Speciation Study of Heavy Metals in Water and Sediments from Asunle River of the Obafemi Awolowo University, Ile-Ife, Nigeria

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Abstract- **A nine-step sequential extraction protocol of Zn, Mn, Cd, Cu, Ni, Co and Pb in sediments from Asunle River that receives effluents from the waste dumpsite of the Obafemi Awolowo University, Ile Ife Nigeria was carried out. Total and dissolved levels of the heavy metals in water samples were also determined using Flame Atomic Absorption Spectrophotometer (FAAS). The results of total metal concentration (μg/mL) in water ranged from 0.04 ± 0.01 Cd to 2.25 ± 0.57 Zn while the mean levels of dissolved metal in water ranged between 0.004 ± 0.000 μg/mL and 0.87 ± 0.17 μg/mL. Mean levels of total heavy metal (μg/g) in the sediment samples ranged between $10.99 \pm 2.18 - 74.62 \pm 11.96$ in Pb and $645.10 \pm 62.15 - 3753.03 \pm 176.29$ in Mn. The apparent mobility and potential bioavailability for each metal in the sediment was >70%. The study showed that both the water and sediment samples were contaminated with heavy metals to varying degrees primarily as a result of effluents discharging into the river from the dumpsite within the vicinity of the river.**

Key words - Heavy Metals; Speciation Studies; Water; Sediment; Asunle River

I. INTRODUCTION

The roles of heavy metals in environmental contamination and the potential dangers they pose to human health are well documented [1 - 6]. The attention given to the presence of heavy metals in the environment is primarily due to their toxicity and threat to human life at elevated levels, and also, because of their tendency to aggravate environmental degradation. Metals are known to constitute highly persistent environmental pollutants [7]. Thus, their tendency to remain as an environmental contaminant for a long period and to be magnified through food chains is high.

Apart from heavy metals added as a result of the natural soil geochemical composition of an aquatic environment, both solubilized and non-solubilized heavy metals and other contaminants can be transferred into the aquatic system by runoffs from contaminated soil sites and agricultural farmlands, and through atmospheric deposition. The types of contaminants brought into the aquatic ecosystem are largely influenced by the kind of anthropogenic activities embarked upon within the surrounding farmlands. There are three possible mechanisms by which heavy metals reaching an aquatic system may be taken up by sediments and suspended matter: physicochemical adsorption from the water column; biological uptake by organic matter or organisms; and physical accumulation of metal-enriched particulate matter by sedimentation.

The various ways by which heavy metals associate with various soil/sediment components determine their mobility and availability [8 - 11]. Determining the total content of heavy metals in the sediment may be useful for the characterization of pollution intensity, however, speciation of heavy metals with selective extracting agents gives further information about the fundamental reactions that govern the behaviour of metals in sediments and helps to assess the environmental impact of contaminated soil and sediment [12 - 14].

Sequential extraction procedure is used to partition heavy metals in soil and sediments in order to assess the forms of heavy metals in contaminated soils and sediments. It provides information on potential mobility as well as bioavailability and plant uptake of trace elements [10, 15, 16]. It also determines the bioavailability of the metal in soil/sediment to other biota within the aquatic ecosystem. Water soluble metals are the most mobile of all the heavy metals and are also the most readily available for plant uptake. Exchangeable metals are primarily bound very weakly to soil or sediment surfaces by cation exchange processes and may be displaced easily to the water-soluble form. Together, the metals in the soluble and exchangeable forms are considered readily mobilized. When changes occur in the oxidation status of soils and sediments, transformations of metals between their soluble and insoluble chemical forms may occur. This affects the mobility and plant availability of those metals.

All heavy metals present in surface waters occur in the form of colloids, particulates and dissolved phases, although dissolved concentrations are generally low [17] compared to their levels in the underlying associated sediments. The solubility of these metals in surface waters is predominantly controlled by water pH, the type and concentration of ligands on which the metals could be adsorbed, the oxidation state of the mineral components and the redox environment of the water/sediment interface [18]. Because their nature is strongly influenced by the action of microorganisms present in water, most metals found in natural water bodies do not exist as simple hydrated cations; their behaviour in natural water is a function of substrate sediment composition and the water chemistry. Ion exchange chromatography is particularly well suited for the separation of

inorganic anions and cations and has been used to monitor the levels of dissolved heavy metals in water samples [17 - 19].

Asunle River, the focus of this study, is a perennial river that has its source located about 0.1 km uphill from the Obafemi Awolowo University, Ile-Ife refuse dumpsite. The dumpsite which lies between latitude 07° 32' 25"N and longitude 004° 31' 16"E at 318 m above sea level started operation in 1971. It serves as the final destination where all refuse collected within the university community are dumped and subjected to open air incineration. The river runs a stretch of more than 10 km, cutting across human communities such as Abagbooro, Agbogbo and Amuta. Commonly planted crops on the farmlands around the stream include cash crops such as cocoa, cola nut, palm trees, etc, and food crops such as cassava, maize, yam, cocoyam, plantain, banana, pineapple, oranges, pepper, and various types of vegetables. This makes human activities around the river vigorous. Downstream, the water from the river is utilized for household purposes while along the river course, farmers use water from the river for palm oil processing, wetting of vegetables, mixing and dilution of pesticides used for spraying of cocoa and other crops.

The aim of this work was to assess the pollution impact of the refuse dumpsite on Asunle River. This was done by monitoring the levels of total heavy metals and their species in the water and sediment samples, and their spatial as well as temporal distribution and variability patterns were evaluated.

<center>II. MATERIALS AND METHODS</center>

A. Reagents Used and Their Sources

The reagents used were of analytical grades and they include: HNO_3 (Riedel-deHaën, Germany), HCl (Sigma-Aldrich, Germany), H_2O_2 (British Drug House (BDH) Chemicals Ltd, Poole, England), NaOH pellets (Merck, Darmstadt, Germany), NaCl (Associated Chemical Enterprises, Glenvista, RSA) and anionic trimethylhyroxyammonium chloride resin (Sigma, USA). Solutions were prepared using doubly distilled water.

B. Pre-treatment and Sterilization of Apparatus

All glass wares used (Erlenmeyer flask, conical flask, beakers, measuring cylinder, volumetric flask, and watch glass) were washed with liquid detergent and rinsed thrice with distilled water followed by oven drying. Polyethylene sample bottles and Teflon beakers were washed with liquid detergent and rinsed with distilled water prior to sample collection [20, 21].

C. Sample Collection and Pretreatment

Samplings were done from six different sites along the river in April, May and June, 2010. The sampling points were Site O (850 m) upstream away from the dumpsite, Site A (680 m), Site B (750 m), Site C (870 m), Site D (1140 m) and Site E (1920 m) as indicated on the study map (Figure 1). Sites A - E are distances downstream away from the dump site. Values in parenthesis are distances of the sampling points from the dump site. Site O represents the reference point upstream, a site very close to the source of the stream where control samples were collected from. Site A is the closest point of the receiving stream to the dump site. The water samples were collected in 2 L treated polythene containers. Before filling, the containers were rinsed thrice with the water sample to be collected at the sampling sites. Samples were adjusted to pH 2 to prevent further microbial degradation. Similarly, sediment samples were collected in polythene bags. The collected sediment samples were air-dried, large unwanted particles were hand-picked and the rest were ground with agate mortar and pestle to powdery form.

D. Speciation Analysis of Heavy Metals in The Sediments

The procedure of Tessier *et al.* (1979, 1985) [22, 23] was used for the speciation study except that water soluble and plant available fractions were included. Thus, the sediment samples were subjected to a nine stage sequential procedure to extract and partition Pb, Mn, Zn, Cd, Cu, Ni and Co into water soluble, exchangeable, bound to carbonate, plant available, bound to Mn oxides, bond to amorphous Fe-oxide, bound to crystalline Fe-oxide, bound to organic matter and residual fractions. One gram of each soil sample was weighed and extractions were made through steps (F1- F9) by centrifugation and filtration at 10,000 rpm placing the sample in polyethylene centrifuge tubes. Distilled water was used to wash the residues following subsequent extraction in order to ensure selective dissolutions and to prevent possible interphase mixing between the extractants. All samples were run in duplicates.

Water soluble metals (F1) Water soluble metals were extracted with a solution of 50 mL distilled water for 2 hours.

Exchangeable metals (F2) The residue from F1 was extracted with 25 mL of 1.0 M CH_3COONH_4. The suspension was shaken for 30 minutes at 28^oC.

Metals bond to Carbonates (F3) The residue form F2 was extracted with 1 M sodium acetate (CH_3COONa) and the suspension was shaken for 5 hours.

Plant available metals (F4) The residue form F3 was extracted by shaking with a solution mixture of 50 mL of 0.025 M HCl + 0.05 M H_2SO_4 for 30 minutes at 28^oC.

Bond to Mn-Oxide (F5) The residue from F4 was shaken for 30 minutes at 28^oC with a solution of 25 mL 0.1 M

$NH_2OH \cdot HCl$ in 25% CH_3COOH.

Bond to Amorphous Fe-Oxide (F6) The residue from F5 was extracted with 25 mL of 0.2 M $(NH_4)_2C_2O_4$ for 30 minutes at 50^oC using a water bath with occasional stirring.

Bond to crystalline Fe-oxide (F7) The residue form F6 was extracted using 25 mL of 0.04 M $NH_2OH \cdot HCl$ in 25% acetic acid and heated in a water bath with occasional stirring at 100^oC for 6 hours.

Bond to organic matter (F8) The residue from F7 was extracted with 1 mL of 0.02 M HNO_3 and 15 mL of 30% H_2O_2. The mixture is then heated to 85^oC for 5 hours with occasional agitation. A second 15 mL of 30% aliquot was added and the mixture heated again to 85^oC for 3 hours with intermittent agitation. After cooling, 5mL of 3.2M CH_3COONH_4 in 20% HNO_3 was added and the samples diluted to 20mL and agitated continuously for 30 minutes.

Residual Metals (F9) The residue from F8 was digested with a mixture of concentrated HNO_3 and $HClO_4$ for 8 hours.

E. Extraction of Dissolved Metals in Water Samples

Ion-Exchange Chromatography (IEC) was used for the extraction of heavy metals dissolved in the water samples. The anion exchange column was prepared using 15g of the resin. The resin was rinsed with distilled water, soaked in 0.5 M HCl for an hour and transferred in a slurry form to pack a 20 cm column length. The column was washed with 100 mL distilled water at a flow rate of 4 mL/min followed by 100 mL of 2 M HCl and 2 M NaOH respectively at the same flow rate. The column was washed with about 50 mL of reagent I (50 g NaCl + 5 mL conc. HCl made up to 500 mL); the solution was drained to about 0.5 mL above the top of the resin. Then 500 mL water sample was allowed to pass through the column at a flow rate of 4 mL/min. The sample was allowed to drain to about 0.5 mL above the top of the resin and the column was washed down with 2.5 mL of reagent I. Next, 150 mL of reagent II (2 M NaOH + 0.34 M NaCl) was passed through the column at a flow rate of 4 mL/min. The eluate containing the dissolved metals was collected in a 250 mL volumetric flask and diluted to volume with distilled water.

F. Digestion of Water Samples

The samples were digested using the method described elsewhere [24]. 20 mL of water sample was placed in a 100 mL Teflon beaker. 5 mL of conc. HNO_3 was added along with a few Hengar granules. This was brought to a gentle boiling on a thermostated hot plate. Replenishing of content was done with 1:1 (v/v) HNO_3:$HClO_4$ until complete digestion was ascertained. The digested sample was cooled down, quantitatively transferred to a 25 mL volumetric flask and made up to the mark with distilled water. A blank determination was carried out.

G. Quantification of Heavy Metals and Their Pollution Intensity in The Samples

The levels of Pb, Mn, Zn, Cd, Cu, Ni and Co in the worked-up samples were profiled using the Atomic Absorption Spectrophotometry (AAS) Buck Model 205/4 (Chem Tech Analytical). The calibration of the AAS was done with 10, 8, 6, 4, 2, 0 ppm solution of the metals obtained by serial dilution of 1000 ppm of the stock metal solution. Each determination was done in triplicate.

Geoaccumulation index (*I-geo*), a widely used empirical relationship for evaluating the degree of metal contamination or pollution in soil or sediment samples of terrestrial or aquatic environments [25], was applied to evaluate the pollution status of the studied area. According to Taylor and McLennan (1995) [26], the geoaccumulation index can be expressed as:

$$\text{I-geo} = \log_2 \left(\frac{C_n}{1.5 B_n} \right),$$

where C_n is the total heavy metal concentration in the sediment sample; B_n is the background value in unpolluted sample; and 1.5 is the background matrix correction factor introduced to minimize variations of heavy metals due to lithogenic effects.

The I-geo values are classified into seven (0 - 6) classes [27]: I-geo $\leq$ 0 (Class 0 for practically unpolluted, PU, samples); 0 < I-geo < 1(Class 1 for practically unpolluted to moderately polluted, MP, samples); 1 < I-geo < 2 (Class 2 for moderately polluted, MP, samples); 2 < I-geo < 3 (Class 3 for moderately polluted, MP, to heavily Polluted, HP, samples); 3 < I-geo < 4 (Class 4 for heavily polluted, HP, samples); 4 < I-geo < 5 (Class 5 for heavily polluted to very heavily polluted, VHP, samples); 5 < I-geo < 6 (Class 6 for very heavily polluted, VHP, samples). The background values of 36, 320, 0.3, 15, 17, 10 and 17µg/g for unpolluted soils [28] for Zn, Mn, Cd, Cu, Ni, Co and Pb respectively were used against the mean total heavy metals in the sediments.

<div align="center">III. RESULTS AND DISCUSSION</div>

A. Levels of Total Heavy Metals in The Sediment Samples

The mean total levels of heavy metals in the sediment samples for April, May and June, 2010 are presented in Table 1. The

range and order of the mean total levels of the metals (µg/g) analyzed in the sediments were: Mn (645.10 ± 62.15 – 3753 ± 176.29) > Ni (170.08 ± 5.30 - 1515.58 ± 106.53) > Co (97.75 ± 52.77– 754.14 ± 55.28) > Zn (132.80 ± 4.79 – 431.26 ± 7.16) > Cu (88.48 ± 15.97– 493.86 ± 53.84), Cd (16.65 ± 3.10 – 77.03 ± 3.33) > Pb (10.99 ± 2.18– 74.62 ± 11.96) with an overall mean levels (µg/g) of 2411.74 ± 968.50, 930.59 ± 539.82, 439.51 ± 226.41, 313.09 ± 88.67, 302.45 ± 137.19, 57.28 ± 21.20 and 34.08 ± 22.98 respectively. The overall mean level of Pb (34.08 ± 22.98 µg/g) obtained in this study was comparable to the mean Pb level of 35.54 ± 5.91 µg/g obtained in the speciation study of roadside dusts of major roads in Ile-Ife [14]. However, the mean Mn level of 2411.77 ± 968.50 µg/g obtained in this study was significantly higher than the Mn level of 51.46 ± 15.10 µg/g obtained in a similar study [14]. As can be seen from Table 1, the total concentration of heavy metals

TABLE I MEAN TOTAL METAL LEVELS (µG/G) IN THE SIX SEDIMENT SAMPLES

Site	Metal						
	Zn	Mn	Cd	Cu	Ni	Co	Pb
O	132.80 ±4.79	645.10 ±62.15	16.65 ±3.10	88.48 ±15.97	170.08 ±5.30	97.75 ±52.77	10.99 ±2.18
A	431.26 ±7.16	3753.03 ±176.29	70.86 ±7.79	493.86 ±53.84	1515.58 ±106.53	754.14 ±55.28	26.92 ±0.90
B	305.84 ±9.09	2875.79 ±50.21	77.03 ±3.33	388.48 ±18.68	1419.01 ±41.05	605.66 ±32.26	25.28 ±1.06
C	361.65 ±14.45	2428.24 ±57.47	68.72 ±8.69	185.06 ±6.35	898.43 ±7.67	295.99 ±30.70	17.41 ±1.04
D	267.71 ±15.74	1698.54 ±13.46	28.23 ±4.24	270.72 ±26.33	554.49 ±17.82	288.41 ±10.08	26.16 ±2.33
E	199.01 ±19.18	1303.28 ±24.10	41.54 ±4.69	174.15 ±4.60	265.47 ±19.03	252.33 ±24.87	74.62 ±11.96
Mean ± s.d.	313.09 ±88.66	2411.77 ±968.50	57.28 ±21.20	302.45 ±137.19	930.60 ±539.82	439.31 ±226.42	34.08 ±22.98
CV	28.32	40.12	37.01	45.36	58.01	51.54	67.43

at A shows a significant increase relative to that of O, and in most cases there is subsequent decrease in their levels in moving downstream from A to E except for Pb and Cd where the highest concentrations of 74.62 ± 11.96 µg/g and 77.03 ± 3.33 µg/g correspond to E and B respectively. This trend suggests that there was a significant input of metals from the dumpsite into the water body in addition to natural differences in soil genesis and properties. The decrease in the levels of the metals downstream might be as a result of dilution influence as the stream widens and increases in volume. The high level of Pb at E may be attributed to anthropogenic inputs as a result of the closeness of E to human dwellings (Figure 1).
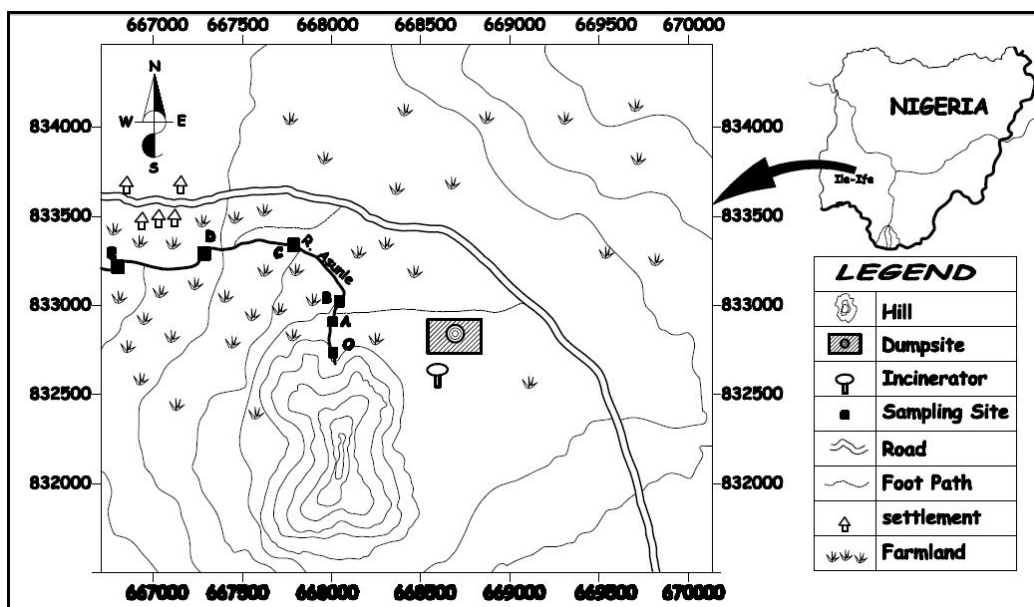
Figure 1 Map showing the study site and sample locations

The inhabitants close to E dump all manners of solid wastes including metal scraps and used batteries carelessly in places where erosion could leach dissolved metals into the stream. The relatively higher than expected levels of the metals at the control upstream O might be due to fly ash deposits all over the place as a result of continuous open space incineration at the dump site over the years.

Coefficient of variation (CV) is a useful statistical tool that can be employed to interpret the spatial and temporal

distribution and variability patterns of pollutants in an environmental matrix. The CV values of the heavy metals in the sediment samples were 67.43 (Pb) > 58.01 (Ni) > 51.54 (Co) > 45.36 (Cu) > 40.12 (Mn) > 37.01 (Cd) > 28.32 (Zn). Clearly, Pb, Ni and Co had the most erratic distribution patterns; Cu, Mn and Cd had moderately uneven distribution pattern; while Zn was, more or less, the most evenly spread of the metals in the sediments. It appears that Pb, Ni and Co enter the aquatic system of the study area as a result of sporadic leaching from the dumpsite.

The levels of Zn, Ni and Cu found in the sediment samples were significantly higher, at $p \leq 0.05$, than levels (µg/g) of Zn (44.5 ± 4.1 - 134 ± 10.5), Ni (11.4 ± 1.0 - 24.2 ± 1.9) and Cu (21.4 ± 2.0 – 102 ± 10) in industrial soils [13], but the levels of Pb and Cd were lower than those reported for the industrial soils [13]. The level of Zn was also higher than that of agricultural soils [9]. The levels of Zn, Pb and Cd in the present study showed significantly higher levels, at $p \leq 0.05$, than the average background levels (Zn, 63.5 µg/g; Pb, 21.4 µg/g; Cd, 0.108 µg/g) obtained in samples from Liaoning Province of China [29]. Also, the concentrations of Ni, Pb, Cd and Zn were higher than the values (Ni, 16.6 ± 5.6 µg/g; Pb, 22.4 ± 10.5 µg/g; Zn, 74.4 ± 29.8 µg/g; Cd, 2.44 ± 0.74 µg/g) obtained in a study of polluted sediment of Waji River reported to have been affected by industrial effluents [30]. The levels of Mn and Co were significantly higher than the concentration of 123±11 - 259±12 µg/g of Mn and 6.02±0.36 - 10.9±0.8 µg/g Co reported elsewhere [31]. To a large extent, the high value of heavy metals detected within the aquatic system in this study is an indication of the heavy metal impact of the dumpsite on the adjoining aquatic environment.

The result of the calculated values of geoaccumulation index (*I-geo*) in the sediment samples is shown in Table 2. The negative values for Pb at O, B and C according to contamination classification [27], showed that the soil was practically unpolluted (PU) by Pb at those sites. However, apart from O which had a status of practically unpolluted to moderately polluted (PU - MP) with respect to all the metals apart from Cd, all the other sites were, at least, moderately polluted with all the metals. In most cases, the site closest to the dumping site (A) had a status of very heavily polluted (VHP) with respect to most of the metals. It should be noted that with respect to Cd, a metal notorious for its toxicity, all the sites investigated had a worrisome very heavily polluted (VHP) status.

TABLE II THE GEOACCUMULATION INDEX (*I-GEO)* VALUES AT THE VARIOUS SITES

Element	Site					
	O	A	B	C	D	E
Zn	1.30 (MP)	3.00 (HP)	2.50 (MP-HP)	2.74 (MP-HP)	2.31 (MP-HP)	1.88 (MP)
Mn	0.42 (PU-MP)	2.96 (MP-HP)	2.58(MP-HP)	2.34 (MP-HP)	1.82 (MP)	1.44 (MP)
Cd	5.21 (VHP)	7.30 (VHP)	7.42 (VHP)	7.26 (VHP)	5.97 (VHP)	6.53 (VHP)
Cu	1.98 (MP)	4.46 (HP-VHP)	4.11 (HP-VHP)	3.04 (HP)	3.59 (HP)	2.95 (MP-HP)
Ni	2.74 (MP-HP)	5.89 (VHP)	5.80 (VHP)	5.14 (VHP)	4.44 (HP-VHP)	3.38 (HP)
Co	2.70 (MP-HP)	5.65 (VHP)	5.34 (VHP)	4.30 (HP-VHP)	4.27 (HP-VHP)	4.07 (HP-VHP)
Pb	-1.21 (PU)	0.08 (PU-MP)	-0.01 (PU)	-0.55 (PU)	0.04 (PU-MP)	1.55 (MP)

PU = practically unpolluted; MP = moderately polluted; HP = heavily polluted; VHP = very heavily polluted

These findings clearly pointed to high levels of heavy metal input from the dump site into the aquatic ecosystem of Asunle River especially when the values are compared with those from upstream O. Thus, the high dependence of the inhabitants within the vicinity of Asunle River as their source of water may lead to serious lead and cadmium induced-pollution problems, for example, in the future.

B. Distribution of Heavy Metals in The Operationally Defined Geochemical Fractions

All the metals studied were found in all the operationally defined geochemical fractions. The result of the speciation analysis of the metals is given in Table 3. The overall mean amount of Zn in the various fractions was in the following decreasing order: water soluble > exchangeable > carbonate > plant available > Mn-Oxide > organic matter > residual > amorphous Fe-Oxide > crystalline Fe-Oxide. The value of Zn ranged from 0.43 ± 0.07 µg/g in crystalline Fe-oxide fraction at O to 179.82 ± 10.73 µg/g in water soluble fraction at A. Higher levels of Zn were associated with the water soluble, exchangeable, carbonate and plant available fractions averaging 78.77% and the other fractions were less that 5% each on the average. Zinc non-residual fraction level gave 95.15% on the average. This is contrary to the earlier report in a similar study where the level of the studied metals was highest in the residual fraction [13]. The high percentage of Zn in the non-residual fractions may be reflective of high cation exchange capacity and pH characteristics of the sediment samples while its low content in the residual and Fe-Mn oxide fractions was probably due to the low association or retention ability of the mineral's crystal structure, such as with detrital silicates and resistant sulfides. The low content of the metals in the organic fraction was probably due to either low level of organic matter itself or the low retention capability of organic matter like humic acids and fulvic acids [32] as a result of weak bonds existing between them.

Like Zn, high levels of Mn in the sediments were present in the non-residual fractions. The percentage of total Mn in the non-residual fractions ranged from 92.3 at O to 96.9 on the average at C with water soluble fraction (avg. 31.14%) having the highest percentage. The sum of Mn in exchangeable, carbonate and plant available fractions in the sites ranged from 14.38% to 19.57% on the average. Despite the affinity of organic matter for Mn [9], the organic bound fraction was one of the smallest in the sediment samples with the values 2.19, 5.86, 1.86, 2.83, 4.20 and 4.67% at O to E respectively. The dominant proportion of Mn in this sediment was found in the water soluble fraction averaging 31.14%. The association of Mn in the sediments was in the order: water soluble > exchangeable > carbonate > plant available > Mn-oxide > amorphous Fe-oxide > crystalline Fe-oxide > organic fraction > residual. The low content of Mn in the residual and Fe-Mn oxide fractions could be due to the low association or retention ability of the mineral's crystal structure, such as with detrital silicates and resistant sulfides.

TABLE III MEAN LEVELS OF HEAVY METALS (μG/G) IN EACH FRACTION OF THE SEDIMENT SAMPLES

Fraction	Site													
	O							A						
	Zn	Mn	Cd	Cu	Ni	Co	Pb	Zn	Mn	Cd	Cu	Ni	Co	Pb
Water soluble	62.87 ±3.70	316.35 ±60.90	5.50 ±1.96	26.76 ±3.79	87.52 ±6.79	77.38 ±51.72	8.46 ±2.26	179.82 ±10.73	968.25 ±77.89	36.41 ±3.65	164.05 ±6.11	515.93 ±18.88	305.65 ±18.26	10.32 ±1.87
Exchangeable	16.08 ±3.64	159.94 ±17.16	4.41 ±0.47	23.89 ±6.14	36.78 ±5.78	11.50 ±2.88	1.02 ±0.20	83.20 ±17.66	628.75 ±32.98	26.72 ±5.12	102.40 ±7.79	309.40 ±10.31	76.46 ±16.67	4.32 ±0.50
Carbonate	13.75 ±4.28	70.24 ±6.91	3.45 ±0.80	14.66 ±6.39	23.68 ±5.66	2.57 ±0.68	0.45 ±0.09	76.72 ±6.55	596.21 ±26.63	1.62 ±0.61	77.14 ±5.81	253.49 ±32.74	163.36 ±19.77	3.66 ±0.56
Plant available	2.64 ±0.57	38.69 ±4.32	2.53 ±0.53	6.52 ±1.00	13.06 ±2.28	1.59 ±0.53	0.26 ±0.06	26.47 ±1.84	403.01 ±6.52	0.73 ±0.22	47.55 ±5.82	248.18 ±35.88	52.86 ±5.96	2.70 ±0.36
Mn-oxide	1.17 ±0.36	20.28 ±2.30	0.20 ±0.03	2.11 ±0.26	4.70 ±0.29	0.41 ±0.05	0.19 ±0.04	21.67 ±3.85	333.86 ±20.62	2.71 ±2.01	40.52 ±7.35	78.24 ±6.75	49.37 ±6.35	1.32 ±0.22
Amorphous Fe-oxide	1.19 ±0.34	13.97 ±2.38	0.31 ±0.34	1.31 ±0.29	2.48 ±0.18	0.84 ±0.12	0.11 ±0.05	13.00 ±2.75	267.39 ±26.73	0.27 ±0.15	32.85 ±3.34	54.08 ±5.88	38.38 ±5.79	1.10 ±0.23
Crystalline Fe-oxide	0.43 ±0.07	10.24 ±1.35	0.14 ±0.03	1.01 ±0.24	1.19 ±0.18	0.63 ±0.21	0.38 ±0.45	5.51 ±0.47	247.55 ±17.79	0.18 ±0.04	23.41 ±3.69	25.48 ±4.84	28.2 ±4.60	0.80 ±0.61
Organic matter	10.36 ±2.76	14.10 ±3.13	0.06 ±0.03	11.94 ±1.38	0.47 ±0.07	2.59 ±0.70	0.07 ±0.04	9.20 ±7.10	220.08 ±27.05	0.16 ±0.03	12.25 ±3.53	28.67 ±4.64	23.59 ±4.25	0.27 ±0.06
Residual	10.38 ±2.37	1.26 ±0.15	0.03 ±0.02	0.29 ±0.06	0.21 ±0.03	0.25 ±0.04	0.05 ±0.02	15.67 ±2.59	87.90 ±11.52	2.06 ±0.22	4.63 ±0.61	2.11 ±0.75	16.31 ±1.84	2.41 ±0.23
%Non Residual	91.27	99.80	99.82	99.67	99.88	99.74	99.55	96.37	97.66	97.09	99.08	99.86	97.84	91.04
% Residual	8.73	0.20	0.18	0.33	0.12	0.26	0.45	3.63	2.34	2.91	0.92	0.14	2.16	8.96
% MF	80.21	90.72	95.55	81.17	94.68	95.17	92.72	84.92	69.18	92.41	77.48	87.56	79.34	78.07

TABLE III (CONT'D) MEAN LEVELS OF HEAVY METALS (μG/G) IN EACH FRACTION OF THE SEDIMENT SAMPLES

Fraction	Site													
	B							C						
	Zn	Mn	Cd	Cu	Ni	Co	Pb	Zn	Mn	Cd	Cu	Ni	Co	Pb
Water soluble	104.42 ±10.47	636.38 ±22.42	25.79 ±3.77	156.05 ±3.80	437.17 ±23.49	189.82 ±7.10	8.04 ±1.57	147.42 ±16.06	640.60 ±14.22	26.69 ±4.88	98.02 ±5.84	382.67 ±13.24	175.23 ±11.96	8.17 ±1.96
Exchangeable	51.96 ±9.24	626.79 ±59.98	25.81 ±8.20	110.40 ±9.98	391.60 ±26.99	73.00 ±7.16	4.89 ±0.54	53.50 ±11.61	536.75 ±42.27	18.87 ±4.29	27.52 ±7.17	262.82 ±38.40	46.85 ±11.32	2.65 ±0.45
Carbonate	29.90 ±5.60	562.70 ±57.36	14.64 ±5.66	52.64 ±6.50	298.52 ±24.07	127.24 ±9.22	4.23 ±0.67	39.15 ±8.10	335.71 ±18.47	6.19 ±0.82	17.44 ±3.63	143.21 ±18.46	28.37 ±10.41	1.08 ±0.22
Plant available	25.44 ±3.60	379.11 ±8.37	5.31 ±0.42	24.27 ±3.32	125.41 ±5.82	56.61 ±3.96	2.69 ±0.61	39.36 ±6.60	262.86 ±20.86	2.60 ±0.44	11.34 ±1.77	49.90 ±6.91	22.43 ±4.12	4.57 ±1.18
Mn-oxide	25.33 ±5.38	270.52 ±22.73	2.48 ±0.57	19.10 ±2.92	46.44 ±3.76	48.81 ±5.03	2.31 ±0.30	34.03 ±4.38	254.47 ±6.26	8.65 ±2.30	10.86 ±2.23	32.84 ±3.39	6.52 ±2.48	0.44 ±0.07
Amorphous Fe-oxide	20.09 ±4.44	187.07 ±23.77	2.19 ±0.38	6.60 ±1.73	68.32 ±7.13	32.63 ±4.43	1.51 ±0.28	17.72 ±5.79	164.64 ±16.01	2.70 ±0.50	4.86 ±0.40	21.96 ±4.44	4.79 ±0.45	0.21 ±0.04
Crystalline Fe-oxide	18.37 ±6.33	121.75 ±6.65	0.56 ±0.22	5.24 ±1.78	27.09 ±4.05	36.97 ±4.05	1.17 ±0.20	5.88 ±0.60	150.60 ±15.37	1.71 ±0.32	2.75 ±0.41	2.33 ±0.28	0.82 ±0.12	0.16 ±0.04
Organic matter	18.34 ±3.86	53.53 ±11.17	0.16 ±0.03	13.35 ±4.19	23.05 ±5.31	23.83 ±5.77	0.33 ±0.05	12.61 ±2.57	68.80 ±11.01	1.01 ±0.10	11.22 ±2.79	0.46 ±0.15	10.85 ±1.25	0.08 ±0.03
Residual	13.78 ±1.57	42.76 ±3.49	5.05 ±0.02	6.19 ±0.11	5.49 ±0.34	14.79 ±1.59	5.17 ±0.02	11.99 ±3.66	13.76 ±1.48	0.31 ±0.03	1.04 ±0.16	2.28 ±0.17	0.15 ±0.04	0.04 ±0.01
%Non Residual	95.52	98.52	93.84	98.43	99.61	97.55	82.96	96.68	99.43	99.55	99.44	99.75	99.95	99.77
% Residual	4.47	1.48	6.16	1.57	0.39	2.45	17.04	3.31	0.57	0.45	0.56	0.25	0.05	0.23
% MF	68.82	76.55	87.27	87.18	88.03	73.99	65.43	77.26	73.13	79.07	83.39	93.34	92.19	94.66

TABLE III (CONT'D) MEAN LEVELS OF HEAVY METALS (μG/G) IN EACH FRACTION OF THE SEDIMENT SAMPLES

Fraction	Site													
	D							E						
	Zn	Mn	Cd	Cu	Ni	Co	Pb	Zn	Mn	Cd	Cu	Ni	Co	Pb
Water soluble	107.19 ±8.69	483.81 ±22.42	12.56 ±2.60	89.66 ±3.36	230.57 ±24.29	175.75 ±9.70	11.44 ±2.78	76.80 ±10.42	457.05 ±14.04	15.59 ±2.81	55.10 ±5.18	148.45 ±4.77	145.910 ±5.75	30.99 ±4.33
Exchangeable	49.43 ±7.61	386.09 ±59.99	12.62 ±2.31	76.58 ±7.16	126.65 ±5.87	26.81 ±3.51	4.37 ±0.42	43.89 ±8.31	277.65 ±24.49	19.42 ±5.61	34.42 ±5.82	85.63 ±7.74	31.37 ±4.29	18.51 ±4.28
Carbonate	33.19 ±4.21	299.61 ±26.33	1.72 ±0.42	30.52 ±7.55	104.42 ±14.63	23.10 ±4.78	4.31 ±1.70	26.68 ±6.04	200.32 ±12.78	3.45 ±0.54	26.65 ±5.73	25.38 ±6.16	31.21 ±7.33	16.64 ±3.97
Plant available	27.86 ±4.64	215.25 ±21.23	0.47 ±0.08	24.51 ±5.06	51.99 ±5.39	22.18 ±5.66	1.55 ±0.21	23.25 ±2.22	128.19 ±4.13	1.57 ±0.25	22.53 ±2.60	2.49 ±0.44	20.71 ±2.33	4.25 ±0.40
Mn-oxide	15.23 ±1.60	113.60 ±4.48	0.33 ±0.02	19.26 ±3.81	24.83 ±2.85	13.44 ±1.79	1.70 ±0.29	11.47 ±3.27	87.73 ±6.60	0.74 ±0.20	11.94 ±2.99	2.74 ±0.88	9.11 ±2.31	1.74 ±0.21
Amorphous Fe-oxide	7.45 ±1.99	65.41 ±4.86	0.26 ±0.06	11.72 ±4.62	13.33 ±0.99	9.54 ±2.09	0.89 ±0.07	5.20 ±0.71	53.42 ±3.66	0.38 ±0.08	8.16 ±1.95	0.37 ±0.07	2.40 ±0.29	1.07 ±0.23
Crystalline Fe-oxide	3.88 ±0.69	47.48 ±10.71	0.14 ±0.05	3.70 ±0.44	1.72 ±0.43	3.29 ±0.31	0.68 ±0.17	3.27 ±0.44	33.56 ±3.34	0.18 ±0.05	2.68 ±0.58	0.23 ±0.03	0.71 ±0.19	0.75 ±0.14
Organic matter	13.35 ±1.76	71.35 ±10.61	0.10 ±0.05	12.79 ±3.19	0.42 ±0.10	13.09 ±1.81	0.32 ±0.11	11.36 ±1.95	60.91 ±4.43	0.13 ±0.04	12.01 ±1.11	0.14 ±0.04	10.83 ±4.11	0.46 ±0.14
Residual	10.12 ±2.73	15.90 ±1.98	0.04 ±0.03	1.99 ±0.15	0.56 ±0.61	1.21 ±0.27	0.90 ±1.18	11.02 ±1.95	4.42 ±0.62	0.09 ±0.03	0.66 ±0.06	0.04 ±0.03	0.08 ±0.03	0.21 ±0.03
%Non Residual	96.22	99.06	99.86	99.26	99.90	99.58	96.56	94.82	99.66	99.78	99.62	99.98	99.97	99.73
% Residual	3.78	0.94	0.14	0.74	0.10	0.42	3.44	5.18	0.34	0.22	0.38	0.02	0.03	0.28
% MF	81.31	81.53	96.91	81.73	92.63	85.93	82.85	80.12	81.58	96.34	79.64	98.67	90.83	94.33

For Cd, up to 98.32% was present in the non-residual fraction on the average. An average of 85.94% of the total Cd in the sediments was present in the carbonate bond, exchangeable and water soluble fraction, with the water soluble fraction accounting for the highest amount of 39.46%, while the exchangeable fraction accounted for 35.76%. Cd levels in the operationally defined extraction sequence followed the order: Water soluble > exchangeable > carbonate bound > plant available > Mn-oxide > amorphous Fe-oxide > crystalline Fe-oxide > organic fraction > residual fractions. Cd does not appear to form stable organic complexes [33] hence its low content in the organic fraction could be due to low adsorption constant of the complex formed with organic matter. The high percentage of Cd in non-residual fraction may be due to high cation exchange capacity and pH effect [33]. The low content of Cd in the residual and Fe-Mn oxide fractions was probably due to the low association or retention ability of the mineral's crystal structure, such as with detrital silicates and resistant sulfides.

Virtually all the Cu content of the sediments was concentrated in the non-residual fraction with an average of about 99.46% of the total concentration of Cu. Water soluble fraction was the highest fraction averaging 36.68%, followed by exchangeable averaging 23% and carbonate fraction averaging about 13% and the organic fraction with an average of about 6% of the total Cu in the sediment. The low association of Cu with organic fraction in this study may be an indication of low organic content of the sediments since it is known that there exists a high formation constant of organic Cu complexes [34] in addition to high retention capability of organic matters like humic acids and fulvic acids for Cu. On the average, percent of total Cu associated with different geochemical fraction in the six sediments samples was in the order: Water soluble > exchangeable > carbonate > plant available > Mn-oxide > organic fraction > amorphous Fe-oxide > crystalline Fe-oxide > residual.

Like every other metals in this study, Ni was mostly concentrated in the non-residual fractions containing up to 99.38% of the total Ni content of all the fractions. Water soluble fraction (42%) > the exchangeable fraction > (26%) > carbonate bond fraction (15%) > plant available fraction > (9%). Although Ni was detected in all the geochemical fractions in the sediments, its composition in the other fractions was insignificantly small with the residual fraction averaging 0.17%. These results are inconsistent with an earlier submission that residual fraction was the most important fraction for Ni [13]. Rather, other factors such as the amount of a metal coming from the anthropogenic input, the prevailing chemistry of the soil/sediment-water interface and the species of the metal all constitute serious factors to be considered when accounting for the levels of metals in a fraction. In this study, Ni association with different geochemical fractions followed the order of decreasing solubility of the geochemical fractions of the sediment: Water soluble > exchangeable > carbonate > plant available > Mn-oxide > amorphous Fe-oxide > crystalline Fe-oxide > organic fraction > residual.

Also, the majority of Co was associated with the non-residual fraction in all the sediment samples. The highest percentage of Co was found at O with 79.15% Co associated with water soluble fraction, followed by exchangeable fraction (11.7%) while all other fractions were responsible for < 3%. Level of Co in water soluble fraction was also the highest fraction at other sites (although lower than the O values). Reasons for the higher levels of Co at O in the water soluble fraction than A to D might be due to variation in the sediment properties such as high cation exchange property and lower organic matter level [13] with respect to Co behaviour and background level in the parent soil/rock upstream. Generally, percent of total Co associated

with different geochemical fraction in the six sediments samples was in the following order: Water soluble > carbonate > exchangeable > plant available > Mn-oxide > organic fraction > amorphous Fe-oxide > crystalline Fe-oxide > residual. The result of speciation analysis of Pb in the samples gave an overall mean amount of Pb in the following order: Water soluble (45%) > exchangeable (16%) > carbonate (13%) > plant available (10%) > residual (5%) > Mn-oxide > amorphous Fe-oxide > crystalline Fe-oxide> organic fraction.

The distribution pattern of the metals was similar with water soluble fraction levels ranking the highest without exception. Thus, expectedly from these results, the mobility factor (MF) for each metal was high. The mean MF for the heavy metals studied were in the order: Zn (78.77%) < Mn (7 8.78%) < Pb (84.67%) < Co (86.24%) < Cu (89.77%) < Cd (91.26%) < Ni (92.48%). With a MF range of 69.18% for Mn to 98.67% for Ni, all the metals can be said to be highly environmentally labile and bioavailable [8, 34]. As such, all the humans, plants, animals and the general biota within the vicinity of this aquatic system are quite vulnerable to the heavy metals exposure.

A. *Levels of Total and Dissolved Heavy Metals in The Water Samples*

Results of the levels (µg/mL) of total heavy metals (Zn, Mn, Pb, Co, Cu, Cd and Ni) in the water samples are shown in Table 4. The mean metal levels at each site showed that Cd level was the least while Zn level was the highest with the following ranges: 0.02 ± 0.00 Cd - 1.35 ± 0.04 Zn at O; 0.06 ± 0.01 Cd - 2.96 ± 0.07 Zn at A; 0.05 ± 0.01 Cd - 2.35 ± 0.23 Zn at B; 0.04 ± 0.01 Cd - 1.98 ± 0.11 Zn at C; 0.03 ± 0.00 Cd - 1.68 ± 0.17 Zn at D; and 0.03 ± 0.00 Cd - 1.53 ± 0.12 Zn at E. Virtually all the metals existed in the water at levels grossly higher than the WHO Guideline Limit [28] for drinking-water (Table 4). This calls for serious caution on the part of the farmers and villagers who may use the water from this River for household purposes and for processing farm products such as palm oil.

The distribution trends of the total and dissolved heavy metals (Tables 4 and 5) in water are similar to what was observed in the sediments. Site O reflected the least values of heavy metal levels while A had the highest levels indicating a direct input of heavy metals from the dumpsite. Also, there was a general decrease in the levels of total metals downstream from A to E (Figure 2). This could be as a result of the dilution effect as the water volume increased

TABLE IV LEVELS OF TOTAL HEAVY METALS (μG/ML) IN THE WATER SAMPLES

Site	Month	Elements						
		Zn	**Mn**	**Pb**	**Co**	**Cu**	**Cd**	**Ni**
O	**April**	1.33±0.21	0.87±0.21	0.04±0.00	0.05±0.01	1.50±0.23	0.02±0.00	0.20±0.01
	May	1.32±0.50	0.89±0.15	0.03±0.00	0.04±0.02	0.94±0.21	0.02±0.00	0.24±0.10
	June	1.39±0.41	0.90±0.00	0.03±0.00	0.05±0.01	0.87±0.20	0.02±0.00	0.23±0.02
	Mean±s.d.	1.35±0.04	0.89±0.02	0.03±0.01	0.05±0.01	1.10±0.34	0.02±0.00	0.22±0.02
A	**April**	2.94±0.34	1.48±0.22	0.09±0.01	0.072±0.02	2.87±0.33	0.05±0.02	0.53±0.16
	May	3.04±0.37	1.55±0.23	0.06±0.02	0.13±0.03	2.62±0.31	0.06±0.01	0.53±0.19
	June	2.91±0.29	1.50±0.21	0.07±0.03	0.09±0.03	2.55±0.30	0.06±0.03	0.58±0.20
	Mean±s.d.	2.96±0.07	1.51±0.04	0.07±0.02	0.10±0.03	2.68±0.17	0.06±0.01	0.55±0.03
B	**April**	2.14±0.24	1.37±0.13	0.08±0.04	0.06±0.01	2.06±0.27	0.04±0.02	0.35±0.17
	May	2.64±0.23	1.27±0.11	0.05±0.03	0.10±0.04	2.49±0.28	0.05±0.03	0.48±0.15
	June	2.27±0.21	1.40±0.15	0.06±0.01	0.08±0.02	2.49±0.30	0.05±0.02	0.48±0.14
	Mean±s.d.	2.35±0.23	1.35±0.07	0.06±0.02	0.08±0.02	2.35±0.25	0.05±0.01	0.44±0.08
C	**April**	1.87±0.20	1.05±0.10	0.07±0.03	0.07±0.02	1.81±0.25	0.04±0.01	0.31±0.11
	May	2.08±0.25	1.00±0.09	0.05±0.04	0.09±0.03	1.87±0.26	0.03±0.00	0.36±0.12
	June	1.98±0.19	1.13±0.07	0.04±0.03	0.07±0.02	2.31±0.30	0.04±0.01	0.31±0.10
	Mean±s.d.	1.98±0.11	1.06±0.07	0.05±0.02	0.08±0.01	2.00±0.27	0.04±0.01	0.33±0.03
D	**April**	1.63±0.17	0.95±0.08	0.06±0.03	0.06±0.01	1.56±0.21	0.03±0.01	0.31±0.11
	May	1.87±0.16	0.98±0.08	0.05±0.02	0.08±0.02	1.81±0.23	0.03±0.01	0.32±0.12
	June	1.53±0.22	0.99±0.04	0.04±0.03	0.06±0.02	1.68±0.24	0.03±0.00	0.28±0.10
	Mean±s.d.	1.68±0.17	0.97±0.02	0.05±0.01	0.07±0.01	1.68±0.12	0.03±0.00	0.30±0.02
E	**April**	1.54±0.23	0.95±0.15	0.08±0.03	0.05±0.00	1.19±0.16	0.03±0.00	0.26±0.08
	May	1.64±0.30	0.97±0.21	0.04±0.02	0.06±0.01	1.56±0.15	0.03±0.02	0.25±0.09
	June	1.41±0.20	0.97±0.03	0.03±0.01	0.05±0.01	1.17±0.17	0.03±0.00	0.25±0.10
	Mean±s.d.	1.53±0.12	0.96±0.01	0.05±0.03	0.05±0.01	1.31±0.22	0.03±0.00	0.25±0.01
WHO*		3.00	0.4	0.01	Not available	2.00	0.003	0.07

TABLE V LEVELS (µG/ML) OF DISSOLVED HEAVY METALS IN THE WATER SAMPLES

Site	Month	Elements						
		Zn	Mn	Pb	Co	Cu	Cd	Ni
O	April	0.43±0.21	0.30±0.07	0.005±0.001	0.005±0.001	0.18±0.00	0.003±0.000	0.05±0.01
	May	0.45±0.16	0.41±0.06	0.006±0.001	0.007±0.000	0.13±0.02	0.003±0.002	0.05±0.01
	June	0.54±0.15	0.39±0.02	0.008±0.002	0.007±0.001	0.20±0.01	0.003±0.000	0.05±0.00
	Mean±s.d.	0.47±0.06	0.37±0.06	0.006±0.001	0.006±0.001	0.17±0.04	0.003±0.000	0.05±0.00
A	April	0.75±0.18	0.78±0.19	0.013±0.002	0.011±0.001	0.38±0.10	0.006±0.001	0.08±0.01
	May	0.94±0.20	1.39±0.31	0.017±0.000	0.017±0.001	0.39±0.09	0.005±0.002	0.18±0.02
	June	1.00±0.21	0.50±0.21	0.016±0.001	0.016±0.003	0.26±0.02	0.005±0.001	0.12±0.01
	Mean±s.d.	0.90±0.13	0.89±0.46	0.015±0.002	0.015±0.003	0.34±0.07	0.005±0.001	0.13±0.05
B	April	0.60±0.25	0.53±0.20	0.010±0.000	0.009±0.000	0.29±0.09	0.006±0.002	0.08±0.03
	May	0.75±0.30	1.00±0.24	0.014±0.000	0.015±0.001	0.36±0.10	0.005±0.000	0.11±0.02
	June	1.00±0.28	0.48±0.23	0.013±0.001	0.013±0.002	0.21±0.11	0.004±0.001	0.08±0.03
	Mean±s.d.	1.00±0.20	0.67±0.29	0.012±0.002	0.012±0.003	0.29±0.08	0.005±0.001	0.09±0.02
C	April	0.58±0.18	0.36±0.11	0.010±0.000	0.008±0.000	0.26±0.13	0.004±0.000	0.07±0.01
	May	0.74±0.20	0.50±0.10	0.011±0.001	0.011±0.000	0.32±0.12	0.004±0.001	0.08±0.03
	June	0.88±0.19	0.46±0.09	0.011±0.000	0.012±0.001	0.21±0.10	0.004±0.002	0.08±0.02
	Mean±s.d.	0.73±0.15	0.44±0.07	0.011±0.001	0.010±0.002	0.26±0.06	0.004±0.000	0.08±0.01
D	April	0.45±0.20	0.51±0.14	0.009±0.001	0.010±0.002	0.25±0.17	0.005±0.000	0.07±0.01
	May	0.70±0.18	0.52±0.07	0.008±0.000	0.010±0.000	0.31±0.19	0.004±0.000	0.07±0.02
	June	0.88±0.19	0.44±0.09	0.012±0.000	0.008±0.003	0.21±0.11	0.004±0.000	0.08±0.01
	Mean±s.d.	0.68±0.22	0.49±0.04	0.010±0.002	0.009±0.001	0.26±0.05	0.004±0.001	0.07±0.01
E	April	0.44±0.20	0.34±0.03	0.008±0.000	0.007±0.001	0.24±0.11	0.004±0.000	0.07±0.01
	May	0.49±0.16	0.49±0.06	0.008±0.002	0.009±0.000	0.24±0.12	0.004±0.001	0.06±0.02
	June	0.58±0.21	0.41±0.08	0.007±0.000	0.005±0.000	0.21±0.10	0.004±0.001	0.06±0.03
	Mean±s.d.	0.50±0.07	0.41±0.08	0.008±0.001	0.007±0.002	0.23±0.02	0.004±0.000	0.06±0.01

downstream and also because of the fact that there was probably no other point source addition of these metals downstream. The other reason could be because the metals had settled in the sediment phase of the aquatic system. This could probably be the case with lead where its high
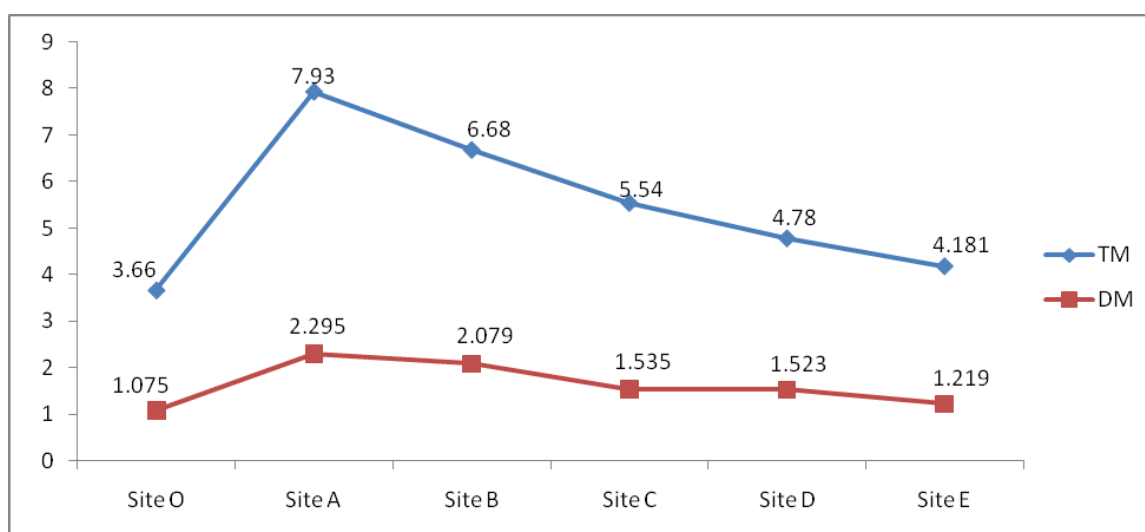

Figure 2 Levels (µg/mL) of total metal (TM) and dissolved metal (DM) in water

level detected in the sediments was not correspondingly reflected in the water phase. Compared with their total levels in the water samples, the dissolved levels of the heavy metals were generally low. This is in agreement with the observation that the levels of dissolved heavy metals in water are usually much lower than their background levels in the sediments [17]. The

dissolution of heavy metals in water is governed by the water pH, the type and concentration of ligands on which the metals could be adsorbed, the oxidation state of the mineral components and the redox environment of the system [18].

IV. CONCLUSION

This study revealed that the aquatic system studied was polluted to varying degrees particularly with notable toxic metals such as Pb and Cd. Also, Zn, Mn, Co, Cu and Ni occurred at levels that could adversely affect the health of plants, animals and humans having a prolonged operation within the vicinity of   the aquatic system. Although, part of the metals was probably a contribution from the geochemical weathering of the parent rocks around and their subsequent juvenile inputs into the river, it was obvious that majority of the heightened heavy metal levels measured could be traced to point source input from the dumpsite. A better method of waste management would certainly be needed to curtail the menace of heavy metal pollution of the dumpsite environment.

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