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Karakteristik logam berat dan penilaian ancaman ekologi dalam air dan sedimen di Eniong Creek, Delta Niger, Nigeria

Heavy metal characteristics and ecological threat assessment in water and sediments of Eniong Creek, Niger Delta, Nigeria

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Abstrak

Karakteristik logam berat dan penilaian ancaman ekologis dalam air dan sedimen Eniong Creek, Nigeria dipelajari antara Agustus 2022 dan Januari 2023 di 3 stasiun. Tujuh logam berat dianalisis dengan metode standar dan dibandingkan dengan standar mutu. Ancaman ekologi dinilai dalam air menggunakan dua indeks pencemaran logam, sementara enam indeks penilaian kualitas sedimen digunakan untuk mengakses kualitas sedimen.Hasil penelitian menunjukkan bahwa konsentrasi rata-rata nikel, tembaga, kadmium, dan seng dalam sampel air melebihi batas yang diizinkan yang ditetapkan oleh peraturan kualitas lingkungan Nasional (air permukaan dan air tanah) untuk kehidupan akuatik, sedangkan tembaga dan kadmium melebihi batas yang diizinkan yang ditetapkan oleh standar kualitas sedimen Kanada untuk perlindungan kehidupan akuatik dalam sedimen di semua stasiun. Nilai indeks pencemaran logam berat (HPI) melebihi ambang batas (100) di seluruh stasiun, berkisar antara 469,53 dan 686,74. Sedangkan indeks pencemaran komprehensif (CPI) berkisar antara 1,405 dan 1,854, menunjukkan air terkontaminasi sedang. Indeks sedimen menunjukkan bahwa kadmium dan tembaga merupakan polutan logam utama. Indeks tersebut menunjukkan hal berikut: faktor kontaminasi - tembaga (sedang) dan kadmium (sangat tinggi), tingkat kontaminasi (sangat tinggi); risiko ekologi - kadmium dan tembaga (tinggi) sedangkan timbal dan seng tergolong sedang; potensi risiko ekologi (tinggi); kuantifikasi kontaminasi - kadmium dan tembaga (antropogenik); indeks akumulasi geografis - kadmium (sangat tercemar). Studi tersebut mengungkapkan bahwa badan air dan sedimen tercemar akibat aktivitas antropogenik.

Kata Kunci: Air; Eniong Creek; Logam Berat; Nigeria; Sedimen

Abstract

Heavy metal characteristics and ecological threat assessment in water and sediments of Eniong Creek, Nigeria was studied between August 2022 and January 2023 in 3 stations. Seven heavy metals were analyzed with standard methods and compared with quality Standard. Ecological threat was assessed in water using two metal pollution indices while six sediment quality assessment indices were used to access the sediment quality. Results showed that the mean concentrations of nickel, copper, cadmium and zinc in water sample exceeded the permissible limits set by National environmental (surface and groundwater) quality regulations for aquatic life, while copper and cadmium exceeded the permissible limits set by Canadian sediment standards quality for the protection of aquatic life in sediments in all the stations. The heavy metal pollution index (HPI) values exceeded the threshold (100) across the stations, ranging between 469.53 and 686.74 while comprehensive pollution index (CPI) ranged between 1.405 and 1.854, indicating moderate contaminated water. The sediment indices indicated that cadmium and copper were the major metallic pollutants. The indices indicated the following –contamination factor: copper (moderate) and cadmium (very high), degree of contamination (very high); ecological risk: cadmium and copper (high) while lead and zinc were moderate; potential environmental risk (high); quantification of contamination: cadmium and copper (anthropogenic); geo-accumulation index: cadmium (very highly polluted). The study revealed that the water body and sediments were polluted, attributed to anthropogenic activities.

Keywords: Eniong Creek; Heavy Metals, Nigeria; Sediment; Water

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1. Introduction

Water and sediment provide essential services in aquatic ecosystems (Jonah *et al*., 2022; Onyena *et al*., 2023). Water provides a medium for the survival and growth of all aquatic organisms while sediment offers a habitat for a wide range of benthic organisms (Ali & Muhammed, 2023). Water bodies and their sediments are overwhelmed with enormous quantities of non-degradable and biodegradable pollutants, including heavy metals (Brraich & Jangu, 2015; Polidoro *et al.* 2017; Onyena *et al*., 2023). Heavy metals are among the most hazardous pollutants in the aquatic environment (Davies et al., 2022; Anyanwu *et al*., 2023) and their harmful nature, persistence and accumulation potential are attracting attention globally (Guan *et al*., 2014; Pandiyan *et al*., 2021; Anyanwu *et al*., 2022). Risks associated with heavy metal contamination in 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). Sediments in most cases become a storage compartment of pollutants and act as sinks and potential sources of heavy metals in aquatic ecosystems (Polidoro *et al.,* 2017; Huang *et al*., 2019). The accumulation of heavy metals in sediments significantly influences its concentration in the water column and the inhabitant biota (Pejman *et al*., 2015; Edokpayi *et al*., 2016). These metals could bioaccumulate in the tissues of aquatic organisms and can damage cells and organs (Erasmus *et al.,* 2020). Benthic invertebrates and other aquatic organisms have been reported to be significantly exposed to risks from contaminants in the water and sediments (Bere *et al*., 2016; Ayoade & Adoh, 2022).

In recent times, bioaccumulation of toxic potentially elements in seafood have been reported (Bhalachandra *et al*., 2011; Singh *et al*., 2012; Jenyo-Oni & Oladele, 2016; Abiaobo *et al*., 2017; Mokarram *et al*., 2020; Anyanwu & Chris, 2023), majorly attributed to the higher accumulation of these elements in water and sediment due to anthropogenic activities (Markmanuel *et al.,* 2022; Davies & Anyanwu, 2023). Metals in water column or sediment can be assimilated through direct uptake across the gill surfaces and other external body parts (Chan *et al*., 2021; Yang *et al*., 2023). Ingestion of contaminated food materials may also expose benthic macro-invertebrates and other aquatic organisms to heavy metal bioaccumulation (Chiba *et al*., 2011), which may in turn accumulate in human body through the consumption of these contaminated aquatic foods (Bere *et al*., 2016). The deleterious health challenges associated with toxicants are considerably increasing due to their penetration and accumulation through the food chain, and their persistence in the ecosystem (Verger & Boobis, 2013).

Metal pollution is of widespread concern for ecological management of aquatic ecosystems (Iwasaki *et al*., 2009; Bentum et al., 2011), due to their toxicity, persistency and bioaccumulative nature; endangering human health and aquatic integrity, and magnified along the food chain (Demirbas, 2008; Zeng *et al*., 2020; Hembrom *et al*, 2020; Jonah & Mendie, 2022; Davies & Anyanwu, 2023). Both anthropogenic pressures (e.g. industrial activities, mining, agriculture, domestic effluents and urban runoff) and natural processes (e.g. weathering of rocks) account for heavy metals in aquatic ecosystems (Bradl, 2005; Iwasaki *et al*., 2009; Bentum *et al*., 2011; Roozbahani *et al*., 2015). The release of heavy metals into aquatic ecosystems through natural processes of weathering is highly dependent on geology (Gupta & Banerjee, 2012) and the surrounding ecosystem conditions (Jonah and Anyanwu, 2023), while mining is regarded as a significant source of mercury (Hg), lead (Pb) and other heavy metals in the environment (Hanson *et al*., 2007; Obiri, 2007; Singh *et al*., 2007).

However, consistent water and sediment quality monitoring is necessary for the ecological protection of aquatic ecosystems. More so, sediment samples have proved useful in studying heavy metal level accumulation because they act as sinks and usually contain historical evidence of natural and anthropogenic fluxes of heavy metals (Nguyen *et al*., 2005; Boamponsem *et al*., 2010). Consequently, several different pollution indices such as the heavy metal pollution index and comprehensive pollution index have been extensively used by researchers to determine the level of a heavy metal contaminant in water bodies (Nasrabadi, 2015; Balakrishnan & Ramu, 2016; Dibofori-Orji *et al*., 2019; Anyanwu & Umeham, 2020; Jonah & Anyanwu, 2023; Jonah *et al*., 2023) while indices like contamination factor, degree of contamination, ecological risk factor, potential ecological risk index, quantification of contamination and geo-accumulation index have been applied to evaluate the contamination and toxicity levels of heavy metals in sediments (Ogbeibuetal., 2014; Shirani *et al*., 2020; Moldovan *et al.,* 2022; Ahirvar *et al*., 2023; Anyanwu *et al.,* 2023; Davies & Anyanwu, 2023).

Eniong Creek is among the most productive ecosystems in Akwa Ibom State; serving as a fishing ground for the indigenous communities. The water body is subjected to anthropogenic activities; the location of a market and other economic activities along the downstream area of the creek could result in the addition of complex pollutants into the water body and sediments. These could have a substantial effect on the ecological system, inhabitant organisms and human health via ingestion of metallic contaminated organisms. Therefore, this study aims to evaluate some heavy metal content in the water and sediment of Eniong Creek, Akwa Ibom State, Niger Delta, Nigeria and the associated ecological risk using applicable assessment indices.

2. Materials and Methods

2.1. Study area and sampling stations

The downstream section of Eniong Creek is located between Ibiono and Itu Local Government Area, Akwa Ibom State, Nigeria; within Latitude 5° 12’7.83 - 5° 12’20.77 North and Longitude 7°58’16.79 - 7°58’54.53. The water body drained from Nkana Ikpe in Ini Local Government Area, transverse through Ikpanya community in Ibiono Ibom Local Government Area, Obot Akpabio to Asang Eniong and empties into the main Cross River (Fig. 1). The study area is characterized by a tropical climate change of long wet season between March and October and short dry season (November – February). The water body commonly called black water attributed to its colour, receives pollutants from point and non-point sources within the watershed and the nearby settlements. For this study, three sampling points were selected along the study stretch, based on accessibility and nature of anthropogenic activities.

Station 1 is upstream after the uncompleted bridge and close to residential settlement with higher anthropogenic activities such as indiscriminate dumping of domestic wastes, fishing, farming and lumbering. The station receives stormwater from the community. Station 2 is located in the middle, about 2 km downstream of station 1 and beside the local market and residential settlement with higher anthropogenic activities which include road construction, indiscriminate dumping of domestic wastes, fishing, farming, boat building, logging, selling of food-stuff (miscellaneous items) and transportation of goods. Station 3 is located downstream, 2 km off station 2 and close to the mainstream of the cross river with minimal human activities such as road construction, fishing, bathing and transportation of goods.

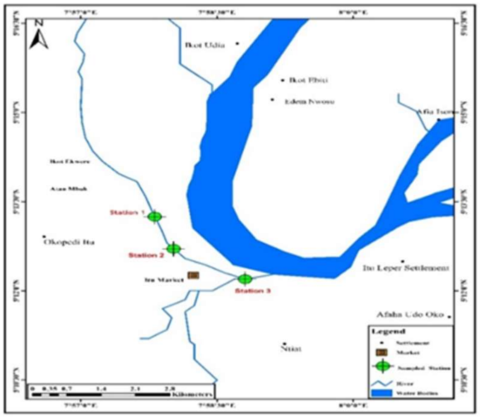

Figure 1. Map of Eniong Creek with sampling stations.

2.2. Samples collection, processing and analysis

2.2.1. Water samples

Water samples for the heavy metals evaluation were collected between August 2022 and January 2023 from three sampling stations with 500mL polyethene bottles and acidified with Nitric acid (HNO_3) immediately after collection. The sampling containers were cleaned with detergent, rinsed with tap water until they were free of detergent and dried under the sun. The containers were rinsed three times with water samples before collection. The samples collected were transported on an ice chest to the laboratory. The water samples were digested according to standard laboratory procedures. After digestion, seven heavy metals – Nickel (Ni), Manganese (Mn), Chromium (Cr), Copper (Cu), Lead (Pb), Cadmium (Cd) and Zinc (Zn) were analyzed using Unicam Atomic Absorption Spectrophotometer 939/959 series.

2.2.2. Sediment samples

Sediment samples from three sampling stations were collected at approximately 3 cm depth with a modified van-veen grab sampler; the sediments collected were wrapped in black polythene bags and transported in ice chests to the laboratory for analysis. In the laboratory, the samples were air-dried to constant weight before being placed in acid-washed ceramic crucibles and further dried in a muffle furnace at 180 °C for 30min to remove any remaining moisture. The dried sediment samples were then homogenized by shaking them vigorously in acid-washed plastic bottles and then passed through a 2 mm sieve to remove large particles. The sediment samples (0.05 g) representing each sampling station were then digested; using the two staged nitric acid and perchloric acid method in a beaker following APHA (1998). The solutions were further filtered with Whatman filter paper after digestion and made up to 25 mL with deionized water. The digested sediments were then analysed for metals - Nickel (Ni), Manganese (Mn), Chromium (Cr), Copper (Cu), Lead (Pb), Cadmium (Cd) and Zinc (Zn) concentrations using Unicam Atomic Absorption Spectrophotometer 939/959 series. For quality control, blanks and sample duplicates were included in the heavy metals analytical process.

2.3. Statistical analysis

All data were summarized with Microsoft Excel. Significant differences in the concentrations of the metals both water and sediments among the stations were tested using single-factor ANOVA. The source of significant difference at P<0.05 was determined with the Tukey pairwise posthoc test.

2.4. Water Quality Assessment Indices

2.4.1. Heavy metal pollution index (HPI)

The pollution status of the heavy metals in the water samples was determined using HPI. The index which is based on the weighted arithmetic mean method was calculated using the formula developed by Mohan *et al.* (1996). In recent times, the index has been used to evaluate the overall contamination of heavy metals in water (Appiah-Opong *et al*., 2021; Jonah *et al.,* 2023; Anyanwu *et al.,* 2022; Anwar *et al.,* 2022). To compute HPI, unit weightage (W*i*) was considered as the inverse of the recommended standard (S*i*) for each metal based on FMEnv (2011). The formula is given in Equation 1:

$$\text{HPI} = \sum \frac{Qi \times Wi}{\sum Wi}; \qquad (1)$$

Where Q*i* is the sub-index of *i*-th heavy metals and W*i* is the unit weightage of the *i*-th parameters while the Q*i* is calculated with the equation below:

$$\text{Qi} = 100 \times \frac{Ci}{Si}; \qquad (2)$$

Where C*i* is the measured value of the *i*-th parameter and S*i* is the standard limit of the *i*-th parameter set by FMEnv (2011). The acceptable range for HPI is 100 for aquatic life and drinking water quality (Prasad & Bose, 2001).

2.4.2. Comprehensive pollution index (CPI)

The CPI provides vital information about the contamination and toxicity of the heavy metals in water samples, which can be used as a tool for effective environmental management (Jonah & Anyanwu, 2023; Jonah *et al.,* 2023). All investigated heavy metals were used to calculate the CPI using the formula below:

$$\text{CPI} = {}^{1}/_{n} \sum_{i=0}^{n} \text{Pli}; \qquad (3)$$

Where n is the number of considered heavy metals while PI*i* is the pollution index number *i*. The PI*i* is calculated using the equation:

$$\text{PI}i = \frac{Ci}{Si}; \qquad (4)$$

Where C*i* is the concentration of each heavy metal and S*i* is the acceptable limit for each heavy metal recommended by FMEnv (2011). The CPI was classified based on Matta *et al*. (2018) as > 0.21 (clean water), 0.21 – 0.40 (sub-clean water), 0.41 – 1.00 (slightly polluted water), 1.01 – 2.00 (moderately polluted water) and >2.01 (heavily polluted water).

2.5. Sediment quality assessment indices

2.5.1. Contamination factor (CF)

The contamination and toxicity of the heavy metals in the sediment were determined using the contamination factor (CF). The CF is expressed as the ratio between the content of each metal to the background value. The CF was calculated using the formula developed by Hakanson (1980) presented in Equation 5.

$$C_F = \frac{\text{Cmetal}}{\text{Cbackground}} \qquad (5)$$

Where; Cmetal is the mean concentration of metals in the sediment sample while Cbackground is the mean natural/geochemical background value (Bn) for each metal**:** (Ni= 31.00mg/kg, Mn = 850 mg/kg, Cr = 67.3 mg/kg, Cu = 22.50 mg/kg, Pb = 21.00 mg/kg and Cd = 0.10 mg/kg) (Guan et al., 2014). The CF is classified into four grades for monitoring the pollution of a single metal over some 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).

2.5.2. Degree of contamination (Cd)

The contamination and toxicity of the heavy metals in the sediment were also determined using a degree of contamination (*Cd*). The index was derived by summation of all the contamination factor (CF) values of the metals. The index expresses the environmental risks posed by the presence of multiple potentially toxic elements in the sediment. The index has been used to assess the contamination and toxicity of heavy metals in sediments (Guan *et al*.,2014; Davies & Anyanwu, 2023; Anyanwu *et al*.,2023). The index was proposed by Häkanson (1980) given in equation 6:

$$Cd = \sum_{i=1}^{n} \mathrm{CF1}; \quad (6)$$

Where; $CF_1$is the contamination factor of each metal. Based on Häkanson (1980), degree of contamination (*Cd*) can be classified as < 6 for low degree of contamination, 6 ≤ – < 12 (moderate degree of contamination), 12 ≤ – < 24 (considerable degree of contamination) and ≥ 24 (very high degree of contamination).

2.5.3. Ecological risk factor (Er)

The index (Er) assesses the potential ecological risk of a single contaminant in the sediment. The Er was calculated using equation 7 as recommended by Edori & Kpee (2017).

$$Er = Tr \times Cf, \quad (7)$$

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 for the heavy metals are Ni (5), Mn (1), Cr (2), Cu (5), Pb (5), Cd (30) and Zn (1). Ecological risk factor is classified as < 40 (low), 40 ≤ – < 80 (moderate), 80 ≤ – < 160 (considerable), 160 ≤ – < 320 (high) and ≥ 320 (very high) (Mugoša *et al*., 2016).

2.5.4. Potential Ecological Risk Index (PERI)

The potential Ecological Risk Index (PERI) was introduced by Häkanson (1980) to assess the risk of several potentially toxic elements in sediment and it was calculated using the formula below:

$$PERI = \sum_{i=1}^{n} E^{i}_{r}; \quad (8)$$

Where *n* is for the number of heavy metals evaluated while *Er* 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 ≥ 600 significantly high ecological risk (Mwakisunga *et al*., 2021).

2.5.5. Quantification of contamination (QoC)

The index was used to evaluate whether the source of heavy metal contamination in sediment is anthropogenic or natural (Zarei *et al*., 2014). The index was calculated using equation 9:

$$QoC(\%) = \left[\frac{(Ci - C\ \ )}{Ci}\right] \times 100 \quad (9)$$

Where, C*i* is the mean concentration of the metal in the sediment samples and C*in* is the background values of each metal (Guan *et al.,* 2014). Negative values indicate metals of natural sources while positive values are attributable to anthropogenic sources (Malvandi, 2021).

2.5.6 Geo-accumulation index (Igeo)

The index of geo-accumulation (*I*geo) 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 (Ahirvar *et al.,* 2023; Anyanwu *et al*. 2023). It was calculated using equation 10 proposed by (Muller, 1969):

$$Igeo = \mathrm{Log2}\frac{Cn}{1.5 \times Bn} \quad (10)$$

Where; *Cn* is the mean concentration of each heavy metal in the sediment. *Bn* is the reference value. A factor of 1.5 was applied to accommodate variation in the background value. Seven classes were designated for *Igeo* index by Abdullah *et al*. (2020): ≤ 0 is for class 0 signifying Unpolluted, 0 ≤ – ≤ 1 is class 1 (Unpolluted to moderately polluted), 1 ≤ – ≤ 2 is for class 2 (Moderately polluted), 2 ≤ – ≤ 3 is for class 3 (Moderately to strongly polluted), 3 ≤ - ≤ 4 is for class 4 (Strongly polluted), 4 ≤ – ≤ 5 is for class 5 (Strongly to extremely polluted) and > 6 is for class 6 (Extremely polluted).

3. Results and Discussion

3.1. Results

3.1.1. Heavy metal concentration in water

The summary of the heavy metal concentrations in the water is presented in Table 1. The mean values of some metals such as nickel (Ni), copper (Cu), cadmium (Cd) and zinc (Zn) exceeded limits while manganese (Mn), chromium (Cr) and lead (Pb) were within limits for aquatic life sustainability set by FMEnv (2011). The nickel (Ni) values ranged from 0.001 to 0.042mg/L with the mean values of 0.02 mg/L. The highest value was recorded in station 3 (August 2022) while the lowest value was recorded in station 2 (December 2022).

Table 1
Summary of heavy metal concentration in waters from Eniong Creek

Heavy ' metals (mg/L)	Station 1 X ±S.E.M	Station 2 X ±S.E.M	Station 3 X ±S.E.M	P value	FMEnv (2011) *
Ni	0.02±0.21 (0.005-0.031)	0.02±0.42 (0.002-0.042)	0.02±0.00 (0.001-0.034)	P >0.05	0.01
Mn	0.03±0.02 (0.03-0.29)	0.03±0.00 (0.01-0.13)	0.04±0.00 (0.02-0.11)	P >0.05	0.05
Cr	0.04±0.01 (0.004-0.05)	0.05±0.04 (0.002-0.08)	0.02 ±0.00 (0.003-0.06)	P > 0.05	0.05
Cu	0.02±0.00 (0.003-0.06)	0.02±0.03 (0.003-0.09)	0.02±0.02 (0.003-0.06)	P >0.05	0.001
Pb	0.01±0.00 (0.008-0.02)	0.01±0.00 (0.005-0.04)	0.01±0.00 (0.008-0.03)	P >0.05	0.01
Cd	0.03±0.23 (0.003-0.05)	0.02±0.41 (0.001-0.04)	0.03±0.64 (0.002-0.06)	P >0.05	0.005
Zn	0.02±0.32 (0.003-0.05)	0.03±0.02 (0.001-0.04)	0.03±0.31 (0.002-0.06)	P >0.05	0.01
HPI	686.74	469.53	686.01		
CPI	1.854	1.405	1.833		

*X = mean; ±S.E.M = standard error of the mean; P < 0.05 indicate a significant difference; HPI= Heavy metal pollution index; CPI = Comprehensive pollution index; *FMEnv = National Environmental (Surface and Groundwater) Quality Regulations.*

The mean values of Ni recorded exceeded the threshold value (0.01mg/L) set by FMEnv (2011) for aquatic life. There were no significant differences between the mean values (ANOVA F= 0.57, P= 0.62). Manganese (Mn) values varied from 0.01 to 0.29mg/L; the highest mean value (0.04mg/L) was in station 3 while the lowest (0.03mg/L) were recorded in stations 1 and 2 respectively. The maximum value (0.29 mg/L) was recorded in station 1 (October 2022) while the minimum value (0.01mg/L) was recorded in stations 1 and 2 (January 2023). The mean values recorded were within the limit value (0.05mg/L) set by FMEnv (2011) for aquatic life. There were no significant differences between the mean values (ANOVA F= 1.32, P= 0.38). The chromium (Cr) values ranged from 0.002 to 0.08mg/L. The mean values recorded were within the acceptable value (0.05mg/L) set by FMEnv (2011) for aquatic life. The lowest and highest values were recorded in station 2 (September and October. 2022) respectively, there were no significant differences between the mean values (ANOVA F= 0.18, P= 0.080). The values for copper (Cu) ranged between 0.003 and 0.09mg/L. The mean values recorded exceeded the acceptable limit (0.001mg/L) set by FMEnv (2011).

The highest value was recorded in station 2 (October 2022) while the lowest values were recorded in all stations (January 2023). The mean values (0.02mg/L) were recorded in all the stations. There were no significant differences between the mean values (ANOVA F= 0.48, P= 0.32). Lead (Pb) values ranged between 0.008 and 0.04mg/L; the highest value was recorded in station 2 (October 2022) while the lowest values were recorded in stations 1 (December 2022) and 3 (January 2023). The mean values of 0.01mg/L were recorded in all the stations, with no significant difference (ANOVA, F= 0.44, P= 0.064). The mean values were within the acceptable limit for aquatic life sustainability (0.01mg/L) set by FMEnv (2011). The spatial concentrations of cadmium (Cd) and zinc (Zn) followed the same trend, with the highest value (0.06mg/L) recorded in station 3 (August and October 2022) while the lowest (0.001mg/L) was recorded in station 2 (December 2022). The mean values exceeded the 0.005mg/L limit for Cd (FMEnv, 2011). There was no significant difference between the mean values (ANOVA, F= 0.66, P= 0.69) across the stations. Zinc recorded the highest mean value (0.03mg/L) in stations 2 and 3 while the lowest (0.02mg/L) was recorded in station 1. The mean values exceeded the 0.01mg/L limit for aquatic life set by FMEnv (2011). There was no significant difference between the mean values (ANOVA, F= 25.5, P= 0.081) among the stations.

3.1.2. Water quality assessment indices

3.1.2.1. Heavy metal pollution and comprehensive pollution index

The results of the heavy metal pollution index (HPI) and comprehensive pollution index (CP1) were also presented in Table 1. The HPI values ranged from 469.53 to 686.74 while CPI values ranged between 1.405 and 1.854. The highest value for both indices was recorded in station 1 while the lowest was in station 2. The HPI values exceeded the threshold value (100) while the CPI values in all the stations were within the range indicating moderate pollution. CPI value > 0.21 (clean water) 0.21 – 0.40 (sub-clean water), 0.41 – 1.00 (slightly polluted water), 1.01 – 2.00 (moderately polluted water) and >2.01 (heavily polluted water).

3.1.3. Heavy metal concentration in sediments

The summary of the heavy metal concentration in the sediments is presented in Table 2. The Nickel (Ni) values ranged between 1.37 and 9.38mg/kg. The lowest value was recorded in station 1 (December 2022) while the highest values were recorded in stations 1 (August 2022) and 3 (October 2022). Station 2 was significantly (ANOVA, F= 6.34, P= 0.000) higher than the others. The CCME (2002) have no limit for Ni concentration in sediments.

Table 2
Summary of heavy metal concentration in sediments from Eniong Creek

Heavy metals (mg/kg)	Station 1 X±S.E.M	Station 2 X±S.E.M	Station 3 X±S.E.M	P value	limit*
Ni	4.67±1.32[a] (1.37-9.38)	5.74±2.42[b] (2.14-8.46)	4.83±1.37[a] (1.43-9.32)	P < 0.05	NI
Mn	34.1±2.52[a] (14.67-66.6)	26.3±2.65[b] (11.8-43.8)	18.3±3.72[c] (9.76-26.6)	P < 0.05	NI
Cr	17.6±5.23[a] (6.34-32.9)	11.8±3.51[b] (6.11-21.3)	13.4±5.37[b] (4.26-31.3)	P < 0.05	37.3
Cu	67.3±18.3[b] (26.7-110)	54.9±35.7[c] (18.0-118.1)	77.2±28.2[a] (40.4-133.0)	P < 0.05	35.7
Pb	8.36±2.56[a] (3.22-19.4)	3.11±3.37[c] (1.23-7.22)	5.62±1.24[b] (2.42-11.6)	P < 0.05	35.0
Cd	5.16±0.34[c] (2.46-11.5)	9.10±1.12[a] (4.18-17.6)	7.28±5.58[b] (3.11-10.64)	P < 0.05	0.6
Zn	39.8±11.4[c] (14.6-69.3)	56.4±26.8[b] (24.4-78.3)	67.9±45.4[a] (32.6-99.8)	P < 0.05	123.0

*X = mean; ±S.E.M = standard error of the mean; P < 0.05 indicates a significant difference; *Canadian sediment standards quality guidelines for the protection of aquatic life (CCME, 2002). NI= Not Indicated*

Manganese (Mn) values varied between 9.76 and 66.6 mg/kg; the lowest value was recorded in station 3 (January 2023) while the highest value was recorded in station 1 (September 2022). The 3 stations were significantly different (ANOVA, F= 14.12, P= 0.020). The CCME (2002) have no limit for Mn in sediments. Chromium (Cr) values ranged from 4.26 to 32.9mg/kg; the lowest value was recorded in station 3 (December 2022) while the highest values were recorded in stations 1 and 3 (August 2022) respectively. All values recorded were within the limit (37.5mg/kg) set by CCME (2022). Station 1 was significantly higher than the others (F= 4.9, P= 0.001). Copper (Cu) values varied between 18.0 and 133.0 mg/kg; the lowest value was recorded in station 2 while the highest was in station 3 in December 2022 respectively. The mean values recorded exceeded the limit (35.7 mg/kg) set by CCME (2002). There was a significant difference in all the stations (ANOVA, F= 5.76, P= 0.000). Lead (Pb) values varied between 1.23 and 19.4mg/kg; the lowest value was recorded in station 2 (December 2022) while the highest was in station 1 (September 2022).

All the values were within the acceptable limit set by (CCME, 2002). There was a significant difference in all the stations (F= 8.14, P 0.001). The cadmium (Cd) varied between 2.46 and 17.6 mg/kg; the lowest value was recorded in station 1 (December 2022) while the highest value was recorded in station 1 (September 2022). All the values exceeded the limit (0.6 mg/kg) set by (CCME, 2002). There was a significant difference in all the stations (ANOVA F=11.6, P =0.000). The Zinc (Zn) values varied between the stations, the lowest value (14.6 mg/kg) was recorded in station 1 (December 2022) and the lowest (99.8 mg/kg) was recorded in station 3 (January 2023). All the values recorded were within the limit (123.0 mg/kg) set by (CCME, 2002). ANOVA revealed significant differences across the stations (F = 6.82, P. 0.020).

3.1.4. Sediments Quality Assessment Indices

3.1.4.1. Contamination factor (CF) and Degree of contamination (DC)

The contamination factor (Cf) values are presented in Table 3. The values of Nickel (Ni), Manganese (Mn), Chromium (Cr), and Lead (Pb) in all the stations, Zinc (Zn) in stations 1 and 2 were less than one and classified as a low degree of contamination.

Table 3
Contamination factor (CF) and degree of contamination (DC) of the heavy metals in sediments from Eniong Creek

Heavy metals (mg/kg)	Station 1	Station 2	Station 3
Nickel (Ni)	0.15	0.18	0.16
Manganese (Mn)	0.04	0.03	0.02
Chromium (Cr)	0.26	0.17	0.19
Copper (Cu)	2.99	2.44	3.43
Lead (Pb)	0.39	0.15	0.26
Cadmium (Cd)	51.6	91.0	72.8
Zinc (Zn)	0.61	0.86	1.04
Degree of Contamination	56.04	94.83	77.90

The Cf values for copper (Cu) ranged between 2.44 and 3.34, the values in stations 1 and 2 signified moderate degree (1 ≤ CF < 3) while in station 3 showed a considerable degree (3 ≤ CF < 6), and the Cf values for cadmium (Cd) ranged between 51.6 and 91.00; the value in station 1 was within the range of 3 ≤ CF < 6, classified as considerable degree while stations 2 and 3 (> 6) were classified as very high degree (Table 3). The degree of contamination (DC) values, which is the sum of the contamination factors (Cf) are also presented in Table 3. The values ranged between 56.04 (station 1) and 94.83 (station 2); the values were higher than 24, indicating an extremely high degree of contamination.

3.1.4.2. Ecological risk (Er) and Potential ecological risk index (PERI)

The ecological risk and Potential Ecological risk index values are presented in Table 4. The values of Nickel (Ni), Manganese (Mn), and Chromium (Cr) in all the stations, Lead (Pb) in stations 2 and 3, and Zinc (Zn) in station 1 had Er values < 40, classified as low ecological risk.

Table 4
Ecological risk (Er) and Potential ecological risk index (PERI) of the heavy metals in sediments from Eniong Creek

Heavy metals (mg/kg)	Station 1	Station 2	Station 3
Nickel (Ni)	23.35	28.70	24.15
Manganese (Mn)	34.10	26.30	18.30
Chromium (Cr)	35.20	23.60	26.80
Copper (Cu)	336.50	274.50	386.00
Lead (Pb)	41.80	15.55	28.10
Cadmium (Cd)	154.80	273.00	218.40
Zinc (Zn)	39.80	56.40	67.90
PERI	665.55	698.05	769.65

The value of Lead (Pb) (station 1) and Zinc (Zn) (stations 2 and 3) were within the moderate ecological risk (40 ≤ Er< 80); Cadmium (Cd) in station 1 had value within the high ecological risk 80 ≤ – < 160 (considerable) while Cd in stations 2 and 3 and Cu in station 2 had Er values within 160 ≤ – < 320 and classified as high. On the other hand, Cu in stations 1 and 3 had the highest Er values and was classified as a very high ecological risk (Er ≥ 320) (Table 4). All the PERI values were > 600, ranging from 665.55 to 769.65 indicating significantly high ecological risk.

3.1.4.3. Quantification of contamination (QoC)

The quantification of contamination values is presented in Table 5. Nickel (Ni), Manganese (Mn), Chromium (Cr), Lead (Pb) and Zinc (Zn) values recorded across the stations were negative while Copper (Cu) and Cadmium (Cd) had positive values in all the stations ranging between 59.02 and 99.89% (Table 4).

Table 5
Quantification of contamination (QoC) of the heavy metals in sediments from Eniong Creek

Heavy metals (%)	Station 1	Station 2	Station 3
Nickel (Ni)	-563.8	-440.0	-541.8
Manganese (Mn)	-2392.66	-3131.93	-4544.80
Chromium (Cr)	-282.38	-470.33	-402.23
Copper (Cu)	66.56	59.02	70.85
Lead (Pb)	-151.19	-575.24	-273.66
Cadmium (Cd)	98.06	99.89	98.62
Zinc (Zn)	-64.32	-15.95	3.681

3.1.4.4. Geo-accumulation index (Igeo)

The Geo-accumulation Index (Igeo) values are presented in Table 6. The values in station 1 ranged from 0.007 to 10.35, station 2 (0.006 to 18.26) and station 3 (0.004 to 14.61). Mn had the lowest values while Cd had the highest across the stations. Ni, Mn, Cr, Cu, Pb and Zn had values less than 1 (0 ≤ Igeo ≤ 1); classified as Class 1 - unpolluted to moderately polluted while Cd values across the stations were greater than the highest Class 6 (Igeo > 6); that is classified as extremely polluted.

Table 6
Geo-accumulation index (Igeo) of the heavy metals in sediments from Eniong Creek

Heavy metals (mg/kg)	Station 1	Station 2	Station 3
Nickel (Ni)	0.030	0.037	0.031
Manganese (Mn)	0.007	0.006	0.004
Chromium (Cr)	0.052	0.034	0.039
Copper (Cu)	0.601	0.488	0.688
Lead (Pb)	0.079	0.029	0.053
Cadmium (Cd)	10.35	18.26	14.61
Zinc (Zn)	0.121	0.172	0.208

3.2. Discussion

The mean values of some heavy metals in water (nickel, copper, cadmium and zinc) exceeded the limits for supporting aquatic life set by FMEnv (2011). The high mean values of nickel, copper, cadmium and zinc recorded in all the stations could be attributed to similar anthropogenic activities in the stations; serving as the major source of these metals into the water body. Constant discharge of domestic wastes and surface runoffs from the surrounding residential settlements and farmlands contribute to higher concentrations of heavy metals in water (Jonah & Anyanwu, 2023). On the other hand, the highest concentration of nickel, copper, cadmium and zinc recorded in August and September 2022 could be linked to allochthonous materials washed into the water body during and after precipitation (Ke *et al.,* 2017; Ling *et al.*, 2017).

The HPI and CPI values varied between the stations. The HPI values in all the stations exceeded the limit for HPI (100) based on Prasad and Bose (2001). This could be ascribed to the accumulation of metallic pollutants in the water, arising from indiscriminate discarding of domestic wastes, which have been reported to contain high concentrations of heavy metals (Jonah *et al.*, 2023). On the other hand, the observed ongoing road construction, transportation, agriculture and other economic activities within the watershed, coupled with surface runoff from contaminated soil could influence the higher values of the heavy metals and HPI in the water (Jonah & Mendie, 2022; Jonah *et al.*, 2023). The recorded CPI values indicated moderate heavy metal pollution in the water. Water with CPI values of 1.01 to 2.00 is classified as moderately polluted (Imneisi & Aydin, 2018; Matta *et al.*, 2018). The HPI and CPI values recorded could be attributed high content of some metals (nickel, copper, cadmium and zinc) that exceeded their respective limits set by FMEnv (2011). This could pose a hazardous threat to both aquatic organisms and human beings exposed to the water body (Bere *et al*., 2016; Ayoade & Adoh, 2022; Jonah *et al.,* 2023). The mean value of copper and cadmium in sediments exceeded the acceptable limits set by Canadian sediment quality guidelines for the protection of aquatic life (CCME, 2002).

The mean values of copper and cadmium in sediments across the stations could be due to deposition from surface water (Ayoade & Adoh, 2022). These could have accumulated over time via complex physical and chemical absorption and dissolution pathways depending on the physico-chemical state of the surface water (Huang *et al.,* 2014; Bing *et al.,* 2016; Ayoade & Adoh, 2022). The cadmium values exceeded the limit (0.6 mg/kg) set by CCME (2002). This could be attributed to both geogenic and anthropogenic sources within the catchment areas especially agriculture (Audu *et al.,* 2022). The findings corroborated with the reports of Nwazue *et al.* (2022) in River Iyiudene, Abakaliki South-Eastern Nigeria and Davies & Anyanwu (2023) in mangrove swamp sediments, Niger Delta, Nigeria. The heavy metals in the sediment, however, could be re-suspended in surface water during turbulence or enter the food chain via a feeding pathway by the benthic organisms or benthic-feeding pelagic organisms (Davutluoglu *et al*., 2011). The higher concentrations of heavy metals in sediments between August and September 2022 suggest the impact of surface runoff (Essien *et al.,* 2019). During and after heavy rainfall, pollutants from contaminated soil and other allochthonous materials are washed into the water (Ling *et al*., 2017), and subsequently sink into the sediment (Pandiyan *et al.,* 2021).

The contamination factor values varied among the metals; the values of Ni, Mn, Cr, Pb and Zn were less than 1 while Cu was classified as moderate degree and Cd was of very high degree in all the stations, indicating that the sediment was contaminated with Cd. The higher CF values of Cd could be attributed to geogenic sources exacerbated by anthropogenic activities, especially the impact of domestic effluent discharges. The higher Cd values corroborated with the reports of Kieri *et al*. (2021) in Silver River, Bayelsa State, and Anyanwu *et al*. (2023) in Ikwu River, Umuahia, Nigeria attributed to anthropogenic input. The degree of contamination (*Cd*) values was ≥ 24 indicating a very high degree of contamination (Häkanson,1980) as ascribed to higher concentrations of Cd and Cu in the sediments as observed by Davies & Anyanwu (2023). The higher values recorded in stations 2 and 3 could be attributed to the high level of human activities (Essien *et al*., 2019), coupled with allochthonous inputs into the water. The Er values for Ni, Mn, Cr (all stations), Pb (stations 2 and 3), and Zn (station 1) were less than 40 indicating low potential ecological damage.

On the other hand, Cu Er values in stations 1 and 3 were higher than the value in station 2; indicating very high ecological risk. The Cd Er in station 1 is considerable, while stations 2 and 3 are high. The higher Er value for Cu agreed with the reports of Rao *et al*. (2018) and Peter *et al*. (2021) in related studies. All the PERI values were > 600 indicating higher ecological risk to the environment (Mwakisunga *et al*., 2021). The significantly higher values recorded were mostly influenced by the concentrations of Cu and Cd which in turn was influenced by anthropogenic activities as observed by Davies & Anyanwu (2023). The QoC index values revealed that the levels of Ni, Mn, Cr, Pb and Zn were attributed to natural sources. The positive values of Cd and Cu in all the stations were attributed to the combined effects of anthropogenic activities such as road construction, transport, domestic wastes and wastewater discharge, agriculture, fishing, surface runoff from contaminated soil and other economic activities within the watershed (Kazemi *et al*., 2012; Jonah & Mendie, 2022 and Jonah *et al*., 2023). The Geo-accumulation Index (Igeo) values recorded in all the stations showed the sediments were extremely polluted by Cd; attributed to anthropogenic influence. The finding corroborates with the report and Davies & Anyanwu (2023).

4. Conclusion

This study revealed that the water and sediment were polluted with potentially toxic metals, attributed to human activities, seasonal factors and the geogenic nature of the watershed. The mean concentration of nickel, copper, cadmium and zinc in the water, copper and cadmium in sediments exceeded permissible limits. The sediment quality assessment and heavy metal pollution indices indicated that cadmium and copper were the major metallic pollutants, which could be detrimental to aquatic organisms and humans within the area through oral and dermal exposures and contamination of seafood. Constant monitoring and remediation processes are strongly recommended to salvage the aquatic ecosystem.

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