Distribution and Seasonal variation of heavy metals in sediments of Urban surface water, South- West Nigeria.

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Absract: This study was carried out to deal with seasonal variation of heavy metals in sediments of Ala River, Southwest, Nigeria from April 2013 to October 2014. Geo-accumulation index (Igeo) , Enrichment Factor (EF), Degree of Contamination (Cd), Pollution Load Index (PLI), potential Ecological Risk Index (PERI) were used to quantitatively assess the influences of heavy metal pollution. Heavy metals were determined by using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). There was significant difference ($p<0.05$) in metals levels between different seasons and stations. The minimum concentration of heavy metals in all the stations were found during the raining seasons and the maximum concentration of heavy metals in all the stations were found during the drying season.

The reason for the pollution was land drainage, irrigation through channels and municipal wastes, agricultural activities, leaching from mechanic village and car wash plant. Among all the metals investigated, Cd was found to be high in all the stations during drying season followed by Cr and Pb. Apart from these three metals, all other six metals were from either cluster or weathering origin. The reason for the high concentration of these metals was due to anthropogenic activities such as Agriculture and Aquaculture, as well as regular inflow and outflow of the river throughout the study duration.

Keywords: Seasonal variation, Heavy metals, Ala river, Geo-accumulation index, Enrichment Factor, Deg Contamination.

1.0 Introduction

Heavy metals are natural constituents of the marine water environments. The aquatic body provides a vital sink for many heavy metals and their compounds. Most of these metals are present in rivers in trace concentrations, whereas excessive concentration can affect marine biota and pose risk to consumers of sea food [1].

Metals are introduced into aquatic environments as a result of various processes which are natural or anthropogenic. The main sources are geological weathering, industrial processing of ores and metals, use of metals and metal components, leaching from dumps and leaching of fertilizers, atmospheric deposition, animal excretion and the discharge of human sewage. They enter aquatic body both from feeder Rivers and from direct discharges. These metals tend to be trapped in rivers and accumulate in sediments. Metals are naturally present in the aquatic environment [2], it is their presence at elevated concentrations which presents a potential threat to aquatic life [3]. Human activities have inevitably increased the levels of metal ions in many of these natural water systems.

Heavy metals such as Cd, Cu, Ni, Zn, Pb, Co, Mn and Fe are regarded as being serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains and ease of accumulation by various organisms [4].

The toxicity of heavy metals arises from their tendency to bind proteins or other molecules and preventing them from functioning in their metabolic role [5]. Even in small amounts metals can cause considerable damage to organisms [6]. Unlike organic pollutants, the heavy metals could not be eliminated from the aquatic system neither by biodegradation nor by chemical means, therefore it

persists in the environment and usually presents in excess of the recommended threshold limit values [7]. Following the fate of heavy metals after they enter the ecosystem becomes difficult; furthermore, they inflict damage as they move from one ecological trophic layer to another.

One of the ways to determine the level of heavy metal pollution in aquatic body is to determine its concentrations in sediment. Sediments serve as the ultimate sink for many contaminants and as a result, they pose the highest risk to the aquatic life as a source of pollution [8]. The sediments are the main repository and source of heavy metals in the marine environment and that they play a major role in the transport and storage of potentially hazardous metals [9]. In addition, heavy metal concentrations in surface sediments can provide historical information on heavy metal inputs at that location, where surface sediments used as environmental indicators to reflect the current quality of marine systems for many pollutants [10, 11]. Monitoring programs are widely known in many aquatic bodies in the world; usually by investigating the water quality and different pollution parameters in water and sediments. Therefore, monitoring and assessing the effects of anthropogenic influence is crucial for protection and sustainable maintaining of the fragile surface water of Ala river.
Therefore the aim of the research is to provide a base line data for the level of pollution of the sediment of Ala River and to provide information on ecological risk of the river.

. 2.0. Method and Materials

2.1 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 [12]. Akure falls between 739000 and 746000 Easting (i.e. between longitude $5^0$06′E and $5^0$38′E) and between 801500 and 807000 Northing (i .e . , between latitude 7^0 07′ N and 7^0 37′ N) as presented in (Fig 1). The capital city is bounded in the North by Ifedore local Government, 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 [13]. 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 22^0C during harmattan (December – February) to 32^0C in March which is the peak temperature. The vegetation is tropical rainforest [13, 15]. The population of the people residing in Akure is about 353,211[16]. Ala river has the total length of about 57 km has a length of about 14.81km with Akure Township (Fig 1). It took its source from north- western part of Akure town and flows towards south - eastern part of the town. Akure township dominated the 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.

2.2 Sample Collection:

Sixty nines sediment samples were collected from ten sites along Ala river (as shown in Fig. 1).Twenty nine sediments were collected from April – October 2014 during raining season and thirty samples were collected between the month of December 2013 to February 2014 representing the drying season. The latitude and longitude for each site are illustrated in Table 1. The samples were collected using an auger at the depth of 0 - 10 cm transported by polythene bag to the laboratory and stored at temperature of 4^oC, after which the sediment samples were air – dried for 2 weeks in the Laboratory. The air – dried sediments were sieved using a 1.7 µm mesh to remove the debris, then lightly ground in an agate mortal for homogenization then ready for heavy metal analysis**.** The analysis was done in triplicates and the mean values were recorded.

Table1 Table1: Monitoing sites and their co - ordinates

Site No	Location	Latitude	Longitude	Sites 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	$005^0$18.53E	Agriculture

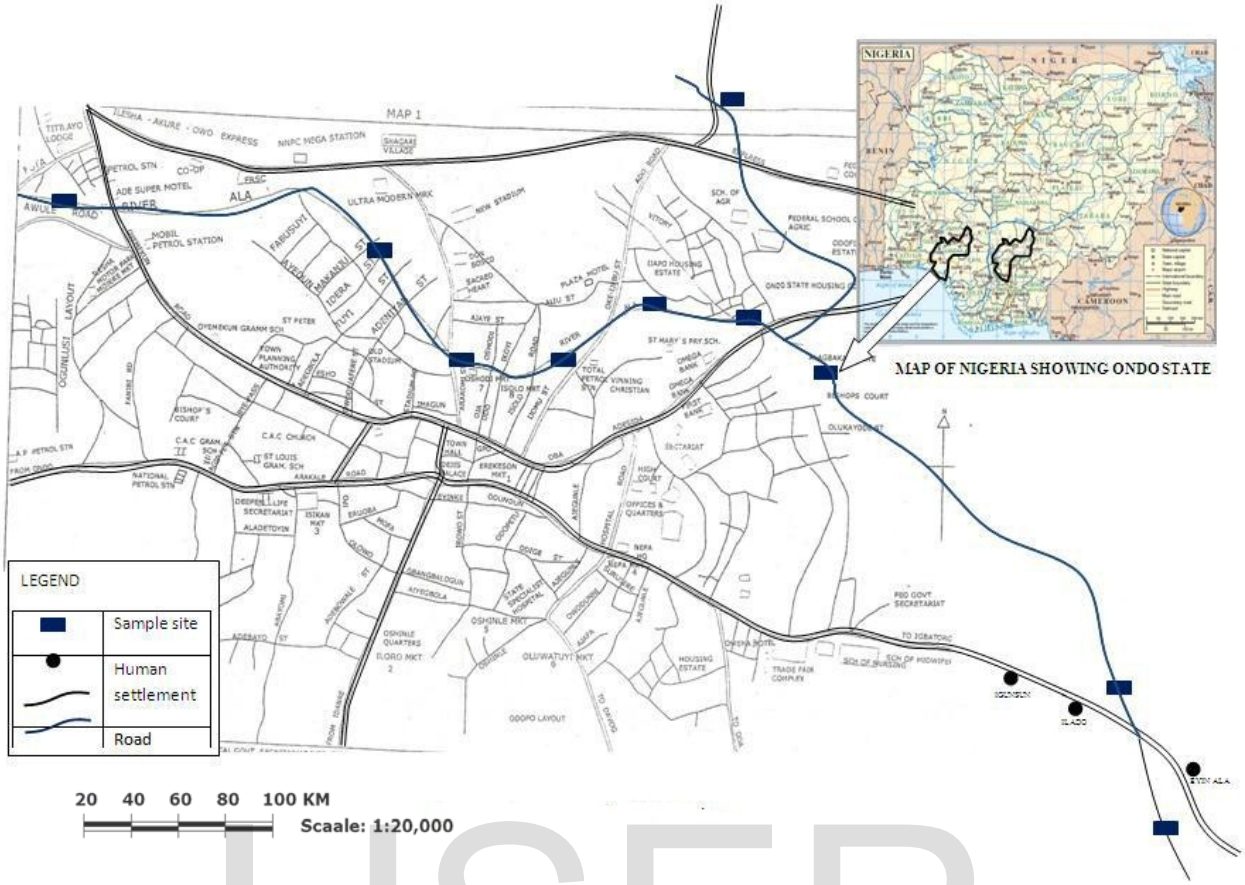

Fig1: Location map of the study area

2.3 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 48 h, then rinsed with Milli-Q water and dried using oven at 60^{o}C.

For heavy metal test, extraction of metals from sediment samples was by mixed acid aqua-regia) digestion the aqua regia was based on the procedure recommended by the Internation Organization for Standardisation [17]. A mixture of HCl and HNO_3 (3:1 v/v) was added to the samples on temperature - controlled hot plate and the mixture was heated at 160^{o}C for at least 2h. Consequently, the mixture was allowed to cool, and then 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.

2.4 Determination of pH

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

2.5 **Determination of Organic Carbon**

The organic matter was determined using [18]. 10ml of 1M $K_2Cr_20_7$ standard solution was added to the soil (2 g) followed by 20 ml of Concentrated H_2SO_4. The system was allowed to stand for 30mins with occasional swirling. After 30 min the content of the conical flask was diluted with 10 Ml of Milli-Q water. The excess $K_2Cr_20_7$ was determined by titrating with standard 1M ferrous sulphate using Ferroin indicators. The blank titration was carried out in the same manner without the soil.

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

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

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

2.6 **Determination of Particle Size**

The particle size was determined by method develop by [19] .

2.7 **Instrumental analysis and quality assurance**

For heavy metals, samples were analysed by using inductively coupled plasma- optical emission spectrometer modeled Perkin Elmer Optma 7300DV from Hiroshima University, Japan.

Procedural blanks, Spiked blank and Spiked Matrix blank were prepared along the extraction process. For heavy metals, concentrations of standard mixtures were prepared; Indium and Yttium were used as recovery standard. Recoveries In and Y were between 98 and 103 %. Detection limits in mg/kg 0.01 for Cd, Cr, Co, Cu, Zn and Ni, while 0.1mg/kg for Fe and Mn. Their detention limit was: Cd and Cu =0.002; Cr= 0.0002; Pb=0.0006; Ni =0.0008; Mn= 0.008; Co= 0.0006; Zn =0.015. The selected wavelength were:Cd 228.8 nm; Cr 205.6 nm; Co 228.6; Cu327.4 nm, Fe 238.2 nm, Mn 259 nm, Ni 231.6 nnm, Pb 220.3 nm and Zn 206.2 nm.

2.7 **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 was used as reference baselines [20]. 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.

2.7.1 **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 [21]. The Igeo of a metal in sediment can be calculated with formula: [22, 23]. In order to characterize the level of pollution in the sediment, geoaccumulation index (I_{geo})values were calculated using the equation,

$$Igeo = Log_2 \frac{Cn}{1.5Bn} \quad \ldots\ldots (3)$$

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 [22]. 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: [24] : $I_{geo} \leq 0$ – 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.

2.7.2. **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 [24].The EF method normalizes the measured heavy metal content with respect to a samples reference such as Fe, Al or Zn [22]. The EF for each element was calculated to evaluate anthropogenic influence on heavy metals in sediments using the following formula [25]:

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

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

Generally, EF values lower than and around 1.0 suggests that a given metal may be entirely from crustal materials or natural weathering process [26]. Samples having enrichment factor > 1.5 was considered to indicate human influence and (arbitrarily) an EF = 1.5 -3 indicates minor enrichment (anthropogenic impact), EF = 3- 5 moderate enrichment; EF = 5 -10 moderately severe enrichment; EF = 10 – 25 severe enrichment; EF = 25 -50 very severe enrichment and EF > 50 extremely severe enrichment [27,28].

2.7.3. **Pollution load Index (PLI) and contamination factor (CF).**

To assess the sediment quality, an integrated approach of pollution load index of the nine metals is calculated according to [29]. The PLI is defined as the nth root of the multiplications of contamination factor of metals (CF)

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

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/ soil [20].

CF metals =Cmetals/ Cbackground ……………………………… (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 [30]. The PLI gave an assessment of the overall toxicity status of the sample and also it is a result of

the contribution of the eight 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 [31, 32]: low degree ($CF < 1$), moderate degree ($1 \leq CF < 3$), considerable degree ($3 \leq CF < 6$), and very high degree ($CF \geq 6$). Thus the CF values can monitor the enrichment of one given metals in sediments over a period of time. The degree of contamination (C_d) is defined as the sum of all contamination factors. The ranges are: Low degree ($Cd < 6$), moderate degree ($6 \leq Cd < 12$), and considerable ($12 \leq Cd < 24$) and very high ($Cd \geq 24$).

2.7.4. **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 [33, 34] were applied to assess the eco -toxicological potential of heavy metals concentrations (a) the effect range –low (ERL) / effect range - median (ERM); and (b) threshold effect level (TEL) /probable effect level (PEL) values (Table 1). Low range values (ERLs/TELs) are concentrations below adverse effects upon sediment dwelling fauna would infrequently be expected. In contrast, the ERMs and PELs represent chemical concentrations above the level which adverse effects are likely to occur [35].

2.7.5 Potential Ecological Risk Index

The ecological risk index for aquatic pollution control had been reported by [36]. Hakanson's method has been used often in ecological risk assessment as a diagnostic tool to potential ecological risk.

The index was calculated using 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.

From the Indices and grades of potential ecological risk (RI) of heavy metals contamination, $E^i_r < 5$ indicates low risk, $5 \leq E^i_r < 10$ (moderate risk); $10 \leq E^i_r < 20$ (Considerable 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) [37].

2.8. **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

Table 2. Heavy metals concentration mg/kg in raining season

Sites/Metals	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	$0.3^{ab}\pm$ 0.03	$8.03^{a}\pm$ 2.2	$27.6^{ab}\pm$ 24.5	$7.4^{a}\pm$ 2.9	$13144^{a}\pm$ 4389	$248^{a}\pm$ 28	$2.3^{abc}\pm$ 1.9	$14.4^{a}\pm$ 4.5	$23.5^{cd}\pm$ 5.2
2	$0.03^{b}\pm$ 0.15	$3.2^{bc}\pm$ 1.0	$33.5^{a}\pm$ 9.5	$5.6^{ab}\pm$ 0.5	$9297^{ab}\pm$ 904	$161^{bc}\pm$ 27	$2.6^{ab}\pm$ 1.0	$8.4^{abc}\pm$ 0.2	$8.4^{d}\pm$ 0.2
3	$0.08^{a}\pm$ 0.05	$2.2^{bc}\pm$ 1.1	$31.4^{a}\pm$ 10.3	$5.7^{ab}\pm$ 0.3	$9230^{ab}\pm$ 1001	$128^{bc}\pm$ 52	$3.7^{a}\pm$ 0.6	$17.1^{a}\pm$ 10.1	$31.3^{bc}\pm$ 5.2
4	$0.11^{a}\pm$ 0.09	$2.4^{bc}\pm$ 0.9	$29.7^{a}\pm$ 3.0	$3.2^{cde}\pm$ 0.3	$10343^{ab}\pm$ 2769	$163^{bc}\pm$ 60	$1.5^{bc}\pm$ 1.3	$10.9^{ab}\pm$ 5.2	$45.7^{abc}\pm$ 24.6
5	$0.03^{ab}\pm$ 0.02	$2.2^{bc}\pm$ 2.0	$21.4^{abcd}\pm$ 1.3	$3.4^{cd}\pm$ 1.4	$10385^{ab}\pm$ 2570	$125^{c}\pm$ 21	$1.1^{bc}\pm$ 1.0	$13.3^{a}\pm$ 4.8	$30.5^{bc}\pm$ 4.7
6	$0.03^{ab}\pm$ 0.03	$4.1^{b}\pm$ 0.3	$21.4^{abcd}\pm$ 1.3	$2.5d^{c}\pm$ 0.4	$8857^{bc}\pm$ 2927	$170^{bc}\pm$ 35	$2.6^{ab}\pm$ 1.1	$12.3^{a}\pm$ 4.9	$59.4^{a}\pm$ 20.3
7	$0.05^{ab}\pm$ 0.06	$3.2^{bc}\pm$ 1.6	$27.2^{abc}\pm$ 6.7	$4.2b^{c}\pm$ 1.1	$8699^{bc}\pm$ 1440	$189^{b}\pm$ 17	$1.2^{bc}\pm$ 1.1	$10.0^{abc}\pm$ 2.6	$45.2^{ab}\pm$ 8.6
8	bdl	2.4bc± 1.4	$11.4^{bcd}\pm$ 0.8	$1.8d^{ef}\pm$ 1.1	$5037^{cd}\pm$ 459	$161^{bc}\pm$ 14	$0.2^{bc}\pm$ 0.6	$8.3^{abc}\pm$ 0.7	$16.8^{cd}\pm$ 1.6
9	$0.004^{b}\pm$ 0.01	$1.4^{c}\pm$ 0.3	$5.8^{d}\pm$ 1.3	$0.33^{f}\pm$ 0.1	$4479^{d}\pm$ 125	$33^{d}\pm$ 6.1	$0.4^{c}\pm$ 0.6	$1.5^{bc}\pm$ 0.1	$8.9^{d}\pm$ 8.5
10	bdl	$1.4^{c}\pm$ 0.6	$27.6^{ab}\pm$ 24.5	$1.1^{ef}\pm$ 0.9	$4498^{d}\pm$ 103	$55^{d}\pm$ 16	$0.23^{c}\pm$ 0.21	$2.7^{bc}\pm$ 0.2	$16.4^{cd}\pm$ 6.4
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

Note: TEL= threshold effect level; PEL =Probable effect level; ERL = Effect range low. The letter a, b, c, d, e, f along the column indicates significance difference at $p \leq 0.5$. Bdl means below detectable Limit.

Table 3. Heavy metal concentration in mg/kg Drying Season

Sites/ Metals	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	2.83^{a} ± 1.8	10.3^{a} ± 4.7	47.8^{ab} ± 3.2	12.4^{a} ± 16.0	12824^{a} ± 3373	237^{abc} ± 70.5	7.1^{a} ± 3.5	16.8^{b} ± 3.0	18.3^{b} ± 7.4
2	1.3^{cd} ± 0.5	2.2^{b} ± 0.3	44.5^{ab}± 30.3	6.2^{ab}± 2.5	10381^{abc}± 1997	322^{ab}± 178	2.3^{bc}± 1.5	10.0^{b}± 2.2	54.7^{b}± 29.5
3	1.3^{cd} ± 0.5	2.8^{b} ± 0.7	37.7^{ab} ± 14.4	6.4^{ab}± 1.4	10139^{abc}± 2039.	140^{bc}± 48	4.2^{b}± 0.7	50.7^{a}± 29.8	265^{a}± 122
4	1.2^{cd} ± 0.4	2.6^{b} ± 0.7	38^{ab}± 7.3	4.4^{ab}± 0.7	9181^{abc}± 2150	138^{bc}± 9.5	1.9^{bc}± 1.7	8.8^{b}± 0.2	42.0^{b}± 17.2.
5	2.1^{ab} ± 1.1	2.2^{b}± 0.6	67.8^{a}± 32.7	6.0^{ab}± 2.7	12097^{ab}± 3260	209^{cd}± 154.8	1.6^{bc}± 0.7	15.8^{b}± 12.3	34.3^{b}± 2.1
6	0.8 ^{cd} ± 0.2	4.4^{b}± 1.4	36.4^{ab}± 29.4	3.7^{ab}± 1.2	8211b^{cd}± 1173	190^{cd}± 30.0	2.4^{bc}± 1.1	13.3^{b}± 1.5	54.3^{b} ± 4.0
7	1.0 ^{cd} ± 0.2	3.4^{b}± 0.9	27.7^{ab}± 11.6	4.9^{ab}± 1.7	8848^{abcd} ± 1089	218^{bc}± 28	1.7^{bc} ± 0.5	8.4^{b} ± 0.4	39.7^{b}± 4.0
8	0.6 ^{cd} ± 0.2	3.7^{b}± 1.5	12.5^{b}± 10.6	1.9^{b}± 0.8	6768^{cde}± 1210	421^{a}± 199	1.23^{c}± 0.5	8.1^{b}± 0.8	17.7^{b}± 7.5
9	0.6 ^{cd} ± 0.3	1.4^{b}± 0.5	11.38^{b}± 5.83	0.9^{b}± 0.8	5978de± 2681	149.7bc ± 64.7	0.9^{c}± 0.5	3.2^{b}± 1.1	10.0^{b}± 3.6
10	0.5^{d} ± 0.3	1.7^{b}± 0.3	11.2^{b}± 2.6	1.4^{b}± 1.1	4523^{e} ± 306	51c± 28	0.5^{c}± 0.4	2.4^{b}± 0.1	17^{b} ± 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

Note: TEL= threshold effect level; PEL =Probable effect level; ERL = Effect range low. The letter a, b, c, d, e, f along the column indicates significance difference at $p \leq 0.5$.

Plots showing seasonal concentrations of heavy metals (mg/kg) .

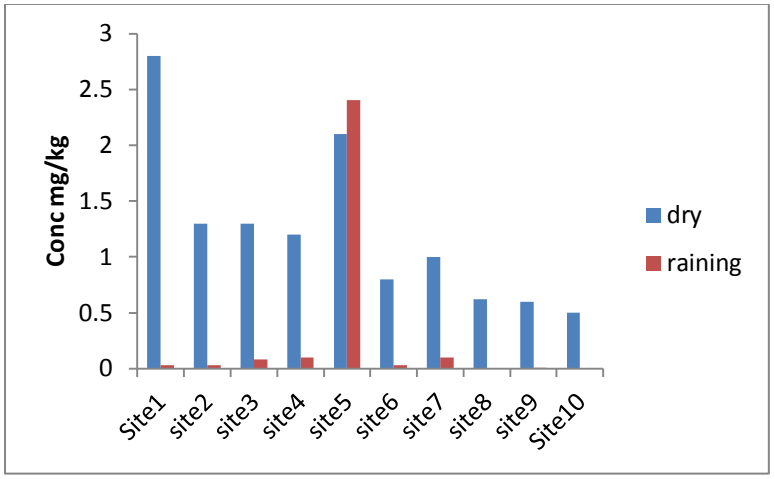

Fig 1. Cadmium concentration.

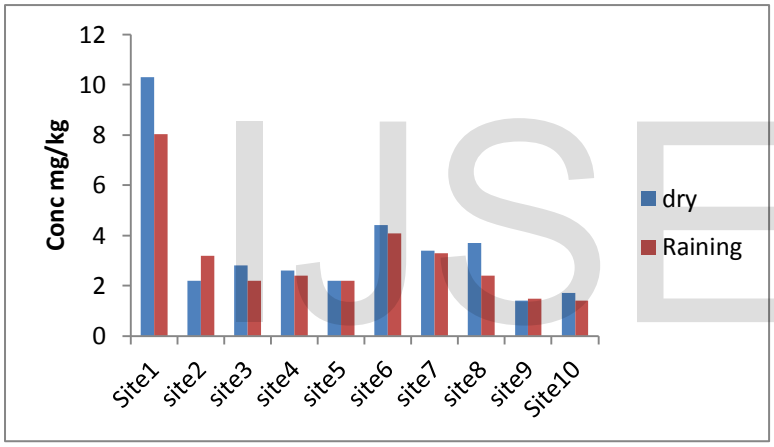

Fig 2 cobalt concentration

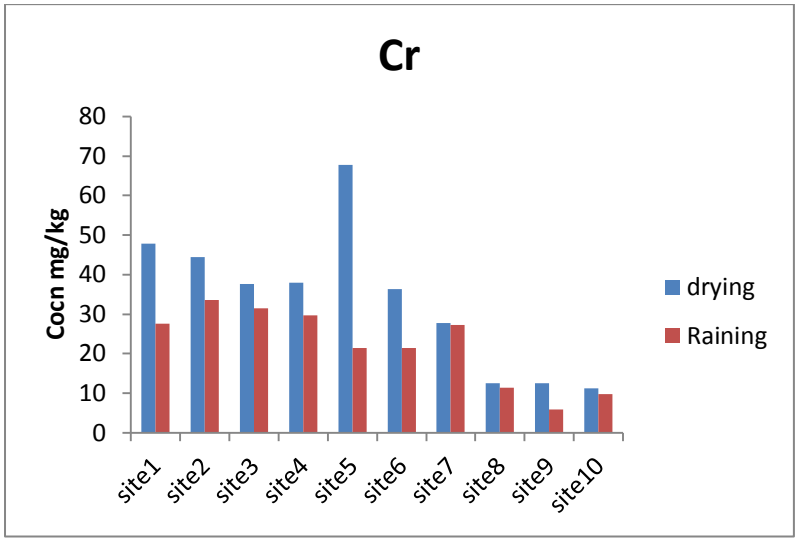

Fig 3. Chromium concentration

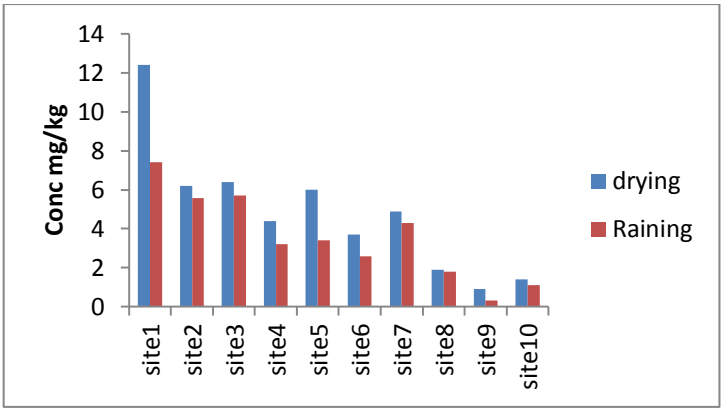

Fig 4. Copper concentration

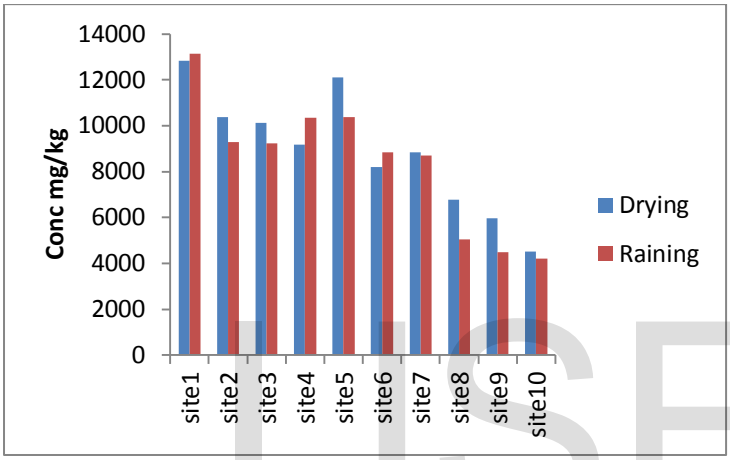

Fig 5. Iron concentration

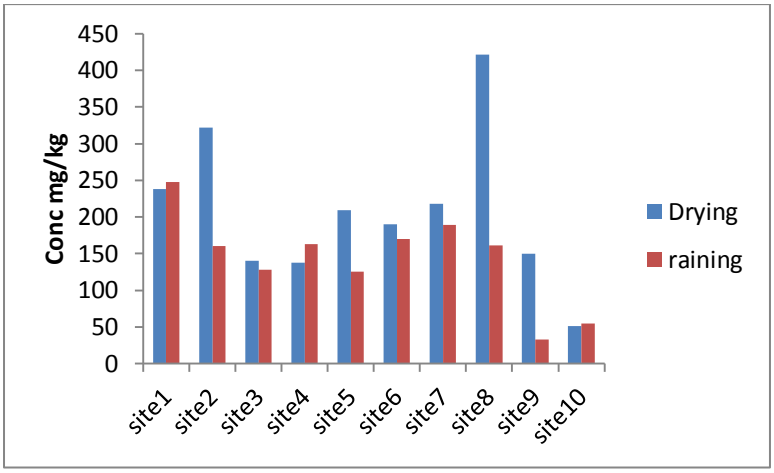

Fig 6. Manganese concentration

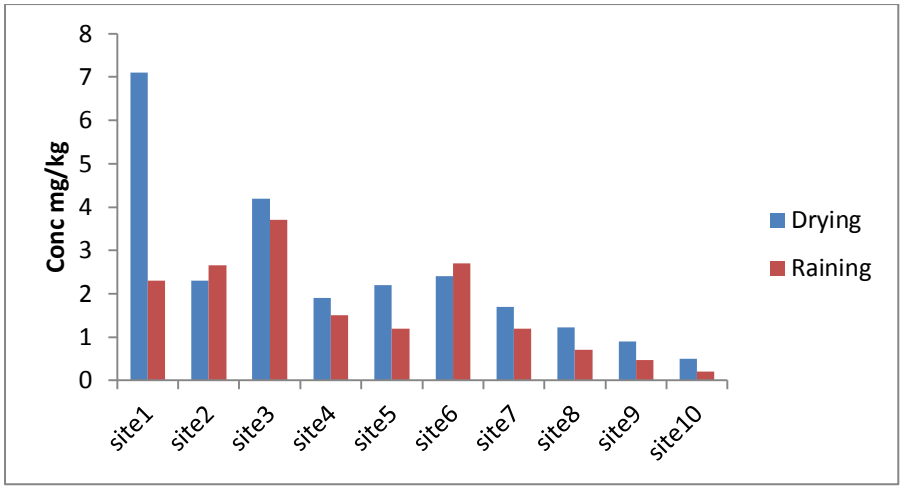

Fig 7.Nickel concentration

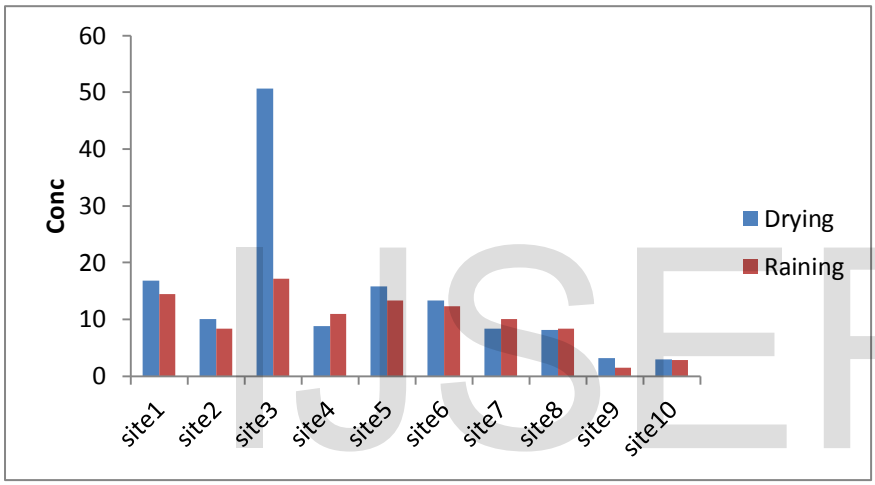

Fig 8. Lead concentration

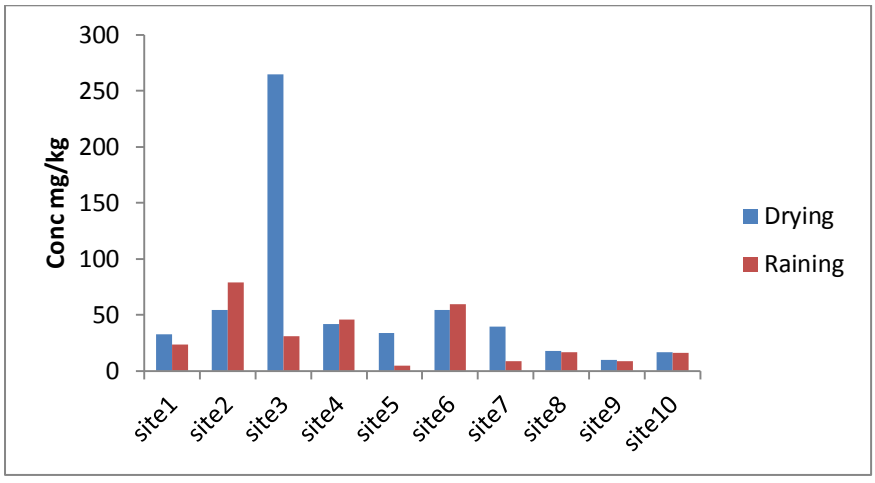

Fig 9.Zinc concentration

The mean concentrations of studied metals in sediment are given in Table 1 and 2. The heavy metals concentration in sediments at all sampling sites occurs in descending order of Fe> Mn>Zn>Cr>Pb> Co>Cu>Ni>Cd, except that the concentration of Cu was higher than Co during the drying season. The mean concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were lower in raining season than in drying season probably due to dilution by rainwater which influences concentration and heavy metal mobility. Also, there was turbulent during the raining season that causes the metals to be transported to different place and new one has to replace them thereby lowering the concentration of the metrals.

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. This implies that the chemical level is above that which frequently affects aquatic organism at this period of analysis [33]. Although during raining season, the concentrations of heavy metals were less than the permissible values of TEL, PEL and ERL (Table 2) which indicate that the metals may not have adverse effect on the biota during this period of raining season. Considering USEPA as guidelines Pb, Cd, Cr, Cu and Zn concentrations are less than the USEPA approved values (Table3).This implies that the chemical level is below that which frequently affect aquatic organism at this period of analysis (Long *et at*., 1995 It was discovered that Cd might be released to the environment through mining and smelting [38]. Cd could also be released through man made activities such as the use of phosphate fertilizer, presence of sewage sludge, NiCd batteries, plating pigment and plastics [38]. 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 a lot of car wash plants where oil, diesel and other forms of oil can be washed into the water, and then dumping of refuse directly into the river is also possible.

Seasonal Variation

Cd

In the sediments at all sampling stations, mean concentration of Cd ranged from bdl – 2.8 mg/kg. The highest mean concentration of Cd was detected at site 1 during drying season and minimum value of below detectable limit (bdl) in site 8 and 10 during raining season, whereas average range (0.6 mg/kg) was recorded from all other stations throughout the study period. There was significant difference ($p<0.05$) in Cd levels between different seasons. The sources of Cd release to the surrounding environment might come from industrial activities and burning fossil fuels. The enrichment of Cd and human exposures are primarily the result of fossil fuel combustion, phosphate fertilizers, natural sources, iron and steel production, cement production, nonferrous metals production and municipal solid waste incineration [39].

Co

The mean concentration of Co ranged from 1.4 – 10.3 mg/kg. The highest mean concentration of Co (10.3 mg/kg) was detected in site 1 during drying season and minimum value 1.4 mg/kg at site 9 during the raining season. There was no significant difference ($p<0.05$) in Co levels during the drying season expect site 1 but there are significant difference in metals level during raining seasons.

Cr

The chromium mean concentration was found to be varied from 5.8 - 67.8 mg/kg. The maximum value of Cr was 67.8 mg/kg in site 5 during drying season and minimum value was 5.8 mg/kg at site 9 during raining season, whereas the average range (27.0 mg/kg) of chromium was recorded from all other stations throughout the study period. There was significant difference ($p<0.05$) in Cr levels

between the different seasons. The increase in concentration during the drying season could be attributed to sewage waste waters released to the fresh water inflow from the mechanic workshop, the high concentrations of heavy metals that enter the river and mix up with surface water. The increase in concentration Cr can also be attributed to the agricultural and industrial activities and sewage waste waters released to the fresh water in which the high concentrations of heavy metals that enter the river and mix up with rivers [40].

Cu

The mean concentration of copper ranged from 0.3- 12.4 mg/kg. The highest mean concentration of 12.4 mg/kg was found in site 2 and minimum value of 0.3 mg/kg in site 9. The average concentration for other sites was found to be 4.1mg/kg. There was a significant difference ($p < 0.05$) in Cu levels between the two different seasons. Earlier reports suggest that naturally occurring elements, such as Cu, Fe, Mn, Mg and Zn are essential micronutrients for plants, but can become toxic at concentrations higher than the amount required for normal growth [41].

Fe

The mean Iron concentration was found significantly varied ($p<0.05$) from 4198 to 13144 mg/Kg. The maximum mean concentration of 13144 mg/Kg was observed in station 1 during raining season and the minimum value of 498 mg/kg in station 10 during raining season. There was significant difference ($p < 0.05$) in Fe levels between the two different seasons.

Mn

The mean concentration of Manganese ranged from 33.0 to 421 mg/kg. The maximum concentration of 421 mg/kg was found in site 8 during drying season and minimum value 33 mg/kg in site 9 during raining season. The average concentration for other sites was found to be 174 mg/kg. There was significant difference ($p < 0.05$) in Cu levels between the different seasons.

Ni

The mean concentration of Ni ranged from 0.2 to 7.1 mg/kg. The maximum concentration of 7.1 mg/kg was found in site 1 during drying season and minimum value of 0.2 mg/kg in site 8 during raining season. The average concentration for other sites was found to be 2.0 mg/kg. There was significant difference ($p < 0.05$) in Ni levels between the different seasons. The concentration of Ni was still rich enough to suggest an anthropogenic contribution.

Pb

The mean concentration of Pb ranged from 1.5 to 50.7 mg/kg. The maximum concentration of 50.7 mg/kg was found in site 1 during drying season and minimum value of 1.5 mg/kg in site 9 during raining season. The average concentration for other sites was found to be 11.8 mg/kg. There was significant difference ($p < 0.05$) in Ni levels between the different seasons. Pb concentration was attributed to several sources, such as boat exhaust systems, spillage of oil, and other petroleum products from mechanic workshops, and the discharge of sewage, into water body, in which all of these sources exist in the studied areas.

Zn

The mean concentration of Zn ranged from 8.4 to 265 mg/kg. The maximum concentration 265 mg/kg was found in site 1 during drying season and minimum value 8.4 mg/kg in site 2 during raining season. The average concentration for other sites was found to be 40.4 mg/kg. There was significant difference ($p < 0.05$) in Zn levels between the different seasons. Zinc always has a tendency for decomposition of soil vegetative remains, which are found to release the accumulated heavy metals back to sediments. This process might be responsible for the strong association of zinc [42].

Significant correlation of heavy metals and physico chemical parameters during raining season

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	OC
Cd	1										
Co	.031	1									
Cr	.432**	.278	1								
Cu	.261	.087	.637**	1							
Fe	.121	.189	.662**	.445**	1						
Mn	.106	.201	.362*	.297	.319*	1					
Ni	.454**	.126	.438**	.365*	.256	.250	1				
Pb	-.066	-.063	.198	.411**	.103	.401*	.137	1			
Zn	.384*	.077	.693**	.411**	.292	.393*	.392*	.210	1		
pH	.000	.067	-.202	-.116	-.195	-.408**	-.278	-.408**	-.219	1	

There was strong correlation ($p \leq 0.5$) between Cu vs Cr, Fe vs Cr and Zn Fe. This suggests that these metals are from similar origin. The good correlation of Fe versus Cr indicates that these metals are contributed by the Fe oxides [43, 44].

Significant correlation of heavy metals and physico chemical parameters during drying season

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	pH	OC
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		

There was strong correlation ($p \leq 0.5$) between Co, Cr Cd, Fe, Ni, Zn, Pb and Fe. This suggests that these metals are from similar origin. The good correlation of Fe versus Cr, Cd, Cu and Ni indicates that these metals are contributed by the Fe oxides [43, 44].

Plots showing seasonal value of EF for the heavy metals under investigation

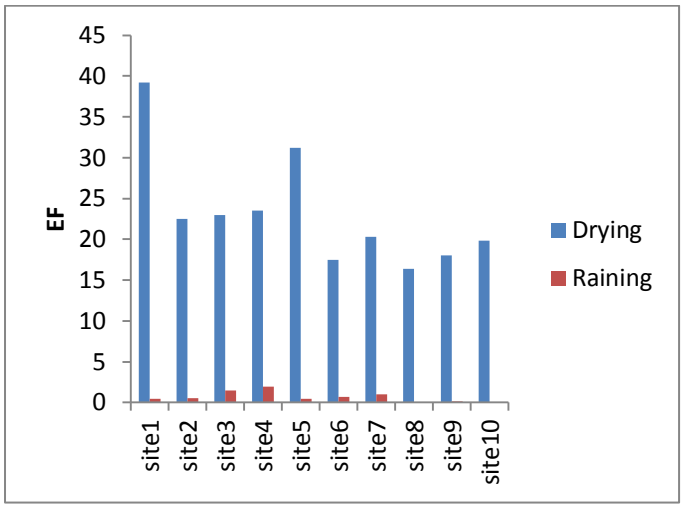

Fig 10: Cd (Enrichment Factor)

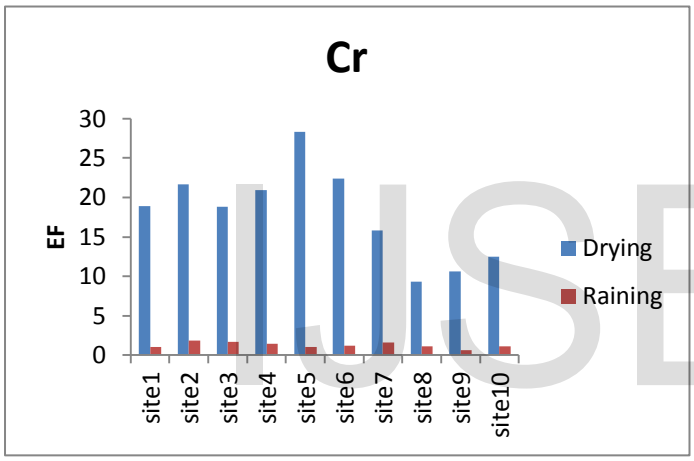

Fig 11: Cr (Enrichment Factor)

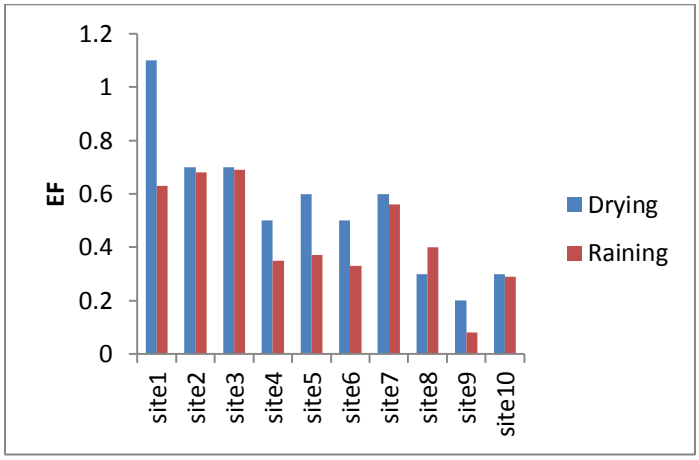

Fig 12:Cu: (Enrichment Factor)

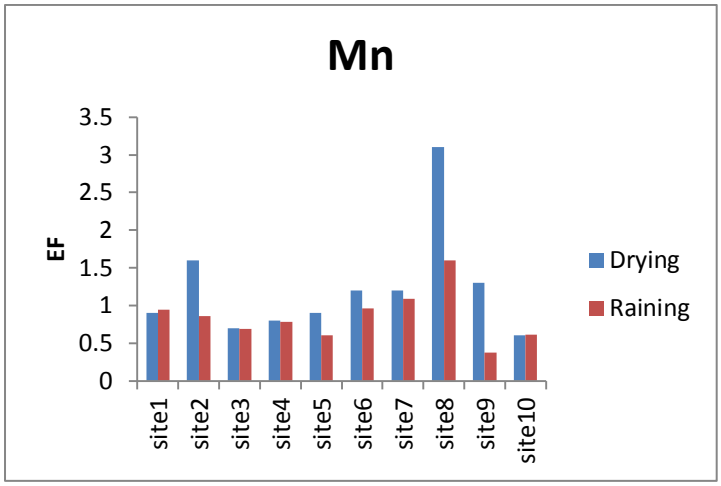

Fig 13: Mn: (Enrichment Factor)

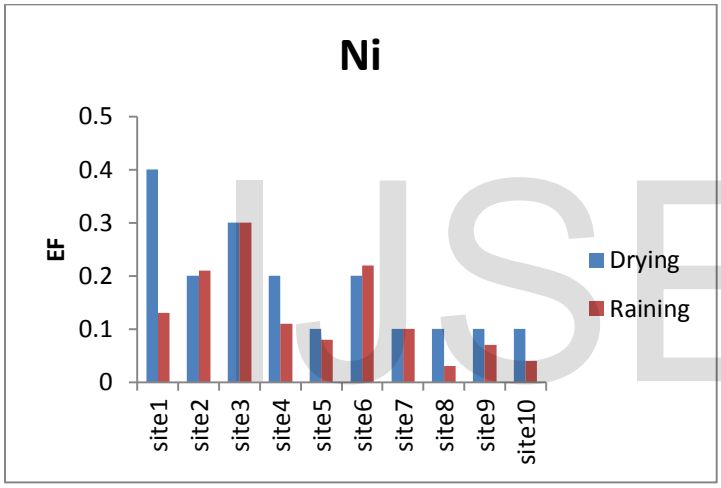

Fig 14: (Enrichment Factor)

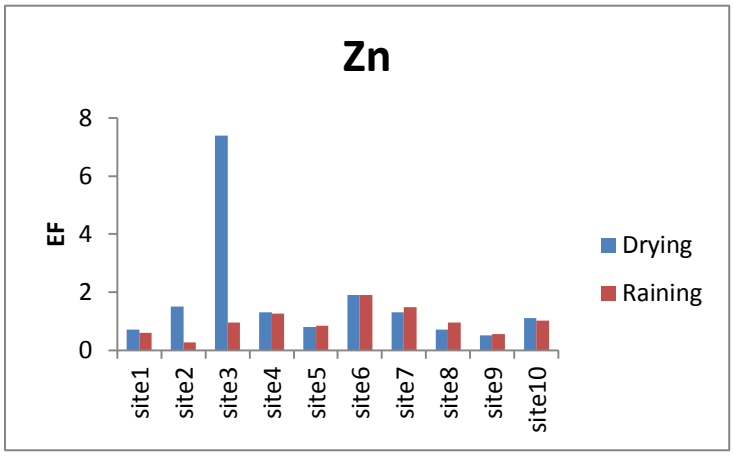

Fig 15: (Enrichment Factor)

The study result show that Cu and Ni were from either crustal or weathering processes for both seasons while Mn was from crustal or weathering process only in drying season. During the raining season, Pb had the highest average EF (4.15) which indicates moderate enrichment. Pb in all the sites except site 9; Cr (sites 2, 3, 4, 7); Co (site 1); Cd (sites 3 and 4) and Zn (sites 6 and 7) were from anthropogenic origin. This might suggest the inputs of fertilizers, pesticides from agricultural activities. During drying season, Cd and Cr were severely enriched in all sites while only Pb and Zn were severely enriched at site 6 and 3 respectively.

Plots showing seasonal values of Igeo for each metal under investigation

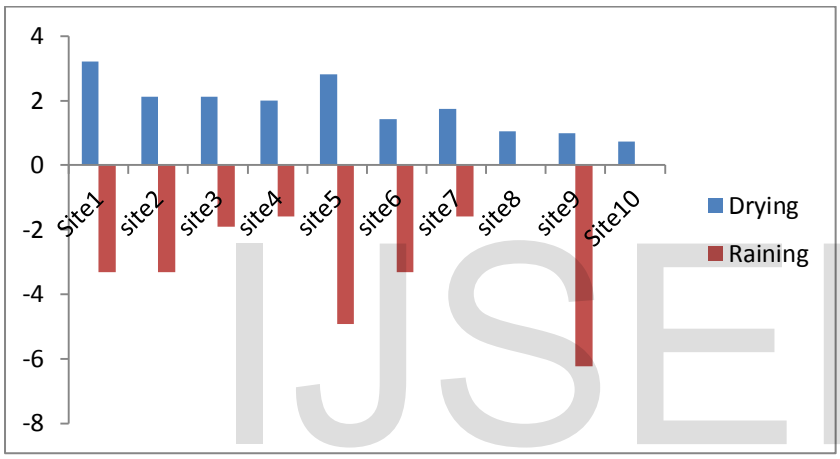

Fig 16: Igeo accumulation index of Cd

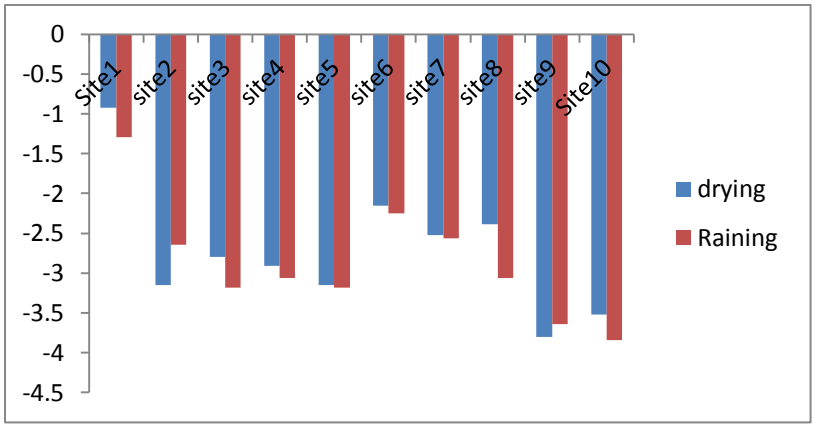

Fig 17: : Igeo accumulation index of Co

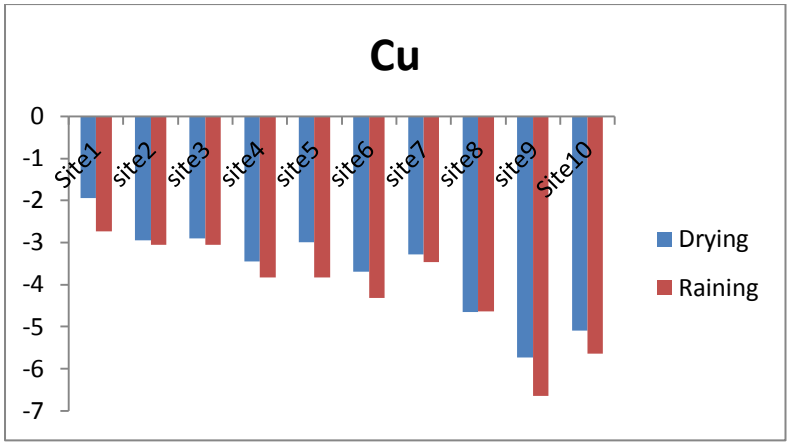

Fig 18: Igeo accumulation index of Cu

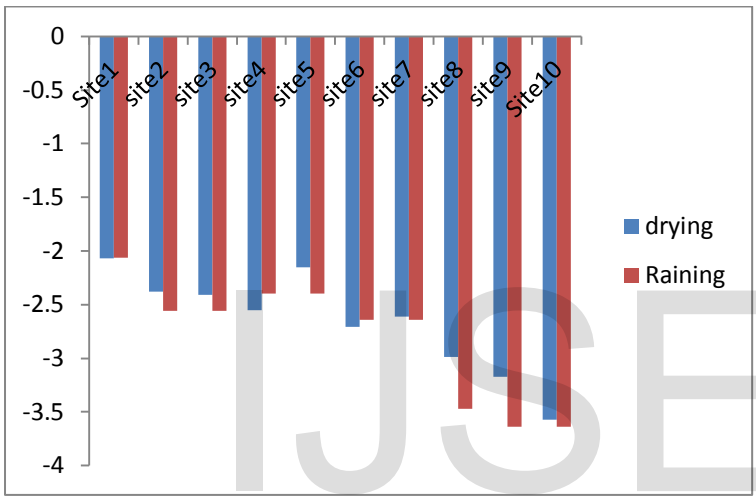

Fig 19: Igeo accumulation index of Fe

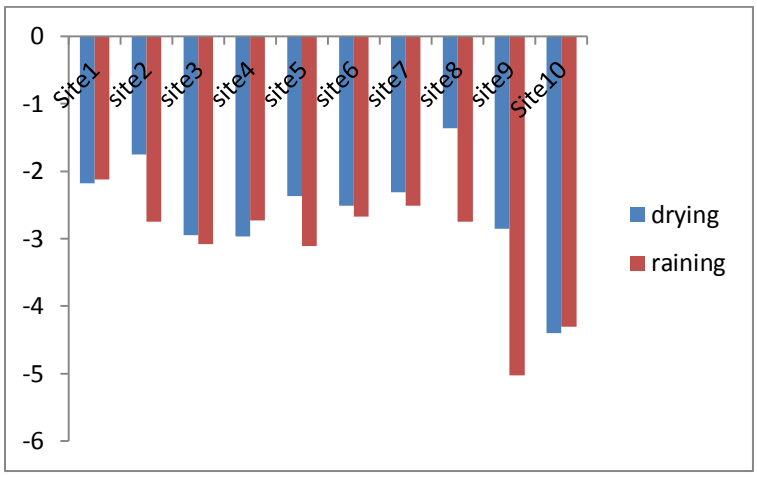

Fig 20: Igeo accumulation index of Mn

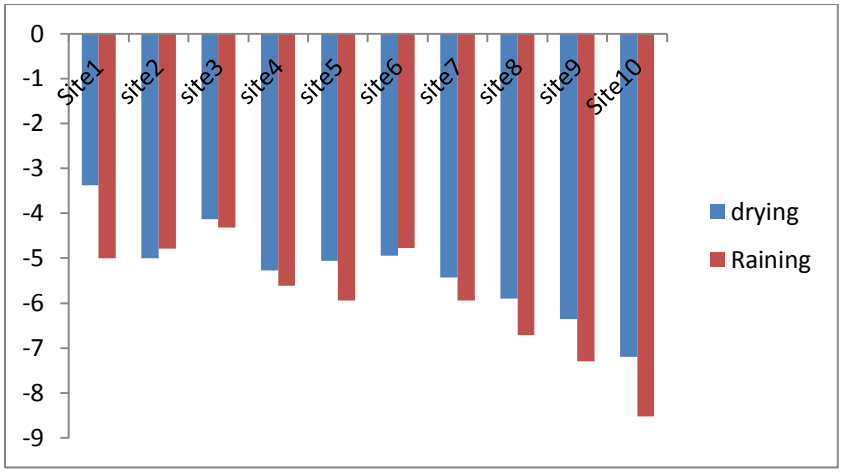

Fig 21: Igeo accumulation index of Mn

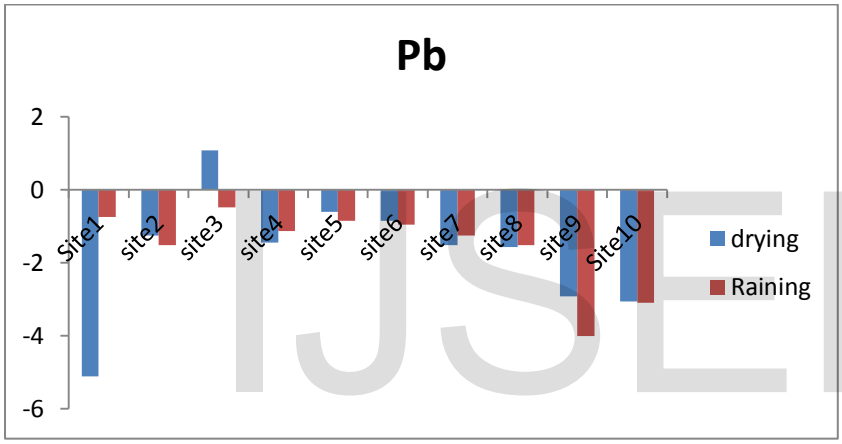

Fig 22: Igeo accumulation index of Pb

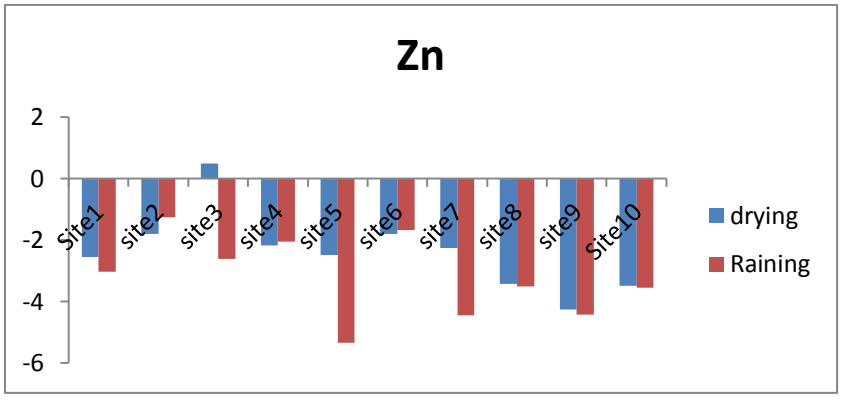

Fig 22: Igeo accumulation index of Zn

The result show that Co, Cr, Cu, Fe, Mn, Ni had Igeo < 1 in both seasons. This implies that, these metals were either from crustal or wreathing origin. But 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 during drying season. 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 during the drying season.

Plots showing seasonal values of CF for each metal under investigation

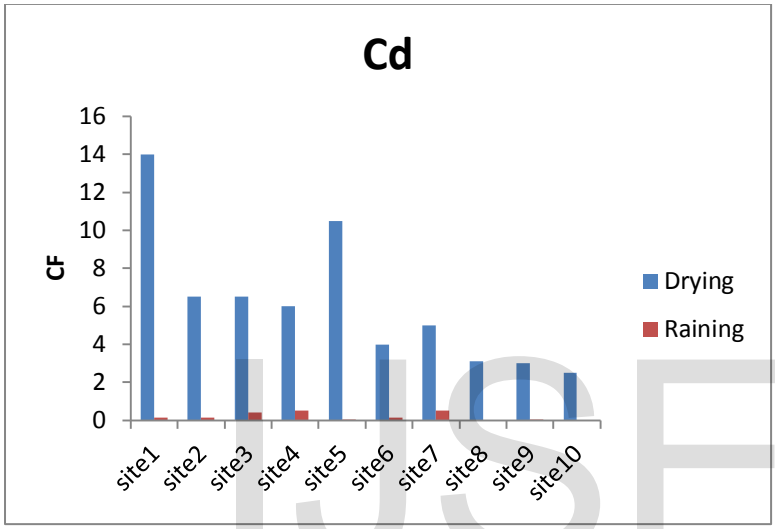

Fig 23: Contamination Factor for Cd

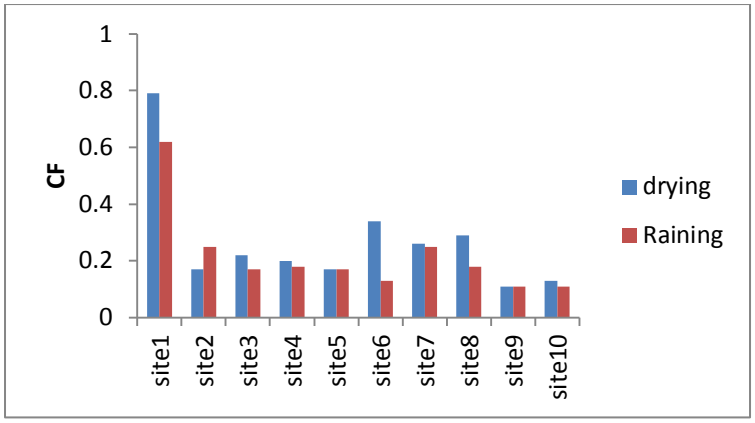

Fig 24: Contamination Factor for Co

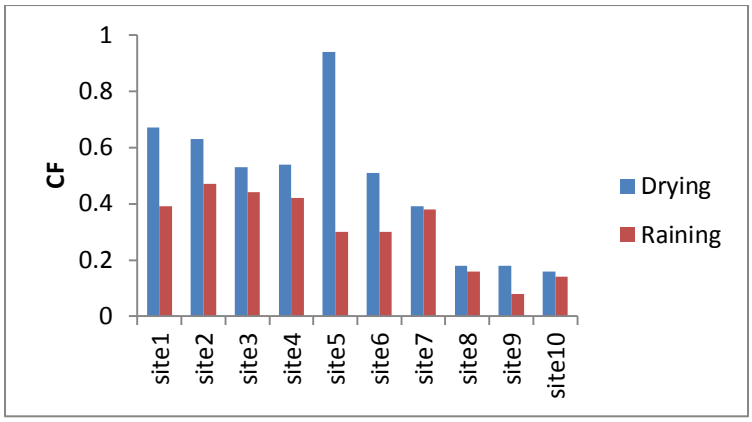

Fig 25: Contamination Factor for Cr

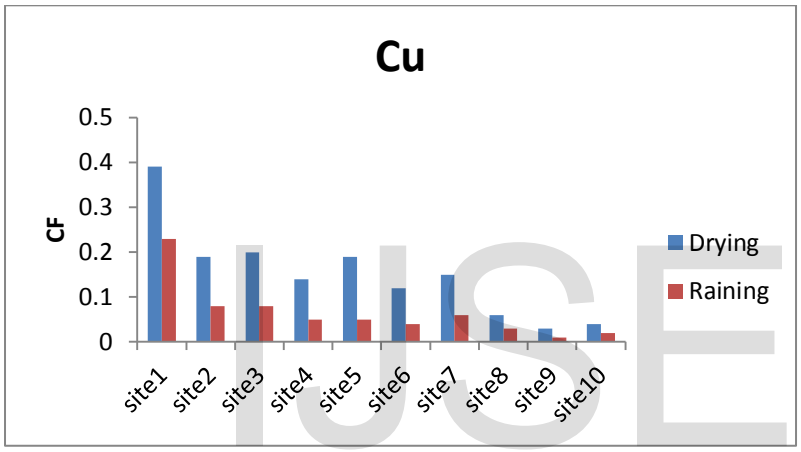

Fig 26: Contamination Factor for Cu

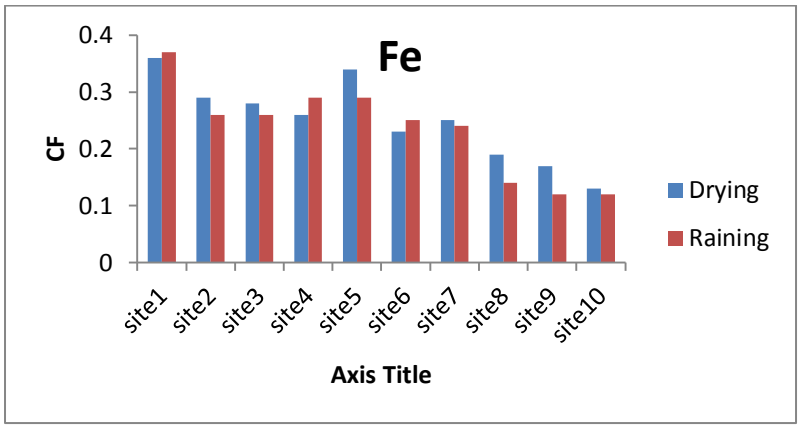

Fig 27: Contamination factor for Fe

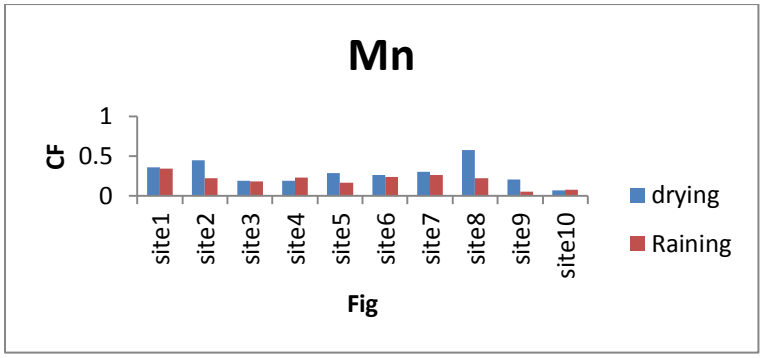

Fig 28: Contamination factor for Mn

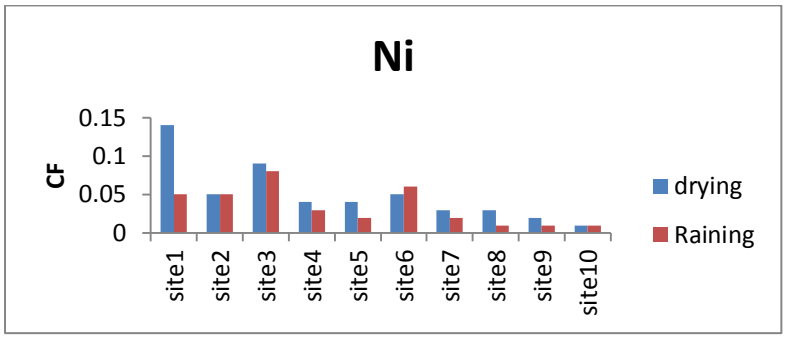

Fig 29: Contamination factor for Ni

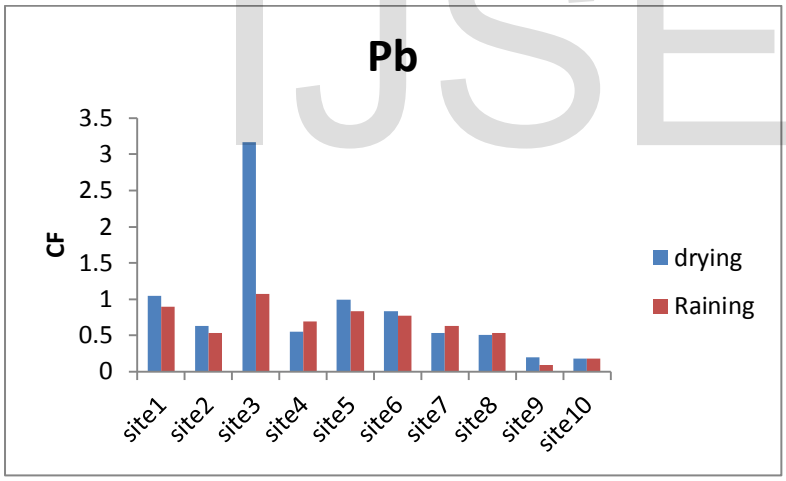

Fig 30: Contamination factor for Pb

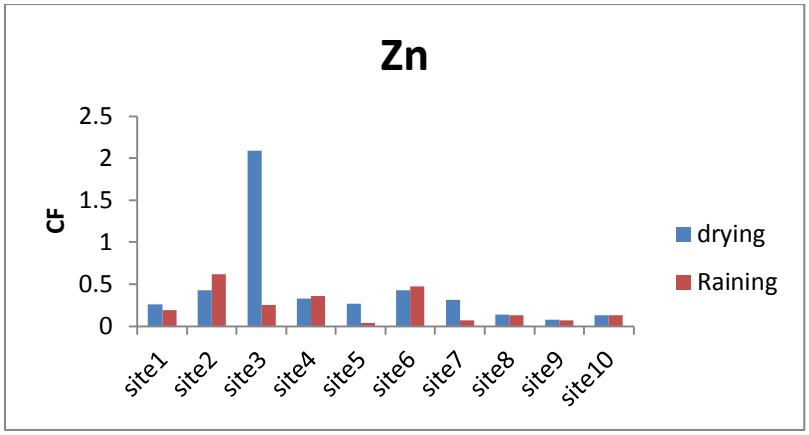

Fig 31: Contamination factor for Zn

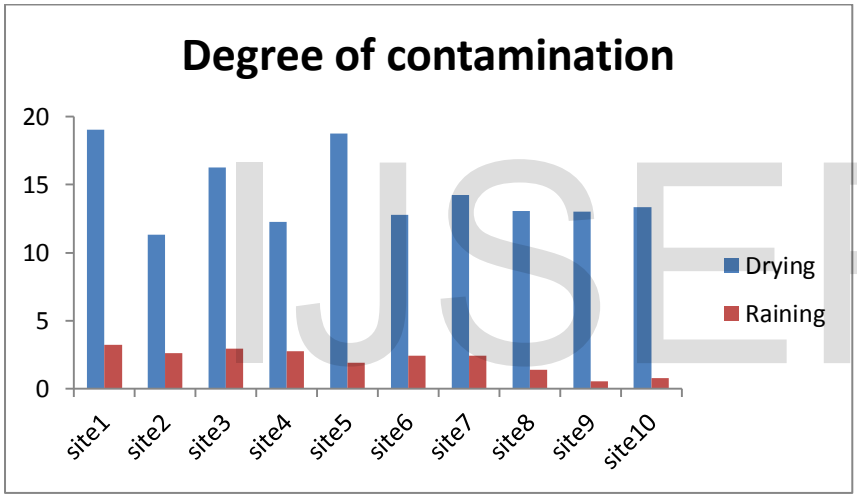

Fig 32: Degree of contamination of seasonal value for each metals

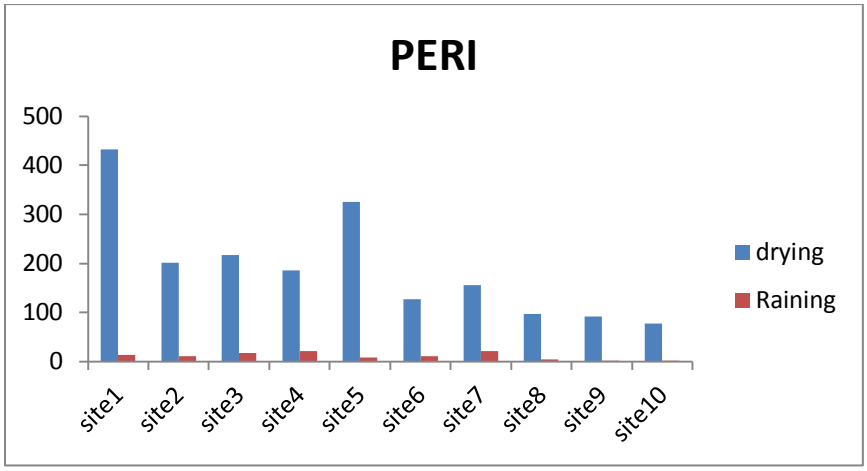

Fig 33: Potential ecological risk index seasonal values for each metal

During the raining season, the degree of contamination of heavy metals indicate low level while during the drying season there was considerate degree of contamination.

The potential ecological risk index was very low during the two seasons. For pollution index load, the values were less than 1 which indicates no pollution.

Conclusion

The mean concentration of the heavy metals under investigation were observed to be lower during raining season compare to dry season, this could be as a result of dilution imminent from persistent rainfall which in turn influences concentration and mobility of heavy metals. Secondly, the water current is very high during raining season and causes a lot of turbulent. The sources of these could be attributed to corrosion of alloyed materials, galvanization and processing of batteries especially Cd. Mn and Co may not only be of natural sources, but also anthropogenic from traffic and industrial inputs. The potential ecological risk was very low during the two seasons, and the value of pollution load index was all less than 1 indicating no pollution.

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