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Heavy metals in sediments collected from Warri River and Akassa Creeks, Delta State, Nigeria

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ABSTRACT
This study assesses the seasonal variation and concentration of heavy metals(HMs) in sediment samples collected from Warri River and Akassa Creeks in Delta State, Nigeria, with the aim of evaluating their environmental status and ecological risks. Sediment samples collected from multiple locations, two distinct rivers during raining season (April to June 2025) and dry seasons (January to March 2025) and analyzed for selected HMs: Lead (Pb), Zinc (Zn), Nickel (Ni) and Copper (Cu), using Atomic Absorption Spectrophotometry (Bulk Scientific VGB 211Model). The results demonstrate a pronounced Dry Season Enrichment. In the Warri region, Pb increased from a wet season mean of 0.0005 mg/kg to a dry season mean of 0.2200 mg/kg. The most significant flux was observed in Ni, which peaked at 10.097 mg/kg at Warri Station 1 during the dry season (Fig1). This indicates that reduced river volume and lower dilution capacity in the dry months exacerbate the concentration of industrial pollutants. There is a massive contrast in Ni levels in Warri between seasons. The Dry season concentration (5.0860mg/kg) is significantly higher than the Wet season (0.0170mg/kg). Akassa's levels remain relatively low and stable across both seasons compared to Warri. Zn increased during the Wet season (0.2510mg/kg to 0.3620mg/kg), which might suggest different runoff or solubility patterns for that specific metal. Using T-test spatial analysis reveals that the Warri River is significantly more impacted by HMs pollution than the Akassa Creeks. The spatial T-test confirms that for Cu (P=0.0000) and Pb (P=0.0007), the differences are statistically significant. These suggest that the anthropogenic sources of these HMs are closely related in the sediments.

Keywords: Heavy metals, Warri River and Akassa Creeks, Anthropogenic sources, T-test spatial analysis, Pollution.

INTRODUCTION
Heavy metals, including mercury, lead and cadmium, occur naturally on earth, but they can be toxic to human health and the environment (UNEP, 2026). Heavy metals are highly toxic emerging environmental contaminants (Briffa, *et al.,* 2020); and are among the most persistent environmental pollutants due to their non-biodegradable nature, toxicity, and ability to accumulate in aquatic systems (Chen, J.P. 2012). Heavy metals are elements found in rocks at concentrations below 0.1% (Rollinson, 1993) and are

generated naturally from geological and natural activities such as weathering of rocks, volcanic eruptions, and the erosion of mineral deposits (Shi *et al.,* 2026). The phenomenon of these elements as regards its geological and environmental activity, have long drawn the interest of researchers, largely because their presence in geological materials such as water, soil, and sediments has become a major source of human health concerns aggravated during the Anthropocene era of homo sapien (Ghosh and Singh,2005). Statistics proved according to Hogstrand and Haux (1991), the toxicity of HM were caused as a result of indiscriminate waste disposal, flared gases from industrial zones, bush burning all from human unsatiable wants to advancement. In recent decades, intensified human activities through urban migration, procreation just to mention a few influencing industrialization, urban expansion, oil exploration, and agricultural practices have greatly increased the discharge of heavy metals into aquatic environments, especially in developing nations like Nigeria (Bulouebibo *et al.,* 2018; Iwegbue *et al.,* 2018; Wogu and Okaka, 2011). These metals are particularly concerning because they tend to accumulate in sediments and can eventually enter the food chain (Olowo, 2025), thereby posing serious risks to aquatic life and human health.

River system a pivotal component of the global water cycle, functioning as major conduits for the convey of water, sediments and contaminants across different geological regions (Simpson and batley, 2016). However, the ripple effect of exponential Anthropocene era over the past decades have significantly disrupted the natural equilibrium of these systems, leading to the widespread accumulation of pollutants, particularly heavy metals, in aquatic environments (Jomova, *et al.,* 2025; Alloway, 2012; Förstner & Wittmann, 2012). Among the listed environmental factors that adversely cling on ecological disequilibrium, river sediments have been widely recognized as critical reservoirs for heavy metal contamination due to their strong capacity to adsorb and retain metallic elements (Abhijit, 2012). River sediments serve as both sinks and potential secondary sources of heavy metals in aquatic ecosystems (Tytla and Kernert, 2023). They play a critical role in the transport, distribution, and storage of contaminants, thereby providing a reliable medium for assessing pollution status over time (Simpson and Batley, 2016). Accumulation of Heavy metals on sediments over a very long period due to their long persistence can be reactivated under human pressures and disturbance making them a threat to aquatic ecosystem health

The Warri River, located in Delta State, is one of the major rivers in the Niger Delta and is subjected to significant environmental pressure from industrial and oil-related activities. Sediment studies in the river have identified the presence of heavy metals such as cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), and zinc (Zn), with variations linked to both natural and anthropogenic sources. Similarly, coastal and estuarine environments around Akassa, including creeks connected to the Nun River system, have been reported to contain heavy metals in sediments due to inputs from oil spillage, agricultural activities, and waste disposal practices. Despite several studies on heavy metal contamination in Nigerian aquatic systems, there is still a need for comparative assessments across different but ecologically connected water bodies within the Niger Delta. Such studies are essential for understanding spatial variations, identifying pollution sources, and evaluating potential ecological risks.

Therefore, this study aims to assess the concentration and distribution of heavy metals in sediments collected from the Warri River and Akassa Creeks in Delta State, Nigeria. The findings will provide valuable insights into the pollution status of these water bodies and contribute to environmental monitoring and management strategies in the Niger Delta region.

MATERIALS AND METHODS

Description of Study Area

The study locations (Fig 1) lie between latitude 5°21'-6°00' N and longitude 5°24'-6°2' E for Warri River, and 5°11' 50'' N and longitude 5°26' 49'' E for Akassa Creeks, Burutu in Delta State, Nigeria. Using standard protocols, samples were collected between January and June 2025. The water bodies are economically essential trade routes for commercial users, fisherfolk, and transportation. The rivers are fed principally by ground seepage from an aquifer in the thick rainforest of Utagba-Uno in Ndokwa, southern Nigeria, and run in a southwest direction, passing Ovu-inland and Ugbolokposo. It turns southward to Effurun and forms a 'W' between Effurun and Warri. It is characterized by extensive mangrove swamps and tidal flats, which are influenced by semi-diurnal tidal regimes.

The area enjoys a tropical climate, with well-demarcated rainy and dry seasons. The dry season stretches from November to April, while the rainy season is usually from May to October (Opute, 2000). The vegetation covers include red mangrove, *Rhizophora racemosa*, *R. mangle*, and the white mangrove *Avicennia africana*.

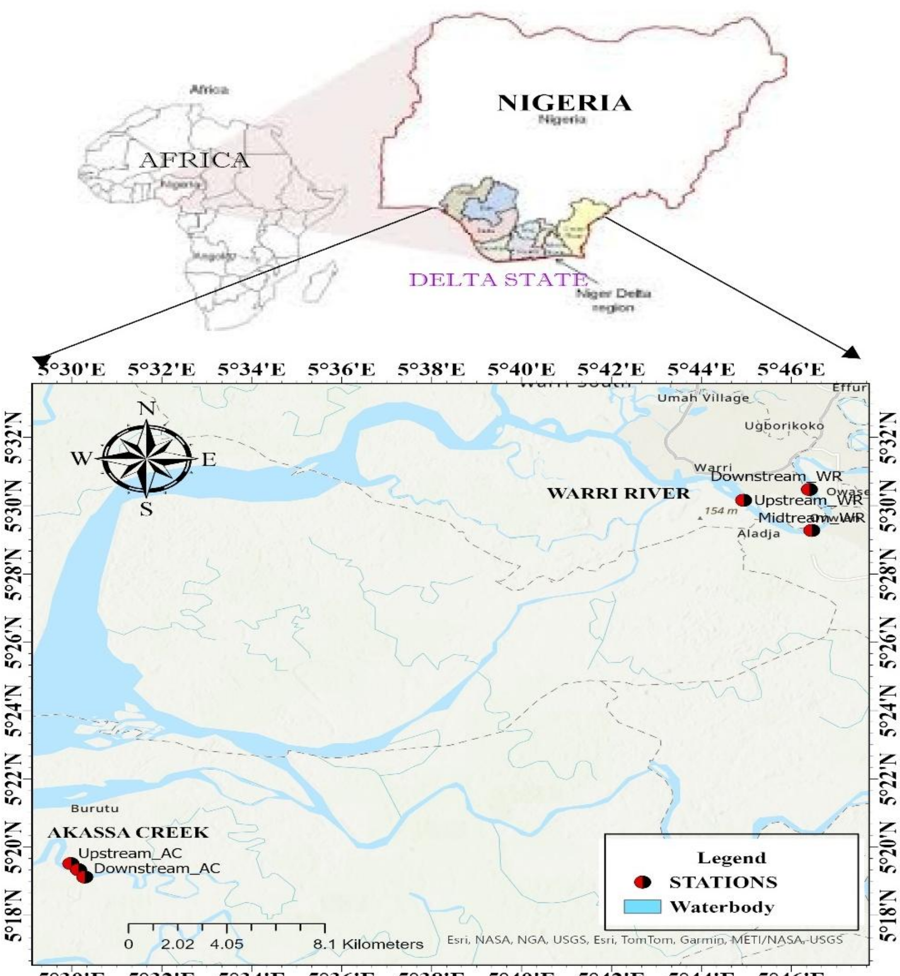

Figure 1: Warri River and Akassa Creeks sampling locations, Delta State, Nigeria

Experimental Design

The study was conducted over a four-month period, from January to June 2025. Sediment samples were systematically collected from the riverbed at three designated sampling stations using a pre-cleaned stainless steel hand trowel to minimize contamination. At each station, samples were obtained from the depth of about 0-5cm sediment layer, placed in acid-washed polyethylene containers, and subsequently wrapped in aluminum foil to prevent photodegradation and external contamination. All samples were properly labeled, stored in ice-packed containers, and transported immediately to the Marine Research Laboratory, Department of Marine Science, University of Delta, Agbor for analysis.

In the laboratory, sediment samples were air-dried at room temperature, homogenized, and sieved through a 2mm mesh to remove debris and ensure uniform particle size distribution. The concentrations of selected heavy metals lead (Pb), nickel (Ni), copper (Cu), and zinc (Zn) were determined following standard acid digestion protocols in accordance with procedures outlined by the Association of Official Analytical Chemists (AOAC).

Specifically, a known weight of each dried sediment sample was subjected to wet acid digestion using a mixture of concentrated nitric acid (HNO_3) and perchloric acid ($HClO_4$) under controlled heating conditions until complete mineralization was achieved. The resulting digest was filtered and diluted to a known volume with deionized water.

Quantitative determination of heavy metal concentrations was carried out using Atomic Absorption Spectrophotometry (AAS) with model Bulk Scientific VGB 211. Calibration was performed using certified standard solutions for each metal, and quality control measures, including reagent blanks and replicate analyses, were employed to ensure accuracy and precision of the results.

Statistical Tools for Data Analysis

Specialized python libraries were utilized for the analysis of data. Pandas was used for structured data management. NumPy was employed for efficient numerical array computations. Matplotlib served as the foundational plotting engine. Seaborn was used for advanced statistical data visualization. SciPy (Stats) was utilized for inferential statistics to perform independent T-tests to determine if observed differences between seasons and locations were statistically significant.

RESULTS

Seasonal Flux

The results 12.432mg/kg during the dry season as against 1.648mg/kg during the wet season according to Table 1 and 2 demonstrate a pronounced Dry Season Enrichment. In the Warri region, Lead (Pb) increased from a wet season mean of 0.0005 mg/kg to a dry season mean of 0.2200 mg/kg. The most significant flux was observed in Nickel (Ni), which peaked at mean value 2.5 mg/kg at Warri Station 1 during the dry season (Fig 2).

This indicates that reduced river volume and lower dilution capacity in the dry months exacerbate the concentration of industrial pollutants. There is a massive contrast in Nickel (Ni) levels in Warri between seasons. The Dry season concentration (5.0860mg/kg) is significantly higher than the Wet season (0.0170mg/kg) according to Table 3. Akassa's levels remain relatively low and stable across both seasons compared to Warri. Zinc (Zn) increased during the Wet season (0.2510mg/kg to 0.3620mg/kg), which might suggest different runoff or solubility patterns for that specific metal.

Table 1: Heavy metals in sediments collected from Warri River and Akassa Creeks, Delta State, Nigeria (mg/kg) (WET SEASON)

Heavy metals	WARRI 1	WARRI 2	AKASSA 1	AKASSA 2
Copper	0.030	0.036	0.00	0.000
Zinc	0.368	0.356	0.450	0.352
Lead	0.001	0.000	0.000	0.000
Nickel	0.021	0.013	0.012	0.009

Table 2: Heavy metals in sediments collected from Warri River and Akassa Creeks, Delta State, Nigeria (mg/kg)(DRY SEASON)

Heavy metals	WARRI 1	WARRI 2	AKASSA 1	AKASSA 2
Copper	0.232	0.231	0.000	0.001
Zinc	0.252	0.250	0.403	0.426
Lead	0.226	0.214	0.000	0.000
Nickel	10.097	0.075	0.012	0.013

Table 3: Mean Metal Concentrations by Location and Season (mg/kg)

Location	Season	Copper (Cu)	Lead (Pb)	Nickel (Ni)	Zinc (Zn)
Akassa	Dry	0.0005	0.0000	0.0125	0.4145
	Wet	0.0000	0.0000	0.0105	0.4010
Warri	Dry	0.2315	0.2200	5.0860	0.2510
	Wet	0.0330	0.0005	0.0170	0.3620

Spatial and Seasonal Variation Analysis

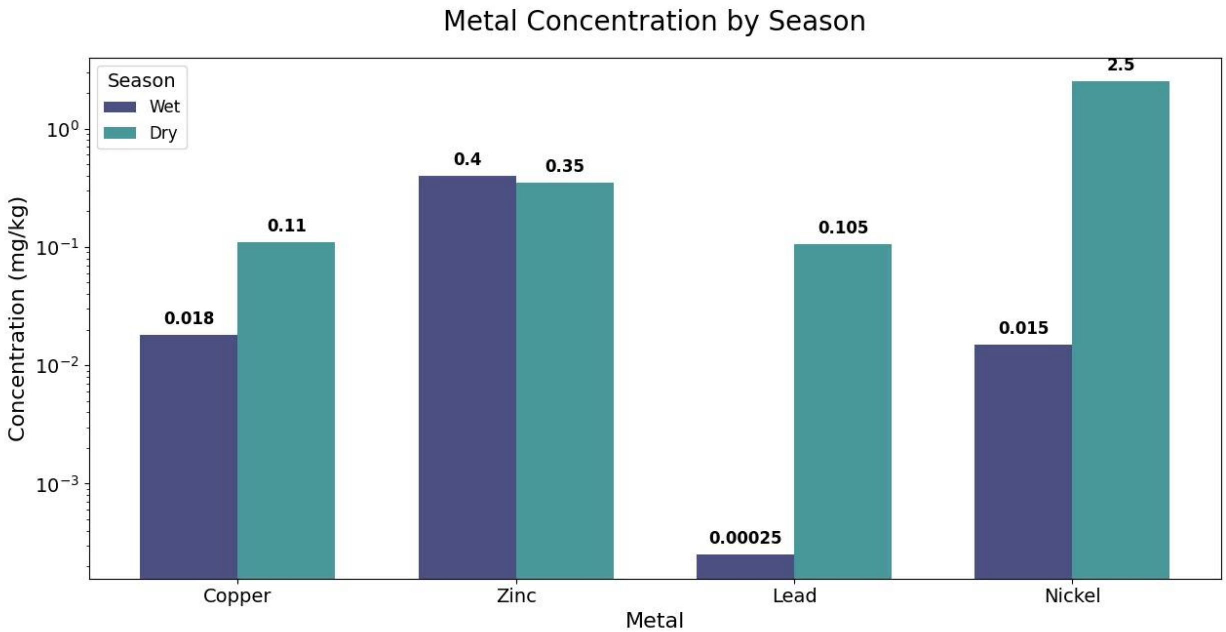

Fig 2: Seasonal Mean Metal Concentration (Grouped Bar Chart) (mg/kg)

Spatial Distri bution Analysis

Spatial analysis reveals that the Warri River is significantly more impacted by heavy metal pollution than the Akassa Creeks. The spatial T-test confirms that for Copper (P=0.0000) and Lead (P=0.0007), the differences are statistically significant. Copper, Lead, and Zinc all show very low P-values (P<0.01). This suggests that the heavy metal load in Warri is distinctly different from Akassa during the Dry season, likely due to localized industrial activity or geological factors.

Table 4: Spatial T-test Results: Warri vs. Akassa (Dry Season)

Metal	P-Value	Significance	Interpretation
Copper	0.0000	Significant	Extremely high confidence that levels differ.
Lead	0.0007	Significant	Strong evidence of spatial difference.
Zinc	0.0049	Significant	Statistically significant difference.
Nickel	0.4179	*Not Significant*	No statistical difference between locations.

A P-value less than 0.05 typically indicates a statistically significant difference.

Correlation of Analysis of Metals

The correlation between Copper and Lead (r = 0.9900) is nearly perfect (Fig 3). This strongly suggests these two metals likely share a common source (such as industrial discharge or a specific type of urban runoff). The value of -0.9165 as seen between Copper and Zinc shows a powerful inverse relationship. As Copper levels increase, Zinc levels tend to decrease significantly. This could indicate different chemical behaviors in the water or mutually exclusive pollution sources. Nickel shows a moderate positive correlation with Copper (r = 0.6548) and Lead (r = 0.6826), suggesting it is somewhat related to their distribution, but likely influenced by additional independent factors.

Table 5: Correlation Matrix: Inter-Metal Relationships

Metal	Copper (Cu)	Zinc (Zn)	Lead (Pb)	Nickel (Ni)
Copper	1.0000	-0.9165	0.9900	0.6548
Zinc	-0.9165	1.0000	-0.8871	-0.5795
Lead	0.9900	-0.8871	1.0000	0.6826
Nickel	0.6548	-0.5795	0.6826	1.0000

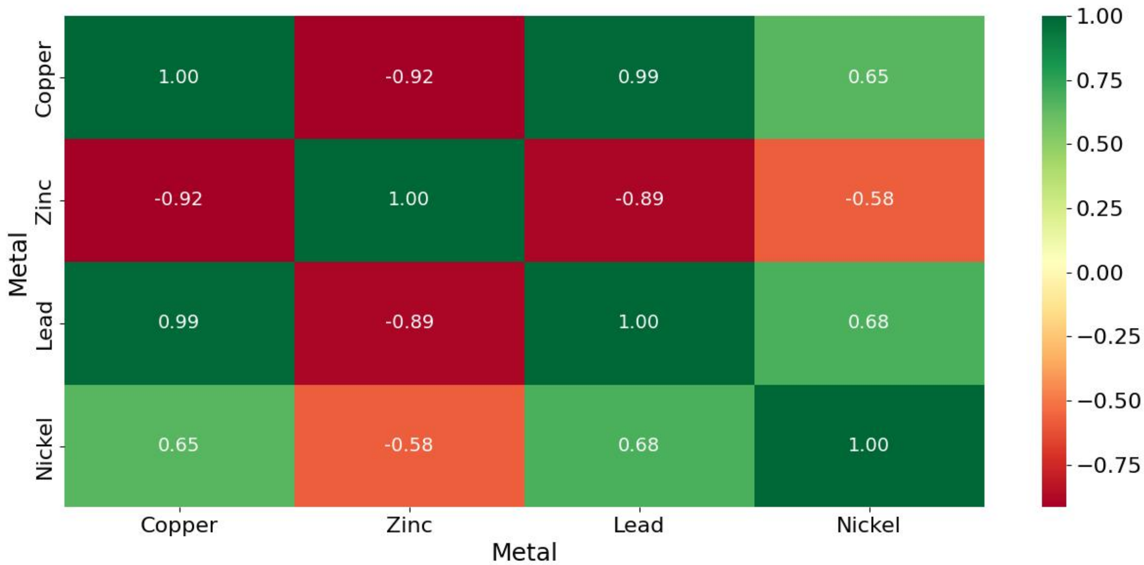

Fig. 3: Correlation Matrix of Heavy Metals

Health Risk Perspective

The elevated levels of Nickel and Lead (Fig 2) in the dry season pose a significant threat. Through biomagnification, these metals enter the food chain via benthic organisms and accumulate in fish species consumed by local populations. Lead is a known neurotoxin, while the high Nickel levels recorded (10.097 mg/kg) (Table 2) are associated with carcinogenic risks and respiratory complications in human receptors. According to

Shetty *et al., 2024* which further buttress the health risk implication of Heavy Metals using Monte Carlo Simulation Approach under the USEPA Human Health Risk Assessment (HRA) Model which proof a 33% carcinogenic effect on those exposed to Heavy Metal along the food chain either exposed through respiration, feeding or in contact. Kamunda *et al., 2016* also give a view on the carcinogenic effect on the absorption of Heavy metals through residential stay in a prone area.

DISCUSSION

The research effectively quantified the concentrations of Copper (Cu), Zinc (Zn), Lead (Pb), and Nickel (Ni) in both study areas. Zinc was the metal that was most often found in all places and at all times of the year, with levels ranging from 0.250 mg/kg to 0.450 mg/kg. The high levels of Zn and its availability in all sample stations might be due to the disposal of solid waste from residential areas which might contain higher levels of these metals. According to report from USGS, Zinc is the 23rd most abundant element in the earth's crust and fourth among all metals in world production exceeded only by iron, aluminum, and copper. Zinc uses range from metal products to rubber and medicines. About three-fourths of zinc used is consumed as metal, mainly as a coating to protect iron and steel from corrosion (galvanized metal), as alloying metal to make bronze and brass, as zinc-based die casting alloy, and as rolled Zinc. The remaining one-fourth is consumed as zinc compounds mainly by the rubber, chemical, paint, and agricultural industries. All these activities are spatially carried out in almost all region of our sample collection, though in bits but these could be a factor that contributed to the diverse spread of zinc in almost all the samples collected. Furthermore, the increase in concentrations of heavy metals might be due to leaching effect, since sediments usually serve as repository of elements in aqueous environment. This conforms to report by Chiaia-Hernández *et al.,* 2022; Stephen et al. (2001); that sediment could act as sink for a wide range of contaminants including heavy metals from various sources.

Nickel (10.097 mg/kg) was the most concentrated metal found at Warri Station 1 during the dry season. The concentration of Ni in the sediment samples of warri river 1 (10.097mg/kg) was higher than every other element in the river in both seasons as analyzed, with Akassa 2 during wet season has the lowest concentration of Ni in its sediment samples. Ni is mostly used for the production of alloys, electronic gadgets, welding, electroplating, in the production of nickel-cadmium batteries and as a catalyst in chemical and food industry. It is estimated that about 65% of the nickel consumed in the Western World and partly Africa is used to make austenitic stainless steel. Another 12% goes into superalloys (e.g., Inconel 600) or nonferrous alloys (e.g., cupronickel). Both families of alloys are widely used because of their corrosion resistance according to USGS in collaboration with (Nickel Institute, 2026). It is estimated that 8% of nickel is used for household appliances (WHO, 2004). The high concentration of Ni warri river 1 during the dry season could be due to several reasons ranging from Calm water conditions in the dry season allow particles (with nickel attached) to settle more easily, sediments remain more stable and accumulate metals, Some aquatic plants and microorganisms may be less active in the dry season leading to less uptake, and possible proximity to region with high density of welding activities. According to WHO 2004, 20 mg/kg showed that the concentrations of Ni in Warri River sediment is below tolerance level and indicate insignificant pollution with it limiting level below contamination.

Lead and copper were often below detectable levels (recorded as 0.000) in the Akassa Creeks. This suggests that the sedimentary environment there is much cleaner than in the Warri River.

The data shows that most metals are much richer in the dry season. During the wet season, more water and faster flow rates probably "scour" sediments and dilute them more, which lowers their concentrations (for example, Warri Lead levels drop to almost zero) which conforms with Roshan and Toolseeram (2002); atoki *et al.,* 2012; Okoro *et al.,* 2013 and Fatoki & Mathabata (2001). In the dry season, on the other hand, there is less flow and more evaporation, which makes pollutants more concentrated. The huge rise in Nickel (5.0860mg/kg mean in Dry vs. 0.0170mg/kg in Wet) in Warri shows how these changes with the seasons. Zinc levels went up a little in some places during the wet season, which is interesting. This means that Zinc could get into the river through runoff from land (like galvanized roofing or agricultural fertilizers) that gets washed away by rain.

The Warri River always had more Cu, Pb, and Ni than the other rivers. The statistical P-values (< 0.05) for Copper and Lead show that the pollution in Warri is not a one-time thing; it is a major environmental feature of the area. Akassa is still pretty clean when it comes to Lead and Copper. But the Zinc levels in Akassa (0.4145mg/kg) were higher than those in Warri (0.2510mg/kg), which means that there is a unique source of Zinc in the Akassa area.

The correlation analysis gives us a lot of information about where pollution comes from. The very close correlation ($r = 0.99$) between Copper and Lead strongly suggests that they come from the same human activity, probably industrial effluent or oil-related activities that are common in the Delta region which align with Pan *et al.,* 2023; Oloruntoba, 2021. The strong negative correlation between Zinc and other metals suggests that Zinc enters the system through different pathways, perhaps more linked to domestic waste or natural geological weathering rather than heavy industrial discharge.

CONCLUSION

The findings highlight potential environmental deterioration of the Warri River, likely associated with contaminant accumulation The Nickel levels during the dry season are especially scary. Nickel stays in the environment and can cause "Nickel itch" or breathing problems in people if it gets into the food chain. The mean Lead levels are low, but the dry season peak in Warri is worrying because Lead is not an essential element and there is no safe biological limit. It is dangerous for the people who live nearby and depend on the river for fishing. Because these metals are stuck in the sediment, they are a direct threat to benthic organisms, which are the base of the aquatic food web in the Delta State.

CONFLICTS OF INTREST

The authors declare no conflicts of interest

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