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ECOTOXICOLOGY AND ENVIRONMENTAL HEALTH

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

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Abstract

The concentration of potentially toxic elements (PTEs) in the aquatic environment can be influenced by naturally occurring activities, anthropogenic and atmospheric deposition. With various multivariate statistical tools, the apportionment of the PTEs in the environment can be established. The source apportionment and concentration of PTEs in surface water and sediments of Okulu-Aleto river, Rivers state Nigeria was determined. Based on laboratory analysis standard (American Public Health Association), PTEs such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Zinc (Zn), Lead (Pb) and Iron (Fe) were considered. The pH of the surface water (6.27 – 6.65) and sediment (6.54-6.85) tends towards neutral while the mean concentration of electrical conductivity (EC) at 13740 µs/cm for surface water and 1376.75µs/cm for sediment. The mean concentration showed that the PTEs descended as Pb > Cr > Ni > Cu > Zn > Cd for surface water and Cu > Zn > Cr > Pb > Ni ≥ Cd for sediment while all concentrations are with WHO limit except Cr across the sampling points. The principal component analysis (PCA) revealed difference correlation level suggesting PTEs of lithogenic and anthropogenic sources. Continuous environmental monitoring is required to ensure environmental sustainability.

KEYWORDS: Potentially Toxic Elements (PTEs), Principal Component Analysis, Source Apportionment, Environmental Sustainability, Aquatic Environment

Introduction

With rapid anthropogenic activities such as urbanisation and industrialisation environmental media such as aquatic environments are increasingly polluted with potentially toxic elements (PTEs) with different level of effect on the aquatic environment and its components (Ahmeed 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 (Carvalho et al., 2022; Pan et al., 2018). PTEs are environmentally concerned due to their persistence, toxicity, bioaccumulation, and biomagnification (Marin et al., 2022). At high concentrations, they pose health risks to organisms, including humans (Afolabi et al., 2022).

The persistent and accumulation of PTEs in the environment have been highly influenced by anthropogenic activities mineral resources development, metal processing and smelting, industrial emissions, application of fertilisers and pesticides, sewage irrigation, and landfill systems and remains a global issue of interest (Chen et al., 2015; Afolabi and Eludoyin, 2021). 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 (Omutange et al., 2022; Goher et al., 2019; Sharma et al., 2021). 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.

The PTEs concentration and sources should be consistently and accurately monitored for sustainable management of the aquatic system (Custodio et al., 2020). The aquatic environment can be assessed based on the water and sediment of the ecosystem (Salem et al., 2015), and the outcome can support the management of the environment (Afolabi *et al*., 2022). Different procedure and statistical analysis techniques are used to determine PTEs sources and concentration in the aquatic environment (Ates et al., 2020). The multivariate statistical techniques such as cluster analysis (CA), principal component analysis (PCA), factor analysis (FA), Hierarchical Cluster Analysis (HCA), and Pearson Correlation Coefficient (PCC) have been widely accepted as efficiently tools in terms of data analyzing and interpreting and have been used to find relationships between elements and determine their sources (Zhang et al., 2016; Ustaoğlu & Islam, 2020; Ates et al., 2020; Zeng et al., 2022; Afolabi et al., 2023a, Afolabi et al., 2024). 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 km^2 and, as of the 2006 census, had a population of 190,884. 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.

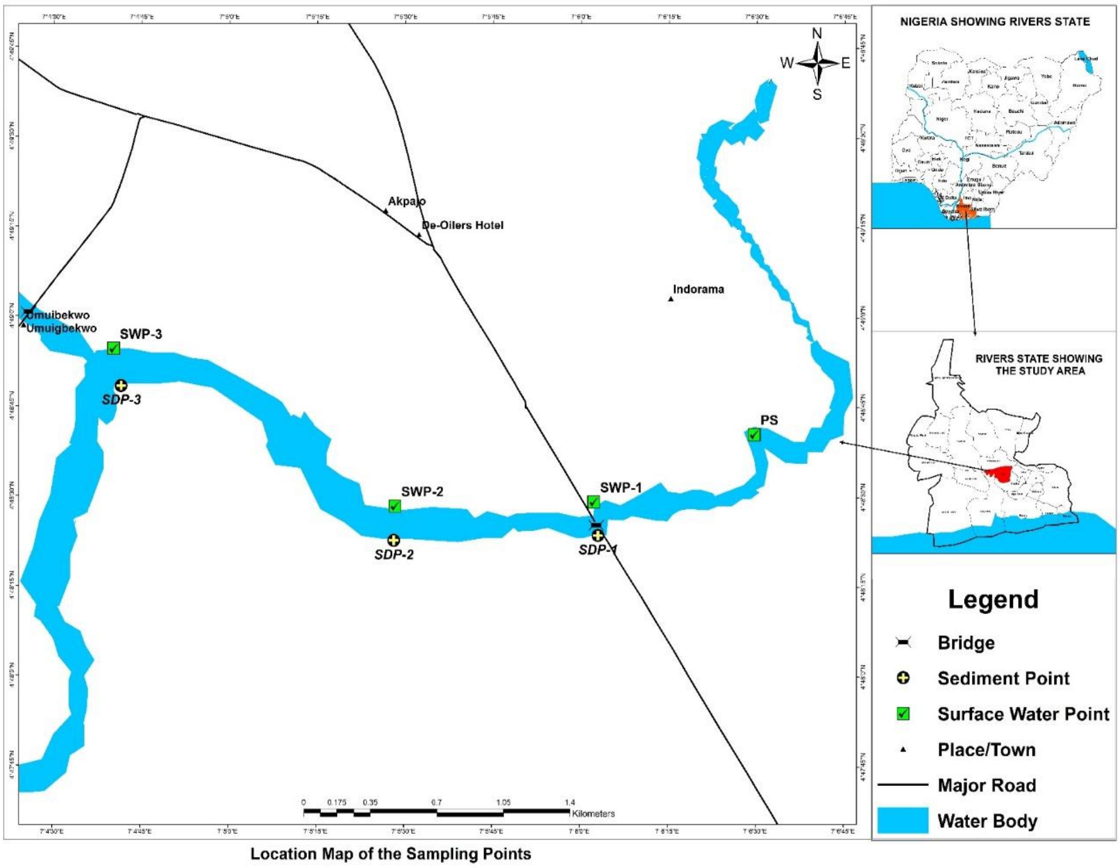


Figure 1: Overview of the Study Area and Sampling Points

Sample Collection

The samples were collected in 21st February 2024 from four sampling points for surface water and three sampling points for the sediment (Table 1).

Table 1: Sampling Points Details and Geographical Information

Description	**Code**	**Latitude**	**Longitude**
Surface Water Details			
Point Source	PS	4° 48' 40.500" N	7° 6' 29.900" E
Surface Water Point 1	SWP1	4° 48' 29.177" N	7° 6' 2.543" E
Surface Water Point 2	SWP2	4° 48' 28.399" N	7° 5' 28.621" E
Surface Water Point 3	SWP3	4° 48' 54.573" N	7° 4' 40.533" E

Sediment Details			
Sediment Point 1	SDP1	4° 48' 23.547" N	7° 6' 3.276" E
Sediment Point 2	SDP2	4° 48' 22.635" N	7° 5' 28.416" E
Sediment Point 3	SDP3	4° 48' 48.379" N	7° 4' 41.823" E

Surface Water: , based on the method described by Ogbonna et al. (2021) and Pan et al. (2018). For the surface water, a sterilised transparent bottle was plunged into the water about 30cm deep, and the bottle was filled to the brim and covered before bringing out the bottle. This was repeated at four different points (sub-composites) about 25m apart, all in the opposite direction of water flow. All the sub-composites (4) were mixed to form a composite sample for each creek and placed in an ice box before transporting to the laboratory (Integrated Scientific and Engineering Solutions Limited) for analysis.

Sediment: The sediment samples 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 Analysis

The PTEs such as Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Zinc (Zn), Lead (Pb) and Iron (Fe) along with physiochemical properties such as pH and electrical conductivity (EC) were analysed for surface water and sediment. All the parameters were analysed based on American Public Health Association standard-APHA (APHA, 2012) and American Standard for Testing Materials- ASTM (ASTM, 2012) accepted standard procedures and analytical method described by Afolabi et al. (2022), while the PTEs concentration was determined by absorption spectrometer (Perkin Elmer 3100 model). Quality assurance/control (QA/QC) ensures that analyses are done at standard procedures, triplicate analyses and mean estimation for accuracy and precision. All analyses were subjected to quality reagents while instruments were sterilized, soaked in 10% HNO3 in 1% HCl solution, washed adequately with deionized water, and desiccated. Detection limits, including LOD and LOQ, were estimated as LOD = 3 σ/S, LOQ = 10 σ/S, respectively, where σ is the SD (standard deviation) of analytical blank measurement (n = 18). At the same time, S is the slope of the calibration curve (y = mx + b) (Ahmad et al., 2021).

Data Analysis

Descriptive statistics such as mean value was adopted, and the findings were presented through tables and charts. The source and distribution of PTEs across the surface water and sediment were analysed through statistical tools such as Pearson's Correlation Coefficient (PCC) and Principal Component Analysis (PCA) using the Statistical Package for the Social Sciences (SPSS) version 21 platform.

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 2. The pH reported for the surface water across the sampling points were below the WHO limit for surface water and within the range of 6.27 – 6.65 which indicated the pH tends toward neutral. Similarly, the pH of the sediment across the sampling points ranged from 6.54 – 6.85 tends toward neutral and within the WHO limit. The reported pH was lower than those reported by Afolabi and Adesope (2022) at 3.35 – 5.13 for surface sediment from similar environment. The pH range reported in the present is similar to those reported by Afolabi et al. (2024) and Ngah et al. (2017) at 6.28 and 6.40 respectively while lower to the value reported by Onojake et al. (2015). According to Ngah et al. (2017), pH tending towards neutral suggests evidence of the presence of waste material which is an attribute to human activity. This may also be attributed to watershed and other human activities. The EC reported for surface water across all the sampling points exceeded the WHO limit for surface water. Similar outcome was observed among the EC concentration of sediments at the upstream and midstream while those reported for downstream and composite sample are within the WHO limit. The concentration reported therein was lower than those reported by Onojake et al. (2015) and Ngah et al. (2017).

Table 2: Concentration of PTEs in Surface Water and Sediment

	Surface Water (mg/l)						**Sediments (mg/kg)**					
PTEs	**PS**	**SWP-1**	**SWP-2**	**SWP-3**	**CS**	**Mean**	**SDP-1**	**SDP-2**	**SDP-3**	**CS**	**Mean**	**WHO**
pH	6.41	6.65	6.27	6.39	6.60	6.464	6.54	6.83	6.85	6.94	6.79	6.5 – 8.5
EC*	6330	8900	15440	17070	13740	12296	1,715	2090	829	873	1376.75	1000
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	0.1185	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

*concentration in µs/cm

For the PTEs reported for the surface water, the mean concentration showed that the PTEs descended as Pb > Cr > Ni > Cu > Zn > Cd and all concentration are within the WHO limit. The PTEs of the sediment shows that the mean concentration descended as Cu > Zn > Cr > Pb > Ni ≥ Cd and all concentration are within the WHO limit except Cr across all sampling points and Cu at the upstream sampling point. The outcome was similar to those reported by Ali et al. (2016) and Onojake et al. (2015) which reported higher concentration of Cr in their study. Cr has no biological function linking human physiological activities; hence, regarded as non-essential to humans/mammals. 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. (2016) 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. According to Afolabi et al. (2024), excessive concentrations of PTEs are attributed to anthropogenic activities such as industrial discharge and engagement of resources from 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),

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 Tables 3-4 and Figure 2-3. 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).

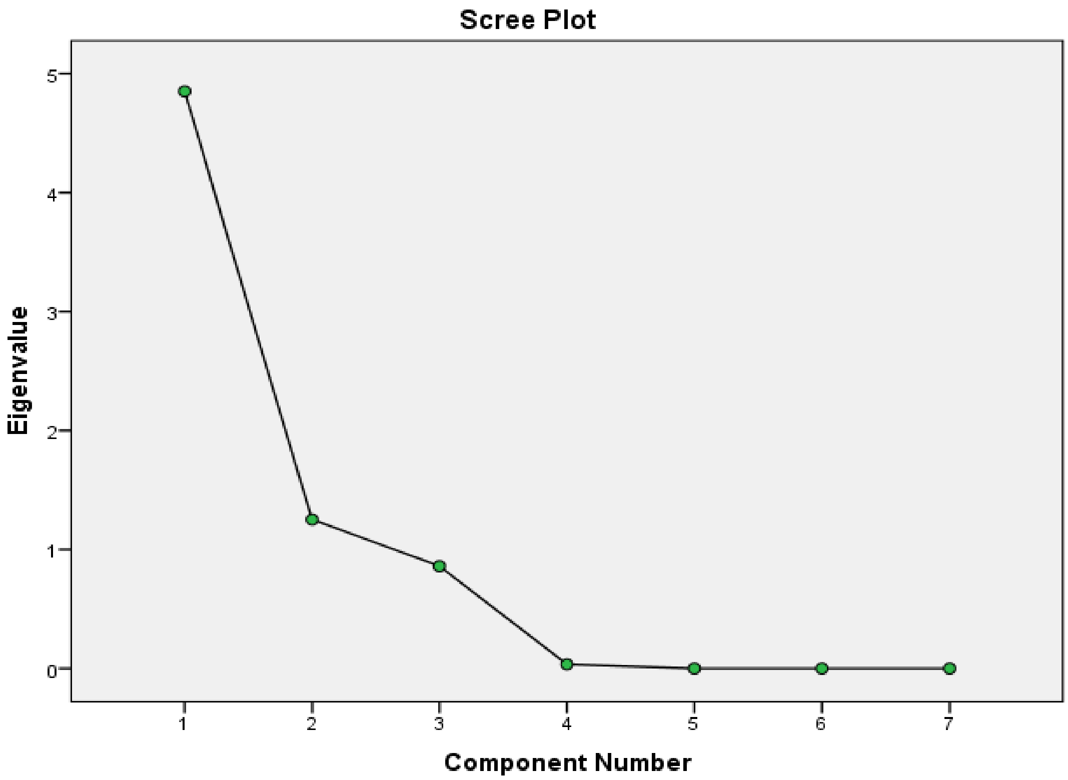
Also, Zn and Fe showed significant weak (and negative) relationship with other PTEs. Furthermore, a significant and positive relationship exist between Cr and Cu (r = 0.710), Ni (r = 0.981) and Pb (r = 0.895), between Cu and Ni (r = 0.684) and Pb (r = 0.945) and between Ni and Pb (r = 0.864). According 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 3: 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		

Table 4: Rotation component matrix of PTEs across the Environmental Mediums

	Surface Water			Sediment		
	PC 1	**PC 2**	**PC 3**	**PC 1**	**PC 2**	**PC 3**
Cd	0.085	0.995	-0.061			
Ni	0.760	0.529	-0.355			
Cr	0.776	0.445	-0.446	0.982	0.068	-0.178
Cu	0.993	-0.115	0.023	-0.079	0.996	-0.036
Zn	-0.953	-0.228	0.159	0.110	0.991	0.074
Pb	0.971	0.150	-0.162	0.982	-0.185	0.022
Fe	-0.128	-0.075	0.989	0.927	0.194	0.322
Eigenvalues	4.851	1.252	0.036	2.828	2.042	0.130
% of Variance	57.716	22.301	19.409	56.115	41.033	2.852
Cumulative %	57.716	80.016	99.425	56.115	97.148	100.00



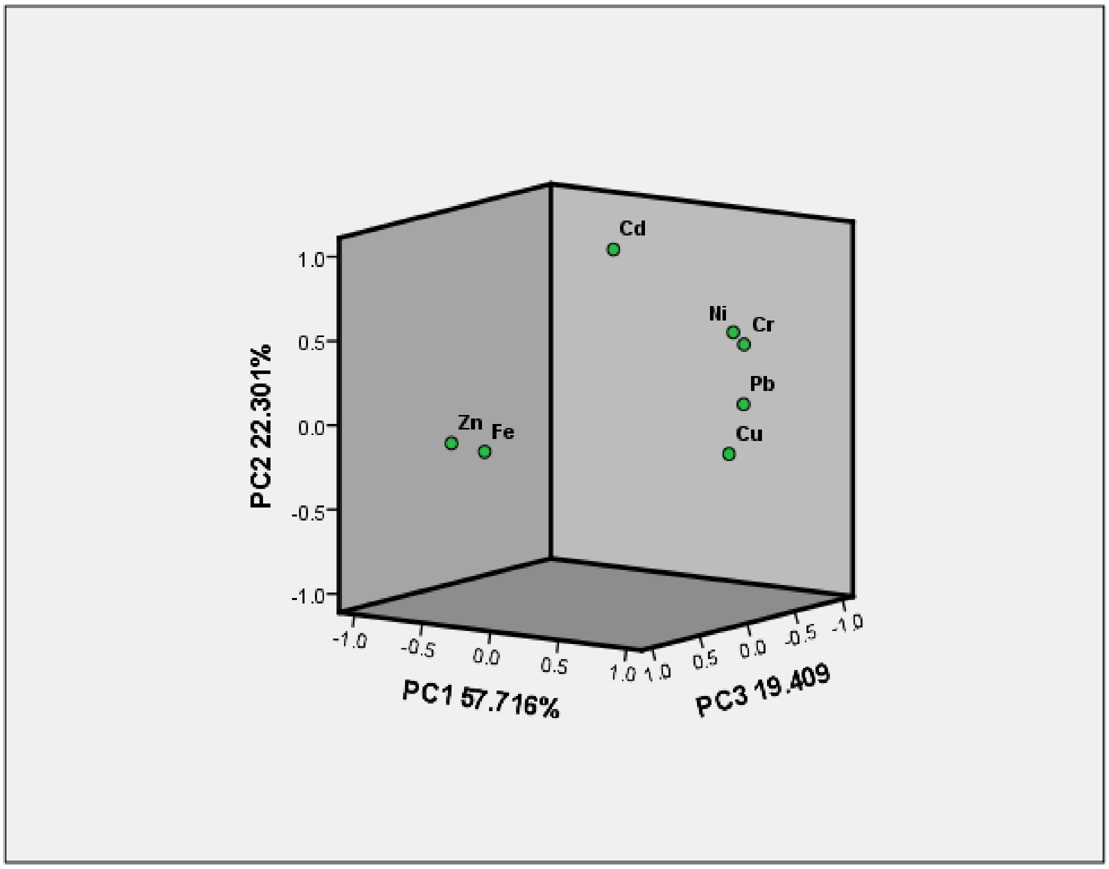
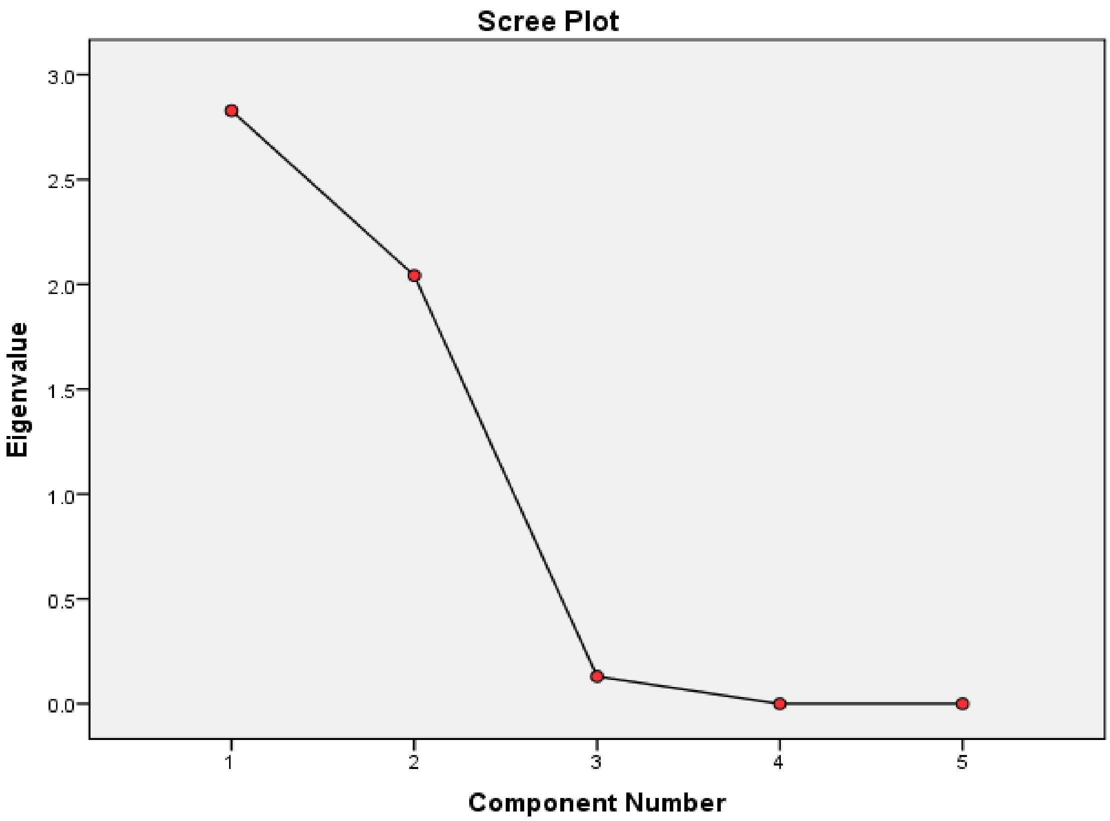


Figure 2: Scree plot of eigenvalues after PCA and rotated component matrix of PTEs in Surface Water



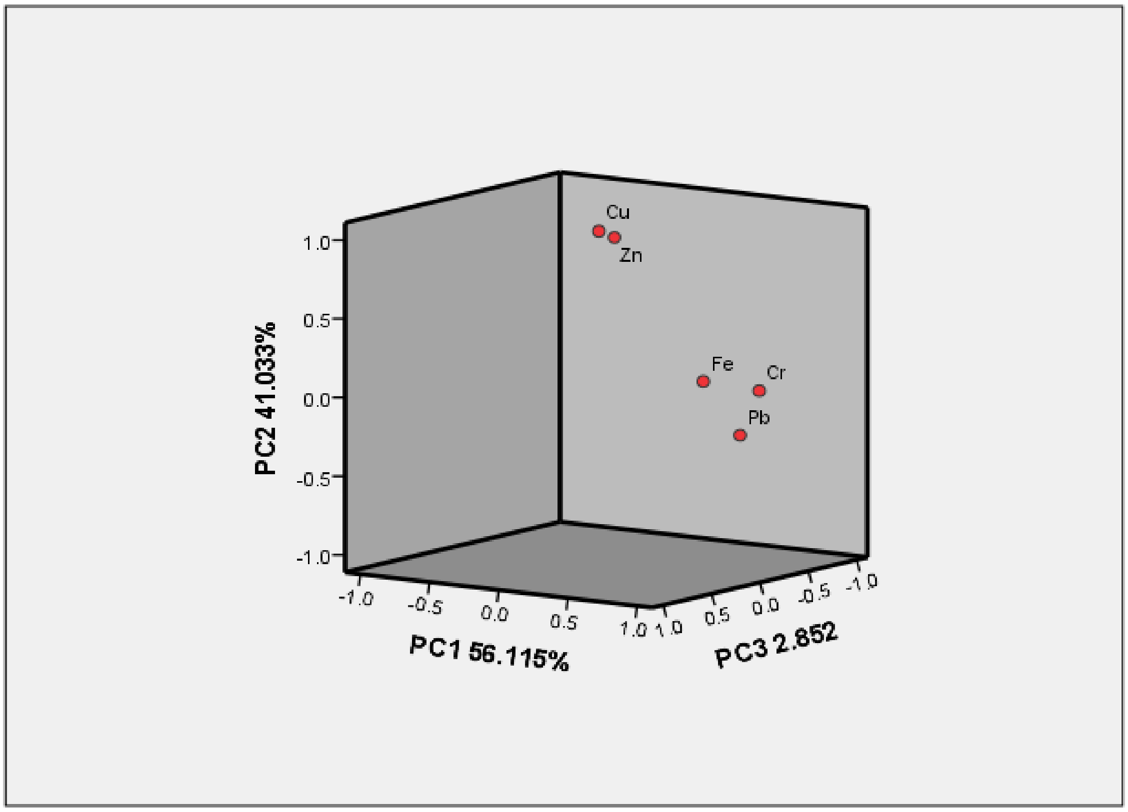


Figure 3: Scree plot of eigenvalues after PCA and rotated component matrix of PTEs in Sediment

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 (Hu et al., 2020; Ustaoglu et al. 2020; Chen et al., 2022). The difference in the PTEs correlation for surface water for suggest difference sources and patherns 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. (2020). Overall, PTEs find their way into the aquatic environment through various sources including atmospheric deposition and series of anthropogenic activities (Shen et al., 2019, 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 PC analysis 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.

List of Abbreviation

Cd	Cadmium
Cr	Chromium
Cu	Copper
Fe	Iron
Ni	Nickel
Pb	Lead
PCC	Pearson Correlation Coefficient
PS	Point Source
PTEs	Potentially Toxic Elements
PCA	Principal Component Analysis
SWP	Surface Water Point
Zn	Zinc

Ethics approval and Consent to Participate

Not Applicable

Consent for Publication

All authors approved the manuscript for publication

Availability of Data and Material

All data for the manuscript is within the text.

Competing Interest

No competing interest from all the authors

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Authors Contribution

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

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