p-ISSN. 2406-9825
e-ISSN. 2614-3178
Acta Aquatica: Aquatic Sciences Journal, 10:3 (December, 2023): 260-268

Acta Aquatica
Aquatic Sciences Journal

Penilaian kandungan logam berat dalam sedimen hutan bakau, niger delta, nigeria, menggunakan indeks resiko ekologi yang berlaku

Assessment of some heavy metal content in sediments of a mangrove swamp, niger delta, nigeria using applicable ecological risk indices

Received: 08 June2023, Revised: 02 November 2023, Accepted: 02 November 2023
DOI: 10.29103/aa.v10i3.11430

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Abstrak

Sedimen dapat berfungsi sebagai tempat penyimpanan polutan dan sumber pencemaran dalam lingkungan perairan. Kami menggunakan teknik-teknik standar dan alat evaluasi untuk menentukan kadar logam berat dalam sedimen permukaan di daerah pasang surut Isaka-Bundu di Niger Delta. Studi ini dilakukan di tiga stasiun antara bulan Januari dan Juni 2022. Ada delapan indeks evaluasi yang digunakan: faktor kontaminasi (CF), tingkat kontaminasi (DC), risiko ekologi (Er), risiko ekologi potensial (PERI), indeks beban pencemaran (PLI), faktor pengkayaan (EF), indeks geo-akumulasi (Igeo), dan kuantifikasi pencemaran (QoC). Lima logam berat yang diperiksa adalah timbal, tembaga, kadmium, nikel, dan seng. Hasil penelitian menunjukkan bahwa kadmium dan tembaga melebihi batas yang diperbolehkan, sementara timbal, seng, dan nikel berada dalam batas yang diizinkan. Stasiun 1 dan 3 mencatat nilai yang signifikan lebih tinggi, menunjukkan pengaruh antropogenik. Kegiatan antropogenik dominan yang diamati di daerah tersebut termasuk kegiatan maritim dan galangan kapal serta pengrajin pabrik minyak bumi mentah. Indeks penilaian mengungkapkan bahwa sedimen memiliki tingkat pencemaran logam berat yang bervariasi, dengan tembaga dan kadmium memainkan peran utama. Indeks tersebut adalah: CF: Cu (tingkat yang signifikan) dan Cd (tingkat yang sangat tinggi), DC (tingkat yang sangat tinggi), Er: Cd (risiko ekologi yang tinggi) dan Cu (risiko ekologi yang sangat tinggi), PERI (risiko ekologi yang signifikan), PLI (tingkat pencemaran yang sangat tinggi), EF: Pb, Zn, Cu (Stasiun 1) dan semua sedimen sangat tercemar dengan logam berat beracun, yang merugikan manusia dan biota perairan.

Kata kunci: Hutan baka; Indeks; Logam berat; Niger Delta; Sedimen.

Abstract

Sediments can act as pollutant sinks and a source of pollution in aquatic environments. We used standard techniques and evaluation tools to find out how much heavy metal was in the surface sediments of the Isaka-Bundu tidal swamp in the Niger Delta. The study was carried out at three stations between January and June 2022. There were eight evaluation indices used: contamination factor (CF), degree of contamination (DC), ecological risk (Er), potential ecological risk (PERI), pollution load index (PLI), enrichment factor (EF), geo-accumulation index (Igeo), and quantification of contamination (QoC). Five heavy metals were looked at: lead, copper, cadmium, nickel, and zinc. Results showed that cadmium and copper exceeded permissible limits, while lead, zinc, and nickel were within limits. Stations 1 and 3 recorded significantly higher values, indicating anthropogenic influence. The dominant anthropogenic activities observed in the area include maritime and dockyard activities and artisanal crude oil refineries. The assessment indices revealed that the sediments had varying degrees of heavy metal pollution, with copper and cadmium playing a major role. These indices were: CF: Cu (considerable degree) and Cd (very high degree), DC (very high degree), Er: Cd (high ecological risk) and Cu (very high ecological risk), PERI (significantly high ecological risk), PLI (very high-level pollution), EF: Pb, Zn, Cu (Station 1) and all the sediments were highly polluted with toxic metals, which are detrimental to humans and aquatic biota.

Keywords: Heavy metal; Indices; Mangrove; Niger Delta; Sediment.

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1. Introduction

Sediment serves as both a pollutant sinks and a source of heavy metals pollution in an aquatic environment (Pejman *et al.,* 2015; Huang *et al.,* 2019). However, under certain environmental and hydrological conditions, the heavy metals deposited in the sediment can be desorbed or re-suspended; resulting in secondary pollution in the water column (Liang *et al.,* 2015; Kouidri *et al.,* 2016). Heavy metals are among the serious pollution sources in the aquatic environment and have been receiving increasing attention globally (Odekina *et al.,* 2021; Davies *et al.,* 2022a). Their harmful nature, persistence in the environment and accumulation in the aquatic ecosystem are of great concern (Guan *et al.,* 2014; Pandiyan *et al.,* 2020; Anyanwu *et al.,* 2022). The presence of pollutants in sediments, such as heavy metals, carbon-based compounds, nutrients, and disease-causing organisms, poses significant hazards to humans and aquatic life (Alabi *et al.,* 2019). Toxic heavy metals tend to accumulate in the superficial sediments, especially the fine fraction and provide a very good means of determining the accumulation of these metals over time (Bai *et al.,* 2011). Determination of heavy metal concentration is not enough to give an insight into their contamination and toxicity levels in the environment (Kumar *et al.,* 2020; Wei *et al.,* 2019).

The critical factors of heavy metal pollution in the environment are their bioavailability and eco-toxicity (Jacob *et al.,* 2018). Consequently, a number of different pollution indices have been applied to determine the contamination and toxicity levels of metals in the environment; despite some of their limitations (Masindi & Muedi, 2018; Davies *et al.,* 2022a; Ahirvar *et al.,* 2023). Assessment indices like contamination factor, contamination degree, ecological risk factor, potential ecological risk index, pollution load index, geo-accumulation index, degree of contamination and enrichment factor have been extensively used by researchers on heavy metals in sediments (Ogbeibu *et al.,* 2014; Shirani *et al.,* 2020; Amin *et al.,* 2021; Moldovan *et al.,* 2022; Ahirvar *et al.,* 2023). Natural and man-made processes are the two major ways through which heavy metals enter the aquatic ecosystem including in the coastal sediments (Pandiyan *et al.,* 2021) and most heavy metals quickly settle in the sediment after entry; resulting in elevated concentration in the sediment in the water column (Liu *et al.,* 2018; Shyleshchandran *et al.,* 2018).

A significant source of heavy metals and other pollutants in the coastal areas emanates from ever-increasing economic activities in such areas around the world (Ansari *et al.,* 2014; Yuan *et al.,* 2016; Abadi *et al.,* 2019). Environmental degradation arising from oil production activities and artisanal crude oil refining is a growing menace in most oil-producing communities in the Niger Delta, Nigeria (Ite *et al.,* 2018; Onuh *et al.,* 2021). Isaka-Bundu mangrove swamp is located within the Bonny Estuary, which is a hub of industrial, agricultural and domestic activities. Wastes from industries, artisanal refineries and densely populated coastal settlements are discharged into the swamp. Therefore, the aim of this study is to evaluate some heavy metal content in sediments of the Isaka-bundu mangrove swamp, Niger Delta, Nigeria using applicable assessment indices.

2. Material and Method

2.1. Study area and sampling stations

Isaka-Bundu mangrove swamp, located along the Upper reaches of Bonny Estuary has been subjected to pollution pressures (Davies *et al.,* 2022b). The swamp receives domestic and industrial waste input from companies (Nigerian Ports Authority, OandO Oil and Gas, Conoil, Ibeto cement factory, dredging companies, etc.), adjoining creeks, and the densely populated coastal settlements on the banks. It is characterized by the wet season (May to October) and dry season (November to April).

Three sampling stations, about 500 meters apart were selected based on anthropogenic activities (Figure 1).

Station 1: Isaka (Latitude 04°45'03.05" N, Longitude 007°00' 45.51" E), located near a heap of sediment, was a dump site marred with oil sheen, and the tidal currents dump off litter and other particulate contaminants. An abandoned bunkering site was also within the station.

Station 2: Bundu-Ama (Latitude 04°44' 55.35" N, Longitude 007°00' 38.40" E) was near the densely populated settlement lining the tidal-swept mangrove swamp. The station witnessed a massive discharge of human, animal, and domestic wastes and runoff that was visible on the shorelines.

Station 3: Dockyard (Latitude 04°45' 03.58" N, Longitude 007°00'57.75" E) and close to the popular Creek Road market. Maintenance fluid and other associated liquid and solid wastes are discharged from the Dockyard while sewage, refuse and other large quantities of commercial wastes from the market are dumped around the station.

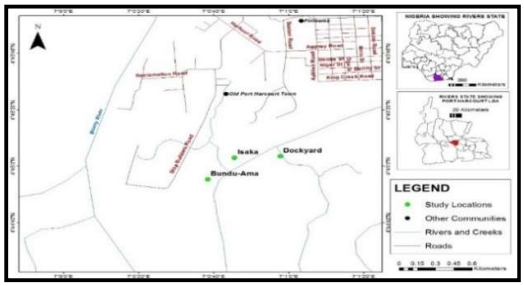

Figure 1. Map of Port Harcourt, Rivers State, Nigeria showing the study area.

2.2. Samples collection and analyses

Sediment samples were collected monthly from the 3 stations between January and June 2022. An acrylic pipe sampler was used to collect the surface sediment (0–5 cm) samples during ebbs. The samples were wrapped in black polythene bags and taken immediately to the laboratory for analysis. The collected samples were dried at 45 °C in an electric oven until a constant weight was attained and then ground into powder using agate mortar and pestle. The ground sample (0.05 g) was digested with mixed acid (5 mL HCl, 3 mL HNO_3, 7 mL HF, 0.25 mL $HClO_4$) in a Teflon beaker. After digestion, the solutions were filtered through Whatman filter paper and diluted to a volume of 25 mL with double-deionized water. The mass fractions of heavy metals (Pb, Cu, Cd, Ni, and Zn**)** in the sediments were determined with a UNICAM Solaar 969 atomic absorption spectrometer (AAS) that uses acetylene-air flame. The chemicals and reagents used throughout the study were Analytical grades.

2.3. Data analysis

The data were summarized with Microsoft Excel while one-way ANOVA was used to test for significant differences in the concentrations of the metals in the sediments among the stations. The source of significant difference at $p<0.05$ was determined with the Tukey pairwise posthoc test.

2.4. Assessment indices

The contamination and toxicity of the heavy metals in the sediments were determined using the assessment indices presented below:

2.5. Contamination factor (CF)

The CF is expressed as the ratio between the content of each metal to the background value.

$$C_F = \frac{\text{Cmetal}}{\text{Cbackground}}$$ (Hakanson, 1980) (1)

Where C_{metal} is the mean metal content in the sample, $C_{background}$ is the mean natural background value of the metal (Table 1). C_F is classified into four grades for monitoring the pollution of a single metal over a period of time (Ali *et al.,* 2016): low degree (CF < 1), moderate degree (1 ≤ CF < 3), considerable degree (3 ≤ CF < 6), and very high degree (CF > 6).

Table 1
Geochemical background value (Bn) (mg/kg).

Metals	Cd	Pb	Zn	Ni	Cu
Values	0.10	21.00	65.40	31.00	22.50

Source: Guan *et al*. (2014)

2.6. Degree of Contamination (Cd)

The degree of contamination (Cd) is the sum of all contamination factors and gives an indication of the environmental risks posed by the presence of multiple trace metals in the sediment. It was developed by Hakanson (1980) and has been used by Essien *et al*. (2019) and Guan *et al*. (2014). The equation is given in equation 2;

$$Cd = \sum_{i=1}^{n} CF_1$$ (2)

Where CF_1 is the contamination factor of metal. Hakanson (1980) proposed the classification of Cd as < 6 = low degree of contamination, 6 ≤ Cd < 12 = moderate degree of contamination, 12 ≤ Cd < 24 = considerable degree of contamination, and Cd ≥ 24 = a very high degree of contamination.

2.7. Ecological risk assessment

The risk factors evaluation (Er and PERI) assesses the ecological risk potential of a single contaminant and that of several metals' pollutants in the sediment.

2.8. Ecological risk factor (Er)

Ecological risk factor (Er) is quantitatively calculated using equation 3 below:

$$Er = Tr \times C_f$$ (3)

T_r = toxic-response factor of a given metal and C_f = the contamination factor for the metal. T_r values are Cd (30), Pb (5), Zn (1), Ni (5) and Cu (5). The ecological risk factor is classified as Er < 40, low; 40 ≤ Er < 80, moderate; 80 ≤ Er < 160, considerable; 160 ≤ Er < 320, high; and Er ≥ 320, very high (Mugoša *et al.,* 2016).

2.9. Potential ecological risk index (PERI)

Potential Ecological Risk Index (PERI) was introduced by Hakanson (1980), and it is calculated using the following equation 4:

$$PERI = \sum_{i=1}^{n} E_r^i$$ (4)

Where, n = the number of heavy metals and E_r = single index of the ecological risk factor

The risks are categorized as PERI < 150 low ecological risks, 150 < PERI < 300 moderate ecological risks, 300 < PERI < 600 high ecological risks and PERI ≥ 600 significantly high ecological risk (Mwakisunga *et al.,* 2021).

2.10. Pollution load index (PLI)

PLI was evaluated using the formula in using equation 5 proposed by Tomilson *et al*. (1980).

$$PLI = (CF1 \times CF2 \times CF3 \cdots \times CFn)\ 1/n$$ (5)

Where CF is the contamination factor and n is the number of metals evaluated. The PLI value of > 1 indicates pollution, whereas < 1 indicates no pollution (Barakat *et al*. 2020).

2.11. Enrichment factor (EF)

The enrichment Factor is a universal index that offers a relatively simple and easy method of evaluating the degree of enrichment as well as a basis for comparing contamination in different environmental media (Nowrouzi & Pourkhabbaz, 2014). It can also be used to confirm whether the heavy metal contamination was of anthropogenic sources (Jahan & Strezov, 2018). It is calculated using equation 6:

$$\text{EF} = \frac{\text{Cn/Cref sample}}{\text{Bn/Bref}}$$ (6)

Where C_n is the concentration of metal analyzed in the sample, C_{ref} is the concentration of the reference material, B_n is the background concentration of the analyzed metal and B_{ref} is the concentration of the reference element. Enrichment factor can be classified based on Abdullah *et al*. (2020) into five categories <2 (Depletion to mineral enrichment), 2≤EF<5 (Moderate enrichment), 5≤EF<20 (Significant enrichment), 20≤EF<40 (Very high enrichment) and EF>40 (Extremely high enrichment). Enrichment factor values close to or < 1 is an indication of heavy metals from natural sources while enrichment factor > 1 point to anthropogenic sources (Habib *et al.,* 2018; Jahan & Strezov, 2018).

2.12. Geo-accumulation index (Igeo)

The index of geo-accumulation (Igeo) is used to evaluate the heavy metals contamination of sediments by comparing the present and pre-industrial concentrations of the metals (Qingjie *et al.,* 2008) and has been extensively used for the assessment of sediment contamination (Islam *et al.,* 2014; Ahirvar *et al.,* 2023). It is calculated using equation 6 proposed by (Muller, 1969):

$$\text{Igeo} = log_2 \frac{c_n}{1.5xB_n}$$ (7)

Where C_n is the mean concentration of the heavy metal in the analyzed sediment samples. B_n is the reference value (Table 1). Factor 1.5 was used to accommodate variation in the background value. I_{geo} indices can be classified based on Abdullah *et al*. (2020) into seven classes as $I_{geo} \leq 0$ (class 0 – Unpolluted), $0 \leq I_{geo} \leq 1$ (class 1 – Unpolluted to moderately polluted), $1 \leq I_{geo} \leq 2$ (class 2 – Moderately polluted), $2 \leq I_{geo} \leq 3$ (class 3 – Moderately to strongly polluted), $3 \leq I_{geo} \leq 4$ (class 4 – Strongly polluted), $4 \leq I_{geo} \leq 5$ (class 5 – Strongly to extremely polluted0 and $I_{geo} > 6$ (class 6 – Extremely polluted).

2.13. Quantification of contamination (QoC)

The Quantification of Contamination (QoC) index was used to evaluate the main sources (anthropogenic or natural sources) of metals (Zarei *et al.,* 2014). The index is estimated in accordance with the following equation 8:

$$\text{QoC (\%)} = \left[\frac{(C_i - C_{in})}{C_i}\right] \times 100$$ (8)

Where C*i* is the mean content of the metal in the sediment samples and C*in* is the background level of the metal in Table 1 (Guan *et al*. (2014). Negative values indicate metals from natural

sources while positive values are attributable to anthropogenic sources (Malvandi, 2021).

3. Results and Discussion

3.1. Results

3.1.1. Heavy Metal content in sediment

The summary of the heavy metal concentrations in the sediment is presented in Table 2. Lead (Pb) values ranged between 5.66 and 12.19 mg/kg. The lowest value was recorded in station 2 while the highest value was recorded in station 1. All the recorded values were within 85 mg/kg set by the Department of Petroleum Resources (2002). The 3 stations were significantly different ($F = 228.8$, $p > 0.05$).

Copper (Cu) values ranged between 57.03 and 99.72 mg/kg. The lowest value was also recorded in station 2 and the highest in station 1. All the recorded values exceeded the acceptable limit of 36 mg/kg set by DPR (2002). All the stations were significantly ($F = 18.2$, $p < 0.05$) different.

Cadmium (Cd) values ranged between 6.12 and 9.91 mg/kg. The lowest value was recorded in station 2 while the highest value was recorded in station 3. All the recorded values exceeded the acceptable limit of 0.8 mg/kg set by DPR (2002). The 3 stations were significantly different ($F = 18.4$, $p > 0.05$).

Nickel (Ni) values ranged between 1.06 and 2.97 mg/kg. The lowest value was recorded in station 2 while the highest value was recorded in station 3. All the recorded values were within 3.5 mg/kg set by DPR (2002). Stations 1 and 3 were also significantly ($F = 26.4$, $p < 0.05$) higher than Station 2.

Zinc (Zn) values ranged between 20.03 and 39.28 mg/kg. The lowest value was also recorded in station 2 while the highest value was also recorded in station 3. All the recorded values were within the acceptable limit of 140 mg/kg set by DPR (2002). Stations 1 and 3 were significantly different ($F = 43.2$, $p > 0.05$) from station 2.

Table 2
Heavy Metal Concentration in Sediment from Isaka-Bundu.

Heavy Metal	Station 1	Station 2	Station 3	F – value	DPR Standard
Pb (mg/kg)	11.68±0.20[a] (11.01 - 12.19)	6.03±0.11[c] (5.66 - 6.41)	8.82±0.23[b] (8.12 - 9.81)	228.8 P< 0.05	85
Cu (mg/kg)	107.71±2.68[a] (98.57 - 117.01)	75.19±5.72[c] (59.72 - 92.23)	93.59±1.97[b] (89.02 - 99.73)	18.2 p < 0.05	36
Cd (mg/kg)	7.82±0.22[a] (7.12 - 8.32)	6.35±0.08[b] (6.12 - 6.64)	8.70±0.42[a] (7.09 - 9.91)	18.4 P < 0.05	0.8
Ni (mg/kg)	2.15±0.03[a] (2.02 - 2.24)	1.38±0.10[b] (1.06 - 1.69)	2.47±0.16[a] (2.04 - 2.97)	26.4 P < 0.05	3.5
Zn (mg/kg)	32.40±1.20[a] (28.42 - 35.80)	20.94±0.40[b] (20.03 - 22.32)	33.31±1.30[a] (30.55 - 39.28)	43.2 P < 0.05	140

3.1.2. Assessment indices

3.1.2.1. Contamination factor (CF) and degree of contamination

The contamination factor values are presented in Table 3. Lead (Pb), Zn and Ni were less than 1 and classified as a low degree while Cu was classified as a considerable degree ($3 \leq CF < 6$). However, Cd recorded the highest contamination factor values (63.50 – 87.00) and was classified as a very high degree ($CF > 6$). Stations 1 and 3 had relatively higher values compared to Station 2.

Table 3
Contamination factor (CF) and degree of contamination of the heavy metals.

Heavy Metal	Station 1	Station 2	Station 3
Cd	78.20	63.50	87.00
Pb	0.56	0.29	0.42
Zn	0.50	0.32	0.51
Ni	0.07	0.04	0.08
Cu	4.79	3.34	4.16
DC	84.12	67.49	92.17

The degree of contamination (DC) values, which are the sum of the contamination factors are also presented in Table 3. The values ranged between 67.49 and 92.17 and were higher than $Cd \geq 24$; classified as a very high degree of contamination. Stations 1 and 3 were relatively higher than station 2.

3.1.2.2. Ecological risk (E_r) and potential ecological risk index

The ecological risk and Potential Ecological Risk Index values are presented in Table 4. Ni, Zn and Pb (station 2) had Er values < 40; classified as low ecological risk. Pb values for stations 1 and 3 were within the moderate ecological risk ($40 \leq Er < 80$) while Cd had values within the high ecological risk ($160 \leq Er < 320$). On the other hand, Cu had the highest Er values and was classified as a very high ecological risk ($Er \geq 320$). All the PERI values were > 600 indicating significantly high ecological risk. For both Er and PERI, stations 1 and 3 had relatively higher values than station 2.

Table 4
Ecological Risk (E_r) of heavy metals in the sediments.

Heavy Metal	Station 1	Station 2	Station 3
Cd	234.60	190.50	261.00
Pb	58.40	30.15	44.10
Zn	32.40	20.94	33.31
Ni	10.75	6.90	12.35
Cu	538.55	375.95	467.95
PERI	874.70	624.44	818.71

3.1.2.3. Pollution load index (PLI)

The PLI values were 3387.48 (station 1), 1473.21 (station 2) and 4612.07 (station 3). All the PLI values exceeded the threshold value of 1 by a wide margin.

3.1.2.4. Enrichment Factor

The enrichment factor values are presented in Table 5. Pb, Zn and Ni values in stations 2 and 3 were <2 indicating depletion to mineral enrichment. Ni (station 1) and Cu (stations 2 and 3) were classified as significant enrichment ($5 \leq EF < 20$) and Pb and Zn (Station 1), Cu (station 1) and all of Cd were classified as extremely high enrichment ($EF > 40$). Though the enrichment factor did not follow any definite trend, generally, stations 1 and 3 and cadmium and copper had relatively higher values.

Table 5
Enrichment Factor of the heavy metals in sediments.

Heavy Metal	Station 1	Station 2	Station 3
Cd	8156.87	144.15	197.49
Pb	58.01	0.65	0.95
Zn	51.68	0.73	1.16
Ni	7.23	0.10	0.18
Cu	499.33	7.59	9.44

3.1.2.5. Geo-accumulation index (Igeo)

The Geo-accumulation Index (Igeo) values are presented in Table 6. The values for Pb, Zn, Ni and Cu were less than 1 ($0 \leq I_{geo} \leq 1$) and are classified as Class 1 - unpolluted to moderately

polluted while all the Cd values were greater than the highest Class 6 (I_{geo} > 6); that is classified as extremely polluted.

Table 6
Geo-accumulation Index (Igeo) of the heavy metals in sediments.

Heavy Metal	Station 1	Station 2	Station 3
Cd (mg/kg)	15.694	12.744	17.460
Pb (mg/kg)	0.112	0.058	0.084
Zn (mg/kg)	0.099	0.064	0.102
Ni (mg/kg)	0.014	0.009	0.016
Cu (mg/kg)	0.961	0.671	0.835

3.1.2.6. Quantification of contamination (QoC)

The quantification of contamination values is presented in Table 7. Lead, Zn and Ni had negative values (-2146.4% to -79.8%) while Cd and Cu had positive values (70.1% to 98.9%) in all the stations. Stations 1 and 3, cadmium and copper had relatively higher values than the others while station 2 had relatively lower values in all the metals.

Table 7
Quantification of contamination (QoC) of the heavy metals in sediments.

Heavy Metal	Station 1	Station 2	Station 3
Cd (%)	98.7	98.4	98.9
Pb (%)	-79.8	-248.3	-138.1
Zn (%)	-101.9	-212.3	-96.3
Ni (%)	-1341.9	-2146.4	-1155.1
Cu (%)	79.1	70.1	76.0

3.2. Discussion

Lead (Pb) values were lower than 5.7 – 22.5 mg/kg recorded by Moslen *et al* (2018) in Azubia and Okujagu Creeks in Port Harcourt and 0.00 – 51.7 mg/kg recorded by Yawo *et al* (2022) in Okoro River, Eastern Obolo, Niger Delta. However, they are higher than 0.97 – 7.05 mg/kg recorded by Jire & Imeokparia (2018) in Warri River, Delta State and 4.7 – 7.9 mg/kg recorded by Kieri *et al* (2021) in Silver River, Bayelsa State. A recent study in the study area had values (6.16 – 12.07 mg/kg) within the same range (Chris & Anyanwu, 2023). All the values were within the acceptable limit of 85 mg/kg. The lowest and highest values were recorded in stations 2 and 1 respectively contrary to stations 1 and 3 recorded by Chris & Anyanwu (2023). This variation could be attributed to season rather than anthropogenic activities. The previous study (Chris & Anyanwu, 2023) was during the wet season, which could result in the transportation of contaminants downstream because station 2 was higher than station 1; while this study was in the dry season.

The copper (Cu) values were substantially lower than 473.19 – 596.73 mg/kg recorded by Chris & Anyanwu (2023) in the study area. This could be attributed to increased contaminant input as a result of increased runoff during the wet season. The spatial variation followed the same trend as Pb and could be attributed to the same factors. All the Cu values exceeded the acceptable limit (36 mg/kg) and were significantly different in the stations suggesting anthropogenic influence. Elsewhere in the Niger Delta, the values were lower. Jire & Imeokparia (2018) recorded 8.86 – 19.44 mg/kg in Warri River, Delta State, Kieri *et al* (2021) recorded 46.15 – 11.91 mg/kg in Silver River, Bayelsa State and Yawo *et al* (2022) recorded 5.9 – 37.6 mg/kg in Okoro River, Eastern Obolo, Niger Delta.

Cadmium (Cd) values were higher than 2.33 – 3.84 mg/kg previously recorded by Chris & Anyanwu (2023) in the study area during the wet season. Pollutants tend to be concentrated during the dry season due to little or reduced precipitation, low flow velocity, high temperatures and evapotranspiration (Ling *et al.,* 2017). All the Cd values exceeded the acceptable limit (0.8 mg/kg) while stations 1 and 3 were significantly higher than station 2; suggesting anthropogenic influence. Elsewhere in the Niger Delta, Moslen *et al* (2018) recorded lower values (0.00 – 0.60 mg/kg) in Azubia & Okujagu Creeks in Port Harcourt, Rivers State and Kieri *et al* (2021) recorded lower values (1.69 – 3.84 mg/kg) in Silver River, Bayelsa State. However, Jire & Imeokparia (2018) recorded higher values (4.14 – 15.92 mg/kg) in Warri River, Delta State.

Nickel (Ni) values were lower than the values recorded elsewhere in the Niger Delta. Jire & Imeokparia (2018) recorded 1.67 – 7.10 mg/kg in Warri River, Delta State while Kieri *et al* (2021) recorded 5.12 – 7.78 mg/kg in Silver River, Bayelsa State. Though all the Ni values were within the acceptable limit (3.5 mg/kg), stations 1 and 3 were also significantly higher than station 2 as observed in Cd; suggesting anthropogenic influence.

The Zinc (Zn) values were substantially lower than 209.02 – 246.41 mg/kg recorded by Chris & Anyanwu (2023) in the study area during the wet as observed in Cu. This could also be attributed to increased allochthonous input as a result of increased runoff during the wet season. Though all the Zn values were lower than the acceptable limit (140 mg/kg), stations 1 and 3 were significantly different from station 2 as in Cd and Ni; suggesting anthropogenic influence. Elsewhere in the Niger Delta, the values were higher. Moslen *et al* (2018) recorded 27.5 – 293.3 mg/kg in Azubia & Okujagu Creeks in Port Harcourt, Rivers State, Jire & Imeokparia (2018) recorded 17.74 – 73.64 mg/kg in Warri River, Delta State and Yawo *et al* (2022) recorded 8.60 – 84.50 mg/kg in Okoro River, Eastern Obolo, Niger Delta. However, Kieri *et al* (2021) recorded lower values (10.71 – 19.14 mg/kg) in Silver River, Bayelsa State.

The contamination factor values for Pb, Zn and Ni were less than 1; indicating a low degree while Cu was classified as a considerable degree ($3 \leq CF < 6$). These values were low compared to values recorded in the area by Chris & Anyanwu (2023); suggesting that the contamination levels of these metals in the sediments were minimal probably due to little or no allochthonous input during the dry season. However, contamination factor values for Cd were high (CF > 6) - very high degree; indicating that the environment was contaminated with Cd (Kieri *et al.,* 2021). The values were higher than the 23.30 – 38.42 recorded by Chris and Anyanwu (2023) in the study area. The high values could be attributed to anthropogenic input; concentrated by the dry season (Ling *et al* 2017). Stations 1 and 3 had relatively higher CF values based on the effects of human activities in the stations. The degree of contamination (DC) was classified as very high (Cd ≥ 24) and influenced by Cd as observed by Kieri *et al* (2021). However, the DC values were significantly lower than 2306.12 – 3811.37 recorded by Chris & Anyanwu (2023) in the study area probably due to allochthonous input during the wet season (Ling *et al* 2017). Stations 1 and 3 were relatively higher than station 2 as observed in CF. Kieri *et al* (2021) recorded CF values of less than 1 in all the metals evaluated in this study except Cd which was between 5.65 and 12.81 in Silver River, Bayelsa State. The DC was also lower. Cadmium is one of the most pervasive heavy metals in the Nigerian environment (Orisakwe, 2014).

The ecological risk (Er) values showed that Ni, Zn and Pb in station 2 posed low ecological risk; Pb in stations 1 and 3 posed moderate ecological risk while Cd posed a high ecological risk. However, Cu posed a very high ecological risk as observed in a previous study (Chris & Anyanwu, 2023). The Er values for Cd were relatively higher than 69.90 – 115.26 while that of Cd was relatively lower than 681.73 - 2983.64 recorded by Chris & Anyanwu (2023). All the PERI values posed a significantly high

ecological risk as observed by Chris & Anyanwu (2023). However, the PERI values (624.44 – 874.70) recorded in this study were influenced by Cu and Cd while the values (2682.16 – 4447.00) recorded by Chris & Anyanwu (2023) were influenced by Cu, Zn and Cd. Er and PERI in stations 1 and 3 were relatively higher suggesting anthropogenic influence. The Er and PERI values recorded in this study are a reflection of a high potential for ecological damage (Peter *et al.,* 2021).

All the Pollution Load Index (PLI) values exceeded the threshold value of 1 by a wide margin; suggesting serious pollution of anthropogenic origin (Barakat *et al*. 2020; Chris & Anyanwu, 2023). Values > 1 are indications that the area was undergoing progressive deterioration (Harikumar & Jisha, 2010). The PLI values (1465.46 – 2860.50) recorded by Chris and Anyanwu (2023) in the study area were lower probably due to dilution during the wet season (Ling *et al.,* 2017). Elsewhere in the Niger Delta, relatively lower values were recorded. Moslen *et al* (2018) recorded 0.00 – 1.14 in Azubia & Okujagu Creeks in Port Harcourt, Rivers State, Kieri *et al* (2021) recorded 1.23 – 1.34 in Silver River, Bayelsa State and Yawo *et al* (2022) recorded 0.42 – 1.77 in Okoro River, Eastern Obolo, Niger Delta.

The enrichment factor (EF) has been extensively used to differentiate between natural and anthropogenic heavy metal sources in the sediment (Ghrefat *et al.* 2011; Ismail & Naji, 2011). The enrichment factor values for Pb, Zn and Ni in stations 2 and 3 were <2 indicating the metals were purely from the natural weathering process (Wang *et al.,* 2008). The Er factor for Ni (station 1) and Cu (stations 2 and 3) were > 2 while Pb and Zn (Station 1), Cu (station 1) and all of Cd were >40. Enrichment factors > 1.5 is an indication that the metal involved was influenced by anthropogenic sources or that a greater portion of the metal is from weathering process that is not natural (Wang *et al*. 2008). Generally, stations 1 and 3 and cadmium and copper had relatively higher values, which could be attributed to anthropogenic influence. The most important sources of metal contamination in water and sediments around coastal areas are municipal and/or industrial wastewater discharges (Zarezadeh *et al.,* 2017) and artisanal crude oil refining wastes in Niger Delta (Ikezam *et al.,* 2021). Chris and Anyanwu reported the enrichment of sediments by Cd, Zn and Cu in a previous study in the area, which was attributed to human activities, especially artisanal crude oil refinery. Elsewhere in the Niger Delta, Moslen *et al* (2018) recorded 0.02 – 3.09 in Azubia & Okujagu Creeks in Port Harcourt, Rivers State and Jire & Imeokparia (2018) recorded 0.11 – 3.69 in Warri River, Delta State.

The Geo-accumulation Index (Igeo) values showed the sediments were not polluted by Pb, Zn, Ni and Cu because they are lower than the baseline contaminated zone (Zarezadeh *et al.,* 2017). However, the sediments were extremely polluted by Cd (>6) suggesting anthropogenic influence (Muller, 1969). This was also confirmed by the relatively higher values recorded is stations 1 and 3 which witnessed most of the anthropogenic activities. Chris and Anyanwu in a related study in the area also reported the sediment was extremely polluted by Cd in the three stations. Elsewhere in the Niger Delta, Moslen *et al* (2018) recorded 0.00 – 0.62 in Azubia & Okujagu Creeks in Port Harcourt, Rivers State and Jire and Yawo *et al* (2022) recorded –0.63 – 0.77 in some of the metals evaluated in this study in Okoro River, Eastern Obolo, Niger Delta.

The Quantification of Contamination Index (QoC) was used to determine possible sources of heavy metals in the sediments (Zarezadeh *et al.,* 2017). This index mainly expressed as a percentage, was applied to identify the effects of anthropogenic and geogenic sources on the level of metals in sediments and differentiate them (Zarei *et al.,* 2014). Out of the 5 heavy metals evaluated, 3 (Pb, Zn, Ni) were negative; ranging from -2146.4% to -79.8% while Cd and Cu were negative; ranging from 70.1% to 98.9%. Negative values indicate metals of natural sources while positive values are attributable to anthropogenic sources based on the QoC index values (Malvandi, 2021). Cd and Cu exceeded geogenic levels in the 3 stations which could be attributed to anthropogenic sources, especially in stations 1 and 3. Human activities such as shipping and transport, domestic wastes and wastewater, agriculture, industrial wastewater from dockyards and other coastal activities like artisanal refinery were observed in the study area and have been reported to contribute to heavy metals in sediments (Kazemi *et al.,* 2012; Zarezadeh *et al.,* 2017; Ite *et al.,* 2018; Onuh *et al.,* 2021).

4. Conclusion

In conclusion, the sediments of the Isaka–Bundu mangrove swamp were polluted by toxic heavy metals. Cadmium and copper exceeded permissible limits while lead, zinc and nickel were within limits. Stations 1 and 3 recorded significantly higher values indicating anthropogenic influence. The assessment indices showed that the sediments were at various levels of heavy metal pollution mainly influenced by copper and cadmium. The levels of these toxic metals in the sediments are detrimental to humans and aquatic biota.

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