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RECEIVED :21/12/2024

ACCEPTED: 16/03/2025

PUBLISHED: 30/06/2025

KEYWORDS:

Heavy metal, Season characteristics, Ecological risk, Qua Iboe River, Nigeria.

Evaluating Spatiotemporal Enrichment and Contamination of Heavy Metals in the Surface Water of Qua Iboe River, Niger Delta, Nigeria

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ABSTRACT

The present study deals with spatial and temporal variation of heavy metals and its contaminant in Qua Iboe River within five sampling locations, from January 2020 to June 2021. Seven heavy metals (Cd, Zn, Pb, Fe, Mn, Cr and Ni) were investigated using standard methods. Contamination factor (C_f), degree of contamination (DC), ecological risk factor (Er) and potential ecological risk index (PERI) were used to determine the contamination status and ecological risk. The spatial mean values of Zn, Pb, Fe and Ni in all the locations, Cd in locations 2, 3, 5; Cd mean value in wet season and the mean value of Zn, Pb, Fe, Ni in both seasons were exceeded the limits. The C_f value for Cd (location 1), Cr (locations 1, 2, 4, 5) and in both seasons were less than 1, DC values across the locations and in both seasons were ≥ 24 (very high degree of contamination), ER values for Zn in locations 1, 4 and 5 were between $40 \leq - < 80$ (moderate), 2 was between $160 \leq - < 320$ (high), location 3 and in both seasons were between $80 \leq - < 160$ (considerable high ecological risk). The PERI values in locations 2, 3, 5 and for the seasons were ranged between $150 < PERI < 300$ indicating moderate ecological risk. These were influenced by human activities, geogenic and seasons. Frequent monitoring is recommended to salvage the aquatic ecosystem and the inhabitant biota.

1. Introduction

Most inland water bodies in Niger delta, Nigeria currently are experiencing a huge amount of pollutants including heavy metals from point and non-point sources. Despite the low level of industrial activities within the catchment of the river, growing levels of metals pollution and its associated effects are still detected (Jonah and Mendie, 2024). The intense farming activities, indiscriminate wastes disposal at the waterside, and local metal fabricated workshops and markets at the nearby communities should be of concern as these activities may further influence the persistence, toxicity and bioaccumulation of pollutants in the water body through surface runoffs. Water pollution have been attributed to the higher level of human activities and poor drainage system (Amah-Jerry et al., 2027; George et al., 2020; Jonah et al., 2020), resulting in shift of the inherent water quality to alteration status. With these, the assessments of metals contaminant in water bodies are significant since freshwaters have been used and identified a dumpsite of waste materials (Egborge, 1994; Jonah et al., 2019). However, some heavy metals in environment are naturally occurred but can be exacerbated by humans (Singh, 2007). Over the years, research conducted in coastal water bodies in Niger delta and other developed countries have reported accumulation of potentially toxic elements, owing to intense application of agro-fertilizers, pesticide and herbicides in agricultural activities, industrial activities and runoffs from municipal contaminated soil (Maitera et al., 2011; Jenyo-Oni and Oladele, 2016; Al-thahaibawi, 2021; Jonah et al., 2023; Jonah and Anyanwu, 2023). This problem may likely be worsened in the future if adequate measures are not taken to mitigate the scenario. Some heavy metals are detriment to living organisms even at little concentration (Rovira and Domingo, 2019; Jonah and Mendie, 2022), these metals can build up through food chain with severe risk to both aquatic biota and humans (George et al., 2015). Qua Iboe River is among the major rivers in Niger Delta, Nigeria. The river is affected by point and non-point sources of pollutants. The river water serves as

source of water for irrigation, industrial and domestic use. There is paucity of research regarding to heavy metals and its contamination in Qua Iboe River. This study aimed to ascertain spatial and temporal level of heavy metals and its contaminant in surface water of Qua Iboe River, Niger delta, Nigeria restricted to the upper segment.

2. Materials and Methods

2.1 Sampling Sites

The studied sections covered Obot Akara and Ukanafun Local Government Area, having the Latitude of 04° 53' to 05° 9' North and Longitude of 07° 39' to 07° 47' East (Figure 1). Five locations were selected along the stretch of the river; which was based on the ecological setting; geological features, land use, nearest to communities and the levels of anthropogenic activities. The first location is upstream (Ikot Amba); 3 kilometers (km) from Obot Akara Local Government Headquarter. The location is characterized by slow water current, higher penetration of sunlight intensity, substrate is sandy and muddy at the right hand side of the river, and human activities (bathing, laundry and farming) are minimal. The second location (Head Bridge at Ikot Osurua) is 6 km from location 1. The location is characterized by higher human activities, ranging from extensive farming, intense sand dredging, laundry, sand loading, stone mining and other domestic activities. The river receives wastes from nearby communities, municipal run-off, direct dumping and from road construction. The third location (Ekpenyong Attai 1) is 5 km from location 2; anthropogenic activities are just like at point one. The substratum is muddy and sandy. The location is near to human habitations. The fourth location (Uruk Ata Ikot Isemin) is 5 km from location 3; human activities were farming at the wetland behind the river, fishing and laundry. The water current is slow especially during the dry season. The fifth location (Head Bridge at Nkek Idim) is 4 km downstream away from location four. The area is characterized by slow water current; sandy substrate while the edge is muddy. Human activities were intense sand dredging and farming. The location is affected by pollutants from nearby communities through surface runoff.

The sampling were carried out once monthly between January 2020 and June 2021. Polyethylene bottles (500 mL) were used for water collection for the determination of dissolved metal concentration and treated with HNO₃ immediately. Before the sampling, bottles were sterilized with distilled water; and the collected samples were transported to the laboratory and kept cool at 4°C prior to analysis (Naveedullah et al., 2014).

2.2 Samples Digestion, Measurement and Data Analyses

In laboratory, a digestion process according to US EPA, Method 200.2 (1999) was considered. Samples were shaken for homogenization before a 50 ml sub-samples was taken for digestion and added to a mixture of concentrated (70%) nitric acid and concentrated (40%) hydrochloric acid (1.0 ± 0.1 ml conc. HNO₃ and 0.50 ± 0.05 ml conc. HCl) in a 250 ml digested beaker and it was thoroughly mixed. The content was heated using water bath which the solution was change to light colour, indicating that the sample is completely digested. After that, it was allowed to cool and distilled water was added to make it to volume (50mL).The same digestion procedure was applied to the Quality Control (QC) samples and the blank. The samples were filtered through 0.45 µm pore size cellulose acetate filters (Naveedullah et al., 2014). After appropriate digestion, seven metals such as Cadmium (Cd), Zinc (Zn), Lead (Pb), Iron (Fe), Manganese (Mn), Chromium (Cr) and Nickel (Ni) were measured using a Unicam Atomic Absorption Spectrophotometer (UNICAM 969 model) as stipulated by APHA (2017) and recorded in milligram per litre (mg/L). All data were subjected to statistical analysis using One-way ANOVA on SPSS while Fisher's LSD was used to compare the mean of each parameter.

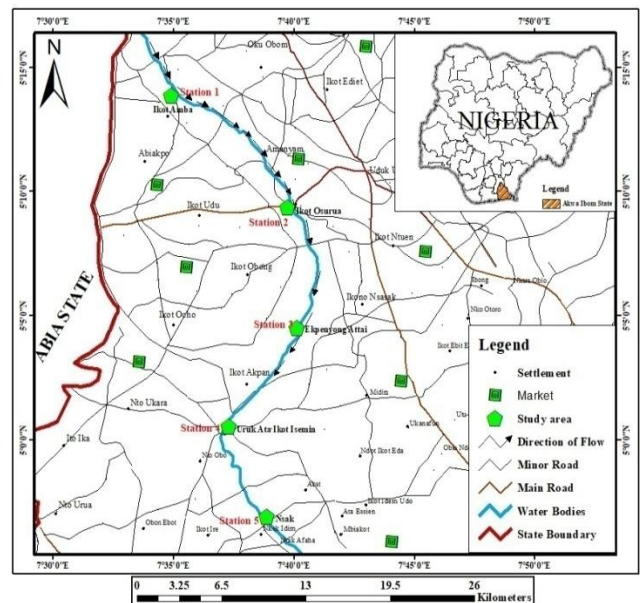


Figure 1: A map showing the stretch of Qua Iboe River and sampling locations

Paired sample **t**-test was used for seasonal comparison with significant difference set at $P < 0.05$ while Pearson correlation co-efficients (r) analysis was applied to ascertain relationship between the heavy metals.

2.3 Water Quality Assessment Indices

2.3.1 Contamination Factor (Cf)

The metal contamination in the water sample was determined using contamination factor (Cf). The index was used by Chris and Anyanwu (2023), to assess the level of contamination in water samples. It expressed as the ratio between the content of each metal to the background value. The Cf was calculated using the formula developed by Håkanson (1980) presented in equation 1.

$$Cf = \frac{C_{\text{metal}}}{C_{\text{background}}} \dots \dots \dots (1)$$

Where; C_{metal} = mean content of metals in the water sample while $C_{\text{background}}$ = standard value for each metal stipulated by FMEnv (2011). The Cf value is rating as low when it < 1 , moderate ($1 \leq Cf < 3$), considerable ($3 \leq Cf < 6$), while value > 6 is classified as very high degree (Ali et al., 2016).

2.3.2 Degree of Contamination (DC)

The contamination of the heavy metals in the river water was also determined using degree of contamination (DC). The index was derived by summation of Cf values of the metals. The index expresses the risks posed by multiple potentially toxic elements and it was determined using equation given below:

$$DC = \sum_{i=1}^n Cf_i \dots \dots \dots (2)$$

Where; Cf_i is the contamination factor of each metal. The DC value < 6 is low contamination, $6 \leq - < 12$ (moderate contamination), $12 \leq - < 24$ (considerable contamination) and ≥ 24 is very high contamination (Häkanson, 1980).

2.3.3 Ecological Risk Factor (Er)

This index appraises the potential risk pose by one contaminant in the water. The index was calculated with equation 3.

$$Er = Tr \times Cf \dots \dots \dots (3)$$

Where; Tr = toxic-response factor of a given metal while Cf = contamination factor of metal. Tr values for the heavy metals are Ni (5), Cr (2), Pb (5), Cd (30) and Zn (1) (Chris and Anyanwu, 2023) and Fe not available. Index value < 40 is classified as low, $40 - 80$ (moderate), $80 - 160$ (considerable), $160 - 320$ (high) and ≥ 320 is very high (Mugoša et al., 2016).

2.3.4. Potential Ecological Risk Index (PERI)

The index assesses the risk of several potentially toxic elements and it was calculated using the formula below:

$$PERI = \sum_{i=1}^n Er_i \dots \dots \dots (4)$$

Where; n = number of heavy metals used while Er = single index of the ecological risk factor. The PERI value < 150 is low, $150 < - < 300$ (moderate), $300 < - < 600$ (high), ≥ 600 is higher ecological risk (Mwakisunga et al., 2021).

3. RESULTS

3.1 Spatial and Seasonal variation

The spatial variation of heavy metal concentration is presented in Table 1, while the seasonal characterization is showed in Table 2. The Cd

values ranged from 0.001 to 0.03mg/L; the maximum average level 0.006mg/L was detected in locations 2, 3 and 5, while the minimum 0.004mg/L was obtained in location 1. The higher mean content 0.006mg/L for Cd was obtained in wet season; while minimum 0.005 mg/L was in dry season. No significant difference between spatial mean ($P = 0.073$) and the seasonal mean values ($t = 2.72$, $P > 0.05$) was obtained. The spatial mean contents of Cd obtained in locations 2, 3, 5, and wet season value exceeded the permissible limit (0.005) for aquatic life recommended by FMEvn (2011). The Zn contents differed among the locations, ranging from 0.14 to 3.45 mg/L. The maximum average content 1.66mg/L was obtained in location 2, while minimum 0.59mg/L was in location 1. The maximum average value 1.28mg/L was obtained in dry season and minimum 0.86mg/L was in wet season. ANOVA showed that locations 2 and 3 were significantly ($P = 0.094$) higher than others, while the dry season was significantly higher ($t = 5.77$, $P < 0.05$) than the wet season. The average values obtained were exceeded 0.01mg/L recommended by FMEvn (2011) for aquatic life. The Pb contents ranged between 0.00 and 0.23mg/L; having the maximum average level 0.08mg/L in location 2 while the minimum value 0.03 mg/L was in location 1. Higher average content was obtained in wet season while minimum was in dry season. The spatial and seasonal average contents were above permissible limit for aquatic life (FMEvn, 2011). No significant variation was detected between the sampling locations ($P = 0.142$), while significant difference ($t = 4.32$, $P < 0.05$) was obtained between the seasons. The Fe was differed among the locations and seasons values. The higher spatial average value 0.48mg/L was obtained in location 2 while the minimum 0.26mg/L was in location 1. For the seasonal regimes, highest mean content 0.38mg/L was obtained in wet season and the lowest 0.33mg/L during dry season. The average levels (spatial and seasons) were above the limit 0.05mg/L for aquatic life by FMEvn (2011). There were a significant difference between the locations ($P = 0.003$), while no significant ($t = 1.77$, $P > 0.05$) was obtained for the seasons. The Mn had its range from 0.02 to 0.19mg/L; with maximum

average level 0.14mg/L obtained in location 3 dry season while minimum 0.06mg/L was while the minimum 0.04mg/L was in location 5. obtained in wet season. The seasonal average level 0.10mg/L was high in

Table 1: Summary of heavy metal contents between locations at the upper segment of Qua Iboe River

Metals (mg/L)	Location 1	Location 2	Location 3	Location 4	Location 5	FMEvn 2011
Cd	0.004±0.004 ^a (0.002- 0.008)	0.006±0.001 ^a (0.002-0.008)	0.006±0.001 ^a (0.002- 0.03)	0.005±0.001 ^a (0.001- 0.009)	0.006±0.001 ^a (0.002-0.01)	0.005
Zn	0.59±0.08 ^a (0.14 – 1.45)	1.66±0.19 ^b (0.39-3.45)	1.32±0.22 ^b (0.23 – 3.37)	0.76±0.13 ^a (0.17 – 1.53)	0.78±0.13 ^a (0.28 – 2.42)	0.01
Pb	0.03±0.22 ^a (0.01 – 0.06)	0.08±0.11 ^a (0.02- 0.23)	0.06±0.18 ^a (0.00 – 0.3)	0.04±0.26 ^a (0.01 – 0.08)	0.05±0.13 ^a (0.02 – 0.4)	0.01
Fe	0.26±0.04 ^a (0.14 – 0.53)	0.48±0.04 ^b (0.12-0.70)	0.32±0.02 ^c (0.14 – 0.52)	0.29±0.03 ^a (0.14 – 0.56)	0.42±0.02 ^b (0.12- 0.62)	0.05
Mn	0.05±0.005 ^a (0.02 – 0.08)	0.09±0.008 ^b (0.04 – 0.16)	0.14±0.05 ^c (0.02 – 0.19)	0.08±0.02 ^b (0.02 – 0.4)	0.04±0.004 ^a (0.02 - 0.08)	NI
Cr	0.03±0.004 ^a (0.01 – 0.08)	0.03±0.004 ^a (0.01 – 0.08)	0.05±0.004 ^a (0.02 – 0.08)	0.03±0.003 ^a (0.01 – 0.06)	0.02±0.002 ^a (0.02 – 0.05)	0.05
Ni	0.02±0.003 ^a (0.00 – 0.06)	0.03±0.003 ^a (0.01 – 0.06)	0.05±0.003 ^a (0.01 – 0.05)	0.04±0.003 ^a (0.01 – 0.06)	0.03±0.003 ^a (0.02 - 0.05)	0.01

±= Standard error; Average with dissimilar superscripts along the same row indicates significant difference; NI = Not indicated; Range values are in parenthesis; FMEvn = National Environmental (Surface and Groundwater Quality Control) Regulations, Abuja, Nigeria.

There is no limit for Mn for aquatic life by FMEvn (2011). There is a significant variation in locations ($P = 0.0001$), while no difference was obtained between the seasons ($t = 2.20$, $P > 0.05$). The Cr varied between the locations; the maximum average content 0.05mg/L was obtained in location 3, while minimum 0.02 mg/L was obtained in location 5. Maximum average level 0.04mg/L was obtained in dry season, while the minimum 0.03mg/L was during wet season. The average values obtained were in line with the limit (0.05mg/L) for aquatic life. ANOVA when applied showed no significant variation between the

sampling locations ($P = 0.53$) and seasons ($t = 2.96$, $P > 0.05$). The Ni value was varied, ranging from 0.00 to 0.06 mg/L; the maximum average level 0.05mg/L was obtained in location 2, while the minimum 0.02 mg/L was in location 1.

The seasonal average content 0.05mg/L was high during dry season, while the minimum 0.02 mg/L was during wet season. All average values were greater than 0.01 mg/L, suitable for aquatic life (FMEvn, 2011). There were no significant differences among the locations ($P = 0.001$) and seasons ($t = 0.03$, $P > 0.05$).

Table 2: Seasonal variation of heavy metal contents in the upper segment of Qua Iboe River

Metals (mg/L)	Unit	Mean (Dry Season)	Mean (Wet Season)	t – value	FMEvn 2011
Cd	mg/L	0.005±0.0003 (0.002 - 0.008)	0.006±0.001 (0.001 - 0.03)	2.72 ^{ns}	0.005
Zn	mg/L	1.28±0.12 (0.37 – 3.37)	0.86±0.09 (0.14 – 2.42)	5.77*	0.01
Pb	mg/L	0.02±0.002 (0.00 – 0.06)	0.18±0.13 (0.01 – 0.23)	4.32*	0.01
Fe	mg/L	0.33±0.02 (0.22 – 0.70)	0.38±0.02 (0.12 – 0.62)	1.77 ^{ns}	0.05
Mn	mg/L	0.10±0.004 (0.02 – 0.14)	0.06±0.02 (0.02 – 0.19)	2.20 ^{ns}	NI
Cr	mg/L	0.04±0.003 (0.02 – 0.08)	0.03±0.002 (0.01 – 0.06)	2.96 ^{ns}	0.05
Ni	mg/L	0.05±0.002 (0.01 - 0.06)	0.02±0.002 (0.00 – 0.05)	0.03 ^{ns}	0.01

± Standard error; * = Significant at $P < 0.05$; ^{ns} = Not significant; NI = Not indicated; FMEvn = National Environmental (Surface and Groundwater Quality Control) Regulations, Abuja, Nigeria.

3.2 Correlation analysis

The spatial correlation between the metals content is presented in Table 3, while the seasonal correlation is shown in Tables 4 and 5. The spatial correlation showed that Cd had positives relationship with Pb ($r = .910^*$) while in dry season it correlated positively with Pb ($r = .942^*$) while Pb had positive correction with Mn ($r = .914^*$). In wet season, Fe was correlated negatively with Cr ($r = -.963^*$) and Ni ($r = -.952^*$).

3.3. Water Quality Indices

3.3.1. Contamination factor (Cf) and Degree of contamination (Cd)

Table 3: Spatial correlation co-efficient (r) between the heavy metals concentrations

Metal s	Cd	Zn	Pb	Fe	Mn	Cr	Ni
Cd	1						
Zn	.662	1					
Pb	.910*	.521	1				
Fe	.760	.505	.467	1			
Mn	.426	.798	.541	-.041	1		
Cr	.375	.588	.497	-.205	.852	1	
Ni	.395	.050	.654	.115	.269	.000	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.05 level (2-tailed).

Table 4: Pearson's correlation co-efficient (r) among the heavy metals in dry season

Metals	Cd	Zn	Pb	Fe	Mn	Cr	Ni
Cd	1						
Zn	-.254	1					
Pb	.942*	.043	1				
Fe	-.753	-.803	.278	1			
Mn	.546	-.034	.914*	-.492	1		
Cr	.964*	-.205	-.857	-.659	.563	1	
Ni	.045	-.002	-.594	-.316	.363	-.364	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.05 level (2-tailed).

Table 5: Pearson's correlation co-efficient (r) among the heavy metals in wet season

Metal s	Cd	Zn	Pb	Fe	Mn	Cr	Ni
Cd	1						
Zn	-.203	1					
Pb	-.685	-.324	1				
Fe	.156	-.063	.553	1			
Mn	.813	-.156	.812	-.412	1		
Cr	.336	-.474	.584	-.963*	-.135	1	
Ni	-.808	-.043	.746	-.952*	-.260	-.018	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.05 level (2-tailed).

The spatial values for Cf are given in Table 6, while for seasonal levels are shown in Table 7. The values Cd in location 1 and Cr in all the locations except 3 were below 1, signifying lowdegree of contamination, while the value in location 3 reflect moderate pollution. The Cf levels of Cd ranged from 0.8 to 1.2; the levels in locations 2 to 5 ranged between $1 \leq Cf < 3$, signified moderatedegree.

Table 6: Spatial variation of contamination factor and degree of contamination of the heavy metals

metals (mg/L)	L. 1	L.2	L.3	L.4	L.5
Cd	0.8	1.2	1.2	1.0	1.2
Zn	59.0	166.0	132.0	76.0	78.0
Pb	3.0	8.0	6.0	4.0	5.0
Fe	5.2	9.6	9.4	5.8	8.4
Cr	0.6	0.6	1.0	0.6	0.4
Ni	2.0	3.0	5.0	4.0	3.0
DC	70.6	188.4	154.6	91.4	96.0

Note: DC = Degree of contamination; L = location

The Cf values for Zn in all the locations were > 6 and classified as very high degree. The Cf values for Pb ranged from 3.0 to 8.0; the values in locations 1, 3 – 5 were considerable

contamination while location 2 was > 6 and classified as very high degree of contamination. The C_f values for Fe in locations 1 and 4 were within the considerable degree of contamination while locations 2, 3 and 5 were > 6 and classified as very high degree of contamination. The C_f values for Fe in locations 2, 3 4 and 5 were classified considerable degree while location 1 is moderately contaminated.

Table 7: Seasonal variation of contamination factor (C_f) and degree of contamination (C_d) of the heavy metals in water from the upper segment of Qua Iboe River

Heavy metals (mg/L)	Seasonal values	
	Dry season	Wet season
Cd	1.0	1.2
Zn	128.0	86.0
Pb	2.0	18.0
Fe	6.6	7.6
Cr	0.8	0.6
Ni	5.0	2.0
Degree of contamination	143.4	115.4

The C_d values, which are the sum of the C_f were given in Table 6. The values ranged from 70.6 (location 1) to 188.4 (location 2); the values were higher than 24, indicating extremely high degree of contamination. For the season, the values Cr in both seasons were < 1 , signifying low contamination. The C_f values for Cd in both seasons, Pb in dry season and Ni in wet season were classified as moderate degree of contamination. The values for Zn, Fe in both seasons and Pb during wet season were greater than 6, and classified as very high degree of contamination, while Ni value during dry season is considerable degree of contamination. The C_d values in both seasons were higher than the threshold (24), though the value during dry season is higher than the wet season, indicating extremely high degree of contamination.

3.3.2. Ecological risk (Er) and Potential ecological risk index (PERI)

The spatial Er and PERI values are given in Table

8, while the seasonal values are shown in 9. The Cd, Pb, Cr and Ni in all the locations had Er values < 40 ; classified as low ecological risk. The Er levels for Zn in locations 1, 4 and 5 were within the moderate ecological risk ($40 \leq - < 80$); location 3 is within $80 \leq - < 160$ (considerable), while location 2 was within the higher ecological risk ($160 \leq - < 320$).

Table 8: Spatial ecological risk and potential ecological risk index of the heavy metals in water from the upper segment of Qua Iboe River

Heavy metals	Location 1	Location 2	Location 3	Location 4	Location 5
Cd	24	36	36	30	36
Zn	59	166	132	76	78
Pb	15	40	30	20	25
Cr	1.2	1.2	2	1.2	0.8
Ni	10	15	25	20	15
PERI	109.2	258.2	225	147.2	154.8

The PERI values ranged from 109.2 (location 1) to 258.2 (location 2); the values in locations 1 and 4 were within the low potential ecological risk (< 150), while locations 2, 3 and 5 were within the moderate potential ecological risk ($150 < PERI < 300$). For the season, the Er levels for Cd, Cr and Ni in both seasons were < 40 ; classified as low ecological risk. The Er levels for Zn in both seasons and Pb during wet season were within the considerable ecological risk ($80 \leq - < 160$). The PERI contents ranged from 194.6 (dry season) to 223.2 (wet season); the values obtained were within the moderate potential ecological risk ($150 < PERI < 300$).

Table 9: Seasonal ecological risk and potential ecological risk index of the heavy metals in water from the upper segment of Qua Iboe River

Heavy metals (mg/L)	Seasonal values	
	Dry season	Wet season
Cd	30.0	36.0
Zn	128.8	86.0
Pb	10.0	90.0
Cr	1.6	1.2
Ni	25.0	10.0
PERI	194.6	223.2

4. DISCUSSION

The concentration of heavy metals varied between the studied locations; the spatial and seasonal mean values of Cr were within the

recommended range set by FMEvn (2011) while other exceeded the standard limits suitable for aquatic life set by FMEvn (2011). Heavy metals such as Cd and Pb are among the potential harmful elements to the living organisms even in minute concentrations (Jonah and Mendie, 2024). The maximum mean content of Cd was obtained in locations 2, 3, 5 and exceeded the FMEvn (2011) standard limit while the mean values in locations 1 and 4 were at the acceptable limit. The mean values were lower compared with the values (0.24 to 0.31) reported by George and Efiom (2018) from Imo river. The obtained values in locations 2, 3 and 5 could be associated with the extravagant used of pesticide, herbicide and fertilizer at the cultivated land at the edge of the river at these locations (Jonah and Akpan, 2024), coupled with geogenic impact exacerbated sand dredging inside the water (Anyanwu et al., 2020). The correlation of Cd with Pb implies that Cd concentration increase with an increase concentrations of Pb. The highest mean content of Cd obtained in wet season could be linked to surface runoff from the land used area. However, Cd is a common impurity of phosphate fertilizer, and the intensity of using fertilizers for agricultural activities as observed at the bank of the river at these locations could be linked to the elevated values during the rainy season through surface runoff (Jonah et al., 2024). The seasonal trend is concord with Silas et al. (2018) in River Mkomon and Okon et al. (2019) in Ikpa River, Nigeria while contradict with the maximum values in dry season report of Anyanwu and Onyele (2018) which recorded higher value of Cd during dry season. The positive correlated of Cd with Pb and Cr indicate that the Pb and Cr contents in the water led to elevated values of Cd in the water during the dry season.

Zn is essential for living organisms (Jonah and Anyanwu 2023); the spatial and seasonal mean values were exceeded the FMEvn (2011) limit, suggesting contamination from geogenic source. The highest mean value obtained in dry season could be link to the reduction of rainfall that would have reduced the pollutant content of Zn and its contaminated materials in the water. The findings are in line with the report of Arazu et al.

(2015) in River Niger, why contradicted with the research conducted by George and Efiom (2018) in Imo River which reported higher mean value during wet season. The low value recorded during the wet season suggests dilution of this parameter through precipitation during the wet months.

Pb is toxic element (Jonah and Mendie, 2024), and no level of Pb in water is recommended (Young, 2005). The concentrations of Pb both in spatial and seasonal values exceeded 0.01 being the limit set by FMEvn (2011). The elevated value in location 2 suggests high exposure to Pb pollutants owing to sand mining, agricultural activities and surface runoffs from contaminated soil during the rainy season. The dredging machines used at the upper region of the location are equipped with standard battery which could add Pb pollutants into the water body during the process of dredging as observed in this study. The sand excavation in the river can stimulate and re-circulate of accumulated Pb pollutants in the sediment which in turn influence its concentration in the water column. The maximum mean value of Pb obtained during the wet season corroborate with the report by Hashim and Ismail (2016) and oppose the findings documented by Appiah-Opong et al. (2021) whose recorded the maximum value of Pb during dry season. In this study, the elevated value during wet season attributed to combining effects of natural phenomenon (soil erosion) and anthropogenic activities added metallic lead-based pollutants into the water. It was observed that Pb was positively correlated with Mn during dry season, indicating that the concentration of Mn contributed to the higher values of Pb contents in the river during dry season.

The average content of Fe was higher in location 2 when compared with others. In this study, the values are low compared to the levels reported by Anyanwu and Nwachukwu (2020) in Ossa River. The spatial and seasonal average levels obtained exceeded the FMEvn (2011) limit for aquatic life. The tremendous average values obtained especially in locations 2 and 5 suggests leaching from the nearby landfills and discarding Fe contaminated materials at these locations. The higher value of this parameter recorded in

wet season than the dry; although the values were not significantly different may be linked with flooding from the nearby communities and contaminated soil into the water body through surface runoff (Asaolu and Olaofe, 2005). However, Okonkwo and Mothiba (2005) affirmed that surface runoffs impose the abundance of heavy metals in water. Iron was negatively correlated with Cr and Ni during the wet season, signifying that increase of these metals together decreases the Fe content in the river water during the wet season.

The maximum average of Mn obtained in location 3 suggests geological and human (2010) near industrial areas, Dhaka. The observed higher mean value in dry season contradicted Silas et al. (2018) and George and Efiom (2018) in their respective studies. The highest average value of Ni was obtained in location 3; this could be associated with intense sand mining. Higher average content of this parameter obtained during the dry season could suggest absence of rainfall, while the low content obtained during wet season could be effect of dilution (Houssou et al., 2017; Anyanwu and Umeham, 2020).

The higher *Cf* values of Zn across the locations could be attributed to geogenic source exacerbated by anthropogenic activities. Zn could be naturally present in water body as well as anthropogenic influence (Jonah and Mendie, 2024). The higher *Cf* value of Pb in location 2 and Fe in locations 2, 3 and 5 suggests intense agricultural activities, while higher values of Zn, Fe in both seasons and Pb in wet season > 6 could suggest impact of surface runoff and sand mining activities. The *DC* values were ≥ 24 indicating very high degree of contamination (Häkanson, 1980) as ascribe to higher contents of metals such as Zn, Pb, Fe and Ni in the water. The higher values obtained in stations 2 and 3 could link to higher human activities (Essien et al., 2019), coupled with allochthonous inputs. The higher *DC* value in dry season over the wet season could be link to higher Zn content, while the low level during wet season suggest dilutions of the river water due to high precipitation.

The *Er* values for Zn in locations and for the both seasons greater than 40 indicating very high

influences (Anyanwu and Nwachukwu, 2020). The slight reductions in value obtained during the dry season suggest low precipitation while the value in wet season may be attributed to rainfall contacting with flooding (Houssou et al., 2017). The Cr is vital element in a normal range to human; it enhances the maintenance of glucose metabolism in the body. The values recorded were in accordance with FMEvn (2011) standards; the elevated mean value recorded in location 3 when compared with others suggests intense domestic effluent (Jonah et al., 2023). The levels of Cr recorded corroborate with the range reported by Ahmad and Goni potential ecological damage. The higher *Er* value of Zn is contradicted with the finding reported by Chris and Ibienebo (2024) in water samples from coastal marine wetland in river state, Nigeria. On the other hand, Pb *Er* value in wet season was > 40 indicating very high ecological risk. Higher content of zinc can be toxic to aquatic organisms, affecting their health and the overall balance of the ecosystem (Okerefor et al., 2020; Jonah et al., 2024) while higher content of Pb may pose a potential risk to water quality and aquatic life (Sonone et al., 2020). The PERI values for locations 1 and 4 were < 150 indicating low ecological risk while the values for locations 2, 3, and 5 were within the range of 154.8 and 258.2 reflecting moderate ecological risk to the environment (Mwakisunga et al., 2021). For the season, higher value for PERI was recorded in wet season; the values were the levels of moderate ecological risk. The significantly higher values recorded were mostly influenced by the concentrations of Zn which in turn was influenced by anthropogenic activities.

5. CONCLUSION

The study revealed that the concentration of heavy metals were significant difference between locations and the seasons. The mean values of heavy metals in location 2, 3 and 5 were generally higher compared to locations 1 and 2. The mean values of zinc, lead, iron and nickel in all the locations; cadmium in locations 2, 3, 5 exceeded the limits. The mean value for cadmium, lead and iron was high during the wet season while zinc, magnesium, chromium and

nickel were in higher during the dry season. The value for water quality indices indicated that the river water was not suitable for aquatic habitations. The values of contamination factor in all the heavy metals except chromium, degree of contamination, ecological and potential ecological risk indices revealed the river water was highly at risk in both seasons. Anthropogenic activities, geogenic influences and surface runoff were the major factors associated with the elevated content of heavy metal. Constants monitoring and remediation processes are strongly recommended to salvage

the aquatic ecosystem and the inhabitant biota.

ACKNOWLEDGEMENTS

The author acknowledges the contribution of Dr Emeka Donald Anyanwu during the sample collections and Mr Utibe Usanga of Department of Geography and Regional Planning, University of Uyo, Uyo, Nigeria for providing the map of the study area insert in this manuscript.

CONFLICT OF INTEREST

The author declares that there is no competing interest.

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