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SEQUENTIAL ANALYSIS, MOBILITY FACTOR AND GEOCHEMISTRY OF HEAVY METALS IN AYETORO COASTAL SEDIMENTS, SOUTHWESTERN NIGERIA

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ABSTRACT: *Previous geochemical investigation of Ayetoro area discovered that its coastal sediments are enriched with sulphide mineralization. However, in order to determine the geochemical phases of the heavy metals in the coastal sediments, random sampling method was utilized across 10 locations, at a depth of 40cm using Van grab sampler at a sampling density of 200m interval. Atomic Absorption Spectrophotometer (AAS) Buck Scientific Model 205A was used to analyze nine (9) heavy metal concentrations namely Ni, Zn, Co, Mn, Fe, Pb, Cr, Cd and Cu in the coastal sediments, followed by sequential extraction of the metals, using five fractional phases. The results revealed that the geochemical concentration of the heavy metals as follows:*

Ni (5.89ppm - 16.82ppm), Zn (2.59ppm - 115.65ppm.), Co (1.22ppm - 22.77ppm), Mn (30.95ppm - 186.49ppm), Fe (6.632ppm - 1925.96ppm), Pb (5.17ppm - 55.96ppm), Cr (0.26ppm - 28.06ppm), Cd (0.13ppm -22.23ppm), and Cu (2.26ppm - 41.94ppm) and showed the concentration order as Residual>Reducible>Organic>Exchangeable>Carbonate. Most of the heavy metals in carbonate and exchangeable phase have low concentration except for Cd. This implied that Cd is of low mobility and bioavailability which is very dangerous as its intake by man leads to kidney diseases and causes bones to become weaker. Also, Mobility factor of Cd stood out because of its high concentration in the exchangeable phase compared to other four non-residual phases. The mobility and bioavailability of the heavy metals are in this order: Cd>Co>Ni>Pb>Cr>Mn>Cu>Zn>Fe respectively. The analysis of variance (ANOVA) revealed that the heavy metals are significantly different in all the phases based on their accumulation index in the sediments while majority of the heavy metals lacked the ability to remobilize but can be released into the environment under reducing and oxidizing conditions.

KEYWORDS*:* ayetoro. coastal sediments, heavy metals, sequential extraction, mobility factor

INTRODUCTION

Sediments are considered to be mixture of several components of mineral species and represent important sinks for various pollutants in aquatic systems including heavy metals. It also plays a prominent role in the assessment of heavy metal contamination. (Alkarhi et al., 2009; Zulkifli et al., 2010). Total amount of heavy metal concentration in sediment is useful to detect net change. Never the less, it does not give any sign about the chemical form of each metals in sediment. (Pagnanelli et al., 2004). Ayeku et al. (2015) studied the pollution status in the bottom sediment in Awoye, Abereke and Ayetoro Area of Ondo state. He concluded that these metals derived from the upstream rivers from the top soil are products of mechanically weathered rock materials and anthropogenic activities while Ololade et al. (2008) agreed that metal speciation should be done to determine the bioavailability of metal in sediment after his own seasonal metal distribution research in Ondo coastal sediment. Heavy metal concentration in the ocean

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ecosystem is determined by three conditions namely; water, sediments and living organism. Usually, heavy metal exists in lowest concentration in water and reach considerable concentration in sediments followed by bioaccumulation in living organism (Kamaruzzamam et al., 2020). According to (Li et al., 2000), heavy metals are released from sediments into water bodies and consequently, to living organisms depending on the speciation of metals and other factors such as sediment pH and organic matter (Yunus et al., 2011). Coastal and marine ecosystems worldwide are continuously bedeviled with pollution, such as eutrophication, acidification, toxic substances, heavy metals, and the likes. Decline in ecosystem productivity, loss of aesthetic beauty of the ocean, impacts on sensitive habitats, impairment on quality of seawater, hazards to human health are some of the consequences of heavy metals accumulation in sediments which makes continuous long term monitoring of heavy metal concentration of coastal sediment extremely important. Therefore, this research attempts to determine the geochemical phases of the heavy metals in the coastal sediments of Ayetoro area using five metal fractional methods, in order to assess the levels of their bioavailability, bioaccumulation and the danger it portends to man and ecology.

Description and Geology of the Study Area

The study area (Ayetoro) is one of the prominent, water-route nodal communities in the coastal region of Ondo State, Nigeria. Ayetoro was established in 1947 and is inhabited by the Ilaje people, a linguistic subgroup of the Yorubas. The town lies east along the coast from Nigeria's largest city, Lagos. Due to oil exploration activities, the community has lost a considerable portion of coastline to the Atlantic Ocean. Ayetoro which is one of the main settlements in Ilaje local government area lies approximately within latitude 6° 12' 33.786" N and longitude 4° 40' 17.051" E respectively. It is bounded in the north-east by Erunna village, on the south-east by Alagbon Village and North-west by Idi Ogba and south-west by the Atlantic Ocean. The people are extractions of the Ilaje sub-ethnic group of the Yoruba's in south western Nigeria. Ayetoro in its hey-days once had the highest per capital income in the whole of Africa and attracted visitors, tourists and researchers from all over the world. The occupational activities in this area include fishing, canoe making, and lumbering. Others are net making, mat making, launch building, farming and trading. Residents say the ocean incursion has impacted on their livelihoods, particularly since the community's entire mangrove vegetation was destroyed. The Atlantic's surges have also destroyed Ayetoro's marine life, thereby crippling people's fishing businesses, which is the mainstay of the local economy.

There are two distinct geological regions in Ondo State. First, is the region of sedimentary rocks in the south, and secondly, the region of Pre Cambrian-Basement Complex rocks in the north. The sedimentary rocks are mainly of the post Cretaceous sediments and the Cretaceous Abeokuta Formation. The basement complex is made up of mainly the medium-grained gneisses. These rocks are strongly foliated most of the times, occurring as outcrops. The surface of these outcrops are rigorously distorted with alternating bands of dark and light-colored minerals. These bands of light-colored minerals are essentially feldspar and quartz, while the dark colored bands contain abundant biotite, a small proportion of the state, especially to the northeast, overlies the coarse-grained granites and gneisses, which are poor in dark ferromagnesian minerals. Troughs and undulating low land surfaces cover Ilaje Local Government Area with silt, mud and superficial sedimentary deposits (Akinnawo *et al*., 2015). There are sand formation at the western part of the local government, extending from the Lekki peninsula in Lagos State to Araromi Sea-side and Zion pepe, Mahin and Ugbonla which are in the eastern part of the local government area. This could be the reason why there is sand deposition on the western side like Igbokoda and clay formation in areas like Ayetoro. Crude oil, which is a major source of income in Nigeria is found in Ilaje Local Government. There are oil wells and fields spreading all over the local government area both onshore and offshore. Oil companies such as Shell, Chevron are believed to be presently harnessing the crude oil found in the area. Apart from petroleum, there are other natural resources and raw materials present in Ilaje land such as glass sand, salt, tar sand, quartz and clay deposits.

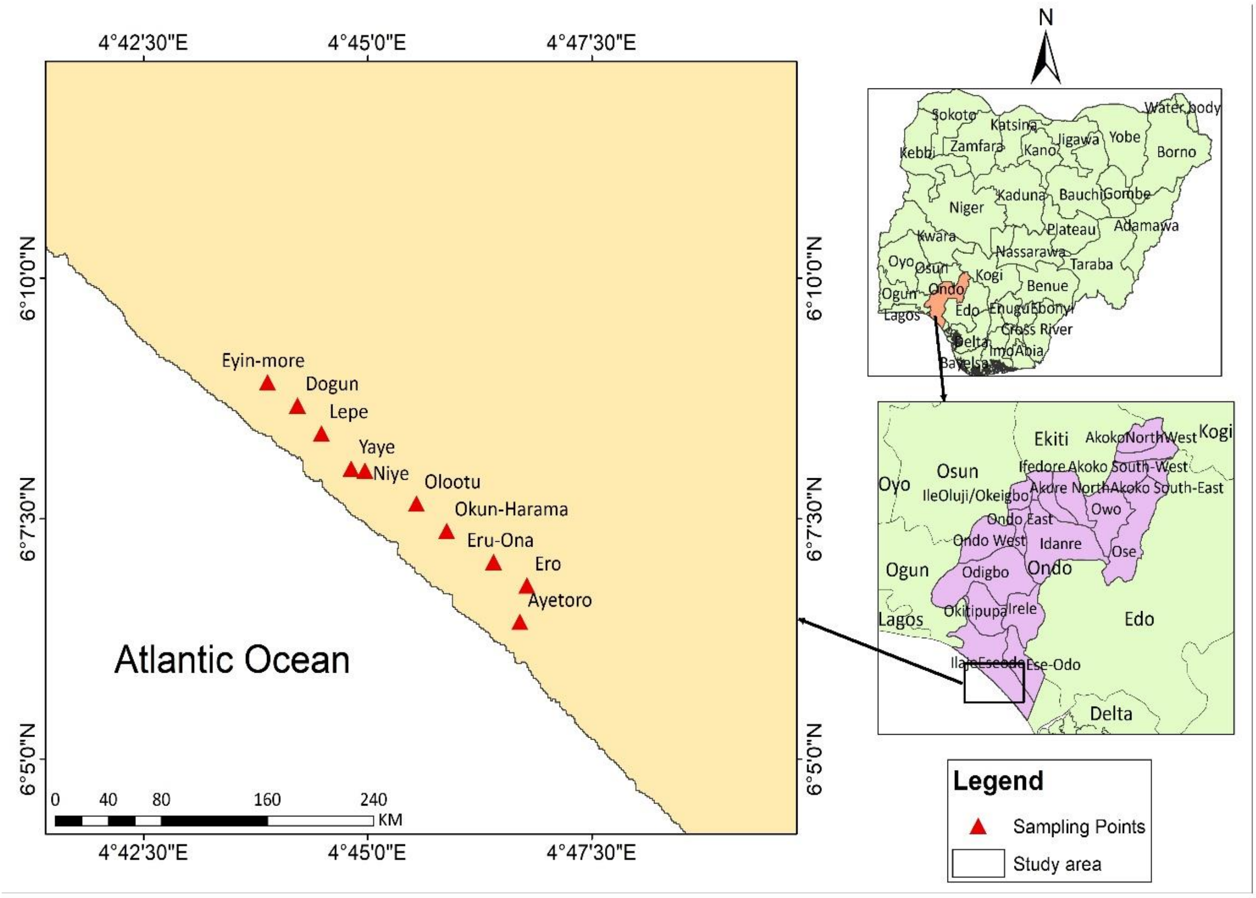

Figure 1: Sampling points of Coastal Sediments.

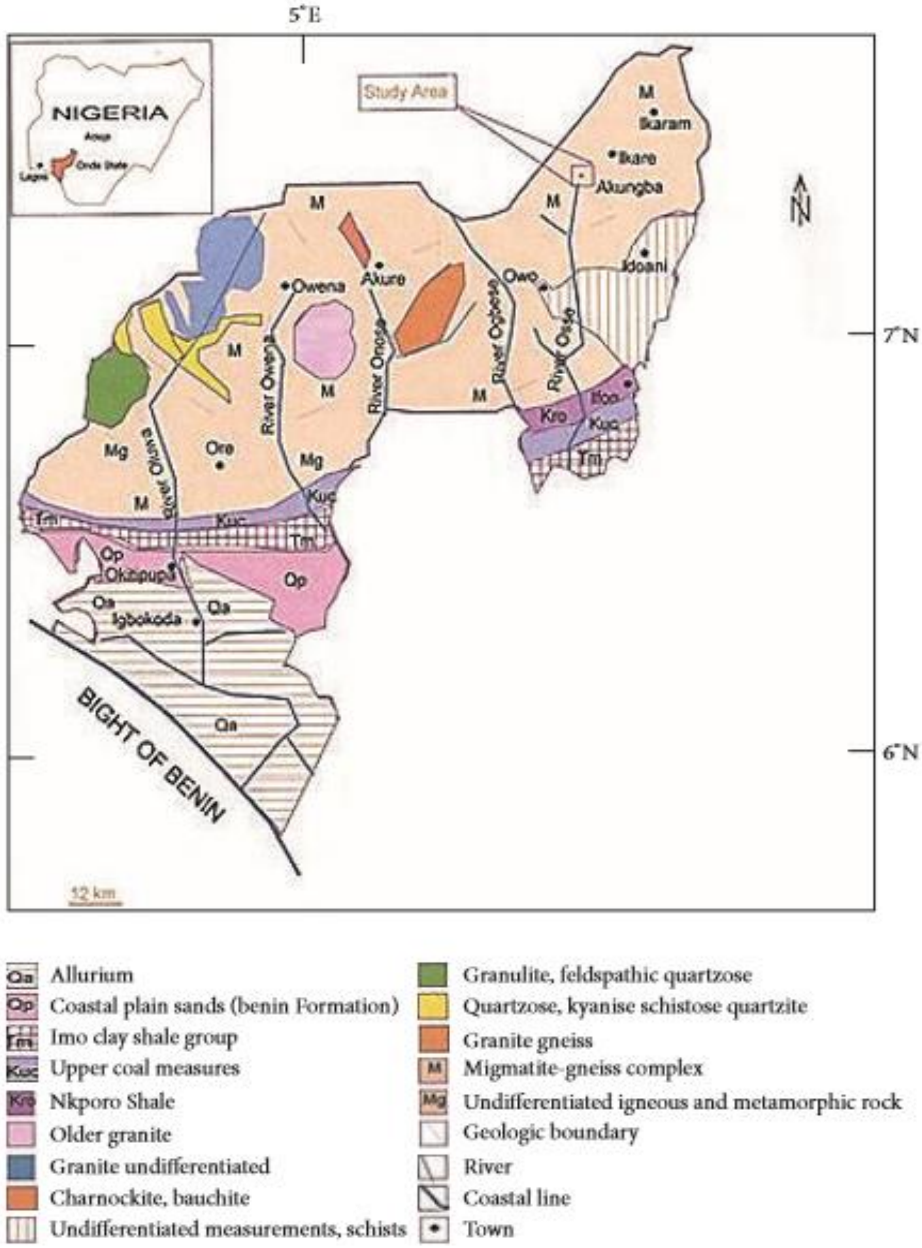

Fig .2: Geological map of Ondo State (Geological survey of Nigeria, 2001)

MATERIALS AND METHODS

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 sample density of 200m intervals. Global Positioning Systems (GPS) G GARMIN eTrex 10 was employed to get the accurate geographical coordinates of each sampling points. A total of ten 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. Observation of geological settings, physical structures and lithology together with human activities were noted and the samples were eventually transmitted to Temsol Consults Laboratory Ltd Shasha, Ibadan for sequential extraction analysis.

Table 4: Field Data and Description of Coastal Sediments

Station ID	**Locations**	**Latitude**	**Longitude**	**Colour**	**Sediment composition**
S1	Ayetoro	6°6′25.76″N	4°46′41.90″E	Dark Grey	Clay
S2	Ero	6°6′48.50″N	4°46′46.50″E	Brownish grey	Clay
S3	Eru-Ona	6°7′3.20″N	4°46′24.30″E	Brown	Silt
S4	Okun Harama	6°7′22.50″N	4°45′52.80″E	Yellowish Brown	Silt
S5	Olootu	6°7′39.60″N	4°45′32.70″E	Grey	Clay
S6	Niye	6°8′0.10″N	4°44′58.20″E	Dark Grey	Clay
S7	Yaye	6°8′1.30″N	4°44′48.90″E	Dark Grey	Clay
S8	Lepe	6°8′23.30″N	4°44′29.00″E	Grey	Clay
S9	Dogun	6°8′40.78″N	4°44′12.98″E	Grey	Clay
S10	Eyin-more	6°8′55.30″N	4°43′53.00″E	Grey	Clay

The field data for the coastal sediment samples is presented in Table 4. Ten coastal sediments were randomly selected from different localities within the study area. Their geographical coordinates as well as their colour and nature of the sediments were taken into consideration. The colour ranges from grey, dark grey, yellowish brown, brown to brownish grey, while the composition of the sediments are clayey and silty in nature.

Laboratory Analysis

Sequential Extraction Procedure

The speciation of toxic metals is important for measuring their bioavailability in the environment, and for evaluating their potential risks to living organisms (Sadhana & Pradhanang, 2014). In the study, the investigated metals speciation revealed differences in the concentrations that were recorded at each step of the extraction. Using a modified version of

Tessier *et al.* (1979) 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 (F5) (Aiyesanmi *et al.* 2020; Rauret *et al.*,1999). 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 ºC 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** ad**de**d **t**o 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 HC1 and 5ml HNO_3.for 6hrs at 120^0c. 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.

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 Cd, Co, Cu,Cr Ni, Pb, and Zn, For 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 $HC10_4$ (2 ml) and HF (10 ml) to near dryness; subsequently, a second addition of HC104 (1 ml) and HF (10 ml) was made and again the mixture was evaporated to near dryness. Finally, HC104 (1 ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in 12ml NHC1 and diluted to 25 ml. The resulting solution was then analyzed by flame atomic absorption spectrophotometry for trace metals using the standard addition techniques.

Mobility Factor =

$$\frac{\mathrm{F1} + \mathrm{F2}}{\mathrm{F1} + \mathrm{F2} + \mathrm{F3} + \mathrm{F4} + \mathrm{F5}} * 100$$

Mobility Factor is used to evaluate the potential mobility of and bioavailability of heavy metal. High percentage represent high potential and vice versa

RESULTS AND DISCUSSION

Geochemical Phases

Exchangeable Phase

Table 5 showed the distribution of the maximum, average and minimum concentration of nine heavy metals in the exchangeable phase. The average concentration of the heavy metals are: Mn>Pb>Fe>Ni>Cr>Co>Zn>Cu>Cd. Also, figures 3.0 and 3.1 showed that Mn is predominantly abundant across all sampling points. The following are the range of concentration of heavy metals in this phase: Ni (6.24 – 9.04), Zn (0.07 – 10.64), Co (1.9 – 5.42), Mn (20.16 - 38.72), Fe (2.64 – 18.32), Pb (9.04 – 14.32), Cr (2.72 – 4.85), Cd (1.29 – 1.74), Cu (0.96 -9.76). Apart from sample point S1, Zn is notably low in all other points. Conc. of Fe in S2, S5 and S10 are notably different from others perhaps because of inflow of some extraneous materials from the land to this particular area.

Table 5: Maximum, Average and Minimum Concentration of heavy metals in the Exchangeable phase

Toxic Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Max conc.(ppm)	9.04	10.64	5.42	38.72	18.32	14.32	4.85	1.74	9.76
Average conc.(ppm)	7.52	2.59	3.10	30.95	8.29	12.51	3.38	1.57	2.26
Min conc.(ppm)	6.24	0.07	1.9	20.16	2.64	9.04	2.72	1.29	0.96

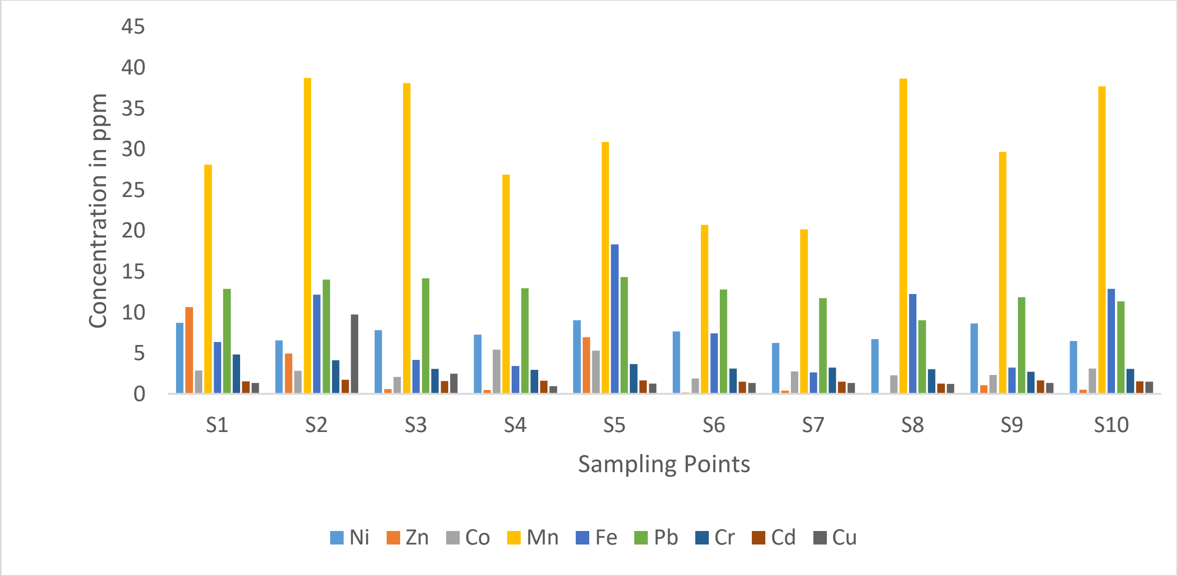

Fig 3.0: **Distribution of Heavy Metal in the Exchangeable Phase with Respect to Sampling Points**

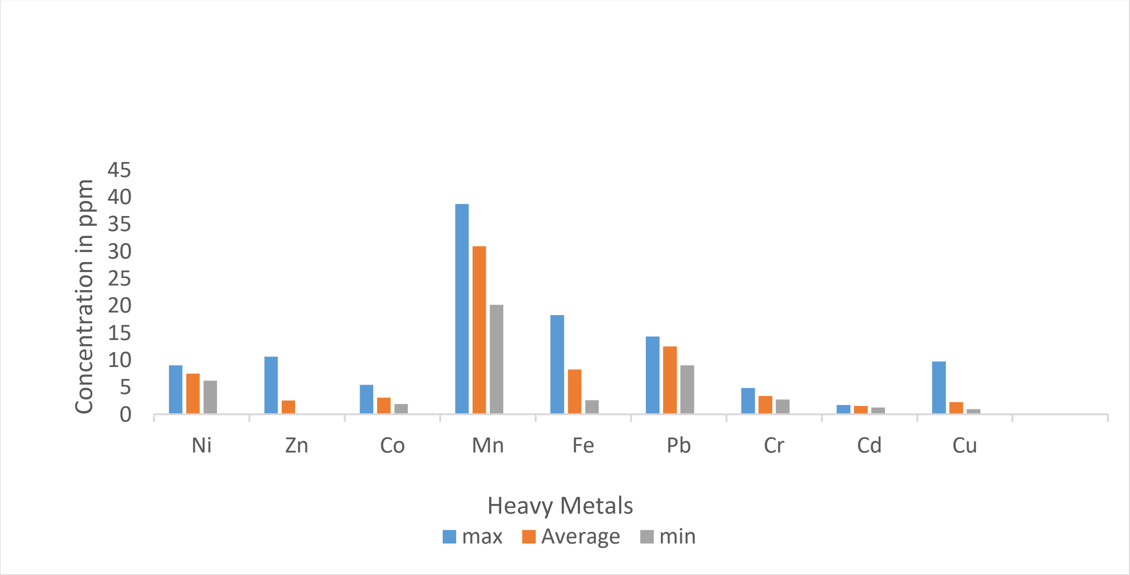

Fig 3.1: Exchangeable Phase with respect to minimum, average and maximum concentration of metals along the sampling points

Carbonate Phase

Table 6 presents the distribution of the maximum, average and minimum concentration of nine heavy metals in the carbonate phase. Average concentration of the heavy metals are in this order: Mn>Fe > Pb >Ni>Zn > Cu>Cr>Co > Cd. The average concentration of Fe is a little higher than Pb in the carbonate phase unlike the exchangeable phase. Likewise, the average concentration of Zn is higher than Cr in the carbonate phase. Except for Zn and Mn the average concentration of all the other heavy metals reduce drastically in the carbonate phase. The following are the ranges of concentration of heavy metals in this phase. Ni (3.25 -6.81), Zn (1.33 – 9.71), Co (0.37 – 1.72), Mn (20.72 – 93.36), Fe (2.08 -11.68), Pb (4.56 – 7.62), Cr (0.12 – 2.3), Cd (0.54 – 0.94), Cu (1.44 - 6.72). Figs 3.2 and 3.3 respectively.

Table 6: Maximum, average and minimum concentration of heavy metals in the carbonate phase

Heavy Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Max conc.(ppm)	6.81	9.71	1.72	93.36	11.68	7.62	2.3	0.94	6.72
Ave conc.(ppm)	5.894	3.37	1.222	66.55	6.632	6.278	1.162	0.743	2.854
Min conc.(ppm)	3.25	1.33	0.37	20.72	2.08	4.56	0.12	0.54	1.44

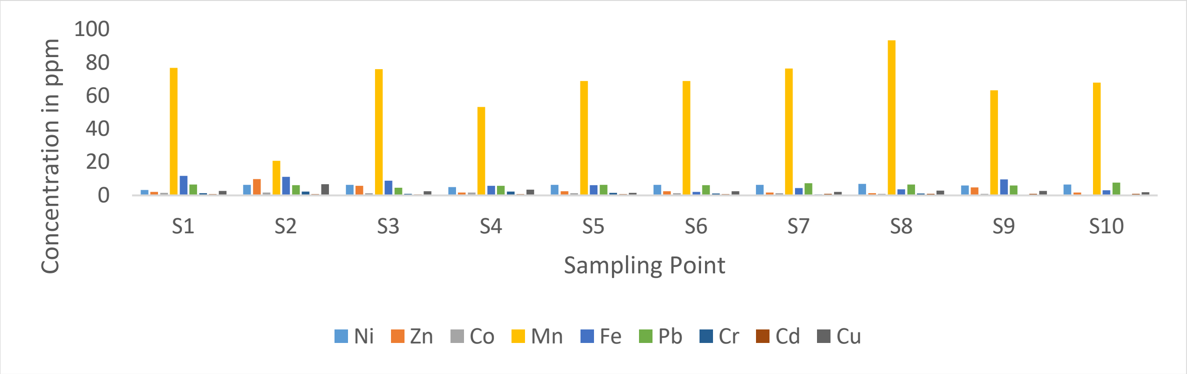

Fig 3.2: Distribution of Heavy Metal in the Carbonate Phase with Respect to Sampling Points

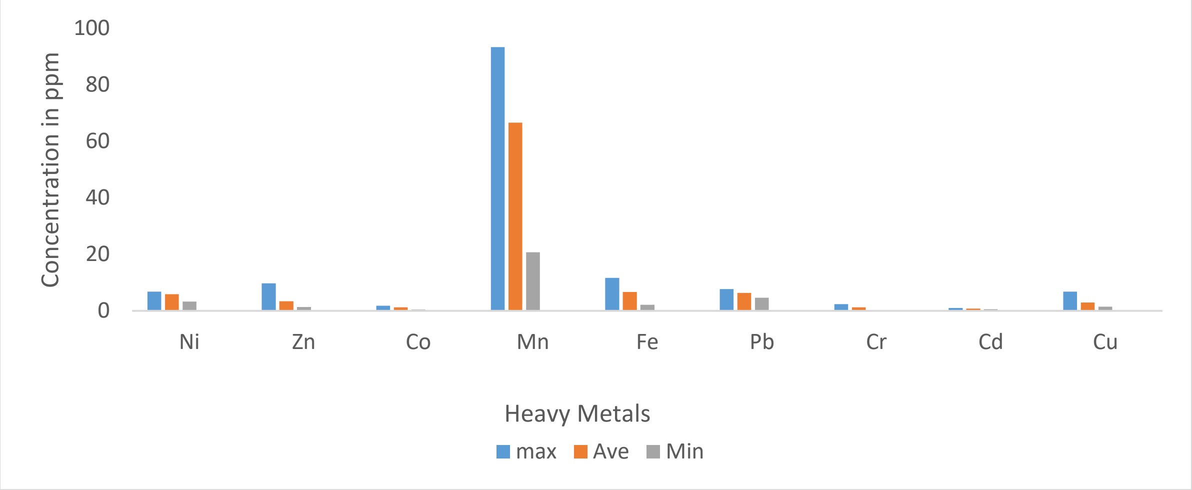

Fig 3.3: Bar chart showing the Carbonate Phase with respect to Maximum, average and Minimum of Heavy Metals Concentration

Reducible Phase

Table 7 presents the distribution of the maximum, average and minimum concentration of nine heavy metals in the Reducible phase. Average concentration of the heavy metals are in this order: Fe> Mn> Zn> Ni> Cu>Pb> Co> Cr> Cd. The concentrations of Fe and Mn has tremendously increased to more than 50% for Mn and 100% for Fe respectively (Figs 3.4 and 3.5). Except for Pb and Cd, the concentration of all other metals increase notably since the previous phase. The following are the ranges of concentration of heavy metal in this phase: Ni (3.66 -13.6), Zn (10.12 – 90.64), Co (1.87 – 9.12), Mn (60.76 – 463.4), Fe (409.89 – 1222.14), Pb (1.34 – 12.8), Cr (0.83 – 6.48), Cd (0.02 – 0.22), Cu (2.23 -12.27).

Table 7: Maximum, Average and Minimum Concentration of heavy metals in the Reducible phase

Heavy Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Max conc.(ppm)	13.6	90.64	9.12	463.4	1222.14	12.8	6.48	0.22	12.27
Ave conc.(ppm)	8.98	35.959	5.093	178.867	735.334	5.165	4.233	0.128	5.99
Min conc.(ppm)	3.66	10.12	1.87	60.76	409.89	1.34	0.83	0.02	2.23

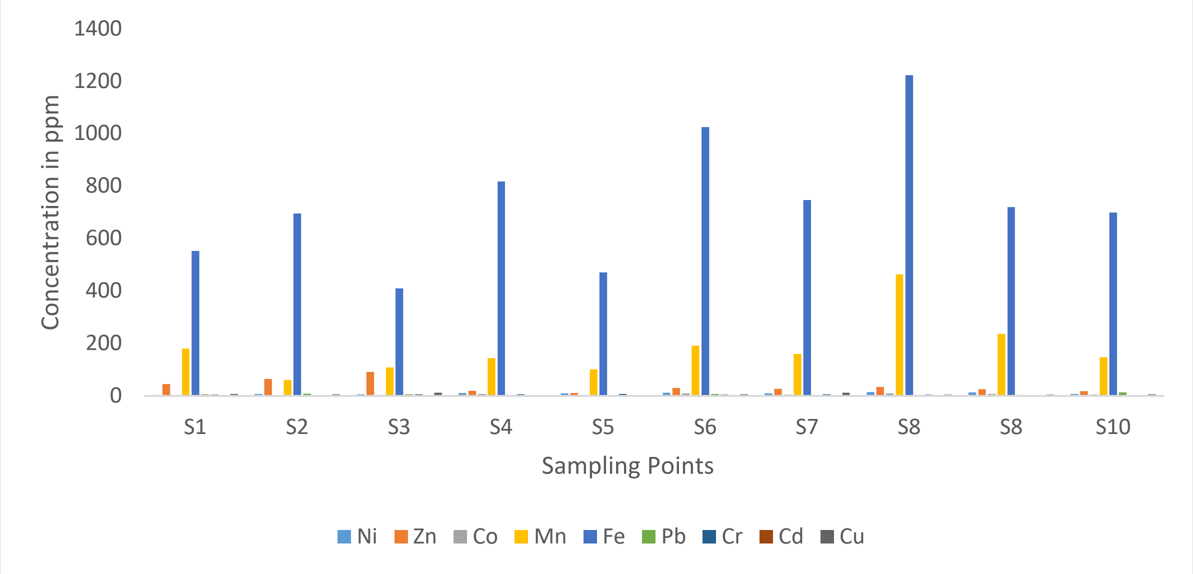

Fig 3.4: Distribution of Heavy Metals in Reducible Phase with Respect to Sampling Points

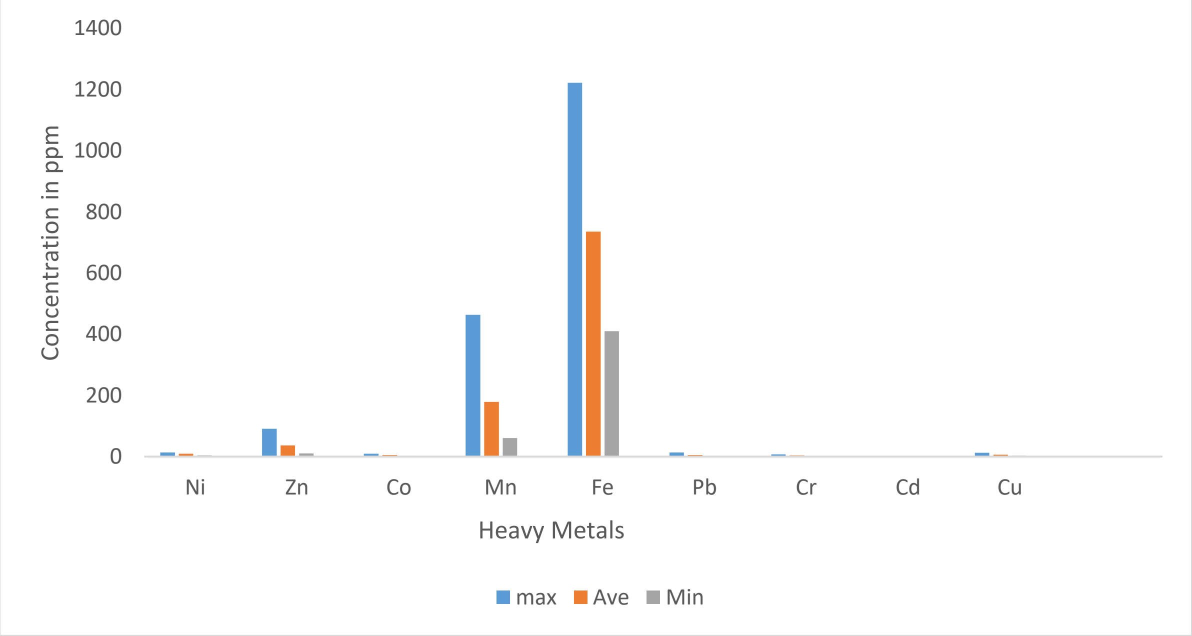

Fig 3.5: Bar chart showing distribution of heavy metals in Reducible phase

Organic Phase

The distribution of the maximum, average and minimum concentration of nine heavy metals in organic phase is presented (Table 8). Average concentration of the heavy metals are in this order: Fe> Cu> Mn> Zn> Ni> Pb> Cr>Cd >Co. The average concentration of Cu over the sampling points in the organic phase increased drastically (figs 3.6 and 3.7)

Table 8: Maximum, average and minimum Concentration of heavy metals in the Organic Phase

Heavy Metals	Ni	Zn	Co	Mn	Fe	Pb	Cr	Cd	Cu
Max conc.(ppm)	16.21	37.34	5.62	47.04	628.59	13.6	9.52	0.62	55.21
Ave conc.(ppm)	9.66	27.75	2.809	31.058	424.267	6.776	6.408	0.26	41.939
Min conc.(ppm)	2.69	15.8	0.74	19.46	245.18	1.29	2.71	0.04	21.26

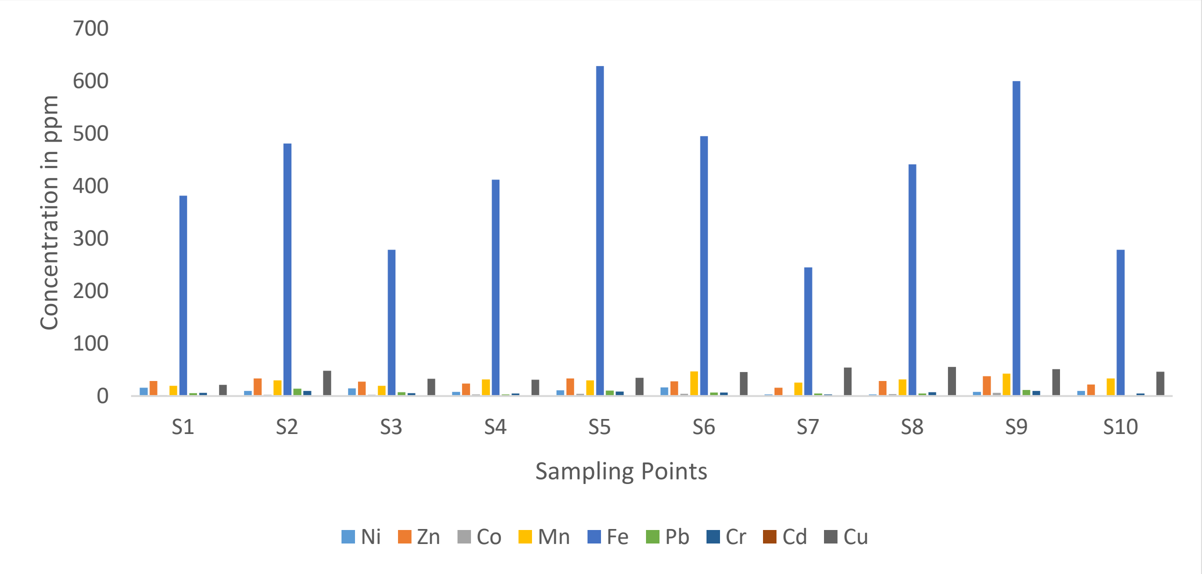

Fig 3.6: Concentration of Heavy Metals in Organic Phase with Respect to Sampling Points

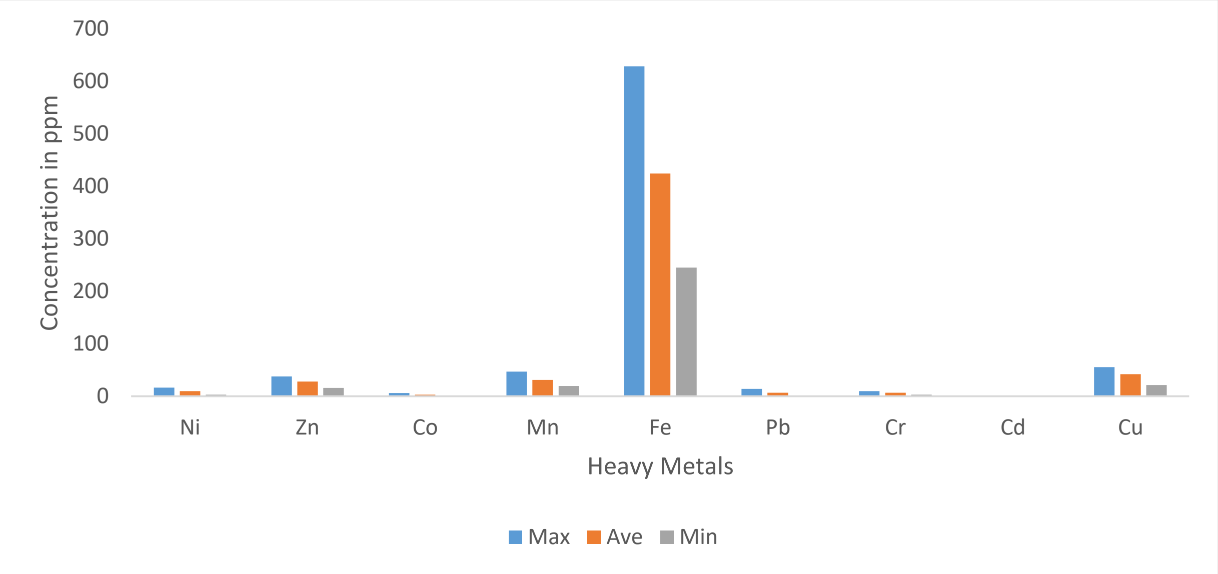

Fig 3.7: Organic Phase with respect Maximum, Average and Minimum Concentration

Residual Phase

Table 9 presents the distribution of the maximum, average and minimum concentration of nine heavy metals in the residual phase. Average concentration of the heavy metals are in this order: Fe> Mn> Zn> Pb> Cu> Cr> Co >Cd Ni. Fe has the highest concentration in this phase (Figs 3.8 and 3.9)

Table 9: Maximum, Average and Minimum Concentration of Heavy metals in the Residual Phase

Toxic Metals	**Ni**	**Zn**	**Co**	**Mn**	**Fe**	**Pb**	**Cr**	**Cd**	**Cu**
Max conc.(ppm)	20.15	127.51	29.65	230.22	4412.61	79.2	40.05	25.1	36.64
Ave conc.(ppm)	16.819	115.647	22.7795	186.498	1925.966	55.963	28.055	22.228	29.434
Min conc.(ppm)	12.66	102.22	2.715	155.65	1000.95	30.3	17.14	17.85	21.16

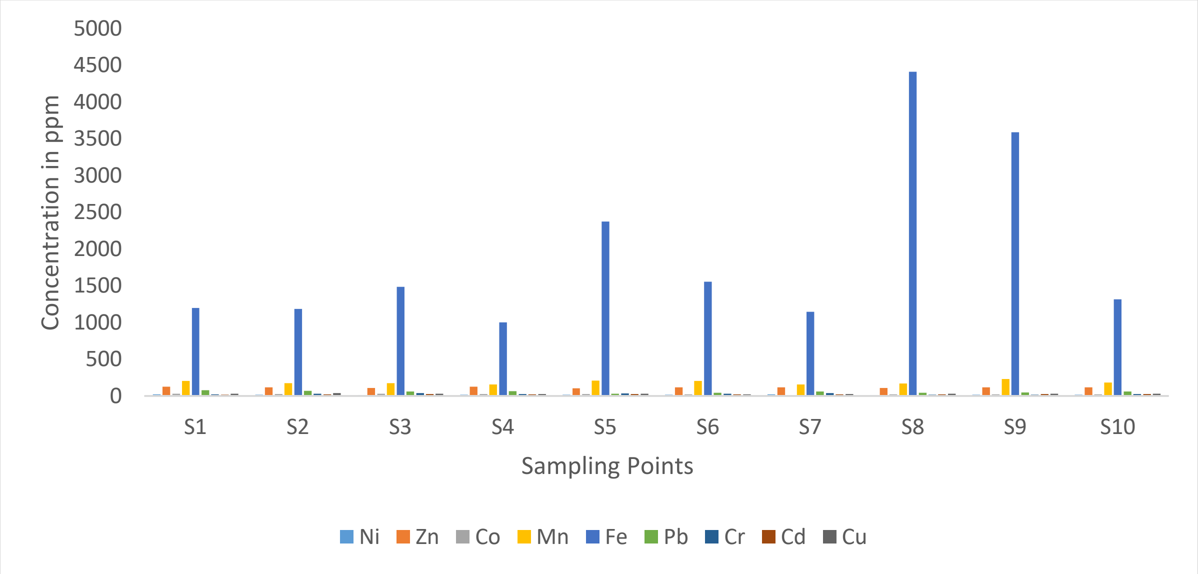

Fig 3.8: Concentration of Heavy Metals in Residual Phase with Respect to Sampling Points

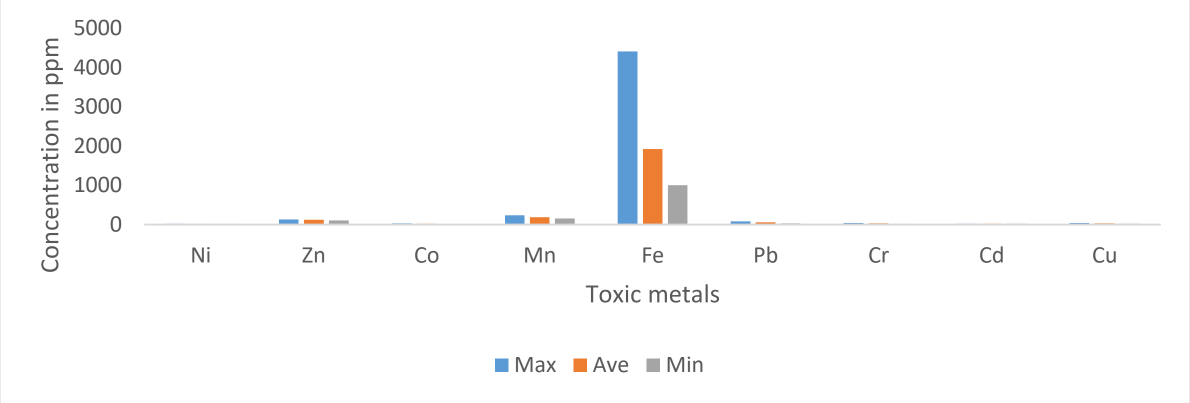

Fig 3.9: Bar chart showing the distribution of heavy Metals in the residual Phase

Analysis of Heavy Metals Across all Phases

Nickel (Ni)

The average concentration of Ni over the sampling points and across all phases is between 5.89ppm to 16.82ppm (Table 10). The concentration increases in this order; Residual>Organic>Reducible>Exchangeable>Carbonate. Ni is predominantly abundant in the residual and organic phases, except for S7 and S8 (Figs 4.0 and 4.01) which have low concentration in the organic phase. This means that it is of mineral origin and do not pose any biological risk. Ni plays an important role in the development of some plants. However, it is not an essential nutrient for human. However, the kidney removes most of the nickel absorbed by humans.

Table 10: Maximum, Average and Minimum Concentration. Of Ni Over all Phases

Phases	Max	Ave	Min
Exchangeable	9.04	7.52	6.24
Carbonate	6.81	5.89	3.25
Reducible	13.6	8.98	3.66
Organic	16.21	9.66	2.69
Residual	20.15	16.82	12.66

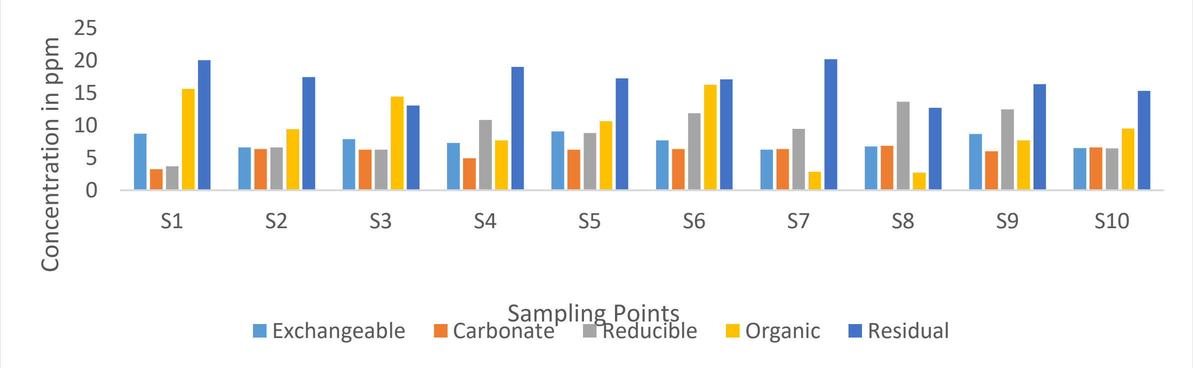

Fig 4.0 Concentration of (Ni) in Respect to Sampling Point and Phases

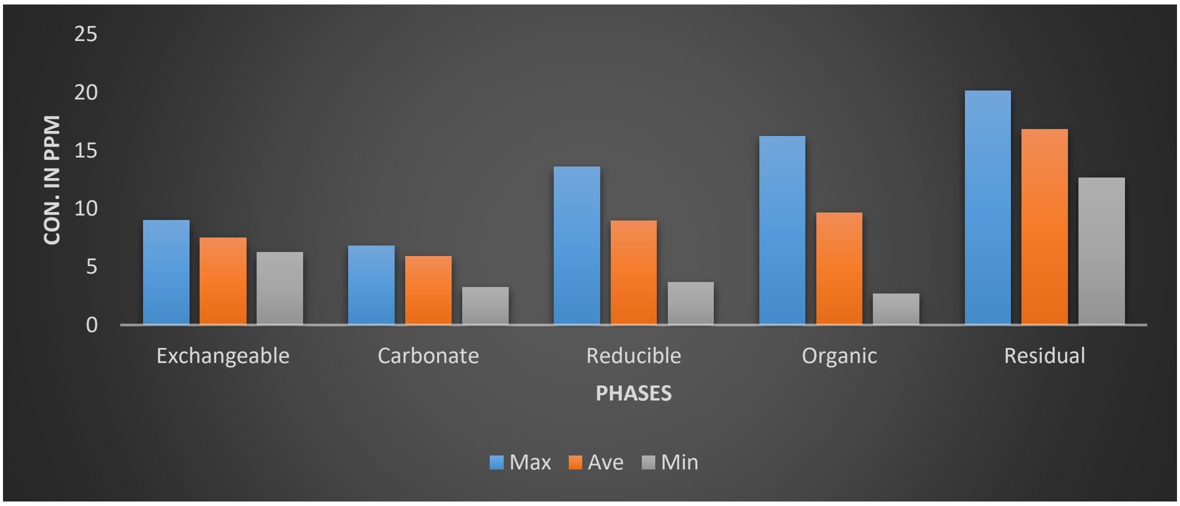

Fig 4.01: Maximum. Average. And Minimum. Concentration of Ni with respect to All Phases

Zinc (Zn)

The average concentration of Zn over the sampling points and across all phases is between 2.59ppm to 115.65ppm (Table 11). The concentration increases in this order; Residual> Reducible>Organic>Carbonate>Exchangeable. Zinc is mostly abundant in the residual phase and S1 and S4, have the highest concentrations while it is of high concentration in other phases. For instance, sampling points such as S3, S4, S6, S7, S8 and S10 showed that it is low in the exchangeable phase. Zinc is an important element in the environment. Its deficiency is connected to many diseases such as delayed sexual maturation, infection susceptibility and diarrhea. Zinc is important for over 300 enzymes and 1000 transcription factors, and is stored and transferred in metallothioneins. Excess zinc is however toxic to plants. Fishes cannot tolerate the amount of Zn, as do plants (Rahaman, 2011). Excess zinc inhibits calcium uptake in fish, which can be deadly (Figs 4.2 and 4.2.1). In this study, it is discovered that the concentration of Zn exceeded the normal concentration expected to be in a sediment hence this necessitates prompt measures to curtail its menace.

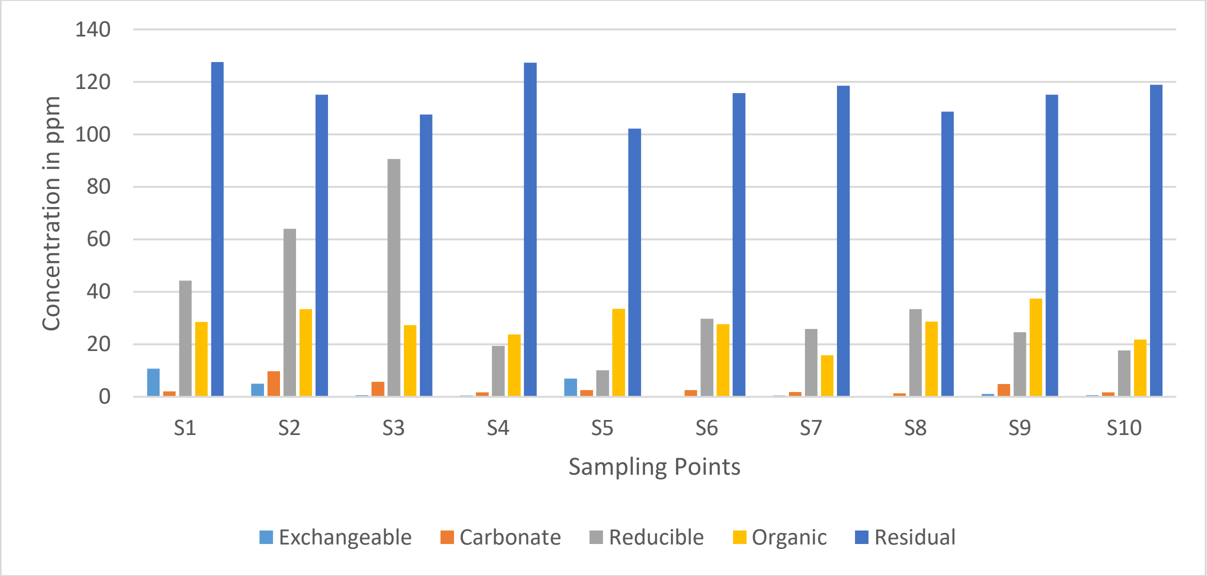

Fig 4.2: Concentration of (Zn) in Respect to Sampling Point and Phases

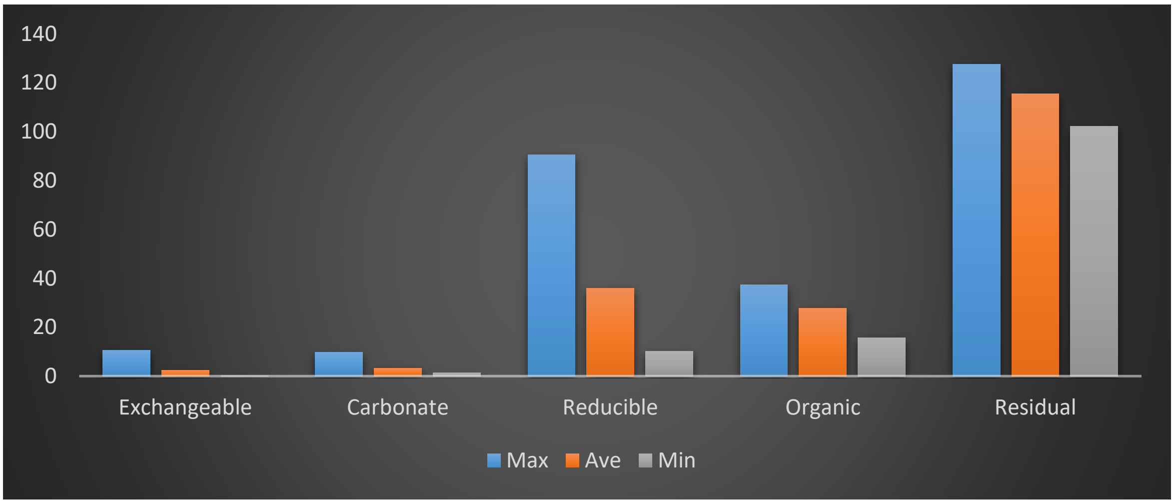

Fig 4.2.1: Maximum, average and minimum concertation of zinc with respect all the Phases

Cobalt (Co)

The average concentration of Co over the sampling points and across all phases is between 1.22ppm to 22.77ppm respectively (Table 11). The concentration increases in this order; Residual> Reducible>Exchangeable>Carbonate>Organic. Co is mostly abundant in the Residual phase and relatively low in other phases with S1 having the highest concentration (figs 4.3 and 4.31). Co is always involved in photosynthesis and nitrogen fixation detected in most ocean basins and a limiting micronutrient for phytoplanktons and cyanobacteria. P value of 5.71E-17 in analysis of variance indicated that there is a significant difference from one phase to another.

Table 11: Maximum, Average and Minimum concentration of Co over all the Phases

Phases	Max	Ave	Min
Exchangeable	5.42	3.09	1.9
Carbonate	1.72	1.22	0.37
Reducible	9.12	5.09	1.87
Organic	5.62	2.80	0.74
Residual	29.65	22.77	2.72

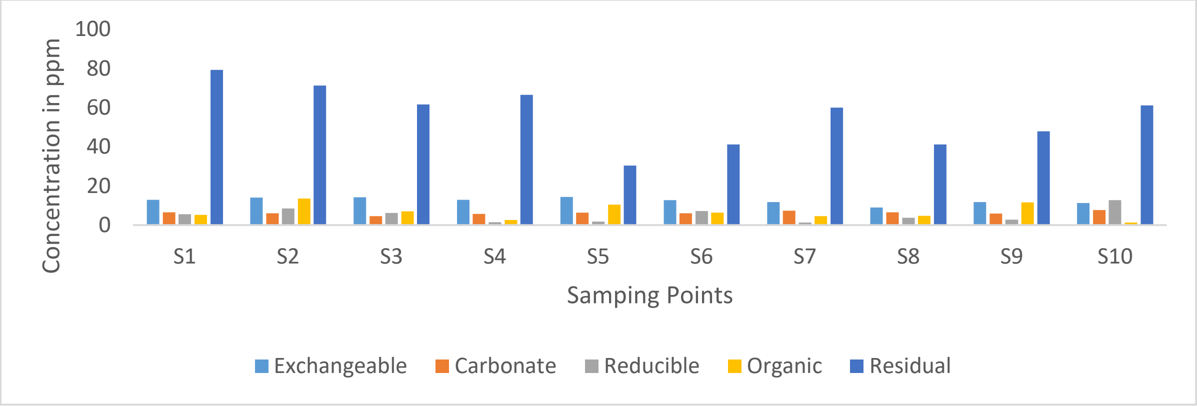

Fig 4.3 Concentration of (Co) in Respect to Sampling Point and Phases

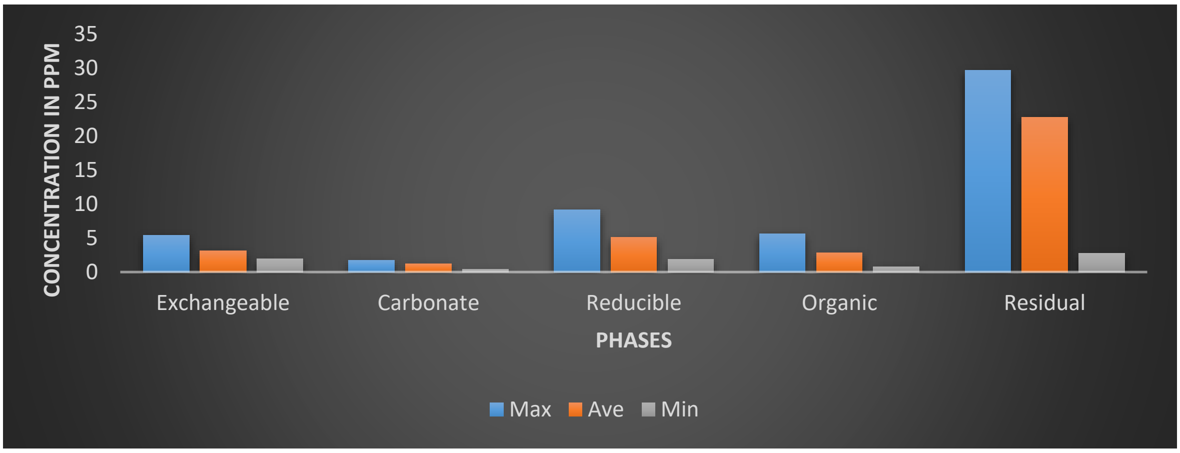

Fig 4.3.1 Maximum, Average and Minimum Concentration of Co over all the Phases

Manganese (Mn)

The average concentration of Mn over the sampling points and across all phases is between 30.95ppm to 186.49ppm (Table 12). The concentration increases in this order; Residual> Reducible> Carbonate Organic>Exchangeable. Except for sampling point S8, which has an extremely high concentration in the reducible phase, Mn is evenly abundant in the residual phase followed by the reducible phase. In the aquatic bodies, many enzymatic systems need Mn to function, but in high levels, Mn can become toxic. At level of 500ppm Mn is dangerous to life, therefore Mn in the study area does not pose any threat to lives in the location. 3.2E-10 P value of annova indicates that there is significant difference between the five phases. (figs 4.4 and 4.4.1)

Table 12: Maximum, Average and Minimum concentration of Mn over all the Phases

Phases	Max	Ave	Min
Exchangeable	38.72	30.95	20.16
Carbonate	93.36	66.55	20.72
Reducible	463.4	178.86	60.76
Organic	47.04	31.06	19.46
Residual	230.22	186.49	155.65

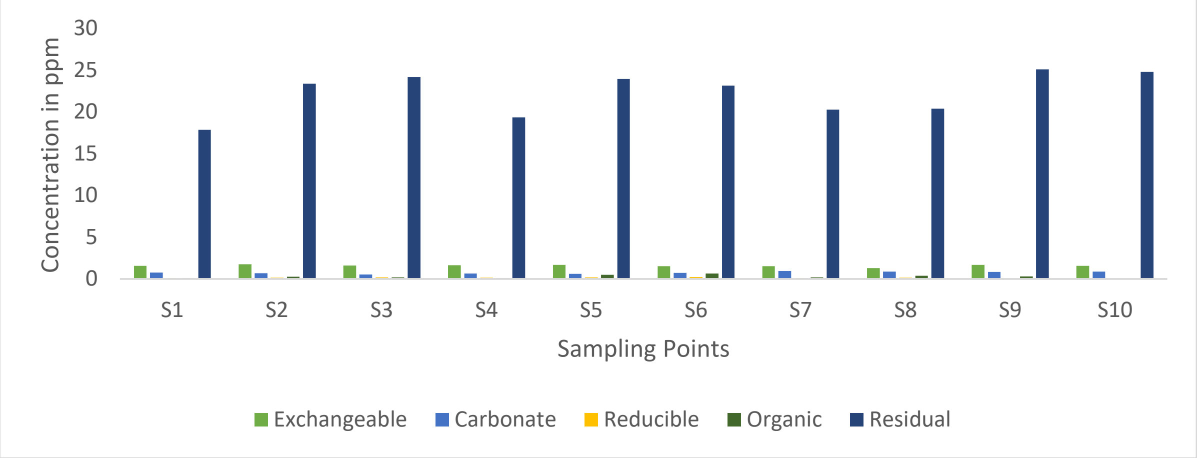

Fig 4.4 Concentration of (Mn) in Respect to Sampling Point and Phases

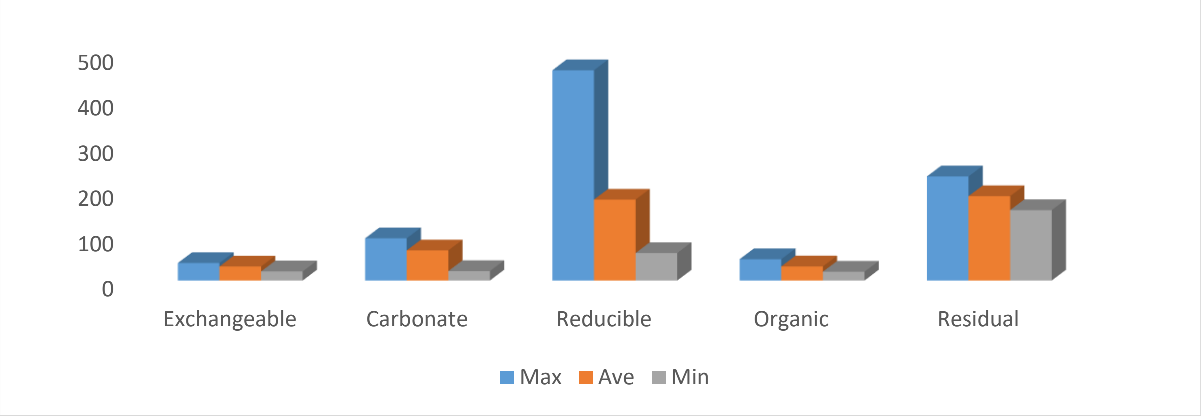

Fig 4.4.1: Maximum, Average and Minimum Concentration of Mn over all the Phases

Iron (Fe)

According to Table 13, the average concentration of Fe over the sampling points and across all phases is between 6.632ppm to 1925.96ppm. The concentration increases in this order; Residual> Reducible > Organic>Exchangeable>Carbonate. (Figs 4.5 and 4.5.1). Iron is extremely low in the carbonate and exchangeable phase but very high in the residual and also present in the reducible phase. Iron accumulation poses a problem for aerobic organisms because ferric iron is poorly soluble near neutral ph. Iron plays an essential role in marine systems and can act as a limiting nutrient for planktonic activity. Its excess may lead to a decrease in growth rates in phytoplantonic organisms. 5.6E-10 P value of ANOVA indicates that there is significant difference between the five phases.

Table 13: Maximum, Average, minimum concentration of Fe over the mineralogical Phases

Phases	Max	Ave	Min
Exchangeable	18.32	8.29	2.64
Carbonate	11.68	6.632	2.08
Reducible	1222.14	735.33	409.89
Organic	628.59	424.27	245.18
Residual	4412.6	1925.96	1000.95

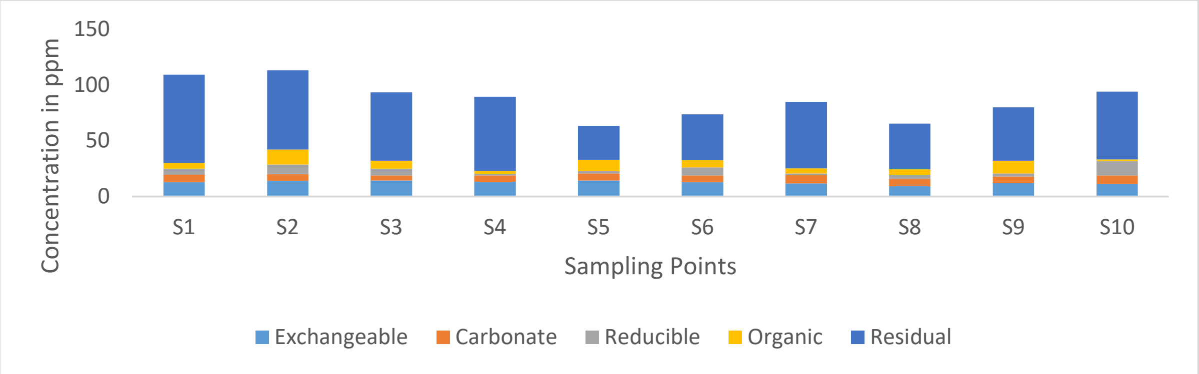

Fig 4.5: Concentration of (Fe) in Respect to Sampling Point and Phases

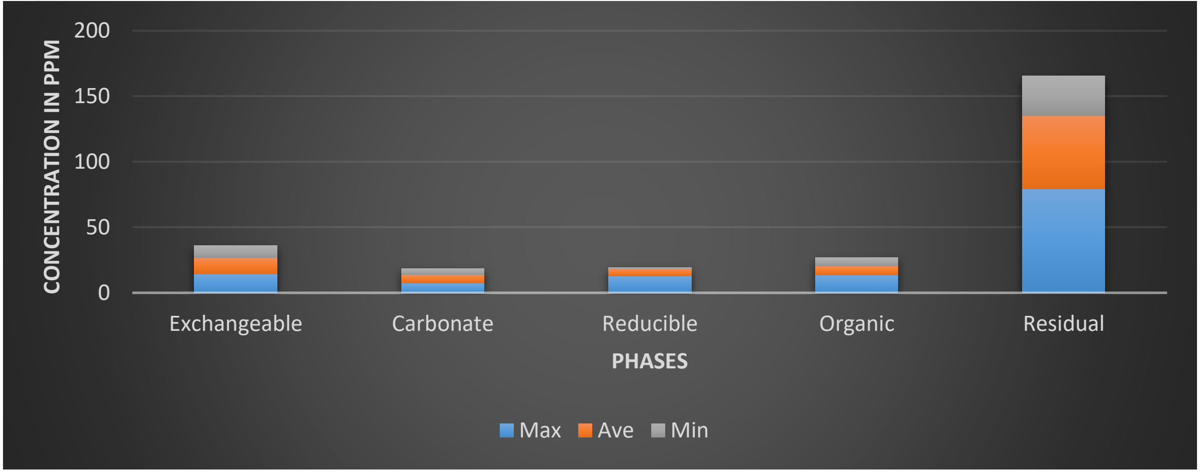

Fig 4.5.1 Maximum, Average and Minimum Concentration of Fe over all the Phases

Lead (Pb)

Table 14 presents the average concentration of Pb over the sampling points and across all phases to be between 5.17ppm to 55.96ppm. The concentration increases in this order; Residual> Exchangeable> Organic >Carbonate>Reducible (figs 4.6 and 4.6.1). Pb is more abundant in the Residual phase and has no confirmed safe level of exposure. Even at level considered to pose little or no risk, Pb may cause adverse mental health outcomes. Pb is a highly poisonous metal both inhaled and swallowed, causing great damage to almost every organs and systems in the human body. High level of Pb causes lead poisoning while low levels cause increase susceptibility to terminal diseases. High concentration of lead has the capacity to inhibit photosynthesis. Bioaccumulation of Pb poses a serious hazard to fishes and other sea mammals. From the results obtained in this study, the concentration is within the residual phase which means that Pb is not bioavailable and will therefore tend not to remobilize. 9.5E-21 P value of ANOVA indicated that there is significant difference between five phases.

Table 14: Maximum, Average and Minimum concentration of Pb over all the Phases

Phases	Max	Ave	Min
Exchangeable	14.32	12.51	9.04
Carbonate	7.62	6.28	4.56
Reducible	12.8	5.17	1.34
Organic	13.6	6.78	6.41
Residual	79.2	55.96	30.3

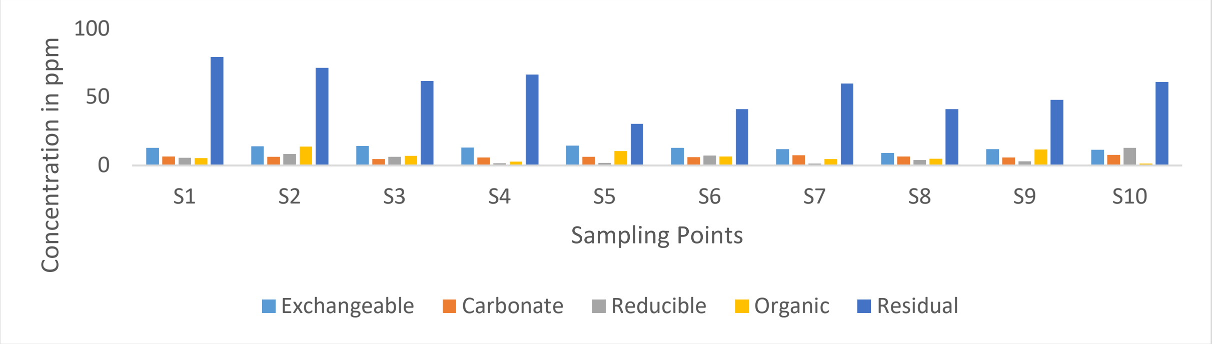

Fig 4.6: Concentration of (Pb) in Respect to Sampling Point and Phases

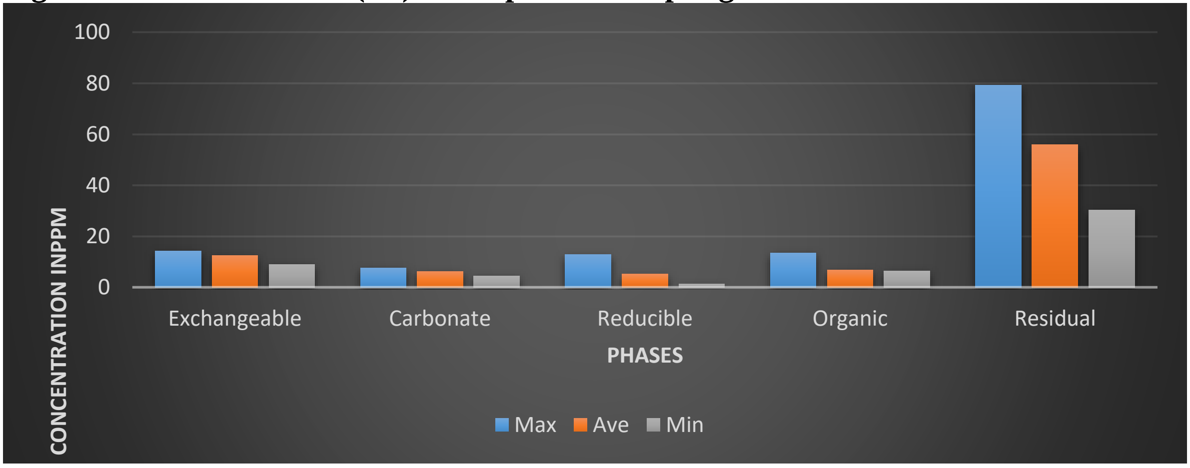

Fig 4 .6.1: Maximum, Average and Minimum Concentration of Pb over all the Phases

Chromium (Cr)

The result of the average concentration of Cr over the sampling points and across all phases is between 0.26ppm to 28.06ppm (Table 15). The concentration increases in this order; Residual >Reducible>Exchangeable>Carbonate>Organic. Cr is more abundant in the residual phase and extremely low in the organic phase (figs 4.7 and 4.7.1). Chromium is highly toxic to fish because it is easily absorbed across gills, readily enters blood circulation, and crosses cell membrane and bio concentrate up the food chain. Acute and chronic exposure to chromium affects fish behavior, physiology, reproduction and survival. Toxicity ranges between 50 and 150 ppm (Katz and Salem 1992). 1.07E-20 P value of ANOVA indicates that there is significant difference between the five phases.

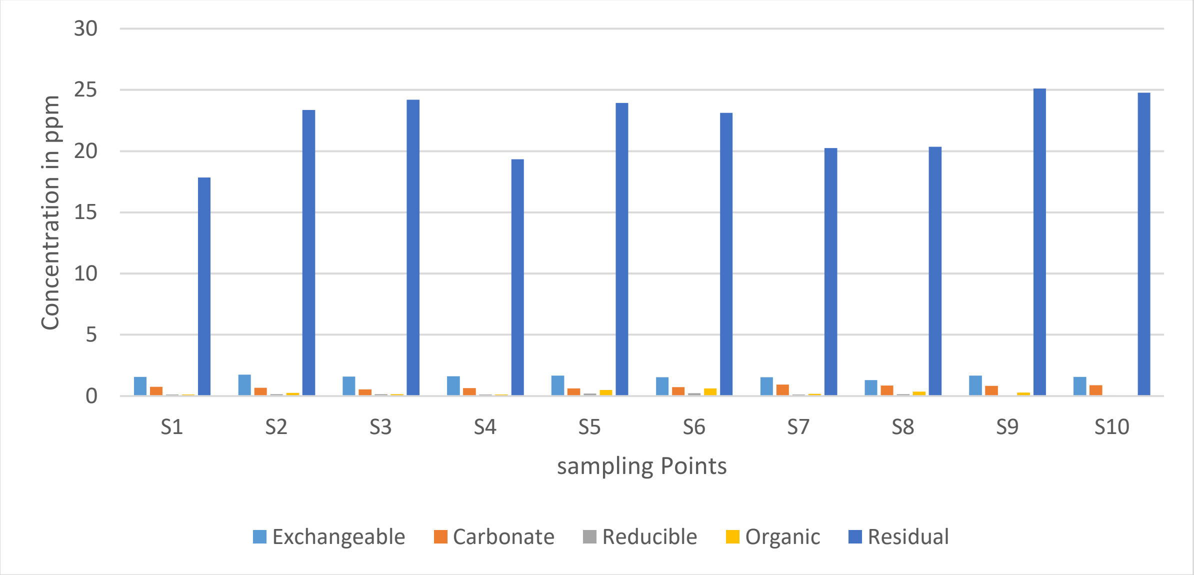

Fig 4.7: Concentration of (Cr) in Respect to Sampling Point and Phases

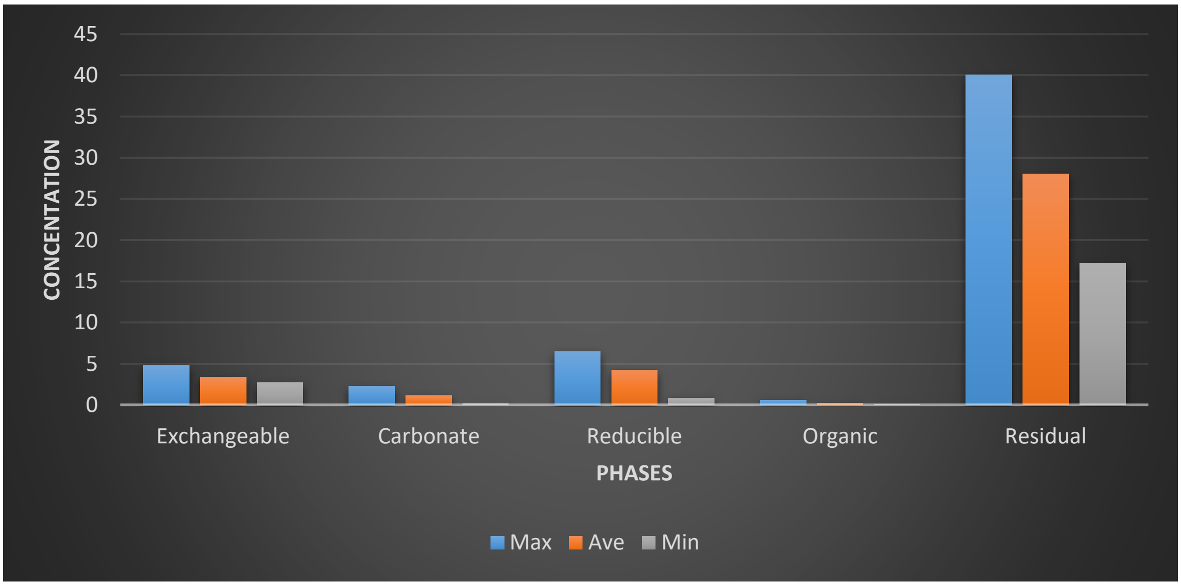

Fig 4.7.1: Maximum, Average and Minimum Concentration of Cr with respect to the mineralogical Phases

Cadmium (Cd)

Table 16 revealed that the average concentration of Cd over the sampling points and across all phases is between 0.13ppm to 22.23ppm. The concentration increases in this order; Residual> Exchangeable> Carbonate>Organic > Reducible. Cd is abundant in the residual and present in an extremely low concentration in other phases (figs 4.8 and 4.8.1) respectively. Cd is considered an environmental pollutant that causes health hazards to living organisms. Anthropogenic sources includes fossils fuel combustion and fertilizers. Cd exposure is associated with a large number of illnesses including kidney disease, early atherosclerosis, hypertension and cardiovascular diseases. 5.11E-40 P value of annova indicates that there is significant difference between five phases. Cd in this location must be monitored because it has good percentage of its concentration in the exchangeable phase.

Table 16: Maximum, Average and Minimum Concentration of Cd over all the Phases

Phases	Max	Ave	Min
Exchangeable	1.74	1.57	1.29
Carbonate	0.94	0.74	0.54
Reducible	0.22	0.13	0.02
Organic	0.62	0.26	0.04
Residual	25.1	22.23	17.85

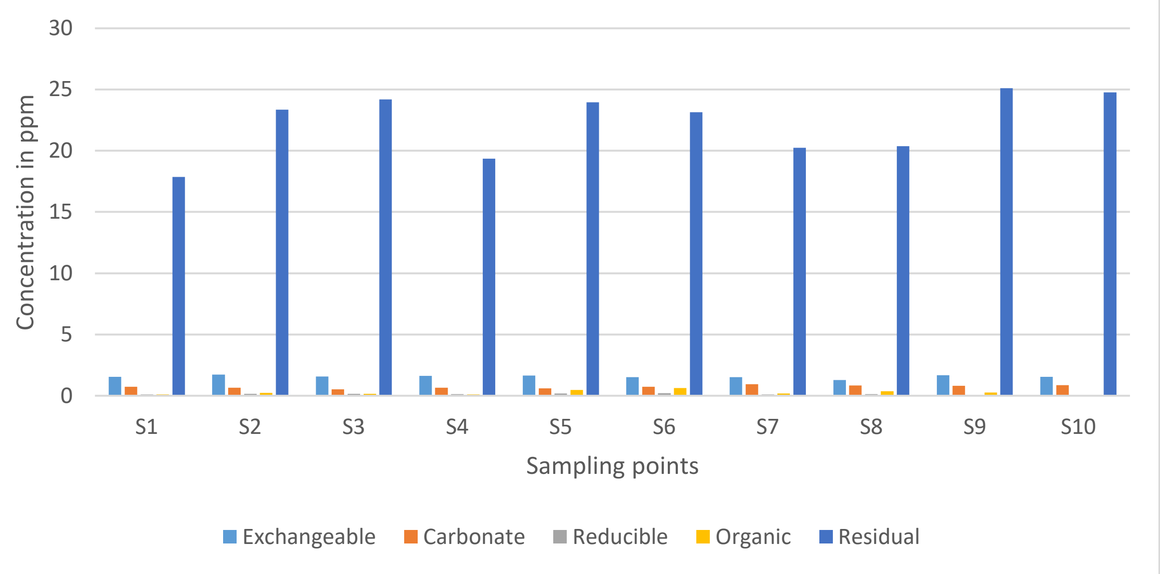

Fig 4.8 Concentration of (Cd) with Respect to Sampling Point and Phases

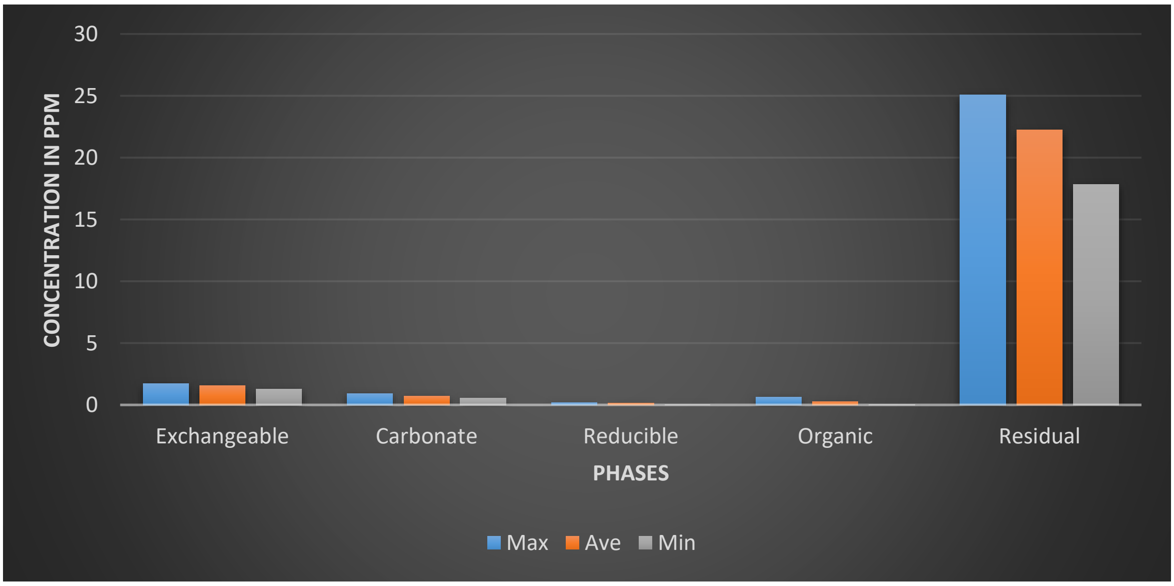

Fig 4.81: Maximum, Average and Minimum Concentration of Cd with respect to mineralogical Phases

Cupper (Cu)

The average concentration of Cu over the sampling points and across all phases is between 2.26ppm to 41.94ppm (Table 17). The concentration increases in this order; Organic> Residual > Carbonate>Reducible. Cu is more abundant in the organic phase (figs 4.9 and 4.9.1). Due to its role in facilitating iron uptake, Cu deficiency can produce anemia-like systems, neutropenia, bone abnormalities and impaired growth. 2.4E-27 P value of annova indicate that there is significant difference between the five phases.

Table 17: Maximum, Average and Minimum concentration of Cu over all the Phases

Phases	Max	Ave	Min
Exchangeable	9.76	2.26	0.96
Carbonate	6.72	2.85	1.44
Reducible	12.27	5.99	2.33
Organic	55.21	41.94	21.26
Residual	36.64	29.43	21.16

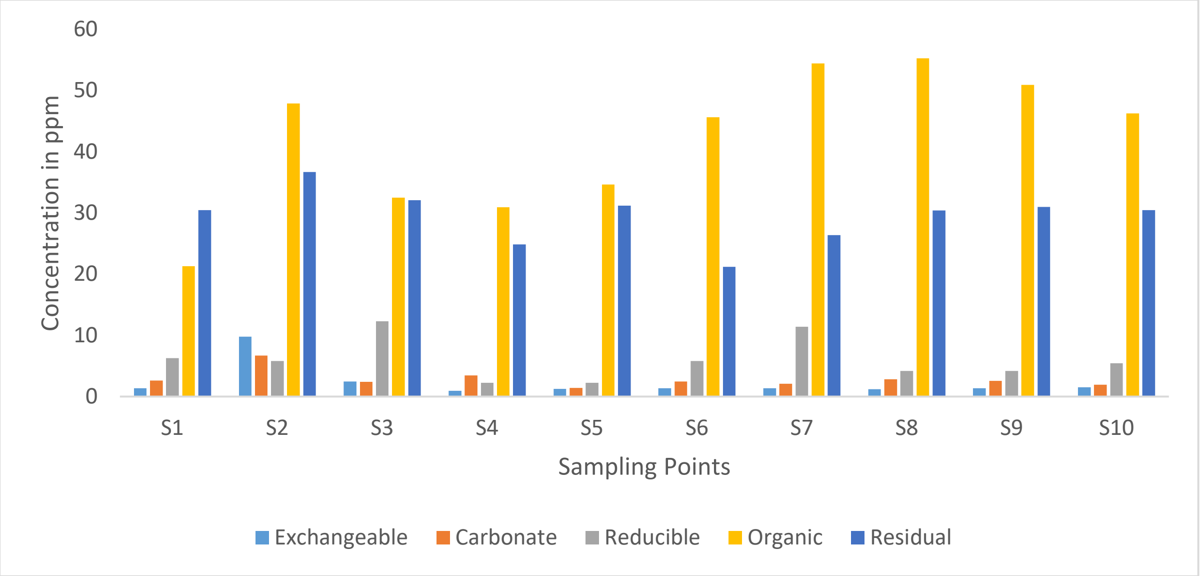

Fig 4.9: Concentration of (Cu) in Respect to Sampling Point and Phases

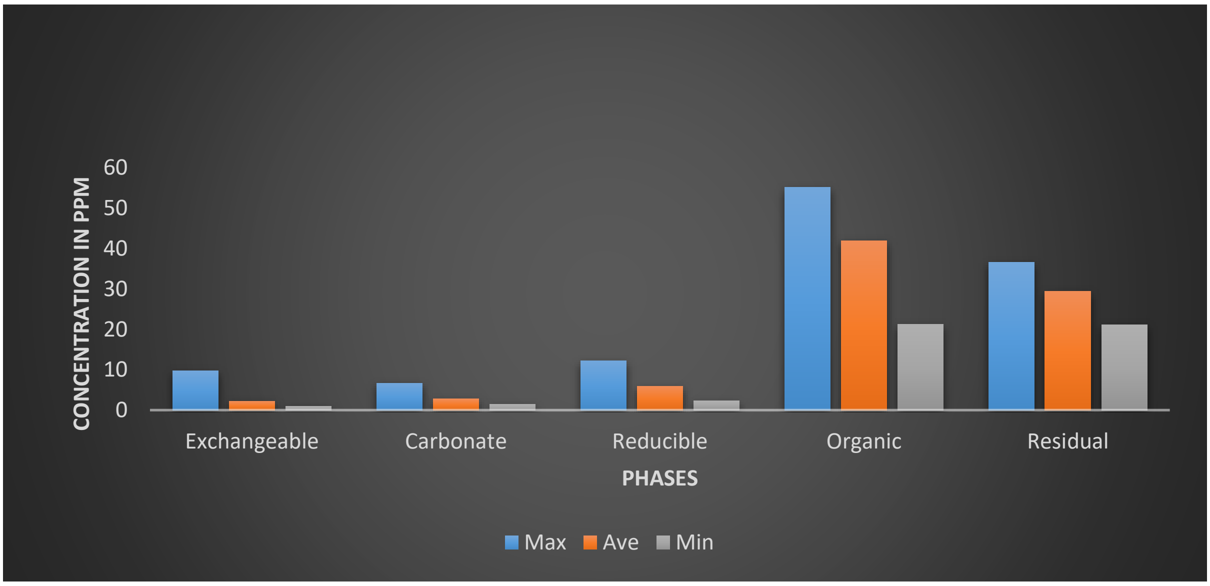

Fig 4.9.1 **Max, Ave and min Concentration of Cu with respect to mineralogical Phases**

Mobility Factor across the Metal fractional phases

The mobility factors of the various heavy metals analyzed is presented in Tables 18-26. It can be deduced that Cd has the highest potential to remobilize across all sampling points because of its high mobility factor (Fig.5.0).

Table 18: Mobility Factor of Ni

Sample Points	F1	F2	F3	F4	F5	Mobility Factor (%)
S1	8.72	3.25	3.66	15.6	20.01	3.65
S2	6.56	6.32	6.57	9.39	17.42	7.04
S3	7.84	6.24	6.22	14.41	13.05	6.76
S4	7.28	4.88	10.8	7.67	19	7.21
S5	9.04	6.24	8.81	10.64	17.2	7.38
S6	7.68	6.32	11.86	16.21	17.05	4.63
S7	6.24	6.32	9.43	2.85	20.15	15.82
S8	6.72	6.81	13.6	2.69	12.66	22.11
S9	8.64	6	12.44	7.66	16.35	9.61
S10	6.48	6.56	6.41	9.48	15.3	7.93

Table 19: Mobility Factor of Zn

Sampling Points	F1	F2	F3	F4	F5	Mobility Factor (%)
S1	10.64	2.07	44.26	28.51	127.51	0.34
S2	4.96	9.71	64.02	33.42	115.05	0.37
S3	0.59	5.71	90.64	27.22	107.57	0.21
S4	0.48	1.66	19.34	23.72	127.25	0.07
S5	6.96	2.46	10.12	33.51	102.22	0.27
S6	0.16	2.46	29.74	27.62	115.71	0.08
S7	0.41	1.74	25.86	15.8	118.55	0.11
S8	0.07	1.33	33.34	28.58	108.58	0.04
S9	1.07	4.85	24.64	37.34	115.09	0.14
S10	0.53	1.71	17.63	21.78	118.94	0.09

Table 20: Mobility Factor of Co

Sampling Points	F1	F2	F3	F4	F5	Mobility Factor (%)
S1	2.88	1.46	3.34	1.82	29.35	7.10
S2	2.84	1.68	1.87	2.15	27.25	6.95
S3	2.09	1.26	3.38	2.42	29.65	4.26
S4	5.42	1.72	6.92	2.96	25.25	8.04
S5	5.31	1.34	3.24	4.18	26.75	5.46
S6	1.9	1.26	8.76	4.04	21.08	3.25
S7	2.75	1.29	4.12	0.98	2.715	37.33
S8	2.3	0.95	9.12	3.18	23.18	3.77
S9	2.34	0.89	6.28	5.62	21.41	2.48
S10	3.13	0.37	3.9	0.74	21.16	15.17

Table 21: Mobility Factor of Mn

Sampling Points	**F1**	**F2**	**F3**	**F4**	**F5**	**Mobility Factor (%)**
S1	28.08	76.88	180.21	19.52	205.18	2.44
S2	38.72	20.72	60.76	30.01	175.46	1.10
S3	38.08	76.08	107.55	19.46	175.23	3.14
S4	26.88	53.21	143.81	31.74	155.82	1.54
S5	30.88	68.8	100.26	29.73	210.02	1.54
S6	20.72	68.82	190.62	47.04	205.11	0.90
S7	20.16	76.48	158.86	25.67	155.65	2.27
S8	38.64	93.36	463.4	31.4	171.45	2.20
S9	29.68	63.23	236.6	42.81	230.22	0.91
S10	37.68	67.92	146.6	33.2	180.84	1.68

Table 22: Mobility Factor of Fe

Sampling Points	F1	F2	F3	F4	F5	Mobility Factor (%)
S1	6.38	11.68	552.04	381.62	1196.8	0.003
S2	12.16	11.22	694.3	481.08	1185.45	0.004
S3	4.16	8.88	409.89	278.84	1484.5	0.003
S4	3.44	5.76	816.28	412.18	1000.95	0.002
S5	18.32	6.08	470.9	628.59	2372.65	0.001
S6	7.44	2.08	1023.8	495.08	1555.3	0.001
S7	2.64	4.46	746.5	245.18	1145.15	0.002
S8	12.24	3.52	1222.14	441.42	4412.61	0.0008
S9	3.24	9.68	718.87	600	3591.2	0.0005
S10	12.88	2.96	698.62	278.68	1315.05	0.004

Table 23: Mobility Factor of Pb

Sampling Points	F1	F2	F3	F4	F5	Mobility Factor(%)
S1	12.88	6.56	5.49	5.22	79.2	4.43
S2	14.01	6.12	8.44	13.6	71.15	2.02
S3	14.16	4.56	6.25	7.02	61.6	4.09
S4	12.96	5.76	1.56	2.68	66.4	9.44
S5	14.32	6.32	1.88	10.42	30.3	6.10
S6	12.8	6.08	7.21	6.46	41.1	6.47
S7	11.76	7.36	1.34	4.64	59.85	6.41
S8	9.04	6.56	3.81	4.82	41.18	7.15
S9	11.84	5.84	2.87	11.61	47.85	3.06
S10	11.36	7.62	12.8	1.29	61	17.18

Table 24: Mobility factor of Cr

Sampling Points	F1	F2	F3	F4	F5	Mobility Factor(%)
S1	4.85	1.34	4.76	5.84	22.05	4.43
S2	4.12	2.3	2.14	9.36	28.54	2.32
S3	3.08	0.96	6.24	5.12	38.35	1.95
S4	2.96	2.24	5.26	4.5	26.41	4.02
S5	3.66	1.54	6.48	8.63	32.56	1.77
S6	3.11	1.17	4.44	6.58	29.95	2.07
S7	3.22	0.51	5.68	2.71	40.05	3.16
S8	3.04	1.12	3.94	7.14	17.14	3.18
S9	2.72	0.32	2.56	9.52	18.05	1.71
S10	3.06	0.12	0.83	4.68	27.45	2.40

Table 25: Mobility factor of Cd

Sampling Points	F1	F2	F3	F4	F5	Mobility Factor (%)
S1	1.55	0.75	0.12	0.11	17.85	52.46
S2	1.74	0.66	0.15	0.25	23.35	28.61
S3	1.58	0.54	0.16	0.16	24.19	34.46
S4	1.62	0.65	0.13	0.12	19.34	48.08
S5	1.66	0.61	0.19	0.48	23.94	16.27
S6	1.52	0.73	0.22	0.62	23.13	13.38
S7	1.52	0.94	0.11	0.18	20.25	39.58
S8	1.29	0.85	0.14	0.36	20.36	22.26
S9	1.67	0.82	0.02	0.28	25.1	26.10
S10	1.55	0.88	0.04	0.04	24.77	70.21

Table 26: Mobility factor of Cu

Sampling Points	F1	F2	F3	F4	F5	Mobility Factor(%)
S1	1.36	2.64	6.29	21.26	30.43	0.60
S2	9.76	6.72	5.81	47.83	36.64	0.92
S3	2.48	2.41	12.27	32.49	32.04	0.46
S4	0.96	3.44	2.23	30.88	24.82	0.56
S5	1.28	1.44	2.26	34.64	31.18	0.25
S6	1.36	2.48	5.81	45.62	21.16	0.39
S7	1.36	2.08	11.4	54.4	26.34	0.24
S8	1.22	2.85	4.2	55.21	30.36	0.24
S9	1.36	2.56	4.21	50.86	30.95	0.25
S10	1.52	1.92	5.42	46.2	30.42	0.24

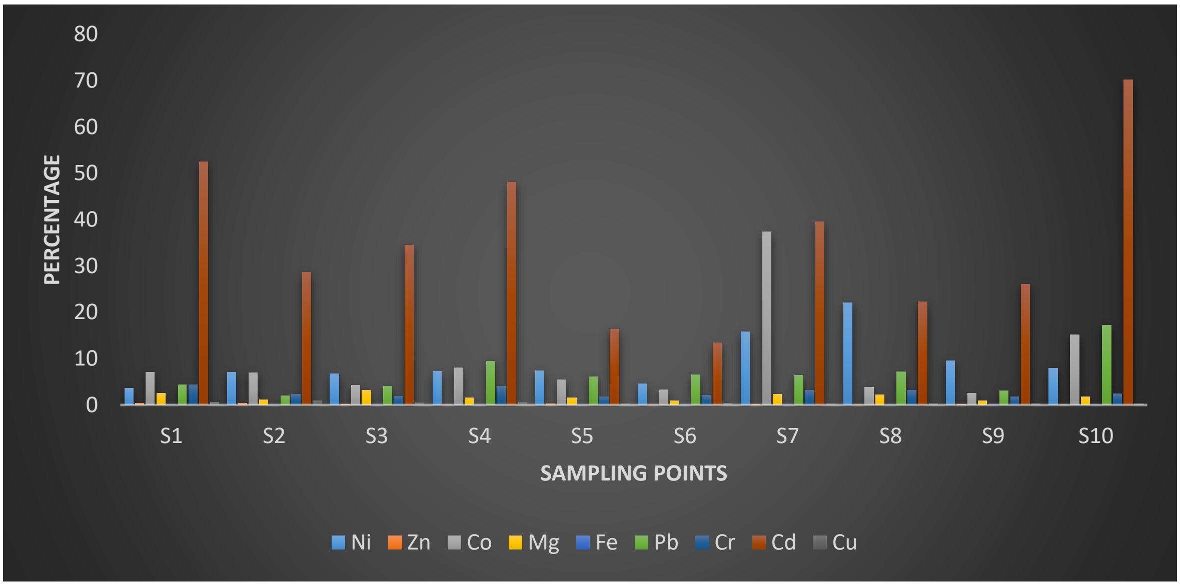

Fig 5.0: Mobility factor chart of the various heavy metals across the sampling points

Statistical Analysis

Analysis of Variance (ANNOVA)

The analysis of variance using single factor for the geochemical phases between and within the geochemical groups are presented in Tables 27-35 using SPSS IBM 15. The results showed that there are no significant variations between the metals except cadmium but there is significant variations between and within the groups of geochemical speciation.

Table 27: Ni

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeble Phase	10	75.2	7.52	1.052444
Carbonate Phase	10	58.94	5.894	1.121849
Reducible Phase	10	89.8	8.98	10.38747
Organic Phase	10	96.6	9.66	22.74793
Residual Phase	10	168.19	16.819	6.736054

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	704.1037	4	176.0259	20.93267	8.39E-10	2.578739
Within Groups	378.4117	45	8.40915			
Total	1082.515	49				

Table 28: Zn

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	25.87	2.587	13.50333
Carbonate Phase	10	33.7	3.37	7.078444
Reducible Phase	10	359.59	35.959	600.1978
Organic Phase	10	277.5	27.75	39.28258
Residual Phase	10	1156.47	115.647	65.64078

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	85872.09	4	21468.02	147.9119	2.82E-25	2.578739
Within Groups	6531.326	45	145.1406			
Total	92403.41	49				

Table 29: Co

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	30.96	3.096	1.575938
Carbonate Phase	10	12.22	1.222	0.160662
Reducible Phase	10	50.93	5.093	6.289912
Organic Phase	10	28.09	2.809	2.294099
Residual Phase	10	227.795	22.7795	60.26222

ANOVA

Source of Variation	*SS*	*Df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3188.203	4	797.0506	56.46207	5.71E-17	2.578739
Within Groups	635.2455	45	14.11657			
Total	3823.448	49				

Table 30: Mn

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	309.52	30.952	51.45948
Carbonate Phase	10	665.5	66.55	368.4856
Reducible Phase	10	1788.67	178.867	12479.66
Organic Phase	10	310.58	31.058	77.58173
Residual Phase	10	1864.98	186.498	617.8134

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	243340.5	4	60835.14	22.37409	3.2E-10	2.578739
Within Groups	122355	45	2719			
Total	365695.5	49				

Table 31: Fe

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	82.9	8.29	28.29149
Carbonate Phase	10	66.32	6.632	12.28304
Reducible Phase	10	7353.34	735.334	59956.47
Organic Phase	10	4242.67	424.267	17505.33
Residual Phase	10	19259.66	1925.966	1378534

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	25075699	4	6268925	21.52736	5.6E-10	2.578739
Within Groups	13104330	45	291207.3			
Total	38180029	49				

Table 32: Pb

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	125.13	12.513	2.560757
Carbonate Phase	10	62.78	6.278	0.734262
Reducible Phase	10	51.65	5.165	13.33385
Organic Phase	10	67.76	6.776	15.67285
Residual Phase	10	559.63	55.963	235.0718

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	18972.33	4	4743.082	88.69767	9.5E-21	2.578739
Within Groups	2406.362	45	53.4747			
Total	21378.69	49				

Table 33: Cr

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	33.82	3.382	0.422818
Carbonate Phase	10	11.62	1.162	0.543796
Reducible Phase	10	42.33	4.233	3.488001
Organic Phase	10	64.08	6.408	5.13164
Residual Phase	10	280.55	28.055	59.15085

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4849.124	4	1212.281	88.18244	1.07E-20	2.578739
Within Groups	618.6339	45	13.74742			
Total	5467.758	49				

Table 34: Cd

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	15.7	1.57	0.014867
Carbonate Phase	10	7.43	0.743	0.016623
Reducible Phase	10	1.28	0.128	0.003751
Organic Phase	10	2.6	0.26	0.032822
Residual Phase	10	222.28	22.228	6.496929

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3728.939	4	932.2348	710.0045	5.11E-40	2.578739
Within Groups	59.08493	45	1.312998			
Total	3788.024	49				

Table 35: Cu

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Exchangeable Phase	10	22.66	2.266	7.090849
Carbonate Phase	10	28.54	2.854	2.136604
Reducible Phase	10	59.9	5.99	11.51213
Organic Phase	10	2.6	0.26	0.032822
Residual Phase	10	294.34	29.434	18.46745

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	5825.948	4	1456.487	185.5877	2.4E-27	2.578739
Within Groups	353.1587	45	7.847972			
Total	6179.107	49				

CONCLUSION

This research has provided a background information on the geochemical speciation of the heavy metals in the coastal sediments of Ayetoro area. The geochemical phases include:

exchangeable, carbonate, reducible, organic and residual. Previous studies carried out in the area had earlier confirmed sulphide mineralization in the study area. However, most of the elements in each of the phases do not show much variation in concentration with respect to each sampling points. For instance, what is observed in a particular phase is almost in the same range throughout the 10 sampling points except a few cases of different geochemical background and bio-availability. This observation confirmed that, the heavy metals are evenly distributed across the sampling points. The exchangeable and Carbonate phases both naturally have high degree of mobility and bioavailability which confirmed that mobility of metals like Cd that had high concentration in those phases were expectedly high and has the tendency to migrate through all the phases unhindered. Cd is a dangerous heavy metal that has devastating effects on the human body when consumed such as causing kidney problems and renal failures in most cases. It can also cause leukemia. The major sources of pollution of this metal is from indiscriminant dumping of wastes from industries, sewage disposals and from organic leachates. Also, heavy metal bound to the reducible phase are easily released into the environment under reducing chemical conditions while those in the oxidizable fraction are easily released into the environment under oxidizing conditions whereas, heavy metals bounded in the residual fraction are not easily released into the environment because the metals are firmly bounded within the crystal structure of the mineral comprising the sediment, hence they have low mobility and not biochemically available to influence mineralization but can concentrate to form ore deposits.

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