

## Spatio-Temporal Concentrations of Toxic Metals in Microplastics of River Sediments, South-South, Nigeria

\*Isaac U. Isaac<sup>1</sup> and Jack D. Nwineewii<sup>2</sup>

Department of Chemistry, Faculty of Science,  
Federal University Otuoke<sup>1</sup>

Department of Chemistry, Faculty of Natural and Applied Sciences,  
Ignatius Ajuru University for Education<sup>2</sup>

\*E-mail of corresponding author: [isaacui@fuotuo.ke.edu.ng](mailto:isaacui@fuotuo.ke.edu.ng)

DOI: 10.56201/ijccp.v10.no3.2024.pg19.28

---

### Abstract

*The accumulation of toxic metals on microplastics in river sediments poses significant risks to aquatic ecosystems and human health. In this study, heavy metals (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Hg) were detected in partial acid digests of microplastic in sediment (MCPS) in the study sites using the GBC 908PBMT model Flame Atomic Absorption Spectrophotometer (FAAS). The spatial distribution of metals in MCPS investigated at Woji, Okujagu and Elelenwo rivers and statistically tested by a one-way analysis of variance (ANOVA) and Principal Component Analysis (PCA) biplot was employed for describing the study locations, possible associations with metals in sediments (MCPS) and study sites using PAST Statistics 1.32. The results showed that the mean concentration of Cd was higher in dry season than in wet season, and Pb was reasonably present during dry season across the sites. Moreover, Cu and Ni were found to be from a common source in the wet and dry seasons. It is recommended that periodic but consistent monitoring of the water bodies in the study area should be conducted in order to ascertain present state of the water and subsequent ameliorative measures taken to arrest potential health and ecological risk.*

**Keywords:** *microplastics, toxic metals, sediments, periodic monitoring*

---

### 1. Introduction

Microplastics, defined as plastic particles of less than 5 mm, in aquatic environments worldwide has drawn more attention to them. Rivers can carry a variety of pollutants, including hazardous metals, and are conduits for the movement of microplastics. To evaluate environmental risks and create efficient mitigation plans, it is essential to comprehend how hazardous metals and microplastics interact in river sediments (Song et al., 2024). Globally, the existence of microplastics in river sediments has been confirmed by numerous investigations. Schell et al. (2020), discovered that in the United Kingdom there are 110 to 915 particles per kilogram of sediment. Similarly, Li et al. In 2018, the concentration of microplastic particles in the Yangtze

River in China was reported to be 230 per kilogram. These results show the widespread distribution of microplastics in the river environment. Toxic metals can be associated with microplastics through various mechanisms, including absorption, adhesion, and collation. The sources of toxic metals in river sediments include industrial discharges, urban drainage, and atmospheric deposits (Bailey et al., 2008). When toxic metals are released into the environment, they accumulate on the surface of microplastics and may pose environmental risks. The interaction between microplastics and toxic metals in river sediments is complex and affected by factors such as particle size, surface area, and chemical composition. Studies have shown that microplastics can be used as vectors for transporting toxic metals and facilitating their absorption into aquatic organisms (Liu et al., 2022). Furthermore, the presence of organics and other pollutants in river sediments can increase the absorption capacity of toxic metal microplastics (Zhang et al., 2020). The accumulation of toxic metals in river sediments poses a serious threat to aquatic ecosystems and human health. The bioaccumulation and bioamplification of toxic metals through the food network may have adverse effects on aquatic organisms and, ultimately, have an impact on human populations dependent on freshwater resources (Huang et al., 2022). Understanding the fate and behaviour of toxic metals associated with river sediments and microplastics is therefore essential for effective environmental management.

## 2. Methodology

### 2.1 Study Area

The study area is located in the brackish water estuary of Woji Creek, Elemenwo Creek and Okujagu Creek as shown in Fig. 1. The creeks are located in the city of Port Harcourt, Rivers State, Nigeria. The creek is one of the tributaries of the Sombreiro River traversing the north down to the south of Rivers State into the North Atlantic, a well-defined route of transportation (Ibezim-ezeani & Ihunwo, 2020). The tidal influence of the North Atlantic upstream is responsible for the saline ocean water brought into the creek thus enriching the creeks with both freshwater and salt water organisms (Dibofori-Orji *et al.*, 2019; Ibezim-Ezeani & Ihunwo, 2020). Woji creek lies along the Bonny River estuary at latitude 7° 2'49.58"E, and longitude 4°48'48.53"N. The Woji Creek has a confluence with the refinery creek at Okujagu to form the main tributary which drains into the Bonny River. The creek has border with the Port Harcourt-Trans-Amadi industrial layout, the industrial hub of Rivers State. There are several anthropogenic activities such as barge and cargo manufacturing, a major abattoir as well as human settlements along the river. The Woji River drainage basin is located at the heart of Obio-Akpor Local Government Areas in Port Harcourt. The Woji River has a meandering flow amid channel blockages upstream as culvert ending creates a fall in the channel (Anya *et al.*, 2017; Iyama *et al.*, 2020). Elemenwo creek is on latitude 7° 3'55.29"E, and longitude 4°49'41.89"N (Table 3.1). The major industrial activities taking place in Elemenwo study area comprise a major abattoir that serves the state, oil servicing company and a computer village designated for sales and repairs of computers. A domestic waste dump site is also noticed at the bank of the Creek. Okujagu creek is on latitude 7° 4'34.22"E, and longitude 4°48'37.49"N (Table 3.1). This study site is an estuarine creek located on the eastern fringes of Port Harcourt city in the upper Bonny estuary of the Niger Delta, Nigeria. Okujagu river just like Woji creek, receives almost equivalent industrial and domestic wastes consequent upon alternate

low and high tides experienced by both creeks by virtue of their locations. There is also obvious dredging, oil bunkering, boat maintenance activities with debilitating effect of anthropogenic activities on-going within the upper Bonny estuary of the Niger Delta compared to the adjacent creeks. Red mangroves (*Rhizophora racemose*) and *Nypa* palms (*Nypa fructican*) line the shores. Apart from the refinery effluents received from refining activities at Okujagu, the most prevalent activities include sand moving, fishing and boat ferrying are the major activities in the study area.

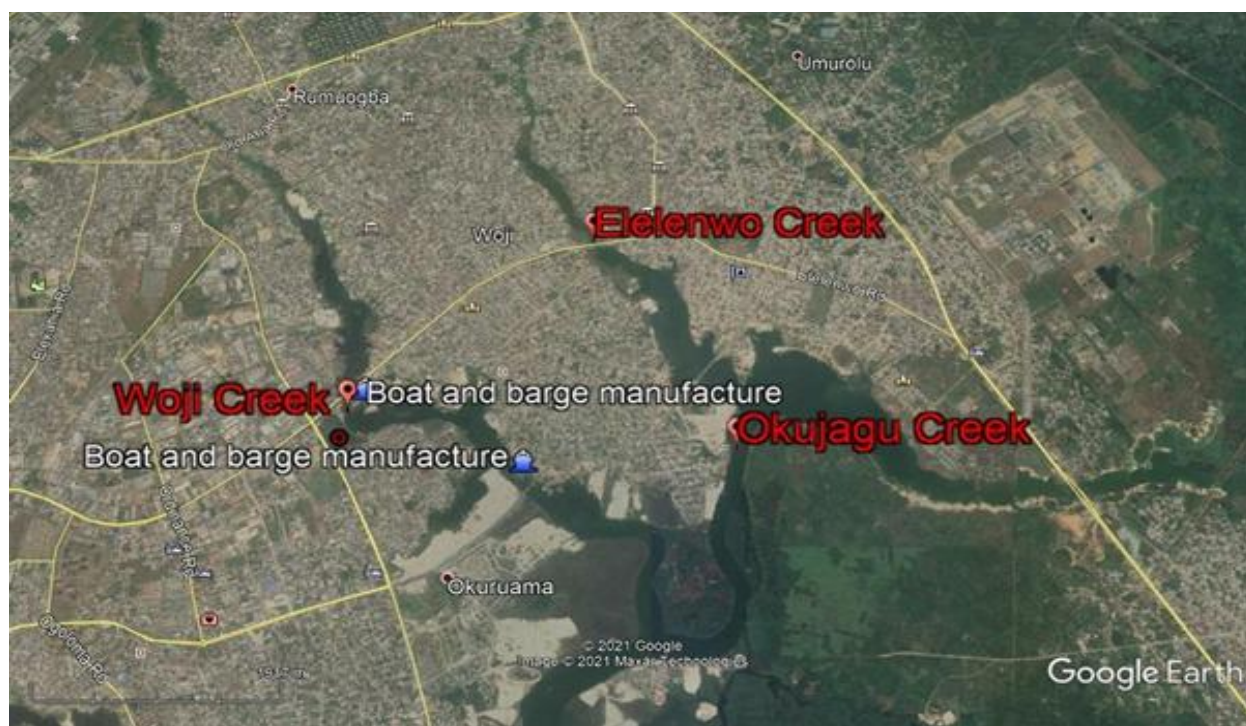


Fig. 1. Map of study area showing sampling locations (Source: Google Earth pro 2020)

## 2.2 Analytical Procedures

### 2.2.1 Sediment Sample Collection and Preparation

Samples were collected monthly from December 2020 to May, 2021 and during low tide event at three stations at approximately 3 km stretch from each creek. Sampling of microplastics in water sample was carried out following the method described by Wang et al. (2017) and Zhu et al. (2019) with slight modification to suit the environment of study. Five liters of surface water sample (0–20 cm in depth) was collected using a one-sided open-ended cylindrical sampling device and made to pass through a 50 $\mu$ m size steel sieve. Three replicates were collected at each station. The residue on the sieve was rinsed with distilled water into a 100 mL glass jar and kept at 4 °C before analysis. Three sediment samples were collected transversely from each station along the creeks using two sets of shovels (plastic and steel), to collect the top layer soft sediment ( $\approx$ 10 cm in depth). The samples were taken approximately 1m from the shore at each station with a steel and a plastic

shovel, each marked differently to differentiate sediments sampled for microplastics and metals respectively. Samples were put into well-labelled foil bags (indicating sampling point information and time of sampling) and placed into ice chest coolers at 4 °C and transferred to the laboratory.

### **2.2.2 Extraction of Microplastics from Sediments and Water Samples**

In the laboratory, separation of microplastics from water and sediment matrices was carried out following standard procedures adopted by Mohsen et al. (2019) and Li et al. (2021) but with slight modifications. The density floatation method as described by the authors was adopted in separation of microplastics from sediments. The sediment samples were dried in an oven at 60 °C for 72 hours to obtain a dry weight. Exactly 50 g of dried sediment were placed in a beaker and mixed with 400 mL of zinc chloride solution of density, 1.60 g/mL. The solution was thoroughly stirred with a clean glass rod, covered with tin foil and left to stand for 2 hours of precipitation. Further, the supernatant was transferred to another clean 500 mL beaker. This was repeated thrice to enhance recovery rate of microplastics. Finally, 15 mL of 30 % hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>) were added to the supernatant to digest the organic matter. The supernatant was filtered through an 8-µm glass microfiber filter paper (Whatman, diameter: 45 mm, pore size: 0.3 µm) with vacuum filtration, and transferred to a new petri dish for later inspection by a dissecting microscope to identify colour, size and number of microplastics in each sample.

### **2.2.3 Metal Analysis in MCPS Samples**

Microplastics in Sediments (MCPS) samples were not analyzed following stipulated guidelines for sediment digestions. However, for MCPS, partial acid digest was adopted following the method US EPA 3050B (USEPA, 1996) and described by Vedolin et al, 2018. Exactly 2g each of MCPS was put in a 50 mL beaker and then 5 mL of concentrated HNO<sub>3</sub>, 3.0 mL of H<sub>2</sub>O<sub>2</sub> (30 % V/V) and 10 mL of HCl were added at 90 °C. Samples were digested on a Corning PC-351 model hot plate at medium to low heat until about 5 ml concentrated extract was left (or with sample concentrate tending towards near-dryness). Afterwards, the content of beaker was left to cool for around 30 minutes. Sample solution was filtered and quantitatively transferred into 50 ml standard volumetric flask. Finally, filtered solutions were made up to the 50 ml graduation mark using distilled water. Thereafter, metals (Cd, Cu, Cr, Fe, Mn, Ni, Pb and Hg) levels were determined using the GBC 908PBMT model Flame Atomic Absorption Spectrophotometer (FAAS). Each sample was individually aspirated. The total metal concentrations are reported in units of mg/kg.

### **2.2.4 Statistical Analysis**

The mean and standard deviation were established using IBM SPSS version 20. The spatiotemporal distribution of metals in microplastics in sediment (MCPS) in the study sites was tested by a one-way analysis of variance (ANOVA) and Principal Component Analysis (PCA) biplot was employed for describing the study sites, possible associations with heavy metals between sediments (SED) and microplastics in sediment (MCPS) and study site using PAST Statistics 1.32 (Hammer, 2006). An effect with  $p < 0.005$  was considered significant.



### 3. Results

#### 3.1 Spatial and Temporal Concentrations of Heavy metals in Microplastics in Sediment

The results of heavy metals analysis detectable in partial acid digests of the microplastics in sediments within the study locations are presented for both dry and wet season (Tables 1 and 2). Spatial distribution of Cd in MCPS samples showed the following trend for the dry season: Woji ( $1.46 \pm 0.62 \text{ mgkg}^{-1}$ ) > Okujagu ( $1.20 \pm 0.73 \text{ mgkg}^{-1}$ ) > Elelenwo ( $0.71 \pm 0.74 \text{ mgkg}^{-1}$ ) and in the wet season: Woji ( $0.18 \pm 0.02 \text{ mgkg}^{-1}$ ) > Elelenwo ( $<0.001$ ) = Okujagu ( $<0.001$ ), respectively. Kruskal Wallis' One Way Analysis of Variance revealed no statistical ( $P > 0.05$ ) significant difference in metal concentrations between study locations. Data showed that temporally, highest mean concentration of Cd was recorded during dry season across the study locations. Cd values during dry and wet seasons except Okujagu and Elelenwo (wet season) were above WHO/FEPA limit ( $0.003 \text{ mg/kg}$ ) set for Cd in sediments (Membere & Abdulwasiu (2020). However, data obtained during both seasons were below threshold effects level (TEL) of  $0.68 \text{ mgkg}^{-1}$  and probable effects level (PEL) of  $4.20 \text{ mgkg}^{-1}$ . Copper concentrations (in  $\text{mgkg}^{-1}$ ) during dry and wet seasons were: Woji ( $24.24 \pm 8.33 \text{ mgkg}^{-1}$ ;  $1.95 \pm 0.04 \text{ mgkg}^{-1}$ ), Okujagu ( $12.73 \pm 5.03 \text{ mgkg}^{-1}$ ;  $1.25 \pm 0.12 \text{ mgkg}^{-1}$ ), Elelenwo ( $10.19 \pm 4.14 \text{ mgkg}^{-1}$ ;  $< 0.001$ ) respectively. Spatial distribution of Cu in MCPS across the study sites varied in the order of Woji > Okujagu > Elelenwo during dry season and wet season. Based on Holmes-Sidak One-Way Analysis of Variance (Appendix C), the difference in concentrations of the metal at different locations was not statistically ( $P > 0.05$ ) significant. However, temporally, highest concentration of Cu was recorded during dry season in MCPS at Woji ( $24.24 \text{ mgkg}^{-1}$ ) indicating a higher concentration of the metal

Table 1: Concentrations of heavy metals (Cd, Cu, Pb & Mn) in MCPS during dry and wet seasons in comparison with sediment quality guidelines

MCPS Location	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Mn (mg/kg)
<b>Dry Season</b>				
Woji	$1.46 \pm 0.62^c$	$24.24 \pm 8.33^c$	$19.66 \pm 2.00^c$	$112.54 \pm 16.30^a$
Okujagu	$1.20 \pm 0.73^c$	$12.73 \pm 5.03^c$	$8.40 \pm 6.42^c$	$85.44 \pm 32.89^a$
Elelenwo	$0.71 \pm 0.74^c$	$10.19 \pm 4.14^c$	$5.14 \pm 4.45^c$	$70.00 \pm 47.23^c$
<b>Wet Season</b>				
Woji	$0.18 \pm 0.02^c$	$1.95 \pm 0.04^c$	$<0.001$	$19.57 \pm 0.35^c$
Okujagu	$<0.001$	$1.25 \pm 0.12^c$	$<0.001$	$19.82 \pm 0.19^c$
Elelenwo	$<0.001$	$<0.001$	$<0.001$	$0.87 \pm 0.03^c$
F-value	2.601	2.422	2.111	12.041
P-value	$P > 0.05$	$P > 0.05$	$P > 0.05$	$P < 0.05$
*FEPA	0.03	1.00	0.01	0.05
**TEL	0.68	18.7	30.24	NA
***PEL	4.2	108	112	NA

Data are expressed as mean  $\pm$  SD (Kruskal Walli Test  $n = 3$ ). values with superscript, a showed significant ( $p < 0.05$ ) difference when compared spatially within group. Values with superscript b, showed significant ( $p < 0.05$ ) difference when compared temporally between groups, values with superscript c, showed no significant ( $p > 0.05$ ) when compared spatially within group while superscript d, showed no significant difference when compared temporally between groups. \*TEL represents Threshold Effect level and \*\*PEL represents probable effect level. Both TEL and PEL are sediment quality guideline as formulated by US EPA to identify heavy metal concentration(s) capable of introducing biological effect in the system

Table 2: Concentrations of heavy metals (Ni, Cr, Fe & Hg) in MCPS during dry and wet seasons in comparison with sediment quality guidelines

MCPS Location	Ni (mg/kg)	Cr (mg/kg)	Fe (mg/kg)	Hg (mg/kg)
<b>Dry Season</b>				
Woji	15.17 $\pm$ 1.22 <sup>a,b</sup>	9.28 $\pm$ 9.35 <sup>c</sup>	4,429.17 $\pm$ 547.81 <sup>a</sup>	0.06 $\pm$ 0.00
Okujagu	9.34 $\pm$ 3.27 <sup>a</sup>	8.17 $\pm$ 3.25 <sup>c</sup>	4,078.76 $\pm$ 56.76 <sup>a</sup>	0.03 $\pm$ 0.00
Elelenwo	5.80 $\pm$ 1.71 <sup>c,b</sup>	7.83 $\pm$ 2.69 <sup>c</sup>	3,369.90 $\pm$ 721.91 <sup>a,b</sup>	0.02 $\pm$ 0.01
<b>Wet Season</b>				
Woji	4.45 $\pm$ 0.37 <sup>a,b</sup>	3.49 $\pm$ 0.20 <sup>c</sup>	3,492.93 $\pm$ 783.15 <sup>a</sup>	<0.001
Okujagu	2.59 $\pm$ 0.24 <sup>b,b</sup>	4.26 $\pm$ 0.15 <sup>c</sup>	3,909.39 $\pm$ 21.97 <sup>b</sup>	<0.001
Elelenwo	2.38 $\pm$ 0.16 <sup>b</sup>	<0.001	736.16 $\pm$ 29.13 <sup>b</sup>	<0.001
F-value	18.546	3.362	6.673	-
P-value	P<0.001	P<0.001	P<0.005	-
*FEPA	0.20	2.00	0.30	-
**TEL	15.9	52.3	NA	0.13
***PEL	42.8	160	NA	0.7

Data are expressed as mean  $\pm$  SD (Holmes-Sidak Test  $n = 3$ ). values with superscript, a showed significant ( $p < 0.05$ ) difference when compared spatially within group. Values with superscript b, showed significant ( $p < 0.05$ ) difference when compared temporally between groups, values with superscript c, showed no significant ( $p > 0.05$ ) when compared spatially within group while superscript d, showed no significant difference when compared temporally between groups. \*TEL represents Threshold Effect level and \*\*PEL represents probable effect level. Both TEL and PEL are sediment quality guideline as formulated by US EPA to identify heavy metal concentration(s) capable of introducing biological effect in the system

in dry season than in wet season although difference in concentration was not statistically ( $P > 0.05$ ) significant. Data obtained showed that mean metal concentration in MCPS were above WHO/FEPA limit (1.0 mg/kg) set for Cu in sediments (Membere & Abdulwasuu (2020). Data further showed that only Cu concentration at Woji study area (24.24 mg/kg) obtained during dry season, was above threshold effects level (TEL) of 18.7 mgkg<sup>-1</sup> but below probable effects level

(PEL) of  $108 \text{ mgkg}^{-1}$ . However, Cu values at other locations including Woji (wet season), all fell below TELL and PEL limits. TEL and PEL limits are sediment quality guidelines recommended by the National Ocean and Administration Agency (NOAA) of United States Environmental Protection Agency (USEPA). Spatial distribution of Pb in MCPS samples showed the following trend for the dry season: Woji ( $19.66 \pm 2.00$ ) > Okujagu ( $8.40 \pm 6.42$ ) > Elemenwo ( $5.14 \pm 4.45$ ) respectively, and in the wet season, Pb concentrations were not detected in MCPS. Kruskal Wallis' One Way Analysis of Variance revealed no statistical ( $P > 0.05$ ) significant difference in metal concentrations between study locations. Data showed that temporally, Pb was reasonably present during dry season across the study locations, and were all above WHO/FEPA limit ( $0.010 \text{ mg/kg}$ ) set for Pb in sediments (Membere & Abdulwasiu (2020) but below threshold effects level (TEL) of  $30.24 \text{ mgkg}^{-1}$  and probable effects level (PEL) of  $112 \text{ mgkg}^{-1}$ . TEL and PEL limits are sediment quality guidelines. During dry and wet seasons, mean manganese concentrations of  $112.54 \pm 16.30$  and  $19.57 \pm 0.35 \text{ mgkg}^{-1}$  was obtained at Woji,  $85.44 \pm 32.89$  and  $29.82 \pm 0.19 \text{ mgkg}^{-1}$  at Okujagu and  $70.00 \pm 47.23$  and  $0.87 \pm 0.03 \text{ mgkg}^{-1}$  at Elemenwo respectively. Spatially, the trend was: Woji > Okujagu > Elemenwo, during dry and wet seasons, respectively. One Way Analysis of Variance revealed that the difference in Mn concentrations in MCPS across locations was statistically ( $P < 0.05$ ) significant. Mean nickel concentrations of  $15.17 \pm 1.22$  and  $4.45 \pm 0.37 \text{ mgkg}^{-1}$  were obtained at Woji,  $9.34 \pm 3.27$  and  $2.59 \pm 0.24 \text{ mgkg}^{-1}$  at Okujagu, and  $5.80 \pm 1.71$  and  $2.38 \pm 0.16 \text{ mgkg}^{-1}$  at Elemenwo respectively. Spatially, the following trend was observed during dry and wet seasons: Woji > Okujagu > Elemenwo. Statistical analysis via One Way Analysis of Variance revealed no statistically significant ( $P > 0.005$ ) difference between locations. However, temporally, the highest concentration of Ni ( $15.17 \pm 1.22 \text{ mgkg}^{-1}$ ) was obtained during dry season at Woji and the lowest at Elemenwo ( $2.38 \pm 0.16 \text{ mgkg}^{-1}$ ). The difference in concentrations of Ni between dry season and wet season was statistically ( $p < 0.05$ ) significant. Data showed that values in the dry and wet seasons were above WHO/FEPA limits ( $0.020 \text{ mg/kg}$ ) set for Ni. Data further revealed that mean metal concentrations in MCPS matrix across the locations were below threshold effects level (TEL) of  $15.20 \text{ mgkg}^{-1}$  and probable effects level (PEL) of  $58.20 \text{ mgkg}^{-1}$  except during dry season at Woji where the metal concentration was slightly above TEL limit ( $15.70 \text{ mgkg}^{-1}$ ). TEL and PEL limits are sediment quality guidelines recommended by the National Ocean and Administration Agency (NOAA) of United States Environmental Protection Agency (USEPA). Chromium detected during dry season followed the trend: Woji ( $9.28 \pm 9.35 \text{ mgkg}^{-1}$ ) > Okujagu ( $8.17 \pm 3.25 \text{ mgkg}^{-1}$ ) > Elemenwo ( $7.83 \pm 2.69 \text{ mgkg}^{-1}$ ). In the wet season, the trend was: Okujagu ( $4.26 \pm 0.15 \text{ mgkg}^{-1}$ ) > Woji ( $3.49 \pm 0.20 \text{ mgkg}^{-1}$ ) > Elemenwo ( $< 0.001$ ) respectively. Data further revealed that the difference in concentrations of Cr in the study locations were not statistically ( $P > 0.05$ ) significant. However, temporally, the highest concentration of Cr was recorded at Woji ( $9.87 \pm 1.87 \text{ mgkg}^{-1}$ ) during dry season and the lowest was at Elemenwo ( $< 0.001 \text{ mgkg}^{-1}$ ) during wet season. Based on Holmes-Sidak One-Way Analysis of Variance (Appendix C), difference in Cr concentrations were statistically ( $P < 0.001$ ) significant. Fe concentrations in dry season and wet season analysis revealed the following trend: Woji > Okujagu > Elemenwo with the values  $4,429.17 \pm 547.81$  and  $3,492.93 \pm 783.15$ ,  $4,078.76 \pm 56.76$  and  $3,909.39 \pm 21.97$ ,  $3,369.90 \pm 721.91$  and  $736.16 \pm 29.13$ , respectively. One-Way Analysis of Variance (Kruskal-Wallis method) showed that spatial concentrations of Fe were statically ( $P < 0.05$ ) significant across study locations. Temporally, the highest concentration of Fe was recorded at Woji ( $4,429.17 \pm 547.8 \text{ mgkg}^{-1}$ ) during dry season

and the lowest at Elemenwo ( $736.16 \pm 29.13 \text{ mgkg}^{-1}$ ) during wet season. The difference in Fe concentrations between study locations in wet season and that of dry season were statistically ( $P < 0.05$ ) significant. Fe values were above WHO/FEPA limit of  $0.3 \text{ mg/kg}$  set for sediments. Mean Hg concentration ranged from  $0.02$  to  $0.06 \text{ mgkg}^{-1}$  across the study locations but was not detected in any of the locations during wet season. Spatially, Hg varied following the trend: Woji > Okujagu > Elemenwo. The values of Mn, Cu and Pb obtained by Li et al. (2017), Wang et al. (2016), Ahmad et al. (2021) were higher than reported in this study. Generally, heavy metal associated with the MCPS were higher than those associated with the corresponding sediment at all the sites in the dry season. This confirms the reports of Mohsen et al., 2019 and Rochman et al., 2015, who attributed it to likely increase over time of heavy metals adsorption on the plastics particles. Surprisingly, on the contrary, heavy metal concentrations in the MCPS were lower in wet season, in all the sites compared to corresponding sediments. This could be attributed to impact of leaching and dilution as a result of incessant rainfall, run-offs, tidal and current effects. The trend of heavy metal accumulation in MCPS was:  $\text{Fe} > \text{Mn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Cd} > \text{Hg}$ . This trend is similar to report of heavy metal concentrations of Cu, Zn, Pb, Cd, Ni that were reported from the isolated MPCs at Beijiang River, China (Wang et al., 2017) but found to be higher than the heavy metals that accumulated in microplastics and pellets at the beach of São Paulo, Brazil (Vedolin et al., 2018).

Temporal variation of iron indicated that Fe value was higher (Okujagu:  $4,429.17 \pm 547.81 \text{ mg/kg}$ ) in dry season than wet season (Elemenwo:  $736.16 \pm 29.13 \text{ mg/kg}$ ) at  $p < 0.05$ . The source is seasonal contamination of sediment. This study also corroborates the works of Vedolin et al. (2018); Dibofori et al, 2021, Ibezim-Ezeani and Ihunwo, 2021 showing that estuaries are filters and accumulators of sediment and contaminants which represent a potential receptor for plastic waste which increases the interaction between plastic pellets and hence, it is the source of combined release of the contaminant (Fe) into the water body. Similarly, spatial variation of metal concentration among the sites revealed that Okujagu had the highest concentration of Fe while Elemenwo had the lowest in both dry season and wet season. The next highest concentration of Fe was found in Woji river ( $4,078.76 \pm 56.76 \text{ mg/kg}$  in dry season and  $3,492.93 \pm 783.15 \text{ mg/kg}$  in wet season and these values were not statistically ( $p < 0.05$ ) different from the highest in both seasons (Table 4). Most MCPS is a potential vector for contaminant metal. Consequently, as a vector, it is capable of taking metal from the water body to the sink (sediment) and vice-versa.

### 3.2 Principal Component Analysis of Heavy metals in the study

Multivariate principal component analysis (PCA) was employed to establish possible factors that contribute towards the heavy metal concentrations and source apportionment. The rotated component matrix, given in Table 3, and illustrated in Figure 4.21 (Appendix B), generated two significant principal components with total variance of 65.6 %. The first axis (PC1) accounted for 45.6 % of the variance with eigenvalue of  $> 6.83$  and the second axis (PC2) accounted for 20.1 % (eigenvalue  $> 3.01$ ). PC1 on one hand, was positively loaded with Mn, Cd, Cr, Cu, Ni & Fe occurring together in the wet season and Pb and Cd co-occurring in the dry season. On the other hand, PC1 was negatively loaded with Fe, Cu and Ni mostly in the dry season, indicating a



common source. However, PC2 was negatively loaded with Mn, Cr & Fe co-occurring mostly in the dry season (irrespective of the matrix), indicating a common source of contamination.

Table 3. Principal component loadings of selected metals in MCPS investigated at Woji, Okujagu and Elelenwo rivers with eigenvalues.

<b>Component Variable</b>	<b>Rotated Component Matrix</b>	
	<b>PC1</b>	<b>PC2</b>
Mn DS	<b>-0.092</b>	<b>-0.476</b>
Mn Ws	<b>0.207</b>	<b>-0.445</b>
Cd Ds	<b>0.313</b>	<b>0.193</b>
Cd Ws	<b>0.256</b>	<b>0.036</b>
Pb Ds	<b>0.334</b>	<b>0.201</b>
Pb WS	<b>0.158</b>	<b>-0.08</b>
Cr Ds	<b>-0.116</b>	<b>-0.343</b>
Cr Ws	<b>0.277</b>	<b>-0.3</b>
Cu Ds	<b>-0.339</b>	<b>0.114</b>
Cu Ws	<b>0.353</b>	<b>-0.115</b>
Ni Ds	<b>-0.323</b>	<b>0.009</b>
Ni Ws	<b>0.253</b>	<b>0.038</b>
Hg Ds	<b>0.09</b>	<b>0.119</b>
Fe Ds	<b>-0.259</b>	<b>-0.406</b>
Fe Ws	<b>0.275</b>	<b>-0.276</b>
Eigenvalues	6.83	3.01
% of total Variance	45.6	20.1
Cumulative Variance (%)	45.6	<b>65.6</b>

### Conclusions and Recommendations

Spatial concentrations of Cd, Cu, Pb, Mn, Ni, Cr and Fe in two matrices (SED & MCPS) were highest in Woji and lowest in Elelenwo relatively. Cd, Cu, Pb, Mn, Ni, Cr, Fe and Hg in MCPS were higher in dry season than wet season Principal component analysis revealed that Cu and Ni were from a common source at Woji and Okujagu. Most of the metals found in both dry and wet season (Cu, Cr, Fe and Mn) were of both anthropogenic and natural sources (dry season). Pb Cu, Fe and Mn (wet season). It is recommended that similar investigation be carried out on the surface water to ascertain the level of pollution of due to microplastic in water body.

## References

- Bailey, B., Lamsal, R., Farzana, N., Walsh, M. E., & Gagnon, G. A. (2008). Water reclamation and reuse.
- Huang, W., Duan, W., & Chen, Y. (2022). Unravelling lake water storage change in Central Asia: Rapid decrease in tail-end lakes and increasing risks to water supply. *Journal of Hydrology*, 614, 128546.
- Li, B., Song, J., Guan, M., Chen, Z., Tang, B., Long, Y., ... & Zhang, Y. (2024). With spatial distribution, risk evaluation of heavy metals and microplastics to emphasize the composite mechanism in hyporheic sediments of Beiluo River. *Journal of Hazardous Materials*, 462, 132784.
- Li, W., Duo, J., Wufuer, R., Wang, S., & Pan, X. (2022). Characteristics and distribution of microplastics in shoreline sediments of the Yangtze River, main tributaries and lakes in China—From upper reaches to the estuary. *Environmental Science and Pollution Research*, 29(32), 48453-48464.
- Liu, S., Huang, J., Zhang, W., Shi, L., Yi, K., Yu, H., ... & Li, J. (2022). Microplastics as a vehicle of heavy metals in aquatic environments: A review of adsorption factors, mechanisms, and biological effects. *Journal of Environmental Management*, 302, 113995.
- Membere, E., & Abdulwasiu, M. (2020). Heavy Metals Concentration in Water, Sediment, and Fish around Escravos River, Nigeria. *World Journal of Research and Review*, 10, 28-37.
- Schell, T., Rico, A., & Vighi, M. (2020). Occurrence, fate and fluxes of plastics and microplastics in terrestrial and freshwater ecosystems. *Reviews of Environmental Contamination and Toxicology* Volume 250, 1-43.
- Wang, W., & Wang, J. (2018). Investigation of microplastics in aquatic environments: an overview of the methods used, from field sampling to laboratory analysis. *TrAC Trends in Analytical Chemistry*, 108, 195-202.
- Zhang, W., Zhang, L., Hua, T., Li, Y., Zhou, X., Wang, W., ... & Li, M. (2020). The mechanism for adsorption of Cr (VI) ions by PE microplastics in ternary system of natural water environment. *Environmental pollution*, 257, 113440.
- Zhu, J., Zhang, Q., Li, Y., Tan, S., Kang, Z., Yu, X., ... & Shi, H. (2019). Microplastic pollution in the Maowei Sea, a typical mariculture bay of China. *Science of the Total Environment*, 658, 62-68.