

Sequential Analysis and Geochemical Characterization of Heavy Metals in Araromi Coastal Sediments, Southwestern Nigeria

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Abstract: Heavy metals are found naturally in the earth and they become concentrated as a result of natural and anthropogenic activities. Numerous researchers have worked on the pollution and contamination of toxic metals in the soils of the study area but none has been able to carry out sequential analysis and extraction of the heavy metals into different geochemical fractions. Therefore, this research adopted random sampling method across five locations at 100-200cm intervals at depth of 40m. The sediments collected were prepared for sequential analysis using standard chemical reagents which fractionate the metals into five defined phases such as exchangeable, carbonate, easily reducible, organic, and residual for heavy metals such as Ni, Zn, Co, Mn, Fe, Pb, Cr, Cd and Cu using atomic absorption spectrophotometer (AAS) Buck Scientific Model 205A. The results revealed that the residual, exchangeable, reducible, and organic fractions were the most active media where Fe, Mn, Zn, Pb and Cu were prominent and the correlation between them indicated a very strong bond. (0.9). Also, the result of mobility factor revealed that Cd has very high mobility and bioavailability in the studied area which constitutes a major threat to the ecosystem. Whereas, the enrichment factor of heavy metals in all the fractions indicated moderate to extremely high enrichment.

Keywords: Araromi, Sequential Extraction, Heavy Metals, Concentration Enrichment Factor, Biodiversity, Correlation Statistics

1. Introduction

Toxic metals are found in sediments in a variety of chemical forms and display a variety of physical and chemical characteristics in terms of chemical interaction, mobility, biological availability, and potential toxicity [1]. As a result, identifying and quantifying the mode of occurrence in which a metal is present in sediment is critical in order to gain a better understanding of the potential and actual impacts of elevated metal levels in sediments, as well as evaluating downstream transport, deposition, and release processes under changing environmental conditions [20]. Earlier research dealt with hazardous metal contamination of sediments, utilizing simply total metal concentration as a criteria to determine its potential

impacts as a pollutant [4]. The overall concentration of metals offers insufficient information to estimate metal bioavailability or toxicity. An assessment of total metal levels in sediment after a strong acid digestion may be useful as a global marker of pollution, but it offers little information about their biodiversity, mobility, and reactivity in sediments [19]. Metal toxicity is determined mostly by their chemical forms rather than their overall elemental amount [14]. Metals in river sediments, for instance, might be associated to distinct compartments, hence sequential extractions can be beneficial for operational classification of metals in different geochemical fractions. Adsorbed on clay surfaces or iron and manganese oxy-hydroxides; present in secondary mineral lattices like carbonates, sulphates, or oxides; occluded in

amorphous materials like iron and manganese oxy-hydroxides; complexed with organic matter or present in primary mineral lattices like silicates [22]. The types of pollutants introduced into the aquatic ecosystem are heavily determined by the anthropogenic activities undertaken in the adjacent farmlands [23]. Toxic metals entering an aquatic system can be taken up by sediments and suspended matter via three different mechanisms: physicochemical adsorption from the water column, biological uptake by organic matter or organisms, and physical accumulation of metal-enriched particulate matter by sedimentation. The varied methods in which hazardous metals connect with distinct soil/sediment components dictate their mobility and availability [15]. The overall amount of hazardous metals in sediment might help characterize contamination severity. Speciation of dangerous metals using selective extracting agents, on the other hand, provides further information on the basic mechanisms that regulate metal behavior in sediments and helps in the

assessment of the environmental effect of contaminated soils and sediments [6]. To analyze the forms of hazardous metals in contaminated soils and sediments, a sequential extraction process is employed to partition harmful metals in soils and sediments. It contains data on possible mobility, bioavailability, and plant absorption of trace elements [7]. It also determines the metals in soil/bioavailability sediment's to other biota in the aquatic ecosystem. Water soluble metals are the most mobile of all hazardous metals, as well as the easiest to absorb by plants. Large inputs of hazardous metals eventually make their way to the estuary zone and on continental shelves, polluted sites, or contaminated seafood, making sediments an effective indication of metal contamination in the coastal environment. The goal of this study is to investigate the geochemical speciation of heavy metals in Araromi's coastal sediments, as well as their transportation factors, enrichment level, and impact on residents and ecosystems.

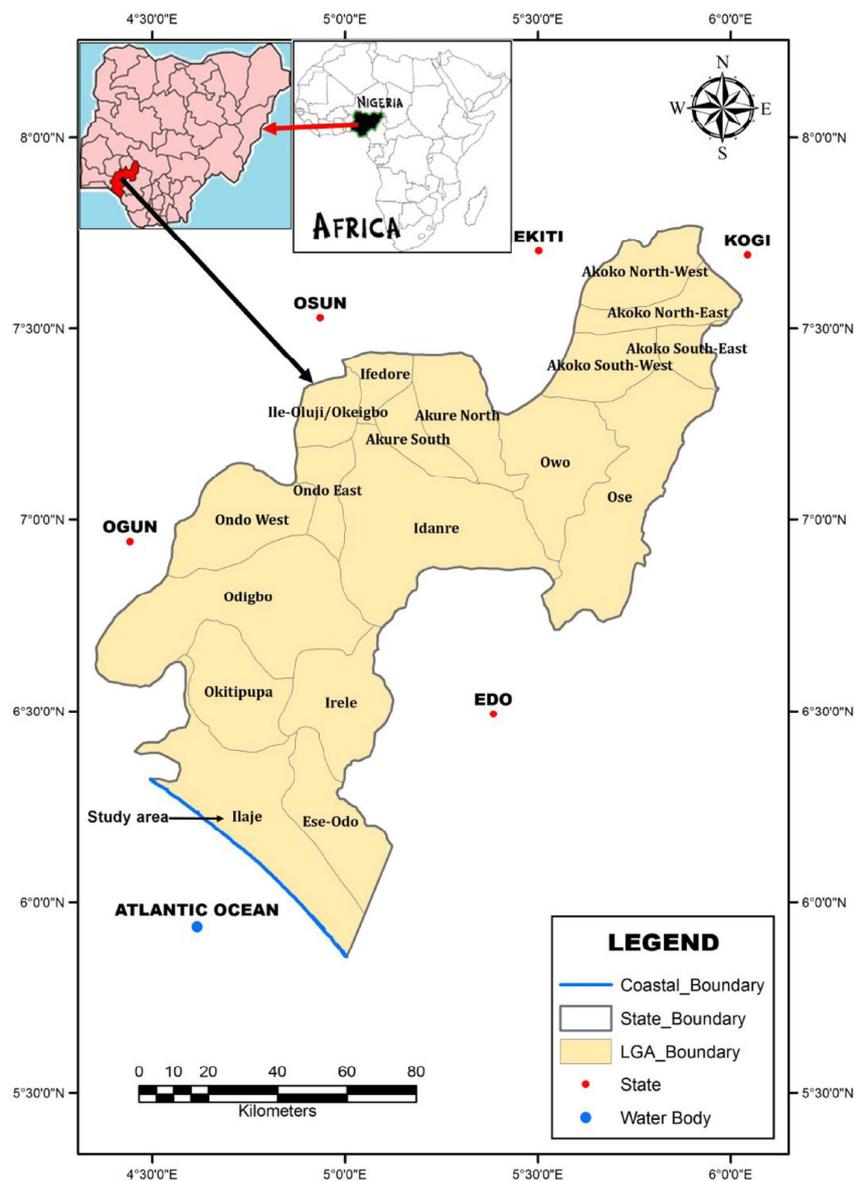


Figure 1. Location Map of the Study Area Inset: Map of Nigeria and Africa showing Nigeria [9].

2. Method of Study

2.1. Description and Geological Setting

The Araromi seaside is a significant river in the western part of Nigeria, located in southwestern Nigeria and bordered geographically on longitudes 5°45 to 6°15 and latitudes 4°30 to 5°00 (Figure 1). The land surface area is approximately 1318 km², with a human population of 290,615 in the 2006 census. The study area is a waterway and is also interconnected with both minor and major road networks which makes it popular among the coastal areas in Nigeria. It is a densely populated town, and the major occupation of the inhabitants are farming and fishing. In addition, sand mining along the channels of Araromi beaches is also one of the major human activities.

Ondo State is divided into two geological areas. The first is the sedimentary rock region in the south, while the second is the Pre Cambrian-Basement Complex rock zone in the north. The post-Cretaceous deposits and the Cretaceous Abeokuta Formation make up the majority of the sedimentary rocks. The medium-grained gneisses make up the majority of the basement complex. These rocks are heavily foliated and appear as outcrops. These outcrops have a deformed surface with alternating bands of dark and light-colored minerals. A tiny region of the state, particularly in the northeast, overlies coarse-grained granites and gneisses, which are lacking in black ferromagnesian minerals and have troughs and undulating low land surfaces.

The sampling coordinates and field description of the coastal sediments are presented in Table 1.

Table 1. Field data and description of coastal sediments.

Sample ID	Location	Colour	Latitude	Longitude	Elevation
A1	OPEN SEA	BLACK	6°17'45.9312"N	4°32'12.3144"E	0.57m asl.
A2	OPEN SEA 2	BROWN	6°17'47.4792"N	4°32'18.3768"E	-1.08m bsl
A3	OKE SIRI 1	BROWN	6°17'53.0196"N	4°32'22.6536"E	0.42m asl.
A4	OKE SIRI 2	BLACK	6°17'55.428"N	4°32'22.8984"E	6.82m asl.
A5	IDI GBEBGEN	BLACK	6°17'58.776"N	4°32'24.144"E	-1.72m bsl.

End note: A1-A5 represents the sampling locations of the study area.

2.2. Method of Sampling and Sample Collection

The samples were collected using random sampling method from Ayetoro to Eyin More. After removing the overburden, the samples were collected randomly at each station at a depth of 40cm and sampling density of 100m-200m intervals (Figure 3). Global Positioning Systems (GPS) G GARMIN eTrex 10 was employed to get the accurate geographical coordinates /

positions of each sampling points. A total of five samples were collected and bagged separately inside the polythene bags and properly labelled to avoid mix up. The samples were air dried and stored in a cool and dry place to avoid contaminations. Observations of geological settings, physical structures and lithology together with human activities were noted in the field notebook and the samples were eventually transmitted to Temsol Consults Laboratory Ltd Shasha, Ibadan for sequential analysis.

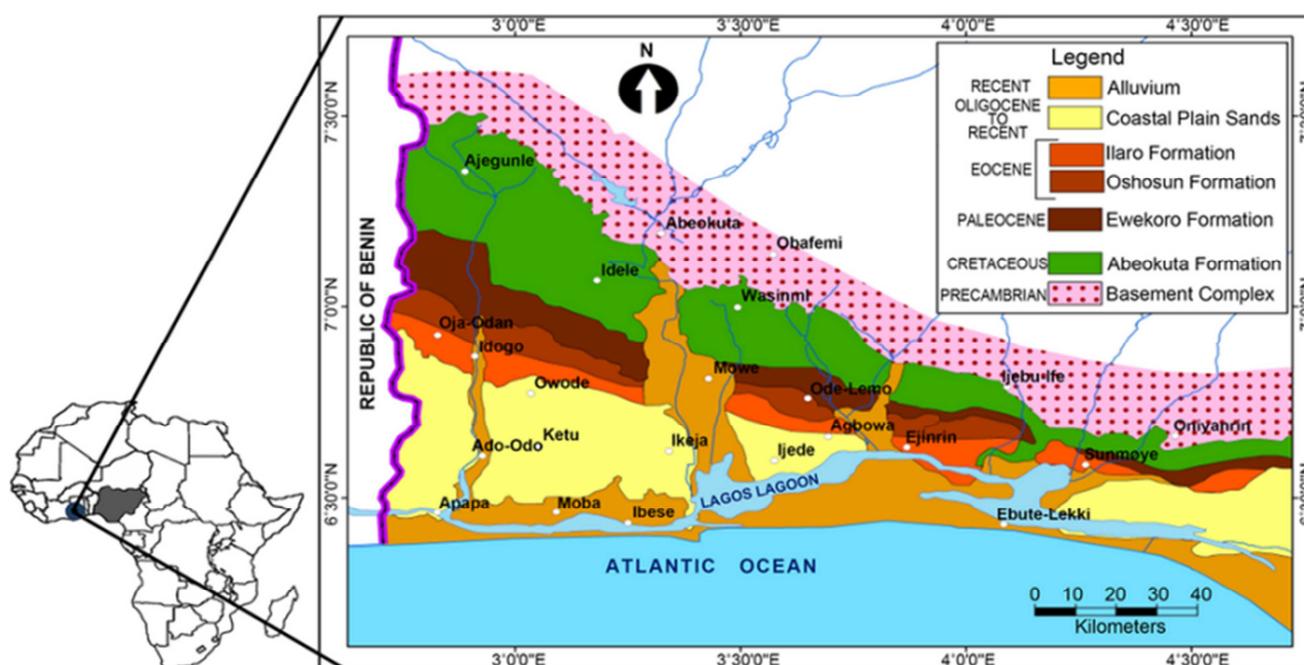


Figure 2. Geological Map of the Study Area [12].2.3. Sequential Extraction Procedure.

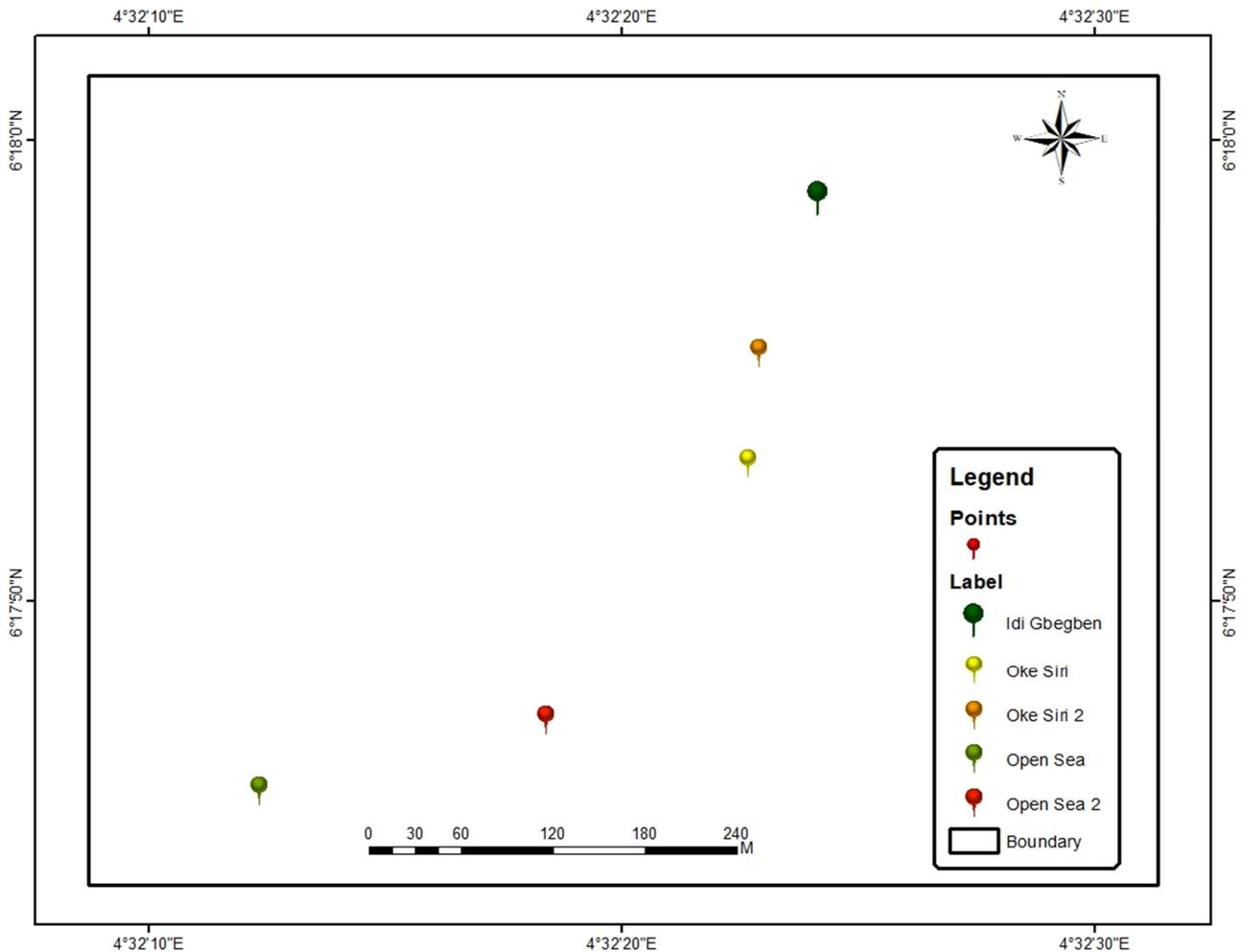


Figure 3. Map of the Study Area showing the sampling points (google Earth).

Toxic metal speciation is critical for determining their bioavailability in the environment and assessing their potential dangers to living organisms [17]. In this study, the investigated metal speciation revealed differences in the concentrations that were recorded at each step of the extraction. Using a modified version of [21] method, the toxic metals were separated into five operationally defined fractions viz. exchangeable (F_1), carbonate-bound (F_2), Fe-Mn oxide-bound (F_4), organic-bound (F_4), and residual (F_5) fractions (F_5) [3]. The sequential extraction procedures are as follows:

- (i) F_1 : 1 g of dried and powdered sediment was extracted at room temperature with 1 M $MgCl_2$ at pH 7.0 for 1 h with continuous agitation. Then, the mixture was centrifuged. The supernatant obtained on standing was filtered to represent F_1 .
- (ii) F_2 : The residue from (i) was leached at 30 °C with 1 M sodium acetate ($NaOAc$) adjusted to pH 5.0 with acetic acid ($HOAc$). The mixture was continuously agitated throughout the extraction using a centrifuge. The extracts were decanted to represent F_2 .
- (iii) F_3 : 20 ml of 0.04 M hydroxylamine chloride ($NH_2OH.HCl$) in 25% (v/v) acetic was added to the

residue from (ii). The mixture was agitated 96°C for 6 h. Then, the extract was decanted to represent F_3 .

- (iv) F_4 : 3ml of 0.02 M HNO_3 and 5ml of 30% H_2O_2 were added to the residue from (iii). The mixture was agitated at 85°C for 5 hours then, 5 ml of 3.2 M NH_4OAc was added and further centrifuging for 30 min before filtering. The supernatant represents F_4 .
- (v) F_5 : The final fraction was obtained by digesting the residual from (iv) with 5ml of 25% of HCl and 5ml HNO_3 . for 6hrs at 120°C. The mixture was centrifuged, and the supernatant was obtained as F_5 .

All reagents used were analytical grade. The supernatant from each extraction was quantitatively transferred into a 25 ml volumetric flask and made up to mark with 1 M HNO_3 before quantifying the trace metals using Atomic Absorption Spectrophotometer (AAS, Buck Scientific Model 205A). All analyses were carried out in triplicates, and reagent blanks were used for quality control.

2.3. Metal Analysis

Trace metal concentrations were determined by atomic absorption spectrophotometry Model 210 VGP of the Buck Scientific AAS series with air-acetylene gas mixture as

oxidant involving direct aspiration of the aqueous solution into an air-acetylene flame. The following techniques were used for the first four fractions for the trace metals such as Cd, Co, Cu, Cr Ni, Pb, and Zn and the metals present in high concentrations (Fe and Mn). The supernatant solution was diluted (20 to 50 X) with deionized water and the concentrations were obtained directly from appropriate calibration curves prepared with the components of the extraction solution diluted by the same factor. For total or residual trace metal analysis, the solid was digested with a 5:1 mixture of hydrofluoric and perchloric acids. For 1g (dry weight) sample, the sediment was first digested in a platinum crucible with a solution of concentrated HClO_4 (2 ml) and HF (10 ml) to near dryness; subsequently, a second addition of HClO_4 (1 ml) and HF (10 ml) was made and again the mixture was evaporated to near dryness. Finally, HClO_4 (1 ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12ml NHCl and diluted to 25 ml. The resulting solution was then analyzed by flame atomic absorption spectrophotometry for trace metals using the standard addition techniques.

2.4. Mobility Factor

$$\text{Mobility Factor} = \frac{F1+F2}{F1+F2+F3+F4+F5} * 100 \quad (1)$$

The Mobility Factor is used to assess heavy metal's potential mobility and bioavailability. A high percentage indicates a high level of potential, and conversely.

2.5. Enrichment Factor

Enrichment factor (EF) is an important indicator that shows the status and the degree of pollution of the environment [16]. It is calculated as:

$$E. F. = \frac{C_n / C_{ref} \text{ sample}}{(B_n / B_{ref}) \text{ background}} \quad (2)$$

Where, C_n sample is the metal concentration in sample, C_{ref} sample is the reference material concentration in sample, B_n background is the metal concentration in reference (background) environment and B_{ref} background is the reference metal concentration in reference (background) environment. There are six levels of enrichment; $EF < 2$ (deficiency to minimal enrichment), $2 < EF < 5$ (moderate enrichment), $5 < EF < 20$ (significant enrichment), $20 < EF < 40$ (very high enrichment), $EF > 40$ (extremely high enrichment).

3. Result and Discussion

The results of investigation are presented in Tables 2-16 and figures 4-12 respectively. The results presented the heavy metals concentration in the sediments (minimum, maximum and average), enrichment factor, correlation statistics and mobility factors of the heavy metals across the different geochemical phases. It also introduces statistical approach to the metal speciation in order to understand the geochemical dynamics of the metal fractions in the different phases. In addition, the study compares its findings with other previous literatures and discovered that recent findings contradicted previous work in the study area which dwelt on bioavailability of heavy metals without taking into consideration the bio-diversity and bioaccumulation which correlates with the works and findings of the following researchers such as [15, 11, 10, 4, 13, 18] amongst others.

3.1 Sequential Extraction of Heavy Metals

3.1.1. Exchangeable Fraction (F1)

The result of heavy metal concentration in the exchangeable fraction is presented in Table 2.

Table 2. Heavy metal concentration in the exchangeable fraction (ppm).

Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Mini	3.64	10.07	2.13	98.04	458.24	9.04	2.04	1.17	1.25
Max	6.12	11.46	3.44	122.56	759.28	11.84	3.26	1.55	2.08
Average	4.976	10.9	2.864	111.244	590.718	10.724	2.62	1.35	1.65

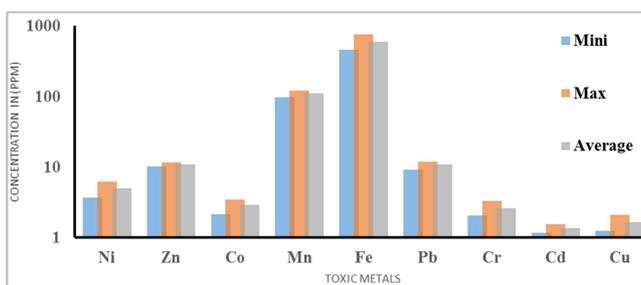


Figure 4. Bar chart of Exchangeable Fractional concentration.

The concentration of heavy metals in the exchangeable phase is presented (Table 2 and Figure 4). The result revealed high concentration of Fe across all the locations. The concentration of Fe ranges from 458.24ppm to 759.28ppm

with an average of 590.718, followed by Mn, Zn and Pb which ranges (98.05ppm to 122.56ppm), (10.07ppm to 11.46ppm) and (9.04ppm to 11.84ppm) respectively. It was also observed that Cd and Cu had the least concentrations. However, the lower concentrations of the exchangeable fractions of Cd and Cu (1.35-1.17 and (1.65-1.35)) ppm in the studied sediments indicated the potential mobility of these metals as well as their potential environmental and ecological risks [8].

3.1.2. Carbonate Bound Metal Fraction (F2)

Similarly, it was also observed that Fe existed more in the carbonate fraction than all other metals ranging from 312.68ppm to 315.71ppm with an average of 313.566ppm. This is closely followed by Mn, Zn and Cu ranging (81.23ppm to 103.08ppm), 13.71ppm to 14.93ppm and 11.85ppm to 12.23ppm respectively. The increased

concentration of Fe, Mn, Zn and Cu in the studied area can be attributed to heavy metal pollution and suggestive of a geochemical province (Table 3 and Figure 5). Most heavy

metals in carbonate and exchangeable phases have low concentration except for Cd which implies that Cd is of low mobility and bioavailability which is very dangerous [4].

Table 3. Heavy metal concentration in the Carbonate fraction (ppm).

Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Mini	5.12	13.71	0.44	81.23	312.68	5.68	1.88	0.62	11.85
Max	6.85	14.93	0.95	103.08	315.71	7.06	2.55	0.88	12.98
Average	6.28	14.32	0.668	90.974	313.566	6.314	2.104	0.79	12.282

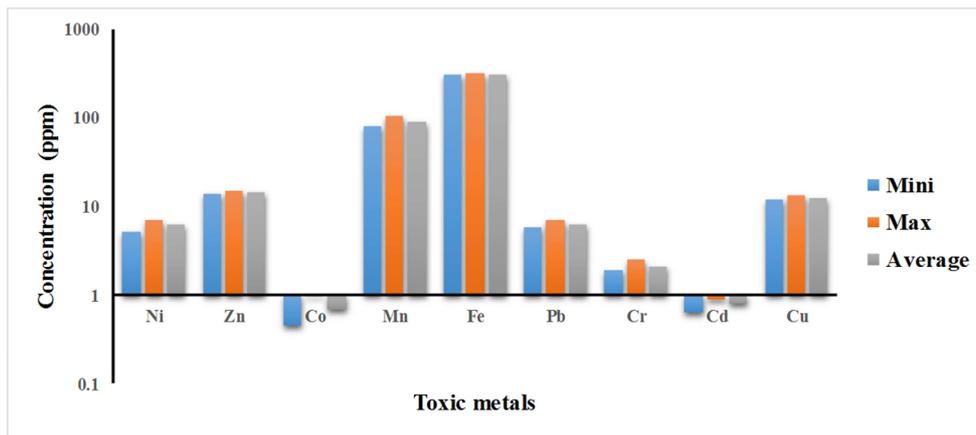


Figure 5. Bar chart of Carbonate bound Metal Fraction.

3.1.3. Reducible Bound Metal Fraction (F3)

In the reducible bound metal fraction, the average concentration of heavy metals are as follows: Fe, Mn and Zn has the maximum value with Fe (124.5448 - 169.81) ppm with an average concentration of 152.44ppm. Mn concentration revealed the highest value at (33.42- 41.18.16)

ppm with an average concentration of 37ppm, while Zn and Ni has (16.41- 18.34) ppm and (8.61 - 10.44) ppm with average concentration of 17.18ppm and 59.22ppm respectively. It was observed that Cd concentration in this fraction was very low due to its bioavailability Table 4 and Figure 6 [4].

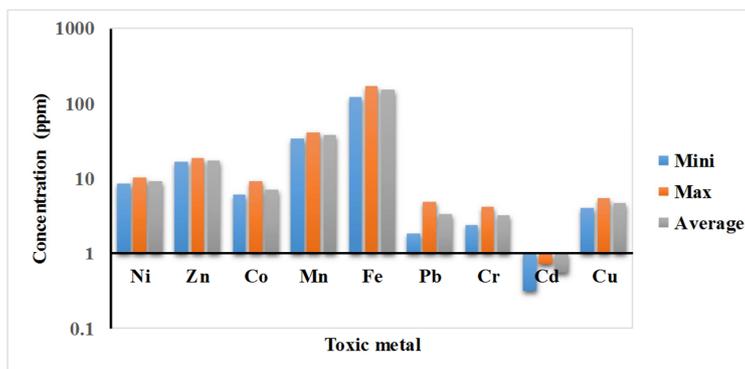


Figure 6. Bar chart of Reducible bound Metal fraction.

Table 4. Heavy Metals Concentration in the Reducible Fraction (ppm).

Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Mini	8.61	16.41	6.06	33.41	124.54	1.85	2.42	0.32	4.04
Max	10.44	18.34	9.15	41.18	169.81	4.82	4.26	0.72	5.43
Average	9.222	17.184	7.18	37.002	152.442	3.372	3.238	0.548	4.682

3.1.4. Organic Bound Metal Fraction (F4)

The Fe concentration was observed to be high across the studied area as in the organic phase (F4). Its maximum to

minimum concentration values range from 243.72ppm - 249.14ppm (246.17ppm) across the area while Cd was observed to be low with mean and average concentration values (0.54ppm -0.82ppm) with 0.61ppm.

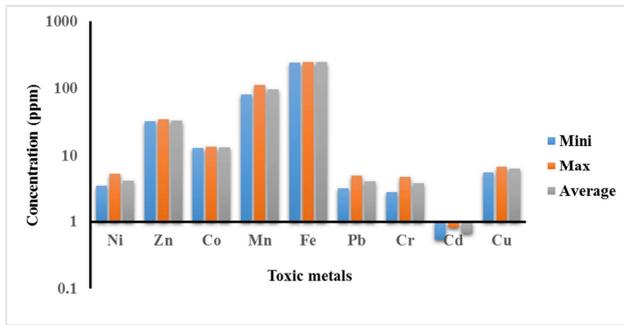


Figure 7. Bar chart of Organic Bound Metal Fraction.

3.1.5. Residual Bound Metal Fraction (F5)

In the residual fraction, Fe also show same preference across all the fractions in the studied area, with an average concentration of 838.62ppm, followed by Zn with an average of 348.26. (Table 6 and Figure 8). The increase in

concentration of Fe in this fraction is likely to be due to anthropogenic activities such as weathering processes and nature of the sediments.

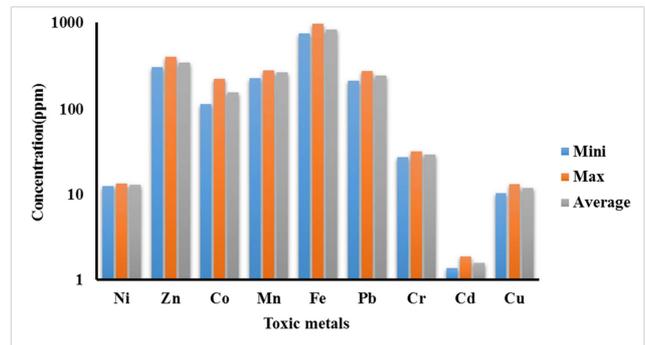


Figure 8. Bar chart of Residual Bound Metal Fraction.

Table 5. Heavy metal concentration in the Organic Fraction (ppm).

Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Mini	3.46	32.96	13.18	82.14	243.72	3.14	2.76	0.54	5.52
Max	5.28	34.58	13.74	114.46	249.14	4.85	4.68	0.82	6.64
Average	4.12	33.772	13.508	97.036	246.172	4.07	3.74	0.674	6.168

Table 6. Heavy Metals Concentration in the Residual Metal Fraction (ppm).

Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Mini	12.5	307.45	116.05	230.62	744.12	214.18	27.14	1.36	10.34
Max	13.35	403.75	225.1	280.95	971.2	278.55	31.51	1.87	13.2
Average	12.972	348.262	157.578	266.98	838.616	244.49	29.09	1.56	12.02

3.2. Mobility Factor of the Heavy Metals

Table 7. Mobility Factors of the Heavy Metals (%).

Sample ID	Location	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
A1	OPEN SEA	32.61	6.15	2.15	31.00	40.28	6.58	10.57	45.89	40.66
A2	OPEN SEA 2	26.69	6.68	1.92	34.15	41.33	6.478	10.42	39.56	38.72
A3	OKE SIRI 1	30.31	5.23	2.56	33.29	39.78	6.381	12.33	46.02	35.78
A4	OKE SIRI 2	31.05	6.65	1.72	34.00	44.58	6.42	13.08	42.40	37.55
A5	IDI GBEBGEN	28.98	5.30	1.67	34.07	44.36	5.90	11.32	43.24	36.81

The mobility factor (MF) of the heavy metals in the studied area is presented in (Table 7). The potential of metals to become environmentally mobile and bioavailable has been attributed to their mobility factor value [13]. It was discovered that Cd had the highest mobility factor in studied area Oke Siri-1 (A3) and Open Sea-1 (A1) respectively with MF values of 46.02% and 45.80%, whereas, in the sampling sites such as Idi Gbebgben-1 and Oke Siri-2, Fe has a mobility factor of 44.36% (A5) and 44.58% (A4) respectively. Therefore, Cd would have higher mobility and bioavailability potentials in Oke Siri-1 and Open Sea-1, thereby rendering Cd a major threat to the ecosystem. The same applies to Fe in Idi Gbebgben-1 and Oke Siri-2. Therefore, it was observed that, the overall order of environmental mobility of the metals are Cd> Fe>Cu >Fe >Mn. (Table 7).

3.3. Enrichment Factor

In order to know the possible natural or anthropogenic input and impact in the sediments, enrichment factor (EF)

was computed. The Enrichment factor value ranges from 2.12 to 404.67 (Table 8). Most of the heavy metals have moderate to very high enrichment level of pollution across the locations in the exchangeable phase, except for Pb that is very highly enriched with its possible source for enrichment to natural mineralization in form of sporadic sulphide occurrence [5]. Cd is extremely highly enriched due to various human activities such as agricultural applications (of fertilizers, metal-containing pesticides, fungicides, and herbicides), waste disposal, and dredging which could have contributed significantly to the very high enrichment of Cd in the exchangeable phase.

The enrichment factor in the carbonate phase ranges from 3.50 to 438.55 (Table 9). Most of the heavy metals have moderate to extremely high enrichment level of pollution across the locations in the carbonate phase, expect Pb that is very highly enriched with enrichment value ranging from (43.00% to 53.24%). However, Cd is observed to be

extremely highly enriched. This can be due to various human activities, for example, agricultural applications (of fertilizers, metal-containing pesticides, fungicides, and herbicides), waste disposal, and dredging, could have contributed significantly to the very high enrichment of cadmium in this phase.

This Enrichment factor value for reducible is high and ranges from 8.03 to 677.59. According to Table 10, most of the toxic metals have significant enrichment to extremely high enrichment level of pollution across the locations in the reducible phase. However, Co and Cd are seen to be extremely highly enriched. Co- 145.48***** (Open Sea) – Cd- 677.59***** (Open Sea 2). This can be due to various human activities such as industrial waste disposal which could have contributed significantly to the very high enrichment of cobalt and cadmium in the reducible phase. This can be due to various human activities such as industrial waste disposal which could have contributed significantly to the very high enrichment of cobalt and cadmium in the reducible phase [10].

The enrichment factor values for the study area is presented in Table 11. It is observed that the Ni value ranges from 9.76*** - 14.71***. The maximum value recorded at

A5 (Idi Gbeben). Zn value range from 70.38***** - 67.71****, the highest at A1 (Open Sea). Similarly, Co values is between 137.70*****- 134.12***** with the highest concentration at A3 (Oke Siri 1). Also, Mn ranges from 25.51*** - 18.68*** with the highest concentration at A4 (Oke Siri 2), Pb ranges from 45.94***** - 30.41**** and the highest concentration is noticed at A5 (Idi gbenben). Cr (9.90*** - 5.81****) with the highest concentration at A3 (Oke Siri 1). Cd value also ranges from 524.44***** - 348.60***** with the highest concentration at A2 (Open Sea 2). Cu (28.58***- 23.72***), also with the highest concentration at A3 (Oke Siri 1). It can be deduced from the table that the enrichment factor varies from one location to the other and can be described as being extremely highly enriched in Co and Cd, very high enrichment of Zn and Cu and significant enrichment of Ni, Mn, Pb and Cr. In addition, locations A2, A3 and A5 are areas of keen interest in this study. The enrichment of heavy metals in these locations could be due to human activities such as dredging works, decay and decomposition of metallic wastes as well as industrial wastes disposal indiscriminately into the streams and soils [13].

Table 8. Enrichment factor for Exchangeable phase across all the sampled locations (%).

Sample No	Location	Ni	Zn	Co	Mn	Pb	Cr	Cd	Cu
A1	OPEN SEA	5.51***	10.92***	11.55***	11.88***	46.56*****	2.33**	401.71*****	2.86**
A2	OPEN SEA 2	6.07***	10.26***	12.31***	10.95***	45.40*****	2.12**	377.54*****	2.78**
A3	OKE SIRI 1	6.65***	10.72***	14.67***	12.68***	52.24*****	2.73**	404.67*****	3.11**
A4	OKE SIRI 2	5.59***	7.91***	11.12***	9.18***	38.28*****	2.26**	323.40*****	3.01**
A5	IDI GBEBGEN	5.59***	7.50***	11.25***	8.96***	36.80*****	2.25**	321.18*****	2.87**

*- deficiency to minimal enrichment
 **- moderate enrichment
 ***- significant enrichment
 ****- very high enrichment
 *****- extremely high enrichment

Table 9. Enrichment factor for Carbonate phase across all the sampled locations (%).

Sample ID	Location	Ni	Zn	Co	Mn	Pb	Cr	Cd	Cu
A1	OPEN SEA	11.37***	21.78****	3.50**	14.43***	49.51*****	3.15**	311.97*****	39.75***
A2	OPEN SEA 2	13.37***	22.11****	4.52**	14.79***	44.42*****	3.27**	392.13*****	40.15****
A3	OKE SIRI 1	14.55***	22.51****	5.00**	15.60***	53.24*****	3.39**	412.24*****	40.35****
A4	OKE SIRI 2	15.14***	23.53****	5.94**	17.58***	42.76*****	3.55**	426.55*****	42.02****
A5	IDI GBEBGEN	15.06***	23.50****	7.48**	18.13***	47.69*****	4.24**	438.55*****	43.12****

**- moderate enrichment
 ***- significant enrichment
 ****- very high enrichment
 *****- extremely high enrichment

Table 10. Enrichment factor for Reducible phase across all the sample location (%).

Sample ID	Location	Ni	Zn	Co	Mn	Pb	Cr	Cd	Cu
A1	OPEN SEA	40.69*****	58.32*****	145.48*****	11.87***	49.54*****	13.23***	543.78*****	32.96****
A2	OPEN SEA 2	43.35*****	49.57*****	103.72*****	12.16***	62.40*****	8.03***	677.59*****	29.80****
A3	OKE SIRI 1	36.13***	52.46*****	103.72*****	11.99***	66.99*****	9.30***	592.98*****	33.54****
A4	OKE SIRI 2	41.38*****	56.45*****	104.23*****	14.27***	40.68****	15.47***	348.56*****	31.08****
A5	IDI GBEBGEN	50.50*****	66.06*****	132.05*****	18.36***	35.06****	10.19***	656.92*****	34.03****

***- significant enrichment
 ****- very high enrichment
 *****- extremely high enrichment

Table 11. Enrichment factor for organic phase across all the sampled location (%).

Sample No	Location	Ni	Zn	Co	Mn	Pb	Cr	Cd	Cu
A1	OPEN SEA	10.41***	70.38*****	134.12*****	18.68***	39.44*****	8.89***	425.36*****	23.72***
A2	OPEN SEA 2	9.76***	68.12*****	137.54*****	19.02***	39.91***	9.06***	524.44*****	25.50***
A3	OKE SIRI 1	11.31***	67.71*****	137.70*****	20.91***	39.23*****	9.90***	469.69*****	25.81***
A4	OKE SIRI 2	11.85***	68.92*****	137.20*****	25.29***	30.41***	6.18***	348.60*****	28.58***
A5	IDI GBEBGEN	14.71***	65.73*****	135.01*****	25.51***	45.94*****	5.81***	385.22*****	27.79***

***- significant enrichment
 ****- very high enrichment
 *****- extremely high enrichment

Table 12. Enrichment factor for Residual phase across all the sampled locations (%).

Sample ID	Location	Ni	Zn	Co	Mn	Pb	Cr	Cd	Cu
A1	OPEN SEA	12.28***	219.39*****	393.94*****	20.28***	679.28*****	19.13***	287.55*****	14.57***
A2	OPEN SEA 2	11.57***	203.94*****	462.12*****	16.87***	769.00*****	19.59***	310.89*****	15.61***
A3	OKE SIRI 1	10.43***	232.98*****	346.69*****	18.76***	741.59*****	17.31***	278.13*****	16.02***
A4	OKE SIRI 2	10.45***	172.19*****	525.15*****	16.94***	588.12*****	18.63***	331.65*****	14.85***
A5	IDI GBEBGEN	9.43***	206.55*****	575.78*****	16.06***	676.87*****	16.74***	259.20*****	14.26***

***- significant enrichment
 ****- very high enrichment
 *****- extremely high enrichment

The enrichment factor values for the reducible area is presented in Table 12. It is observed that the Ni value ranges from 9.43*** - 12.28***. The highest recorded at A1 (Open Sea). Zn values also range from 172.19***** - 232.98*****, the highest at A3 (Oke Siri). Similarly, Co values is between 346.69*****- 575.78***** with the highest concentration at A5 (Idi gbengben). Also, Mn ranges from 16.06*** - 20.28*** with the highest concentration at A1 (Open Sea), Pb ranges from 588.12***** - 769.00***** and the highest concentration is noticed at A2 (Open Sea 2). Cr (16.74*** - 19.59***) with the highest concentration at A2 (Open sea 2). Cd value also ranges from 259.20***** - 331.65***** with the highest concentration at A4 (Oke siri 2). Cu (14.26*** - 16.02***) also with the highest concentration at A3 (Oke Siri 1). It can be deduced from the table that the enrichment factor varies from one location to the other and can be described as being extremely highly enriched in Co and pb, very high enrichment of Zn and Cd and significant enrichment of Ni, Cu, Cr and Mn. In addition, locations A2, A3 and A5 are areas of anomaly in this study where adequate attention is required to mitigate the effects of these metals on the environment and aquatic lives. The enrichment of heavy metals in these locations could be due to agricultural applications (of fertilizers, metal-containing pesticides, fungicides, and herbicides), nearness to abattoir, waste disposal, and dredging [18].

3.4. Correlation and Regression Analysis

Correlation is a statistical term that describes how closely two variables are connected linearly (meaning they change together at a constant rate). The relationships between the fraction phases are described in this way. Regression analysis is a statistical tool for determining whether factors have an influence on a certain issue. This regression approach has enabled us to clearly identify which geochemical phases are heavily coupled and how these geochemical phases interact. The grading standards for this statistical analysis is presented

in Table 13.

Table 13. Extent of correlation degree based on the factor values.

Grading Standards	Correlation Degree
$\rho = 0$	No correlation
$0 < \rho \leq 0.19$	Very weak
$0.20 \leq \rho \leq 0.39$	Weak
$0.40 \leq \rho \leq 0.59$	Moderate
$0.60 \leq \rho \leq 0.79$	Strong
$0.80 \leq \rho \leq 1.00$	Very strong
1.00	Monotonic correlation

Spearman's correlation <http://www.statstutor.ac.uk/resources/uploaded/spearmans.pdf>

Table 14. Correlation between Exchangeable and Carbonate phases.

	Exchangeable	Carbonate
Exchangeable	1	
Carbonate	0.994768837	1

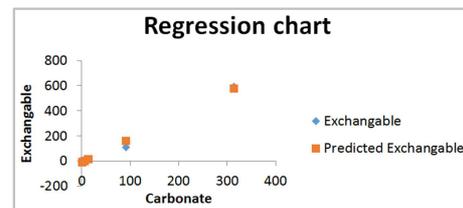


Figure 9. The Regression between Exchangeable and Carbonate fraction.

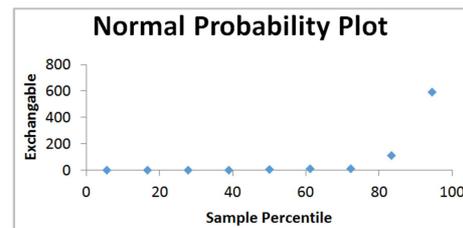


Figure 10. The percentage regression between Exchangeable and Carbonate fractions.

Correlation and regression analysis was used to deduce the correlation between exchangeable and carbonate fraction phases which gives 0.9 mean value (Table 13) indicating a very strong relationship between the two phases using the correlation standards and grading degree. This showed that there is a strong bond between the exchangeable and carbonate phases (Table 14, Figures 9 and 10). However, the strong correlation of heavy metals between the exchangeable and carbonate phases from this result may pose a serious threat to life for humans and aquatic lives either as a pollutant or increasing the acidity and the biological oxygen demand (BOD) of streams and rivers in the study area [2, 10, 4].

Table 15. The Correlation between Reducible and Organic phases.

	Reducible	Organic
Reducible	1	
Organic	0.986337652	1

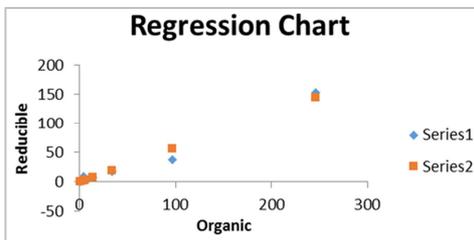


Figure 11. The percentage regression between Reducible and Organic fractions.

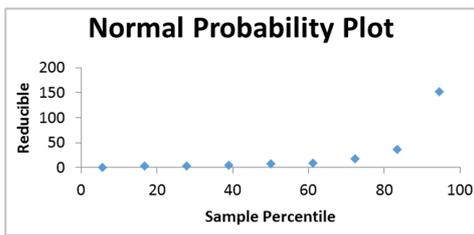


Figure 12. The percentage regression between Reducible and Organic fraction.

The correlation between Reducible and Organic fraction also revealed 0.9 a very strong bond between the two metal fractions (Table 15 and Figure 12). However, the strong correlation between the reducible and organic fraction is an indication of unguarded release of heavy metals or harmful substances into the environment when reducing conditions are favorable. It also poses serious threat to both living and aquatic organisms as well as posing chronic health challenges to the inhabitants [15].

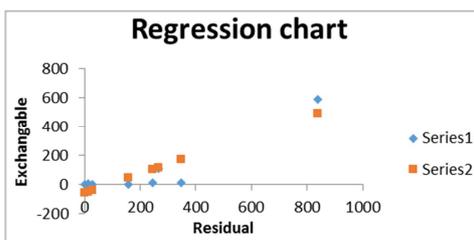


Figure 13. The regression between exchangeable and residual fractions.

Table 16. The Correlation between Exchangeable and Residual Phases.

	Exchangeable	Residual
Exchangeable	1	
Residual	0.905252938	1

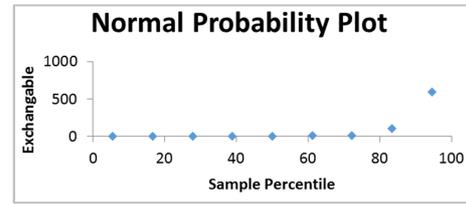


Figure 14. The percentage regression between exchangeable and residual fraction.

The correlation between exchangeable and residual fraction phase also revealed 0.9 mean value (Table 16, Figures 13 and 14), which affirmed a very strong relationship between the two metal fractions. It revealed that metals in these fractions are strongly bonded to the matrix of the sediments. The result also revealed a very strong pollution indicator to the environment which can result to serious ecological risks and untimely death of human and aquatic lives [14, 8].

4. Conclusion

Geochemical speciation of heavy metals has been carried out on Araromi coastal sediments. This research has been able to establish that strong bond relationship between the exchangeable and the carbonate, residual and the organic metal fractions when subjected to statistical correlation and regression analysis and becomes bioavailable in all the geochemical phases and such metals include Cu, Zn, Fe or have low mobility factor and becomes bioavailable such as Cd, Co and Pb, or can be held within the mineral grains of sediments e.g Mn. O Also, it showcased that metals such as Cu, Zn, Fe, or have low mobility and becomes bioavailable. Whereas, Cd, Co and Pb. Or can constitute mineralization by their association under oxidizing or reducing conditions such as CU-Zn-Fe (massive sulphide mineralization). The geochemistry of these metals also revealed their bioavailability and bioaccumulation in sediments which can be harmful or beneficial to humans and aquatic lives through consumption of the agricultural products grown on polluted/contaminated soils and sediments which may lead to brain damage, excessive bleeding (Hemorrhage) and other terminal and life threatening diseases. From the foregoing, it can be concluded that Fe, Mn, Zn, Pb, Co is found in residual phase > exchangeable phase > carbonate phase > reducible phase > organic phase. However, the heavy metals in the exchangeable and carbonate phases can be released into the environment under reducing and oxidation conditions. The sources of contamination of heavy metals are through excessive use of fertilizers, agrochemical, metal-containing pesticides, antimicrobial agent, offshore filling stations, and mechanical work from boats. In addition, the enrichment factor of the heavy metals analyzed also showed that Cd, Co, Pb, Zn and Cu are extremely high in all the phases and are

linked to anthropogenic activities such as agricultural applications, waste disposal, and dredging activities. This could have contributed to extremely high enrichment in the reducible, organic, carbonate, exchangeable and residual phases of the metal fractions in the sediments studied.

Conflict of Interest

All the authors do not have any possible conflicts of interest.

Declaration

All the data used for this research are available whenever it is requested.

Significance Statement

This study has revealed that mobility factor and bioavailability of Cd is very high in all the metal fractions analyzed. Its mobility and bioavailability in the studied area constitutes a major threat to the ecosystem, thereby resulting in hazardous ecological risks and geo-environmental pollution on human and aquatic lives. Whereas, the enrichment factor of heavy metals such as Pb, Zn and Cu in all the fractions indicated moderate to extremely and high enrichment which may constitute mineralization potentials (massive sulphide enrichment) in the studied area.

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