Scientia Africana, Vol. 23 (No. 2), April, 2024. Pp361-374
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ECOTOXICITY OF TRACE METAL ENRICHMENT AND THE DEGREES OF CONTAMINATED SEDIMENT AND WATER FROM RIPARIAN COMMUNITIES IN RIVERS STATE, NIGERIA.

Davies, I. C.[1]*, Sulaiman Y.[2] and Efekemo, O.[3]
[1]Department of Fisheries, Faculty of Agriculture, University of Port Harcourt, Port Harcourt, Rivers State, Nigeria.
[2]Department of Zoology, Faculty of Natural and Applied Sciences, Nasarawa State University, Keffi, Nasarawa State.
[3]Department of Chemical Sciences, Biochemistry Programme, Faculty of Science, Edwin Clark University, Kiagbodo, Delta State, Nigeria.
*Corresponding Author:davies.chris@uniport.edu.ng

Received: 21-03-2024
Accepted: 23-04-2024

https://dx.doi.org/10.4314/sa.v23i2.34

Journal Homepage: http://www.scientia-african.uniportjournal.info
Publisher: *Faculty of Science, University of Port Harcourt.*

ABSTRACT

This study assessed trace metal enrichment and contamination levels in Tema, Sangama, and Degema communities in Rivers State, Nigeria. Samples were collected monthly from October 2021 to April 2022. Trace metals such as Pb, Cu, Fe, Cd, Zn, and As were analysed using an Atomic Absorption Spectrophotometer (AAS). The contamination factor, degree of contamination and enrichment factor for trace metals were used to evaluate the impact of pollution levels. There was a descending order of heavy metal concentrations in water at the three stations: Fe > Cu > Zn > Cd > Pb. Sediment heavy metal concentrations were descending from Fe > Zn > Cu > Pb > Cd at the same stations. Heavy metal levels were consistently higher at Sangama. The result revealed that compared to Pb and Zn, Cd contamination was moderate to considerable. Fe contamination was relatively low, but Cu contamination was moderate to high. Water and sediment were contaminated to varying degrees. The contamination levels of Pb, Zn, and Cu were low to moderate. Sangama, Tema, and Degema all had varying degrees of contamination, with some areas having higher contamination levels. This study recommends the need for effective environmental management practices in these coastal marine wetlands.

Keywords: Trace metals, enrichment factor, communities, contamination factor, pollution

INTRODUCTION

The coastal marine wetlands of Rivers State, Nigeria, are vital areas that offer essential services while also contributing to the preservation of coastal integrity. These dynamic ecosystems, particularly mangroves thriving in estuaries and intertidal zones of subtropical and tropical coasts, play a crucial role in shoreline stabilisation, habitat provision, and carbon sequestration (Rafique et al, 2018; Ayyam et al., 2019; Anu et al., 2024). However, rapid urban expansion and intense industrial activities have led to a range of environmental problems, with trace metal contamination emerging as a significant concern in these delicate environments (Masindi et al., 2018; Mishra et al., 2019).

Nigeria, currently experiencing rapid urbanization and industrial expansion, is facing a growing concern over heavy metal pollution in its water sources (Egbueri and Unigwe, 2020; Müller et al., 2020; Fashae and Obateru, 2021; Onyena et al., 2024). With the development of urban and industrial areas, there is a significant increase in the risk of contaminants infiltrating aquatic environments. Consequently, it is crucial to monitor and assess the extent of heavy metal contamination in coastal marine wetlands to comprehend the potential risks and impacts on the ecosystem and human health. Trace metals like copper (Cu), zinc (Zn), manganese (Mn), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) present specific dangers due to their toxic properties and resistance to natural breakdown (Obasi et al., 2020; Jadaa et al., 2023).

These pollutants stem from various sources, such as household sewage, industrial waste, and marine operations, causing detrimental impacts on the environment and human well-being (Kolawole and Iyiola, 2023). Heavy metals, originating from natural geological processes and human actions, garner significant attention due to their enduring nature, potential for bioaccumulation, and toxicity (Moore, 2019; Mukhopadhyay 2022; Awasthi et al., 2022). These contaminants not only pollute water, soil, and food but also amass aquatic organisms, permeate the food chain, and affect human health through the consumption of marine products (Chris and Anyanwu, 2023; Chris et al., 2023; Maqbool et al., 2023). The physical and chemical properties of water profoundly influence the health, productivity, and long-term viability of aquatic ecosystems.

Temperature, pH, salinity, dissolved oxygen, and nutrient levels all play crucial roles in determining the well-being of water sources, with changes in these factors indicating shifts in ecological balance and ecosystem health (Akankali and Davies 2021; Yadav and Kumar, 2023). By evaluating trace metal pollution in these ecosystems, the project aims to gather valuable insights into the extent of contamination, potential risks, and overall ecological well-being of these vital coastal habitats. Understanding the intricate interplay between urbanization, industrialization, and heavy metal pollution is essential, and the findings of this study could help inform targeted environmental interventions to safeguard the biological diversity of Rivers State's coastal marine wetlands.

The study involves thorough field sampling and lab analysis to assess heavy metal levels in water and sediments from various sites in coastal marine wetlands. This study will utilize probabilistic ecological risk assessment methods to identify potential risks to environmental health due to heavy metal contamination. This approach will offer valuable data for evidence-based decision-making, targeted remediation, and conservation efforts. Ultimately, the study's findings will support the ecological health and sustainability of coastal marine wetlands in Rivers State, Nigeria.

MATERIALS AND METHODS

Study Area

The study sites comprised three riparian settlements in Rivers State, Nigeria namely Degema, Tema, and Sangama. In Degema, southeast of the Niger Delta, illicit garbage processing, dumping, dredging, and fishing are frequent. Sangama, in the same region, is known for its residential garbage, illicit refining overflow, rubbish disposal, and fishing activities, while Tema is known in the same region for garbage and human waste disposal, as well as dredging and fishing. These sites have typical Niger Delta mangrove vegetation.

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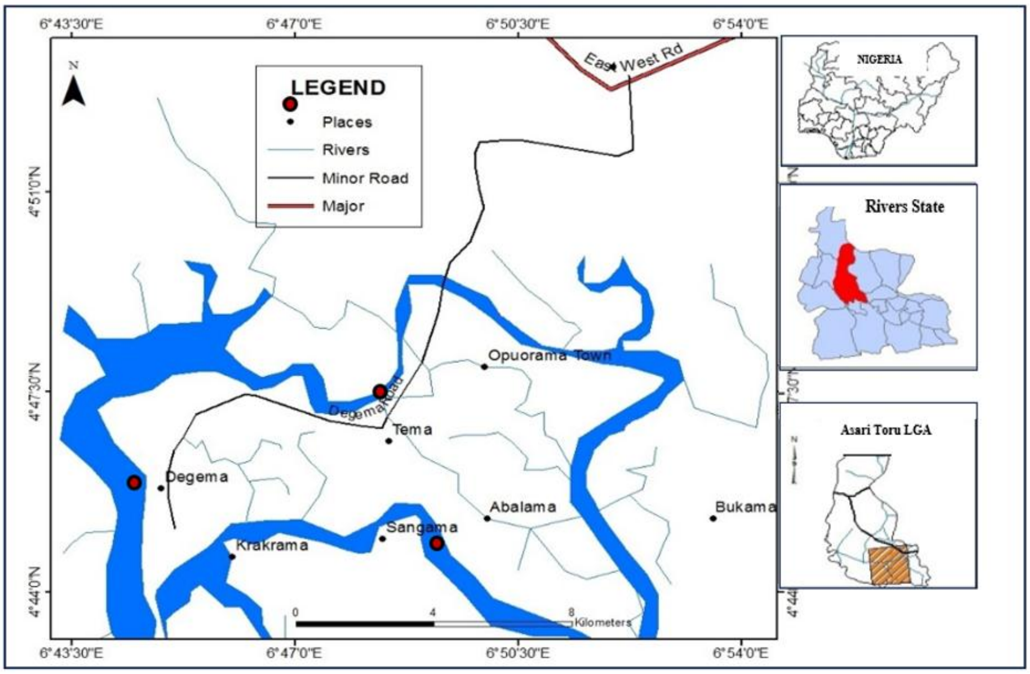

Figure 1: Map of the sampled locations along the Creeks

Sample and Sampling Procedure

To reflect catchment activities, sampling stations were selected from each community based on their features and relevance as pollution locations. To represent various activities, each watercourse was tested at least 1000 m apart. Heavy metals of interest were lead (Pb), copper (Cu), iron (Fe), cadmium (Cd), zinc (Zn), and arsenic (As) in industrial and home effluents from the research region. At each site, sediment and water samples were taken. All sample locations (longitudes and latitudes) were georeferenced using GPS receivers (Magellan GPS 315). Between October 2021 and April 2022, samples were collected once every month. Every month, sampling was carried out during the first week.

Water Analysis

Surface water samples were collected from Schott glass bottles that were pre-cleaned by washing with detergent, rinsing with tap water, and soaking in 50% hydrochloric acid for 24 hr. To prevent metal contamination, the bottles were rinsed with tap water and then triple-distilled water. The samples were carefully packaged in ice packs, labelled, and stored in ice chests for transportation to the laboratory to maintain their integrity. Heavy metal levels were analyzed using standard methods (APHA, 2000), ensuring that the sampling locations accurately represented pollution hotspots in the study area.

Sediment Analysis

An 'Ekman grab' sampler was utilized to collect a combined sediment sample from three distinct locations in each stream monthly for six months. The sampler was placed in a polypropylene container and soaked in 10% nitric acid for 24 hr. The frozen samples were then taken to the lab and stored at 20°C for subsequent analysis using the API-RP 45 Atomic Absorption Spectrophotometric Machine. The sampling distance was one meter away from the shore was chosen to detect pollution hotspots in the study area, ensuring a precise representation of actual contamination.

Quality Assurance and Control

The study utilized NIST-certified atomic absorption standards to create a calibration curve for heavy metals in water, sediment, and biota samples. A reagent blank was run after every 10 samples for verification. Recovery rates varied from 82 to 110%. The methodology and wavelength adhered to Davies et al. (2024) procedures. Each sample underwent duplicate analysis, and the findings reflect the mean. This meticulous quality assurance and control procedure enhances the precision and reliability of the outcomes.

Statistical Analysis

Descriptive statistics and ANOVA were conducted using SPSS v16. At 0.05, the Duncan Multiple Range Test identified significant means. Sediment and water concentrations were determined based on the mean values. Means and standard errors were utilized in Microsoft Excel for data management during the analysis.

Contamination Factor

The contamination factor (CF) ratio was calculated by dividing the metal concentration in sediment and water by the background/control value, as depicted in equation (1). Rahman et al. (2012) categorizes contamination levels as CF<1 for low contamination, 1≤CF<3 for moderate contamination, 3≤CF<6 for significant contamination, and CF≥6 for very high contamination.

$$CF = \frac{\text{Cmetal}}{\text{C−background}} \ldots\ldots\ldots\ldots\ldots (1)$$

Degree of Contamination

The degree of contamination level in equation 2 was evaluated following Rehman et al. (2018) and was classified into different risk categories as: CD < 8 signifies low risk, 8 ≤ CD < 16 indicates moderate risk, 16 ≤ CD < 32 suggests significant risk, and CD > 32 represents very high risk.

Degree of contamination = ∑Pb +∑Cd +∑Cu +∑Hg+∑Cr……∑n… (2)

Enrichment Factor (EF)

The enrichment factor calculation according Chris et al. (2023) in the equation was followed.

$$EF = \frac{\text{Cn/Cref sample}}{\text{Bn/Bref}} \ldots\ldots\ldots\ldots (3)$$

Where C_n represents the metal concentration in the sample, C_{ref} denotes the reference concentration, Bn stands for the background metal concentration, and B_{ref} indicates the reference element concentration. In a study by Abdullah et al. (2020), enrichment factors were categorized as EF < 2 (depletion to mineral enrichment), EF ≤ 5 (moderate enrichment), EF ≤ 20 (major enrichment), EF < 40 (very high enrichment), and EF > 40 (extremely high enrichment). A value of enrichment factor less than one suggests that heavy metals were from natural sources, whereas a value greater than one indicates anthropogenic sources (Habib et al., 2018).

RESULTS AND DISCUSSION

Water

The results in Figures 2a and 2b display average concentrations of heavy metals at different sites and media. Sangama had the highest Fe value (37.92±3.95 mg L^{-1}), followed by Degema (36.25±4.01 mg L^{-1}), while Tema had the lowest (35.90±4.12 mg L^{-1}). Sangama poses a greater risk due to high Fe levels compared to Degema and Tema. Elevated Fe levels can impact water quality and aquatic ecosystems, potentially harming aquatic life (Akhtar et al., 2021). Various natural and manmade factors were believed to contribute to the decline in water quality. Häder et al. (2020) suggested that human pollution could raise Fe levels, affecting aquatic ecosystems and leading to global consequences. Zn concentrations were highest in Sangama (10.99±1.71 mg L^{-1}), followed by Tema (10.76±1.253 mg L^{-1}), and lowest in Degema (9.94±1.25 mg L^{-1}). The high Zn levels in Sangama raise concerns about water quality. Zn can be harmful to aquatic organisms, impacting their health and the overall environmental balance (Okereafor et al., 2020; Kolarova and Napiórkowski, 2021). This aligns with Singh et al. (2022), who observed that heavy metal pollution in water negatively affects living beings. Pb levels were highest in Degema (0.12±0.02 mg L^{-1}) and lowest in Sangama (0.07±0.01 mg L^{-1}). Degema, with the highest Pb levels, could pose a threat to water quality. Pb, a heavy element, has adverse effects on human health and aquatic life (Sonone et al., 2020). Sangama had the highest Cu content in water (149.24±4.89 mg L^{-1}), while Degema had the lowest (145.95±3.66 mg L^{-1}). The high Cu

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levels in Sangama raise concerns about its detrimental impact on aquatic life and the ecological balance of water systems (Mebane, 2023). The significant differences among the three locations indicate various challenges and environmental characteristics. These results underscore regional variations in heavy metal levels, pointing to potential ecological risks and the necessity for further research on environmental influences on water quality in these areas.

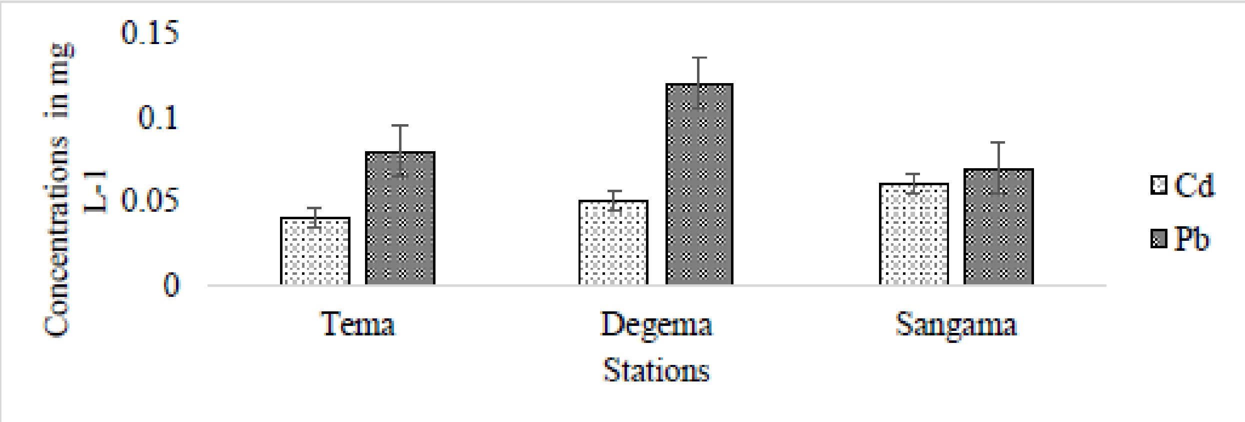

Figure 2a: The mean concentration of heavy metals in the water across the three stations

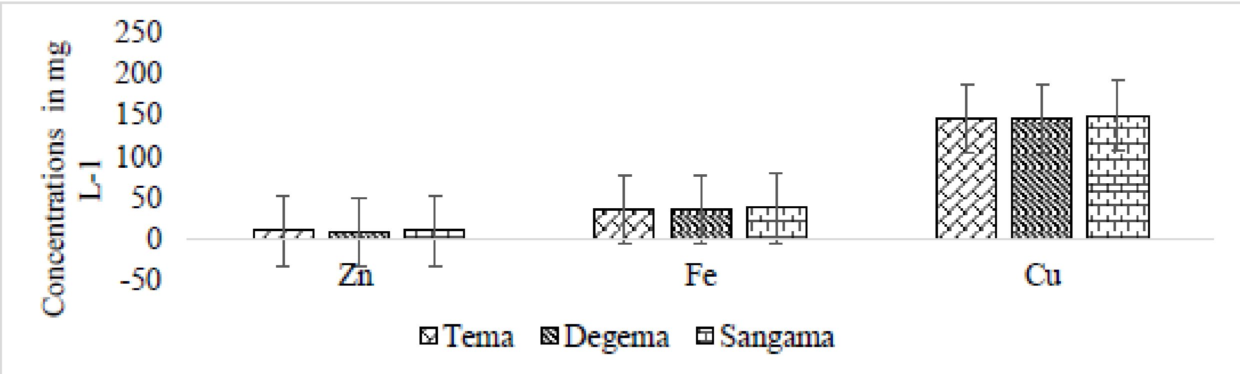

Figure 2b: The mean concentration of heavy metals in the water across the three stations

Sediment

The results in Figures 3a and 3b revealed that Sangama exhibited the highest Fe content (1748.44±88.22 mg kg^{-1}), with Tema following closely behind (1643.88±83.5 mg kg^{-1}), and Degema showing the lowest levels (1577.60±107.5 mg kg^{-1}). The elevated Fe levels in the sediment of Sangamamay indicate pollution, impacting sediment quality and benthic species (Arisekar et al., 2023). Zn levels peaked in Sangama (225.31±7.83 mg kg^{-1}) and hit a low in Degema (205.76±1.88 mg kg^{-1}). The high Zn content raises concerns about potential ecological repercussions, as it may accumulate in sediments and harm bottom-dwelling organisms (Ezekwe et al., 2022). Pb concentrations were highest in Sangama (10.57±0.62 mg kg^{-1}) and lowest in Degema (6.93±1.03 mg kg^{-1}). The levels of lead in the sediment of Sangama indicate likely pollution, posing a threat to sediment-dwelling organisms and the food chain (Luo et al. 2016). Cd levels were highest in Sangama (3.15±0.33 mg kg^{-1}) and lowest in Degema (2.48±0.32 mg kg^{-1}). The increased Cd content in Sangama suggests potential contamination following its known toxicity and probable adverse effects on benthic animals (Enuneku et al., 2018; Zhang et al., 2020). Furthermore, Cu concentrations were highest in Degema (563.48±14.82 mg kg^{-1}) and lowest in Tema (451.58±40.29 mg kg^{-1}).

The exceedingly high Cu content in Degema raises concerns about possible ecological impacts, as Cu can accumulate in sediments and harm benthic organisms (Birch et al., 2012; Jafarabadi et al., 2020). There was no detectable variation in As content (<0.01 mg kg^{-1}) in sediment samples across all three locations. Sangama displayed the highest levels of Fe, Zn, Pb, Cd, and Cu, followed by Tema, while Degema had the lowest concentrations of all heavy metals examined.

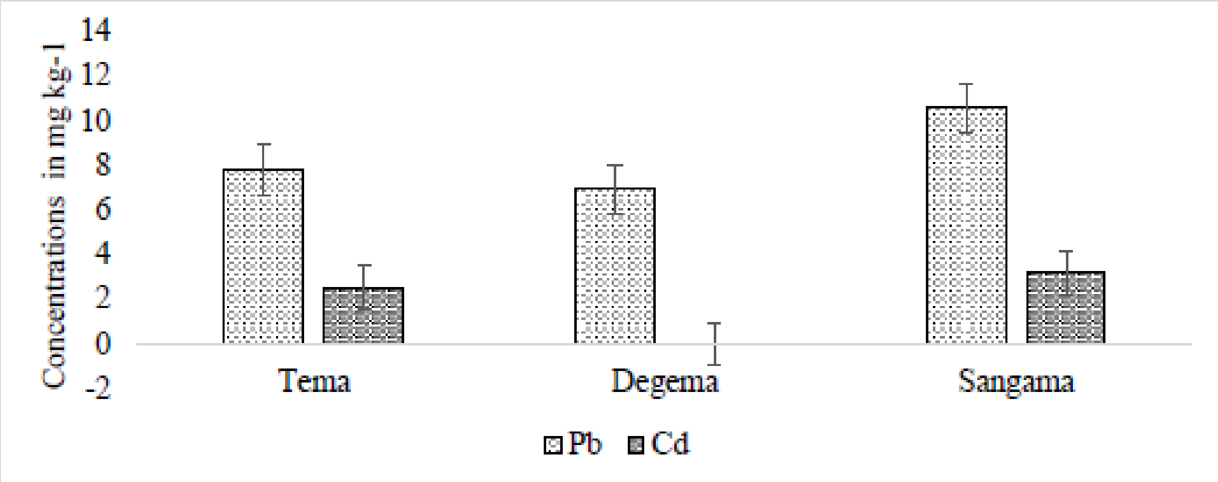

Figure 3a: The mean concentration of heavy metals in the Sediment across the three stations

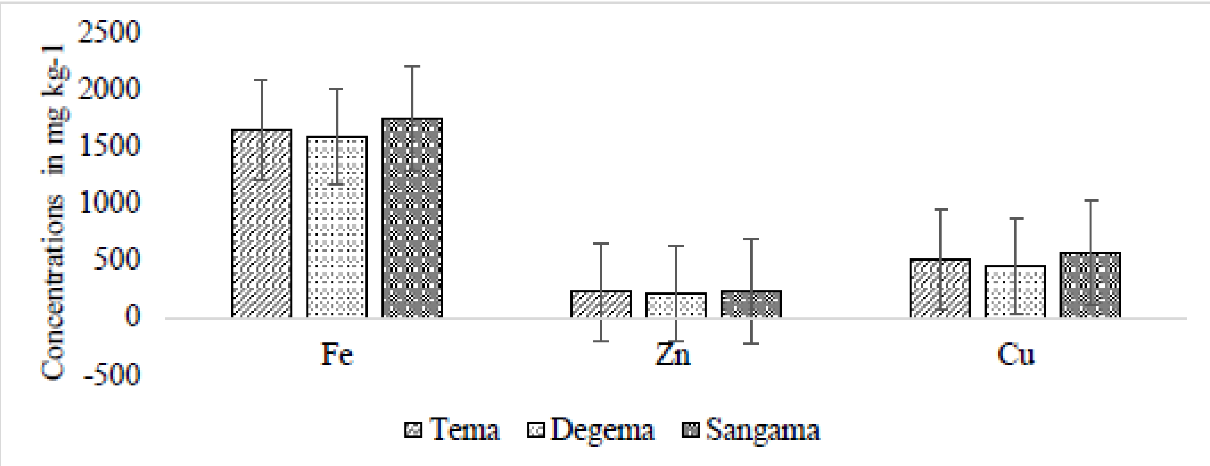

Figure 3b: The mean concentration of heavy metals in the Sediment across the three stations

Contamination Factor and Degree of Contamination in Water

The result for contamination factor and degree of contamination for water in Table 1 revealed that Cadmium (Cd) contamination ranges from moderate to considerable at all sites, with contamination factor (CF) values varying from 24.80 to 31.50. Lead (Pb) concentrations range from 0.33 to 0.50, indicating low to moderate contamination. Zinc (Zn) levels suggest moderate contamination, with consistent values ranging from 3.15 to 3.44. Iron (Fe) contamination was relatively low at all sites, with values ranging from 0.41 to 0.45. However, Copper (Cu) exhibits significant variability, with contamination levels ranging from 2.26 to 25.04, indicating moderate to very high contamination (Rahman et al., 2012). Tema and Degema fall within the moderate risk

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category (ur Rehman et al., 2018), with CD values of 192.41 and 193.68, respectively. Sangama also fell within the moderate risk category, with a CD value of 198.22. The findings show varying levels of contamination across parameters and sites, with some areas facing higher contamination levels and associated risks compared to others. Moderate to considerable Cd contamination poses potential risks to aquatic ecosystems, potentially impacting water quality, aquatic life, and the broader environment (Zaynab et al., 2020; Singh et al., 2022). While contamination levels were not significantly elevated, the presence of Pb raises potential environmental concerns that may necessitate monitoring and management strategies (Tóth et al., 2016). Moderate Zn contamination indicates potential impacts on aquatic environments, underscoring the need for further assessment to grasp the extent of ecological risks (Yap and Al-Mutairi, 2021). Lower Fe contamination levels suggest a relatively lower impact on water quality compared to other heavy metals (Singh et al., 2022). The wide range of Cu contamination levels signals potential risks to aquatic ecosystems, with some sites experiencing very high contamination (Ustaoğlu et al., 2020) and requires effective management strategies to address these risks. Chris et al. (2023) indicates that specific heavy metals in water, particularly Cd and Cu, pose moderate to considerable risks in certain locations. Therefore, ongoing monitoring, assessment, and implementation of mitigation measures are vital to safeguard the ecological health of the water environments in Sangama, Tema, and Degema.

Table 1: Contaminations Factor and Degree of Contamination in Water

Trace metal	**Tema**	**Degema**	**Sangama**
Cd	25	24.80	31.50
Pb	0.37	0.33	0.50
Zn	3.39	3.15	3.44
Fe	0.43	0.41	0.45
Cu	2.26	20.07	25.04
DC	193.68	192.41	198.22

Contamination Factor and Degree of Contamination in Sediment

Sediment contamination assessment in Table 2 for the three locations (Tema, Degema, Sangama) reveals distinct patterns in various parameters. The contamination factor and degree of contamination in sediment for the specified parameters across the three locations reveal a distinctive pattern. The contamination factors for Cd, Pb, Zn, Fe, and Cu exhibit varying degrees across Tema, Degema, and Sangama. Specifically, for Cd, the contamination factor follows a descending order: Tema (0.40) > Degema (0.50) > Sangama (0.60). Pb demonstrates contamination factors in descending order of Degema (0.01) >Tema (< 0.01) > Sangama (< 0.01). Zn exhibits contamination factors in descending order of Tema (0.16) > Degema (0.15) > Sangama (0.17). For Fe, the contamination factors (0.01) were constant in all three locations. Lastly, Cu showed contamination factors in descending order of Sangama (6.63) >Tema (6.53) > Degema (6.49).

The degrees of contamination across the three locations follow an ascending order: Tema (1926.79) > Degema (2244.41) > Sangama (2550.95). This systematic evaluation underscores the distinct contamination levels and patterns across the three locations, following a descending order of contamination degree from Tema to Sangama. Cadmium (Cd) shows low to moderate contamination in all locations, while lead (Pb) concentrations remain consistently low. Zinc (Zn) levels indicate low to moderate contamination, and iron (Fe) contamination was consistently low in all locations. However, copper (Cu) contamination levels were relatively high, suggesting significant contamination (Yerima et al., 2020; Luoand Jia, 2021).

Based on the degree of contamination (CD), the overall risk assessment underscores the need for prompt environmental management interventions. The greatest contamination risk was seen in Sangama, indicating a crucial need for focused remediation strategy (Yap and Al-Mutairi, 2021). Degema and Tema also showed extremely high contamination risk, underscoring the widespread urgency for comprehensive risk mitigation strategies. The findings indicate that the sediment in Tema, Degema, and Sangama was confronted with varying degrees of contamination, with significant risks linked to copper levels. According to Chris et al. (2023b), immediate and targeted environmental management measures may be crucial to address these risks and protect the ecological health of the sediment environments in these areas.

Table 2: Contaminations Factor and Degree of Contamination in Sediment

Trace metal	Tema	Degema	Sangama
Cd	0.4	0.5	0.6
Pb	<0.01	0.01	<0.01
Zn	0.16	0.15	0.17
Fe	0.01	0.01	0.01
Cu	6.53	6.49	6.63
DC	1926.79	2244.41	2550.95

Metal Enrichment Factor for Water

The Metal Enrichment Factor (EF) values obtained for water samples from Tema, Degema, and Sangama as seen in Table 3 play a crucial role in assessing the sources and levels of metal enrichment, according to the classification by Abdullah et al., (2020). These EF classifications range from <2 (depletion to mineral enrichment) to EF > 40 (extremely high enrichment), with values below 1 suggesting natural sources and values above 1 indicating anthropogenic sources (Habib et al., 2018).

Across all stations, the results provide insights into the enrichment levels of various metals in the water: EF values for Cd and Pb remain significantly below 1, indicating a depletion or natural enrichment rather than anthropogenic influence. This suggests that Cd and Pb in the water were likely derived from geological or natural sources.

The EF values for Zn fell within the moderate enrichment category ($2 \leq EF < 5$) for all stations, signifying a moderate degree of anthropogenic influence contributing to Zn levels in the water. This suggests that human activities may be contributing to the observed levels of Zn contamination. Cu EF values exceed 1 across all stations, indicating anthropogenic sources. However, the values fell within the range of moderate enrichment ($2 \leq EF < 5$), suggesting a moderate level of anthropogenic impact on Cu concentrations in the water.

The results offer a nuanced understanding of metal enrichment in water, with Cd and Pb influenced by natural sources and Zn and Cu showing some degree of human influence (Yap and Al-Mutairi, 2021). While the ecological risk linked to Cd and Pb may be lower due to natural sources, the moderate enrichment of Zn and Cu suggests the need for targeted interventions to manage human contributions and preserve water quality (Nag et al., 2022). However, Shotyk et al., (2023) stated that the metal enrichment factor results highlight a mixed influence of natural and human sources on metal concentrations in water. The moderate enrichment of Zn and Cu implies a potential ecological risk, underscoring the importance of proactive

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environmental monitoring and management strategies in Tema, Degema, and Sangama to mitigate the impacts of metal contamination on water quality and ecosystem health.

Table 3: Metal Enrichment Factor for Water

Metals	Tema	Degema	Sangama
Cd	0.04	0.05	0.06
Pb	0.08	0.12	0.07
Zn	10.76	9.94	10.99
Cu	146.9	146	149.2

Metal Enrichment Factor for Sediment

The Metal Enrichment Factor (EF) values for sediment samples from Tema, Degema, and Sangama were crucial indicators for assessing the sources and levels of metal enrichment in these aquatic environments. The EF values in Table 4 for Cd and Pb at all stations fell within the range of moderate enrichment ($2 \leq EF < 5$), indicating a moderate degree of anthropogenic influence contributing to Cd and Pb levels in the sediment (Abdullah et al., 2020). These findings suggest that human activities may be responsible for the observed concentrations of Cd and Pb, leading to a moderate enrichment of these metals in the sediment.

The Zn EF values for Tema, Degema, and Sangama exceeded20, indicating very high enrichment, suggesting a significant anthropogenic influence contributing to the elevated levels of Zn in the sediment across all three locations. The exceptionally high EF values underscore the substantial impact of human activities on Zn concentrations in the sediment. The EF values for Cu in Degema and Sangama were notably higher than those for Tema, with values exceeding 20, indicating very high enrichment, suggesting a significant anthropogenic contribution to Cu levels in the sediment, particularly in Degema and Sangama. According to Jung et al. (2024), extremely high EF values underscore the substantial impact of human activities on Cu concentrations in the sediment.

The analysis revealed varying degrees of anthropogenic influence across different metals and locations. Cd and Pb showed moderate enrichment and Zn and Cu exhibited very high enrichment. However, the findings highlight a significant ecological risk associated with elevated concentrations of Zn and Cu in the sediment (Habib et al., 2018). This emphasizes the imperative for immediate and effective environmental management strategies to mitigate metal contamination impacts.

Table 4: Metal Enrichment Factor for Sediment

Metals	Tema	Degema	Sangama
Cd	2.50	2.48	3.15
Pb	7.79	6.93	10.60
Zn	221.90	205.80	225.30
Cu	50.80	451.60	563.50

CONCLUSION

The Geo-Ecological Risk Assessment of trace metals in sediment and water from coastal marine wetlands in Rivers State, Nigeria, has revealed complex dynamics of metal contamination, ecological risks, and pollution levels. The study found varied metal contamination levels across water and sediment samples, with Sangama consistently showing higher levels. Cadmium contamination ranged from moderate to considerable, while lead and zinc showed low to moderate contamination. Iron contamination was relatively low, but copper displayed significant variability. Degema, Tema, and Sangama showed varying degrees of contamination, with some areas experiencing higher contamination levels and associated risks. The Ecological Risk Assessment revealed low individual metal risks but a significantly high cumulative risk in all locations, requiring urgent and coordinated environmental management strategies. The findings call for sustained environmental conservation efforts, policy-making, and community involvement in the region.

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