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Evaluating Toxicological and Pollution Indices of River Sediments: Safeguarding Aquatic Biodiversity and Coastal Economies in Cross River State

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ABSTRACT

This study evaluated the pollution status, ecological risk and potential toxicity implications of ten heavy metals: cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), mercury (Hg), copper (Cu), zinc (Zn), iron (Fe), manganese (Mn) and cobalt (Co), in 72 sediment samples from six rivers representing the Southern, Central and Northern Senatorial Districts of Cross River State, Nigeria. Sediment quality was assessed using the Contamination Factor (CF), Geo-accumulation Index (Igeo), Enrichment Factor (EF), Pollution Load Index (PLI), Potential Ecological Risk Index (PERI), Mean Probable Effect Level Quotient (mPEL-Q), Mean Effect Range Median Quotient (mERM-Q), Toxic Risk Index (TRI), Hazard Quotient (HQ) and Modified Hazard Quotient (mHQ). Pearson correlation, Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were used to examine metal associations and multivariate patterns. Iron had the highest mean concentration (16,470 mg/kg), whereas mercury was lowest (0.020 mg/kg). Idundun generally recorded the highest metal concentrations, while Abeb recorded the lowest. Cd and Hg were the principal risk-driving metals. PLI classified Idundun (1.68), Akpabuyo (1.49), Adun (1.29) and Ikom (1.12) as moderately polluted, whereas Abakpa (0.96) and Abeb (0.84) were unpolluted. PERI indicated moderate ecological risk at Idundun (179.39) and low risk at the remaining rivers. Toxicity indices similarly identified Idundun and Akpabuyo as priority sites, with generally lower concern toward the Northern Rivers. PCA retained three components explaining 83.70% of total variance, separating a Cd−Hg−Pb−Cr−Ni association from Cu−Zn−Co and the Fe→Mn geogenic group. HCA produced three river clusters consistent with the contamination gradient. The findings indicate localized rather than statewide severe contamination and support targeted monitoring, catchment management and pollution prevention to protect aquatic biodiversity and river-dependent livelihoods and maintain the ecological integrity of connected coastal systems.

Keywords: River sediments; heavy metals; ecological risk; pollution indices; sediment quality; Cross River State.

1.0. Introduction

Heavy-metal contamination of aquatic environments remains an environmental concern because metals are persistent, can accumulate in sediments and may subsequently become available to aquatic organisms. River sediments are particularly important because they act as repositories for contaminants transported from surrounding catchments and may also become secondary sources when changes in pH, redox conditions, organic matter or physical disturbance favour remobilisation. Sediment assessment therefore provides information on contaminant accumulation that may not be apparent from measurements of overlying water alone. Recent investigations in Nigerian aquatic systems continue to demonstrate the usefulness of sediment-based assessment for characterising the occurrence, distribution and potential significance of trace metals (Anya & Odo, 2023; Ololade et al., 2024; Egun et al., 2025).

The ecological implications of sediment-associated metal levels depend not only on their absolute values. First, metals vary in their geochemical properties and in their toxicological effects, so a "low" concentration of a metal could constitute a major factor of an ecological-risk index, through its toxic-response weighting. Second, high concentrations of naturally-occurring elements (e.g. Fe and Mn) in the sediment are not in themselves indicative of anthropogenic pollution. The method used in modern metals-risk assessment is placed more importance on the differences between total concentration, enrichment, potential risk, and bioavailability (Adams & Garman, 2024). It is therefore not correct to interpret pollution indices as measures of biological injury or harm, especially where total sediment concentrations are used without direct measures of metal speciation, of target or non-target organism tissue burdens, or of biological effects.

Sediment contamination across space is exemplified in Nigerian rivers. Eight trace metals significantly varied spatially and seasonally among six major rivers in southwestern Nigeria (Ololade et al 2024) and among them Cd, was an important factor in ecological risk. Phillips and Fajemila (2024) similarly documented potentially toxic elements in Ogun River estuarine sediments and combined contamination and ecological-risk indices with multivariate analyses. Egun et al. (2025), working on River Siluko, further demonstrated that sediment contamination and ecological-risk patterns need not correspond simply with absolute metal concentrations. Together, these observations demonstrate the benefits of integrating concentration data with supplementary contamination and risk indicators, and hint that evidence from one environmental settings should not be blindly transferred or extrapolated into another.

The Cross River system provides a particularly relevant setting for such assessment. More recently (Dan et al., 2022a) examined selected trace metals (Zn, Pb, Cu and Cd) of surface sediment in the Cross River estuary and nearshore environment. The contamination factor, Igeo, ecological-risk and bioavailability methods were applied and were useful in identification of Cd and Zn as potential contaminations, with their distribution related to sedimentary organic matter and land inputs. Another recent work by Dan et al. (2022b) focuses on Ni, Cr, Cu, Zn, Pb and Cd of Cross River estuary sediments based on speciation analyses. This work however indicated differences in the proportion of metals among residual and non-residual fractions and Cd showing the most severe pollution load and concerns of bio-availability. Anya and Odo (2023) also documented Mn, Fe, Zn, Pb, Cu, Cr and As, in water and sediment from the Cross River within the Afikpo catchment, although that study was located outside the present six-river sampling framework. More recently, Omayeli and Osabor (2025) assessed Fe, Zn, Mn, Mg, Ni, Cd, Cr and Pb in five stations of the Cross River Estuary during dry and wet seasons and reported predominantly low contamination and ecological-risk classifications. Although the studies produce valuable local information, they are about specific environment compartments, estuarine stations and particular metals, not a common comparative analysis of geographically separated inland river systems.

The present work attempts to address the problem in the formulation of the fragmented available evidence. Whereas site specific investigations on a few Cross River Rivers have generated sound information on sediment contamination. However, no common framework for comparison of sediment contamination and potential ecological risk among selected river systems present in the Southern, Central and Northern Senatorial Districts has emerged. The present work therefore focuses on six selected rivers, namely: Idundun, Akpabuyo, Adun, Ikom, Abakpa and Abeb chosen to provide a geographical coverage for comparison of sediment-metal distributions among selected river systems in Cross River State across the three senatorial districts.

A further analytical dimension is the question of how the approaches to contamination assessment adopted for the study interconnected. The previous Cross River research has drawn on some particular contamination, ecological-risk and speciation methods, but this study utilises a range of the measures (concentrations, contamination, enrichment, pollution-load and ecological-risk) together and also provides specialised measures (CF, Igeo, EF, PLI and PERI). The CF measures contamination relative to background, the Igeo logarithmically assesses accumulation; EF assesses departure from background relationships and normalisation, the PLI sums the area contamination 'load' while the PERI measures the contamination severity by weighting for specific toxic responses. A number of other sediment-quality screening tools (mPEL-Q,

mERM-Q, TRI, HQ and mHQ) were used and complemented with correlation analysis, PCA and HCA in order to assess the metal associations and spatial grouping. These measures are complementary rather than interchangeable and aimed to examine whether the same locations and metals emerge as comparatively important across various analytical perspectives.

It is thus not the presence of heavy metals in the Cross River environment – this has been established in existing research, but rather the behaviours of ten metals across a wider range of river systems using an internally consistent framework. The study seeks to determine the concentrations of Cd, Cr, Ni, Pb, Hg, Cu, Zn, Fe, Mn and Co; evaluate their contamination and accumulation using CF and Igeo; assess enrichment and integrated pollution using EF and PLI; estimate potential ecological risk using individual risk factors and PERI; evaluate potential sediment-quality or toxicological significance using mPEL-Q, mERM-Q, TRI, HQ and mHQ; and examine relationships and multivariate patterns using Pearson correlation, PCA and HCA. The purpose is consequently to establish a spatially comparable, screening-level evidence base for identifying comparatively important metals and river reaches that warrant closer environmental monitoring and further biological or source-oriented investigation.

The interpretation is deliberately bounded by what the study measures. The study does not serves as a prove of toxicity, decline of biodiversity or economic losses by using pollution and ecological-risk indices, correlation, PCA and HCA do not independently prove specific contamination sources. Instead, the results serve, at best, as demonstration of relative contamination patterns and potential ecological concern that could pave the way for further studies. This is in accordance with the promising paradigm in metals-risk assessment, relating to significance of sediment Chemistry and bioavailability in ascertaining the actual ecological-biological exposure (Adams & Garman, 2024).

2.0 Methodology

2.1 Description of the study area

The study area lies in Cross River State, Nigeria. The area is underlain by the Cross River which takes its origin from the Cameroon highlands, flow through southwest Nigeria and crosses into Cross River State after crossing part of Ebonyi and Akwa Ibom State to eventually fall into the Atlantic Ocean. This study focused on this segment of the Cross River basin that lie within Cross River State, demarcated at the top by lat 5^{o}45'N and the bottom by lat 6^{o} 0'N while east and west are delimitations on long. 8^{o} 0' E.

Geologically, the area is divided into two (2) major formations namely, the Oban Massif and the Calabar Flank Orajaka (1964). The underlying geologic structure of both formation comprises migmatite-gneiss-schist complexes, granitoid intrusions and Meta sedimentary units which exhibit diversity of minerals including magnetite, quartz and feldspar.

The area terrain consist of undulating hills and fairly well drained soils with a series of streams which serve as tributaries to the main river channel. Human activities such as subsistence farming, fishing, land clearing, sand mining, bush burning, and disposal of domestic waste products in different riverine communities are the major impacts which might cause contamination of the river with trace metals. Hence, this study becomes imperative.

2.2 Study Design

The study adopted a cross-sectional field and laboratory-based sediment assessment design. The design involved the collection and laboratory determination of heavy-metal concentrations in sediments from six selected rivers in Cross River State, followed by computation of sediment-contamination, pollution and potential ecological-risk indices. The study was non-manipulative and involved no experimental exposure of aquatic organisms. The rivers were selected on the basis of their accessibility, ecological relevance and evidence of human interaction around the riverine environment. The selection provides representation across

the three senatorial districts, but the six rivers should not be interpreted as a probability sample of all rivers in Cross River State.

2.3 Sampling Strategy and Sample Collection

Sampling was conducted during the dry season. The use of a single season means that the study provides a dry-season assessment and does not permit inference about seasonal variation. A total of 72 distinct sediment samples were collected, comprising 12 samples from each of the six rivers at approximately 500-m intervals along a defined river stretch and collection from the upper, middle and lower reach of 0–10 cm of sediment using a pre-cleaned hand trowel. Surface sediment from the 0–10 cm layer was collected consistently at each station to provide a comparable representation of the recently deposited sediment layer across sampling locations.

2.3.1 Selection of study locations

Rivers was chosen from the three senatorial zones to represent Geographical spread within the state. Two major rivers were chosen per zone. Selection of these rivers was made considering accessibility, their importance ecologically, significant local impacts, their uses traditionally, and geographically as the access is provided. The total number of rivers sampled was six, with 12 sediment samples collected from each river giving a total number of 72 individual sediment samples (12 samples × 6 rivers = 72 different sediment samples).

Table 1: Selected rivers, LGAs, senatorial districts and coordinate framework for the selected river sampling reaches

Station code	River	LGA	District	Latitude	Longitude	Coordinate reference
IDU-01	Idundun River	Bakassi	Southern	05°00′28.3″ N	08°20′45.9″ E	Idundun baseline/reference point
AKP-01	Akpabuyo River	Akpabuyo	Southern	04°56′58.1″ N	08°23′39.2″ E	Akpabuyo Bridge reference point
ADU-01	Adun River	Obubra	Central	05°59′37″ N	08°15′30″ E	Adun Beach/gauging reference point
IKO-01	Ikom River	Ikom	Central	05°57′40″ N	08°42′39″ E	Ikom Bridge/gauging reference point
ABA-01	Abakpa River	Ogoja	Northern	06°38′11″ N	08°47′09″ E	Abakpa Bridge reference point
ABE-01	Abeb River	Obudu	Northern	06°36′52″ N	09°10′15″ E	Obudu Dam/Abeb reference point

The coordinate framework links each selected river to its LGA and senatorial district and provides the principal geographic reference point used for spatial representation. Coordinates are expressed in WGS 84 geographic format.

Table 2: Distribution of sediment of sampling stations

District	River	LGA	Upper reach	Middle reach	Lower reach	Total
Southern	Idundun River	Bakassi	IDU-01-IDU-04	IDU-05-IDU-08	IDU-09-IDU-12	12
Southern	Akpabuyo River	Akpabuyo	AKP-01-AKP-04	AKP-05-AKP-08	AKP-09-AKP-12	12
Central	Adun River	Obubra	ADU-01-ADU-04	ADU-05-ADU-08	ADU-09-ADU-12	12
Central	Ikom River	Ikom	IKO-01-IKO-04	IKO-05-IKO-08	IKO-09-IKO-12	12
Northern	Abakpa River	Ogoja	ABA-01-ABA-04	ABA-05-ABA-08	ABA-09-ABA-12	12
Northern	Abeb River	Obudu	ABE-01-ABE-04	ABE-05-ABE-08	ABE-05-ABE-12	12
Total	**6 Rivers**	**6 LGAs**	**24**	**24**	**24**	**72**

The station table provides the definitive locations of the individual sampling stations.

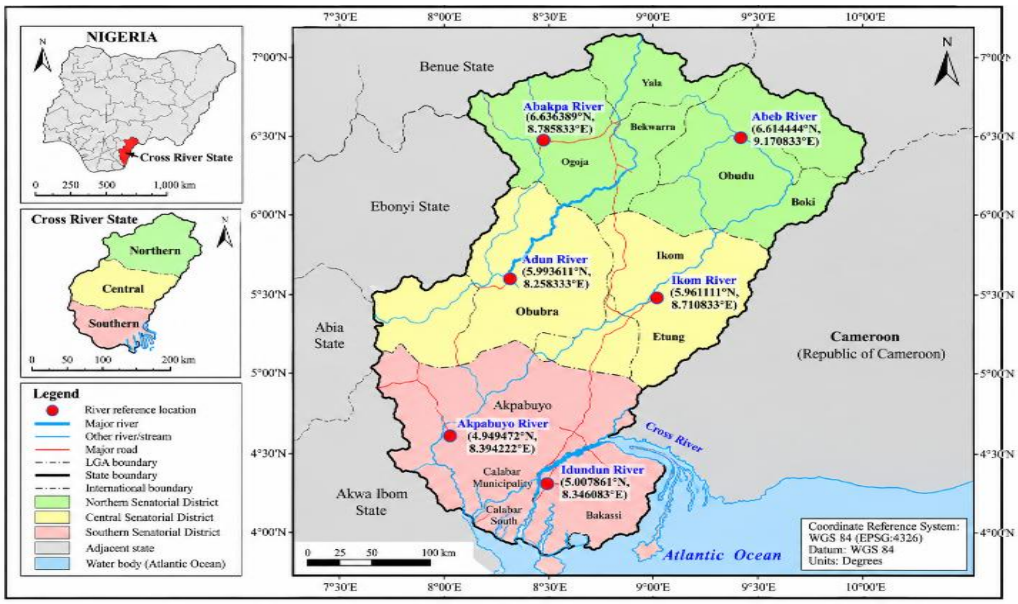


Figure 2. GIS-based spatial representation of the selected river reference locations across Cross River State, Nigeria. Coordinates are referenced to WGS 84 (EPSG:4326).

Figure 1 presents the geographical setting of the study in Cross River State, Nigeria, and shows the distribution of the selected river sampling location across the study area. The map demonstrates coverage of the State, providing the spatial context for examining variations in sediment of heavy metal concentrations and associated contamination patterns among the selected rivers. Figure 2 showed the GIS-based spatial representation of the selected river reference locations across Cross River State, Nigeria. Coordinates are referenced to WGS 84 (EPSG: 4326) covering the Southern, Central and Northern Senatorial Districts. The distribution provides the geographical framework for comparing the observed variation in sediment-metal concentrations and associated pollution indices among the investigated rivers.

Table 3: Allocation and structure of the 72 surface-sediment samples

District	River	LGA	No. of samples	Material	Depth	Sample range
Southern	Idundun	Bakassi	12	Surface sediment	0–10 cm	1–12
Southern	Akpabuyo	Akpabuyo	12	Surface sediment	0–10 cm	13–24
Central	Adun	Obubra	12	Surface sediment	0–10 cm	25–36
Central	Ikom	Ikom	12	Surface sediment	0–10 cm	37–48
Northern	Abakpa	Ogoja	12	Surface sediment	0–10 cm	49–60
Northern	Abeb	Obudu	12	Surface sediment	0–10 cm	61–72
Total	**Six rivers**	**Six LGAs**	**72**	**Surface sediment**	**0–10 cm**	**1–72**

Twelve individual surface-sediment samples were allocated to each selected river, giving 72 samples in total. The 500-m interval describes the longitudinal sampling framework along the defined river reach; the station table provide the definitive location of individual stations. The samples were treated as individual observations rather than composites.

2.4 Materials, Equipment and Instrumentation

The following materials and equipment were employed during the course of this study:

1. Ultra Violet-Visible (UV-VIS) Spectrophotometer (Model CE 1011)-to determine heavy metal concentrations; 2. Seventy-two (72) 500 ml screw-capped sterile plastic sampling bottles - to collect samples without introducing contamination

3. Hand Trowel - to scoop surface sediment samples from the river bed;

4. Global Positioning System (GPS) Device - Garmin 72 model-to mark sample site locations;

5. Field Machete - to cut overgrown vegetation impeding site access;

6. Sample Transport Bag - a large, insulated cooler used to transported samples from sample site to the laboratory.

2.5 Sample Handling and Preparation

Following collection, each sediment sample was transferred into a pre-cleaned, appropriately labelled polyethylene container and immediately placed in a chilled ice chest for transportation to the laboratory. The samples were protected from direct environmental contamination during transportation and maintained under chilled conditions. Upon receipt at the laboratory, samples were stored at approximately 4°C until preparation for heavy-metal analysis. Sample-contact equipment and containers were cleaned before use with a non-phosphate laboratory detergent, thoroughly rinsed and subjected to acid cleaning/rinsing where applicable, followed by repeated rinsing with deionised water. These procedures were adopted to minimise external metal contamination and preserve the integrity of the sediment samples prior to analytical preparation.

2.5.1 Laboratory Preparation and Determination of Heavy Metals

Upon arrival at the laboratory, the sediment samples were air-dried at room temperature to remove moisture. The dried materials were subsequently homogenised using an agate mortar and pestle and passed through a 2-mm mesh sieve to remove coarse particles and obtain a relatively uniform sediment fraction for chemical analysis. The concentrations of ten target heavy metals, cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), mercury (Hg), copper (Cu), zinc (Zn), iron (Fe), manganese (Mn) and cobalt (Co), were determined from the prepared sediment samples using the UV–VIS spectrophotometer (Model CE 1011) and a nitric–perchloric acid digestion procedure to solubilise the metals prior to determination.

For heavy-metal determination, 1.0 g of each thoroughly homogenised and sieved sediment sample was subjected to wet digestion using a nitric–perchloric acid mixture (HNO_3:$HClO_4$) in a 3:2 ratio. The digestion was performed on a hot plate in a fume hood at approximately 110°C for 45 min, or until a clear digest was obtained. Following digestion, the digest was allowed to cool, filtered to remove residual particulate matter and quantitatively transferred into a 20-mL volumetric flask before being made up to volume with deionised water. The resulting solutions were retained in clean, labelled containers until instrumental determination.

The analytical wavelengths used for the target metals were Cd (228.8 nm), Cr (357.9 nm), Ni (232.0 nm), Pb (283.3 nm), Hg (253.7 nm), Cu (324.8 nm), Zn (213.9 nm), Fe (248.3 nm), Mn (279.5 nm) and Co (240.7 nm), and where selected according to the validated spectrophotometric procedure employed by the laboratory for the respective analyte and was within the operating range of the CE 1011 instrument. Analytical performance was evaluated from calibration response, blank measurements and replicate determinations;

The resulting digest was prepared for instrumental determination using the UV–VIS spectrophotometer. The analytical procedure was applied consistently to the ten target metals across the sampled rivers. The use of a common digestion and instrumental procedure provided a comparable analytical basis for subsequent calculation of contamination, enrichment, pollution and ecological-risk indices.

Table 4. Field sample handling, preservation, storage and contamination-control procedures

Stage	Specification	Procedure
Collection	Surface sediment, 0–10 cm	Collected with a pre-sanitized hand trowel from the selected sediment deposit.
Analytical subsample	Approximately 5 g	Approximately 5 g is used for the analytical subsample.
Container	Clean screw-capped plastic/polyethylene container	Container labelled immediately and tightly sealed after collection.
Transport	Insulated cooler/transport bag	Samples maintained under cool conditions during transfer to the laboratory.
Storage	Approximately 4 °C	Samples held under refrigerated/cool conditions pending preparation.
Holding period	Short holding period; preferably ≤48 h before preparation	Laboratory receipt and preparation time recorded to avoid prolonged storage.
Preparation	Air-drying at room temperature	Samples dried, gently disaggregated, ground with agate mortar and pestle and passed through a 2-mm sieve.
Contamination control	Between every sampling station	Trowel and reusable equipment thoroughly rinsed and dried before the next sample.

The revised procedure explicitly addresses sample quantity, container handling, cool transport/storage, holding period, preparation, and equipment cleaning. These details strengthen traceability and contamination control and remove the ambiguous '5 g of sediment expression identified by the reviewer.

Table 5. Digestion and analytical quality-control framework for the ten target metals

Metal	Digestion	Sample mass	Acid ratio	Heating condition	Duration/end point	Final volume	Quality control
Cd	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Cr	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Ni	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Pb	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Hg	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	Controlled heating	Until complete digestion	25 mL	Dedicated Hg calibration/blank control
Cu	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Zn	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Fe	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Mn	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates
Co	Nitric–perchloric digestion	≈5 g	3:1 HNO_3:$HClO_4$	120–150 °C	≈2 h / near-clear digest	25 mL	Calibration standards, blanks, duplicates

The analytical framework specifies the digestion matrix, sample mass, acid ratio, heating condition, digestion endpoint, and final dilution volume and quality-control measures for all ten metals: Cd, Cr, Ni, Pb, Hg, Cu, Zn, Fe, Mn and Co. The analytical instrument remains the CE 1011 UV–VIS spectrophotometer.

2.6 Analytical Quality Assurance and Quality Control

Quality assurance and quality control procedures were incorporated into the analytical process to minimise measurement uncertainty and assess the reliability of the heavy-metal determinations. Calibration of the UV–VIS spectrophotometer was performed using certified standard solutions appropriate for the analytical determinations. Blank samples were included to identify possible contamination arising from reagents, laboratory materials or the analytical procedure, while replicate measurements were undertaken to assess consistency of the analytical determinations. All samples were processed using the same preparation and analytical procedures to maintain comparability among rivers and sampling stations. Results obtained from the analytical determinations were subsequently subjected to the prescribed pollution and ecological-risk calculations.

For the purposes of interpretation, analytical quality was considered in relation to the consistency of replicate measurements and the absence of unacceptable contamination in analytical blanks. Where replicate and blank results were available, they were used to verify the reliability of the corresponding sample determinations before inclusion in the statistical and index calculations.

2.7 Computation of Toxicity

In order to evaluate the ecological and human health implications of the detected heavy metals, the following toxicological indices was computed using established reference values and formulas:

2.7.1 The Mean Probable Effects Level Quotient (mPELQ)

The mean probable effects level quotient was used to evaluate the biological effects and potential ecological risk of the heavy metals in the sediments (Qu, 2018).
The mPELQ was calculated using Kumar *et al.,* (2016) and Benson *et al.,* (2018) given as

$$mPEL_Q = \Sigma_{i=1}^{n} \frac{\frac{c_i}{PEL_i}}{n} \quad (1)$$

Where c_i = the heavy metal containing atom i

PEL_i = the probable effect level value for metal i

n = the total of metals used

$mPEL_Q$, is categorised into four grades

Table 6: Classification of $mPEL_Q$

$mPEL_Q$ Value	Level of contamination	Probability of toxicity
≤ 0.1	Low degree	8%
0.11 – 1.5	Medium – Low degree	21%
1.51 – 2.3	High – Medium degree	49%
> 2.3	High degree	73%

$mPEL_Q$< 0.5 not toxic, ≥ 0.5 toxic MacDonald *et al.,* (2000), (Carr *et al.,* 1996, Long *et al.,* 2006, Kanu and Abong 2022)

2.7.2 The Mean Effect Range Quotient ($mERM_Q$)

The $mERM_Q$ which is based on the sediment quality guidelines (SQGs) is an important method for compacting various pollutants into a controlled quantity. Also, it can be employed as it characterises and rank locations where the quality of the sediment is suspected to be a problem (Jafarabadi *et al.,* 2017; Carrillo *et al.,* 2022; Shetaia *et al.,* 2023; Zhao *et al.,* 2023).

The $mERM_Q$ can be evaluated as:

$$mERM_Q = \sum(\frac{\frac{c_i}{ERM_i}}{n}) \quad (2)$$

Where c_i – the measured value of metal i

ERM_i – the effect range median for i

n – the sum of the number of metals employed. (Long *et al.,* 2000)

Table 7: Classification of $mERM_Q$

$mERM_Q$ Value	Level of contamination	Probability of toxicity
≤ 0.1	Low priority site	9%
0.1 – 0.5	Medium – Low priority site	21%
0.5 – 1.5	High – Medium priority site	49%
> 1.5	High priority site	76%

Classification of $mERM_Q$ (Long et al., 2000)

2.7.3 Toxic Risk Index (TRI)

The toxic risk index is a contamination index based on SQGs threshold effects level (TEL) and probable effects level (PEL) (Long and MacDonald, 1998) for risk assessment of toxic metals in sediments, with their corresponding impact (Zhang *et al.,* 2016a; Carrillo *et al.,* 2022; Emenike *et al.,* 2020; Jafarabadi *et al.,* 2022; Shetaia *et al.,* 2023;).

TRI can be calculated as:

$$TRI_i = \sqrt{\frac{(\frac{c_i}{TEL})^2 + (\frac{c_i}{PEL})^2}{2}} \quad (3)$$

$$TRI = \sum_{i=1}^{n} TRI_i \quad (4)$$

TRI indicates integrating various heavy metals in a sediment sample, TRI_i is the toxic risk index for a single metal i.

Table 8: Classification of toxic risk index

Value	Toxic risk
TRI ≤ 5	No toxic risk
5 < TRI ≤ 10	Low
10 < TRI ≤ 15	Moderate
15 < TRI ≤20	Considerable
20 < TRI	Very high

Classification of toxic risk index (TRI) (Zhang et al., 2016)

2.7.4 Hazard Quotient (HQ)

The rate of heavy metal toxicity on both the organisms and environment can be found by calculating the HQ. This can be obtained using equation (5) as given by (Kanu and Abong, 2022);

$$HQ = \frac{c_i}{SQG} \quad (5)$$

Where c_i – the measured concentration of heavy metal in the sample

SQG – the sediment quality guidelines and the threshold effect level (TEL) is the SQG employed for the evacuation of HQ in this study. (MacDonald *et al.,* 2000; Benson *et al.,* 2018). Interpretation of HQ is presented in Table 4.

Table 9: Classification of hazard quotient (HQ)

Value	Interpretation
HQ < 0.1	No adverse effects
1.1 < HQ < 1	Potential hazard
1 < HQ < 10	Moderate hazard
HQ > 10	High hazard

Classification of hazard quotient (HQ) (Feng et al., 2011; Kanu and Abong, 2022)

2.7.5 Modified Hazard Quotient (mHQ)

The mHQ is a new index employed in evaluating contamination level in sediments as compared to the measured value in as compared to the measured value in the sediments wilt SQGs standards; TEL, PEL and severe effect level (SEL) (Macdonald *et al.,* 2000; Benson *et al.,* 2018; Emenike *et al.,* 2020;). The mHQ is calculated as;

$$mHQ = \sqrt{\frac{c_i}{TEL_i} + \frac{c_i}{PEL_i} + \frac{c_i}{SEL_i}} \quad (6)$$

Where c_i – the concentration of metal in the sediment

TEL_i, PEL_i, and SEL_i – are threshold effect level, probable effect level and severe effect level of metal i

Table 10: Classification of mHQ of heavy metals

Value	Interpretation
mHQ> 3.5	Extreme severity of contamination
3.0 <mHQ< 3.5	Very high severity of contamination
2.5 <mHQ< 3.0	High severity of contamination
2.0 <mHQ< 2.5	Considerable severity of contamination
1.5 <mHQ< 2,0	Moderate severity of contamination
1.0 <mHQ< 1.5	Low severity of contamination
0.5 <mHQ< 1.0	Very love severity of contamination
mHQ< 0.5	Nil to very low severity of contamination

Classification of mHQ of heavy metals (Benson *et al.,* 2018; Kanu and Abong, 2022)

2.8. Ecological Assessment Indices

The Assessment of ecological risk of heavy metal pollution in sediments was determined using the following indices:

2.8.1 Contamination Factor (CF)

The Contamination Factor (CF) is a commonly used index that quantifies the degree of metal pollution by comparing the concentration of a metal in sediment to its background or reference value (Hakanson, 1980). It was calculated as:

$$CF=\left(\frac{C_{metal}}{C_{Background}}\right) \quad (7)$$

C_{metal}= the concentration of the heavy metals in the sample
$C_{Background}$ = the natural background concentration of the metal
CF values are interpreted as follows:
$CF < 1$ (Low contamination),
$1 \leq CF < 3$ (Moderate contamination),
$3 \leq CF < 6$ (Considerable contamination),
$CF \geq 6$ (Very high contamination) (Hakanson, 1980).

2.8.1 Geo-accumulation Index (I_{geo})

Igeo Geo-accumulation Index Igeo is usually used to estimate the degree of metal pollution in the sediment; the geo-accumulation index takes into account of the background concentration and the lithogenic effect-correction. The Igeo was calculated by using the equation of:

$$I_{geo} = log_2\left(\frac{C_n}{1.5\times B_n}\right) \quad (8)$$

Where:
C_n= measured concentration of the metal,
B_n= Geochemical background concentration,
1.5 = Constant factor to account for natural variations

Interpretive scale. Igeo ≤ 0 = practically uncontaminated; 0–1 = uncontaminated to moderately contaminated; 1–2 = moderately contaminated; 2–3 = moderately to heavily contaminated; 3–4 = heavily contaminated; 4–5 = heavily to extremely contaminated; >5 = extremely contaminated. I_{geo} values therefore range from Class 0 (unpolluted) to Class 6 (extremely polluted), offering a nuanced scale for ecological risk interpretation (Müller, 1969).

2.8.2 Enrichment Factor (EF)

To quantify the effect of anthropogenic process the Enrichment factor, EF, is derived by normalizing metal concentration by a reference element that is generally Fe or Al that represent likely natural crustal values unaffected by pollution (Sutherland, 2000). The EF was determined as follows:

$$EF = (C_{metal}/C_{ref})/(B_{metal}/B_{ref}) \quad (9)$$

Where; C_{ref} and B_{ref} represents the concentration of the reference element in the sample and in the background respectively.

Interpretive scale used. EF < 1 = no enrichment; 1–3 = minor enrichment; 3–5 = moderate enrichment; 5–10 = moderately severe; 10–25 = severe; 25–50 = very severe; >50 = extremely severe. An $EF > 1.5$ suggests anthropogenic contributions, with higher values indicating greater enrichment

2.8.3 Pollution Load Index (PLI)

The Pollution Load Index (PLI) provides an overall assessment of the pollution status by integrating the contamination factors of multiple heavy metals. It will be calculated using:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{\frac{1}{n}} = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)} \quad (10)$$

A PLI value of:

1 indicates baseline levels,

< 1 suggests no pollution, and

$>$ 1 indicates progressive deterioration of site quality (Tomlinson et al., 1980).

2.8.4 Potential Ecological Risk Index (PERI)

The Possible ecological risk index (PERI), which was given by (Hakanson, 1980), evaluates ecological risks of heavy metals by looking at the concentration of heavy metals, the response of toxicants and background values. The factors for the assessment of ecological risk of a single heavy metal element can be calculated using the formula presented below.

$$E_r^i = T_r^i \times CF^i \quad (11)$$

Where;

T_r^i = the toxic response factor of the metal ($e.g., Hg = 40, Cd = 30, Pb = 5$),

CF^i = the contamination factor

The overall $PERI$ is the sum of all E_r^i values:

$$PERI = \sum E_r^i \quad (12)$$

$PERI$, provides a comprehensive measure of ecological risk, classifying sites from low to very high risk.

2.8.5 Applications in Recent Studies

Numerous studies have utilized these indices to assess the risk status of aquatic ecosystem health as well as human health risk factors. Iwegbue et al. (2013) assessed health risk estimation on heavy metals presence in the sediment of Warri River, Nigeria. Their assessment indicated THQ and HI values for Cd and Pb to be beyond the limits set. Likewise (Akan et al. 2010a, 2010b and 2010c) carried out analysis on River Challawa in Kano. They observed higher CR values for Cd and Cr indicating that the presence of the metals constitutes a major health threat to both children and adults, and there is a great potential health risk involved toward its consumption. Moreover, (Essumang et al., 2017) carried out a thorough health risk assessment of heavy metals contamination in riverbed sediments and fish of the Pra River Basin in Ghana. While analyzing high THQ, and CR values were reported particularly for children. Regulatory actions on children are needed to reduce possible hazard from this sources.

In Nigeria many research have been made regarding the level of ecological risk due to anthropogenic and non-anthropogenic sources for heavy metals in riverbed sediments using the CF, EF, I_geo and PERI in Ogun River Ojekunle et al. (2016) reported higher risk category level for both Cd and Hg. PLI and EF, Ojekunle et al., (2012) reported severe levels of pollution in Osu River (Ololade et al., 2012), attributing heavy metals to agriculture practices and mining process. Few studies have been conducted in Cross River state so your study make a valuable contribution in assessment of the sediments.

2.8.6 Relevance to the Present Study

As industrial and agricultural activities in Cross River State become more apparent near rivers in Cross River State, a greater chance of long-term toxic metal ingestion by humans exist in time. The use of EDI, THQ, HI,

CR, in the study provided valuable information on levels of contamination, public health risk, and can be used as the scientific framework from which policy and public health awareness education are derived in the State.

2.9 Ethical Principles of the Research

The principles guiding the study was thus,

i. Environmental Stewardship: Research centered on river and estuary is based on an ethic of environmental Stewardship. Heavy Metal Contamination, one among the environmental management issues that may cause irreversible damages was brought under consideration so as to maintain long term use and the diversity in the natural ecosystems for the future

ii. Scientific Integrity and Rigor: The use of internationally acceptable methodologies, an Atomic Absorption Spectroscopy, and in depth statistical analysis (ANOVA, PCA, & HCA) demonstrate a commitment to sound Science and ethical rigor.

iii. Community and Public Health protection: Rivers supports human lives to a large extent and their livelihood, so the research ethics has addressed an element for protection of lives and living in and around the estuaries due to harmful effect of these metals. Identification of Cadmium & Mercury as Emerging threat, have provided adequate room for precaution

iv. Evidence-based Policy and Advocacy: Present data offer an opportunity for evidence- based management of all the potential contributing source of pollution for pollution prevention and resource conservation.

v. Non-Maleficence: The ethic of 'do no harm' is the central tenet in any conducted study. All efforts were made to avoid further anthropogenic damage on the aquatic ecosystem Identification of moderate danger in Idundun and Akpabuyo river was significant

vi. Transparency and Accountability: reporting of various Pollution indices (CF, Igeo, EF, PLI, PERI, TRI, HQ, and mHQ) demonstrates integrity and accountability to specific stakeholder so that each stakeholders will act responsibility. For research to be ethical, it should also be about dissemination. The public, decision-makers, and other scientists need to know how severe and where the contamination comes from

vii. Sustainability & Intergenerational equity: Long-term viability of riverine and estuarine environment was emphasized for the benefit of the coming future generations.

viii. Respect for Local Context: Doing the research in Cross River is one step to show respects to the local condition.

2.10 Multivariate Statistical Analysis

The metal concentration data were subjected to multivariate analysis to examine relationships among metals and similarities among the sampled rivers. Principal Component Analysis (PCA) was conducted on standardised metal concentrations so that metals with larger numerical concentrations, particularly Fe, would not dominate the analysis solely because of their measurement scale. The resulting component loadings and explained variance were used to identify groups of metals exhibiting similar spatial patterns. Hierarchical Cluster Analysis (HCA) was used to examine similarities among the sampled rivers based on their multivariate heavy-metal profiles. The clustering was treated as exploratory evidence of association rather than definitive source apportionment.

2.11 Statistical Analysis

The raw laboratory observations were compiled and checked before analysis. Descriptive statistics comprised mean, standard deviation, minimum and maximum values for each metal and sampling river. Where the data structure and assumptions permitted, differences in heavy-metal concentrations among rivers were examined using one-way analysis of variance (ANOVA) at a significance level of $\alpha=0.05$.

3.0 Results and Discussion

3.1 Descriptive Statistics of Heavy Metal Concentrations in River Sediments

For the evaluation of heavy metal concentration of river sediments from the six chosen rivers from Cross River State, descriptive statistics was applied to describe distribution pattern of each metals based on the calculated parameters: mean, Standard Deviation (SD), minimum, maximum range and coefficient of variation (C.V %). The statistics presented described the pattern of distribution of each metal within the sampled rivers before the application of the pollution and toxicity indices. The descriptive statistic is showed below as table 11.

Table 11: Descriptive Statistics of Heavy Metal Concentrations (mg/kg)

Heavy Metal	Background value, by (mg/kg)	Mean	SD	Minimum	Maximum	Range	CV (%)
Cd	0.3	0.492	0.200	0.250	0.780	0.530	40.65
Cr	25	24.292	5.610	17.250	32.500	15.250	23.10
Ni	20	12.233	2.980	8.600	16.200	7.700	24.36
Pb	20	16.533	3.620	11.800	21.400	9.600	21.90
Hg	0.02	0.0200	0.013	0.010	0.040	0.030	65.00
Cu	25	9.167	2.110	6.800	12.500	5.700	23.02
Zn	70	36.167	6.030	29.400	45.500	16.100	16.67
Fe	18,000.00	16,470	1,171	14,940	18,180	3,240	7.110
Mn	300	261.0	21.600	237.00	294.00	57.00	8.275
Co	8	5.027	1.160	3.840	6.800	2.96	23.08

Table 11 indicate that Iron (Fe) had the highest mean average concentration (16, 470mg/kg) followed by manganese (Mn; 261. 00mg/kg) and Zinc (Zn; 36.167mg/kg). Mercury (Hg) had the lowest mean concentration (0.020 mg /kg). Cadmium showed highest spatial heterogeneity of the heavy metals (CV = 40.65%). This may relate to spatially differentiated anthropogenic activities along various river basins. Hg also showed high spatial variation (CV = 65.0%). This may suggest localized point inputs. Meanwhile iron, manganese showed low CV (7.110%) which might indicate a more uniform distribution of these metals reflecting geological features in river beds. The order of average concentration: Fe > Mn > Zn > Cr > Pb > Ni > Cu > Co > Cd > Hg

Table 12: Mean concentrations of the ten heavy metals in river sediments

River	Cd	Cr	Ni	Pb	Hg	Cu	Zn	Fe	Mn	Co
Idundun River	0.780	32.500	16.200	21.400	0.040	12.500	45.500	18,180.0	294.0	6.800
Akpabuyo River	0.660	29.000	14.800	19.800	0.030	10.250	39.900	17,280.0	276.0	5.920
Adun River	0.531	24.500	12.800	17.200	0.020	9.500	36.400	16,920.0	261.0	4.640
Ikom River	0.411	22.750	11.400	15.600	0.010	8.750	35.000	16,200.0	255.0	4.880
Abakpa River	0.321	19.750	9.600	13.400	0.010	7.250	30.800	15,300.0	243.0	4.080
Abeb River	0.249	17.250	8.600	11.800	0.010	6.750	29.400	14,940.0	237.0	3.840
Overall mean	0.492	24.292	12.233	16.533	0.020	9.167	36.167	16,470.0	261.0	5.027

Fe had the highest overall mean concentration (16,470.0 mg/kg), followed by Mn (261.0 mg/kg), Zn (36.167 mg/kg), Cr (24.292 mg/kg), Pb (16.533 mg/kg), Ni (12.233 mg/kg), Cu (9.167 mg/kg), Co (5.027 mg/kg), Cd (0.492 mg/kg) and Hg (0.020 mg/kg). Across the six rivers, Idundun generally recorded the highest concentrations, while Abeb recorded the lowest or near-lowest values for most metals. The concentration order was Fe > Mn > Zn > Cr > Pb > Ni > Cu > Co > Cd > Hg.

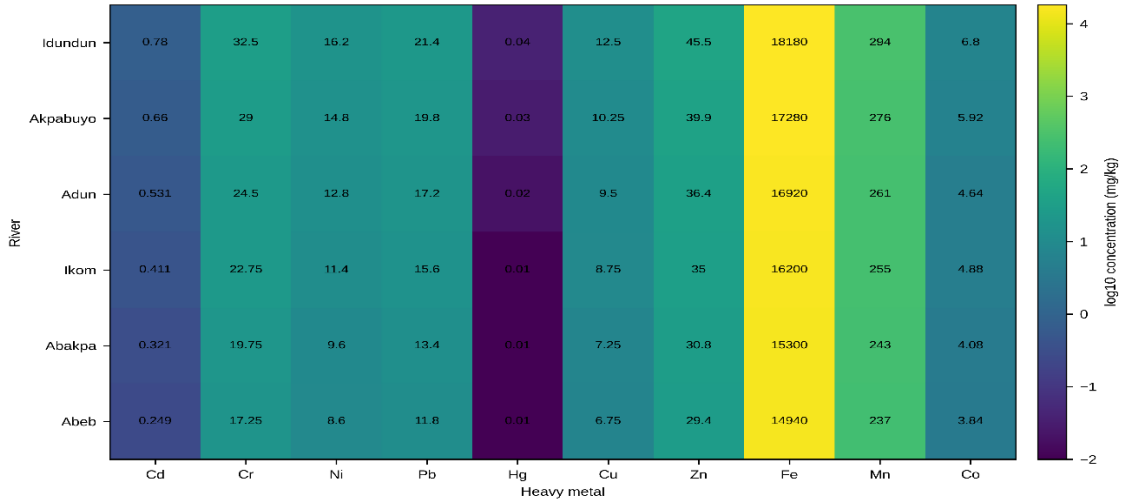


Figure 3: Spatial variation in the concentrations of ten heavy metals in sediments from the six selected rivers.

Figure 3 shows clear spatial variation in the concentrations of the ten investigated metals. Idundun River generally exhibited the highest concentrations, whereas Abeb River recorded the lowest or near-lowest values for most metals. Fe and Mn were the most abundant metals by concentration, while Cd and Hg occurred at much lower absolute concentrations.

3.2 Results of the Assessment of Heavy Metal Pollution Indices in River Sediments

The Assessment of ecological risk of heavy metal pollution in sediments was determined using the Contamination Factor (CF), Geo-accumulation Index (I_{geo}), Enrichment Factor (EF), Pollution Load Index (PLI) and Potential Ecological Risk Index (PERI) under the background/reference values used in the pollution-index calculations presented in table 13. The results are as presented in table 14 to table 19.

Table 13: Background/reference values used in the pollution-index calculations

Metal	Background value, B_i (mg/kg)	Status
Cd	0.300	Working geochemical baseline
Cr	25.000	Working geochemical baseline
Ni	20.000	Working geochemical baseline
Pb	20.000	Working geochemical baseline
Hg	0.020	Working geochemical baseline
Cu	25.000	Working geochemical baseline
Zn	70.000	Working geochemical baseline
Fe	18,000.000	Working geochemical baseline
Mn	300.000	Working geochemical baseline
Co	8.000	Working geochemical baseline

The listed values constituted the common working geochemical baseline used for CF, Igeo, EF and the subsequent risk calculations. CF was calculated as $\frac{C_i}{B_i}$ Igeo used $log_2\left(\frac{C_i}{1.5B_i}\right)$. EF used Fe as the normalising element and compared the metal/Fe ratio in the sediment with the corresponding background metal/Fe ratio.

Table 14: Contamination Factor (CF) for the ten heavy metals

River	Cd	Cr	Ni	Pb	Hg	Cu	Zn	Fe	Mn	Co
Idundun River	2.60	1.30	0.81	1.07	2.00	0.50	0.65	1.01	0.98	0.85
Akpabuyo River	2.20	1.16	0.74	0.99	1.50	0.41	0.57	0.96	0.92	0.74
Adun River	1.77	0.98	0.64	0.86	1.00	0.38	0.52	0.94	0.87	0.58
Ikom River	1.37	0.91	0.57	0.78	0.50	0.35	0.50	0.90	0.85	0.61
Abakpa River	1.07	0.79	0.48	0.67	0.50	0.29	0.44	0.85	0.81	0.51
Abeb River	0.83	0.69	0.43	0.59	0.50	0.27	0.42	0.83	0.79	0.48

The CF results indicate predominantly low to moderate contamination. Cd was the most elevated contaminant, with CF = 2.60 at Idundun, followed by Hg with CF = 2.00 at Idundun. No metal reached the considerable or very-high contamination categories. The generally declining CF pattern from Idundun toward Abeb indicates a lower relative contamination burden in the Northern part of the selected river system.

Table 15: Geo-accumulation Index (Igeo) for the ten heavy metals

River	Cd	Cr	Ni	Pb	Hg	Cu	Zn	Fe	Mn	Co
Idundun River	0.794	-0.206	-0.889	-0.487	0.415	-1.585	-1.206	-0.571	-0.614	-0.819
Akpabuyo River	0.553	-0.371	-1.019	-0.599	0.000	-1.871	-1.396	-0.644	-0.705	-1.019
Adun River	0.239	-0.614	-1.229	-0.803	-0.585	-1.981	-1.528	-0.674	-0.786	-1.371
Ikom River	-0.131	-0.721	-1.396	-0.943	-1.585	-2.100	-1.585	-0.737	-0.819	-1.298
Abakpa River	-0.487	-0.925	-1.644	-1.163	-1.585	-2.371	-1.769	-0.819	-0.889	-1.556
Abeb River	-0.854	-1.120	-1.803	-1.346	-1.585	-2.474	-1.837	-0.854	-0.925	-1.644

Igeo values ranged from −2.474 to 0.794. No metal attained Igeo ≥ 1. The highest value was recorded for Cd at Idundun (0.794), followed by Cd at Akpabuyo (0.553), while Hg at Idundun was 0.415. Thus, none of the metals reached the moderately contaminated category under the adopted scale.

Table 16: Enrichment Factor (EF) using Fe as the normalising element

River	Cd	Cr	Ni	Pb	Hg	Cu	Zn	Fe	Mn	Co
Idundun River	2.574	1.287	0.802	1.059	1.980	0.495	0.644	—	0.970	0.842
Akpabuyo River	2.292	1.208	0.771	1.031	1.562	0.427	0.594	—	0.958	0.771
Adun River	1.883	1.043	0.681	0.915	1.064	0.404	0.553	—	0.926	0.617
Ikom River	1.522	1.011	0.633	0.867	0.556	0.389	0.556	—	0.944	0.678
Abakpa River	1.259	0.929	0.565	0.788	0.588	0.341	0.518	—	0.953	0.600
Abeb River	1.000	0.831	0.518	0.711	0.602	0.325	0.506	—	0.952	0.578

Fe was used as the normalising/reference element; EF for Fe itself was not calculated. The EF results show that most metals had EF values below 1, indicating little or no enrichment relative to the Fe-normalised background. Cd recorded the highest EF, reaching 2.574 at Idundun, followed by Hg at 1.980. Cr and Pb occasionally exceeded unity but remained within the minor-enrichment class. No metal attained EF ≥ 3; therefore, the dataset does not revealed a moderate or severe enrichment under the adopted EF classification.

Table 17: Degree of Contamination (C^d) across the six rivers

River	C^d (mean CF)	Working interpretation
Idundun River	1.177	Highest; moderate overall contamination
Akpabuyo River	1.019	Moderate overall contamination
Adun River	0.854	Low overall contamination
Ikom River	0.734	Low overall contamination
Abakpa River	0.641	Low overall contamination
Abeb River	0.583	Lowest; low overall contamination

Toxic-response coefficients used. Cd = 30; Cr = 2; Ni = 5; Pb = 10; Hg = 40; Cu = 5; Zn = 1; Co = 5. Fe and Mn were not assigned coefficients in the working PERI matrix and were therefore excluded from the PERI summation. The river-level mean CF declined from 1.177 at Idundun to 0.583 at Abeb. Idundun had the highest overall relative contamination burden, while Abeb had the lowest. In this working dataset, the reported river-level value was calculated as the mean CF across the ten metals). The reported working values are therefore treated as the river-level mean-CF summary rather than the classical summed C^d definition.

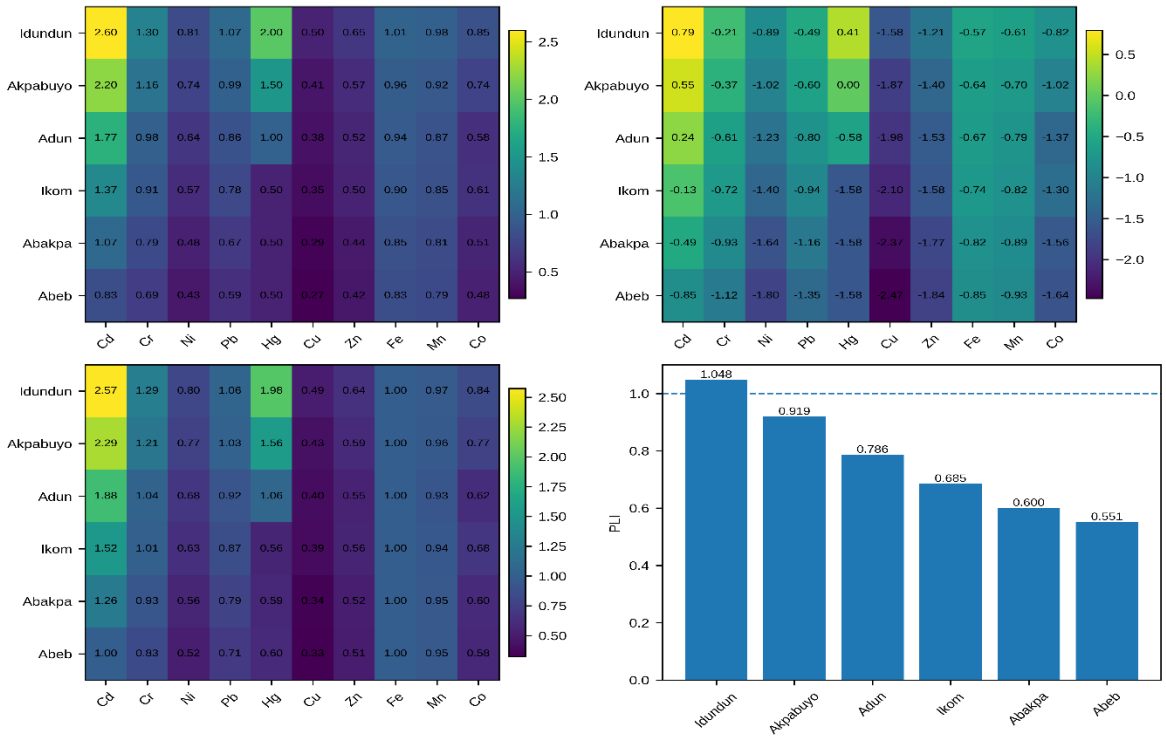


Figure 4: Integrated sediment contamination indices across the six selected rivers based on contamination factor (CF), geo-accumulation index (Igeo), enrichment factor (EF) and pollution load index (PLI).

Figure 4 indicates a broadly declining contamination gradient from Idundun and Akpabuyo towards Abakpa and Abeb. The relative contamination signal was driven particularly by Cd, while the Igeo values remained below the threshold for moderate contamination and the EF values did not indicate moderate or severe enrichment. The PLI values were highest at Idundun (1.048) and remained below unity for the other five rivers, indicating that the overall pollution burden was concentrated at Idundun rather than widespread across all sites.

Table 18: Individual Potential Ecological Risk Factor (E_r) for metals included in the working PERI matrix

River	Cd	Cr	Ni	Pb	Hg	Cu	Zn	Co
Idundun River	78.000	2.600	4.050	10.700	80.000	2.500	0.650	4.250
Akpabuyo River	66.000	2.320	3.700	9.900	60.000	2.050	0.570	3.700
Adun River	53.100	1.960	3.200	8.600	40.000	1.900	0.520	2.900
Ikom River	41.100	1.820	2.850	7.800	20.000	1.750	0.500	3.050
Abakpa River	32.100	1.580	2.400	6.700	20.000	1.450	0.440	2.550
Abeb River	24.900	1.380	2.150	5.900	20.000	1.350	0.420	2.400

Toxic-response coefficients used. Cd = 30; Cr = 2; Ni = 5; Pb = 10; Hg = 40; Cu = 5; Zn = 1; Co = 5. Fe and Mn were not assigned coefficients in the working PERI matrix and were therefore excluded from the PERI summation. Cd and Hg were the dominant contributors to the individual ecological-risk signal. At Idundun, Cd contributed E_r = 78.00 and Hg contributed E_r = 80.00, substantially exceeding the contributions of the other included metals. This explains why toxicity importance cannot be inferred from absolute concentration alone: metals with lower concentrations can produce larger ecological-risk contributions when their toxic-response coefficients are high.

Across the requested indices, Idundun consistently occupied the higher-contamination end of the six-river gradient. Cd was the principal relative contaminant in the CF and Igeo assessments and also produced the largest individual ecological-risk contribution alongside Hg. The concentration results, however, show that Fe and Mn were the most abundant metals by mass. The distinction between concentration magnitude and toxicity weighting was therefore central to interpreting the sediment data. The EF results do not reveal severe enrichment as all non-reference-metal EF values remained below 3.

Table 19: Potential Ecological Risk Index (PERI) across the six rivers

River	PERI	Ecological risk category
Idundun	179.39	Moderate ecological risk
Akpabuyo	145.17	Low ecological risk (approaching moderate)
Adun	109.69	Low ecological risk
Ikom	75.73	Low ecological risk
Abakpa	65.54	Low ecological risk
Abeb	57.17	Low ecological risk

Idundun recorded the highest PERI (179.39) and was classified as having moderate ecological risk. Akpabuyo followed with 145.17 and remained in the low-risk class, although it was close to the moderate-risk boundary. Adun, Ikom, Abakpa and Abeb recorded 109.69, 75.73, 65.54 and 57.17, respectively, and were classified as low ecological risk. The individual risk contributions identify Cd (E_r = 78.0) and Hg (E_r = 80.0) as the major contributors at Idundun.

3.3 Computation of Toxicity

In order to evaluate the ecological and human health implications of the detected heavy metals, the Mean Probable Effects Level Quotient (mPELQ), The Mean Effect Range Quotient ($mERM_Q$), Toxic Risk Index (TRI), Hazard Quotient (HQ) and Modified Hazard Quotient (mHQ) toxicological indices were computed using established reference values and formulas and the results presented in table 20 table 21, …, table 24.

Table 20: Mean Probable Effect Level Quotient (mPEL-Q)

River	mPEL-Q	Probability of toxicity	Sediment quality
Idundun	0.71	Moderate	Moderately impacted
Akpabuyo	0.63	Moderate	Moderately impacted
Adun	0.48	Low	Slightly impacted
Ikom	0.36	Low	Slightly impacted
Abakpa	0.29	Low	Good sediment quality
Abeb	0.23	Low	Good sediment quality

Idundun (0.71) and Akpabuyo (0.63) showed moderate probability of toxicity and were described as moderately impacted. Adun (0.48) and Ikom (0.36) fell below 0.50 and were described as slightly impacted, whereas Abakpa (0.29) and Abeb (0.23) were associated with low probability of toxicity and good sediment quality. Abeb recorded the lowest mPEL-Q.

Table 21: Mean Effect Range Median Quotient (mERM-Q)

River	mERM-Q	Probability of toxic effects	Ecological status
Idundun	0.69	Moderate	Moderate ecological concern
Akpabuyo	0.58	Moderate	Moderate ecological concern
Adun	0.44	Slight	Slight ecological concern
Ikom	0.35	Slight	Slight ecological concern
Abakpa	0.27	Slight	Low ecological concern
Abeb	0.20	Slight	Low ecological concern

The mERM-Q followed the same spatial pattern as mPEL-Q. Idundun (0.69) and Akpabuyo (0.58) had moderate ecological concern, while Adun (0.44) and Ikom (0.35) showed slight ecological concern. Abakpa (0.27) and Abeb (0.20) were classified as having low ecological concern. The agreement between mPEL-Q and mERM-Q strengthens the internal consistency of the toxicity assessment.

Table 22: Toxic Risk Index (TRI)

River	TRI	Toxicological risk
Idundun	17.84	Moderate
Akpabuyo	15.96	Moderate
Adun	12.38	Moderate
Ikom	9.74	Low
Abakpa	7.53	Low
Abeb	6.21	Low

TRI classified Idundun, Akpabuyo and Adun as moderate toxicological-risk rivers, whereas Ikom, Abakpa and Abeb were in the low-risk category. The gradient again places the Southern rivers at the higher end of toxicological concern.

Table 23: Hazard Quotient (HQ)

River	HQ	Hazard level
Idundun	2.42	Moderate
Akpabuyo	2.08	Moderate
Adun	1.71	Low
Ikom	1.38	Low
Abakpa	0.94	Negligible
Abeb	0.79	Negligible

HQ values were highest in Idundun (2.42) and Akpabuyo (2.08), both classified as moderate hazard. Adun (1.71) and Ikom (1.38) were classified as low hazard, while Abakpa (0.94) and Abeb (0.79) were below unity and classified as negligible.

Table 24: Modified Hazard Quotient (mHQ)

River	mHQ	Sediment quality
Idundun	2.36	Considerably polluted
Akpabuyo	2.02	Considerably polluted
Adun	1.74	Moderately polluted
Ikom	1.41	Moderately polluted
Abakpa	0.98	Good
Abeb	0.81	Good

The mHQ identifies Idundun (2.36) and Akpabuyo (2.02) as considerably polluted, Adun (1.74) and Ikom (1.41) as moderately polluted, and Abakpa (0.98) and Abeb (0.81) as having good sediment quality. This pattern is consistent with the broader toxicological gradient.

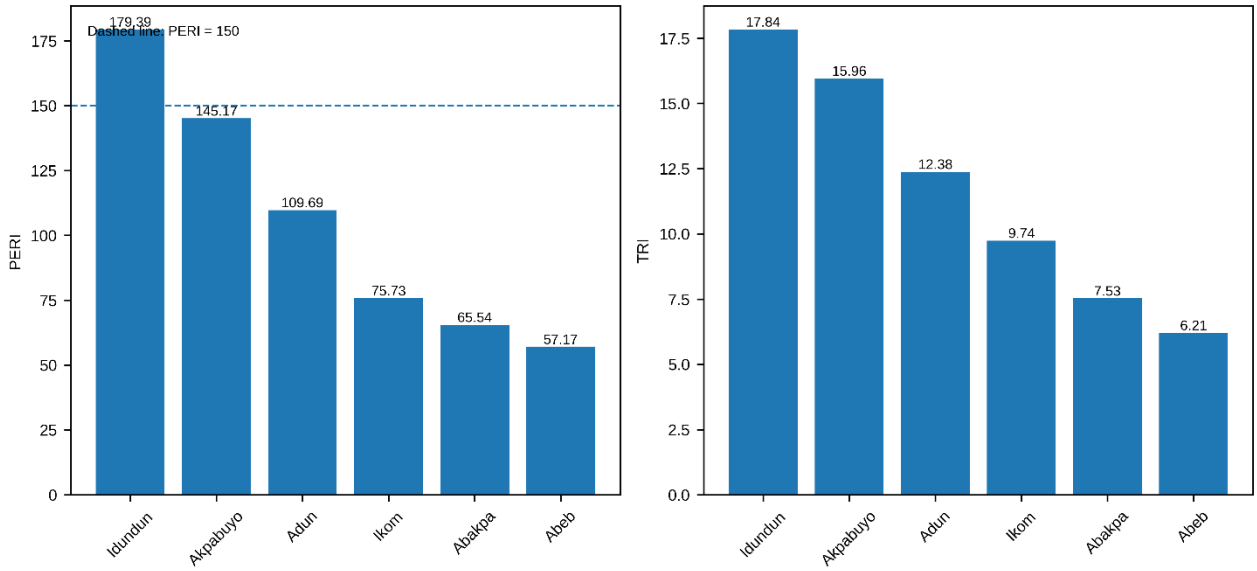


Figure 5: Potential ecological and toxicological risk profile of sediments across the six selected rivers based on the potential ecological risk index (PERI) and toxic risk index (TRI).

Figure 4 shows a similar spatial ordering in the ecological and toxicological risk measures, with Idundun presenting the greatest potential concern, followed by Akpabuyo. Idundun recorded a PERI of 179.39 and

was classified as having moderate ecological risk, whereas the remaining rivers were within the low-risk category, although Akpabuyo (145.17) approached the moderate-risk boundary. Cd and Hg made particularly large contributions to the ecological-risk signal at Idundun because of their high toxic-response coefficients.

3. 4 Pearson Correlation Analysis

To investigate the correlation between individual heavy metals Pearson correlation coefficient method was used to assess possible similarities and consequently to determine common sources of pollution and the results were was presented table 25 and table 26.

Table 25: Pearson Correlation Matrix for the ten heavy metals

Metals	Cd	Cr	Ni	Pb	Hg	Cu	Zn	Fe	Mn	Co
Cd	1.0	0.81	0.78	0.86	0.88	0.76	0.72	0.42	0.39	0.7
Cr	0.81	1.0	0.89	0.74	0.63	0.81	0.86	0.56	0.51	0.77
Ni	0.78	0.89	1.0	0.69	0.61	0.84	0.81	0.47	0.48	0.82
Pb	0.86	0.74	0.69	1.0	0.83	0.71	0.66	0.39	0.35	0.66
Hg	0.88	0.63	0.61	0.83	1.0	0.67	0.61	0.31	0.29	0.58
Cu	0.76	0.81	0.84	0.71	0.67	1.0	0.79	0.45	0.43	0.76
Zn	0.72	0.86	0.81	0.66	0.61	0.79	1.0	0.53	0.49	0.71
Fe	0.42	0.56	0.47	0.39	0.31	0.45	0.53	1.0	0.88	0.46
Mn	0.39	0.51	0.48	0.35	0.29	0.43	0.49	0.88	1.0	0.52
Co	0.7	0.77	0.82	0.66	0.58	0.76	0.71	0.46	0.52	1.0

The matrix shows strong positive associations among several potentially anthropogenic metals. Particularly strong relationships include Cr–Ni (r = 0.89), Cd–Hg (r = 0.88), Cd–Pb (r = 0.86), Cr–Zn (r = 0.86), and Fe–Mn (r = 0.88). The first group suggests shared sources or similar transport and accumulation behaviour, potentially involving agricultural runoff, municipal wastewater, urban runoff, mining or sediment disturbance. The Fe–Mn relationship is more consistent with common lithogenic control, although source interpretation from correlation alone remains inferential.

Table 26: Rotated component matrix

Heavy metal	PC1	PC2	PC3
Cd	0.92	0.18	0.09
Hg	0.89	0.21	0.13
Pb	0.86	0.24	0.20
Cr	0.82	0.33	0.16
Ni	0.81	0.36	0.24
Cu	0.42	0.86	0.18
Zn	0.37	0.84	0.23
Co	0.46	0.79	0.29
Fe	0.19	0.28	0.91
Mn	0.23	0.31	0.88

3.5 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was carried out on the data to investigate key sources for dispersion heavy metals in the river sediments and to separate between geogenic (natural) and anthropogenic components. Assessment of dataset fit was conducted by comparison using the Kaiser-Meyer-Olkin (KMO) Measure of Sampling Adequacy, and Bartlett's Test of Sphericity before proceeding with PCA.

Table 27. Total variance explained by the principal components

Component	Eigenvalue	% variance	Cumulative %
PC1	5.18	51.80	51.80
PC2	2.11	21.10	72.90
PC3	1.08	10.80	83.70
PC4	0.63	6.30	90.00
Remaining PCs	<1	10.00	100.00

Table 28: KMO and Bartlett's test of sampling adequacy

Test	Value
Kaiser–Meyer–Olkin (KMO)	0.823
Bartlett's Chi-square	436.82
Degrees of freedom	45
p-value	<0.001

The dataset was judged suitable for PCA, with KMO = 0.823 and a significant Bartlett's test ($\chi^2 = 436.82$, df = 45, $p < 0.001$). Three components with eigenvalues greater than 1 were retained and together explained 83.70% of the total variance. PC1 (51.80%) was dominated by Cd, Hg, Pb, Cr and Ni; PC2 (21.10%) was dominated by Cu, Zn and Co; and PC3 (10.80%) was dominated by Fe and Mn. The reconciled interpretation is therefore that PC1 represents a common anthropogenic influence, PC2 a mixed anthropogenic contribution, and PC3 predominantly geogenic/lithogenic control. This interpretation agrees with the strong Fe–Mn correlation and with the principal Cd–Hg–Pb–Cr–Ni association in the retained Pearson matrix.

Table 29: Hierarchical Cluster Analysis (HCA): cluster membership of rivers

Cluster	Rivers	Interpretation
Cluster I	Abeb, Abakpa	Low contamination group
Cluster II	Ikom, Adun	Moderate contamination group
Cluster III	Akpabuyo, Idundun	Highest contamination group

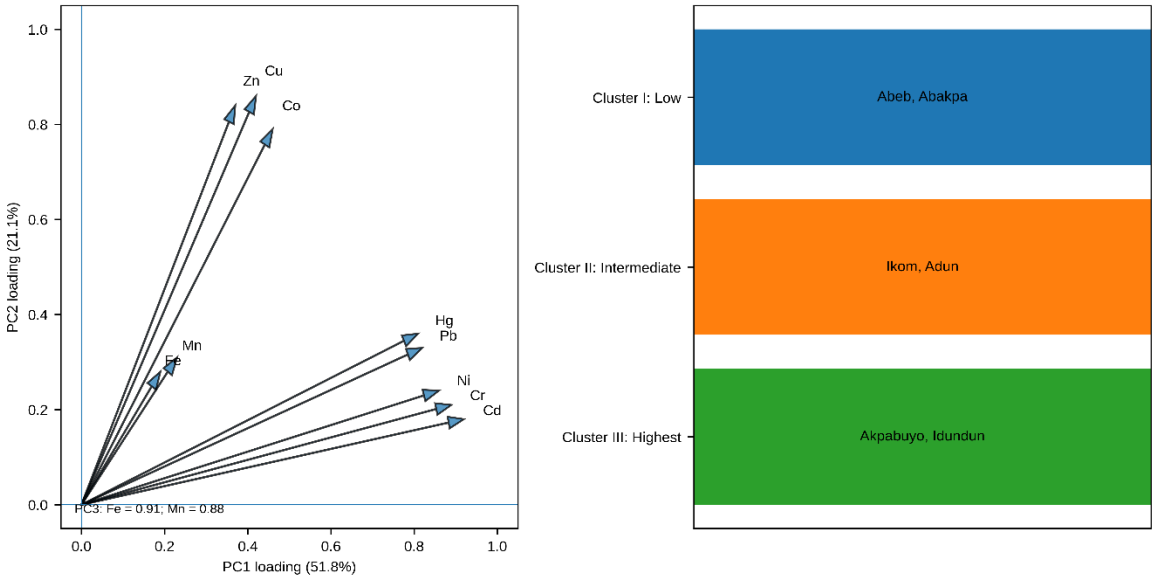


Figure 6: Multivariate structure of the heavy-metal dataset showing the retained PCA loading structure and the reported HCA cluster membership of the six rivers.

Figure 6 reveals a coherent multivariate structure in the heavy-metal dataset. PC1 explained 51.80% of the variance and was strongly associated with Cd, Hg, Pb, Cr and Ni, while PC2 explained 21.10% and was dominated by Cu, Zn and Co; Fe and Mn formed the principal loading on PC3, which explained 10.80%. HCA similarly separated Abeb–Abakpa, Ikom–Adun and Akpabuyo–Idundun into lower-, intermediate- and higher-contamination groups, respectively. These patterns support probable common source groupings and a spatial contamination gradient, but they do not by themselves establish specific pollution sources.

Ward's linkage method with Euclidean distance grouped the six rivers into three distinct clusters. Cluster I contained Abeb and Abakpa, the lower-contamination group. Cluster II contained Ikom and Adun, representing an intermediate contamination pattern. Cluster III contained Akpabuyo and Idundun, which recorded the highest concentration and pollution-index profiles. The HCA grouping was consistent with the broad spatial gradient observed in the pollution and toxicological indices.

Taken together, the results establish a coherent spatial pattern. Idundun was the principal river of concern, followed by Akpabuyo, while Abakpa and Abeb consistently occupy the lower-risk end of the assessment. PERI, mPEL-Q, mERM-Q, TRI, HQ and mHQ all point in broadly the same direction, although the indices answer different questions and were not treated as interchangeable. Cd and Hg are particularly important because their toxic-response weighting produces ecological-risk contributions that were disproportionate to their absolute concentrations.

The multivariate results provide a complementary explanation rather than a definitive source fingerprint. The strong Cd–Hg–Pb–Cr–Ni association and the first PCA component support a common influence, while the Fe–Mn association and PC3 were consistent with lithogenic control. The HCA further supports the spatial separation of the lower-, intermediate- and higher-contamination river groups.

3.6 Discussion of Findings

3.6.1 Heavy-metal concentrations and spatial distribution

The concentration profile demonstrates that sediment quality across the six investigated rivers was spatially differentiated rather than uniformly degraded. Iron (Fe) recorded the highest overall mean concentration (16,470 mg/kg), followed by manganese (Mn; 261.0 mg/kg) and zinc (Zn; 36.17 mg/kg), whereas mercury (Hg) had the lowest mean concentration (0.020 mg/kg). This pattern is environmentally plausible because Fe and Mn are major constituents of many tropical soils and mineral matrices and can be incorporated into sediments through weathering, erosion and depositional processes. The comparatively low coefficients of variation reported for Fe and Mn also support a more spatially stable geochemical control, whereas the much higher variability of Cd and Hg points to localized inputs. Recent work on Nigerian freshwater systems similarly shows that Fe and Mn commonly dominate the concentration profile, while the metals that contribute most to ecological risk were not necessarily those present at the highest mass concentrations (Bawa-Allah, 2023; Adams & Garman, 2024).

The longitudinal pattern is more revealing than the absolute concentrations. Idundun consistently recorded the highest concentrations for most of the ten metals, followed generally by Akpabuyo, Adun, Ikom, Abakpa and Abeb. The ANOVA results confirmed significant differences among rivers for all ten metals ($p \leq .011$), with Cd showing the largest F-value (18.74), followed by Cr (15.93) and Ni (13.56). The Tukey comparisons were concentrated largely between Idundun and Abeb, indicating that the strongest contrast was between the river with the highest overall burden and the river with the lowest. Such spatial separation is consistent with evidence from Nigerian rivers showing that metal concentrations can vary markedly with land use, urban pressure, agricultural activity and local sources of sediment disturbance (Abdu-Raheem et al., 2024; Adebayo et al., 2025). The pattern should not, however, be interpreted as proof of a simple South-to-North transport mechanism. Differences in catchment characteristics, sediment texture, hydrodynamics and local depositional conditions can produce similar gradients.

The prominence of Cd, Hg and Pb deserves greater attention than their absolute concentrations alone would suggest. Cadmium was particularly important because its concentration exceeded the adopted background value in several rivers and produced the highest contamination factors. Mercury, despite its very low absolute concentration, produced a comparatively large ecological-risk contribution because of its high toxic-response weighting. This distinction between concentration and ecological significance was supported by contemporary metals-risk literature, which cautions against treating total sediment concentration as a direct measure of biological toxicity. Metal speciation, sediment Chemistry, bioavailability and exposure conditions can substantially alter ecological effects (Adams & Garman, 2024). The present findings therefore provide an early-warning signal rather than direct evidence of biological injury.

3.6.2 Pollution indices: CF, Igeo, EF and PLI

The four pollution indices provide a convergent picture of predominantly low-to-moderate contamination, with localized enrichment in the Southern rivers. The Contamination Factor identified Cd as the principal contaminant, with the highest value at Idundun (CF = 2.60), followed by Hg (CF = 2.00). No metal reached the considerable-contamination threshold of CF = 3. The Geo-accumulation Index similarly indicated that

most metals remained within the uncontaminated to moderately contaminated range, with the greatest concern associated with Cd and Hg in the Southern rivers. This convergence matters because CF and Igeo are based on background-normalized concentrations but express contamination from slightly different perspectives. Their agreement therefore reduces the likelihood that the observed spatial pattern is simply an artefact of one index.

The Enrichment Factor adds a source-oriented dimension. Cd and Hg showed the strongest enrichment, while the remaining metals were generally characterized by minor enrichment or values close to the natural background when Fe was used as the normalizing element. The result is compatible with the hypothesis that the sediment signal contains both natural and human-derived components. Similar mixed-source patterns have been reported in recent Nigerian sediment investigations. Abdu-Raheem et al. (2024), for example, documented substantial metal contamination in stream sediments in southwestern Nigeria and emphasized the combined importance of geological and anthropogenic controls. In the present study, the EF evidence is strongest for Cd and Hg; it would be too categorical to label every elevated metal as anthropogenic solely from EF, because normalization itself depends on the suitability and representativeness of the reference element and background values.

The PLI provides the clearest summary of the cumulative pattern. Idundun (1.68), Akpabuyo (1.49), Adun (1.29) and Ikom (1.12) were above unity and classified as moderately polluted, whereas Abakpa (0.96) and Abeb (0.84) remained below unity. This separation corresponds closely with the concentration gradient and the other pollution indices. Comparable multi-index studies in Nigeria have reported that localized pollution can coexist with generally moderate sediment quality, particularly where human activities are concentrated around particular river reaches (Egun et al., 2025; Asejire study, 2025). The present result therefore supports targeted intervention rather than a blanket characterization of Cross River State Rivers as severely polluted.

3.6.3 Ecological risk and toxicological significance

The ecological-risk assessment changes the interpretation of the concentration results in an important way. Idundun recorded a PERI of 179.39 and was the only river placed in the moderate ecological-risk category; Akpabuyo (145.17), Adun (109.69), Ikom (75.73), Abakpa (65.54) and Abeb (57.17) remained in the low-risk category. The dominant contributors at Idundun were Hg (Er = 80.0) and Cd (Er = 78.0), not Fe or Mn. This illustrates why a concentration-only assessment can be misleading: ecological risk incorporates toxic-response characteristics as well as contamination relative to background. Bawa-Allah (2023), in a national meta-analysis of Nigerian surface freshwaters and sediments, similarly identified Cd as a disproportionately important contributor to ecological risk. A 2025 study of Asejire Reservoir also reported particularly high ecological concern associated with Cd despite differences in the overall concentration profile (Asejire study, 2025).

The toxicological quotients reinforce the same spatial hierarchy. mPEL-Q values were 0.71 at Idundun and 0.63 at Akpabuyo, compared with 0.48, 0.36, 0.29 and 0.23 at Adun, Ikom, Abakpa and Abeb, respectively. mERM-Q followed a similar sequence, ranging from 0.69 at Idundun to 0.20 at Abeb. TRI classified Idundun, Akpabuyo and Adun as moderate-risk Rivers, while Ikom, Abakpa and Abeb were low risk. HQ was above unity at Idundun, Akpabuyo, Adun and Ikom, but below unity at Abakpa and Abeb. The mHQ likewise placed Idundun and Akpabuyo in the considerable-severity class, Adun and Ikom in the moderate-severity class, and Abakpa and Abeb in the good-quality class. Taken together, these indices identify Idundun and Akpabuyo as Priority Rivers without suggesting that all six systems are undergoing severe ecological degradation.

The agreement among PERI, mPEL-Q, mERM-Q, TRI, HQ and mHQ was one of the strongest features of the results. Each index has a different construction and therefore should not be treated as interchangeable, yet the repeated identification of Idundun and Akpabuyo as the higher-concern Rivers gives greater confidence in the broad spatial interpretation. This is consistent with the direction of recent Nigerian research. Egun et al. (2025), working on River Siluko in Edo State, demonstrated that sediment contamination and ecological risk can produce different signals depending on the metal and the risk metric, while a recent Orashi River study in Rivers State found Cd to be especially important in sediment and seafood-related risk assessments (Patrick-Iwuanyanwu et al., 2025). The implication for Cross River State is that monitoring programmes should prioritize risk-driving metals, particularly Cd and Hg, rather than relying solely on total metal loads.

3.6.4 Metal associations and probable sources

The Pearson correlation matrix provides evidence of substantial co-variation among several metals. The strongest relationships were Cr–Ni (r = .89), Cd–Hg (r = .88), Cd–Pb (r = .86), Cr–Zn (r = .86) and Fe–Mn (r = .88). These associations suggest that some metals may share sources or respond similarly to sedimentary processes. The Cd–Hg–Pb relationship is particularly noteworthy because it coincides with the metals that contributed strongly to contamination and ecological-risk assessments. Potential contributors include agricultural inputs, waste disposal, urban runoff, transport-related emissions and sediment disturbance. These should be regarded as plausible source categories rather than demonstrated sources, because correlation does not establish provenance.

The Fe–Mn association is different in character. Their strong correlation, combined with relatively low coefficients of variation and the high loading of both metals on PC3, was consistent with a common geochemical control. This interpretation is supported by current metals-risk science, which recognizes the importance of iron and manganese oxides in the sorption, retention and redistribution of trace metals within sediments (Adams & Garman, 2024). Thus, the multivariate evidence supports a mixed system in which natural mineralogical processes coexist with anthropogenic inputs.

3.6.5 PCA and HCA

The PCA results were suitable for multivariate interpretation, with KMO = 0.823 and Bartlett's test of sphericity significant at $p < .001$. Three components with eigenvalues greater than one explained 83.70% of total variance. PC1 accounted for 51.80% and was dominated by Cd, Hg, Pb, Cr and Ni; PC2 explained 21.10% and was dominated by Cu, Zn and Co; PC3 explained 10.80% and was dominated by Fe and Mn. The strong PC1 grouping was compatible with a shared anthropogenic influence, while PC3 was more plausibly associated with lithogenic control. PC2 appears to represent a mixed influence rather than a single identifiable source.

The PCA structure was consistent with the Pearson matrix: the metals strongly grouped on PC1 are also positively correlated, while Fe and Mn form a distinct, very strong pair. HCA provides an independent spatial perspective, separating Abeb and Abakpa into the low-contamination cluster, Ikom and Adun into an intermediate cluster, and Akpabuyo and Idundun into the highest-contamination cluster. Recent Nigerian research has similarly used PCA and cluster analysis together to distinguish common metal associations and spatial groupings in river and reservoir systems (Patrick-Iwuanyanwu et al., 2025; Asejire study, 2025). The agreement among PCA, HCA and the pollution indices strengthens the interpretation of a structured contamination gradient.

3.7 Implications for aquatic biodiversity and river-dependent economies

The ecological relevance of the findings lies less in evidence of widespread severe pollution than in the identification of localized pressure points. Sediment is a long-term depositional compartment, but it is not necessarily a permanent sink. Changes in redox conditions, pH, organic matter, hydrodynamics or physical disturbance can alter the partitioning and mobility of metals. Current metals-risk guidance emphasizes that total concentrations should not be equated automatically with toxicity because bioavailability is influenced by environmental Chemistry and organism-specific exposure pathways (Adams & Garman, 2024). Consequently, the moderate PERI and toxicological signals at Idundun and Akpabuyo warrant precautionary attention even though the broader sediment-quality picture remains largely low to moderate.

This distinction is particularly relevant to Cross River State because river and coastal resources support fishing, food supply and other livelihood activities. Recent work from River Siluko and the Orashi River illustrates how sediment-associated metals can intersect with aquatic organisms and human exposure pathways (Egun et al., 2025; Patrick-Iwuanyanwu et al., 2025). The present study did not measure metal accumulation in fish or benthic fauna, so it cannot claim demonstrated biological effects or human-health outcomes. Its contribution is instead to identify where sediment monitoring and subsequent biological

investigations should be concentrated. Idundun and Akpabuyo emerge as the most defensible priorities, with Adun and Ikom warranting continued surveillance.

4.0 Conclusion

The study shows that heavy-metal levels among the six river sediments studied were spatially variant and not homogeneously high. Fe and Mn showed the most high-prevalence contribution to the concentration profile while Cd and Hg account significantly and disproportionately to the ecological-risk indices. Idundun showed the highest contamination and risk levels at the high-proportion extreme of the spatial variation series, followed by Akpabuyo with Abakpa and Abeb on the low profile levels. The convergence of the CF, Igeo, EF, PLI, PERI and the supporting sediment-quality screening indictors forms a coherent basis for exploring relatively localized areas of greater concern. The general environmental implication was one of localised pressure rather than widespread contamination across the selected river basins. Idundun had the highest PLI and was the only river that showed moderate ecological risk as per PERI, whilst Akpabuyo was also in the 'moderate' zone for risk and toxicological screening values. Cd and Hg had the largest risk contributions, as their risk contributions show the effect of the weightings associated with a toxic response, and their own contributing concentrations. The multivariate results indicate different associations between metals, with a significant Fe-Mn association, consistent with geochemical control, and a Cd-Hg-Pb-Cr-Ni grouping, consistent with shared effect or interaction influence, though these remain tentative or provisional as the work has not focused on source apportionment.

The results facilitate a direction for specific management actions. Idundun and Akpabuyo merit priority follow-up sediment studies with focus on Hg and Cd contamination and activities that might cause primary or secondary deposition or redistribution of metals in their catchments. Adun and Ikoms merits routine surveillance as much as being treated equally and with the high-priority sites. Environmental Protection Agency can employ index results as warrant screening information for site-specific assessments and avoid regulatory decisions based on index classification alone.

A more comprehensive monitoring programme where appropriate, should extend sampling across contrasting hydrological seasons, since present study is a dry-season snapshot and did not assess temporal stability. Grain-size distribution, organic carbon and other relevant physicochemical sediment properties, and at least where resources or funds allow, metal speciation or other techniques that can discriminate potentially mobile fractions from total concentrations should be included in future work. Investigations of resident fish or benthic fauna and relevant ecotoxicological endpoints would yield evidence not accessible through examination of sediment Chemistry alone and would also help determine whether the potential risks found in present study aligns with measurable biological responses.

Finally, future monitoring should adhere to high standards of laboratory quality assurance, by routine calibration verification, procedural blanks, duplicate analysis, recovery correction and, where possible, use of certified reference materials. In combination these would provide better comparability over sampling occasions and greater confidence in the indices of pollution and risk. This study is most useful in terms of spatial sediment-quality baseline for these rivers; it highlights sites and pollutants requiring further study and provides a defensible foundation for seasonal monitoring, bioavailability, ecological work and source attribution.

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