

ASSESSMENT OF HEAVY METALS IN SEDIMENTS AND ASSOCIATED ECOLOGICAL RISKS IN IKWU RIVER, UMUAHIA, NIGERIA

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Abstract. Sediments can act as pollutant sink as well as source of secondary contamination in aquatic ecosystems. The pollution characteristics of eight heavy metals in the sediments of Ikwu River, Umuahia were investigated using eight assessment indices. The study was carried out between January and June 2022 in three stations. Results showed that cadmium exceeded permissible limit, copper exceeded limit only in February 2022 while others were within limits. The values in Stations 2 and 3 were slightly higher, attributed to localized anthropogenic influence; though other human activities in the watershed especially agriculture were not ruled out in the area. Different levels of heavy metal pollution were observed in the sediments as indicated by the indices but Cd was the principal pollutant. The indices indicated the following – Contamination Factor: Zn and Cu (moderate) and Cd (very high), Degree of Contamination (very high), Ecological Risk: Cd (high) and Cu (considerable), Potential Ecological Risk (high), Pollution Load Index (>1), Enrichment Factor: Zn and Cu (moderate) and Cd (extremely high), Geo-accumulation Index: Cd (very highly polluted) and Quantification of Contamination: Cd and Cu (anthropogenic). The sediments were polluted with toxic metals that may be detrimental to humans and aquatic biota.

Keywords: sediment, heavy metal, indices, anthropogenic, pollution.

1. Introduction

Sediments play an important role in aquatic ecosystem and greatly influence its services and functions; aquatic biota prefers certain sediment quality and quantity depending on their life stages (Ali,

Muhammed, 2023). Sediment serves as a pollutant sink and under certain environmental circumstances; pollutants (including heavy metals) in the sediments are re-suspended; thereby serving as a source of secondary pollution in the water column (Liang et al., 2015; Pejman et al., 2015). Heavy metals are among the most hazardous pollutants in the aquatic environment (Odekina et al., 2021; Davies et al., 2022) and their harmful nature, persistence and accumulation potential is attracting attention globally (Guan et al., 2014; Pandiyan et al., 2021; Anyanwu et al., 2022a). Risks associated with heavy metal contamination in the aquatic ecosystems could persist for a long time because of their long residence time and low biodegradability when compared to other organic substances (Kumar et al., 2020). Evaluation of heavy metal concentration does not give enough information on their level of contamination and toxicity in the environment (Wei et al., 2019; Kumar et al., 2020). Bioavailability and eco-toxicity are the life-threatening factors of heavy metal pollution in the environment (Jacob et al., 2018). As a result, pollution indices are used to assess the toxicity and environmental contamination of metals; despite some inherent challenges (Masindi and Muedi, 2018; Davies et al., 2022; Ahirvar et al., 2023). Researchers have evaluated heavy metal contamination in sediments using different assessment indices like contamination factor, contamination degree, ecological risk factor, potential ecological risk index,

pollution load index, geo-accumulation index, degree of contamination, enrichment factor and quantification of contamination (Ogbeibu et al., 2014; Shirani et al., 2020; Amin et al., 2021; Malvandi, 2021; Moldovan et al., 2022; Ahirvar et al., 2023). Heavy metals enter the waterbodies through two major ways – geogenic process and anthropogenic activities (Pandiyan et al., 2021) and most of the metals get deposited in the sediment after entry; contributing to elevated concentration in the sediment compared to the water column (Liu et al., 2018; Shyleshchandran et al., 2018). Assessing heavy metal pollution in sediments is very necessary for the ecological protection of waterbodies (Li et al., 2022) because such pollution is becoming a major contributor to environmental risks in aquatic ecosystems globally (Mohajane, Manjoro, 2022). Ikwu River is located in the rural area and utilized for various purposes (Anyanwu et al., 2022b) but is being subjected to increasing anthropogenic pressures. Therefore, the objective of this study is to appraise some heavy metals in sediments of Ikwu River, Umuahia, Nigeria using index method.

2. Materials and Methods

2.1. Study area

Ikwu River is located in Umuire Community, Umuahia, Nigeria within $5^{\circ}34'11.988''$ –

$5^{\circ}34'48.000''$ N and $7^{\circ}28'44.400''$ – $7^{\circ}28'52.764''$ E (Fig. 1). The river went through Umuire and Umuegwu Okpula communities and discharged into the Imo River Basin. The study stations were selected based on accessibility and observed human activities. The reference site was Station 1, located upstream on the right of the Uzuakoli road. No activities were observed in the station during the study. However, evidence of periodic watering of cattle was observed. On the left side was Station 2, about 350 metres south of Station 1. Human activities were more intense some distance upstream before the sampling point. Some of the activities include washing of vehicles, children swimming, bathing, abstraction of drinking water, washing of fruits and vegetables by market women as well as low scale sand mining. Station 3 was about 430 meters south of Station 2 within Umuire community. Due to the location of the station, it is a major source of water for most domestic activities – abstraction of drinking water, washing of clothes. Other activities in the station include bathing, swimming and low level sand mining. The community disposes their solid wastes on the bank of the river, effluents and stormwater from the community are discharged into the river during rainfall events.

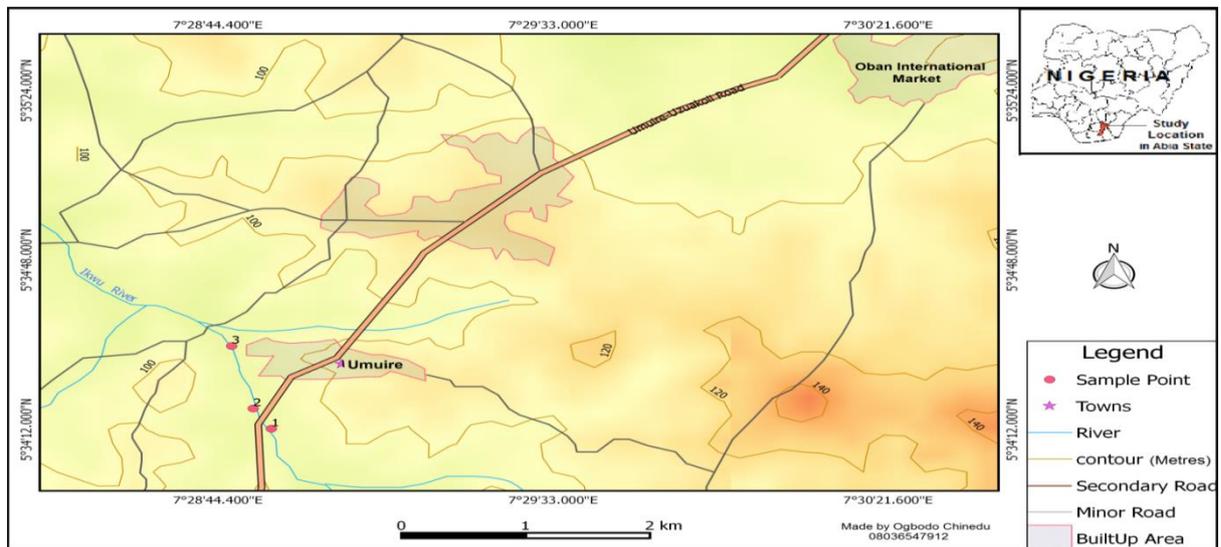


Fig. 1. Map of Umuahia, Southeast Nigeria showing the Sampling stations of Ikwu River

2.2. Sediment Samples

The samples were collected from the surface sediments of Ikwu River on monthly basis between

January and June 2022. The samples were collected with hand trowel, wrapped in black polythene bags and transported in ice chests to the laboratory for analysis. The collected samples were dried at 45°C in an electric

oven to attain constant weight, pounded into powder with mortar and pestle. The ground sample (0.05 g) was digested with mixed acid (5 mL HCl, 3 mL HNO₃, 7 mL HF, 0.25 mL HClO₄) in a Teflon beaker. The solution were filtered with Whatman filter paper after digestion and made up to 25 mL with deionized water. A total of eight heavy metals (Fe, Cd, Ni, Mn, Pb, Cu, Cr, and Zn) in the sediments were determined with UNICAM Solaar 969 atomic absorption spectrometer (AAS) that uses acetylene-air flame. The chemicals and reagents used throughout the study were Analytical grade.

2.3. Statistical Analysis

The heavy metal results were summarized with Microsoft Excel. Significant differences in the concentrations of the metals in the sediments among the stations were tested using single-factor ANOVA. The source of significant difference at p<0.05 was determined with 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:

2.4.1. Contamination Factor (CF)

Contamination factor is expressed as the ratio of each metal to the background level.

$$C_F = \frac{C_{\text{metal}}}{C_{\text{background}}} \text{ (Hakanson, 1980),} \quad (1)$$

where C_{metal} is the mean metal content in the sample, $C_{\text{background}}$ is the mean natural background value of the metal (Table 1). C_F has been classified into low degree ($CF < 1$), moderate degree ($1 \leq CF < 3$), considerable degree ($3 \leq CF < 6$), and very high degree ($CF > 6$) for the assessment of pollution from a single metal for a certain duration (Ali et al., 2016).

risks posed by the presence of multiple trace metals in the sediment. Hakanson (1980) proposed the index while Guan et al. (2014) and Essien et al. (2019) have applied it in their studies. The equation is given by

$$Cd = \sum_{i=1}^n CF_i, \quad (2)$$

where CF_i is the contamination factor of each metal. Based on Hakanson (1980), degree of contamination (Cd) can be classified as < 6 for low degree of contamination, $6 \leq - < 12$ (moderate degree of contamination), $12 \leq - < 24$ (considerable degree of contamination) and ≥ 24 (very high degree of contamination).

2.4.3. 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.

2.4.3.1. Ecological risk factor (Er)

Ecological risk factor (Er) was calculated using equation 3 as recommended by Edori and Kpee (2017).

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

where T_r is the toxic-response factor of a given metal while C_f is the contamination factor for each of the metals. T_r values are Pb (5), Zn (1), Ni (5), Mn (1), Cr (2), Cd (30), and Cu (5). T_r for iron (Fe) is not available. Ecological risk factor is classified as < 40 (low), $40 \leq - < 80$ (moderate), $80 \leq - < 160$ (considerable), $160 \leq - < 320$ (high) and ≥ 320 (very high) (Mugoša et al., 2016).

2.4.3.2. Potential Ecological Risk Index (PERI)

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

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

where n is for the number of heavy metals evaluated while, E_r is the single index of the ecological risk factor.

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

Table 1

Geochemical background value (Bn), mg/kg (Guan et al., 2014)

Metals	Cd	Pb	Zn	Ni	Cu	Fe	Cr	Mn
Values	0.10	21.00	65.40	31.00	22.50	3850	67.3	850

2.4.2. Degree of Contamination (Cd)

Degree of contamination (Cd) is the sum of all contamination factors, which expresses the environmental

2.4.4. Pollution load index (PLI)

PLI was evaluated using the formula proposed by Tomilson et al. (1980).

$$PLI = (CF_1 \times CF_2 \times CF_3 \dots \times CF_n)^{1/n}, \quad (5)$$

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).

2.4.5. Enrichment Factor (EF)

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 of contamination in diverse environmental component (Nowrouzi, Pourkhabbaz, 2014). It can also be used confirm whether the heavy metal contamination was of anthropogenic sources (Jahan, Strezov, 2018). It is calculated using:

$$EF = \frac{C_n/C_{ref} \text{ sample}}{B_n/B_{ref}}, \quad (6)$$

where C_n is the concentration of metal evaluated in the sample, C_{ref} is the reference material concentration, B_n is the background level of the evaluated metal while B_{ref} is the reference element concentration. Abdullah et al. (2020) classified EF into five categories viz: < 2 (Depletion to mineral enrichment), $2 \leq EF < 5$ (Moderate enrichment), $5 \leq EF < 20$ (Significant enrichment), $20 \leq EF < 40$ (Very high enrichment) and $EF > 40$ (Extremely high enrichment). Enrichment factor values close to or < 1 is an indication of heavy metals from natural process while enrichment factor > 1 point to anthropogenic sources (Habib et al., 2018; Jahan, Strezov, 2018).

2.4.6. 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). It has been used in sediment contamination assessments (Islam et al., 2014; Ahirvar et al., 2023). It is calculated as:

$$I_{geo} = \log_2 \frac{C_n}{1.5 \times B_n} \quad (\text{Muller, 1969}), \quad (7)$$

where C_n is the mean concentration of each heavy metal in the sediment. B_n is the reference value (Table 1). A factor of 1.5 was applied to accommodate variation in the background value. Seven classes was designated for I_{geo} index by Abdullah et al. (2020): ≤ 0 is for class 0

signifying Unpolluted, $0 \leq - \leq 1$ is class 1 (Unpolluted to moderately polluted), $1 \leq - \leq 2$ is for class 2 (Moderately polluted), $2 \leq - \leq 3$ is for class 3 (Moderately to strongly polluted), $3 \leq - \leq 4$ is for class 4 (Strongly polluted), $4 \leq - \leq 5$ is for class 5 (Strongly to extremely polluted) and > 6 is for class 6 (Extremely polluted).

2.6.7. Quantification of contamination (QoC)

The Quantification of Contamination (QoC) index was used to evaluate whether the source of heavy metal contamination is anthropogenic or natural (Zarei et al., 2014). The index was calculated using equation 8:

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

where C_i is the mean concentration 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 of natural sources while positive values are attributable to anthropogenic sources (Malvandi, 2021).

3. Results and Discussion

3.1. Sediment Heavy Metal content

The summary of the heavy metal concentrations in the sediments are presented in Table 2. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life was used as standard for evaluating the metals (CCME, 2002). The heavy metals did not show any significant differences ($p > 0.05$) in the stations. Stations 2 and 3 also had relatively higher mean values though not significant; reflecting anthropogenic activities – bathing, washing of motorcycles, tricycles and cars, children swimming, washing of clothes, abstraction of drinking water, washing of fruits and vegetables by market women, sand mining and solid wastes disposal in the stations. The values of chromium (Cr) were 7.41–30.11 mg/kg and within 37.3 mg/kg set by CCME (2002). Station 1 had lowest value in January 2022; attributable to little or no allochthonous input in the dry months (Haque et al., 2019) while station 2 had the highest in February 2022; attributed to the effect of the first rain of the year few days before sampling. Ramos et al. (2015) made similar observations in Enxoé temporary River in southern Portugal after the first major rainfall following a period of dryness. The chromium (Cr) had

higher values when compared to 1.10–2.54 mg/kg recorded by Amodu et al. (2021) in River Evbuarhue in Edo State, Nigeria and 0.00–1.60 mg/kg recorded by Chinemelu and Okumoko (2022) in Warri River, Niger

Delta, Nigeria. However, Ibezim-Ezeani and Owhonda (2021) recorded value as high as 136.6 mg/kg in a station associated with metal works in Sombreiro River, Rivers State, Nigeria.

Table 2

Heavy Metal Concentration in the Sediments of Ikwu River, Umuahia, Nigeria

Heavy Metal, mg/kg	Station 1	Station 2	Station 3	F – value	CCME (2002)
Cr	13.42±4.37 (7.41–19.70)	15.98±8.22 (8.77–30.11)	17.06±7.13 (9.6–28.4)	0.46 P> 0.05	37.3
Cd	6.95±1.78 (3.33–10.61)	7.25±2.84 (3.39–10.74)	8.32±3.75 (5.01–15.33)	0.32 p > 0.05	0.6
Ni	4.16±0.22 (1.75–6.51)	4.38±1.72 (1.88–6.66)	4.95±2.55 (2.17–9.46)	0.24 P > 0.05	–
Pb	9.45±2.94 (4.68–13.37)	11.27±4.78 (4.85–17.41)	12.09±4.59 (7.33–19.73)	0.63 P > 0.05	35.0
Fe	108.08±43.39 (51.20–174.00)	112.55±47.01 (48.3–175.5)	113.75±45.29 (55.6–177.0)	0.03 P > 0.05	–
Mn	42.17±14.20 (20.10–59.4)	45.7±17.35 (19.30–73.40)	48.47±12.21 (28.6–66.10)	0.28 P > 0.05	–
Zn	72.77±21.84 (38.60–96.10)	74.63±26.54 (30.40–98.70)	75.48±21.32 (40.70–98.30)	0.02 P > 0.05	123.0
Cu	27.48±14.24 (17.30–55.40)	28.85±19.77 (11.30–66.70)	31.78±15.12 (18.00–58.30)	0.11 P > 0.05	35.7

CCME (2002) = Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.

The Cadmium (Cd) values were 3.33–15.33 mg/kg. All the cadmium (Cd) values exceeded the limit (0.6 mg/kg) set by CCME (2002). This could be attributed to anthropogenic activities in the watershed especially agriculture (Audu et al., 2022). Fertiliser and pesticides are common sources of cadmium in waterbodies (Cui et al., 2019). Station 1 had the lowest value in January 2022; attributable to little or no allochthonous input during the dry months (Haque et al., 2019). On the other hand, highest recorded in station 3 in June 2022 could be linked materials washed into the station during the wet months (Ke et al., 2017). Dumping of refuse on the banks of the river in the station could also be a contributor. Cd pollution was also recorded by Ibezim-Ezeani and Owhonda (2021) and Nwazue et al. (2022), which was attributed to both geogenic and anthropogenic sources. Orisakwe (2014) reported Cd as one of the most pervasive metals in the Nigerian environment. The concentrations recorded were higher than values in related studies in Nigeria. Offor and Okerulu (2019) recorded 0.05–0.18 mg/kg in Obii stream, Ufuma, Anambra State, Nigeria, 0.07–1.10 mg/kg recorded by Amodu et al (2021) in River Evbuarhue in Edo State, Nigeria, Ibezim-Ezeani and Owhonda (2021) recorded 0.04–5.29 mg/kg in Sombreiro River, Rivers

State, Nigeria, 0.00–0.79 mg/kg recorded by Chinemelu and Okumoko (2022) in Warri River, Niger Delta, Nigeria and Nwazue et al (2022) recorded 0.10–9.70 mg/kg in River Iyiudene, Abakaliki, Ebonyi State, Nigeria.

The values of nickel (Ni) were 1.75–9.46 mg/kg. CCME (2002) has no limit for Ni. Station 1 in January 2022 and station 3 in June 2022 had the lowest and highest values respectively as observed in Cd. The recorded values were higher than values recorded in related studies in Nigeria. Offor and Okerulu (2019) recorded 0.11–0.88 mg/kg in Obii stream, Ufuma, Anambra State, Nigeria, 1.16–2.10 mg/kg recorded by Amodu et al (2021) in River Evbuarhue in Edo State, Nigeria, Ibezim-Ezeani and Owhonda (2021) recorded 0.38–0.96 mg/kg in Sombreiro River, Rivers State, Nigeria, 0.00–0.69 mg/kg recorded by Chinemelu and Okumoko (2022) in Warri River, Niger Delta, Nigeria and Nwazue et al. (2022) recorded 0.10–7.80 mg/kg in River Iyiudene, Abakaliki, Ebonyi State, Nigeria.

The lead (Pb) values were 4.68–19.73 mg/kg. All the values were lower than 35.0 mg/kg set by CCME (2002). Station 1 in January 2022 and station 3 in June 2022 had the lowest and highest values

respectively as observed in Cd and Ni. The recorded values were higher than some values recorded in related studies in Nigeria. Offor and Okerulu (2019) recorded 0.00–0.56 mg/kg in Obii stream, Ufuma, Anambra State, Nigeria, 0.25–0.53 mg/kg recorded by Amodu et al. (2021) in River Evbuarhue in Edo State, Nigeria, Ibezim-Ezeani and Owhonda (2021) recorded 0.03–13.97 mg/kg in Sombreiro River, Rivers State, Nigeria, 0.00–3.36 mg/kg recorded by Chinemelu and Okumoko (2022) in Warri River, Niger Delta, Nigeria and Nwazue et al (2022) recorded 1.30–9.30 mg/kg in River Iyiudene, Abakaliki, Ebonyi State, Nigeria.

The Iron (Fe) values were 28.42–177.00 mg/kg. CCME (2002) has no limit for Fe. Iron exhibited a different trend. Station 2 had the lowest value in May 2022; which could be due to dilution as a result of the onset of the wet season. However, station 3 had the highest in January 2022; attributable to concentration due to dry season. Some parameters get concentrated in water and sediments during the dry season due to high temperatures and evapotranspiration coupled with reduced rainfall and associated reduction in flow velocity (Etesin et al., 2013; Ling et al., 2017). The recorded Fe values were higher than some values recorded in related studies in Nigeria. Offor and Okerulu (2019) recorded 16.62–91.97 mg/kg in Obii stream, Ufuma, Anambra State, Nigeria, 11.76–12.97 mg/kg recorded by Amodu et al. (2021) in River Evbuarhue, Edo State, Nigeria. However, some higher values were also recorded – Ibezim-Ezeani and Owhonda (2021) recorded 129.80–3111.70 mg/kg in Sombreiro River, Rivers State, Nigeria and 56.77–1250.22 mg/kg recorded by Chinemelu and Okumoko (2022) in Warri River, Niger Delta, Nigeria.

The manganese (Mn) values were 19.30–73.40 mg/kg. CCME (2002) has no limit for Mn. Station 2 had the lowest and highest values in May and February 2022 respectively probably due to rainfall. There was dilution in May 2022 as a result of the onset of the rains while higher value recorded in February 2022 could be due to introduction from the watershed as a result of the first major rain of the year (Ramos et al., 2015; Ling et al., 2017). Akintade et al (2022) recorded lower values (10.32–13.36 mg/kg) in Asa River, Ilorin, Kwara State, Nigeria.

The zinc (Zn) values were 30.40–98.70 mg/kg. All the values were within the limit (123.0 mg/kg) set by CCME (2002). Station 2 had the lowest and highest values in May and February 2022 respectively probably due to rainfall as observed in Mn. Lower levels were observed in related studies in Nigeria. Offor and Okerulu (2019) recorded 0.79–19.80 mg/kg

in Obii stream, Ufuma, Anambra State, Nigeria, 4.52–5.49 mg/kg recorded by Amodu et al. (2021) in River Evbuarhue, Edo State, Nigeria, 0.91–9.22 mg/kg recorded by Chinemelu and Okumoko (2022) in Warri River, Niger Delta, Nigeria, 11.10–38.50 mg/kg recorded by Nwazue et al. (2022) in River Iyiudene, Abakaliki, Ebonyi State, Nigeria, 32.29–37.11 mg/kg recorded by Akintade et al (2022) in Asa River, Ilorin, Kwara State and 7.50–79.00 mg/kg recorded by Olutona (2023) in Asunla stream Ile – Ife, Osun State, Nigeria.

The Copper (Cu) values were 11.30–66.70 mg/kg and within the limit (35.7 mg/kg) set by CCME (2002). However, February 2022 had values higher than the limit throughout the stations; due to introduction from the watershed as a result of the first major rain of the year (Ramos et al., 2015; Ling et al., 2017). Station 2 had the lowest and highest values in May and February 2022 respectively probably due to rainfall as observed in Mn and Zn. Lower levels were observed in related studies in Nigeria. Offor and Okerulu (2019) recorded 0.05–0.51 mg/kg in Obii stream, Ufuma, Anambra State, Nigeria, 3.72–7.46 mg/kg recorded by Amodu et al. (2021) in River Evbuarhue, Edo State, Nigeria, 0.21–5.51 mg/kg recorded by Chinemelu and Okumoko (2022) in Warri River, Niger Delta, Nigeria, 0.10–13.30 mg/kg recorded by Nwazue et al. (2022) in River Iyiudene, Abakaliki, Ebonyi State, Nigeria, 47.68–47.71 mg/kg recorded by Akintade et al (2022) in Asa River, Ilorin, Kwara State and 5.60–25.00 mg/kg recorded by Olutona (2023) in Asunla stream Ile – Ife, Osun State, Nigeria.

3.2. Assessment Indices

3.2.1. Contamination Factor (CF) and Degree of contamination (Cd)

The contamination factor values are presented in Table 3. The contamination factor values for Cr, Ni, Pb, Fe and Mn were < 1; an indication of low degree of contamination while Zn and Cu were classified as moderate degree ($1 \leq < 3$). These values were low to moderate suggesting minimal anthropogenic impact (Offor and Okerulu, 2019; Olutona, 2023). However, the Cd values (69.45–83.20) revealed very high degree of contamination (> 6); suggesting environmental input beyond natural level (Kieri et al., 2021; Audu et al., 2022). Though all the CF recorded in Obii stream sediment in Ufuma, Anambra State, Nigeria were less than 1, the Cd-CF (0.52) was higher (Offor and Okerulu, 2019). Kieri et al. (2021) recorded CF values

less than 1 in all the metals evaluated in this study except Cd that was between 5.65 and 12.81 in Silver River, Bayelsa State. Elsewhere Cd-CF values were also highest – Ibezim-Ezeani and Owhonda (2021) in Sombreiro River, Rivers State, Nigeria and Audu et al. (2022) in selected waterbodies of south senatorial district of Niger State, Nigeria

because its toxicity coefficient is about 3 to 30 times greater than other heavy metals (Li et al., 2022; Said et al., 2022). The value recorded in Obii stream sediment by Offor and Okerulu (2019) in Ufuma, Anambra State, Nigeria was very low (1.04).

Table 3

Table 4

Contamination Factor (CF) and Degree of contamination (DC) of the heavy metals in the sediments

Heavy Metal, mg/kg	Station 1	Station 2	Station 3
Cr	0.20	0.24	0.25
Cd	69.45	72.53	83.20
Ni	0.13	0.14	0.16
Pb	0.45	0.54	0.58
Fe	0.03	0.03	0.03
Zn	1.11	1.14	1.15
Cu	1.22	1.28	1.41
Mn	0.05	0.05	0.06
DC	264.11	277.38	286.52

The sum of the contamination factors is the degree of contamination (DC) and ranged between 264.11 and 286.52. The degree of contamination (DC) was very high ($DC \geq 24$) compared to moderate (≤ 18) recorded by Audu et al (2022). The CFs and DC were influenced by Cd as observed by Kieri et al. (2021). The danger of cadmium in the Nigerian environment has been highlighted (Orisakwe, 2014).

3.2.2. Ecological Risk (Er) and Potential Ecological Risk Index (PERI)

The ecological risk and Potential Ecological Risk Index values are presented in Table 4. The ecological risk (Er) levels showed that Cr, Ni were low (< 40) while Pb, Zn and Mn were moderate ($40 \leq - < 80$) ecological risks. However, Cu and Cd were considerable ($80 \leq - < 160$) and high ($160 \leq - < 320$) ecological risks respectively. For Cu, these values do not constitute much ecological threat since they were all lower than the limit except in February 2022. However, Cd was quite different because all the values exceeded acceptable limit set by CCME (2002). When the concentration exceeds the acceptable limit, the pollution rate could result in deleterious consequences on aquatic flora and fauna (Calmuc et al., 2021; Muhammad et al., 2022). Cd, at low concentrations could result in serious damage to biological health

Ecological Risk (Er) of heavy metals in the sediments

Heavy Metal, mg/kg	Station 1	Station 2	Station 3
Cr	26.84	31.96	34.12
Cd	208.35	217.59	249.60
Ni	20.80	21.90	24.75
Pb	47.25	56.35	60.45
Zn	72.77	74.63	75.48
Cu	137.40	144.25	158.90
Mn	42.17	45.70	48.47
PERI	320.39	342.83	368.05

All the PERI values were within $300 < PERI < 600$ indicating high ecological risk (Mwakisunga et al., 2021). The Er and PERI values were a reflection of a high potential for ecological damage (Peter et al., 2021; Usman et al., 2021).

3.2.3. Pollution Load Index (PLI)

All the PLI value exceeded the threshold value of 1 by wide margin and ranged between were 1366.80 (station 1) and 1860.49 (station 3). The values were very higher than the threshold value of 1; suggesting serious pollution of anthropogenic origin (Barakat et al. 2020; Chris and Anyanwu, 2023). Harikumar and Jisha (2010) observed that PLI values > 1 are indications that the sediment was deteriorating progressively. Very low PLI value (0.00545) was recorded in Obii stream, Ufuma, Anambra State, Nigeria by Offor and Okerulu (2019).

3.2.4. Enrichment Factor

The enrichment factor values are presented in Table 5. Natural and anthropogenic sources of heavy metals in sediments can be differentiated by using Enrichment factor (Ghrefat et al. 2011; Ismail and Naji, 2011). Values recorded for Cr, Ni, Pb, Fe and Mn in all the stations were < 2 ; indicating that the metals were purely of geogenic sources (Wang et al., 2008).

Zn and Cu reflected moderate enrichment while Cd values reflected extremely high enrichment as observed by Audu et al. (2022). Generally, an enrichment factor > 1 suggest that the metal concerned is of anthropogenic origin (Wang et al. 2008; Cevik et al., 2009). The results of Zn, Cu and Cd in all the stations could be attributed to the fact that some heavy metals can have either natural or anthropogenic enrichment, depending on location (Mohajane and Manjoro, 2022). Chinemelu and Okumoko (2022) recorded EF of 0.65 to 1.93 in Warri River, Niger Delta, Nigeria.

Table 5

Enrichment Factor of the heavy metals in the sediments

Heavy Metal, mg/kg	Station 1	Station 2	Station 3
Cr	0.45	0.54	0.58
Cd	157.65	164.65	188.87
Ni	0.30	0.32	0.36
Pb	1.02	1.22	1.31
Fe	0.06	0.07	0.07
Zn	2.53	2.59	2.62
Cu	2.77	2.91	3.21
Mn	0.11	0.12	0.13

3.2.5. Geo-accumulation Index (Igeo)

The Geo-accumulation Index (Igeo) values are presented in Table 6. The values were generally less than 1 ($0 \leq I_{geo} \leq 1$) indicating unpolluted environment. However, all the Cd values pointed to very highly polluted environment ($I_{geo} > 6$) based on Singh et al. (2002); suggesting anthropogenic influence (Muller, 1969). Audu et al. (2022) recorded moderate to strong polluted levels in selected waterbodies of south senatorial district of Niger State, Nigeria.

Table 6

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

Heavy Metal, mg/kg	Station 1	Station 2	Station 3
Cr	0.040	0.048	0.051
Cd	13.938	14.556	16.697
Ni	0.027	0.028	0.032
Pb	0.090	0.108	0.116
Fe	0.006	0.006	0.006
Zn	0.223	0.229	0.232
Cu	0.245	0.257	0.283
Mn	0.010	0.011	0.011

3.2.6. Quantification of contamination (QoC)

The QoC values are presented in Table 7. The QoC expressed as percentage was used to identify the possible sources of heavy metals in the sediments (Zarei et al., 2014; Zarezadeh et al., 2017). Five (5) metals – Pb, Ni, Cr, Fe and Mn were negative; ranging from – 3462.18 to – 73.70 % while Cd, Zn and Cu were positive; ranging from 10.13 to 98.90 %. Negative values indicate metals of geogenic sources while positive values were attributable to anthropogenic sources based on the QoC index values (Malvandi, 2021). Cd, Zn and Cu exceeded geogenic levels in all the stations; attributed to activities especially agricultural activities in the watershed (Cui et al., 2019; Audu et al., 2022).

Table 7

Quantification of contamination (QoC) of the heavy metals in the sediments

Heavy Metal, %	Station 1	Station 2	Station 3
Cd	98.56	98.62	98.90
Pb	-122.22	-86.34	-73.70
Zn	10.13	12.337	13.35
Ni	-645.19	-607.76	-526.26
Cu	18.22	22.10	29.20
Cr	-401.49	-321.15	-294.49
Fe	-3462.18	-3320.70	-3284.62
Mn	-1915.65	-1759.96	-1653.66

4. Conclusion

In conclusion, the sediments of the Ikwu River were polluted by toxic heavy metals. Cadmium exceeded permissible limit, Cu exceeded limit only in February 2022 while others were within limits. Cadmium was influenced by anthropogenic activities in the watershed especially agriculture. Stations 2 and 3 recorded higher values in all the metals suggesting anthropogenic influence. The indices used showed that the sediments were at different levels of heavy metal contamination basically influenced by copper and cadmium. The level of cadmium in the sediments is considered detrimental to humans and aquatic biota.

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