

Geochemical Partitioning of Some Heavy Metals in Bottom Sediment of River Delimi in Jos, Nigeria

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Abstract— The determination of total metal content is usually insufficient to fully assess the environmental impacts of contaminated sediments. In order to differentiate metals of lithogenic from those of anthropogenic origin and assess their bioavailability and potential toxicity, detail information on their partitioning to various geochemical fractions of the sediment is necessary. In recent times there has been a lot of concern on the rate at which River Delimi ecosystem deteriorate as it passes through Jos city. This study was aimed at determining the geochemical partitioning of Cd, Cu, Pb and Zn in River Delimi sediment with a view to determining the extent to which they might be remobilized and affect the quality of the river ecosystem. The study was conducted at three sites along River Delimi and one control site at Lamingo Dam all within Jos city. The total metals content in sediment were extracted using aqua-regia. A five-step sequential extraction procedure was used to determine the partitioning of the metals into different geochemical fractions of the sediment. The metals extracted were determined using Atomic Absorption Spectrophotometer (AAS). The total metals content in sediment were generally higher at the study compared to the control site. The mean values of Cd in sediment (1.330mg/kg, 1.515mg/kg, 1.301mg/kg and 0.900mg/kg) respectively for stations I, II, III and IV were all above the limit of 0.68mg/kg recommended by USEPA. Sediment samples obtained from River Delimi had more metals associated with the non-residual fractions compared to those from Lamingo Dam. The high amount of these metals recovered in non – residual fractions mean that the metals are in potentially available forms and could pose a serious threat to the river ecosystem. Measures should therefore be put in place by the relevant authorities to curtail indiscriminate dumping of domestic and industrials wastes into the river.

Keywords— Bioavailability, Heavy metals, Partitioning, Sediment, Toxicity.

I. INTRODUCTION

The excess accumulation of heavy metals in sediment could have significant impacts on the river water quality and on the local communities. Studies on the distribution of heavy metals in sediment can provide evidence on human impact inflicted on the aquatic ecosystem and will in a way assist in determining the risk associated with dumping of domestic wastes and discharge of industrial effluents into the ecosystem [1].

It should be noted however that determining the total metal content is usually insufficient to fully assess the environmental impacts of contaminated sediments [2]. Detail information on the geochemical partitioning of the metals in sediments as pointed out by [3] is necessary to fully understand the different sediment sources, element distribution pattern and evaluating the environmental conditions existing in an area.

Metal partitioning into various geochemical fractions is also very useful for determining the extent to which they might be remobilized into the environment as well as differentiating metals of lithogenic from those of anthropogenic origin [4]. Another report by [5] states that delineating various forms of elements and their speciation in sediments is essential for assessing their bioavailability and toxicity.

River Delimi is one of the major inland water bodies in Nigeria serving as habitat to numerous species of plants and animals. In recent time however there has been a lot of concern on the rate at which the quality of the river deteriorate due to dumping of industrial and domestic wastes. Earlier studies by [6] revealed that the river water contained excess amount of metal pollutants. However, there is insufficient information on the geochemical partitioning of the metals in the river sediment. This study

was therefore aimed at determining the partitioning of Cd, Pb, Cu and Zn in various geochemical fractions of bottom sediment obtained from River Delimi with a view to determining the magnitude of human impact on the river ecosystem

II. MATERIAL AND METHODS

2.1 Study Area

The study was conducted at designated points along River Delimi in Jos city (Figure 1) in north-central Nigeria. The city is about 1250mm above sea level located on Lat. 9° 52'59"N and Long. 80°54'26"E. The average monthly temperatures range between 21 and 25°C. The mean

annual rainfall ranges from 2000 – 3250 mm between May and September [7]. River Delimi is located in the north central and north eastern parts of Nigeria. It mainly originates from Delimi village located few kilometers to the southern outskirt of Jos Plateau State. The river is characterized by low base flows in dry season and relatively high peak flows in rainy season, thus responds very quickly to rainfall in its catchments' area. High peak flow results in flooding of the river, which is mainly due to the geomorphological composition of the river system. The river covers a distance of about 15 km as it passes through Jos and serves as the major source of water for vegetable crop irrigation in the city.

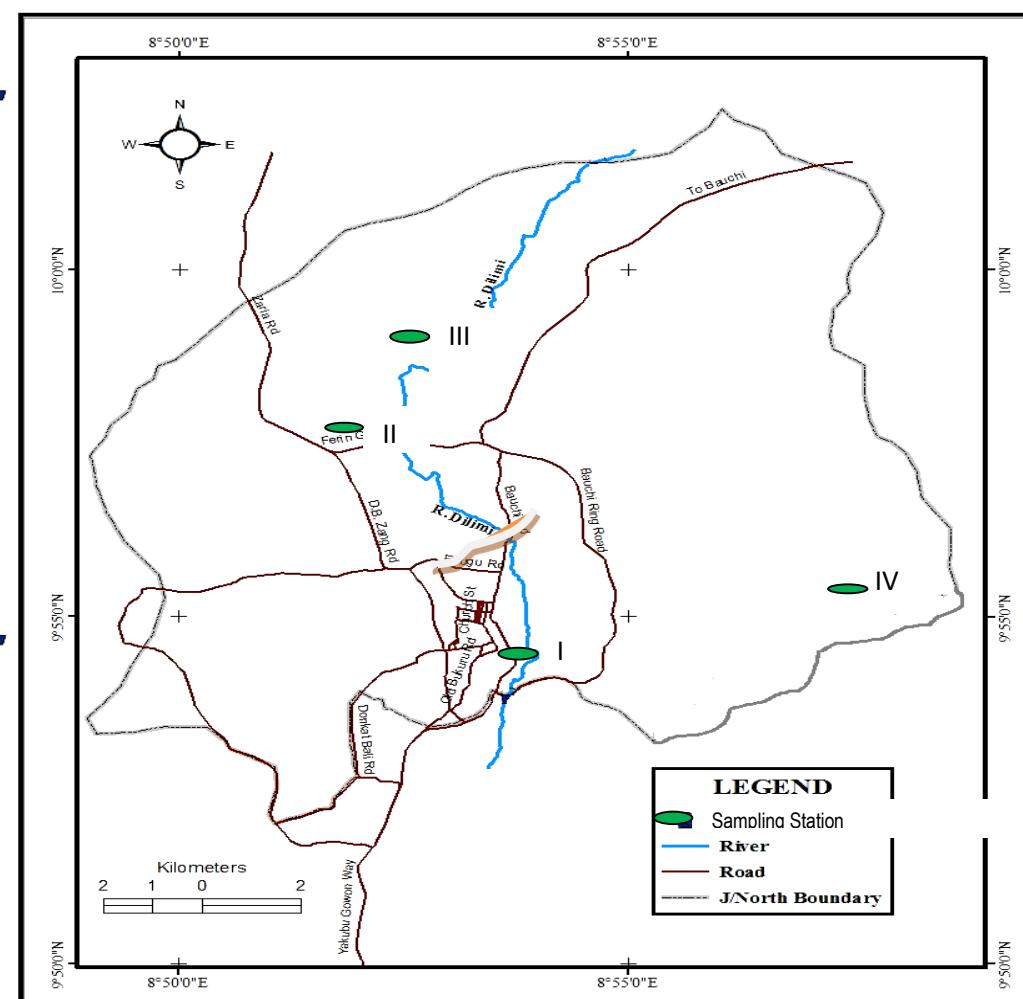


Fig.1: Map of Jos metropolis showing the sampling stations. Source: University of Jos (2012)

2.2 Sampling strategy

Sediment samples (top 10cm) were collected using soil auger at 3 different sampling stations along the river (study site) as follows:

- Station I = Gangare (Lat. 9° 53' 22"N, Long. 80°52'57"E)

- Station II = Farin Gada (Lat. 9° 57'36"N, Long. 80°52'27"E)
- Station III = University of Jos main campus (Lat. 9° 58'52"N, Long. 80°52'54"E)
- Station IV (Control Site) = Lamingo Dam (Lat. 9° 53'07" Long. 80°54'55")

2.3 Samples Preservation and Pretreatment

Sediment samples were collected in a polythene bags and kept on ice. The samples were subsequently transported to the laboratory and kept at low temperature (4°C). Sediment samples meant for total metal analysis were placed in porcelain crucibles and oven dried at 80°C for 24 hours. The dried samples were ground using a previously acid washed porcelain mortar and pestle. The samples were then kept in desiccators to attain constant weights before being transferred into air-tight plastic bottles. All the samples were sieved with a $200\mu\text{m}$ sieve before metal analysis.

2.4 Analysis of Sediment Samples

2.4.1 Determination of pH, Organic Matter and Total Metal Content in Sediment

Sediment pH was determined using a pH meter after shaking 5g of each sample with 5ml water and allowed to stay overnight. The organic matter content was determined by Loss on Ignition (LoI) using 5g each of soil and sediment samples heated at 450°C for 1 hr [8]. The total metal concentrations were determined using Atomic Absorption Spectrophotometer (AAS) after digestion with Aqua-regia.

2.4.2. Geochemical partitioning of metals in sediment

1g each of air dried sediment samples were extracted in accordance with Tessier's extraction scheme [9]. At the end of each extraction step, the samples were centrifuged for 10 minutes and the supernatant decanted, filtered and analyzed for metal content using AAS. Each step was followed by a wash stage in which 8ml of deionized water was added to the residue and centrifuged for 10 minutes to remove any trace of previous extracting solution and the supernatant discarded. The extractions were carried out as follows;

2.4.2.1 Exchangeable fraction:

1g each of the air dried sediment samples was leached with 8ml of 1M MgCl_2 at pH 7 (adjusted with NaOH) for 1hr with continuous shaking using mechanical shaker. The solution was then filtered using a Whatman filter paper No. 1 into a 100ml volumetric flask. The filtrate was made up to the mark with distilled water.

2.4.2.2 Carbonate bound fraction

8ml of NaOAc at pH 5 (adjusted with acetic acid) was added to the residue obtained from exchangeable fraction and leached for 5hrs at room temperature with continuous agitation using mechanical shaker. The leachate was filtered and transferred into a 100ml conical flask and made up to the mark with distilled water.

2.4.2.3 Iron-Manganese Oxide fraction

To the residue obtained from the carbonate fraction, 20ml of 0.04M $\text{NH}_2\text{OH.HCl}$ (Hydroxylamine hydrochloride) in 25% acetic acid (v/v) was added. The sample was placed

in a water bath at 90°C and leached for 6hrs with occasional shaking. The leachate was then transferred into a 100ml volumetric flask and made up to the mark with distilled water.

2.4.2.4 Organic bound fraction

To the residue obtained from the Iron-Manganese fraction, 3ml of 0.02M nitric acid (HNO_3) and 5ml of 30% hydrogen peroxide (H_2O_2) at pH 2 (adjusted with HNO_3) were added. The mixture was heated in water bath at 85°C for 2hrs with occasional shaking. 9ml of 30% H_2O_2 at pH 2 was further added and the mixture continuously heated at 85°C for 3hrs. Another 9ml of 3.2M ammonium acetate $\text{CH}_3\text{COONH}_4$ in 20% (v/v) HNO_3 was then added and the mixture shaken for 0.5hr at a low temperature of about 25°C . The supernatant was filtered and transferred into a 100ml volumetric flask and made up to the mark.

2.4.2.5 Residual fraction

The concentration of metals in the residual fraction of the sediment and soil was calculated by subtracting the concentration in the first four fractions from the total content previously determined by the aqua-regia digestion [8].

2.5 Quality control/Assurance

Sediment samples were collected with plastic bags to avoid contamination. Samples were kept in polythene bags well covered while transporting them from field to the laboratory to avoid contamination from the external environment. Reagent blanks were used in all to check reagent impurities and other environmental contaminations during analysis [10]. Analytical reagent (AnalaR) grade chemicals and distilled water were used throughout the study. All glassware and plastic containers used were washed with detergent solution followed by 20% (v/v) conc. HNO_3 acid and then rinsed with water and finally with distilled water [11]. All the instruments used were calibrated before use. Tools and work surfaces were carefully cleaned for each sample during grinding to avoid cross contamination [10].

2.6 Statistical analysis

Tests for significant difference were carried out using the analysis of variance (ANOVA) of the Statistical Package for Social Sciences (SPSS) computer programme. Means were separated using the Tukey test.

III. RESULTS AND DISCUSSION

3.1 Sediment Analysis

3.1.1 pH, Organic Matter and Total Metal Content in Sediment

The mean values of pH and OM (%) and total metal content in sediment obtained from the four stations at River Delimi and Lamingo Dam within Jos metropolis are shown in Table 1.

Table 1 Mean pH, Organic Matter (OM) and total metal contents (mg/kg) in sediment from the four sampling stations at River Delimi and Lamingo Dam in Jos city.

| STATION | pH | OM | Cd | Cu | Pb | Zn |
|-------------|------------------|------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| I | 6.5 ^c | 4.5 ^c | 1.330(±0.390) ^a | 3.701(±0.767) ^a | 1.840(±1.775) ^a | 3.558(±0.537) ^a |
| II | 6.6 ^c | 4.6 ^c | 1.515(±0.350) ^a | 3.966(±1.844) ^a | 1.673(±1.111) ^a | 4.390(±0.377) ^a |
| III | 6.6 ^c | 4.1 ^c | 1.301(±0.371) ^a | 1.898(±0.947) ^b | 2.053(±1.886) ^a | 2.680(±0.477) ^b |
| IV | 7.3 ^t | 4.9 ^c | 0.900(±0.314) ^b | 1.983(±0.176) ^b | 1.111(±0.793) ^a | 2.405(±0.645) ^b |
| USEPA LIMIT | - | - | 0.68 | 18.70 | 30.20 | 124.00 |

Means followed by same letter within column are not statistically different at 95% level of confidence

Data analysis revealed that there was a significant variation in the mean pH values of sediment samples collected at the study compared to the control site. Thus, a significantly higher value of 7.3 was recorded for sediment samples obtained from station IV compared to statistically similar value of 6.5 for station I and 6.6 each for stations II and III.

The acidic nature of the sediment at the study site is an indication that the metals can easily be desorbed from the sediment into the water column making them more bioavailable to biota. The high pH value (above 7) at the control site means that the metals cannot be easily desorbed from the sediment to the water phase and therefore less bioavailable to biota.

There was no significant variation in the mean OM content in sediments collected from the various sampling stations. The mean values of 4.5%, 4.6%, 4.1% were recorded for samples collected from stations I, II and III respectively (study site), while station IV (control site) had a mean OM value of 4.9%. However, the relatively higher organic matter content in the sediment at the control station means that the metals are less likely to be released into the water column due to formation of metal-organic matter complex. Organic matter in the sediment is known to play an important role in the adsorption and retention of heavy metals.

3.1.2 Total Metal Contents in Sediment

Sediment samples collected at stations I, II and III had statistically similar ($p > 0.05$) mean Cd values of 1.330mg/kg, 1.515mg/kg and 1.301mg/kg respectively. These values were significantly higher ($p \leq 0.05$) than 0.900mg/kg recorded in samples collected at station IV.

There was significant variation ($p \leq 0.05$) in the mean Cu concentration in sediment obtained from the various sampling stations. The mean Cu concentrations in sediment obtained from stations I (3.701mg/kg) and II (3.966mg/kg) were statistically similar ($p > 0.05$), but significantly higher ($p \leq 0.05$) than 1.898mg/kg and 1.983mg/kg obtained from stations III and IV respectively. No significant variation ($p \leq 0.05$) was observed in the mean Pb concentrations in sediment samples collected at the various sampling stations in the study as well as the

control sites. The mean values of 1.840mg/kg, 1.673mg/kg and 2.053mg/kg recorded in sediment samples obtained respectively at stations I, II, and III and 1.111mg/kg recorded at station IV were all statistically similar ($p > 0.05$).

The concentrations of all the metals were generally at their maximum in the study site compared to what were obtained in the control site. This corroborates the findings of [12] who collected sediment samples from Yamuna River which passes through Delhi and Agra urban centers and analysed them for concentration and distribution of nine heavy metals and obtained the following results; Cr (157–817 mg/kg), Mn (515–1015 mg/kg), Fe (28,700–45,300 mg/kg), Co (11.7–28.4 mg/kg), Ni (40–538 mg/kg), Cu (40–1204 mg/kg), Zn (107–1974 mg/kg), Pb (22–856 mg/kg) and Cd (0.50–114.8 mg/kg). The levels of metals were compared with the average shale concentration and showed exceptionally high values for chromium, nickel, copper, zinc, lead and cadmium in the two urban centers. The authors concluded that high levels of these metals were found in sediments obtained from the urban centers because they received domestic and industrial wastes. Another analysis conducted by [13], however reported the detection limit of heavy metals in sediment of two freshwater lakes as 0.02 mg/kg for Cd, 0.36 mg/kg for Cu, 0.48 mg/kg for Pb, and 7.8 mg/kg for Zn which were below the values obtained in this investigation except for Zn mean concentration. The lower values were obtained by the author because the lake is located at a site far away from urban environment and therefore has less anthropogenic influence. A comparison of the mean metal concentrations obtained in this study with [14] threshold effect limits (Cd, 0.68mg/kg; Cr, 52.30mg/kg; Cu, 18.70mg/kg; Pb, 30.20mg/kg and Zn, 124.00mg/kg) in sediment revealed that the concentrations of all the metals under investigation except Cd falls within the recommended threshold limits.

3.2 Geochemical partitioning of metals in sediment

3.2.1 Partitioning of Cadmium in sediment

In sediment samples obtained at station I, II, and III of the study site, Cd was mostly concentrated in exchangeable phase, while in station IV – the control site the metal was

mostly found in residual fraction (Figure 1). Mean values of 38.3%, 14%, 7.1%, 15.5% and 25.1% were recovered from exchangeable, carbonate, Fe/Mn oxide, organic and residual fractions respectively in sediment samples collected from station I. The percentage recoveries of the metal at station II were; exchangeable (32.4%), carbonate (9.0%), Fe/Mn oxide (9.6%), organic (19.6%) and residual (29.4%). At, station III, the metal behaved in a similar manner with the exchangeable fraction having the highest metal load of 44.7% recovery, The percent recoveries in carbonate, Fe/Mn oxide, organic and residual fractions were 9.1%, 5.6%, 12.2% and 28.4% respectively. On the contrary however, a greater portion of Cd (47.0%) in sediment at station IV (control site) was found associated with the residual and the least (7.7%) with the exchangeable fractions. Partitioning to other fractions were carbonate (13.4%), Fe/Mn (9.9%) and organic (22.0%). The binding of Cd to the non-residual fractions especially the exchangeable and organic phase is generally reflective of sites with anthropogenic contamination. This corroborates the findings of [15] who opined that Cd is generally a mobile and bioavailable element that tends to preferentially accumulate more in exchangeable fraction. At station IV – the control site however much more (47.0%) Cd was recovered in residual fractions. The Cd at this site is therefore not readily available since in geochemical partitioning, metals bound to residual fraction are notably fixed within the crystal lattice and are usually considered to be of primary mineral phase. A substantial amount (22.0%) of this metal was also found associated with organic phase of the non-residual fractions. This further reduces its bioavailability since metals bound to this fraction are only released under low pH (oxidizing condition) and the sediment pH value (7.3) at this station is relatively high.

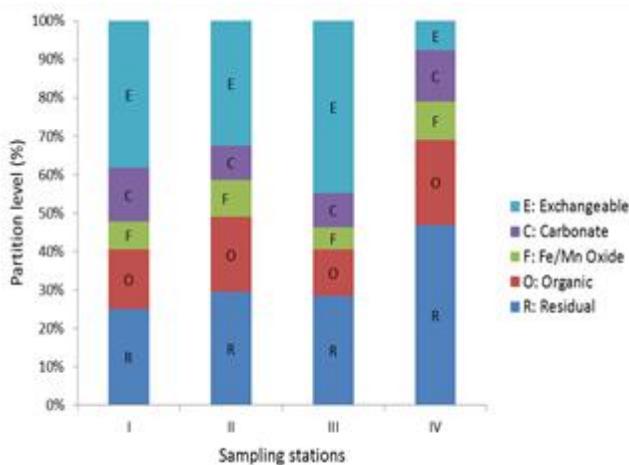


Fig.1: Partitioning of cadmium into different geochemical fractions of sediment obtained from four sampling stations along River Delimi and Lamingo Dam in Jos metropolis

3.2.2 Partitioning of Copper in sediment

The partitioning of Cu in sediment is as presented in Figure 2. At station I, Cu was mainly concentrated in residual fraction with mean value of 27.8%. This is closely followed by 22.2% recovered from exchangeable fraction. The carbonate bound, Fe/Mn oxide and carbonate fractions had 13.4%, 18.2% and 18.4% mean recoveries respectively. The dominant fraction with respect to the distribution of Cu in sediments obtained from station II is exchangeable with mean value of 37.3%. The lowest value (12.2%) was however recovered in carbonate phase. The mean recovery values of 15.9%, 13.8% and 20.8% were obtained in Fe/Mn oxide, carbonate bound and residual fractions respectively. The metals partitioning in sediment at station III is such that highest mean value of Cu (34.4%) was obtained in residual while the least was recorded in the exchangeable phase with mean value of (13.3%). The carbonate, Fe/Mn oxide and organic fractions had 16.6%, 13.5% and 22.2% mean metal recoveries respectively. The distribution of the metal at station IV was equally dominated by the residual fraction. The mean recovery were exchangeable (10.2%), carbonate (18.3%), Fe/Mn oxide (16.3%), organic (17.2%) and residual (38.0%).

The partitioning of Copper in the sediment samples obtained from the study site revealed a somewhat proportionate distribution of the metal in the various geochemical fractions although the metal tends to accumulate more in non – residual fractions especially the easily exchangeable fraction at stations I and II and organic fraction at station III. At station IV, the residual fraction had 38% of the total metal concentration with the remaining portion distributed among the non-residual fractions especially carbonate, Fe/Mn oxides and organic fractions. The metal in the sediments at stations I, II and III is easily available while at station IV it is only available under specific environmental conditions. For example, under reducing condition, the metal in Fe/Mn oxide can be released. The oxidizing condition however will lead to the release of those portions associated with organic fraction. However since the pH value of sediment at this sampling station is 7.3, the release of Cu will be more in the portion associated with the Fe/Mn oxide fraction.

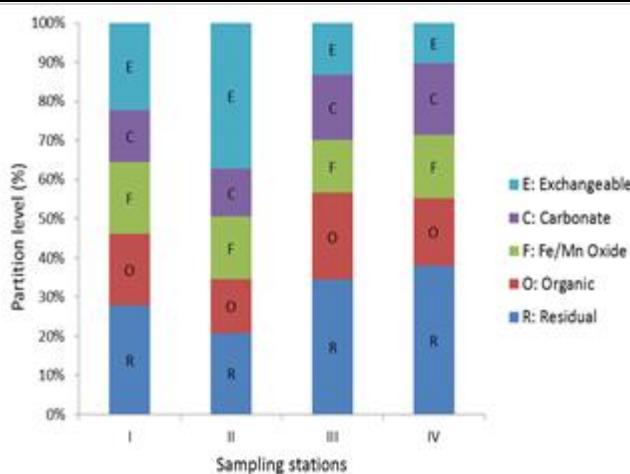


Fig.2: Partitioning of copper into different geochemical fractions of sediment obtained from four sampling stations along River Delimi and Lamingo Dam in Jos metropolis.

3.2.3 Partitioning of Lead in sediment

At station I, residual was the dominant fraction for Pb (mean = 40.9%), while the exchangeable was the least (mean = 12.8%). The carbonate, Fe/Mn oxide and organic fractions had 17.2%, 14.3% and 18.4% mean Pb recoveries respectively (Figure 3). There was a similar higher mean Pb recovery (43.9%) from residual fraction at station II, however the least value (12.0%) was recorded in Fe/Mn oxide fraction. The mean concentrations in exchangeable, carbonate and Organic fractions were 15.7%, 11.9% and 16.5% respectively. Relatively higher mean Pb value (36.1%) was recovered from residual at station III. The next important fractions were carbonate and organic fractions having 18.9% and 17.0% mean metal recoveries respectively. The mean concentrations recovered in the other fraction were exchangeable (13.8%) and Fe/Mn oxide (14.2%). The residual fraction also dominated the distribution of the metal at station IV with mean recovery of 59.1%. The exchangeable, carbonate, Fe/Mn oxide and organic fractions had 6.0%, 4.1%, 7.5% and 23.3% mean values respectively.

The substantial amount recovered in the non – residual phase also confirmed that there has been a lot of anthropogenic interference on the sediment quality. At the control site however, the metal tends to be partitioned predominantly into the residual and organic fractions with the exchangeable accumulating the least amount. The metal at station IV may be considered to be less mobile because of its preference to the residual fraction and its high stability constants for the formation of lead–organic matter complexes.

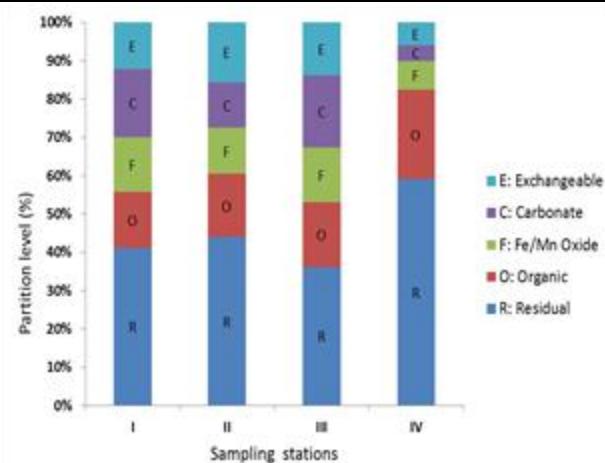


Fig.3: Partitioning of lead into different geochemical fractions of sediment obtained from four sampling stations along River Delimi and Lamingo Dam in Jos metropolis

3.2.4 Partitioning of Zinc in sediment

Zn partitioning in sediment samples (collected from both study and control sites) is dominated by residual fraction (Figure 4). At station I, the result showed that residual had the highest mean Zn value of 28%, followed by 23.8% in exchangeable, 18.2% in Fe/Mn oxide, 15.6% in organic and the least 14.4 recovered in carbonate fraction. The portioning at station II revealed a higher mean recovery value of 34.5% in residual, followed by 22.3% in exchangeable, 15.9% in organic and the least values of 13.4% each in carbonate and Fe/Mn oxide. At station III, greater portion (50.7%) of Zn was present in residual while the non-residual fractions exchangeable, carbonate, Fe/Mn oxide and organic fractions had 8.6%, 11.1%, 13.7% and 15.9% mean concentrations respectively. Residual was also the dominant fraction in the distribution of Zn at station IV. The mean metal concentrations in ascending order were exchangeable (7.4%), carbonate (12.6%), organic (12.8%), Fe/Mn oxide (15.2%) and residual (52.0%).

The partitioning of Zn follows almost the same pattern to that of Pb with the non-residual fraction dominating the distribution of the metal, although unlike Pb, substantial amount of Zn was also found in exchangeable fraction of the non – residual phases especially at stations I and II. It is not surprising that there was high accumulation of Zn in exchangeable fraction at stations I and II considering the fact that the two stations had the busiest human activities notably mechanic workshops and other metal works.

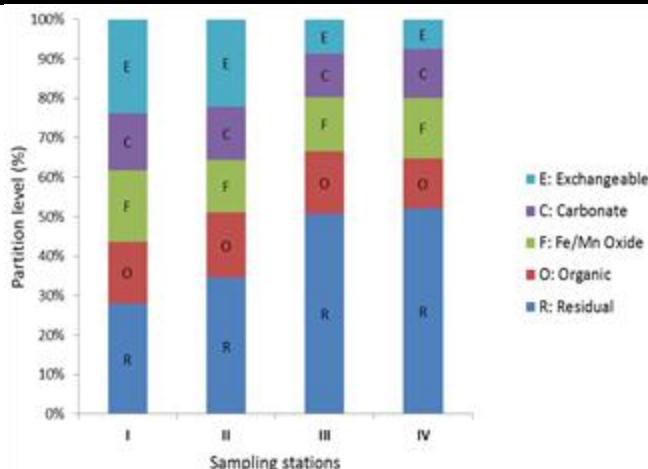


Fig.4: Partitioning of Zinc into different geochemical fractions of sediment obtained from four sampling stations along River Delimi and Lamingo Dam in Jos metropolis

IV. CONCLUSION

The result of this investigation revealed that high concentrations of Cd, Cu, Pb and Zn were recovered in bottom sediment obtained from River Delimi compared to the control site. Partitioning of these heavy metals into different geochemical fractions of sediment also revealed that sediment samples obtained from the River Delimi had more metals associated with non-residual mobile fractions than those from the control sites. This suggests that there are more anthropogenic and potentially available metal species in sediments obtained from River Delimi compared to the control site. This may not be unconnected to the indiscriminate dumping of domestic and industrial wastes into the Delimi River contrary to the situation at Lamingo Dam, the control site where no intentional dumping of such wastes occurs being a protected drinking water reservoir. It is recommended that measures should be put in place by the Plateau State Environmental Protection Board and other relevant government agencies to check the unnecessary dumping of domestic and industrial waste into the Delimi River.

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