sediments; as a result, suspended particulate matter and sediments are responsible for the majority of heavy metal compound load in aquatic systems. (Calmano et al., 1993).

Heavy metals can accumulate in stream sediments due to both natural and anthropogenic sources. Natural sources of heavy metals in stream sediments include weathering of parent rocks, volcanic eruptions, and wildfires, while anthropogenic sources include industrial effluents, sewage disposal, urban storm, water runoff, leaching of heavy metals from refuse disposed at open waste dump sites etc. However, long-term human impact have considerably raised heavy metal concentrations in the

Quick Response Code	Access this article online	
	Website: www.geologicalbehavior.com	**DOI:** 10.26480/gbr.02.2022.68.75

Cite The Article: Chinemelu, E.S., Okumoko, D. P. (2022). Assessment of Temporal Variation of Heavy Metals in Sediments of Warri River, Southwestern Nigeria. *Geological Behaviour 6(2): 68-75.*

environment and this poses a threat to humans, flora and fauna if not adequately managed. Therefore, in order to maintain the marine ecosystem of Warri River, and develop appropriate measures for its sustainable environmental management, knowledge of the concentration of heavy metals in the sediment is crucial.

The present work will thus provide information relevant for the management and sustainable development of heavy metals, in the rapidly developing study area. This study will also enlighten the authorities in environmental management on the concentration, source and trend of heavy metals in the stream sediments of Warri River. The accumulation of heavy metals in stream sediments has been examined by various researchers (Davies et al., 2006; Li et al., 2007; Andem et al., 2015; Remeikaite-Nikiene et al., 2018). However, few studies have examined the impact of seasonal variation as a critical component in understanding the origins of contaminants in the sediments of the study area. Further, the majority of these research mainly focused on a few suites of the heavy metals lead, zinc, copper, cadmium, while a few focused-on chromium and nickel which are known to have significant effects on the environment.

The goal of this research was to investigate the concentration of heavy metals and other physico-chemical parameters in the sediments of Warri River in order to determine their pollutant levels using the environmental pollution indexes: Geoaccumulation Index, Enrichment Factor (EF), and Contamination Factor (CF) (Wang et al., 2015; Muller, 1969; Rastmanesh et al., 2010). These contamination indexes aid in the quantification of the potential risks, heavy metals may pose at elevated levels, and this provides a more accurate assessment of the impact of human activities on heavy metal content in the studied area. Furthermore, because of their grain-size distribution and mineralogical characteristics, the absolute concentration of metals in river sediments never reveals the degree of contamination originating either from natural processes or human activities. (Zheng et al., 2008; Rubio et al., 2000). These indexes are commonly used approaches for determining the influence of human activities on soils and sediments and they involve computing the contamination factors for heavy metal concentrations against uncontaminated baseline levels (Wang et al., 2015; Bonnail et al., 2016; Lin et al., 2016).

2. Materials and Methods

2.1 Location and Geology of Study Area

The study was carried out along some parts of Warri River in Warri and its environs, southwestern Nigeria (Figure1). Warri River is one of the main coastal rivers of the Niger Delta area of Nigeria, which comprises of a network of rivers and creeks which drain into various tributaries and finally into the Atlantic Ocean (Nwajide, 2013). It is a relatively large water body with a length of about 150 km, and an estimated surface area of about 25558 square kilometres (NEDECO, 1954). The source of the river is near Utagba-Uno, from which it flows in a Southwest direction across several industrial areas such as Aladja, Enerhen, Udu, before connecting to the Forcados Estuary and finally flows into the Atlantic Ocean. The studied area's geologic map reveals three major sub-surface lithostratigraphic units beneath the surface: the Benin Formation, Agbada Formation, and Akata Formation.

The Benin Formation is overlain by the Sombreiro-Warri Deltaic Plain sands, which are superficial alluvium deposits of Quaternary to Recent age. The study area consists mainly of lowland and its climate is mainly tropical with two distinct alternating wet and dry seasons. Annual average temperatures range from about 22⁰C to 34⁰C, while yearly rainfall ranges between 1,501 and 2000 mm, evapotranspiration is 1117 mm, and humidity is high (NIMET, 2003; Akpoborie, 2011; Olobaniyi et al., 2007). The study area is a well-known centre of commercial activities in southern Nigeria. The economic activities along the river course include markets, Warri Ports, oil production, sawmills, steel production, auto-mechanic repair workshops, agriculture, dredging, fishing and recreational activities. In addition, one of Nigeria's three refineries is located in the study region, as are numerous other oil and gas firms.

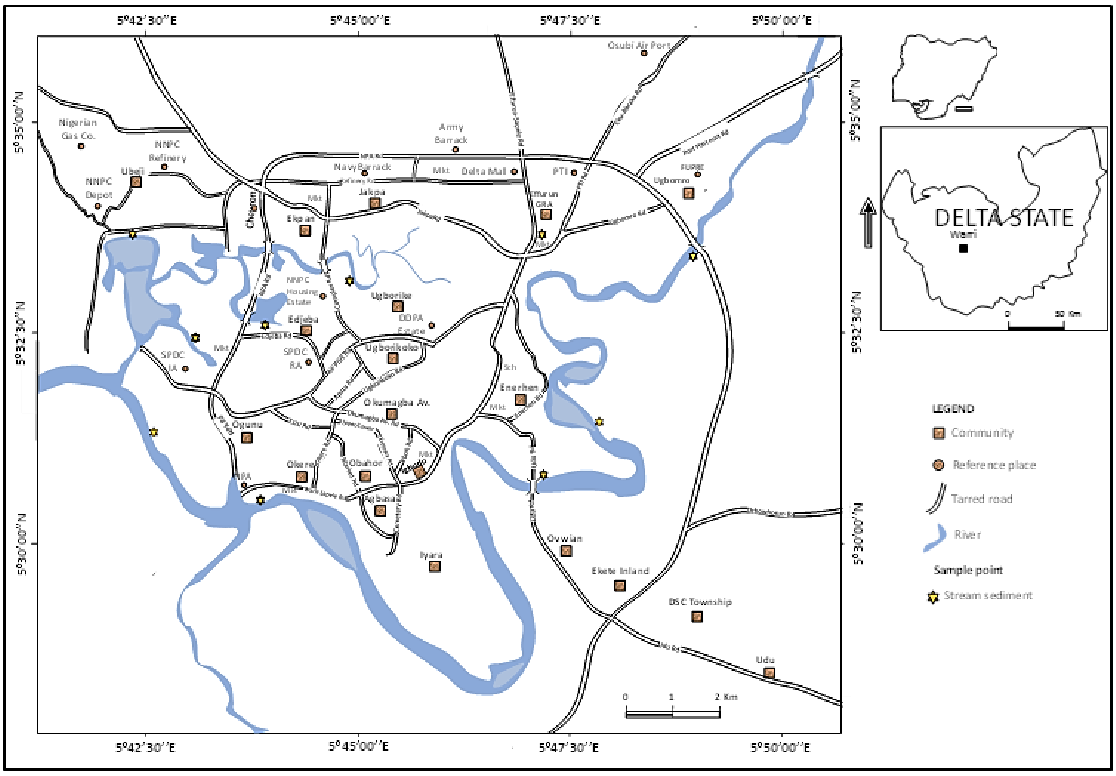

Figure 1: Map of the study area showing sampling points.

2.2 Sampling and Analysis

Stream sediment sampling was carried out in the dry season (December to February) and the rainy season (May to July), in order to identify the seasonal trends, as the environment is heterogeneous and changes with time. A total of 20 stream sediment samples were taken, and the geographical coordinates of each sampling site were determined using a Garmin model GPS device. Ten stream sediment sampling points were selected, and samples were collected with the aid of an Ekman grab sampler at a depth of approximately twenty centimeters from each sampling station, conserved in acid washed plastic bottles and properly labelled. In order to minimize contamination during sample collection, distilled water was used to wash and clean all sampling materials. The samples were prepared and digested using Wet Oxidation method according to (Allen et al., 1986). The digests were tested for heavy metals As, Cd, Fe, Pb,Cr, Cu,Ni, Zn, using Varian Spectra Model 220 (Fast Sequential) Atomic Absorption Spectrophotometer (AAS). Standard techniques were used to determine the other physical and chemical parameters.

2.3 Statistical Analysis

To know more about the sources of heavy metals in the study area's stream sediments multivariate statistical analysis was employed using

Hierarchical Cluster Analysis (HCA) and Pearson's correlations. Pearson's significant correlation analysis, which is used to find out association among heavy metal concentrations in the study area, was also determined using the SPSS 20.0 software. The range and mean values of different physico-chemical parameters and heavy metals concentration was calculated by using Microsoft Excel statistical functions.

The following were the environmental indicators used to assess heavy metals in sediment:

Geo-accumulation (Igeo)

Equation (1) was used to calculate the Geoaccumulation Index.

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \quad (1)$$

Here Cn is the determined concentration of the metal of interest at a specific location, and Bn is the soil's geochemical baseline value (Muller, 1969).

Contamination Factor (CF)

The C^i_f was calculated by dividing the quantity of each element in sediments by the background value, and is calculated by the equation (2) (Bonnail et al., 2016):

$$C^i{}_f = \frac{C^i{}_{o-1}}{C^i{}_n} \quad (2)$$

Where C^i_f is the element of interest's contamination factor, C^i_{o-1} is the element's concentration in the sample, while C^i_n is the background concentration.

Enrichment factor (EF)

Enrichment factor was calculated using equation (3):

$$EF_X = \frac{[X_S / E_{S(ref)}]}{[X_C / E_{C(ref)}]} \quad (3)$$

Here EF_X = the element X enrichment factor,

X_S= the concentration of element of interest in sample,

$E_{S(ref)}$ = the concentration of the reference element in the sample used for standardization,

X_C = the concentration of the element in the crust and

$E_{C(ref)}$ is the crust's concentration of the reference element used for standardization. (Taylor and Meclenan, 1985).

3. Results and Discussion

3.1 Stream Sediment Physico-chemical Properties

Aside from the sources, the physical and chemical properties of sediments also have an effect on the concentration of heavy metals in stream sediments. Total organic matter and pH amongst others physico-chemical properties are essential parameters which influence the accumulation and bioavailability of heavy metals in the environment (Nyamangara and Mzezewa, 1999). Therefore, it was important that these parameters were investigated with respect to heavy metal accumulation in the stream sediments. Table 1 shows the results of the physico-chemical parameters of stream sediments in the studied area. The pH result of sediments showed values which ranged from 5.07 to 6.87 in the rainy season, with the overall average value of 6.15. In the dry season pH values ranged from 5.25 to 7.21, with the overall average value of 6.55.

This pH of the sediments in both rainy and dry seasons implies that the sediment samples were generally slightly acidic. Increasing acidity in the sediment implies that the solubility, bioavailability and mobility of heavy metals will be greatly increasing (Alloway, 1995). Electrical conductivity values for sampled sediments ranged from 85.2 µS/cm to 542.3 µS/cm. Generally, significant variations were observed in the EC values recorded at all the sampled sites for both seasons. All sampled sediment had a predominantly mud-sand composition. Total organic matter (TOM) content and total organic carbon (TOC) ranged between of 0.62% to 5.21% and 1.33% to 7.25% across the sample locations.

Generally, the values were slightly increased when compared to those obtained from control samples. Increased organic matter in the sediment implies that the mobility and bioavailability of heavy metals will increase (Alloway, 1995). Furthermore, research has shown that about 50% of the total heavy metals in organic rich sediments are retained with organic substances (Siegel, 2002). Cation Exchange Capacity (CEC) measures the quantity of cations that can be adsorbed and held by a sediment. CEC is used to evaluate the capacity to protect water bodies from cation contamination. The cation exchange capacity of a sediment influences the transport rate of heavy metals in the sediment, as it increases with increasing pH values. Cation exchange capacity (CEC) results varied from 1.08 meq/100g to 5.89 meq/100g with a mean value of 3.08 meq/100g in the rainy season. CEC values for the dry season ranged from 3.23 meq/100g to 7.82 meq/100g with a mean value of 4.79 meq/100g.

Table 1: Summary Statistics of Physico-Chemical Properties of Stream Sediments in The Study Area

Parameter	Rainy Season (n=20)		Dry Season (n=20)	
	Range	Mean	Range	Mean
pH	5.07 - 6.87	6.15	5.25 - 7.21	6.55
EC (µS/cm)	85.2 - 542.3	223.36	91.2- 556.7	235.02
TOC (%)	0.36 - 1.95	0.95	0.77 - 2.38	1.45
TOM (%)	0.62 - 5.21	1.91	1.33- 7.25	3.78
CEC (meq/100g)	1.08 -5.89	3.08	3.23 - 7.82	4.79

3.2 Heavy Metal Concentrations in Stream Sediments

Tables 2 and 3 show descriptive data for average heavy metal contents in stream sediment samples throughout rainy and dry seasons, respectively. During the rainy season, lead concentrations in sediments varied between 0.001 mg/kg to 2.15 mg/kg, with an average of 0.27 mg/kg. Lead concentrations in the dry season were slightly higher, with values between 0.03 to 3.36 mg/kg. An average value of 0.5 mg/kg was obtained in the dry season. Cadmium levels in the sediments varied between < 0.001 mg/kg to 0.26 mg/kg, with an average value of 0.0689 mg/kg. Chromium concentration in the sediments during the rainy season varied from < 0.001 mg/kg to 0.88 mg/kg with an overall average value of 0.33 mg/kg. Chromium concentrations were marginally higher during the dry season, varying from 0.03 to 1.60 mg/kg. During the dry season, an average value of 0.70 mg/kg was recorded. During the dry season, arsenic concentrations in the sediments fluctuated between below 0.001 mg/kg to 0.02 mg/kg, with an average value of 0.0051 mg/kg.

Arsenic concentrations were barely higher during the dry season, varying between 0.01 to 0.04 mg/kg. During the dry season, an average value of 0.201 mg/kg was observed. During the rainy season, nickel concentrations in the sediments varied between below 0.001 mg/kg to 0.36 mg/kg, with an average value of 0.07 mg/kg. The levels of Nickel recorded in this study are similar to those of a similar study (Andem et al., 2015). Nickel enters into the water resources through several sources such as runoff from petroleum contaminated areas or oil spills, wearing a way of industrial machines, and disposal of sewage and untreated effluent into a river system (Zahra et al., 2014). Copper concentrations in the sediments varied from 0.21 mg/kg to 3.23 mg/kg during the wet season, with an average of 1.62 mg/kg. Copper concentrations in the dry season ranged from 1.30 mg/kg to 5.51 mg/kg. During the dry season, an overall average value of 3.17 mg/kg was obtained. When the copper concentrations in this study were compared to those reported in previous investigations, it was established that the levels obtained in this study were comparable to those obtained (Fagbote et al., 2010).

Copper is essential to life in aquatic ecosystems, but it can become toxic in large concentrations. Copper can enter the aquatic system through human activities which are transported through industrial, urban and municipal runoff. Natural sources of copper to sediments are through volcanic eruptions and the decay of organic materials (Hanif et al., 2016). During the wet seasons, measured levels of Fe in the sediments varied between 56.77 mg/kg to 1110.67 mg/kg, with an overall average of 501.85 mg/kg During the dry season, iron concentrations were marginally higher, varying between 75.44 mg/kg to 1250.22 mg/kg. During the dry season, an average value of 566.41 mg/kg was recorded. During the rainy season, zinc concentrations in stream sediments varied between less than 0.001 mg/kg to 2.15 mg/kg, with an overall mean of 0.27 mg/kg. In the dry season, lead concentrations were slightly higher, varying between 0.03 to 3.36 mg/kg.

During the dry season, an average value of 0.5 mg/kg were measured. Zinc can be incorporated into surface water bodies through runoff from farmland where fertilizers have been applied (Hanif et al., 2016). From the findings of the present work, the mean concentration of all heavy metals in the sediments of Warri River are higher during the dry season than during the wet season. This is probably due to heavy rainfall which causes dilution in the rivers which in turn affects the mobility and availability of heavy metals in sediment. Generally, the sediment quality of the Warri River were low, with respect to heavy metal levels and they decreased as one moved away from the sources of contamination.

Table 2: Average Metal Concentration of Stream Sediment Samples in The Study Area in The Rainy Season (mg/kg)								
Location	**Lead**	**Cadmium**	**Chromium**	**Arsenic**	**Nickel**	**Copper**	**Iron**	**Zinc**
Ekpan	.1655	.0040	.4240	.0025	.1140	1.4975	124.74	3.2170
Refinery	2.1520	.0860	.1045	.0155	.0480	3.2255	889.51	4.6500
Ubeji	.0040	.2625	.4965	.0035	.3600	2.3555	935.49	7.1100
NPA	.0500	.0050	.0835	.0040	.0030	.7510	1110.67	1.3870
Jakpa	.0050	.0130	.6050	.0040	.0035	.2100	106.03	.9145
Ejeba	.0170	.0035	.0035	.0030	.0035	.2785	76.98	1.2845
Ogunu	.0130	.1295	.0445	.0045	.0045	2.2250	152.74	4.3760
Udu	.0070	.0045	.3065	.0035	.0040	1.0365	1063.75	2.1860
Otokutu	.0120	.1120	.8775	.0050	.1025	2.9530	56.76	5.1115

Table 3: Average Metal Concentration in Stream Sediment Samples in The Study Area in The Dry Season (mg/kg)								
Location	**Lead**	**Cadmium**	**Chromium**	**Arsenic**	**Nickel**	**Copper**	**Iron**	**Zinc**
Ekpan	.7710	.0460	.8945	.0125	.5715	3.4875	143.9000	4.2355
Refinery	3.3550	.1260	.3490	.0360	.0880	5.5105	950.1100	5.4600
Ubeji	.0270	.7875	.9920	.0160	.6855	4.6090	1000.0000	9.2220
NPA	.0460	.0555	.1465	.0200	.0130	1.5045	1250.2200	3.3000
Jakpa	.0330	.0545	1.4290	.0185	.0150	1.2965	146.5000	1.5485
Ejeba	.0670	.0400	.0300	.0155	.0175	1.7215	91.3500	3.2380
Ogunu	.0785	.1985	.0985	.0215	.0200	1.7975	199.2250	6.6035
Udu	.0555	.0700	.7880	.0175	.0175	3.2895	1241.0000	4.3560
Otokutu	.0655	.1680	1.6010	.0235	.1375	5.3170	75.4400	7.3250

Table 4: Descriptive Statistics of Heavy Metal Concentration in Stream Sediment Samples During The Dry Season (mg/kg).				
Heavy Metal	Min.	Max.	Mean	Std. Dev.
Pb	0.00	2.15	0.27	0.71
Cd	0.00	0.26	0.07	0.09
Cr	0.00	0.88	0.33	0.29
As	0.00	0.02	0.01	0.00
Ni	0.00	0.36	0.07	0.12
Cu	0.21	3.23	1.61	1.13
Fe	56.77	1110.67	501.85	477.51
Zn	0.91	7.11	3.36	2.10

Table 5: Descriptive Statistics of Heavy Metals Concentration in Stream Sediment Samples During The Rainy Season (mg/kg).				
Heavy Metal	Min.	Max.	Mean	Std. Dev.
Pb	0.03	3.36	0.49	1.09
Cd	0.04	0.79	0.17	0.24
Cr	0.03	1.60	0.70	0.58
As	0.01	0.04	0.02	0.01
Ni	0.01	0.69	0.17	0.26
Cu	1.30	5.51	3.17	1.68
Fe	75.44	1250.22	566.41	526.10
Zn	1.55	9.22	5.03	2.37

3.3 Contamination Assessment Using Environmental Indexes

The results of the quantitative assessment of stream sediments were calculated using geo-accumulation index (*Igeo*), contamination factor (CF), and enrichment factor (EF) methods, for both dry and rainy seasons. The results are presented in Figures 2 – 6. The results on the calculation of *Igeo* of the heavy metals investigated at the research area's stream sediment sampling locations in both rainy and dry season showed that the *Igeo* values for all heavy metals were lower than zero(<0), suggesting that the stream sediments were uncontaminated with heavy metals, implying that there were no significant contributions from anthropogenic activities. The calculated values of CF in stream sediment samples in the dry season revealed values ranging from 0.003 to 0.673. All the heavy metals had values lower than 1, which indicates a low contamination factor. The calculated values of CF in soil samples in the rainy season varied from 0.003 to 0.772. All the heavy metals have values lower than 1, thus suggesting a low contamination factor (Muller, 1969). The calculated values of CF in soil samples during the dry season varied from less than 0.01 to 0.677.

All the heavy metals had values lower than 1, which indicates a low contamination factor (Akoto, 2008). The calculated EF values for all stream sediment samples collected over both seasons ranged from 0.65 to 1.93. The mean EFs for the sediments were in the order As (1.09) > Cd (1.10) > Cu (1.46) > Zn (1.61) > Pb (1.09) > Ni (1.09) > Fe (0.83), showing that level of heavy metals in the sediment samples were minimally enriched. The EF levels for some heavy metals were more than 1.5 for some sites. According to a study, EF values between 0.5 and 1.5 imply that the heavy metals are totally lithogenic or natural, whereas EF values greater than 1.5 indicate that the source is most likely from humans (Zhang and Liu, 2002). Increasing EF values means that anthropogenesis is likely contributing more to heavy metal levels in the sediments (Surthland et al., 2000). This means that, based on the estimated EF values, human activities influenced the concentration of heavy metals in the sediments of Warri River to some extent, but the effect was minor at the time of data collection.

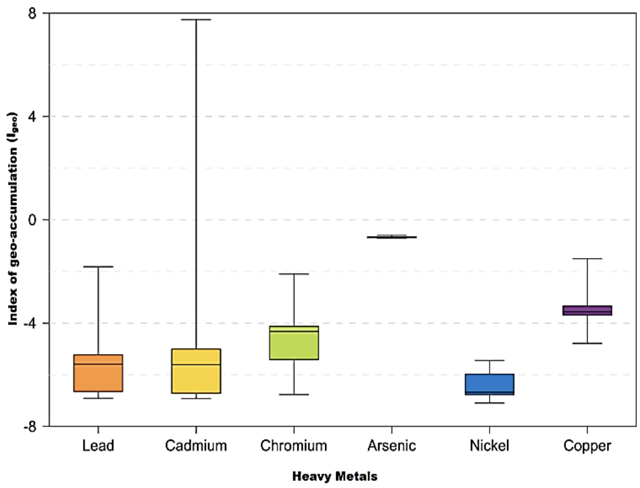

Figure 2: Index of geo-accumulation of stream sediments, in all sampled locations during the dry season.

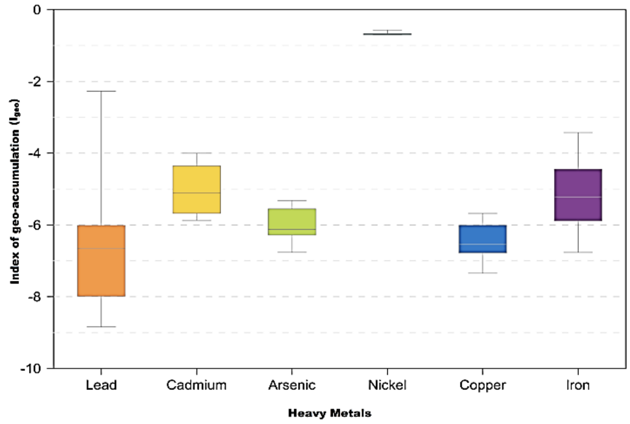

Figure 3: Index of geo-accumulation of stream sediments, in all sampled locations during the rainy season.

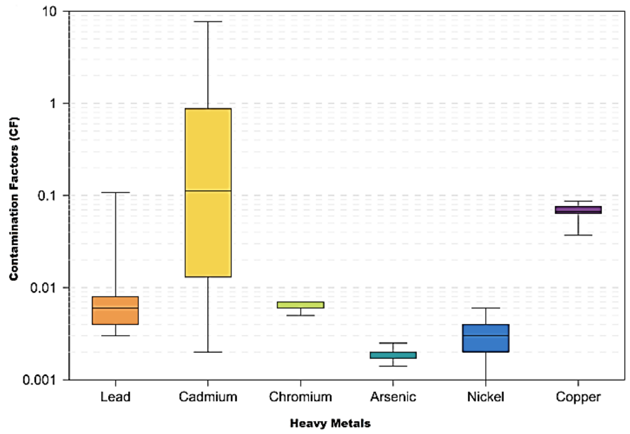

Figure 4: Contamination factors of heavy metals in stream sediments in the study locations in the dry season

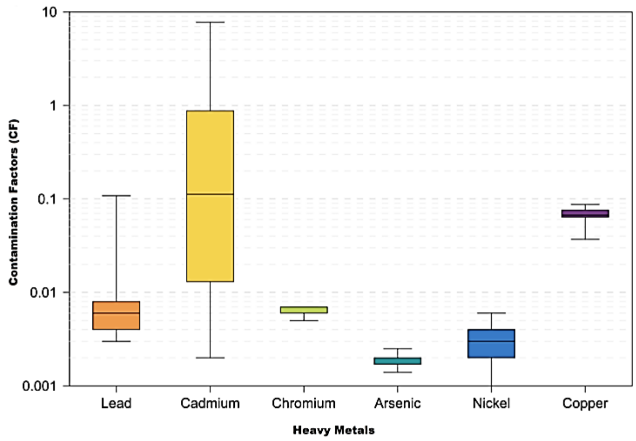

Figure 5: Contamination factors of heavy metals in stream sediments in the study locations in the rainy season

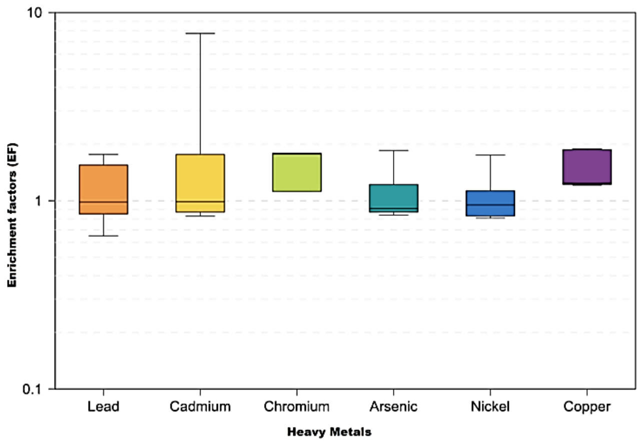

Figure 6: Enrichment factors of metals in stream sediments of the study area in the dry season

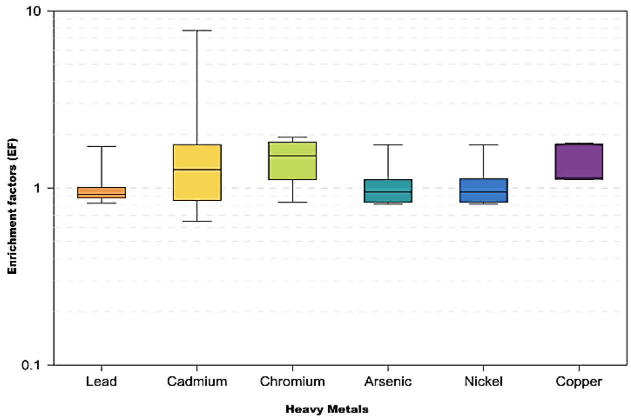

Figure 7: Enrichment factors of metals in stream sediments of the study area in the rainy season.

3.4 Correlation Analysis

The geochemical data was statistically examined using Pearson's Correlation to determine the important correlations between the heavy metals studied. The Pearson correlation results are presented in Tables 5 – 6. From the correlation matrix given in Table 5, there was a significant correlation among the heavy metal levels in the sediment samples during the rainy season. When the p-value is less than 0.05, the correlation is considered to be significant. Lead had a strong positive correlation with Arsenic with a correlation value of 0.971 and a *p*-value of 0.000. Cadmium had a strong positive correlation with both Zinc and Nickel. Their correlation values are 0.915 and 0.805 respectively while their *p*-values are 0.001 and 0.009.

Copper has a strong positive correlation with Zinc with a correlation value of 0.866 and a p-value of 0.003. Zinc had a strong positive correlation with Nickel, with a correlation value of 0.789 while *p*-value of 0.012. During the dry season, the Pearson correlation of heavy metal concentrations in the sediments of the studied area revealed significant correlations. Lead had a strong positive correlation with Arsenic with a correlation value of 0.789 and a *p*-value of 0.012. Cadmium had a strong positive correlation with both Zinc and Nickel. Their correlation values are 0.678 and 0.800 respectively while their *p*-values are 0.045 and 0.010. Copper has a moderate positive correlation with Zinc with a correlation value of 0.675 and a *p*-value of 0.046.

Table 6: Pearson Correlation Coefficient of Heavy Metal Concentrations in The Sediments of Warri River During The Rainy Season.

	Pb	Cd	Cr	As	Cu	Fe	Zn	Ni
Pb	1							
Cd	.046	1						
Cr	-.282	.244	1					
As	.971**	.130	-.215	1				
Cu	.532	.664	.217	.601	1			
Fe	.292	.146	-.288	.284	.105	1		
Zn	.222	.915**	.300	.270	.866**	.129	1	
Ni	-.073	.805**	.413	-.101	.432	.192	.789*	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 7: Pearson Correlation Coefficient of Heavy Metal Concentration in Sediments of Warri River During The Dry Season.

	Pb	Cd	Cr	As	Ni	Cu	Fe	Zn
Pb	1							
Cd	-.123	1						
Cr	-.208	.190	1					
As	.789*	-.093	-.135	1				
Ni	-.006	.678*	.311	-.379	1			
Cu	.539	.403	.378	.479	.444	1		
Fe	.203	.258	-.252	.223	.019	.178	1	
Zn	.041	.800**	.145	.166	.539	.675*	.129	1

3.5 Clustering Analysis

The heavy metal source apportionments in stream sediment samples are shown using cluster multivariate analysis. Cluster multivariate analysis of the metal content of sediment sample collected in the dry season followed a similar trend with the rainy season results. From the dendrograms two cluster groups were identified, there were two types of sources: crustal or geogenic (Iron) and anthropogenic (Fe, Cd, As, Ni, Pb, Cr, Cu and Zn).

4. Conclusion

Due to urbanization and increasing population, Warri River receives industrial and domestic waste from various sources in addition to discharge from drains and as a result of several activities which occur along its banks. Anthropogenic activities identified to contribute to heavy metal contamination in this present work were discharge of untreated effluent, sewage disposal, urban storm, water runoff, leaching of metals, and hazardous e-waste from garbage and open waste dump sites oil spillage, agrochemicals and wastewater used for irrigation. More so, considerable amounts of heavy metal may enter the study area through precipitation and atmospheric deposition. The weathering of parent rocks was identified as the primary source of heavy metals in the study area.

The stream sediments of the research area were found to be unpolluted when contamination indexes such as enrichment factor, geo-accumulation index, and contamination factor values were computed from heavy metal concentrations. It was therefore concluded that the metals had not accumulated significantly. Pearson's correlation analysis for the dry and rainy seasons showed significant correlations among the heavy metal concentration in the sediment samples. Hierarchical cluster analysis (HCA) revealed that the heavy metals in all the samples were associated with two cluster groups of anthropogenic and geogenic sources. When compared to the data obtained during the wet season, all of the heavy metals examined had higher concentrations during the dry season; however, the differences observed in the seasons were not significant.

However, the metal concentrations in the sediment were elevated at some sampled points. Based on the aforementioned, it is therefore recommended that annual monitoring of the stream sediments of the study area is undertaken. Monitoring the physiochemical characteristics and sediment quality of Warri River is important because it will aid in preserving and restoring its biological integrity, as well as protecting aquatic life and human health. Also, sustainable practices should be employed in order to conserve the resources of the Warri River. Mitigation measures such as establishing water protection areas and imposing penalties for illegal activities that degrade the river are required to reduce heavy metal influx into the river by anthropogenic activities.

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