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Heavy Metal Pollution Risk Assessment and Source Analysis in Warri River Sediments

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Contaminated river sediment poses a threat to aquatic life and public health. The focus of this study was to investigate possible contamination of sediments from the Warri River. Triplicate samples were collected from ten sites of intense industrial activities. The sediments were analysed for heavy metals (HMs), anions, and physicochemical properties, including total hydrocarbon content (THC), an indicator of hydrocarbon contamination. The contamination level was evaluated using the following indices: contamination factor index (CF), geo-accumulation index (I_{geo}), enrichment factor (EF), ecological risk index (ERI), modified degree of contamination (mC_d), pollution load index (PLI), risk index (RI) and sediment quality guidelines (SQG). Principal component analysis (PCA) and hierarchical clustering analysis (HCA) were used to identify the sources of HM contamination. The aggregate contamination indices (mC_d, PLI and RI) indicate no contamination/pollution or ecological risk. Similarly, the single contamination indices (CF, I_{geo}, and ERI) showed low contamination and ecological risk for almost all heavy metals except for Cd, which was high in many sample locations. Most of the heavy metals exhibited values below both the threshold-effects level (TEL) and the probable-effects level (PEL), except for Cd, where 80% of locations recorded levels between TEL and PEL, suggesting possible ecological risk for Cd. PCA suggests that PC1, loaded with Fe, Zn, Ni, Cd and Cr, indicates anthropogenic activity. PC2, loaded with Mn and Pb, suggests both anthropogenic and geogenic origins. In conclusion, the possible HM contamination necessitates urgent government intervention to protect aquatic ecosystems and public health.

Keywords: Warri River, heavy metal contamination, sediment quality, pollution indices, anthropogenic processes, industrial activities.

Introduction

The sedimentation of weathered and eroded minerals, organic matter, and soils results in the formation of sediments. These are naturally essential and integral components of rivers, lakes, etc. (Hauer et al., 2018; Bylak and Kukuła, 2022). They serve as a source of substrate nutrients as well as the micro- and macrobiota that form the backbone of support for aquatic living resources. The origin of heavy metals (HMs) in river sediments can be traced to geogenic (e.g., weathering and erosion) and anthropogenic (e.g., mining, agriculture, industry) processes (Vertimurugan et al., 2018; Akinwole et al., 2022). HMs are particularly concerning due to their toxicity, persistence, and non-degradability in the environment (Ali et al., 2019; Briffa et al., 2020). Lead, nickel, and mercury demonstrate high toxicity even at minute levels (Algül and Beyhan, 2020).

HMs enter river systems through several pathways, such as surface runoff, industrial effluents, sewage discharges, direct atmospheric deposition, or sedimentation. They are usually precipitated, adsorbed, and stored in the sediments at the bottom of the river systems (HM sinks), and may re-enter the river water through dissolution under different redox conditions (Jiao et al., 2017; Fang et al., 2019; Nawrot et al., 2021; Li et al., 2022; Chen et al., 2022). HMs enter the food chain through plants and sediment-eating and burrowing organisms, which consume sediment and soil potentially containing HMs. Subsequently, these organisms are consumed by other organisms higher up in the food chain, leading to bioaccumulation. Other organometallic compounds that may be more toxic could be formed from HMs (Gao and Chen, 2012). When toxic metals bioaccumulate in aquatic biota, they are eventually transferred to human beings through the food chain or direct absorption (Chen et al., 2016; Sonone et al., 2021; Tahity et al., 2022). Heavy metal exposure in humans has been associated with several detrimental health effects such as cancer, diminished IQ, organ and neurological system damage, and stillbirth (Li et al., 2022). Therefore, the health of aquatic ecosystems is threatened by heavy metal contamination of river sediments, making sediment crucial in establishing the pattern of aquatic environmental contamination. Sediment quality is also a good indicator of water column contamination because it provides a clearer view of the nature and sources of contaminants in a water body. It reflects the history of pollution and provides a record of water quality of rivers (Aladesanmi et al., 2016; Akkajit et al., 2018). The analysis of heavy metals in sediments enables the identification of contaminants that may be absent or present in only trace amounts in the water column.

Many indices of contamination have been developed to assess the level of contamination at a given site (soil, sediments, water). The most common include the geo-accumulation index (I_{geo}), pollution load index (PLI), contamination factor index (CF), modified degree of contamination (mC_d), enrichment factor (EF), and ecological risk index (ERI) (Attah et al., 2021; Chen et al., 2022; Li et al., 2022; Anoop et al., 2022; Chinemelu and Okumoko, 2022). Combining several indices of contamination when evaluating the level of contamination within a site can provide a robust and accurate picture of the contamination at a given location (Luo et al., 2021). Recently, several researchers have investigated the quality of river sediments. For example, Li et al. (2022) have characterized the ecological risk of sediments from the Yellow River in China, finding Pb, Cr, Ni, and V to pose ecological risk. Chen et al. (2022) have investigated an HM pollution risk in sediments from Lake Gehu in China and found a serious Cd pollution. Chinemelu and Okumoko (2022) used I_{geo}, CF, and EF of HMs to evaluate the sediments of the Warri River, revealing a geogenic origin for the HMs. Malvandi (2017) have examined HM contamination in Zarrin-Gol River (Iran) sediments using four contamination indices, including CF, EF, PLI, and I_{geo}. Similarly, Alahabadi and Malvandi (2018) have assessed HMs in sediments from the Tajan River (Iran) using CF, I_{geo}, ERI, and PLI.

To investigate and pinpoint the sources of HMs in river sediments, multivariate statistical analysis can be utilized (Vetrimurugan et al., 2017; Xiao et al., 2019). This may be important in designing any river basin management plan that addresses contamination (Chen et al., 2022). Several studies have utilised multivariate statistical analysis to infer HM sources in sediments. For example, Li et al. (2022) have used Pearson correlation analysis, principal component analysis (PCA), and cluster analysis to investigate the possible sources of HMs in Yellow River sediment in China. A high correlation coefficient indicated interrelated transportation, principal components represented similarity of sources, and

cluster analysis was used for categorizing heavy metals and sediment samples. Similarly, Chen et al. (2022) have used correlation analysis and the positive matrix factorization (PMF) model to investigate the sources of HMs in Lake Gehu. Dye and print textiles and metal manufacturing plants were identified as the anthropogenic sources of the HMs. Chinemelu and Okumoko (2022) have used cluster analysis to reveal the sources of HMs in the Warri River. Fe was attributed to geogenic sources, while Cd, As, Ni, Pb, Cr, Cu, and Zn were attributed to anthropogenic sources.

The population of inhabitants around the Warri River catchment has grown recently due to urbanization. This growth has led to a corresponding increase in the industrial and domestic waste that the river receives from various sources (Chinemelu and Okumoko, 2022). One of the main sources of pollution in the area is the activities of crude oil and related industries. Despite the significance of the Warri River to local populations, not much is known about the river's health because there have been few studies on it. Understanding the distribution and sources of HMs in the river sediments is important for safeguarding the aquatic ecosystem and ensuring public safety. Adequate measures need to be taken to reverse any detected contamination or pollution trends. The objectives of this research are to investigate HM variation and distribution, evaluate the level of contamination and environmental risk, and infer the sources of HMs in the Warri River sediments.

Methods

Study area

The studied area of the Warri River (*Fig. 1*) is located between latitude 5°25'00"N – 5°45'00"N and longitude 5°25'00"E – 5°45'00"E, with an area of approximately 1400 km^2. The Warri River is a relatively large body of water and one of the most important coastal rivers in the Niger Delta region in terms of navigation, with two ports sited on the river. The headwater of the Warri River is located at Utagba-Uno and flows south-westward, where it empties into the Forcados River. The studied area is characterized by a tropical climate with an annual rainfall of 3000 mm and an average temperature 28°C (Olele, 2011; Ejere et al., 2014; Mogborukor, 2022). Geologically, the Warri River is located within the Niger-Delta Basin, which has been documented to consist of approximately 8 km of Tertiary to Quaternary sedimentary rock layers. These are divided into Akata, Agbada, and Benin Formations with decreasing age (Weber, 1975). The Warri River flows on the Sombreiro-Deltaic Plain, which consists of up to 30 m of fine-medium and coarse-grained sands, with discontinuous silty clay-to-clay layers. In boreholes up to 100 m in depth, black-grey clays interbed majorly sand units (Akpoborie, 2012; Akpoborie, 1996).

Sampling and laboratory procedures

Samples were collected in October 2022 and June 2023. Ten sampling points along the Warri River were surveyed and distributed based on major human activities such as tank farms, transportation, human settlements, and ecological conditions (*Fig. 1*). The various activities and specific coordinate information of the sampling points are shown in *Table 1*. Sediment samples were collected at ten sampling points in triplicate, resulting in thirty (30) sediment samples. These were obtained using a Van Veen grab sampler (250 cm^2) from the first 10 cm of the sediment surface and transferred into well-labelled polyethylene sample bags, without any chemical pre-treatment. The samples were stored in a portable refrigerator at 1 to 4°C and transported to the laboratory, Jacio Environmental Limited, Effurun, Nigeria, where all analyses were performed. In the laboratory, the sediments were spread on plastic films to air-dry at room temperature; stones, branches, and other plant materials were removed manually. After

Fig. 1. *Map of the study area showing sediment sampling points*

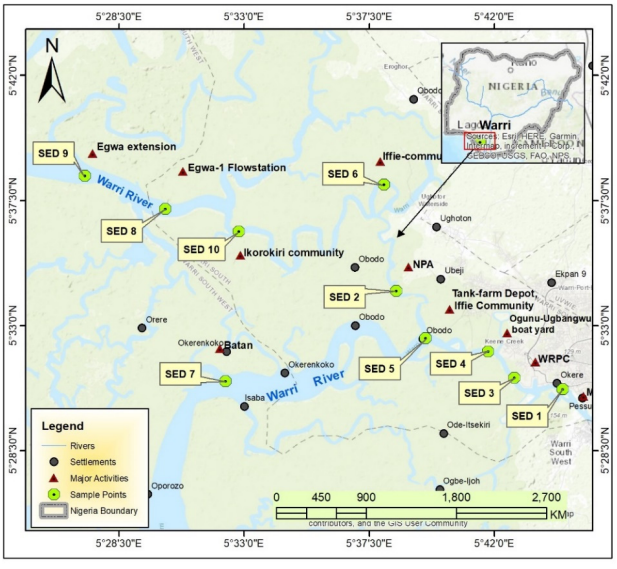


Table 1. *Sediment sample points coordinates and surrounding major human activity*

ID	Coordinates	Sample description	Human activity
SED1	5°30'54.840"N 5°43'55.292"E	Miller Jetty, Warri	Sales of petroleum products such as diesel, kerosene, boats and vessels transportation, mini market
SED2	5°32'10.367"N 5°40'30.646"E	NPA, Warri	Boats and vessels anchor there, though not fully operational
SED3	5°30'52.814"N 5°42'47.273"E	WRPC	Warri refinery and petrochemical company with petroleum vessels anchoring at its jetty
SED4	5°32'0.870"N 5°41'48.136"E	Ogunu-Ugbangwue boat yard, Warri	Boat and vessels anchoring
SED5	5°32'3.340"N 5°41'12.421"E	Tank-farm Depot, Iffie community	For storage, sales and distribution of petroleum products such as Gas, PMS, DKP, AGO
SED6	5°32'38.073"N 5°39'47.948"E	Iffie-community extension	Industrial activities related to tank-farms depot
SED7	5°31'56.658"N 5°32'11.291"E	Batan	Crude oil exploration and production
SED8	5°35'55.767"N 5°27'19.951"E	Egwa-1 flow station	Crude oil exploration and production
SED9	5°37'47.024"N 5°26'29.403"E	Egwa extension	Crude oil exploration and production
SED10	5°36'4.667"N 5°32'21.485"E	Ikorokiri community	Fishing

PMS, premium motor spirit; DKP, diesel kerosene premium; AGO, automotive gas oil.

the samples were well dried, they were ground with an agate mortar and sieved through a 230 ASTM sieve mesh (mesh size 63 μm) to remove small debris.

In the process of determining HMs in sediment samples, 1 g of the sample was digested in Teflon tubes with a mixture of 2 mL of HNO_3, 5 mL of $HClO_4$, and 2 mL of HF. The digestion process was carried out on a hotplate at 140°C for 20 to 30 minutes, which is generally considered sufficient for complete digestion. After digestion and cooling, the extracted solutions were filtered through filter paper and diluted with double deionized water to a volume of 25 mL (Bai et al., 2011). Heavy metal concentrations were determined after digestion using a Flame Atomic Absorption Spectrometer (Varian SpectrAA 600 model, Varian Inc., Palo Alto, California, USA). The analytical method has the following limits of detection (LOD): 0.072 mg/kg for Cr, 0.042 mg/kg for Mn, 0.105 mg/kg for Ni, 0.008 mg/kg for Cu, 0.089 mg/kg for Zn, 0.016 mg/kg for Cd, and 0.069 mg/kg for Pb. Values below detection limits were replaced by half the detection limit values in line with the recommendation of Farnham et al. (2002).

The physicochemical properties of the sediment samples were also determined, including pH, electrical conductivity (EC), total organic carbon (TOC), moisture content (MC), chloride (Cl^-), sulphate (SO_4^{2-}), and nitrate (NO_3^-), total phosphate (TP), and total hydrocarbon content (THC). The Hanna HI9829 multi-parameter meter was utilized for measuring pH and EC. The meter was calibrated using Hanna Quick Cal solution (HI9829-27) (Omoruyi and Amadi, 2022). To measure pH and EC, a sediment-water suspension (using distilled water) in a 1:2 ratio (10g:20g) was prepared and allowed to stand for 30 minutes. The meter probe was inserted into the mixture and allowed to stabilize in the sediment-water sample mixture for 5 minutes before recording readings (Sathyanarayana, 2020). TOC determination involved the use of the Walkley and Black (1934) chromic acid wet oxidation method using a finely divided sieved sediment sample. Then, 5 g of representative samples were used for THC determination based on the ASTM D3921 method using infrared spectrophotometry with the Infracal-2 instrument. Oven drying at 105°C to a constant weight was done to determine the moisture content of sediments. ASTM D512, ASTM D516, and ASTM D3867 standards were employed for the determination of Cl^-, SO_4^{2-}, and NO_3^- ions in the sediments, respectively. TP was determined using the Bray P-1 method. Further, 10 g of the air-dried sediment was used, and the extracted solution of the sediment was treated. The absorbance was measured after 5 minutes at a wavelength of 880 nm using a 752N Searchtech Instrument UV-VIS spectrophotometer.

Data analysis

In this study, the quality of sediments was evaluated using empirical sediment quality guidelines (SQG) based on threshold-effects level (TEL) and probable-effects level (PEL) recommendations from the Canadian

Freshwater Sediment Guideline (MacDonald et al., 1996). TEL is the concentration of sediment contamination at which benthic organisms start to show toxic responses, while PEL is the concentration at which a significant proportion of the benthic population exhibits toxic responses. The TEL and PEL are as follows (mg/kg): Cd (TEL: 0.6, PEL: 3.53), Cr (TEL: 37.3, PEL: 90), Cu (TEL: 35.7, PEL: 197), Pb (TEL: 35, PEL: 91.3), Ni (TEL: 18, PEL: 36), and Zn (TEL: 123, PEL: 315) (CCME, 1999; Thompson and Wasserman, 2015).

The CF is the ratio of heavy metal concentration to its background values in a soil or sediment sample. CF was proposed by Håkanson (1980) and is a simplistic and reliable measure of anthropogenic influences at a given site (Usman et al., 2021). The background values for this study are average shale values (ASV) of Turekian and Wedepohl (1961). The I_{geo}, proposed by Müller (1981), is another method that involves normalization of the concentration of HMs in a sample with background values. However, it differs from CF in that it involves normalization by a factor of 1.5 and taking the log_2 of the normalized values. Chester and Stoner (1973) proposed the EF as a method to assess heavy metal contamination in sediment/soil samples. EF is defined as the ratio of a HM concentration in a sample, normalized against a reference element concentration (typically Fe or Al) in the same sample, to the ratio of the heavy metal concentration normalized against Fe or Al in the background. For this study, Fe was the normalizing element.

Tomlinson et al. (1980) proposed the PLI as a method to assess heavy metal contamination in sediment/soil samples. PLI is defined as the nth root of the product of computed CFs for each heavy metal in a sample. The mC_d is a method proposed by Abrahim (2005) to assess heavy metal contamination in sediment/soil samples. It is derived from Hakanson's Degree of Contamination (Håkanson, 1980) and is calculated as the average of CFs for each HM in a sample. The ERI involves the multiplication of the CF with a toxic response factor, which factors in the migration, transformation, and toxicity of certain HMs (Håkanson, 1980; Lin et al., 2016). The toxic response factor for Cd, Cu, Cr, Mn, Ni, Zn, and Pb are 10, 5, 2, 1, 5, 1, and 5, respectively (Chai et al., 2017). The RI is the summation of the ERI of each sediment/soil sample. The equation and classification ranges of CF, I_{geo}, EF, PLI, mC_d, ERI and RI are presented in *Table 2*.

Table 2. *Pollution indices (PI) computation and classification*

PI	Formula	Variable definition	Enrichment/contamination classification
CF	$\frac{C_i}{B_i}$	C_i is sample HM content; B_i is background value	CF < 1 (low); 1 ≤ CF < 3 (moderate); 3 ≤ CF < 6 (considerable); CF ≥ 6 (very high)
I_{geo}	$\log_2 \frac{C_i}{1.5B_i}$	C_i is sample HM content; B_i is background value	I_{geo} < 0 (no); 0 ≤ I_{geo} < 1 (no to moderate); 1 ≤ I_{geo} < 2 (moderate); 2 ≤ I_{geo} < 3 (moderate to strong); 3 ≤ I_{geo} < 4 (strong); 4 ≤ I_{geo} < 5 (strong to extreme); I_{geo} ≥ 5 (extreme)
EF	$\frac{\left(\frac{C_i}{Fe_i}\right)_i}{\left(\frac{B_i}{Fe}\right)}$	C_i is sample; HM content; B_i is background values; Fe_i is sediment Fe; Fe is background Fe	EF < 2 (minimal); 2 ≤ EF < 5 (moderate); 5 ≤ EF < 20 (significant); 20 ≤ EF < 40 (high); EF ≥ 40 (extremely severe)
PLI	$\sqrt[N]{\prod_{i=1}^{N} CF_i}$	CF_i is contamination index; N is number of HM	PLI < 1 (no pollution); PLI ≥ 1 (elevated pollution)
mC_d	$\frac{\sum_{i=1}^{N} CF_i}{N}$	CF_i is contamination index; N is number of HM	mC_d < 1.5 (nil to low); 1.5 ≤ mC_d < 2 (low); 2 ≤ mC_d < 4 (moderate); 4 ≤ mC_d < 8 (high); 8 ≤ mC_d < 16 (very high); 16 ≤ mC_d < 32 (extremely high); mC_d ≥ 32 (ultra-high)
ERI	$T_i \times CF_i$	T_i is the toxic factor; CF_i is contamination index	ERI < 40 (low risk); 40 ≤ ERI < 80 (moderate risk); 80 ≤ ERI < 160 (considerable); 160 ≤ ERI < 320 (high risk); ERI ≥ 320 (extremely high)
RI	$\sum_{i=1}^{N} ERI_i$	RI_i is ecological risk index; N is number of HM	RI < 150 (low risk); 150 ≤ RI < 300 (moderate); 300 ≤ RI < 600 (considerable); RI ≥ 600 (high risk)

These PI were computed for each HM analyzed.

Three statistical methods were employed to infer the source of the heavy metals: correlation analysis (CA) using the Pearson method, principal component analysis (PCA) with varimax rotation, and hierarchical cluster analysis (HCA). PCA reduces the number of variables into a few uncorrelated components with eigenvalues greater than 1, while preserving a high percentage of information or variability in the original variables. The new components are interpreted based on their possible meaning, which in this study was related to the source of HMs. CA is a bivariate measure of the relationship between two variables, ranging from –1 to 1, with values close to 0 indicating no relationship. Similarity in transportation was inferred in this study for CA coefficients that are above 0.65 at 95% and 99.9% confidence levels. HCA involves the determination of similar sediment samples/sites and related HMs, with similarity of source being inferred and presented in a dendrogram. The distance between samples/sites was measured with the Euclidean method, and the agglomerative method of linkages (Ward and Hook, 1963) was used.

Results and Discussion

Physicochemical parameter in sediment

The average values and standard deviations (± SD) of physicochemical parameters from triplicate sediment samples from the Warri River are presented in *Table 3*. The pH, electrical conductivity (EC), and moisture content (MC) of sediments ranged from 4.08 to 6.08, 616.67 to 6029.67 µS/cm, and 21.7 to 26.07%, respectively. The observed pH levels suggest acidic to slightly acidic conditions, particularly in areas associated with crude oil exploration and production, such as SED7 (4.67), SED8 (4.59), and SED9 (4.08). These observations could imply a connection between sediment pH and industrial activities near the sampling points. These pH values are also similar to findings that have been reported in Niger Delta sediments (Iwegbue, 2007; Akporido and Ipeaiyeda, 2014; Ibanga and Nkwoji, 2019; Onajite and Ovie, 2022; Eguvbe, 2023; Ibekwe, 2023). The EC values recorded displayed a significant rise from upstream to downstream (SED1 to SED10), particularly from SED7 (3260.67 µS/cm) to SED9 (6029.67 µS/cm), suggesting similar potential contamination sources as the pH. These sources could be effluents or the indiscriminate discharge of drilling fluids and untreated produced water, notably oilfield brines containing salts, minerals, heavy metals, and trace metal elements. These elements, being electrically conductive and dense, settle and remain in sediment. The higher EC values could also be attributed to estuarine conditions resulting from the intrusion of saline water from the Atlantic Ocean during high tides, flushing into freshwater upstream (Davies and Tawari, 2010). These EC values are consistent with earlier research by Davies and Tawari (2010), who found EC values ranging from 4080 to 4577.78 µS/cm in the sediment of Trans-Okpoka Creek, Upper Bonny Estuary. Olumukoro et al. (2022) have similarly noted high EC values at Otumara,

Table 3. *Average ± SD of the physicochemical measures of the sediment samples*

ID	pH	EC (µS/cm)	Cl^- (mg/kg)	SO_4^{2-} (mg/kg)	TOC (%)	MC (%)	NO_3^- (mg/kg)	PO_4^{3-} (mg/kg)	THC (mg/kg)
SED1	4.78 ± 0.21	616.67 ± 2.52	218.61 ± 10.24	134.62 ± 1.47	1.02 ± 0.03	23.71 ± 0.65	4.88 ± 0.19	2.03 ± 0.08	99.64 ± 4.17
SED2	5.95 ± 0.08	921.33 ± 2.31	327.02 ± 9.00	161.87 ± 2.42	0.98 ± 0.01	26.07 ± 0.32	4.12 ± 0.13	1.46 ± 0.09	85.8 ± 1.45
SED3	4.63 ± 0.03	1401.67 ± 3.06	531.75 ± 0.02	209.09 ± 1.80	3.19 ± 0.06	22.07 ± 1.00	4.04 ± 0.01	1.98 ± 0.10	40.89 ± 1.57
SED4	6.06 ± 0.01	1623.67 ± 4.04	667.64 ± 10.23	228.5 ± 2.45	1.87 ± 0.00	23.05 ± 1.45	3.40 ± 0.02	1.96 ± 0.07	38.12 ± 1.03
SED5	6.08 ± 0.03	1301 ± 1.73	492.76 ± 12.78	197.14 ± 2.75	2.31 ± 0.04	21.7 ± 0.81	3.46 ± 0.06	1.67 ± 0.06	36.95 ± 0.67
SED6	5.09 ± 0.04	1627 ± 1.73	710.18 ± 5.41	260.21 ± 3.11	2.89 ± 0.07	25.33 ± 0.23	4.13 ± 0.14	2.18 ± 0.09	51.24 ± 1.97
SED7	4.67 ± 0.11	3260.67 ± 2.08	1022.14 ± 10.23	671.74 ± 2.95	4.05 ± 0.02	24.1 ± 0.70	3.62 ± 0.40	1.91 ± 0.11	50.91 ± 1.78
SED8	4.59 ± 0.27	5177.67 ± 3.21	2310.68 ± 7.3	1410.71 ± 10.09	3.75 ± 0.08	24.99 ± 0.91	3.49 ± 0.00	1.86 ± 0.09	209.17 ± 9.81
SED9	4.08 ± 0.09	6029.67 ± 45.94	2268.8 ± 17.73	1308.09 ± 1.47	2.98 ± 0.06	25.51 ± 0.66	4.00 ± 0.64	2.04 ± 0.07	223.39 ± 3.39
SED10	5.17 ± 0.29	5661.67 ± 565.23	2448.08 ± 3.52	1463.66 ± 32.62	3.8 ± 0.10	25.17 ± 0.46	3.99 ± 0.07	2.05 ± 0.06	258.08 ± 1.92

Saghara, and Escravos flow stations in Delta State, with mean values of 6058.33, 11 907.50, and 10 223.33 µS/cm, respectively. However, these results differ from those reported by Chinemelu and Okumoko (2022) (85.2–556.7 µS/cm) in Warri River sediments, Onajite and Ovie (2015) in Okpare Creek (131.99–295.16 µS/cm), and Adesuyi et al. (2015) (23.0–567.0 µS/cm) in Nwaja Creek.

The TOC levels in the sediments ranged from 0.98% at SED2 to 4.05% at SED7. The THC varied from 38.12 mg/kg at SED4 to 258.08 mg/kg at SED10. Notably, the lowest observed value of THC is higher than the 30 mg/kg limit recommended by the Nigeria Federal Ministry of Environment (FME, 1991). The high THC concentrations (> 200 mg/kg) detected at SED8 and SED9 suggest significant contributions from petroleum exploration and production activities in the vicinity. This indicates a considerable impact of human activities on the sediment quality within the Warri River. However, the THC-to-TOC ratios, which ranged from 11.99 to 77.7, indicated little to no hydrocarbon pollution, as they are below the threshold of 100 (Marchand and Roucache, 1981). The fluctuating levels of TOC observed align with patterns found in various settings across the Niger Delta region. Upstream of the Sombreiro River, where numerous petroleum installations are present, the average TOC values were reported as 1.3% for the wet season and 2.6% for the dry season (Ehi-Douglas et al., 2018). At Nwaja Creek, TOC values ranged from 1.99% to 3.65% (Adesuyi et al., 2016). In contrast, THC in this study showed wide variation across the region. In the sediments of Kau/Kinabere Creek, THC ranged from 1403 to 3755 mg/kg, which are higher than the values reported in the current study. These elevated THC levels were attributed to pollution from illegal oil bunkering and refining activities (Wokoma, 2015). Similarly, in Mgboshimili Creek, the average THC of sediment was found to be 495.49 mg/kg, with a range of 2.23 to 1190.58 mg/kg (Owoh-Etete et al., 2023).

The Cl^-, SO_4^{2-}, NO_3^{2-}, and PO_4^{3-} concentrations recorded in the sediments of the Warri River are in a wide range, reflecting the diverse environmental influences present across various sampling sites. The observed range of Cl^- and SO_4^{2-} concentrations were 218.61 to 2448.08 mg/kg and 134.62 to 1463.66 mg/kg, respectively, with the highest values for both parameters observed at SED10 and the lowest values at SED1. NO_3^- and PO_4^{3-}, which are essential plant nutrients, had concentrations ranging from 3.4 mg/kg at SED4 to 4.88 mg/kg at SED1, and from 1.46 mg/kg at SED2 to 2.18 mg/kg at SED6, respectively. These results align with previous studies conducted in Niger Delta coastal areas, which have attributed the variations in chemical constituents and nutrient levels to both natural processes and human activities, including surface runoff, industrial effluents, domestic waste discharges, and industrial activities (Iyama and Edori, 2014; Ngoka et al., 2021). In the Sombreiro River, reported values for SO_4^{2-}, NO_3^-, and PO_4^{3-} were 21.0–30.0 mg/kg, 2.6–4.1 mg/kg, and 8.90–15.7 mg/kg, respectively. The NO_3^- levels were similar to those reported in this study, while the SO_4^{2-} levels were lower and the PO_4^{3-} levels were higher. Although SO_4^{2-} values in the region can vary widely, they are generally considered normal even when higher values are observed. The elevated levels of NO_3^- and PO_4^{3-} in the Sombreiro River are attributed to inputs from agricultural runoff rich in super-phosphate fertilizer (Ezekiel, 2011).

Heavy metals in sediments

Studies have indicated that over 99% of heavy metals entering aquatic ecosystems were stored in sediments through various mechanisms and eventually transferred to humans via the food chain (Gwimbi et al., 2020; Xu et al., 2018; Algül and Beyhan, 2020). Therefore, analyzing sediment heavy metals provides a deeper understanding of the long-term pollution status of aquatic environments. The average values and standard deviation (± SD) of the heavy metals of the triplicate sediment samples are presented in *Table 4*. The heavy metal concentrations showed significant variability across different sediment locations. Cu ranged from 1.64 mg/kg in SED6 to 8.25 mg/kg in SED10. Fe levels were lowest in SED2 (484.93 mg/kg) and highest in SED7 (831.28 mg/kg). Zn was least concentrated in SED2 (13.2 mg/kg) and over three times higher in SED8 (40.11 mg/kg). Mn, Pb, Ni, and Cd ranged from 15.06 mg/kg (SED4) to 32.52 mg/kg (SED9), 1.99 mg/kg (SED1) to 6.99 mg/kg (SED9), 2.61 mg/kg (SED2) to 6.79 mg/kg (SED7), and 0.01 mg/kg (SED1) to 2.63 mg/kg (SED8), respectively. Cr levels were highest in SED8 (3.01 mg/kg), while SED1, SED5, and SED10 all had the lowest concentration (0.04 mg/kg). Overall, SED1 and SED2, where the primary human activities were boat and vessel anchoring and transportation, had the

Table 4. *Average ± SD of heavy metal in triplicate sediment samples*

ID	Cu, (mg/kg)	Fe, (mg/kg)	Zn, (mg/kg)	Mn, (mg/kg)	Pb, (mg/kg)	Ni, (mg/kg)	Cd, (mg/kg)	Cr, (mg/kg)
SED1	3.37 ± 0.43	501.7 ± 11.12	19.03 ± 0.13	22.13 ± 0.25	1.99 ± 0.05	3.84 ± 0.17	0.01 ± 0.00	0.04 ± 0.00
SED2	5.69 ± 0.46	484.93 ± 9.45	13.2 ± 0.19	15.81 ± 0.01	2.53 ± 0.01	2.61 ± 0.06	0.57 ± 0.05	0.72 ± 0.59
SED3	2.76 ± 0.16	515.41 ± 7.69	14.36 ± 0.01	27.01 ± 0.42	3.24 ± 0.08	3.33 ± 0.04	0.75 ± 0.01	1.67 ± 0.02
SED4	3.07 ± 0.04	729.96 ± 31.76	20.73 ± 0.04	15.06 ± 0.24	2.54 ± 0.06	4.27 ± 0.07	1.36 ± 0.05	0.34 ± 0.06
SED5	2.00 ± 0.06	647.29 ± 8.93	13.99 ± 0.11	29.77 ± 0.01	5.90 ± 0.03	3.66 ± 0.18	0.61 ± 0.04	0.04 ± 0.00
SED6	1.64 ± 0.22	732.03 ± 3.17	16.2 ± 0.04	19.66 ± 0.75	2.10 ± 0.03	2.84 ± 0.24	0.71 ± 0.03	1.02 ± 0.05
SED7	4.06 ± 0.07	831.28 ± 4.23	38.79 ± 0.35	29.05 ± 0.27	4.92 ± 0.07	6.79 ± 0.10	2.25 ± 0.04	2.69 ± 0.07
SED8	5.18 ± 0.07	718.99 ± 7.52	40.11 ± 0.41	21.96 ± 0.24	3.58 ± 0.03	6.21 ± 0.12	2.63 ± 0.04	3.01 ± 0.04
SED9	6.66 ± 0.19	677.06 ± 11.24	27.94 ± 0.37	32.52 ± 0.47	6.99 ± 0.05	5.82 ± 0.02	1.85 ± 0.04	1.19 ± 0.19
SED10	8.25 ± 0.06	502.35 ± 10.21	23.21 ± 0.60	18.99 ± 0.04	4.14 ± 0.04	3.65 ± 0.01	1.13 ± 0.14	0.04 ± 0.00

lowest levels of heavy metal concentration. The lowest levels of Cu, Cd, and Cr occurred at SED1, while the lowest levels of Fe, Zn, and Ni occurred at SED2. As observed, SED7, SED8, and SED9, associated with crude oil exploration and production, had the highest heavy metal concentrations: SED7 had the highest Fe, Zn, and Ni; SED8 had the highest Zn and Cd; SED9 had the highest Pb and Mn. Surprisingly, SED10, associated with fishing, had the highest level of Cr. In comparative studies of Warri River sediment, previous research has reported the highest values for Cu, Zn, Pb, Ni, and Cd at 19.43 mg/kg, 73.64 mg/kg, 7.05 mg/kg, 7.1 mg/kg, and 15.91 mg/kg, respectively (Jire and Imeokparia, 2018). These values were 2.35, 1.84, 1.01, 1.04, and 6.05 times higher than those found in the present study, suggesting that their sampling areas experienced more intense human activities, leading to greater heavy metal enrichment in the sediments. In a more recent study of Warri River sediment, the highest values for Pb, Cd, Cr, Ni, Cu, and Zn were 2.15 mg/kg, 0.26 mg/kg, 0.88 mg/kg, 0.36 mg/kg, 3.22 mg/kg, and 9.22 mg/kg, respectively (Chinemelu and Okumoko, 2022). These values were 3.25, 3.5, 10.11, 3.42, 18.86, 2.56, and 4.35 times lower than those reported in the present study. When compared with previous studies, the values of the current study suggest lower contamination levels than reported in Jire and Imeokparia (2018) but higher than those reported in Chinemelu and Okumoko (2022), indicating variability in heavy metal contamination linked to differing intensities of human activity across study sites.

Aggregate contamination indices

The aggregate contamination indices (PLI, mC_d, RI) across the study locations (*Fig. 2a-c*) revealed that mC_d ranged from 0.06 in SED1 to 1.21 in SED8. SED1 had the highest PLI, while SED7 had the lowest, with values ranging from 0.03 to 0.13. For RI, SED1 had the lowest, and SED8 had the highest, with values ranging from 1.72 to 90.11. Overall, SED8 stood out as a location with substantial environmental risk. Classification of the sediment locations based on thresholds for mC_d reveals that all the samples exhibited nil to low contamination (mC_d < 1.5). Similarly, based on PLI and RI, all the samples showed no pollution (PLI < 1) and low ecological risk (RI < 150). Related studies across the Niger Delta revealed various levels of sediment contamination. In the Maa-Dee-Tai River, it was reported that the sediment PLI and RI indicated an absence of contamination (Bale and Adowei, 2024), which aligns with the findings of this study. At Kolo Creek, sediment PLI values ranged from 0.54 to 1.90, and RI values ranged from 24.30 to 87.10 (Uzoekwe and Aigberua, 2019). A previous study on Warri River sediment reported lower PLI values, ranging from 0.95 to 1.58 (Jire and Imeokparia, 2018). In the Ikwu River, RI values fell within the range of 300 to 600, which is considered very high, and PLI values ranged from 1366.80 to 1860.49 (Anyanwu et al., 2023). All of these values from Kolo Creek, Warri River, and Ikwu River are significantly higher than those reported in this study.

Fig. 2. *Distribution of PLI, mC_d, and RI of sediment samples from the Warri River*

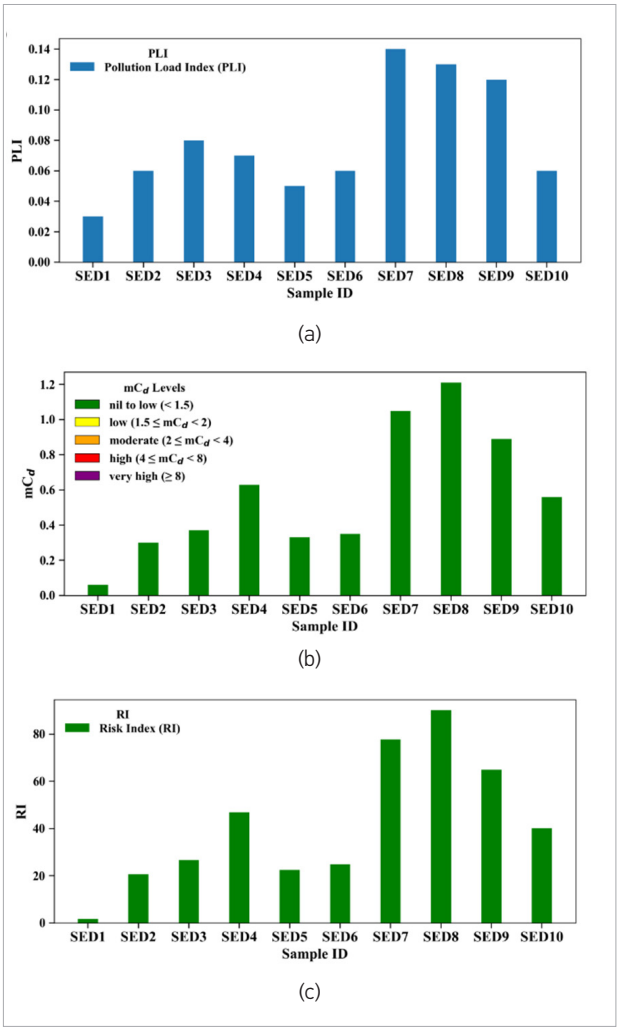
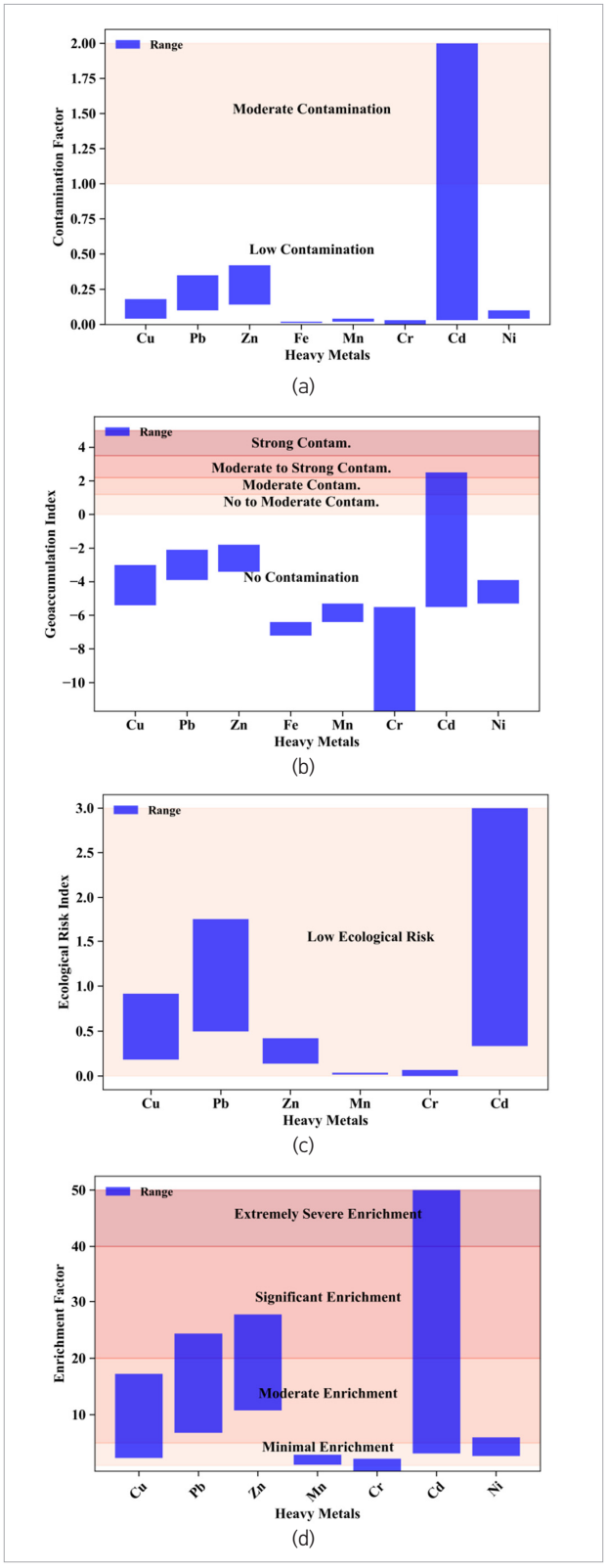


Fig. 3. *Waterfall diagram (blue bars) illustrating the range of (a) CF, (b) Igeo, (c) ERI, (d) EF. Classification ranges are indicated*



Single contamination indices

Fig. 3a-d is a waterfall diagram that depicts the range values of sediment heavy metal single contamination indices CF, I_{geo}, ERI, and EF, respectively. The CF, I_{geo}, and ERI for Cu ranged from the lowest at SED6 (CF = 0.04, I_{geo} = −5.4, ERI = 0.18) to the highest at SED10 (CF = 0.18, I_{geo} = −3.0, ERI = 0.92); Pb was lowest at SED1 (CF = 0.10, I_{geo} = −3.9, ERI = 0.50) and highest at SED9 (CF = 0.35, I_{geo} = −2.1, ERI = 0.75); Zn has minimum values at SED2 (CF = 0.14, I_{geo} = −3.4, ERI = 0.14) and maximum at SED8 (CF = 0.42, I_{geo} = −1.8, ERI = 0.42); Cr ranged from the lowest at SED1 (CF = 0.000, I_{geo} = −11.7, ERI = 0.00) to the highest at SED8 (CF = 0.033, I_{geo} = −5.5, ERI = 0.42); Cd was lowest at SED1 (CF = 0.03, I_{geo} = −5.5, ERI = 0.33) and highest at SED8

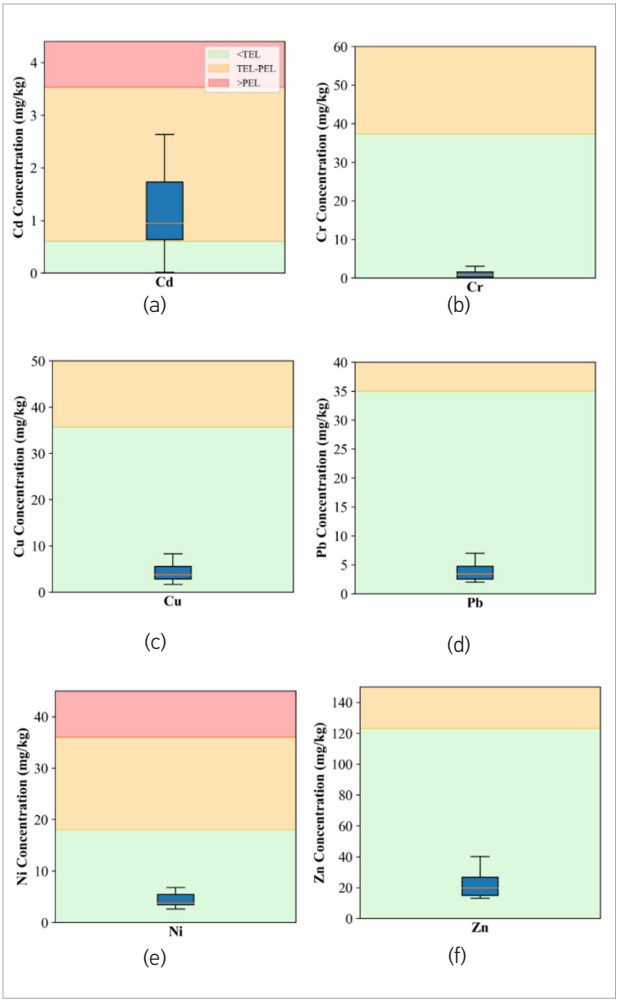
(CF = 0.10, I_{geo} = 2.5, ERI = 87.67); Ni had minimum values at SED2 (CF = 0.04, I_{geo} = –5.3, ERI = 0.19) and maximum at SED7 (CF = 0.10, I_{geo} = –3.9, ERI = 0.50). EF variability across locations: Cu ranged from 2.35 (SED6) to 17.23 (SED10); Pb from 6.77 (SED6) to 24.36 (SED9); Cr from 0.03 (SED5) to 2.20 (SED8); Cd from 3.14 (SED1) to 575.51 (SED8); Ni from 2.69 (SED6) to 6.00 (SED8). Overall, SED8 showed consistently high contamination levels for multiple heavy metals, indicating it as a potential hotspot for pollution, while SED1 and SED6 generally exhibited lower contamination levels. In terms of threshold value classification, single contamination indices (CF, I_{geo}, and ERI) revealed low contamination / ecological risk for Cu, Pb, Zn, Fe, Mn, Cr, and Ni. EF revealed minimal to significant enrichment of these heavy metals. However, all the single contamination indices revealed high levels of Cd contamination across several sampling sites (SED2–SED10).

Previous studies of Warri River sediment and related studies across the Niger Delta revealed similar single contamination indices. CF less than 1 (low contamination), I_{geo} less than zero (no contamination), and minimal to moderate enrichment based on EF have been reported previously at Warri River (Jire and Umeokparia, 2018; Chinemelu and Okumoko, 2022). Similar results were obtained at Kolo Creek, with an additional finding of ERI < 49 (low ecological risk) (Uzoekwe and Aigberua, 2019). Elsewhere, the sediments of the Zarrin-Gol River (Iran) all have negative I_{geo}, CF < 1, and mostly EF < 2 (minor contamination) (Malvandi, 2017). All these findings align with the single contamination indices of all the heavy metals in this study, except for Cd, which was found to be unusually high.

Sediment quality guidelines

The Box-Whisker plot in *Fig. 4a-f* shows the comparison of sediment heavy metal concentrations with sediment quality guidelines (SQG) (TEL and PEL). Only SED1 and SED2 had Cd concentrations below the TEL, while other sample locations fell between the TEL and PEL, indicating a possible toxic effect of Cd on sediment-dwelling biota. The concentrations of other heavy metals in the samples were generally below their respective TEL values. In related studies in the Niger Delta, at Worji Creek and Bonny Estuary, all the heavy metals including Cr, Ni, Cu, Zn, Cd, and Pb had concentrations below PEL (Ibanga, 2016), aligning with the findings of this study. Elsewhere, the Mohammad Abad River in Iran had Cr concentrations between TEL and PEL, while other metals were below TEL (Malvandi, 2021). In stream sediments from the Durgapur industrial zone in India, only Ni and Cu concentrations were below TEL, whereas Pb, Cd, and Cr exceeded PEL, highlighting significant contamination and potential ecological risk (Pobi et al., 2019). Sediments from a lake in East Antarctica had Pb concentrations below TEL, with Cr, Ni, and Zn mostly between TEL and PEL, and some samples of Cr and Ni exceeding PEL, indicating varied levels of contamination (Joju et al., 2024). These comparisons indicate varying degrees of heavy metal contamination across different regions where industrial activities contribute to differences in metal concentrations. Our study indicates moderate contamination for Cd and relatively lower contamination for other metals.

Fig. 4. *Boxplot showing comparison of sediment heavy metal concentration with SQG (TEL and PEL)*



Pearson correlation coefficient

The correlation coefficients (r) between heavy metals in the sediment samples, as presented in *Table 5*, revealed several significant relationships. Zn, Ni, and Cd exhibited very strong correlations, with Zn and Ni (0.94), Zn and Cd (0.91), and Ni and Cd (0.87) showing particularly high positive correlations. Additionally, Cr was significantly correlated with Zn (0.75), Ni (0.69), and Cd (0.78). Fe displayed strong positive correlations with Ni (0.66) and Cd (0.68). These strong correlations suggest that these elements might share common sources or environmental pathways. Other correlations between the heavy metals, though not significant, were mostly positive. Comparing these findings with other studies across the Niger Delta revealed some common patterns and notable differences. In the Warri River, significant correlations (*P* value < 0.01) for Cd with Zn and Ni, and Cu with Zn were observed in both dry and rainy seasons, aligning with the present study's findings of strong Zn-Ni-Cd inter-correlations (Chinemelu and Okumoko, 2022). In the Ethiope River, the correlations of Zn with Ni and Cd are reported as 0.44 and 0.05, respectively, while the strongest correlations were between Cr and Zn (0.66) and Cr and Ni (0.63) (Osakwe and Peretiemo-Clarke, 2013). This shows some variability, as the current study found stronger correlations involving Zn, Ni, and Cd. At Kolo Creek, strongly significant correlations (> 0.72) were reported between Cd, Pb, Ni, and Fe (Uzoekwe and Aigberua, 2019), consistent with the strong Fe-Ni and Fe-Cd correlations observed in the present study. However, at Agbor, significant correlations (> 0.7) were reported at two stations of Arogodo River between Cr, Cd, Cu, Fe, and Pb, although the correlations of Ni and Zn with other heavy metals showed greater variability (Issa et al., 2011). This suggests that while some heavy metals show consistent patterns of correlation across different studies, others may vary significantly, reflecting the influence of local environmental factors, sources of contamination, and sediment characteristics.

Table 5. *Pearson correlation coefficient (r) of heavy metals*

	Cu	Fe	Zn	Mn	Pb	Ni	Cd	Cr
Cu	1							
Fe	–0.30	1						
Zn	0.36	0.61	1					
Mn	–0.07	0.26	0.26	1				
Pb	0.32	0.28	0.33	0.80*	1			
Ni	0.25	0.66*	0.94**	0.50	0.53	1		
Cd	0.35	0.68*	0.91**	0.25	0.44	0.87**	1	
Cr	0.02	0.54	0.75*	0.30	0.14	0.69*	0.78*	1

**P value < 0.05 (statistically significant), and ** P value < 0.001 (highly statistically significant)*

Principal component analysis and cluster analysis

PCA revealed that the first two principal components (PC) accounted for 74.07% of the variability, similar to the 74% of variability explained by the first two PCs in the PCA of HM in the Tajan River (Iran) (Alahabadi and Malvandi, 2018). *Fig. 5* displayed the PCA variable map of the first 2 PCs. The first three PCs accounted for 96.56% of the variability. PC1, PC2, and PC3 explained 55.88%, 18.19%, and 16.49% of the variance, respectively. PC1 is highly loaded with Fe, Zn, Ni, Cd, and Cr, similar to the high PC1 loading for Fe and Cr found in the Alahabadi and Malvandi (2018) study, attributing it to anthropogenic contamination. PC2 is loaded with Mn and Pb, and PC3 with Cu. This suggests three potential anthropogenic non-point HM sources in the area, possibly unrelated to petroleum activities. PC1 could be linked to agricultural and urban runoffs with improper sewage and industrial effluent disposal. A combination of PC1 and PC2, indicating both geogenic and anthropogenic input, may explain the Mn, Pb, and Cu contents in the sediments. This is supported by the positive matrix factorization (PMF) in the study of Mahanadi River

Fig. 5. *Variable factor map*

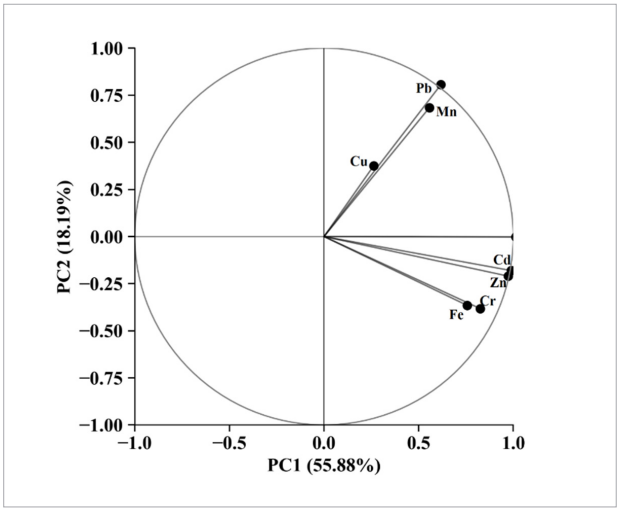
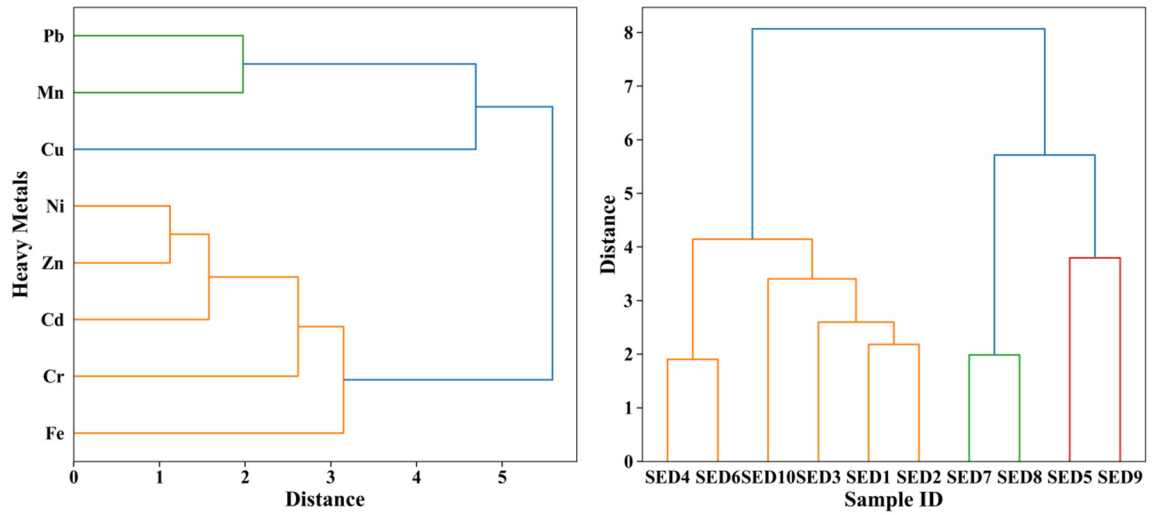


Fig. 6. *Vertical and horizontal hierarchical cluster dendrogram*



sediment (India), which attributed Pb sources to a combination of anthropogenic and geogenic sources (Samal et al., 2022). A similar pattern of sediment heavy metal sources and distribution was identified in Okpare Creek, Niger Delta by Onajite and Ovie (2022). Interestingly, the factor analysis results from the study by Jire and Imeokparia (2018) identified four factors responsible for sediment contamination in the area, including petroleum spills resulting from petroleum production and pipeline vandalism due to bunkering activities, metal filings from iron/steel industries, emissions from vehicles, and the dumping of wastewater into the river.

The hierarchical cluster dendrogram (*Fig. 6*) revealed two groups of samples and two groups of heavy metal sources. Pb, Mn, and Cu were grouped, while Ni, Zn, Cd, Cr and Fe were grouped. Uncertainty surrounds the exact sources of HMs in these two groupings of heavy metals. Several studies with related activities observed at the site have suggested potential sources for these metals. Cu, Fe, and Zn have been found in lubricating oils (Supriyanto, 2018), while Cu, Zn, and Fe have been associated with gas flaring (Obiudu et al., 2021). Cd has been linked to domestic sewage discharges, municipal wastewater, industrial wastes, and harbour fishing activities (Perumal et al., 2021). Minor increases in Mn and Fe have been observed in areas where non-aqueous fluids have been used in oil and gas drilling (Pozebon et al., 2009). Enrichments of Cd, Pb, and Cu have been found in soils around petroleum tank farms (Emoyan et al., 2020). Port activities have been associated with Cu, Ni, and Zn (Delshab et al., 2017). Increased levels of Pb, Cd, Zn, Ni, and Cr have been linked to emissions from diesel and petrol engine boats, operations at the dock, and discharge areas near the oil terminal. These pollutants also originate from refinery waste that travels through channels dug from the petroleum tank farm to the discharge points (Onojake et al., 2015). Sample IDs SED4, SED6, SED10, SED3, SED1, and SED2 were grouped, while sample IDs SED7, SED8, SED5, and SED9 were also grouped and are related to oil and gas-related activities.

Conclusions

This study provided insights into the contamination of Warri River sediments, particularly focusing on heavy metals. The concentrations of the heavy metals, including Cu, Fe, Zn, Mn, Pb, Ni, Cd, and Cr, varied widely across different sediment locations, with the highest levels typically found in areas associated with crude oil exploration and production (SED7, SED8, SED9). The aggregate contamination indices (mC_d, PLI, and RI) revealed no pollution or ecological risk across the site. Single contamination indices (CF, I_{geo}, ERI) and Sediment Quality Guidelines (SQG) revealed low-level contamination / ecological risk for most heavy metals except Cd, which was found to be high in several locations (SED2–SED10). SQG indicated that Cd levels across the sites fell

between TEL and PEL, potentially posing some ecological risk. All the indices identified SED8 as a hotspot of heavy metal contamination. Correlation and PCA analyses revealed strong interrelationships among heavy metals, suggesting common sources or environmental pathways. The PCA identified three main components that accounted for the majority of variability, pointing to multiple anthropogenic sources such as agricultural runoff, industrial effluents, and domestic sewage, alongside geogenic inputs. Authorities can immediately employ monitoring and regulation of industrial activities, along with the implementation of sustainable policies, to prevent further contamination of the Warri River system and avert the negative consequences of industrial activities on the aquatic ecosystem.

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