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Pollution Status and Potential Ecological Risk of Toxic Metals in Sediments of the Lower Calabar and Great Kwa Rivers, Nigeria

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ABSTRACT

Contaminants present in sediments serve as vital indicators of environmental health in aquatic ecosystems. This study aimed to investigate the current heavy metals pollution status and potential biological effects of the surface sediments of Great Kwa and Calabar Rivers, Nigeria, from October 2021 to August 2022. The concentrations of lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) were determined. The total metals concentrations in the sediment of both eivers ranged between: 4.457-11.341mg/ kg, 0.311-0.978mg/ kg, 0.034-0.096mg/ kg, and 0.134-0.755mg/ kg for lead, cadmium, mercury and arsenic, respectively. Metal concentrations in the sediment of Calabar River were significantly ($P \leq 0.05$) higher than the Great Kwa River, except for arsenic. Both rivers did not exhibit significant seasonal variations in metal concentrations. Assessment of metals using United States Environmental Protection Agency, and the Australian and New Zealand sediment quality guidelines indicated that neither river was polluted with respect to the metals under study. The contamination factor for the metals corresponded to a low contamination level, except for lead, which showed a moderate contamination factor during the dry season. The average contamination degree for each river corresponded to low contamination degree. The pollution load index (PLI) also supported the conclusion that both rivers were not polluted. However, the concentration of cadmium at Esuk Nsidung exceeded the Threshold Effect Level (TEL), indicating potential risks to organisms in this specific location. The ecological risk factor analysis revealed that Pb, Cd, Hg, and As posed a low potential ecological risk to other components of the environment. This study emphasizes the importance of periodic monitoring of water and sediment quality in the Great Kwa and Calabar Rivers to ensure sustainable management and to safeguard human and environmental health.

INTRODUCTION

Any entity that causes harmful effects on individuals, communities, populations, or ecosystems is termed a stressor. Ecological risk assessment focuses on studying physical, biological, or chemical stressors that have the potential to induce negative impacts and disrupt the structures of ecosystems **(Fagasova, 2016)**. The goal of an ecological risk assessment is to determine whether there could be contamination and ecological effects resulting from human activities, identify the ecological components most at risk, assess the nature and likelihood of risks, and quantify their magnitude **(Suter & Norton, 2019)**. The assessment considers not only the potential effects of stressors on individual organisms or species but also acknowledges the intricate ecological relationships within the ecosystem. Indirect impacts are taken into accounts as species often depend on one another and the abiotic components of the environment. A stressor may not directly affect a particular species, but its influence on other species within the ecosystem can pose risks. Furthermore, stressors can affect biogeochemical processes, leading to significant alterations in ecological relationships **(U.S. EPA, 2012)**.

Ecological risk assessment is commonly employed to examine chemical stressors, which are chemical agents accidentally or intentionally introduced into the ecosystem, resulting in adverse impacts **(Ahmed *et al*., 2022; Elhaddad *et al*., 2022; Salaah *et al*., 2022)**. Such stressors include industrial chemicals, hazardous waste, agrochemicals, and domestic and municipal waste. Heavy metals are one of the most dangerous of these chemical stressors due to their extensive dispersion, inability to biodegrade, and extreme environmental persistence **(NGCERA, 1999)**.

Anthropogenic activities, particularly those related to the petroleum sector, have resulted in extensive degradation of wetlands, causing rapid ecological changes in the Niger Delta wetlands and raising serious concerns for the health of the ecosystem and the well-being of communities dependent on ecosystem services **(US-NOAA, 2017; Chijioke *et al*., 2018; Khedr *et al*., 2024)**. Other accompanying activities, such as urbanization, industrialization, invasive plant infestation, dredging, and global climate change, have also significantly impacted the ecosystem. The vast network of rivers, tributaries, creeks, and estuaries that make up the Niger Delta creates a rich mangrove swamp habitat that is home to large mud flats and swamps. Additionally, these bodies of water serve as substantial sinks for pollutants like pesticides, herbicides, heavy metals, and plastics **(US-NOAA, 2017)**.

Water sediments are the result of bedrock and soil erosion **(Namiesnik & Rabajczyk, 2010; Yuan *et al*., 2014)**. Sediments are contributed to rivers from both channel and non-channel sources. Rivers transport sediments in two ways based on their particle sizes. Bed load refers to larger particles that cannot remain suspended in the moving water for extended periods and tend to stay at the bottom of the channel, sliding or rolling downstream. Suspended sediment, on the other hand, consists of finer particles that are small enough to be carried along with the flowing water. Deposition of sediment occurs starting with the larger particles **(Yuan *et al*., 2014)**. A typical sediment cross-section in a river reveals four distinct layers: silt, silt soil, floating mud, and flowing mud **(Yuan *et al*., 2014)**. Silt and silt soil, which have larger particle sizes and higher densities, significantly lower adsorption capacities, and are relatively difficult to disturb, floating mud and flowing mud (0-80cm depth) are easily disturbed and serve as the major contaminant adsorbing layer of river sediment **(Zahra *et al*., 2013; Yuan *et al*., 2014)**, Sediments offer a food source and habitat for benthic organisms. Metals' bioavailability to these organisms is influenced by their chemical form, the geochemical characteristics of the sediment, and the organisms' exposure routes. Bioavailable metals can be taken up by organisms and potentially transferred to higher trophic levels. When harmful heavy metals build up to dangerous levels in the aquatic ecosystem, there is a substantial risk to public health from consuming contaminated water and water resources, in addition to ecological disruption **(Ubiogoro & Adeyemo, 2017)**.

Notably, while contaminant concentrations in surface water are more transient in lotic systems, sediments store episodic inputs and are considered a more suitable medium to reflect the contamination status of the ecosystem **(Lutgen *et al*., 2020; Tiwari, 2020; Nkopuyo & Everard, 2021)**. A combination of processes, such as river hydrodynamics, environmental factors, and biogeochemical processes, give sediment its ability to absorb and retain pollutants. Therefore, toxic metals present in sediment serve as important markers of environmental changes in aquatic ecosystems. Maintaining sediment quality is crucial for protecting surface water quality, conserving fisheries, and safeguarding the health of benthic ecosystems **(Zhang *et al*., 2014)**.

While some studies have been reported on the heavy metal content of surface water and sediment in the Great Kwa and Calabar Rivers **(Ewa *et al*., 2013; Ephraim & Ajasi, 2015; Ekpo *et al*., 2021; Otogo *et al*., 2021)**, there is yet no published report on the ecological risk assessment of the sediment in these rivers. This study was designed to evaluate the ecological risk and current pollution status of toxic metals in the sediments of the Great Kwa and Calabar Rivers in the lower parts of the Niger Delta, Nigeria.

MATERIALS AND METHODS

Study location

Nine states, including all of the states that produce oil, are included in the enormous 75,000-square-kilometer Niger Delta region of Nigeria. Cross River State, with its capital in Calabar, is one of the states in this region. Calabar is situated between latitudes 4° 55' and 4° 58'N and longitudes 8º 15' and 8.26E, and it had an estimated population of 579,000 as of the year 2020 **(Populationstat, 2020; Udiba *et al*., 2020)**. The city is bordered to the west by the Calabar River and to the east by the Great Kwa River, which both empty into the Cross River Estuary before entering the Atlantic Ocean in the Gulf of Guinea **(Udofia *et al*., 2016)**. The rivers originate from Oban Hill and form an intricate network of tributaries and creeks. The flow in the upper reaches of the rivers is unidirectional. The shoreline is characterized by dense vegetation, transitioning from freshwater swamp ecology to the ecosystem of mangrove swamps nearer the mouth of the estuary. The area has a tropical climate, and the rivers' lower portions are tidal. The River Cross, Great Kwa River, Calabar River, and their tributaries make up the river system, which has an approximate total size of 54,000 square kilometers. In both rivers, the mangrove creek system provides spawning habitats for fish, shrimp, crabs, and clams. The rivers flow through a rich agricultural basin. Farmers in the region use fertilizers, pesticides, and other pesticides, which eventually end up in the rivers **(Udiba *et al*., 2020)**. A large amount of municipal solid waste and wastewater disposed of in open landfills and drainage systems end up in the surrounding rivers and marshes during the intense rainy season. Furthermore, the United Cement Company (UNICEM) and numerous quarries are located in the Great Kwa River basin.

The Nigeria Port Authority's Calabar port, an important player in the oil and gas industry, the Nigerian Export Processing Zone (NEPZ), and the Free Trade Zone are in the Calabar River basin.

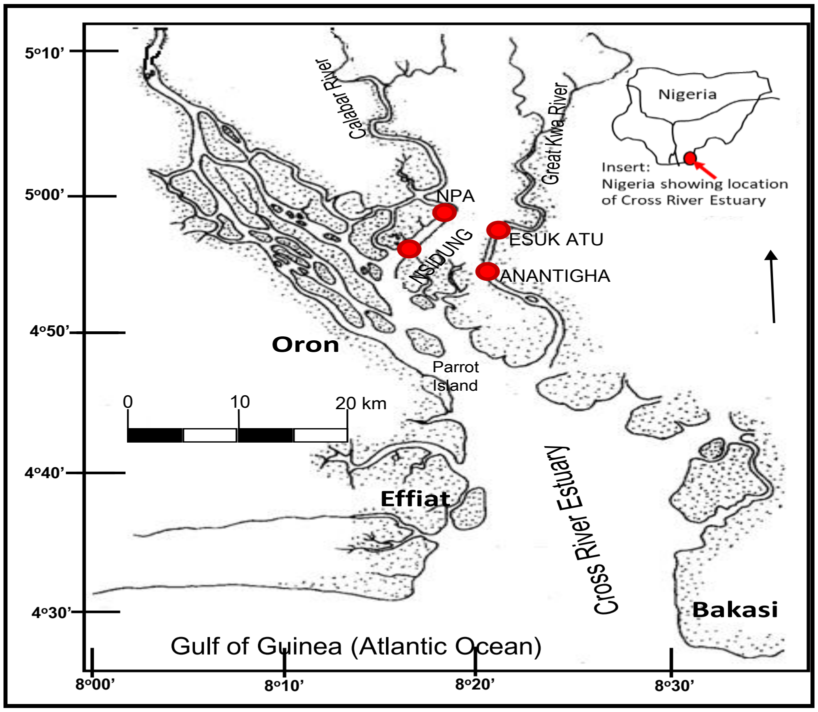

Fig. 1. Map of Cross River Estuary showing Calabar River and Great Kwa River with the sampling points

Collection, preparation, and analysis of samples

The guidelines outlined in **APHA (2005)** were followed in sample collection and preparation. Two sampling points, namely Esuk Atu and Obufa Esuk for the Great Kwa River, and Nigerian Port Authority Jetty and Esuk Nsidung for the Calabar River, were established along the lower reaches of both rivers. Every month (from October 2021 to August 2022) sediment samples were taken from each sampling point using an Ekman grab that was pushed under pressure into the water to extract sediment layers at a depth of about 10cm. Each sample was put in a polyethylene bag, placed in an ice chest, and transported to the laboratory.

Following a five-day air-drying period, the samples were pulverized and sieved through a 60-mesh (0.3-inch) sieve. One gram of a thoroughly mixed and sieved sample was weighed, placed in a beaker of 250mL capacity, and subjected to a digestion process on a hot plate using a 20ml solution of HF, $HCLO_4$, and HNO_3 (ratio 1:1:3). The sediment digestion procedure was adapted from **Martin (1996)**.

The metal concentrations in the digest were measured at atomic absorption spectrophotometer/ultra violet visible spectrometer laboratory in NARICT, Zaria, Nigeria, using a Shimadzu model AAS-6800 atomic absorption spectrophotometer (Japan).

Analytical quality assurance

To prevent sample cross-contamination, precautions were taken. Only analytical grade reagents (HNO3, HF, and HCIO4 obtained from Riedel-deHaen, Germany, British Drug House Chemicals Limited, England, and Sigma Aldrich, Germany, respectively) were employed. Blank and combined standards were created and analyzed for every batch of samples to ensure analytical consistency and to detect any background contamination. The accuracy of our results was assessed by evaluating a standard reference material (Lichen coded, IAEA-336) alongside the samples using the same process.

Statistical analysis

Significant statistical testing was performed on the acquired data. Independent t-test was used to compare metal concentrations between the Calabar River and the Great Kwa River and between the wet and dry seasons. A probability of 0.05 or less ($P \leq 0.05$) was considered statistically significant. For all statistical studies, IBM SPSS version 23 for Windows was used.

Evaluation of metal pollution status of surface sediments

- **Contamination factor (CF)**

To describe sediment contamination, a contamination factor (CF) was employed, following **Hakanson (1980)** and **Qingjie *et al*. (2008)**. The following equation was used for the computation of CF.

$$CF = Cs / Cp \ldots (1),$$

Where, Cp is the metal's pre-industrial reference level and Cs is the mean concentration of that metal in sediments from the sampling sites.

- **Contamination degree (CD)**

At a specific site, the total of all contamination factors is known as the contamination degree (CD). It gives a general idea of the extent of contamination that exists in sediments from a particular location. CD was computed using equation (2) **(Hakanson, 1980; Qingjie *et al*., 2008)**.

$$\boldsymbol{CD} = \sum_{i=1}^{n} CF \ldots (2).$$

- **Index of geo-accumulation (Igeo)**

The index of geo-accumulation (Igeo) is a quantitative measure that was used to evaluate the degree of metal pollution in the sediment of the Calabar and Great Kwa Rivers. Igeo was computed using equation 3 **(Qingjie *et al*., 2008)**:

$$Igeo = \log_2 [C_n / (1.5\ B_n)] \ldots (3),$$

Where:

C_n is the concentration of metals in sediment, B_n is the geo-chemical background concentration of the given metal, and 1.5 is a correctional value to account for variation in background concentrations due to the lithogenic effect.

- ***Pollution load index (PLI)***

In accordance with **Thomilson *et al*. (1980)**, the pollutant load index (PLI) was also employed to assess the degree of heavy metal pollution of sediment from the study area. PLI was computed following equation 4:

$$PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \ldots \times CFn)} \ \ldots (4),$$

Where, CF_1 is the contamination factor for each metal 1; CF_2 is the contamination factor for each metal 2, CF_n is the contamination factor for each metal n, and n = the number of metals studied.

Evaluation of potential ecological risk

- ***Threshold and probable effects levels***

Various empirical approaches for sediment guidelines have been developed based on the occurrence of macro-invertebrate effects and total sediment concentrations. These methods typically establish two threshold levels. According to **Burton (2001)**, the first one is the 'effects range low/effect range median', below which adverse consequences are rare, and the second is the 'threshold/probable effect level', above which adverse consequences are more likely to occur. These threshold levels were used to evaluate the ecological danger that the metals under study posed, according to Table (1).

Table 1. Effects range low/effects range median (ERL/ERM) and threshold/probable effect level (TEL/PEL*)* sediment guidelines

	Lead	**Cadmium**	**Mercury**	**Arsenic**
Threshold effect level (TEL)	35	0.6	0.17	5.9
Effects range low (ERL)	35	5	0.15	3.3
Probable effect level (PEL)	91.3	3.53	0.486	17
Effects range median (ERM)	110	9	1.3	35

- ***Ecological risk factor***

The potential ecological risk posed by a specific heavy metal was expressed quantitatively using an ecological risk factor (Er) **(Hakanson, 1980; Qingjie *et al*., 2008)**. Er was computed using equation 5:

$$Er = Tr \text{ x } CF \ \ldots (5),$$

Where, CF denotes the contamination factor and Tr denotes the toxic-response factor for a particular metal.

RESULTS

1. Analytical quality assurance

Table (2) displays the results of the certified standard reference material analysis (Lichen designated IAEA-336) that was done concurrently with our samples. The analysis's findings show that the values fall within the certified reference values' confidence interval for the metals under study, confirming the precision and accuracy of the metal determination techniques.

Table 2. Results of analyzed standard reference materials (Lichen coded IAEA-336) compared to the certified reference values

Metals Mg/Kg	**Pb**	**Cd**	**Hg**	**As**	**Cr**
Analyzed value	4.8	1.46	0.19	0.63	1.00
Reference value	4.3-5.5	0.100-0.134	0.16-0.24	0.55-0.71	0.89-1.23

2. Concentration of metals in surface sediment

Table (3) presents the concentrations of lead, cadmium, mercury, and arsenic in sediments of the Great Kwa and Calabar Rivers for both the dry and rainy seasons.

Concentrations of the metals in sediments were in the ranges of 4.457-11.341mg/ kg, 0.311-0.978mg/ kg, 0.034-0.096mg/ kg, and 0.134-0.755mg/ kg for lead, cadmium, mercury, and arsenic, respectively (Table 3). The highest concentrations of each metal were found at Esuk Nsidung in March, while the lowest values were found at Esuk Atu in August. The difference in lead, cadmium, and mercury concentrations between the Great Kwa and Calabar Rivers was significant ($P \leq 0.05$), with concentrations in the Calabar River being significantly higher than in the Great Kwa River for both wet and dry seasons. Calabar River sediments displayed a significantly higher arsenic concentration than Great Kwa River in the dry season. The difference was, however, not significant ($P > 5$) in the wet season.

3. Evaluation of metal pollution status of surface sediments

The pollution status of surface sediments was evaluated in this study using a variety of metal pollution indices, such as the contamination factor, contamination degree, pollution load index, and index of geo-accumulation. Table (4) presents the 'pre-industrial reference levels and toxic response factors' **(Hakanson, 1980)** that were used to compute the contamination factor and ecological risk factor. Metal pollution indices computed for sediments of the Great Kwa and Calabar Rivers are presented in Tables (5-8).

Table 3. Lead, cadmium, mercury and arsenic concentrations of surface sediments of Great Kwa River and Calabar River for dry and wet season

Metals	**Months**	**Dry Season**				**Months**	**Wet Season**			
		Esuk Atu	Esuk Anantigha	NPA Jetty	Esuk Nsidung		Esuk Atu	Esuk Anantigha	NPA Jetty	Esuk Nsidung
Lead	October	5.963	6.735	8.936	9.941	April	6.786	7.776	8.732	10.112
	January	6.836	8.467	9.992	10.342	June	6.236	6.458	7.971	8.328
	March	7.734	8.986	9.898	11.341	August	4.457	5.214	6.984	6.938
	Mean±SD	6.844±0.72	8.063±0.96	9.608±0.48	10.541±0.59	Mean±SD	5.826±0.99	6.483±1.05	7.896±0.72	8.459±1.30
	Range		5.963-11.341			Range		4.457-10.112		
Cadmium	October	0.354	0.396	0.432	0.785	April	0.374	0.605	0.699	0.878
	January	0.385	0.463	0.394	0.898	June	0.326	0.419	0.394	0.833
	March	0.396	0.675	0.754	0.978	August	0.311	0.321	0.404	0.762
	Mean±SD	0.378±0.02	0.511±0.11	0.527±0.16	0.887±0.08	Mean±SD	0.337±0.03	0.448±0.12	0.499±0.14	0.824±0.05
			0.354-0.978			Range		0.311-0.878		
Mercury	October	0.043	0.053	0.057	0.068	April	0.044	0.053	0.067	0.090
	January	0.052	0.051	0.059	0.074	June	0.034	0.046	0.061	0.061
	March	0.046	0.062	0.072	0.096	August	0.034	0.043	0.043	0.056
	Mean±SD	0.047±0.01	0.055±0.01	0.063±0.01	0.079±0.01	Mean±SD	0.037±0.04	0.047±0.05	0.057±0.06	0.069±0.07
	Range		0.043-0.096			Range		0.034- 0.067		
Arsenic	October	0.154	0.256	0.342	0.541	April	0.411	0.411	0.398	0.621
	January	0.342	0.347	0.451	0.623	June	0.328	0.323	0.371	0.564
	March	0.432	0.432	0.418	0.755	August	0.134	0.234	0.319	0.453
	Mean±SD	0.309±0.11	0.345±0.07	0.404±0.05	0.640±0.09	Mean±SD	0.291±0.12	0.323±0.07	0.363±0.03	0.546±0.07
	Range		0.154-0.755			Range		0.134-0.621		

Table 4. The pre-industrial reference level (µg/g) and toxic- response factor used for the computation of the contamination factor and the ecological risk factor

Elements	Ni	Hg	Cd	As	Cu	Pb	Cr	Zn
Pre-industrial reference level	50	0.25	1.0	15	50	7.0	90	175
Toxic-response factor	5	40	30	10	5	5	2	1

Source: **(Hakanson, 1980)**.

3.1 Contamination factor and contamination degree

Contamination status of sediments of the Great Kwa and Calabar Rivers was evaluated using the metal contamination factor to determine the level of contamination posed by each metal (the contribution of each metal to the overall contamination) and the contamination degree to assess the overall contamination at each site due to the cumulative impact of all the metals under study. The average value of contamination factors computed for the Great Kwa River in dry and wet seasons were: 1.065 and 0.879 for lead, 0.445 and 0.393 for cadmium, 0.204 and 0.168 for mercury, and 0.022 and 0.021 for arsenic, respectively. For Calabar River, the average contamination factors were 1.440 and 1.168, 0.707 and 0.662, 0.284 and 0.251, and 0.035 and 0.030 for Pb, Cd, Hg, and As, respectively (Table 5).

The average contamination degree for dry and wet seasons were: 1.736 and 1.460 for the Great Kwa River and 2.466 and 2.110 for the Calabar River (Table 5)

3.2 Index geo-accumulation

Average values of the geo-accumulation index computed for Great Kwa River in the two seasons were: lead at -0.509 and -0.773, cadmium at -1.772 and -1.949, mercury at -2.883 and -3.169 and arsenic at -6.108 and -6.198. For Calabar River, the average values were: -0.376 and -0.361, -1.134 and -1.226, 2.411 and 2.580, and -5.468 and -5.255 for lead, cadmium, mercury, and arsenic, respectively (Table 6)

3.3 Pollution load index

Average values of PLI were: 0.163, 0.219, 0.251, and 0.341 for Esuk Atu, Esuk Anantigha, NPA Jetty, and Esuk Nsidung, respectively (Table 7).

4. Evaluation of potential ecological risk posed by lead, mercury, cadmium, chromium, and arsenic in sediments

4.1 Ecological risk factor

The average values of the ecological risk factor computed for the Great Kwa River were: 5.325 and 4.395 for lead, 13.355 and 11.775 for cadmium, 8.160 and 6.720 for mercury, and 0.220 and 0.205 for arsenic. The average values of the ecological risk factor computed for Calabar River were: 7.198 and 5.840, 15.810 and 19.865, 11 360 and 10.080, and 0.350 and 0.300 for lead, cadmium, mercury, and arsenic, respectively (Table 8)

Table 5. Contamination factor (CF) and contamination degree (CD)

Sampling Station	Sampling point	Dry Season					Wet Season				
		Contamination Factor				Contamination Degree	Contamination Factor				Contamination Degree
		Pb	Cd	Hg	As		Pb	Cd	Hg	As	
Great Kwa River	Esuk Atu	0.978	0.378	0.188	0.021	1.565	0.832	0.337	0.148	0.019	1.336
	Esuk Anantigha	1.152	0.511	0.220	0.023	1.906	0.926	0.448	0.188	0.022	1.584
	Average	**1.065**	**0.445**	**0.204**	**0.022**	**1.736**	**0.879**	**0.393**	**0.168**	**0.021**	1.460
Calabar River	NPA Jetty	1.373	0.527	0.252	0.027	2.179	1.128	0.499	0.225	0.024	1.876
	Esuk Nsidung	1.506	0.887	0.316	0.043	2.752	1.208	0.824	0.276	0.036	2.344
	Average	**1.440**	**0.707**	**0.284**	**0.035**	2.466	**1.168**	**0.662**	**0.251**	**0.030**	2.110

Table 6. Index of geo-accumulation (I_{geo})

Sample Location	Sampling point	Dry Season				Wet Season			
		Pb	Cd	Hg	As	Pb	Cd	Hg	As
Great Kwa River	Esuk Atu	-0.618	-1.989	-2.996	-6.187	-0.850	-2.154	-3.342	-6.273
	Esuk Anantigha	-0.400	-1.554	-2.770	-6.028	-0.696	-1.744	-2.996	-6.123
	Average	**-0.509**	**-1.7715**	**-2.883**	**-6.1075**	**-0.773**	**-1.949**	**-3.169**	**-6.198**
Calabar River	NPA Jetty	-0.128	-1.509	-2.574	-5.800	-0.411	-1.588	-2.718	-5.145
	Esuk Nsidung	-0.623	-0.758	-2.247	-5.136	-0.311	-0.864	-2.442	-5.365
	Average	**-0.376**	**-1.134**	**-2.411**	**-5.468**	**-0.361**	**-1.226**	**-2.580**	**-5.255**

Table 7. Pollution load index (PLI)

Seasons	Esuk Atu	Esuk Anantigha	NPA Jetty	Esuk Nnsidung
Dry season	0.195	0.233	0.265	0.367
Wet season	0.131	0.204	0.236	0.315
Average	**0.163**	**0.219**	**0.251**	**0.341**

Table 8. Ecological risk factor (EC)

Sample Location	Sampling point	Dry Season				Wet Season			
		Pb	Cd	Hg	As	Pb	Cd	Hg	As
Great Kwa River	Esuk Atu	4.890	11.340	7.520	0.210	4.160	10.110	5.920	0.190
	Esuk Anantigha	5.760	15.330	8.800	0.230	4.630	13.440	7.520	0.220
	Average	**5.325**	**13.335**	**8.160**	**0.220**	**4.395**	**11.775**	**6.720**	**0.205**
Calabar River	NPA Jetty	6.865	15.810	10.080	0.270	5.640	14.970	9.120	0.240
	Esuk Nsidung	7.530	26..610	12.640	0.430	6.040	24.760	11.040	0.360
	Average	**7.198**	**15.810**	**11.360**	**0.350**	**5.840**	**19.865**	**10.080**	**0.300**

DISCUSSION

1. Concentration of metals in surface sediments

Given that the water column above and the surface sediments are often in a condition of dynamic equilibrium, exchanging matter and energy, sediment pollution is considered one of the largest risks not only to benthic communities but also to the entire aquatic environment. Sediment quality in this study was assessed using **US-EPA (1999)** sediment quality guidelines (Table 9). The results indicated that both the Calabar and the Great Kwa Rivers were not polluted, with respect to the studied metals. The US-EPA's sediment quality criteria are helpful in identifying places that may have detrimental biological consequences, even though they do not provide a clear indication of toxicity **(Nkopuyo & Everard, 2021)**. This is because they have a high predictive capacity.

Table 9. United States Environmental Protection Agency sediment quality guideline (mg/kg)

Pollution status	Pb	Hg	Cd	Cr	As
Not polluted	< 40	NA	*	< 25	< 3
Moderately	40 – 60	NA	*	25 – 70	3 – 8

polluted					
Heavily polluted	> 60	NA	>6	> 70	> 8

** Lower limits not established, Not available.*

Sediment quality in the study was also evaluated using Australian and New-Zealand's sediment quality criteria, (**ANZECC, 2000)**. The criteria make use of lower and higher limits for sediment quality assessment. The lower and upper guideline values (mg/kg) for lead, mercury, cadmium, chromium, and arsenic are: 50 and 220, 0.15 and 1, 1.5 and 10, and 20 and 70, respectively **(ANZECC, 2000)**. ANZECC guideline numbers are trigger values that when exceeded, prompt further action. First level screening compares metal concentrations with the lower guideline value (trigger value) for the given metal. If it is not exceeded, the metal is not likely to result in any biological disturbance for organisms in the sediment. On the other hand, if the trigger value is exceeded, it triggers further investigation to determine whether the exceedance poses risks to the ecosystem. Furthermore, if the upper guideline number is exceeded, the site is said to be highly polluted. This then triggers an immediate management or a remedial action. The concentrations of lead, mercury, cadmium, chromium, and arsenic in sediments measured in this study were all found to be below the lower guideline values, indicating also that, the sediments of the Great Kwa River and Calabar River were not polluted.

The significantly higher metals concentrations observed in the Calabar River may be due to the higher levels of anthropogenic activities in the basin, including periodic dredging to accommodate cargo vessels, offloading of petroleum products, discharge of ballast water, and regular sand mining during ebb tides. On the other hand, the Great Kwa River experiences relatively lower anthropogenic influence, leading to lower sediment metal concentrations compared to the Calabar River. The increase in sediment metal concentration toward the sea may be attributed to the continual transit of polluted sediments by the rivers and their deposition at downstream sites, as observed by **Udiba *et al*. (2012)**. Sampling stations such as Esuk Nsidung (Calabar River) and Esuk Anantigha (Great Kwa River) are predominantly depositional areas. The two rivers did not display significant seasonal variations in metal concentrations, except for lead concentrations in the Calabar River, which were significantly higher in the dry season than the wet season. The observation may be due to tidal influence on the rivers. Tidal currents play a crucial role in the mixing and distribution of metals in sediments, thereby reducing the impacts of seasonal variations.

2. Evaluation of metal pollution status of surface sediments

2.1. Contamination factor and contamination degree

The contamination factor was classified as follows: a low contamination factor for Cf less than 1, moderate contamination for Cf between 1 and 3, considerable contamination for Cf between 3 and 6, and very high contamination for Cf greater than 6 **(Qingjie *et al*., 2008)**. The contamination factors for cadmium, mercury, and arsenic corresponded to low contamination factors throughout the study. However, lead corresponded to a moderate contamination factor in the dry season. The low contamination factor recorded for these metals suggests minimal anthropogenic influence and that the self-purification mechanism of the rivers has not been overloaded, as it is sufficient to restore their quality. The moderate contamination factor recorded for lead in the season may be due to the reduced volume of fresh water discharged to the tide-dominated lower reaches of the rivers during the dry season.

The contamination degree expresses the overall contamination status of a site, taking into consideration the contribution of all the metals put together. The study categorized contamination levels as follows: Cd less than 7 represent low degree of contamination, Cd between 7 and 14 indicates moderate degree of contamination, Cd between 14 and 21 reflect high degree, and Cd greater than 21 represent a very high degree of contamination (**Qingjie *et al*., 2008)**. Table (6) reveals that the contamination degree for all the sampling points corresponds to a low level of contamination. The presence of higher concentrations of the metals under investigation in sediments above the area's typical background level is referred to in this study as contamination. The biological effects of these metals, if unchecked, could reduce one or more levels of biological organizations, from cells to ecosystems, which is considered pollution.

2.2. Index of geo-accumulation (Igeo)

Qingjie *et al*. (2008) identified seven distinct classes for the index of geo-accumulation: class 0 (Igeo ≤ 0) as unpolluted, class 1 ($0 <$ Igeo ≤ 1) as unpolluted to moderately polluted, class 2 ($1 <$ Igeo ≤ 2) as moderately polluted, class 3 ($2 <$ Igeo ≤ 3) as moderately to strongly polluted, class 4 ($3 <$ Igeo ≤ 4) as strongly polluted, class 5 ($4 <$ Igeo ≤ 5) as strongly to extremely polluted, and class 6 (Igeo > 5) as extremely polluted. Based on the values of Igeo computed, the Great Kwa and the Calabar rivers could be said to be unpolluted concerning lead, cadmium, mercury, and arsenic (pollution status corresponding to group 0). In both wet and dry seasons, the metal pollution intensity of the Great Kwa and Calabar rivers' sediments ranked according to the following trend: Pb > Cd > Hg > Cr > As.

2.3. Pollution loud index (PLI)

According to **Qingjie *et al*. (2008)**, the PLI was interpreted as follows: PLI > 1 implies pollution; PLI = 1 indicates that pollutants are at baseline levels; and PLI < 1 indicates no pollution. The pollution load index computed for the study suggests that there is no pollution in the two rivers. The PLI followed the trend: Esuk Nsidung > NPA Jetty > Esuk Anantigha > Esok Atu

3 Evaluation of potential ecological risk posed by lead, cadmium, mercury and arsenic in sediments

3.1. Ecological risk factor

This study's ecological risk factor shows how sensitive different biological communities are to metal contamination and highlights the possible ecological risk that heavy metals may pose. This study expressed the possible ecological damage posed by heavy metals by utilizing the ecological risk factor, which reflects the vulnerability of different biological communities to metal contamination. The ecological risk factor was categorized as follows: Er less than 40 indicates a low potential risk, Er between 40 and 80 suggests a moderate risk, Er between 80 and 160 represents a significant risk, Er between 160 and 320 shows a high risk, and Er greater than 320 indicates a very high potential ecological risk **(Qingjie *et al*., 2008).** According to the results of this investigation, Pb, Cd, Hg, and As pose low potential ecological risk to other components of the ecosystem.

3.2: Threshold and probable effects levels

The potential ecological risk posed by sediment contamination in this study was also estimated by comparing the heavy metal concentrations with the threshold and probable effects levels (effects range low/effect range median and threshold effect/probable effect levels). The sediments from both rivers had concentrations of all the metals below effects range low (ERL) and the threshold effects levels (TEL) suggesting rare occurrence of adverse effects on sediment dwelling fauna, except for Esuk Nsidung, where cadmium concentrations exceeded the TEL (Table 1). The exceedance of TEL by cadmium at Esuk Nsidung suggests that possible adverse effects on biological communities are expected from cadmium at this site. It is important to emphasize here that even though the cadmium contamination factor corresponded to a low contamination factor, the concentration exceeded the TEL at Esuk Nsidung, indicating that adverse effects on sediment-dwelling fauna could be expected **(Enuneku *et al*., 2018)**. Cadmium is one of the known toxic metals that exhibits deleterious effects, even at low concentrations.

CONCLUSION

Sediments in aquatic systems serve as repositories of heavy metals, and their concentrations can be influenced by natural and human activities, leading to potential ecological hazards due to bioaccumulation and biomagnification along the food web. The concentration of metals in the Calabar River sediments was significantly greater than that in the Great Kwa River sediment, except for arsenic during the wet season. There were no significant seasonal fluctuations in the concentrations of metals in the two rivers. Evaluation based on US-EPA and Australian, and New Zealand sediment quality standards indicated that neither river had any metal pollution, with particular reference to the metals under study. Low levels of contamination were also suggested by the contamination factor and contamination degree. The pollutant load index further confirmed that the rivers were not polluted. However, it was noted that cadmium concentrations at Esuk Nsidung exceeded the threshold effect level, potentially posing adverse effects on biological communities". The ecological risk factor analysis revealed that lead, cadmium, mercury, and arsenic pose a low potential ecological risk to the environment. The authors emphasized the importance of periodic data collection on water and sediment quality to ensure sustainable management of the two rivers and to safeguard human and environmental health in the city of Calabar

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