Accumulation and Risk Assessment of Heavy Metals in Sediments from Dredged Tributaries and Creeks of River Ethiope, South-South, Nigeria

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ABSTRACT: *The presence of heavy metals in rivers in the Niger Delta region has become a source of concern due to its associated health challenges. The present study was conducted to assess the risk of heavy metal accumulation in surface sediments obtained from creeks and dredged tributaries of the River Ethiope, Delta State, South-South, Nigeria. Heavy metals in the sediments were extracted using the three-step sequential extraction method of the European Commission Standard Measurement and Testing Program. The heavy metals; magnesium (Mn), iron (Fe), zinc (Zn), lead (Pb), copper (Cu), cobalt (Co), arsenic (As), chromium (Cr), cadmium (Cd) and barium (Ba) were quantified by employing inductively coupled plasma-mass spectrometry (ICP-MS). Assessment of the extent of sediment contamination was carried out by determining the contamination factor (CF), degree of contamination (C_d), modified degree of contamination (mC_d), pollution load index (PLI), ecological risk factor (E_r), potential ecological risk index (PI) and geo accumulation index (1_{geo}). Pearson's correlation coefficient and principal component analysis (PCA) were used to determine the sources and the relationship between pollutants across sediments. The values of heavy metals ranged from 12.5 mg kg^{-1}–116 mg kg^{-1} and 21.6 mg kg^{-1}–71.1 mg kg^{-1} in the wet and dry seasons, respectively. The trend of heavy metals for risk index (RI) in this study is Cd > Pb > Cr > Co > Zn > Cu > Mn (wet*

season) and Cu > Cd > Pb > Zn > Cr > Mn > Co = As (dry season). It showed that heavy metal pollution was a result of Cd for extreme contamination, while moderate to high contamination levels were due to Pb and Cu. The Pearson's correlation coefficient analysis and PCA displayed strong positive loadings for Mn, Fe, Zn, Pb, Cu and Cd across seasons as a result of high contamination levels in the study sites. The pollution load index revealed that the sediments were polluted by the metals, and the mean and median analyses revealed that the metals datasets were normally distributed, except for Cu with an irregular distribution.

1.   INTRODUCTION

Dredging entails, the removal of soil, water-way sediments, river bank and plants, as well as the discharge of dredging spoils at the bank of the river. This has resulted in the death of aquatic life, reducing the quality and number of fish, and destroying many plants.[1] Sediments are known to be important nutrient sources in water bodies. Under stable hydrodynamic conditions, nutrients and other contaminants enter the dredged river systems, and the sediments then act as sinks through adsorption, sedimentation and particle mineralisation.[2] It is well known that water sediments serve as the final destination for the majority of pollutants that enter water bodies as a result of anthropogenic activities.[1] On the other hand, wind-wave action, flooding, dissolved oxygen, pH, water temperature and anthropogenic activities can cause a constant change in these natural conditions, which can result in the release of nutrients and suspended particles from the sediments.[3,4] Dredging and wind-wave action have a deleterious impact on water bodies by increasing turbidity, which affects plant photosynthesis and the state of eutrophication.[2]

The impact of local agricultural practices, run-off from erosion and other anthropogenic activities can cause changes in water quality. As a result of urbanisation, anthropogenic activities are increasing. The accumulation of heavy metals in sediments as a result of dredging and other human activities is determined by the compositional peculiarities, structure and qualities of the sediments, as well as the absorbed metals.[5] Accumulation can happen through various processes such as ion exchange, acid complex formation, clay adsorption, as well as the formation of iron, manganese and other hydroxides in solid-phase interactions.[5] This has led to an increase in the number of heavy metals and other solid waste dumped in the river, necessitating an assessment of the buildup of heavy metal contaminants in the dredged sediments along the tributaries and creeks of the River Ethiope.

Toxicity, biomagnification, and bioaccumulation caused by heavy metal persistence in the environment have resulted in an adverse effect on the ecosystem, living organisms, human health,[3–5] as well as animal health.[6–8] Heavy metal contamination in surface sediments poses a significant concern to aquatic bodies due to its prevalence, persistence and toxic effects.[9,10] According to studies, dredging introduces toxins into bodies of water.[11] Due to the long-standing problems caused by the act, such as submerged aquatic vegetation, coral reefs, fish and others, evaluating the environmental risk connected with it becomes a critical issue during the management of dredging operations. Although some risks cannot be prevented during the operation, such as noise from the dredging machine, some species may be threatened into abnormal behaviour.[12] Dredging may remove a huge amount of sediment, alter habitation features, change structure and mobility in the bottom community, and raise turbidity, which will reduce primary productivity and hence impede the food chain in aquatic ecosystems. It has been reported that dredging caused changes in the physicochemical qualities of the aquatic environment. It decreased pH from 7.2 to 4.0, and dissolved oxygen decreased from 6.0 mg/l to 0.4 mg/l.[13] Despite the implementation of environmental contamination management techniques that have significantly reduced the amounts of these contaminants, the pollution concerns in the dredged river have not been resolved. Therefore, it is critical to evaluate risk assessment and heavy metal contamination levels in this community. The present study aimed at evaluating heavy metal accumulation and risk assessment in dredged tributaries and creeks of the River Ethiopia, South-South, Nigeria.

2.   EXPERIMENTAL

2.1   Description of the Study Area

The river Ethiope is a freshwater river with tributaries and creeks where dredging activities are carried out daily. The river flows from Umuaja in Ukwuani Local Government Area to Sapele in Okpe Local Government Area, where it discharges into the Benin River in Delta State, South-South, Nigeria, at latitude 5° 47' 20" N, longitude 6° 4' 47" E for Sapele tributaries. The river covers a distance of 10 km from its source to where it discharges.[12] Across the route of the river, there are several institutions, factories and domestic activities that deposit their wastes into the river. Some of these wastes are from soils washed through erosion from the cities into the water bodies. Because it is a freshwater river, it is used for drinking, fishing, sand excavations and other activities for the people of Delta State. Currently, there is a significant decline in the number of fishermen and

women due to a decrease in the quality and quantity of fish, which may be related to poor water quality caused by dredging activities that create challenges in the aquatic environment.[14] The tributaries and creeks of River Ethiope where the samples were collected are located at latitude 5° 47' 17" N, longitude 6° 4' 49" E for Abraka tributaries, latitude 5° 47' 11" N, longitude 6° 4' 32" E for Obiaruku tributaries' and latitude 5° 47' 20" N, longitude 6° 4' 47" E for Sapele tributaries. About 40% of the land associated with the tributaries and creeks is known to be agricultural land, 50% is built-up land and 10% is water bodies across the study area (Figure 1). The region is associated with heavy rainfall (1600 mm–2300 mm) from the southeast to the south-west in April–September for the wet season and in the dry season, the temperature of the same range cut across the whole state and ranged from 30°C–35°C as the maximum value and 20°C–23°C as the minimum value. The dredged rivers cut across several communities, including Umuaja, which links Obiaruku, Abraka, Eku, Aghalokpe, Sapele and Mosogar.[14] A total of 18 sediment samples were collected from the bottom of the water bodies at depths of 3 m from three communities in Abraka, Eku and Sapele from April to June and November to January 2021, for the wet and dry seasons, respectively. The sediments were obtained using a Van Venn grab sampler. The samples were placed in plastic containers, placed in coolers at 4°C, and transported to the laboratory for analysis. The frozen samples were dried at room temperature for 5 days, ground, and passed through a 2 mm-mesh sieve.

2.2   Sample Collection

Samples of surface sediments were collected from the base of the water at a depth of 3 m from three communities of Abraka, Eku and Sapele. The samples were collected in rainy season (April, May and June 2020) and in the dry season (November, December 2020 and January 2021). These sediments were collected with the aid of Van Veen grab surface sampler. The sampling sites cut across the stretch of the river. The samples were stored in plastic containers, embedded in cooler bags at 4°C and conveyed to the laboratory.
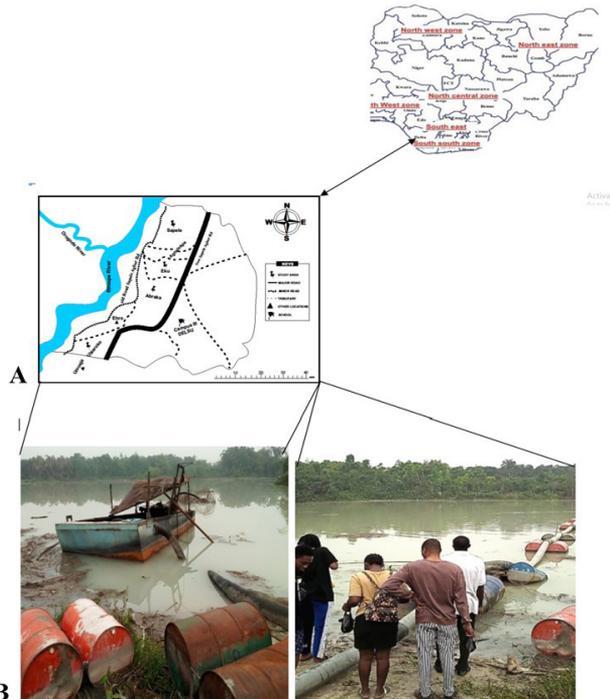
Figure 1: Sampling area showing the designated sampling points. A: Map; B: Pictures.

2.3   Geochemical Analysis

This analysis was performed with a previously used method,[4] with slight modifications. One gram of dry sediment samples was digested using HNO_3, 30% H_2O_2, and HCl (5:4:2). The sample was then heated using microwave digestion equipment (CEM/MARS6) in the following order: the temperature was increased to 170°C for 30 min at 1,600 W of power, and allowed to stay for 20 min, followed by another heating at 210°C for 40 min and allowed to stay for 30 min. The digested samples were then placed in an acid purifier at 150°C, which increased the acid volume to 1 ml. Following that, 50 ml of distilled water was used to dilute the sample, which was then filtered through No. 45 Whatman filter paper. Inductively coupled plasma-mass spectrometry (ICP-MS) was used to measure metal concentrations in samples extracted by microwave digestion and sequential extraction (PE Optima 8,000, Crystal City, WA, USA). A flame atomic absorption spectrophotometer was used for the analysis of cadmium (Cd) and iron (Fe).

2.4   Sequential Extraction Procedure

This was accomplished by utilising the European Commission's proposed three-step Standard Measurement and Testing Program (formerly BCR). In the first step, acid-soluble fractionation (F1, 0.11 mol/l CH_3COOH), reducible fractionation (F2, 0.5 mol/l NH_2OH-HCl, pH 1.5), oxidisable fractionation (F3, 1.0 mol/l CH_3COONH_4, pH 2.0) and residual fractionation (F4, HF–HNO_3–$HClO_4$) of sediments.[16] One gram of weighted sample was placed in a 100 ml polypropylene centrifuge tube. After each extraction, the centrifuge tube was placed in a 4,000 rpm centrifuge for 10 min. The filtrate was collected, and the residue was washed twice with distilled water before being placed in a 50 ml volumetric flask, fixed with 3% HNO_3, and filtered with No. 45 Whatman filter paper before loading the centrifuge tube with 50 ml of the filtrate.

2.5   Assessment of Sediment Pollution Levels

The contamination levels of heavy metals through dredging and other sources were evaluated using the contamination factor (CF), degree of contamination (C_d), modified degree of contamination ($_mC_d$), pollution load index (PLI), potential ecological risk index (RI), geo accumulation index (1geo), potential contamination index (Cp), and human health risk.

2.5.1   Contamination factor

CF was used to assess the contamination level of the surface sediment using the equation below:

$$C_f^i = \frac{C_{o-1}^i}{C_n^i} \tag{1}$$

Where C_f^i is the contamination factor for the target element, C_{o-1}^i is the concentration of the element in the sample, and C_n^i is the background concentration of the continental crustal average.[12] The CF categories are as follows: 1: CF < 1 (low); 2: 1 < CF < 3 I (moderate); 3: 3 < CF < 6 (considerable), and 4: CF > 6 (very high).

2.5.2   Degree of contamination (C_d)

The total values of all the CF for all the sampling sites are the degree of contamination.[15]

$$C_d = \sum_1^8 = {}_1 CF \tag{2}$$

It is classified as follows: 1: $C_d < 6$ (low); 2: $6 < C_d < 12$ (moderate); 3: $12 < C_d < 24$ (considerably high); 4: $C_d > 24$ (high).

2.5.3   Modified contamination degree

Modified contamination degree ($_mC_d$) is the addition of the contamination factor of the sample element to the analysed number of elements, and it is expressed as follows:

$$_mC_d = \sum_{i=1}^{i=n} \frac{CF}{n} \tag{3}$$

$_mC_d$ is based on the following categories: 1: $_mC_d < 1.5$ (nil to very low); 2: $1.5 \leq {_mC_d} < 2$ (low); 3: $2 \leq {_mC_d} < 4$ (moderate); 4: $4 \leq {_mC_d} < 8$ (high); 5: $8 \leq {_mC_d} < 16$ (very high); 6: $16 \leq {_mC_d} < 32$ (extremely high); 7: $_mC_d \leq 32$ (ultra-high).

2.5.4   The pollution load index

The assessment of PLI was based on a previous index description, which was used to measure the pollution level of the heavy metals through the formula below:[15]

$$\text{PLI for a site} = \sqrt[2]{CF1 \; X \; CF2 \; CF3 \; X \ldots\ldots CF_n} \tag{4}$$

Where n is the number of heavy metals

$$\text{PLI for zone} = \sqrt[n]{Site \; 1 \; X \; Site \; X \; Site \; 3 \; X \ldots\ldots\ldots .Site n} \tag{5}$$

It is categorised as (i): PLI < 1.0 (no pollution); (ii): 1.0 < 2 (moderate pollution); (iii): 2.0 < 3 (heavy pollution); (iv): PLI > 3 (extreme pollution).

2.5.5   Potential ecological risk index

This estimates the characteristic and environmental behaviour of the heavy metal contaminant in the surface sediment.[19] RI is the total of all risk factors for the detected heavy metal contamination in the surface sediment. The calculation is based on:

$$C_r^i = \frac{C^1}{C_n^i} \tag{6}$$

$$E_r^i = T_r^i X \; C_r^i \tag{7}$$

$$RI = \sum_{i=1}^{n} T \; X \; C_r^i = \sum_i^n T_r^i X^{\frac{C^i}{C_n^i}} \tag{8}$$

Where, *RI* is the sum of the potential ecological risk of each heavy metal, T_r is the toxic response factor, which depicts the toxicity of the individual heavy metal.

These factors as proposed are as follow:[14] copper (Cu) = 5, zinc (Zn) = 1, Cr = 2, nickle (Ni) = 5, lead (Pb) = 5, cadmium (Cd) = 30, cobult (Co) = 5 and magnesium (Mn) = 1. This is to determine the concentration of heavy metal, n in the sediment and is the accepted concentration of heavy metal, and present in the sediment. It is categorised in the following order:[5] (i): $E_r^i < 40$ (low); (ii): $40 < E_r^i < 80$ (moderate); (iii): $80 < E_r^i <$ (considerably high); (iv): $160 < E_r^i < 320$ (high); (v): $E_r^i < 320$ (very high); (vi): $RI < 95$ (low); (vii): $95 < RI < 190$ (moderate); (viii): $190 < 380$ (considerably high); (ix): $RI > 380$ (very high).

2.5.6   Geo accumulation index

The analysis of level and the concentration degree of heavy metal pollution in the surface sediments were measured with 1 geo.

$$I\,geo = \log 2\,[Cn/k*Bn] \qquad (9)$$

Where C_n is the determined concentration of the heavy metal in sediments; B_n is the background value of each element; 1.5 is used to multiply the concentration of the individual geochemical background concentration to reduce the possibility of variation in the value of individual elements present in the environment. The categories are as follows: (i): 1 geo > 5 (extreme contamination); (ii): 4–5 (strong to extreme contamination), (iii): 3–4 (strong contamination); (iv): 2–3 is moderate to strong contamination; (v): 1–2 (moderate contamination); (vi): 0–1 is uncontaminated to moderate contamination; (vii): < 0 (uncontaminated).

2.6   Statistical Analysis

Mean, standard deviation, median, Pearson's correlation coefficient, and principal component analysis (PCA) were performed to determine the sources and the relationship between the sediments and contaminants. This was done using Microsoft Excel (Windows 10 version). A one-way analysis of variance (ANOVA) was used to determine the difference between wet and dry seasons at a p-value less than 0.05, which is statistically significant.

3.   RESULTS AND DISCUSSION

The mean, median concentrations and the range of the various heavy metals under study in the dredged sediments in wet and dry seasons are presented in Table 1 and Table 2. Mn concentrations were low across sites and months, much below the Environmental Protection Agency's (EPA) acceptable limit of 512 mg kg^{-1}.[18] During the wet season, the readings ranged from 12.5 mg kg^{-1} to 116 mg kg^{-1}. The Mn concentration in the sediment was lower than that reported for surface sediment,[5] from the Thondi Coast, Palk Bay, South India (686.1 mg kg^{-1}), and 392 mg kg^{-1} and 297 mg kg^{-1} from sediments and dredged sediments in Niger Delta, Nigeria, respectively.[18] Wet season concentrations were greater than dry season concentrations, which varied from 21.6 mg kg^{-1} to 71.1 mg kg^{-1}. This might be attributed to runoff from the nearby farmlands into the dredged river. Across months, the concentrations of Mn in sediments follow the trend of Abraka < Eku < Sapele (April), Abraka < Sapele < Eku (May), Abraka < Eku < Sapele (June) and Abraka < Sapele < Eku (November), Abraka < Eku < Sapele (December), Eku < Abraka < Sapele (January). According to the pattern, Abraka had the highest concentrations over months, which could be attributed to much of the dredging and other anthropogenic activities as a result of the population increase. Since the levels of Mn are below the acceptable limit of EPA guidelines for sediments, it poses no threat when the sediment is used in the upland site where drainage and concurrent oxidation would take place. There is no significant difference between the mean and the median values of Mn, which implies that the datasets are properly distributed and log transferred.[17,18]

Fe had mean values that were less than the EPA's permissible limit of 20,000 mg kg^{-1}.[18] The results varied from 37.3 mg kg^{-1}–5,474 mg kg^{-1} (wet season) to 516 mg kg^{-1}–1,026 mg kg^{-1} (dry season). The higher level in the rainy season than in the dry season may be attributed to agricultural runoff into the dredged river. These values are higher than previous reports (5.92 mg kg^{-1} and 4.12 mg kg^{-1}),[18] but lower than other comparable reports (52,802 mg kg^{-1})[5] and (2,780 mg kg^{-1}).[5,21] Fe concentrations are listed in the following order: Abraka, Eku, Sapele (April), Abraka, Sapele, Eku (May), Abraka, Eku, Sapele (June), Abraka, Sapele, Eku (November), Abraka, Eku, Sapele (December) and Eku, Sapele, Abraka (January). According to the pattern, Abraka had the highest concentrations across all months except December, which could be attributed to much of the dredging and other human activities as a result of population expansion. Since the levels of Fe are within the acceptable limit for dredged sediments proposed by the EPA, their level would pose no threat if the sediments were used in the uplands where drainage and concurrent oxidation would take place. This implies

Table 1: Concentration (mg kg⁻¹) of heavy metals for sediments across study locations in the wet season.

	Metals	April			May			June		
		Abraka	Eku	Sapele	Abraka	Eku	Sapele	Abraka	Eku	Sapele
Mean ± SD	Mn	17.6 ± 2.13	63.1 ± 7.65	90.0 ± 10.9	21.9 ± 1.29	92.2 ± 5.42	70.6 ± 4.15	12.5 ± 2.44	27.7 ± 5.39	116 ± 22.7
	Fe	250 ± 172	2957±2038	4729±3259	461 ± 319	5437±3767	3996±2768	37.3 ± 25.5	464 ± 317	5474±3741
	Zn	63.0 ± 9.49	81.6 ± 12.3	100 ± 16.5	31.9 ± 4.67	132 ± 19.3	88.2 ± 12.9	93.8 ± 14.5	31.6 ± 4.90	131 ± 20.3
	Pb	43.2 ± 11.7	111 ± 29.9	169 ± 45.6	44.8 ± 14.4	166 ± 53.2	155 ± 49.8	42.2 ± 8.55	50.6 ± 10.3	188 ± 38.0
	Cu	55.4 ± 9.98	80.8 ± 18.2	118 ± 29.9	36.8 ± 9.66	112 ± 18.0	102 ± 27.4	73.7 ± 10.1	48.5 ± 17.9	134 ± 33.3
	Co	ND	ND	ND	ND	ND	144 ± 39.7	ND	ND	ND
	As	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Cr	59.8 ± 17.4	92.9 ± 26.9	187 ± 54.3	72.6 ± 26.8	99.4 ± 36.7	247 ± 91.2	47.3 ± 7.72	89.8 ± 14.7	123 ± 20.1
	Cd	ND	ND	ND	ND	55.3 ± 36.2	48.6 ± 31.8	ND	ND	102 ± 69.3
	Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND
Median	Mn	17.6	63.1	90.0	21.9	92.2	70.6	12.6	27.7	117
	Fe	249	2957	4729	461	5437	3996	37.3	464	5474
	Zn	63.0	81.6	109	31.9	132	88.2	93.8	31.6	131
	Pb	43.2	111	169	44.8	166	155	42.2	50.6	188
	Cu	20.2	36.9	60.6	21.5	39.9	60.8	18.7	33.1	61.6
	Co	ND	ND	ND	ND	ND	143.8	ND	ND	ND
	As	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Cr	59.8	92.9	187	72.6	99.4	247	47.3	89.8	123
	Cd	ND	ND	ND	ND	55.3	48.6	ND	ND	102.05
	Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND
Range	Mn	7.30 – 10.3	26.2 – 36.9	37.3 – 52.7	10.1 – 11.9	42.3 – 49.9	32.2 – 38.2	4.55 – 8.00	10.1 – 17.7	42.3 – 74.3
	Fe	3.15 – 247	37.2 – 2919	59.6 – 4669	4.66 – 457	55.0 – 5383	40.4 – 3956	0.63 – 36.7	7.77 – 457	91.6 – 5382
	Zn	24.8 – 38.2	32.1 – 49.5	43.1 – 66.5	12.7 – 19.3	52.4 – 79.7	35.0 – 53.2	36.6 – 57.2	12.3 – 19.3	51.0 – 79.7
	Pb	13.4 – 29.8	34.3 – 76.6	52.3 – 117	12.2 – 32.6	45.4 – 121	42.4 – 113	15.1 – 27.2	18.1 – 32.6	66.9 – 121
	Cu	3.05 – 17.2	5.58 – 31.4	9.15 – 51.5	3.90 – 17.6	7.25 – 32.7	11.1 – 49.8	2.20 – 16.5	3.90 – 29.2	7.25 – 54.3
	Co	ND	ND	ND	ND	ND	43.8 – 100	ND	ND	ND
	As	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Cr	17.6 – 42.2	27.4 – 65.5	55.0 – 132	17.3 – 55.3	23.7 – 75.7	58.9 – 188	18.2 – 29.1	34.5 – 55.3	47.3 – 75.7
	Cd	ND	ND	ND	ND	2.05 – 53.3	1.80 – 47.8	ND	ND	2.05 – 100
	Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: *ND: Below the limit of detection by the equipment

Table 2: Concentrations (mg kg^{-1}) of heavy metals for sediments across study locations in the dry season for three months.

		November			December			January	
	Metals	Abraka	Eku	Sapele	Abraka	Eku	Sapele	Abraka	Eku	Sapele
Mean ± SD	Mn	23.7 ± 9.96	54.4 ± 22.8	47.5 ± 19.9	21.6 ± 8.86	34.0 ± 13.9	71.1 ± 29.1	35.5 ± 17.9	31.6 ± 15.9	49.7 ± 25.0
	Fe	642 ± 411	811 ± 519	688 ± 440	518 ± 332	595 ± 381	1026 ± 658	771 ± 488	521 ± 329	599 ± 379
	Zn	57.5 ± 1.61	79.2 ± 2.22	71.6 ± 2.01	43.0 ± 0.63	49.2 ± 0.72	112 ± 1.65	82.4 ± 4.77	47.8 ± 2.77	54.7 ± 3.17
	Pb	42.3 ± 19.9	52.0 ± 24.5	25.7 ± 12.1	27.5 ± 12.3	39.5 ± 17.7	55.4 ± 24.8	51.6 ± 23.6	28.6 ± 13.1	41.1 ± 18.8
	Cu	65.5 ± 358	85.3 ± 443	57.5 ± 203	53.2 ± 408	41.9 ± 219	109 ± 680	71.4 ± 311	65.2 ± 400	48.3 ± 215
	Co	ND	ND	ND	ND	ND	ND	ND	ND	ND
	As	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Cr	24.8 ± 11.3	61.9 ± 28.2	35.0 ± 15.9	14.3 ± 6.06	26.8 ± 11.4	83.9 ± 35.6	48.3 ± 25.6	22.9 ± 12.2	43.0 ± 22.9
	Cd	100 ± 70.5	ND	ND	100 ± 70.6	ND	ND	75.5 ± 52.7	25.2 ± 17.6	ND
	Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND
Median	Mn	23.7	54.3	47.5	21.6	33.9	71.1	35.5	31.6	49.7
	Fe	643	811	688	518	595	1027	772	521	599
	Zn	57.5	79.2	71.6	43.0	49.2	112	82.4	47.8	54.7
	Pb	42.3	52.0	25.7	27.5	39.6	55.4	51.6	28.7	41.1
	Cu	577	715	327	640	344	1066	508	652	349
	Co	ND	ND	ND	ND	ND	ND	ND	ND	ND
	As	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Cr	24.8	61.9	35.0	14.3	26.8	83.9	48.3	22.9	43.0
	Cd	100.3	ND	ND	100.15	ND	ND	75.45	25.15	ND
	Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND
Range	Mn	4.83 – 18.9	11.1 – 43.3	9.65 – 37.8	4.55 – 17.1	7.15 – 26.8	15.0 – 56.1	5.10 – 30.4	4.55 – 27.1	7.15 – 42.6
	Fe	30.0 – 613	37.9 – 773	32.1 – 656	24.2 – 494	27.8 – 567	48.0 – 979	40.8 – 731	27.6 – 494	31.7 – 567
	Zn	27.6 – 29.9	38.0 – 41.2	34.4 – 37.2	21.1 – 22.0	24.1 – 25.1	54.9 – 57.2	37.8 – 44.6	22.0 – 25.9	25.1 – 29.6
	Pb	7.08 – 35.2	8.70 – 43.3	4.30 – 21.4	5.05 – 22.5	7.25 – 32.3	10.2 – 45.2	9.10 – 42.5	5.05 – 23.6	7.25 – 33.9
	Cu	35.6 – 541	44.1 – 670	20.2 – 307	31.2 – 609	16.8 – 327	52.0 – 1014	33.6 – 474	43.2 – 609	23.2 – 327
	Co	ND	ND	ND	ND	ND	ND	ND	ND	ND
	As	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Cr	4.43 – 20.4	11.1 – 50.9	6.25 – 28.8	2.85 – 11.4	5.35 – 21.4	16.8 – 67.1	6.00 – 42.3	2.85 – 20.1	5.35 – 37.7
	Cd	0.30 – 100	ND	ND	0.15 – 100	ND	ND	0.45 – 75.0	0.15 – 25.0	ND
	Ba	ND	ND	ND	ND	ND	ND	ND	ND	ND

Note: *ND: Below the limit of detection by the equipment.

that the datasets were properly distributed and log transformed.[19,20] The elevated Fe concentrations detected in this study could be related to the convergence of ephemeral streams and the tiny mangrove forest system along the creeks and tributaries of the River Ethiope where dredging is practiced.[5,22] Furthermore, to prevent corrosion, the dredging boat and drums used as a platform for crossing the dredged river were painted with an inorganic pigment containing iron (III) oxide to avoid corrosion. This can cause the co-precipitation of heavy metals as a result of the iron oxide present in them, and in their concentration in the sediments.[5,23]

Zn had mean values ranging from 31.6 mg kg^{-1}–132 mg kg^{-1} (wet season) to 43.0 mg kg^{-1}–112 mg kg^{-1} (dry season). Values of 31.6 mg kg^{-1} (wet season) at Eku and 43.0 mg kg^{-1} (dry season) at Abraka were lower, and also 132 mg kg^{-1} (wet season) at Eku and 112 mg kg^{-1} (dry season) at Sapele were higher than the acceptable limit of 75.0 mg kg^{-1} established by EPA.[18] This implies that there is evidence of pollution of Zn as a result of anthropogenic activities. The Zn concentrations throughout the two seasons were lower than previously reported (252.9 mg kg^{-1}),[5] but consistent with others (37.7 mg kg^{-1}) in the Cuddalore, south-east coast of India[16] and (124 mg kg^{-1}) in surface sediments of the Chennai coast.[24] The trend of Zn across sites and months are as follows, Abraka < Eku < Sapele (April), Abraka < Sapele < Eku (May), Eku < Abraka < Sapele (June), and Abraka < Sapele <Eku (November), Abraka < Eku < Sapele (December), and Eku < Sapele < Abraka (January). This is consistent with previous research.[17,18] The concentration of Zn that is above the accepted limit of EPA sediments guideline might be attributed to the paints used on boats and drums to avoid corrosion, which consist of $ZnSO_4$ that is acted upon by ocean currents versus transport activities.[5]

The concentrations of Pb across sites and seasons (Table 1) displayed high concentrations that range from 42.2 mg kg^{-1}–188 mg kg^{-1}. Eku and Sapele (wet season) displayed concentrations of 111 mg kg^{-1} and 369 mg kg^{-1}, 166 mg kg^{-1} and 155 mg kg^{-1}, as well as 50.6 mg kg^{-1} and 188 mg kg^{-1}, respectively, which are higher than the EPA's acceptable guidelines for dredged sediment for Pb (50 mg kg^{-1}). Pb levels in Table 2 range from 25.7 mg kg^{-1} to 55.4 mg kg^{-1}. High quantities were found in Eku, Sapele, and Abraka (during the dry season). This could be attributed to a higher concentration of hydrocarbon fuel from vehicle exhaust along the creeks and tributaries of the Ethiopian River. Pb poisoning can build up in the bone marrow, which is where red blood cells are formed. Cu levels in some locations and seasons exceed the EPA threshold of 50.0 mg kg^{-1}. The values varied from 36.8 mg kg^{-1} to 134 mg kg^{-1} (wet season) and 41.9 mg kg^{-1} to 109 mg kg^{-1} (dry season), with only Abraka (wet season) and Eku (both wet and dry seasons) falling within the EPA threshold. These elevated Cu contents in the rainy season vs the dry season are an indicator of riverine runoff resulting in

a high concentration of Cu pollutants at the dredged river's confluence point due to e-waste from circuit boards and electroplating.[5] There is a significant variation between the mean and the median values of Cu, which indicates that the datasets of Cu were irregularly distributed. Cr concentrations in Sapele were higher; 187 mg kg^{-1}, 247 mg kg^{-1} and 123 mg kg^{-1} (wet season) were greater than the EPA guideline value of 100 mg kg^{-1}, but values in all other locations were lower in both wet and dry seasons. The values of Cr in this study corroborate previous reports (14.1 mg kg^{-1}, 130 mg kg^{-1} and 61.2 mg kg^{-1}).[25,26] This high accumulation of Cr in the sediments might be attributed to natural and anthropogenic sources.

The mean concentrations of Co, As, Cd and Ba were below the detectable limit across locations and seasons, except in Sapele during the wet season (144 mg kg^{-1}) for Co, Eku, Sapele during the wet season (55.3 mg kg^{-1} and 48.6 mg kg^{-1}), for Cd and Abraka during the dry season (100 mg kg^{-1}), Abraka and Eku during the dry season (75.5 mg kg^{-1} and 25.2 mg kg^{-1}). Due to the non-detectable limit observed in many sites across months, they are considered insignificant in the sediments. Their presence at some sites might be due to riverine runoff and other anthropogenic activities. The values of Cd are far higher when compared to previous reports (0.6 mg kg^{-1}–2.5 mg kg^{-1} and 0.4 mg kg^{-1}).[5,27] The non-significant variation observed between the mean and median values of detected metals indicates that the datasets were normally distributed.

3.1   Assessment of Sediment Contamination

Figure 2 and Figure 3 display the contamination factors of each heavy metal with locations and seasons. Based on the categories, the values fell within the range of low to very high contamination, with Mn, Fe and Cu exhibiting low contamination during the wet season and Mn, Fe, Zn and Cr exhibiting low contamination during the dry season. Zn and Co displayed low and moderate contamination across the locations in the wet season, while Pb, Cu and Cd showed significant and very high contamination in both seasons. The degree of C_d across the locations and seasons is presented in Figure 4. Only Abraka in April, May and June, Eku in June, and Sapele in November had low C_d based on the category of $6 < C_d$. All the other locations across seasons displayed a moderate, considerably high, and high degree of contamination based on the categories of $6 < C_d < 12$, $12 < C_d < 24$ and $C_d > 24$. Figure 5 is a profile depicting the modified degree of contamination across seasons. The profile showed moderate to high contamination based on the categories of $2 \leq {_m}C_d < 4$ and $4 \leq mC_d < 8$ across seasons. The mean value of ${_m}C_d$ was less than 4, which indicates that anthropogenic activities are primarily responsible for the contamination.
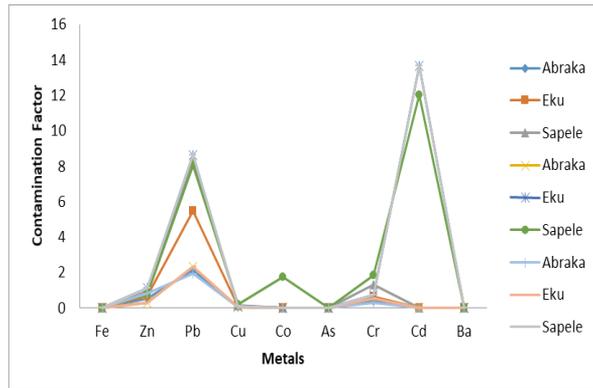
Figure 2: Contamination factors of all the heavy metals under study in the wet season.
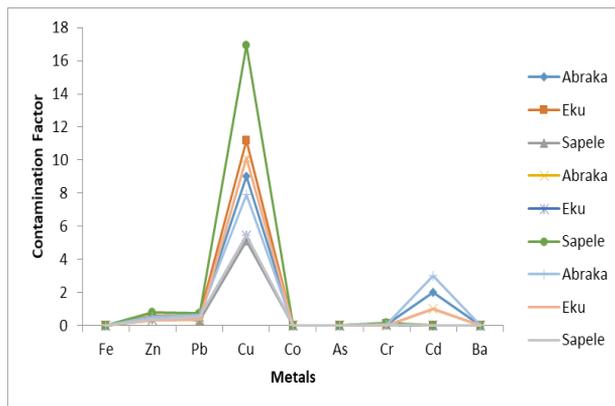
Figure 3: Contamination factors of all the heavy metals under study in the dry season.
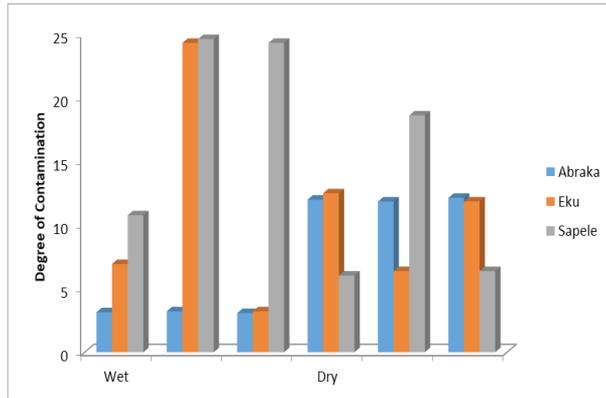
Figure 4: Degree of contaminations of all the heavy metals under study across the wet and dry seasons.
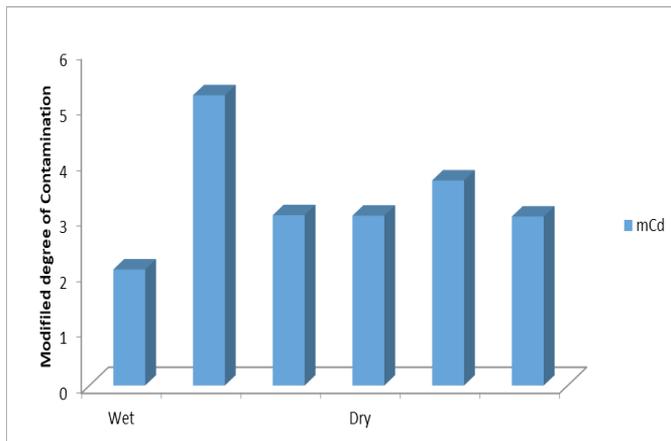
Figure 5: Modified degree of contamination of all the heavy metals under study in the dry season.

Figure 6 shows the PLI varying by location and season, with values ranging from 5.27 in Abraka to 33.2 in Sapele (wet season). These data suggest that all of the sediments in the study area were polluted by heavy metals, as their values were greater than 3, based on the PLI $\geq$ 3.0, which is extreme pollution. Figure 7(a) and 7(b) showed the results of environmental risk factors of heavy metals under study across seasons. The average values of Mn (1), Zn (4), Pb (5), Cu (5), Co (5), As (4), Cr (2) and Cd (30) were less than 40 for all metals except Pb and Cd that displayed low and moderate, low and very high. Eighty percent of all the heavy metals fell into the category of low–potential risk. On the other hand, the high ecological risk observed in Pb (41.7, 43.1, 40.3) and Cd (410, 360) across some locations in the

wet season might be attributed to the discharge of domestic sewage waste at the study site. These results are in agreement with a previous report for Cd (367.5).[5] During the dry season [(Figure 7(b)], all heavy metals displayed low ecological risk factors except Cu, which displayed moderate ecological risk factors across some locations, 45.1, 55.9, 50.8, 84.5 and 50.7, respectively.
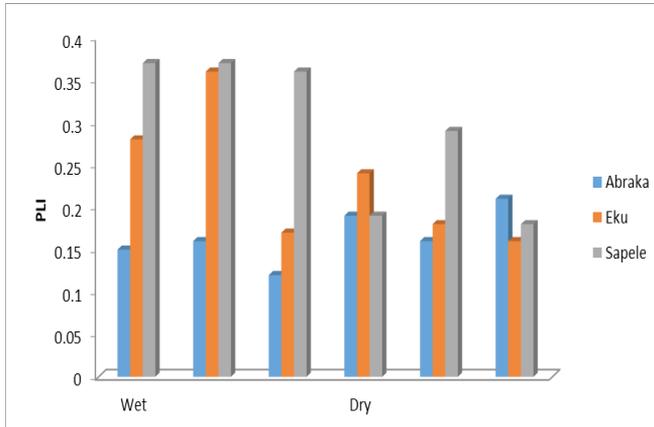
Figure 6: PLI of all the heavy metals under study across seasons.
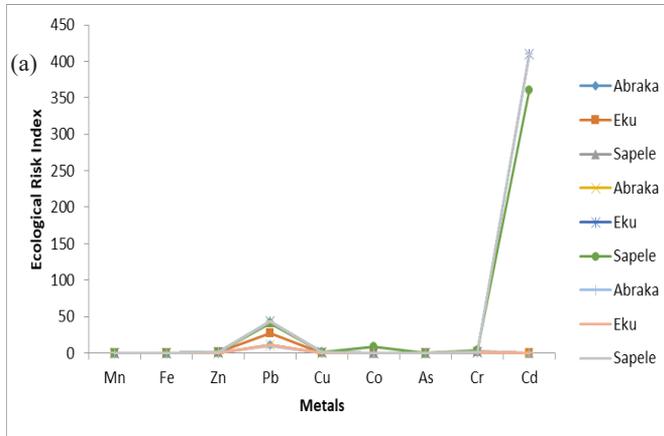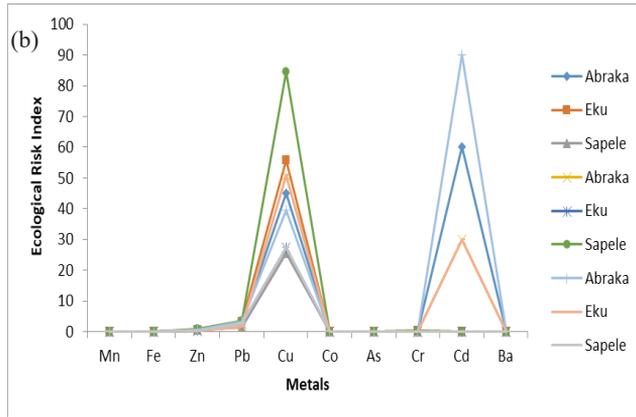
Figure 7: Ecological risk factor of all the heavy metals under study (a) in the wet season; (b) in the dry season.

A profile showing the potential ecological RI of each heavy metal across seasons (Figure 8) indicate that in the wet season, the RI values of Mn (0.21), Zn (6.61), Cu (4.44), As (0.00), Co (98.76) and Cr (14.1) exhibit low potential ecological risk since their values are less than 95 of the category of RI < 95. Pb (239) and Cd (1,180) depict high and very high RI since the values fell within the categories of 190 RI < 380 and RI > 380, respectively. Cd had the highest RI. This is similar to a previous study,[5] which found a much higher RI value with Cd 4,197. The trend of heavy metals RI in this study is Cd > Pb> Cr > Co > Zn > Cu > Mn. In the wet season, Mn (0.07), Zn (4.25), Pb (22.8), Co (0.00), As (0.00) and Cr (1.20) depict low RI, while Cu (407) and Cd (180) depict very high and moderate RI, respectively. The trend of heavy metals RI in the dry season is as follows, Cu > Cd > Pb > Zn > Cr >Mn > Co = As.

Figure 8: Potential ecological RI of all the heavy metals under study across seasons.

3.2 Pearson's Correlation Coefficient Values (p < 0.05) Between Metals

Pearson's correlation analysis of the heavy metals in sediments (Table 3 and Table 4) shows the relationship between heavy metals and their contributions. In the wet season, there was a strong correlation of Mn with Fe ($r^2 = 1.00$), Zn ($r^2 = 0.79$), Pb ($r^2 = 0.99$), Cu ($r^2 = 0.83$), Cr ($r^2 = 0.60$), Cd ($r^2 = 0.75$) and a weak correlation with other metals such as Co. Fe was strongly correlated with Zn ($r^2 = 0.82$), Pb ($r^2 = 0.99$), Cu ($r^2 = 0.83$), Cr ($r^2 = 0.60$) and Cd ($r^2 = 0.75$). Zn, Pb, Cu and Co also undergo the same trend of strong correlation with other metals. Meanwhile, in the dry season, Mn, Fe, Zn, Pb and Cu showed a strong positive correlation with another element. For example, Mn displayed a strong positive correlation with Fe ($r^2 = 0.85$), Zn ($r^2 = 0.86$), Cr ($r^2 = 0.94$), Pb ($r^2 = 0.51$) and Cu ($r^2 = 0.53$). Fe was strongly correlated with Zn ($r^2 = 0.99$), Pb ($r^2 = 0.79$), Cu ($r^2 = 0.64$) and Cr ($r^2 = 0.95$). Pb was strongly correlated with Cu ($r^2 = 0.63$), Cr ($r^2 = 0.94$) and with Cu ($r^2 = 0.51$), Cr ($r^2 = 0.74$). Cu was strongly correlated with Cr ($r^2 = 0.69$) in the dry season. The positive correlation observed between some of these metals could be attributed to a common source and chemical behaviour similarities, which is consistent with a previous report.[26] A high correlation between metals indicates common lithological or crucial sources.[26] However, just because a metal concentration in an environment is considered to be a naturally occurring background does not mean that the concentration is not causing an adverse ecological effect.[5,8] The presence of one metal can have a considerable impact on another metal's impact on an organism, which can be synergistic, additive, or antagonistic.[29] The negative and non-correlation observed in Cd, Co, As and Ba showed that there was no evidence of pollution by these metals.

Table 3: (Dry season) Pearson's correlation coefficient values (p < 0.05) between metals.

	Mn	Fe	Zn	Pb	Cu	Co	As	Cr	Cd	Ba
Mn	1.00									
Fe	0.85	1.00								
Zn	0.86	0.99	1.00							
Pb	0.51	0.79	0.69	1.00						
Cu	0.53	0.64	0.63	0.51	1.00					
Co	0.00	0.00	0.00	0.00	0.00	1.00				
As	0.00	0.00	0.00	0.00	0.00	0.00	1.00			
Cr	0.94	0.95	0.94	0.74	0.69	0.00	0.00	1.00		
Cd	–0.62	–0.12	–0.14	0.10	–0.04	0.00	0.00	–0.38	1.00	
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00

Table 4: (Wet season) Pearson's correlation coefficient values (p < 0.05) between metals.

	Mn	Fe	Zn	Pb	Cu	Co	As	Cr	Cd	Ba
Mn	1.00									
Fe	1.00	1.00								
Zn	0.79	0.82	1.00							
Pb	0.99	0.99	0.80	1.00						
Cu	0.83	0.83	0.52	0.89	1.00					
Co	0.21	0.22	0.03	0.33	0.65	1.00				
As	0.00	0.00	0.00	0.00	0.00	0.00	1.00			
Cr	0.60	0.60	0.28	0.69	0.94	0.81	0.00	1.00		
Cd	0.75	0.75	0.67	0.75	0.63	0.44	0.00	0.45	1.00	
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00

Table 5 shows that PCA results for the metals studied over the seasons. It is a multivariate approach used to distinguish the natural and anthropogenic contributions of each metal based on different levels of relationship.[5,30,31] PCA was utilised in this study to determine the association between heavy metal and season. According to the results, two principal components were found for each season, PC1 accounts for 91.0% (wet season) and 88% (dry season) of the total and cumulative percentage of 57.6% and 90.8% for components 1 and 2, respectively, (wet season) and 64.2% and 88.3% for components 1 and 2, respectively (dry season). PC1 of the wet season explained 58.0% of the sum of variation, which is majorly loaded positively by Mn, Fe, Zn, Pn and Cd with their variance values of 0.948, 0.956, 0.916, 0.919 and 0.748, respectively. PC2 for the wet season explained 91.0% of the sum of variation, which is majorly loaded positively by Cu, Co and Cr having variance values of 0.736, 0.954 and 0.907, respectively. PC1 for the dry season explained 64.0% of the sum of variation, which is majorly loaded positively by Mn, Fe, Zn, Pb, Cu and Cr with variance values of 0.734, 0.969, 0.934, 0.861, 0.756 and 0.913, respectively. Meanwhile, PC2 for the dry season explained 88.0% of the sum of variation, which is majorly loaded positively by Mn with a variance value of 0.982. The high positive loading of Mn, Fe, Zn and Pb in PC1 (wet season) suggests that these metals may be dispersed in all areas from the same anthropogenic sources. This applies to the wet season for Cu, Co and Cr, PC1 (dry season) for Mn, Fe, Zn, Pb, Cu, Cr and PC2 (dry season) for Mn. From the PCA results, PC1 is polluted by anthropogenic causes such as riverine runoff dredging and domestic sewage during both seasons.

Table 5: PCA results for heavy metals in the study locations across seasons.

Metals	Wet Season		Dry Season	
	Components		Components	
	1	2	1	2
Mn	0.948	0.263	0.734	0.673
Fe	0.956	0.261	0.967	0.177
Zn	0.916	–0.051	0.934	0.222
Pb	0.919	0.377	0.861	–0.150
Cu	0.647	0.736	0.756	0.022
Co	0.003	0.954	–	–
Cr	0.361	0.907	0.913	0.407
Cd	0.748	0.328	0.027	–0.982
Variance %	57.524	33.287	64.189	24.088
Cumm Variance %	57.524	90.811	64.189	88.277

Considering the values of 1 geo, sediments of the dredged creek and its tributaries in the studied river (Table 6), the values displayed uncontaminated, uncontaminated to moderate contamination, moderate contamination, moderate to strong contamination, and strong contamination to extreme contamination, in all the metals under study across sites and months, except Fe, which showed extreme contamination in all the sites and seasons. Strong contamination and strong to extreme were mostly observed in Mn (wet season) and Cu (dry season). The extreme contamination observed in Fe and strong to extreme contamination observed in Mn and Cu in this study might be attributed to anthropogenic activities such as dredging, paints used for boats and drums, oil pollution from the dredging machine, and natural sources like tick mangrove forests along the study area. These results are consistent with previous report.[5]

Table 6: Geo accumulation index for heavy metals across the study sites and seasons.

Season		Mn	Fe	Zn	Pb	Cu	Co	As	Cr	Cd	Ba
	Abraka	3.67	8.97	3.25	2.45	2.09	ND	ND	3.46	ND	ND
	Eku	4.22	100.00	3.10	2.85	2.35	ND	ND	3.65	ND	ND
	Sapele	4.37	10.20	3.49	3.04	2.56	ND	ND	3.95	ND	ND
	Abraka	3.80	9.23	2.95	2.48	2.15	ND	ND	3.58	ND	ND
WET	Eku	4.43	10.30	3.57	1.98	2.46	ND	ND	3.71	0.21	ND
	Sapele	4.31	10.20	3.40	3.02	2.65	2.91	ND	4.11	–0.75	ND
	Abraka	3.46	8.14	2.67	2.40	1.95	ND	ND	3.29	ND	ND
	Eku	3.80	9.23	2.95	2.48	2.19	ND	ND	3.56	ND	ND
	Sapele	4.43	10.30	3.57	3.05	2.46	ND	ND	3.71	0.21	ND
	Abraka	3.49	9.36	3.14	1.82	4.34	ND	ND	2.48	–0.48	ND
	Eku	3.85	9.46	3.28	1.91	4.43	ND	ND	2.88	ND	ND
	Sapele	3.79	9.39	3.24	0.21	4.09	ND	ND	2.63	ND	ND
	Abraka	3.46	9.27	3.01	1.67	4.39	ND	ND	0.36	–1.82	ND
DRY	Eku	3.45	9.33	3.07	1.83	4.12	ND	ND	2.56	ND	ND
	Sapele	3.98	9.57	3.43	1.98	4.61	ND	ND	3.06	ND	ND
	Abraka	3.51	9.44	3.25	1.93	4.28	ND	ND	2.61	–1.35	ND
	Eku	2.88	9.27	3.01	1.67	4.39	ND	ND	2.29	–1.82	ND
	Sapele	3.66	9.33	1.17	1.83	4.12	ND	ND	2.56	ND	ND

4.   CONCLUSION

The findings of this study show that the concentration trend of heavy metals across sites follows the wet season > the dry season. The pollution indices determined with CF, $C_{d,\ m}C_d$, E_r, 1 geo and RI revealed that Pb, Cu and Cd were the major metals responsible for high contamination in the study sites except for 1 geo result. The PCA findings showed that Mn, Fe, Zn, Pb, Cu, Cr and Cd are responsible for high contamination due to their strong positive loading. This suggests that the volume of heavy metals discharged into the dredged river exceeded its potential for self-remediation. An assessment of the sediment contamination showed that the sampling sites were enriched with these heavy metals, indicating that their pollutants were introduced by humans. Heavy metals are entering the study sites from multiple sources at the same time, and if this continues, the level of toxicity will rise, thereby affecting the aquatic ecosystem and even the whole food chain. Therefore, strict monitoring of home sewage outflow is required to protect the aquatic ecosystem.

5. AKNOWLEDGEMENTS

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