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Source Apportionment and Concentration of Potentially Toxic Elements in Surface Water and Sediments of Okulu-Aleto River, Rivers State, Nigeria

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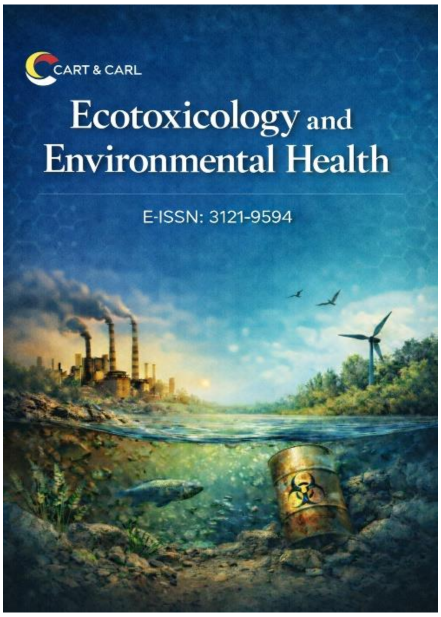

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Abstract

Urbanization and industrial activities continuously introduce potentially toxic elements (PTEs) into the terrestrial and aquatic environments, leading to various health-related challenges. This study evaluates the concentration of PTEs (Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Zinc (Zn), Lead (Pb) and Iron (Fe)) and sources identification in the surface water and sediment of Okulu-Aleto River, Rivers State, Nigeria. Using the Atomic Absorption Spectroscopic technique, the concentration of the studied PTEs were monitored for 4 surface water and 3 sediment samples. The mean concentration showed that the PTEs descended as Pb (0.126) > Cr (0.122) > Ni (0.061) > Cu (0.051) > Zn (0.039) > Cd (0.005) and all concentrations are within the WHO limit for surface water. The mean concentration descended as Cu (1.482) > Zn (1.215) > Cr (0.265) > Pb (0.119) > Ni ≥ Cd and all concentration are within the WHO limit except Cr across all sampling points and Cu at the upstream sampling point. Multivariate statistical analyses, including Pearson Correlation Coefficient and Principal Component Analysis, identified both lithogenic and anthropogenic sources, with industrial discharges, wastewater inputs, and sand mining activities contributing significantly to contamination. Strong positive loadings of Cr, Cu, Ni, and Pb indicated shared anthropogenic origins, while variations in Fe and Zn suggested mixed sources. Continuous monitoring and integrated pollution management strategies are therefore recommended to safeguard ecosystem integrity and public health.

Keywords : Aquatic Environment, Potentially Toxic Elements (PTEs), Principal Component Analysis, Sediment Contamination, Source Apportionment, Surface Water

Introduction

With rapid anthropogenic activities such as urbanisation and industrialisation, aquatic environments are increasingly polluted with potentially toxic elements (PTEs) with different level of effect on the aquatic environment and its components (Mohiduzzaman et al., 2015; Ali et al., 2016; Bai et al., 2023). The PTEs are naturally occurring elements in the human environment consisting of metals, semimetals, and non-metals (Afolabi et al., 2024) which are formed as a result of weathering action of parent materials with or without biological importance to living organisms (Pan et al., 2018; Carvalho et al., 2022). PTEs are regarded as concerned environmental substances as a result of their bio-accumulation, bio-magnification, persistence and toxicity (Marín et al., 2022). According to Afolabi et al. (204), PTEs are capable of health susceptibility at higher concentrations.

The persistent and accumulation of PTEs in the environment have been highly influenced by anthropogenic activities including those related to industrial processing, manufacturing, and applications, agricultural practices and waste management (Chen et al., 2015; Afolabi & Eludoyin, 2021) and remains a global issue of interest. However, the naturally occurrence actions such as such as metal corrosion, atmospheric deposition, soil erosion of metal ions, volcanic eruptions and weathering and their contribution to the environmental concentration of PTEs should be considered (Goher et al., 2019; Sharma et al., 2021; Omutange et al., 2022). The PTEs concentration in the aquatic environment could be as a result of anthropogenic actions such as urbanisation and industrialisation or nature-related activities; however, anthropogenic contribution has significantly increased in recent centuries (Afolabi, 2024).

Anthropogenic contributions to PTEs increased concentration in aquatic environment have been highly documented; for instance, Gu et al. (2022) reported high concentration of PTEs such as Zn, Cr, Cu, As, Cd and Pb in urban rivers due to intensive industrialization and urbanization Qingdao, East China. Mining activities have been reported to increase the concentration of PTEs in an aquatic environment leading to health concerns and ecological degradation (Yan et al., 2024; Merga et al., 2025). Omutange et al. (2022) suggested an influenced concentration of PTEs (Pb, Cd, Cu and Zn) in a riparian zone due to effluent discharge from Kraft pulp and paper mill activities in western Kenya. In Nigeria, increased concentration of PTEs (such as Cr, Pb, Fe, Ni, Cd, Zn and Cu) in aquatic environment has been reported due to industrialization, urbanization and mining activities (Sulaiman et al., 2024; Afolabi et al., 2024).

The PTEs concentration and sources should be consistently and accurately monitored for sustainable management of the aquatic system (Custodio et al., 2020). For aquatic ecosystem, the water and sediment can be monitored through various PTEs assessment (Saleem et al., 2015), and the findings can highlight the effective management practices for the ecosystem (Afolabi et al., 2022). Okulu-river have been supporting various anthropogenic activities within and beyond the environment such as serving as the wastewater receiving river for various industries, abattoirs and sand mining which suggest the need for monitoring program. Therefore, the study intends to carry out preliminary quantifications of the PTEs in the surface water and sediment of the river and identify the source allocations of PTEs using statistical techniques.

Method and Materials

Study Area

The study was undertaken within Okulu-Aleto, Eleme Local Government Area, Rivers State of Nigeria. Eleme is located between latitude 4° 44'0"N and 4°50'0"N and longitude 7°6'0"E and 7°12'0"E (**Figure 1**). It covers an area of 138 km2 and, as of the 2006 census, had a population of 190,884 (Afolabi & Adesope, 2022). The area's climate condition is endowed with abundant sunshine and rainfall due to its location near the equator, which can also influence the rate of dispersing and environmental fate of the pollutants. Considering various activities surrounding the Okulu-river such as activities of petrochemical industrial, abattoir, sand mining, fishing and other human activities that influence the water chemistry and such makes the river important for the study. The map of the study area and sampling points was presented in Figure 1.

Sample Collection

The samples were collected in 21st February 2024 from four sampling points for surface water and three sampling points for the sediment (Supplementary Table (ST) 1). The surface water collection followed the procedure described by Pan et al. (2018) and Ogbonna et al. (2021). With the aid of sterilised lucid bottle, surface water samples (n =4) were collected, filled to the brim and covered before bringing out the bottle. All samples collected were placed in ice box before transporting to the laboratory (Integrated Scientific and Engineering Solutions Limited) for analysis. The sediment samples (n=3) were collected across the three sections of the river with the aid of an Eckman grab, dip down into each medium and turned 360° before being withdrawn and samples taken. At each section, 3 sediments samples were randomly collected to make the composite sample and a total of 3 composite samples were collected across the sample area. Collected samples were instantly wrapped in foil papers and appropriately label and taken to the laboratory for analysis.

Laboratory Analyses

The PTEs such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Zinc (Zn), Lead (Pb) and Iron (Fe) were analysed for surface water and sediment samples collected from Okulu-Aleto River, Rivers State, Nigeria. The sample digestion was based on United State-Environmental Protection Agency (US-EPA) (1983) procedure similar to the one described and adopted by Merga et al. (2025) for surface water sample and Afolabi and Adesope (2022) for sediment sample. For the surface water, the digestate was filtered using 0.45µm membrane filter into 100 mL volumetric flask. Lastly, the volume of the filtrate was adjusted to 100mL and immediately the aliquot was analysed for the selected PTEs using Flame Atomic Absorption Spectroscopy (FAAS). Similarly, the diluted sample was then filtered using acid-washed Whatman No. 44 filter paper into a 50 ml volumetric flask and diluted to mark. The sample was then aspirated into an FAAS machine at the interval for readings of selected PTEs concentration in the sample.

Quality assurance/control (QA/QC)

The laboratory analyses were performed under strict and standard QA/QC procedures which ensure that samples were analysed in triplicate and mean estimation for accuracy and precision. Glassware and digestion vessels were acid-washed (10% HNO_3) and rinsed with ultrapure water prior to use. Instrument calibration was performed using multi-element calibration standards prepared from certified stock solutions.

Accuracy and precision of the result was evaluated using spike recovery tests (%) and percent relative standard deviation (%RSD). Recoveries for analysed elements ranged between 86% - 99% and the %RSD (1.9 - 11.9% for surface water and 0.3 - 12.3% for sediment) indicating the procedure for determination of PTEs were within the acceptable range. The limit of detection (LOD) and limits of quantification (LOQ) were calculated individually for each element based on blank standard deviations and calibration slope. The LOD and LOQ values ranged from 0.001–0.055 mgL-1 and 0.004–0.16 mgL-1 for surface water and 0.002-0.054 mgL-1 for the sediment. Calibration linearity was verified with coefficients of determination (R^2) exceeding 0.995 for all elements across samples. All the indicators asset the accuracy and robustness of the procedure for the analysis while the values for the individual elements was present in Table S3-4.

Data Analysis

Descriptive statistics such as mean value was adopted, and the findings were presented through tables and charts. With the aid of statistical tools such as Pearson's Correlation Coefficient (PCC) and Principal Component Analysis (PCA), the source(s) and distribution of PTEs in surface water and sediment were analysed using the Statistical Package for the Social Sciences (SPSS) version 26 platform.

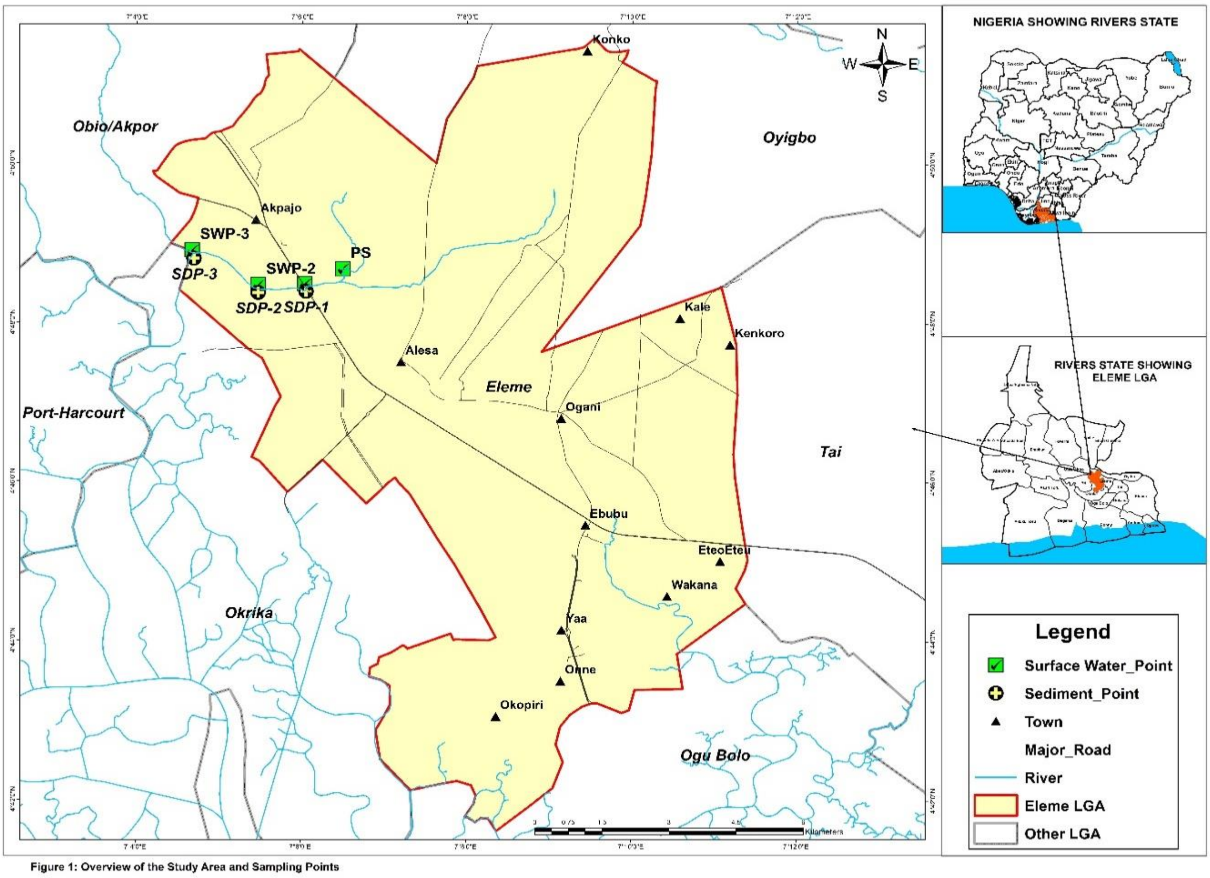

Figure 1: Overview of the Study Area and Sampling Points

Result and Discussion

Concentration of PTEs in the Surface Water and Sediment

The concentration of PTEs in surface water and sediment of the study area was presented in **Table 1**. For the PTEs reported for the surface water, the mean concentration showed that the PTEs descended as Pb (0.126) > Cr (0.122) > Ni (0.061) > Cu (0.051) > Zn (0.039) > Cd (0.005) and all concentration are within the WHO limit. The PTEs of the sediment shows that the mean concentration descended as Cu (1.482) > Zn (1.215) > Cr (0.265) > Pb (0.119) > Ni ≥ Cd and all concentration are within the WHO limit except Cr across all sampling points and Cu at the upstream sampling point. According to Afolabi et al. (2024), various human activities such as industrial and agricultural practices have contributed to the high concentration of PTEs in the environment which increases the health risk such as anaemia and cancer, nervous system and kidneys, allergies, cardiovascular and kidney diseases, lung fibrosis, and lung and nasal cancer (Mugica et al., 2002; Tiwari et al., 2015; Bazrafshan et al., 2015; Afolabi, 2024).

Table 1: Concentration of PTEs in Surface Water and Sediment

	Surface Water (mg L^{-1})						Sediments (mg kg $^{-1}$)					
PTEs	**PS**	**SWP-1**	**SWP-2**	**SWP-3**	**CS**	**Mean**	**SDP-1**	**SDP-2**	**SDP-3**	**CS**	**Mean**	**WHO**
Cd	<0.001	<0.001	0.001	0.015	0.001	0.005	<0.001	<0.001	<0.001	<0.001	-	0.03
Cr	0.097	0.097	0.139	0.139	0.139	0.122	0.265	0.223	0.265	0.307	0.265	0.1
Cu	0.039	0.049	0.059	0.059	0.049	0.051	5.574	0.128	0.118	0.108	1.482	2.0
Ni	<0.001	0.013	0.077	0.093	0.061	0.061	<0.001	<0.001	<0.001	<0.001	-	0.07
Zn	0.076	0.046	<0.001	0.015	0.021	0.039	3.097	0.204	0.843	0.716	1.215	5.0
Pb	0.007	0.081	0.230	0.156	0.156	0.126	0.081	0.007	0.156	0.230	0.119	0.01
Fe	0.211	1.942	0.084	0.321	0.084	0.528	22.27	18.90	23.24	23.29	21.925	0.3

The Cd concentration was below detected limit across the various sampling points and well below the stipulated WHO standard for both surface water and sediment. The reported concentration was lower than those reported for surface water and sediment from Tumet River in Ethiopia (Merga et al., 2025), Bay of Callao in Peru (Guabloche et al., 2024), and Sava River in southeastern Europe (Jonjev et al., 2024). According to Jomova et al. (2024), the exposure to Cd lead to effect such as fever, body pain vomiting, salivation, muscle cramps, vertigo, shock, loss of consciousness and convulsions while chronic exposure can affect organs including brain, lung and kidney.

The Cr concentration reported for this study was lower than those reported by Gu et al. (2022) and Ahamad et al. (2024) for surface sediment in Pakistan and China respectively. Similarly, higher concentration was reported by Afolabi et al. (2024) for Bonny River (Fibiri and Iwoama Creek) for surface water and sediment. Cr is regarded as non-essentials to human and mammals as there is no evidence-based of the biological function of Cr to human physiological activities. Cr in its compounded forms, such as chromates of Ca, Zn, Sr, and Pb, are highly soluble in water, toxic and carcinogenic (Nwaichi et al., 2016). Ali et al. (2021) suggested that Cr concentration in sediment was higher than other metals as a consequence of direct discharging untreated wastes from petroleum, fertilizers and textile industries.

The Cu concentration of the present study was lower than those reported for surface water in a mining area in South Africa (Belle et al., 2023) and China (Yan et al., 2024), while higher concentration was reported for surface sediment in Morocco (Basraoui et al., 2024). This study Cu concentration was higher than those reported for remediated oil spill site for surface sediment in Nigeria (Afolabi & Adesope, 2022).

The Ni concentration was below detected limit in the sediment samples while the concentration was with allowable limit in surface water samples. The reported concentration for this study was lower that those reported for similar environment in Nigeria (Afolabi & Adesope, 2022; Adewumi & Laniyan, 2021), China (GU et al., 2022), and Peru (Guabloche et al., 2024). As trace nutrient for human, nickel is classified as possibly essential element. However, human's exposure to high level of nickel can poses different health problems including allergy, cardiovascular and kidney diseases, lung fibrosis, lung and nasal cancer (Genchi et al., 2020).

The Zn reported for the surface water and sediment were within the WHO stipulated limit indicating that the environment is not contaminated with Zn. Although, Zn is an essential trace element regulating different metabolic activities in human body. However, exposure to high concentration of Zn can pose health effects including stomach pains, rashes, vomiting, nausea, anemia, liver failure, and renal failure (Khalef et al., 2022). The concentration reported for this study is lower than those reported for similar environment in Nigeria (Afolabi et al., 2024; Bubu et al., 2018), Ethiopia (Merga et al., 2025), Morocco (Basraoui et al., 2025) and Pakistan (Ahamad et al., 2024).

The concentration of the Pb for the study exceeded the WHO limit at some of the sampling points indicating progressive accumulation of Pb in the environment.

Continuous accumulation of Pb in the studies river could pose risk to human and aquatic organisms of the river. The concentration of Pb reported for this study was lower than those reported by Merga et al. (2025) and Basraoui et al. (2025) but higher than those reported by Omutange et al. (2022) for similar environment. Merga et al. (2025) suggested that Pb being a toxic non-essential element can cause neurological, cardiovascular, hematologic, and reproductive effects and high-level exposure can have severe impact on children, young people, and pregnant women.

The Fe concentration for the study exceeded the WHO limit for surface water and sediment; although, higher concentration of Fe was recorded in sediment samples. The reported concentration for surface water was lower than those reported by Merga et al. (2025) and Afolabi et al. (2024) while the concentration for sediment samples for this study were higher than those reported by Basraoui et al. (2025) and Afolabi and Adesope (2022). Despite Fe being an essential micronutrient for human, excessive exposure to Fe can promote the formation of oxidative stress (e.g. reactive oxygen species), which further cause damage to lipid membranes (Carocci et al., 2018).

Source Apportionment Analysis for Surface Water and Sediment

The source and distribution of PTEs across the surface water and sediment were analysed through PCA, PCC, rotation component matrix of HM, and screen plot, which are summarised and presented in **Table 2** and Supplementary **Figure-SF 1-2 and Table 5**. Prior to PCA, sampling adequacy and data suitability were verified using the Kaiser–Meyer–Olkin (KMO) measure and Bartlett's Test of Sphericity. The KMO values of 0.74 and 0.76 were deduced for surface water and sediment respectively, exceeded the minimum acceptable threshold 0.5, confirming dataset suitability for multivariate analysis. The Pearson correlation mix of the surface water indicated that Cd has a significant and relatively strong relationship (> 0.5) with Cr and Ni with a correlation coefficient (r) of 0.536 and 0.612 respectively and week and negative relationship with Cu (-0.031), Zn (-0.317), Pb (0.242) and Fe (-0.146). Also, Zn and Fe showed significant weak (and negative) relationship with other PTEs. Furthermore, a significant and positive relationship exist between Cr and Cu (r = 0.710), Ni (r = 0.981) and Pb (r = 0.895), between Cu and Ni (r = 0.684) and Pb (r = 0.945) and between Ni and Pb (r = 0.864). According to Afolabi et al. (2023), PTEs of strong correlation indicated similar sources and distribution patterns noted among Fe, Ni, Se, Zn and Cu. In same vein, Ustaoğlu et al. (2020) asserted that the lack of correlation between and among parameters indicate a lack of mutual forms of source and distribution pattern.

Table 2: Pearson's Correlation Coefficient (PCC) Analysis

	Cd	Cr	Cu	Ni	Zn	Pb	Fe
Surface Water							
Cd	1.000						
Cr	0.536	1.000					
Cu	-0.031	0.710	1.000				
Ni	0.612	0.981	0.684	1.000			
Zn	-0.317	-0.910	-0.915	-0.917	1.000		
Pb	0.242	0.895	0.945	0.864	-0.975	1.000	
Fe	-0.146	-0.573	-0.095	-0.488	0.297	-0.295	1.000
Sediment							
	Cr	Cu	Zn	Pb	Fe		
Cr	1.000						
Cu	-0.003	1.000					
Zn	0.163	0.976	1.000				
Pb	0.948	-0.263	-0.074	1.000			
Fe	0.866	0.108	0.318	0.881	1.000		

For the surface water, the principal component (PC) of the PTEs showed strong positive correlation for Ni:0.760, Cr:0.776, Cu:0.993 and Pb:0.971 for PC1, Cd:0.995, Ni:0.529 for PC2 and Fe:0.989 for PC3 while negative or weak positive correlation was common with Zn across the PCs, Cd with PC1 and PC3, Ni with PC3, Pb and Cr with PC2 and PC3. The eigenvalues indicated that the PC1 and PC2 has > 1 and PC1 has 57.716 % of the total variance capable of explaining the factor. For the sediment, the PC of the PTEs showed a strong positive correlation for Cr:0.982, Pb:0.982 and Fe:0.927 for PC1, Cu: 0.996 and Zn:0.991 for PC2 while negative or weak positive correlation was common with PC3. The eigenvalues indicated that the PC1 and PC2 has > 1 and PC1 has

56.115 % of the total variance capable of explaining the factor. According to the Liu et al. (2022), PTEs sources can be categorized based on the extent of positive loading value with 0.75 - 1.0 being strong positive loading, 0.5 - 0.75 moderate positive loading (0.5–0.75), and weak positive loading (0.3–0.5). Therefore, the PTEs in PC1 and PC2 of the surface water (such as Ni, Cr, Cu, Pb and Cd) and sediment (such as Cr, Cu, Zn, Pb and Fe) are presumed to be an anthropogenic source related with industrial activities.

The outcome was similar to the study conducted by Zeng et al. (2022) and Afolabi et al. (2024). Furthermore, Chen et al. (2022) suggested that a weak positive and negative values of PTEs across the PCA is a confirmation of the influence of multiple sources. Also, PTEs with similar(strong and positive OR weak and negative) correlation suggest similar sources and transport pathway (Chen et al., 2022; Ustaoğlu & Islam, 2020; Hou et al., 2019). The difference in the PTEs correlation for surface water for suggest difference sources and patterns such that Ni, Cr, Cu and Pb in PC1 are lithogenic source while Cd, Zn and Fe are anthropogenic source. For sediment, PTEs such as Cr, Pb and Fe suggest lithogenic source while Cu and Zn suggest anthropogenic source. The outcome is similar to the findings reported by Zeng et al. (2022) and Wang et al. (2022). Overall, PTEs find their way into the aquatic environment through various sources including atmospheric deposition and series of anthropogenic activities (Shen et al., 2021; Afolabi, 2024).

Conclusion

Having considered the apportionment of PTEs in the aquatic environment based on multivariate statistical techniques such as principal component analysis (PCA) and Pearson Correlation Coefficient (PCC), the study deduced that various human activities have contributed to the concentration of the PTEs in the surface water and sediment of the aquatic environment; however, the concentration are within the WHO allowable limit except for Cr and Cu in the sediment. The PCA of the PTEs further established that the PTEs in the aquatic environment has both the lithogenic and anthropogenic influence. There is need for continuous monitoring of the aquatic environment for effective sustainability that will ensure safety of the aquatic organism and human being at large.

This study offers a thorough evaluation of the concentration and source apportionment of potentially toxic elements (PTEs) in the surface water and sediments of the Okulu-Aleto River, an essential aquatic system affected by various anthropogenic activities. The results indicate that while the majority of PTE concentrations fell within the permitted limits set by the WHO, except chromium (Cr) in sediments and localised increases of lead (Pb) and iron (Fe) suggest emerging environmental and public health issues. The observed distribution patterns indicate that Pb and Cr predominate in surface water, while Cu and Zn are prevalent in sediments, reflecting distinct partitioning and accumulation processes within the aquatic system. Multivariate statistical analysis (PCA and PCC) indicated that the PTEs derive from both lithogenic and anthropogenic sources. The robust correlations between Cr, Cu, Ni, and Pb indicate substantial input from industrial effluents, wastewater discharge, and other anthropogenic activities in the studied area. The interplay of natural and human-induced inputs highlights the intricacy of pollutant behaviour in the aquatic environment.

The study emphasises that sediments function as both sinks and potential secondary sources of contamination, posing long-term ecological concerns through remobilisation processes. Consequently, although concentration levels are normally adequate, the ongoing introduction and accumulation of PTEs may result in future degradation of water quality if not properly managed. Given these findings, there is an urgent necessity for continuous environmental monitoring, more stringent regulation of industrial and municipal effluents, and the execution of comprehensive watershed management policies. This would guarantee the preservation of aquatic ecosystems, preserve public health, and encourage sustainable use of water resources in the Niger Delta region.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit Authorship Contribution Statement

Afolabi, O. O.: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Visualization, Project administration, Writing-original draft, Review & Editing. **Nwankwoala, H. O. and Hart, A.I.**: Supervision, Methodology, Validation, Formal analysis, Data curation, Visualization, Review & Editing.

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