CONTAMINATION AND ECOLOGICAL RISK ASSESSMENT OF HEAVY METAL IN THE SEDIMENT OF ALA RIVER, SOUTH - WEST NIGERIA: AN INDEX -ANALYSIS APPROACH

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Abstract-Heavy metal concentrations were determined in sediments from Ala River in Akure Metropolis.Nine heavy metals were determined using Inductively Coupled Plasma -Optical Emission Spectroscopy (ICP-OES). The concentrations of the metals between the sites were Fe > Mn > Zn > Cr > Pb > Cu > Co> Ni> Cd and their concentrations (mg/kg) range are Fe: 4523- 12824, Mn: 51 -421, Zn: 10- 265, Cr: 11.2 - 67.8, Pb: 2.9- 50.7, Cu: 0.9- 12.4, Co: 1.4 - 10.3, Ni: 0.5 -7 and Cd: 0.5- 2.8. The organic carbon (OC), organic matter (OM) and particle size were also determined. With reference to US EPA sediment quality guideline, Cr was moderately polluted while Zn was heavily polluted in one of the sites. The heavy metal contamination in the sediments was also evaluated by applying Index of geo- accumulation (Igeo), enrichment Factor (EF), Contamination factor (CF), Pollution Load Index (PLI) and Potential Ecological Risk Index (PERI).Cd exceeds the ERL and TEL while Cr and Zn exceeded TEL values. Cd was heavily contaminated and has a considerably degree of contamination according to Igeo and degree of contamination respectively. Pb, Zn and Cd were severely enriched from anthropogenic origin while Cu and Ni were of natural origin. Potential risk index showed that the sites in Ala River have high potential risk index which need monitoring. The extent of pollution by heavy metals in Ala river implies that the condition may affect the biota and inhabitants in its if not properly remediated.

Index Term- Heavy metals; Sediments; Ala river; Geoaccumulation index; Contamination factor; Enrichment Factor

1. INTRODUCTION

Pollution of natural environment by heavy metals is a universal problem because these metals are indestructible and most of them have toxic effects on living organisms when permissible concentration levels are exceeded [1]. Heavy metals frequently reported in literature with regards to potential hazards and occurrences in contaminated soils/ sediments are Cd, Cr, Pb, Zn, Fe and Cu [2]. Vehicular emissions as well as several industrial activities emit these heavy metals so that soils, plants and even residents along roads with heavy traffic loads are subjected to increasing levels of contamination with heavy metals [1]. Heavy metals contamination in aquatic environment is of critical concern, due to toxicity of metals and accumulation in aquatic habitats. Trace metals in contrast to most pollutants are not biodegradable, and they undergo a global ecological cycle in which natural water are the main pathways. Of the chemical pollutants, heavy metal being non-biodegradable, can concentrate along the food chain, producing their toxic effect at points far from the source of pollution [3,4]. Exposure to heavy metals has been linked to several human diseases such as development of retardation or malformation, kidney damage, cancer, abortion, effect on intelligence and behavior, and even death in some cases of exposure to a very high concentration. The symptoms of toxic heavy metal poisoning and the symptoms of autism, Pervasive Development Disorder (PDD), aspersers, and Attention Deficit Disorder (ADD)/ Attention Deficit Hyperactivity Disorder (ADHD) are very similar [3,4]. Perhaps, toxic metals could be the cause of illness experienced by humans such as memory loss, increased allergic reactions, high blood pressure, depression, mood swings, irritability, poor concentration, aggressive behavior, sleep disabilities, fatigue, speech disorders, cholesterol, triglycerides, vascular occlusion, neuropathy,

autoimmune diseases, and chronic fatigue are just some of the many conditions resulting from exposure to toxins [1,4]. Heavy metals poison us by disrupting our cellular enzymes, which run on nutritional minerals such as magnesium, zinc, and selenium. The heavy metals most often implicated in human poisoning are lead, mercury, arsenic, and cadmium. Some heavy metals, such as zinc, copper, chromium, iron, and manganese, are required by the body in small amounts, but these same elements can be toxic where they are trace in larger quantities. Toxic heavy metals may lead to a decline in the mental, cognitive and physical health of the individual [3].

Sediments are normally mixtures of several components including different mineral species as well as organic debris. Sediments are an important element of aquatic ecosystems. They constitute ecological niches supporting benthic organisms, that is, animals and plants living on the bottom of bodies of water, and are a source of nutrients for aquatic organisms such as small invertebrates and protozoans [5,6]. Sediments are considered a suitable medium to study the contamination of aquatic environments because they represent the sink of multiple contaminant sources. Removed sediments are often heavily contaminated, resulting in waste management problem [7]. Actually, pollutants are not necessarily permanently immobilized in dredged sediments, and heavy metals and organic compounds remobilisation from sediments due to bioturbation and re-suspension constitutes a potential danger. [7]. In Ala river till now, little or no scientific research regarding ecological risk assessment had been conducted. Therefore, the objectives of this study are to assess the level of heavy metal concentrations in the sediment of Ala river, its spatial distribution and compare it with the USEPA quality guideline and to select different pollution indices to assess heavy metal contamination and the ecological risk due to sediment contamination.

2. Method and Materials

Description of the study area

Akure is the Capital City of Ondo State Nigeria and it is located in the Central Senatorial District of the State [8]. Akure falls between 739000 and 746000 Easting (i.e. between longitude 5°06′E and 5°38′E) and between 801500 and 807000 Northing (i .e . , between latitude 7° 07′ N and 7 37′ N) (Fig 1). The capital city is bounded in the North by Ifedore Local Govt area, in the west by Ile – Oluji Oke -Igbo Local Government area, in the South by Idanre Local Government and East by Ore – Odigo Local Government area [9]. The study area experiences a frequent rainfall between April and July with a short break in August and continues between September and November, with the heaviest rainfall in July. The average daily temperature ranges from 22^0 C - during harmattan (December – February) to 32 °C in March which is the peak temperature. The vegetation is a tropical rainforest [10, 11]. The population of the people residing in Akure is about 353,211 [12]. Ala river with total length of about 57 km has a length of about 14.81km in Akure Township (Fig. 1). It took its source from North Western part of Akure township and flows towards South - Eastern part of the town. Akure Township is located upstream of Ala river while rural towns such as Ilado, Ehinala, Ajegunle, Owode Aiyetoro and Araromi are located in downstream where the water is used for domestic purposes.

Samples Collection:

Twenty nine sediment samples were collected from ten sites along Ala river (as show in Fig.1) during drying season between December 2013 and February 2014. The latitude and longitude for each site are illustrated in Table1. The samples were collected using an auger at 0 - 10 cm stored inside polythene bags, later transported to the laboratory and preserved at temperature of 4 ^{0}C, after which the sediment samples were air – dried for 2 weeks in the laboratory. The air –dried sediments were sieved through a 1.7 μm mesh to remove the debris, then lightly ground in an agate mortal for homogenization then ready for heavy metal analysis.

Table1: Monitoing sites and their coordinates

Site No	Location	Latitude	Longitude	Site descriptions
1	Aule	$07^0$16.45N	$005^0$09.99E	Mechanic workshops, petrol stations
2	Ayedun	$07^0$15.82N	$005^0$11.48E	refuges
3	Araromi	$07^0$15.67N	$005^0$11.67E	Car wash, saw mill,refuges
4	Oke-Ijebu (Cocola deport)	$07^0$15.75N	$005^0$12.31E	Car wash, refuges
5	Oke- Ijebu (3-Ages Hotel)	$07^0$16.44N	$005^0$12.44E	refuges
6	Fiwasaye	$07^0$15.33N	$005^0$13.23E	refuges
7	Alagbaka	$07^0$15.43N	$005^0$12.67E	refuges
8	Odudu	$07^0$19.16N	$005^0$14.31E	refuges
9	Kojola- Ilado	$07^0$11.60N	$005^0$17.58E	Agriculture
10	Ehin- Ala	$07^0$11.51N		Agriculture

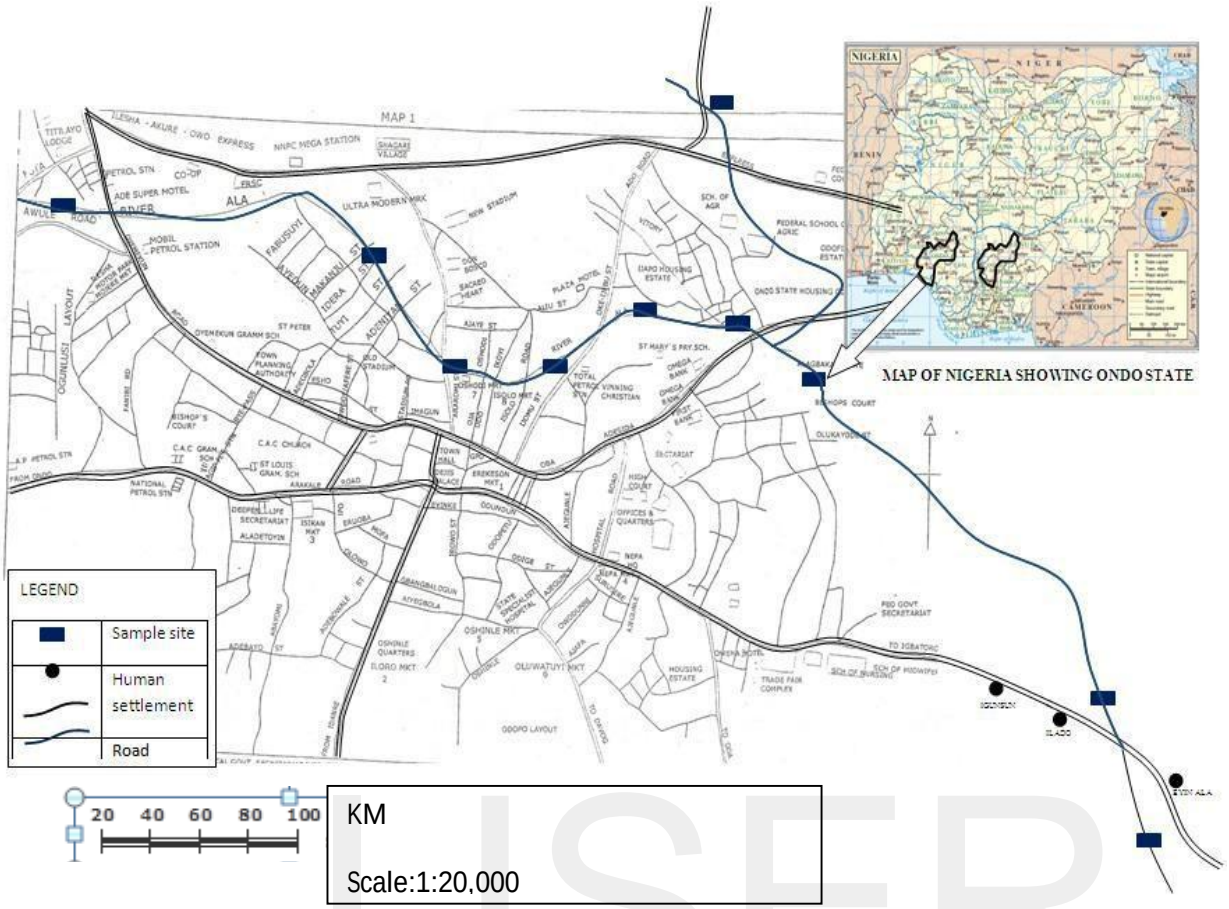

Fig 1: Location map of the study area.

Sample digestion and metal extraction

All chemicals used were of analytical grade, Milli-Q water was used for solution preparation. The Teflon vessel and polypropylene containers were cleaned, soaked in 10 % HNO_3 for 48h, then rinsed with Milli-Q water and dried using oven at 60 ^{O}C.

For heavy metal analysi, extraction of metals from sediment samples was usihg mixed acid aqua- regia digestion. The aqua regia was based on the procedure recommended by the International Organization for Standardization[13]. A mixture of HCl and HNO3 (3:1v/v) was added to the samples on temperature-controlled hot plate and the mixture was heated at 160^0C for at least 2 h. Consequently, the mixture was allowed to cool, the 1ml of HNO_3 was added followed by Milli-Q water and filtered through a filter paper (70 mm) into 50 ml volumetric flask and made up to the mark with Milli-Q water.

Determination of pH

Sediment to Milli-Q water (2:1) was prepared. The mixtures were mixed thoroughly and filtered using filter paper (70 mm).The filterate was measured by using Horiba pH D-51.

Determination of Organic Carbon

The organic matter was determined using the method described by [14]. 10 mL of 1M $K_2Cr_20_7$ standard solution was added to 2 g sediment followed by 20 mL of concentrated H_2SO_4. The system was allowed to

stand for 30 min with occasional swirling. After 30 min, the content of the conical flask was diluted with 10 mL of Milli-Q water. The excess $K_2Cr_2O_7$ was determined by titrating with standard 1M ferrous sulphate using Ferroin indicators. The blank titration was carried out in the same manner without the sediment.

$$\%C = \frac{(B-S)XMofFe^{2+}X12X100}{gofse\,\mathrm{dim}\,entX\,4000} \quad 1$$

$$\%OM = \frac{\%totalCX1.72}{0.58} \quad 2$$

B = mL of Fe^{2+} solution used for blank;
S = mL of $Fe2^{+}$ solution used to titrate sample

Determination of Particle Size

The particle Size was determined using method [15].

Instrumental analysis and quality assurance

For heavy metals, samples were analysed by using Inductively Coupled Plasma- Optical Emission Spectrometer (ICP- OES) modeled Perkin Elmer Optma 7300DV from the Hiroshima University, Japan.

Procedural blanks, spiked blank and spiked matrix blank were prepared for qualification. For heavy metals, concentrations of standard mixtures were used. Indium (In) and Yttium (Y) were used as recovery standard. Recoveries In and Y were between 98 and 103 %. The machine detection limit for the metals analysed were given in mg/kg below: 0.01 for Cd, Cr, Co, Cu, Zn, Ni while 0.1mg/kg for Fe and Mn. The selected wavelength were: Cd 228.8 nm; Cr 205.6nm; Co 228.6; Cu327.4 nm, Fe 238.2 nm, Mn 259 nm, Ni 231.6 nm, Pb 220.3 nm and Zn 206.2 nm

Metals Assessment in Sediment

The choice of background values plays an important role in metal assessment. For the purpose of this experiment, the world surface average values were used as reference baselines [16]. The degree of contamination from heavy metals could be assessed by USEPA guides lines,contamination factor, geo-accumulation index (Igeo), enrichment factor (EF), pollution load index and ecological pollution risk index.

Geoaccumulation index (I_{geo})

Index of Geo-accumulation (Igeo) has been used widely to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environment [17]. The Igeo of a metal in sediment can be calculated with formula: [18, 19]. In order to characterize the level of pollution in the sediment, geoaccumulation index (I_{geo})values were calculated using the equation

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$$\mathrm{Igeo} = \mathrm{Log}_2 \frac{Cn}{1.5Bn} \quad \text{.....(3)}$$

where Cn is the measured concentration of metal n in the sediment and Bn is the geochemical background value of the element n in the background sample [20]. The factor 1.5 is introduced to minimize the possible variations in the background values which may be attributed to lithogenic effects. The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as

follows: [20]: $I_{geo} \leq 0$ – practically uncontaminated; $0 \leq I_{geo} \leq 1$ -uncontaminated to moderately contaminated; $1 \leq I_{geo} \leq 2$ –moderately contaminated; $2 \leq I_{geo} \leq 3$ –moderately to heavily contaminated; $3 \leq I_{geo} \leq 4$ – heavily contaminated; $4 \leq I_{geo} \leq 5$ – heavily to extremely contaminated; and $5 > I_{geo}$ - extremely contaminated.

Enrichment Factor (EF)

A common approach to estimate how much the sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above un-contaminated background levels [20]. The EF method normalizes the measured heavy metal content with respect to a samples reference such as Fe, Al or Zn **[18].** The EF for each element was calculated to evaluate anthropogenic influence on heavy metals in sediments using the following formula [21].

$$EF = \frac{CM/CFEsample}{(CM/CFe)\ background} \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where C_M/C_{Fe} is the ratio of concentration of heavy metals C_M to that of Iron(Fe) in the sediment sample, and (C_M/C_{Fe})background is the same reference ratio in the background sample.

Generally, EF value of about 1suggests that a given metal may be entirely from crustal materials or natural weathering process [22]. Samples having enrichment factor > 1.5 was considered to indicate human influence and EF of 1.5 -3; 3- 5; 5 -10 and > 10 are considered the evidence of minor, moderate, severe, and very severe modification represented by [23].

Pollution Load Index (PLI) and Contamination factor (CF)

To assess the sediment quality, an integrated approach of pollution load index of the eight metals is calculated according to [24]. The PLI is defined as the nth root of multiplications of contamination factor of metals (CF).

$$PLI = (CF_1 \, x CF_2 \, x \, CF_3 \, x \ldots\ldots x \, CFn)^{1/n} \quad \ldots\ldots\ldots\ldots(5)$$

where CF metals is the ratio between the content of each metal to the background value (background value from the world average values for sediment [16]

$$CF\ metals = C_{metals}/\ C_{background} \quad \ldots\ldots\ldots\ldots(6)$$

The PLI value of zero indicates perfection, a value of one indicates the presence of only baseline level of pollutants and values above one would indicate progressive deterioration of the site [24]. The PLI gave an assessment of the overall toxicity status of the sample and also it's a result of the contribution of the nine metals. The ratio of the measured concentration to natural abundance of a given metal had been proposed as the index contamination factor (CF) being classified into four grades for monitoring the pollution of one single metal over a period of time [25, 26]: low degree (CF < 1), moderate degree (1 ≤ CF < 3), considerable degree (3 ≤ CF < 6), and very high degree (CF ≥ 6). The degree of contamination (C_d) is defined as the sum of all contamination factors. The ranges are: Low degree (Cd < 6), moderate degree (6 ≤ Cd < 12), and considerate (12 ≤ Cd < 24) and very high (Cd ≥ 24).

Effect Range Low (ERL), Effect Range Median, (ERM), Threshold Effect Level (TEL) and Probable Effect Level (PEL)

To evaluate the sediment contamination and potential ecotoxicology effects associated with concentration of contaminants, two sets of SQGs developed for marine and estuarine ecosystems [27,28] were applied to assess the eco -toxicological potential of heavy metal concentrations;

(a) the Effect Range –Low (ERL) / Effect Range - Median (ERM); and (b) the Threshold Effect Level (TEL) /Probable Effect Level (PEL) values (Table 2). Low range values (ERLs/TELs) are concentrations below which adverse effects upon sediment dwelling fauna would infrequently be expected. In contrast, the ERMs and PELs represent chemical concentrations above which adverse effects are likely to occur [29].

Potential Ecological Risk Index

The ecological risk index for aquatic pollution control had been reported by [30]. Hakanson's method has been used often in ecological risk assessment as a diagnostic tool to potential ecological risk.

The index calculated as the following equations:

$$C^i_f = \frac{C^i_D}{C^i_R} \quad (7)$$

$$C_H = \sum_{i=1}^{m} C^i_f \quad (8)$$

$$E^i_f = T^i_f \times C^i_f \quad (9)$$

$$RI = \sum_{i=1}^{m} E^i_f \quad (10)$$

C^i_f is the pollution coefficient of single metal; C^i_D is the measured concentration of sample; C^i_f is the background concentration of sediments; C_H is the polluted coefficient of many metals; E^i_f is the potential ecological risk factor of single metal; T^i_f is the biological toxicity factor of different metals; and RI is the potential ecological risk index of many metals. The toxicity Response Factor for metals is: Cd =30; Cr =2, Cu = Mn = Pb = Co =5, Zn = Fe =1 [31]

From the Indices and grades of potential ecological risk (RI) of heavy metal contamination, $E^i_r < 5$ indicates low risk, $5 \leq E^i_r < 10$ (moderate risk); $10 \leq E^i_r < 20$ (Considerate risk); $20 \leq E^i_r < 40$ (High risk); $E^i_r \geq 40$ (Very high risk). For potential ecological risk of the environment, the grades of, PERI < 110 (Low risk); PERI: 110 -220 (moderate); PERI: 220 – 440 (high risk); PERI > 440 (Significantly high risk) [32].

Statistical analysis

The data were statistically analysed using the statistical package, SPSS 18.0 (SPSS, USA). The means and standard deviations of the metals concentrations in sediments were calculated. The principal component analysis (PCA) was used as an approach to reduce the size of the variable space and substitute a large number of parameters by a small number of independent factors (principal components), which allows data interpretation and data structure explanation.

3. RESULTS AND DISCUSSION

3.1 Mean concentrations (mg/Kg) of sediments of Ala River

The mean concentrations of sediments sample are presented according to the Table 2. The mean

concentration ranges over the following intervals: Cd: 0.5 – 2.8; Co: 1.4 – 10.3; Cr: 11.2 – 67.8; Cu: 0.9 – 12.4; Fe: 4523 – 12824; Mn: 51- 421; Ni: 0.5 -7.1; Pb: 2.9 – 50.7; and Zn: 10– 265. The highest values for Cd, Co, Cu, Fe, Ni were found in site 1, while Pb and Zn have the highest value in site 3, Cr in site 5 and Mn in site 8. The concentrations of the metals between the sites were Fe > Mn > Zn > Cr > Pb > Cu > Co > Ni > Cd [33]. The metals in study followed the same trend when compared with the part of the work done by the author during the raining season Abata *et al.,* 2013.The values in this study were higher than the values of heavy metal concentration obtained across the sites. This might probably due to dilution which influences concentration and heavy metal mobility during the raining season

The average pH of the sediment from the sites range from 5.7 -6.2 (Table 4). The composition of the organic carbon in sediment samples was varied among the sites due to its origin in the aquatic environment. The organic carbon and OM in sediments ranged from 0.04 – 0.12 and 0.13- 0.36% respectively. The particle size (silt, clay and sand) ranged from 0.30 – 1.47, 0.3- 7.5 and 89.7- 94.0% respectively (Table 4).

3.2 Assessment of metal pollution in sediment.

From the data obtained from this study Cd exceeded the ERL and TEL values in Site 1 to 6 while Cr exceeded TEL value in Site 5. Zn also exceeded the TEL and ERL in Site 3 (Table 2). According to USEPA guidelines from Table 3, the sediment was found to be moderately polluted with Cr in sites 1 to 6 but heavily polluted with Zn in site 3. It was discovered that Cd might be released to the environment through mining and smelting [34] (ATSDR 1999).Cd could also be released through man made activities such as the use of phosphate fertilizer, presence of sewage slude, NiCd batteries, plating pigment and plastics [34] (ATSDR 1999). Generally located in site 1 is mechanic village where a lot can be deposited on the soil and leached into the river. In site 3, there are lot of car wash plant where oil, diesel can be washed into the water and there dumping of refuge directly the river.

Enrichment factor (EF) is a normalization technique used to categorise the metal fractions that is associated with sediments [18]. The spatial distribution of calculated EF for each of the studied metals is shown in (Table 6). Cd and Cr were severely enriched in all sites while only Pb and Zn were severely enriched at site 6 and 3 respectively. Sample having enrichment factor > 1.5 was considered indicative of human influence. For most of the sites EF values were higher than 1.5 except for Cu and Ni which were less than 1.5 which indicate that they are not of human influence they might be from crustal materials or natural weathering. Most of the sites, the EF greater than 1.5 indicating that anthropogenic inputs were probably the major contributors for the enrichment of the sites with metals on the surface sediments of the studied river. It is presumed that high EF values indicate an anthropogenic source of heavy metals, mainly from activities such as industrialization, urbanization, deposition of industrial wastes, and others. Since the bioavailability and toxicity of metals in sediments depend upon the chemical form and concentration of elements [35] it can be inferred that trace elements with the highest EF in sediments have a potential for mobility and bioavailability in the aquatic ecosystem. Among the studied metals, the Igeo showed that Cd has the highest values. Cd ranged from heavily contaminated in site1, uncontaminated to moderately contaminated in sites 6 to 9 and moderately contaminated at site 2 to 4. Pb and Zn ranged from uncontaminated to moderately contaminate in both in site 3. Among the remaining sites, the I_{geo} for Co, Cr, Cu, Fe, Mn, Pb, Ni and Zn indicate uncontaminated (Table 5). The higher value of Cd might be due to the higher concentration in sediment and lower level in the background samples.

The calculated pollution index (PLI) values of metals in sediment are summarized in Table7 which ranged from 0.12 – 0.60 confirming the sediment of the studied river was not polluted.

The contamination factors of the various metals in the sediment of Ala river are presented in Table 7. The concentration of Cd was reported to be high in all the sites. Pb has moderate and considerate contamination in sites 1 and 3 respectively. Cd had a considerate degree of contamination in all the sites except in site 2 where it had moderate degree of contamination (Table 7). From the contamination factor calculations, it was found

that a regular monitoring for the concentrations of Cd and Pb is essential since the contamination factor at all sites especially for Cd exceeded the desirable limit for CF values and can cause potential pollution risk. Also from Table 7, the ecological risk index (PERI) ranged from low risk in sites, 8 to 10 but moderately risk, in site 2 to7 and significantly risk in site 1 respectively.

There is correlation among the heavy metals. The correlation was very strong among Cd, Cr and Fe, and strong correlation between Cr, Co, Cu, Cd, Ni, Fe, Zn and Pb. This may suggest that the metals may be from the same origin (Table 9).

Table 2: Mean Concentrations of Heavy metals (mg/Kg dry weight) of sediments of Ala River (drying season)

Site	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	2.8± 1.8	10.3 ± 4.7	47.8 ± 3.2	12.4± 16.0	12824 ± 3373	237± 70.5	7.1± 3.5	16.8 ± 3.0	18.3± 7.4
2	1.3± 0.5	2.2± 0.3	44.5± 30.3	6.2± 2.5	10381± 1997	322± 178.0	2.3± 1.5	10.0± 2.2	54.7± 29.5
3	1.3± 0.5	2.8± 0.7	37.7±1 4.4	6.4± 1.4	10139± 2039	140± 48.0	4.2± 0.7	50.7± 29.8	265± 122.0
4	1.2± 0.4	2.6± 0.7	38± 7.3	4.4± 0.7	9181± 2150	138± 9.5	1.9± 1.7	8.8± 0.2	42.0± 17.2
5	2.1 ± 1.1	2.2± 0.6	67.8± 32.7	6.0± 2.7	12097± 3260	209± 154.8	1.6± 0.7	15.8± 12.3	34.3± 2.1
6	0.8 ± 0.2	4.4± 1.4	36.4± 29.4	3.7± 1.2	8211± 1173	190± 30.0	2.4± 1.1	13.3± 1.5	54.3 ± 4.0
7	1.0 ± 0.2	3.4± 0.9	27.7± 11.6	4.9± 1.7	8848 ± 1089	218 ± 28.0	1.7 ± 0.5	8.4 ± 0.4	39.7± 4.0
8	0.62± 0.2	3.7± 1.5	12.5± 10.6	1.9± 0.8	6768± 1210	421± 199.0	1.23± 0.5	8.1± 0.8	17.7± 7.5
9	0.6 ± 0.3	1.4± 0.5	11.38± 5.8	0.9± 0.8	5978± 2681	149.7± 64.7	0.9± 0.5	3.2± 1.1	10.0± 3.6
10	0.5± 0.3	1.7± 0.3	11.2± 2.6	1.4± 1.1	4523± 306	51.0± 28.0	0.5± 0.4	2.4± 0.1	17.0± 7.9
TEL	0.7	-	52.3	18.7	-	-	15.9	30.2	124.0
PEL	4.2	-	160.4.	108.2	-	-	42.8	11.2	271.0
ERL	1.2	-	81	34	-	-	20.9	46.7	150.0
TEL =Threshold Effect Level; PEL = Probable Effect Level; ERL = Effect Range Low; ERM = Effect Range Low.									

Table3. USEPA Guidelines for sediments (mg/Kg)

Metals	Not polluted	Moderately Polluted	Heavily polluted
Pb	<40	40- 60	>60
Cd	-----	-----	>60
Cr	<25	25 -75	>75
Cu	<25	25 – 75	>50
Zn	<90	90 -200	>200

Table 4.Physico– chemical Properties of the sediments of Ala river (drying season).

Sites	pH	OC	OM	Silt	Clay	Sand
1	5.7 ± 0.50	0.11± 0.03	0.30± 0.10	1.30± 0.60	7.5± 1.2	89.7± 3.8
2	5.7 ± 0.03	0.11± 0.03	0.32 ± 0.03	1.3± 0.06	7.5± 1.2	89.7± 3.8
3	5.7 ± 0.30	0.06± 0.01	0.14± 0.01	0.08± 1.10	7.3± 1.2	92.0± 1.3
4	6.0 ± 0.10	0.05± 0.04	0.14± 0.10	0.33± 0.20	5.7± 2.1	94.0± 1.9
5	6.0 ± 0.10	0.05± 0.04	0.14± 0.10	0.33± 0.20	0.3± 2.1	94.0± 1.9
6	5.7 ± 0.30	0.05± 0.04	0.13± 0.10	1.13± 0.50	5.7± 2.4	93.0± 2.6
7	5.8 ± 0.20	0.08± 0.03	0.24± 0.10	1.10± 0.70	6.3± 2.7	92.6± 3.4
8	5.9 ± 0.10	0.12± 0.05	0.36± 0.10	1.40± 0.90	6.6± 3.5	92.0± 3.2
9	6.2 ± 0.10	0.04± 0.03	0.13± 0.80	1.47± 0.10	6.7± 3.0	91.2± 2.8
10	6.2 ± 0.20	0.08± 0.07	0.24± 0.20	0.9± 0.40	5.9± 3.4	92.9± 4.0

Table 5: Geo-accumulation Index of heavy metals from Ala river (drying season).

Sites	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	3.22	-0.92	-1.16	-1.95	-2.07	-2.18	-3.37	-5.10	-2.55
2	2.12	-3.15	-1.26	-2.95	-2.38	-1.75	-5.00	-1.26	-1.8
3	2.12	-2.80	-1.50	-2.91	-2.41	-2.95	-4.13	1.08	0.48
4	2.00	-2.91	-1.49	-3.45	-2.55	-2.97	-5.27	-1.45	-2.18
5	2.81	-3.15	-0.65	-3.00	-2.15	-2.37	-5.06	-0.60	-2.48
6	1.42	-2.15	-1.55	-3.70	-2.71	-2.51	0.7	-0.85	-1.81
7	1.74	-2.52	-1.94	-3.29	-2.61	-2.31	1.5	-1.51	-2.26
8	1.05	-2.39	-3.09	-4.66	-2.99	-1.36	7.4	-1.57	-3.43
9	1.00	-3.80	-3.09	-5.74	-3.17	-2.85	-6.35	-2.91	-4.25
10	0.74	-3.52	-3.25	-5.10	-3.57	-4.40	-7.20	-3.05	-3.49

Table 6: Enrichment Factor of heavy metals from Ala river (drying season).

Site	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
1	39.2	2.2	18.9	1.1	0.9	0.4	2.9	0.7
2	22.5	0.6	21.7	0.7	1.6	0.2	2.2	1.5
3	23.0	0.8	18.8	0.7	0.7	0.3	11.2	7.4
4	23.5	0.8	20.9	0.5	0.8	0.2	2.2	1.3
5	31.2	0.5	28.3	0.6	0.9	0.1	2.9	0.8
6	17.5	1.5	22.4	0.5	1.2	0.2	3.6	1.9
7	20.3	1.1	15.8	0.6	1.2	0.1	2.1	1.3
8	16.4	1.5	9.3	0.3	3.1	0.1	2.7	0.7
9	18.0	0.6	10.6	0.2	1.3	0.1	1.2	0.5
10	19.8	1.0	12.5	0.3	0.6	0.1	1.4	1.1

Table 7: Contamination factor, degree of contamination and pollution index of heavy metals (drying season).

Sites	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	degree C	PLI
1	14.0	0.79	0.67	0.39	0.36	0.36	0.14	1.05	0.26	19.02	0.62
2	6.5	0.17	0.63	0.19	0.29	0.45	0.05	0.63	0.43	11.34	0.42
3	6.5	0.22	0.53	0.20	0.28	0.19	0.09	3.17	2.09	16.27	0.55
4	6.0	0.2	0.54	0.14	0.26	0.19	0.04	0.55	0.33	12.25	0.32
5	10.5	0.17	0.94	0.19	0.34	0.29	0.04	0.99	0.27	18.73	0.41
6	4.0	0.34	0.51	0.12	0.23	0.26	0.05	0.83	0.43	12.77	0.36
7	5.0	0.26	0.39	0.15	0.25	0.30	0.03	0.53	0.31	14.22	0.31
8	3.1	0.29	0.18	0.06	0.19	0.58	0.03	0.51	0.14	13.08	0.31
9	3.0	0.11	0.18	0.03	0.17	0.21	0.02	0.20	0.08	13.00	0.14
10	2.5	0.13	0.16	0.04	0.13	0.07	0.01	0.18	0.13	13.35	0.12

Table 8: Ecological risk index of heavymetals from Ala river (drying season).

Sites	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	PERI
1	420	1.34	1.95	0.36	1.95	0.7	5.30	0.26	431.8
2	195	0.85	0.95	0.29	0.95	0.25	3.20	0.43	201.9
3	195	1.06	1.00	0.28	1.00	0.45	15.9	2.09	216.8
4	180	1.08	0.70	0.26	0.70	0.20	2.75	0.33	186.0
5	315	1.88	0.95	0.34	0.95	0.20	4.95	0.27	324.5
6	120	1.02	0.60	0.23	0.60	0.25	4.15	0.43	127.3
7	150	0.78	0.75	0.25	0.75	0.15	2.65	0.31	155.6
8	93	0.38	0.30	0.19	0.30	0.15	2.55	0.14	97.0
9	90	0.36	0.15	0.17	0.15	0.10	1.00	0.08	92.0
10	75	0.32	0.20	0.13	0.20	0.05	0.90	0.13	76.9

Tabble 9 Coefficient correlation between the elements on sediments in Ala river (drying season).

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1								
Co	.699**	1							
Cr	.771**	.306	1						
Cu	.790**	.726**	.594**	1					
Fe	.886**	.513**	.817**	.631**	1				
Mn	.138	.248	.122	.235	.226	1			
Ni	.775**	.792**	.468**	.780**	.708**	.167	1		
Pb	.271	.096	.286	.257	.403*	.036	.402*	1	
Zn	.063	-.090	.164	.148	.214	-.132	.287	.635**	1

Note: Very Strongly correlation (>0.8); Strong (0.6 -0.8); moderate (0.4- 0.6); Regular: Low (<0.4) *Correlation is significant at the 0.05 level

Table 10 Component Plot of heavy metals in Ala river (drying season.

Extraction of total variance of sediments sample with eigen values and Component Matrix (2 components selected)			
Extraction method, principal component analysis.			
Components	Total	% of Variance	Cumulative %
1	4.691	52.127	52.127
2	1.628	18.086	70.213

3.3 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was used to deduce the variables. The percentage (%) variance in each of the original variables extracted by the components is explained by communalities (Table11). Fe had the largest variance (80.4%) being extracted by the PCA. The variables were strongly extracted apart from Mn which had a weak extraction value of 18.9 % by the components. The results of the PCA indicated that the heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) could be reduced to two components, which accounted for 70.2 % of the total variance for the data. The first component has vast and strong relationship among one another while only Zn and Pb were extracted by component 2 (Table12). Table 13 show the loading of the two components when rotated with Varimax rotation method. The largest loading variables explained by the components are displayed and sorted out by size.

The total variance of 52.1% was characterized by high loadings for Cd, Fe, Ni, Cu, Cr and Co in component 1. Most PCA loading for Cu, Cd, Fe, Ni, Co and Cr were in Component 1 and high concentration of them also had similar locations, which indicated that the six metals might have the same origin. Cd and Cu in the component suggested that incineration of waste might be a major source of the metals [36] (Ediabgonya *et al.*,2013). Total variance 18.1 % was characterized by high loadings for Zn and Pb in component 2. These two metals had a high correlation indicating that they may have similar sources. The loading might suggest vehicular related emission as a source of the heavy metals [36] (Ediabgonya *et al*., 2013). After rotation by Varimax rotation method, the highest loading parameters are: Component 1 (Cu, Cd, Fe, Ni, Co and Cr); and (Zn and Pb) from component 2.

Finally, it was discovered that the two components loading of variables are inter- related. There was strong correlation among the elements in component 1 while only Zn and Pb had strong correlation between one another in component 2. The two components were not statistically significant which implies that they are of the same source pollution.

Table 11. PCA Communalities

Variables	Intial	Extraction
Cd	1.000	.895
Co	1.000	.719
Cr	1.000	.584
Cu	1.000	.776
Fe	1.000	.804
Mn	1.000	.189
Ni	1.000	.790
Pb	1.000	.747
Zn	1.00	.816

Table 12 PCA, component extracted

Component	1	2
Cd	.935	-.145
Fe	.895	.052
Ni	.889	.011
Cu	.868	-.148
Cr	.762	.057
Co	.748	-.399
Zn	.255	.866
Pb	.448	.739
Mn	.255	-.351
Cd	.935	-.145

Table 13 PCA, Rotation method: Oblimin with Kaiser Normalization

Component	1	2
Cd	.946	.079
Fe	.881	.060
Ni	.874	.220
Cu	.873	.260
Cr	.806	-.212
Co	.741	.235
Zn	.312	-.282
Pb	.104	.902
Mn	.316	.823
Cd	.946	.079

3.3 Cluster analysis.

A cluster analysis was performed in order to group the heavy metals having close similarities. The dentogram separates the studied metals into two main groups. The cluster confirms two major clusters arrangement of heavy metals concentration and distribution at ten monitoring sites. In order to discriminate the distinct groups of heavy metals of natural or anthropogenic sources, the results obtained from a hierarchical cluster enabled the identification of elements. Cd, Ni, Co, Cu, Pb, Cr, Zn and Mn are of a common origin (Fig 3). Anthropogenic input had a greater influence on the sediment content of these elements as evident from cluster. The cluster containing Fe and Zn is most likely to have a common natural origin without much anthropogenic interference

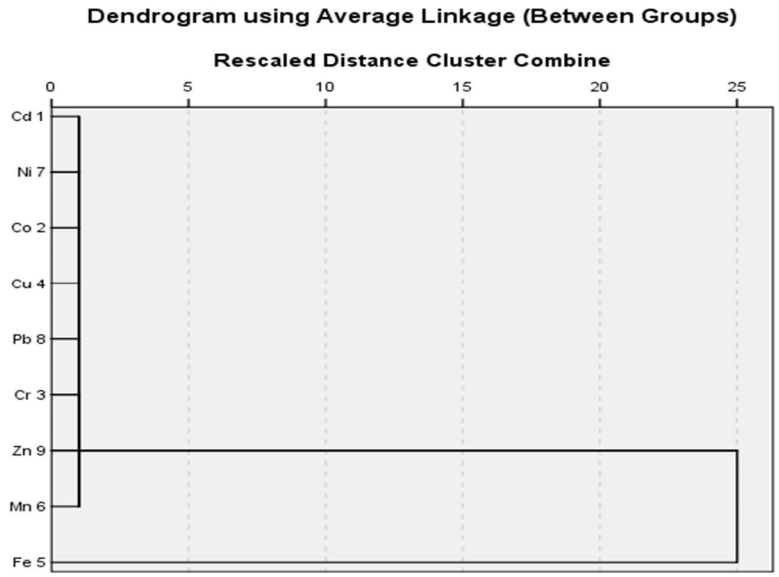

Fig3. Plot of cluster analysis.

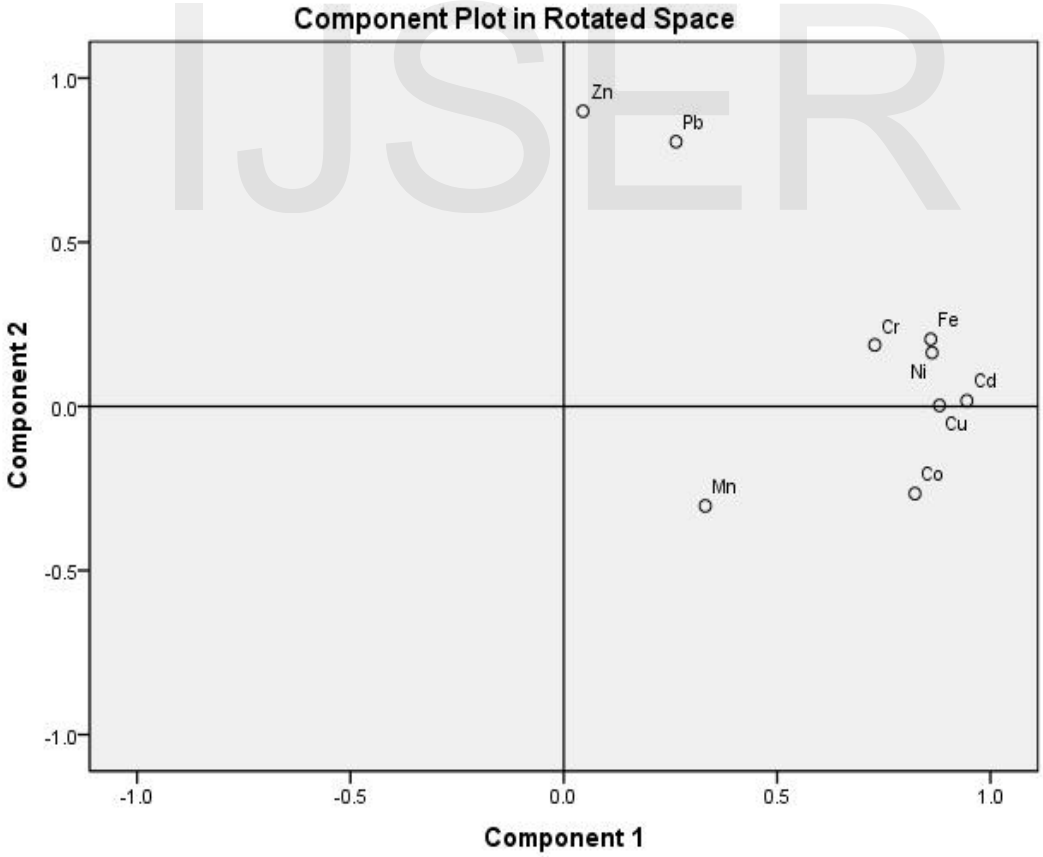

Fig 4 Component Plot of the extracted variables

4 Conclusions

In the present investigation, it was discovered that Cd, Cr and Pb were higher than the value of TEL and ERL which implies that the concentrations below which adverse effects upon sediment dwelling fauna would infrequently be expected. The implication is that the heavy metals might create an adverse effect on the riverine ecosystem if not properly treated. The contamination factor (CF), geo-accumulation index (I_{geo}) and enrichment factor (EF) and index of ecological risk revealed that sediments in this study were of very high degree of contamination with Cd and moderately polluted with Pb.

From PCA, the parameters were reduced to two components. The cumulative extracted variance was 70.2% in which component 1, extracted 52.12% while component 2, 18.08% of the total extraction.

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