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# Assessment of River Asa Catchment Soil for Heavy Metal Pollution Using Indices Methods

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**ABSTRACT**
Lack of water for irrigation purpose has in recent time led to the use of catchment soil of polluted river for agricultural practice of farming. This study was aimed at investigating the contamination status of catchment soils of Asa River, Ilorin, Nigeria. Soil samples were collected from four sampling stations; Before Asa Bridge, In front of Asa Bridge, Emir Bridge and at Unity Bridge. The samples were analysed to determine their heavy metals (Fe, Cu, Mn, Pb and Zn) concentrations using Atomic Absorption Spectrophotometer (AAS). The obtained results for the metal concentration were used for Pollution Index computation. The contamination factor, degree of contamination, modified degree of contamination, pollution load index and geoacummulation indices were all employed. The values of all the metals considered, except Fe were higher at second to fourth location than those from the first location (control) suggesting probable influence of anthropogenic activities on the catchment soil. The indices results which reflect the cumulative effects of all the metals showed that the first location has a relatively low level of contamination while other locations indicated contamination status of the soil. The implication is that there is every tendency of transmission of heavy metal to man from plant through food chain and thus planting of edible phytoplant on the soil should be avoided.

***Keywords:*** *Asa River, Heavy metals, Ilorin, Industrial effluents, Pollution index*

## 1. INTRODUCTION

Soil is a vital component of the environment which sustain most living organism, being the ultimate source of mineral nutrient. It is formed by the decomposition of rock and organic matter over many years (Hannah *et al.*, 2009). Its properties vary from place to place due to the variations in bedrock composition, climatic condition and other natural and anthropogenic activities. Thus, soil at a particular place may has its elements constituent exceeding the level recommended for plants, animals and ultimately man who get exposed to them through food chain (Hannah *et al.*, 2009).

Though, some of the naturally occurring heavy metals (such as Mn, Cu and Fe) are sources of nutrients, others (such as Pb and Cd) that are mainly of anthropogenic sources are harmful even at a lower concentration (Opaluwa, *et al*., 2012). At elevated level Zn, Cu and Mn are not only dangerous to plant but also to man when consumed. While some (Zn, Pb) may cause corrosion, some others (Mn, Pb) are carcinogenic affecting the vital organs of the body. While Cu and Pb affect the nervous system, the kidney or liver, Cu and Cr affect the skin, bone and teeth (Zevenhoren and Kilpinne, 2001). Poisoning incidents with symptoms of gastrointestinal distress, nausea and diarrhea have been reported after a single or short-term exposure to concentration of Zn in beverages (WHO, 2001).

Soil pollution with these metals often results from improper management of the enormous solid waste being generated in the urban cities, which are more often than not deposited along the bank of the river (Ajadi and Tunde, 2010). More so, irrigation with rivers which often serve as recipient of industrial effluents and urban runoff could also increase the heavy metal content of the soil. Soil contamination with heavy metals through the use of untreated or poorly treated wastewater or use of river receiving such wastewater have been reported in many urban cities in developing nation (Ashraf *et al.,* 2010; Egun, 2010). Plant cultivated on such polluted soil takes up the metals and accumulates them in their edible and non edible part in quantity high enough to cause critical problem to man who consume them either directly or indirectly and there is no good mechanism for their elimination from human body (Syed *et al*., 2012, Animashaun *et al.*, 2015).

Early study by Adekola and Eletta (2007) showed that the sediment of river Asa is highly polluted with Mn, Cr, Zn, Cu and Fe. Due to insufficient or non-availability of water for agricultural practice of farming, the banks of the same river is being used for farming such as to have the river as the source of irrigation water to farm land. Hence, there is the need for the evaluation of the catchment soil for heavy metal presence. This work thus aimed at assessing the concentration of some heavy metals in Asa river catchment soil.

## 2.0 METHODOLOGY

### 2.1 Study Area

Soil samples at the depth of 0-30 cm were collected from four sampling stations. First station was before Asa Bridge, the sample collected there was used as control sample. Second sample was collected in front of Asa

Bridge. Third station was at Emir's road close to the bridge. Fourth station was at Unity which is also close to the Bridge (Figure 1). The choice of the locations was informed by the human activities of waste disposal and agricultural practice of farming.

### 2.2 Soil Sampling

Five samples were collected randomly at each of the locations using hand auger into polyethylene bags previously cleaned with detergents and distilled water and properly labelled. The samples were then taken to the laboratory for analysis.

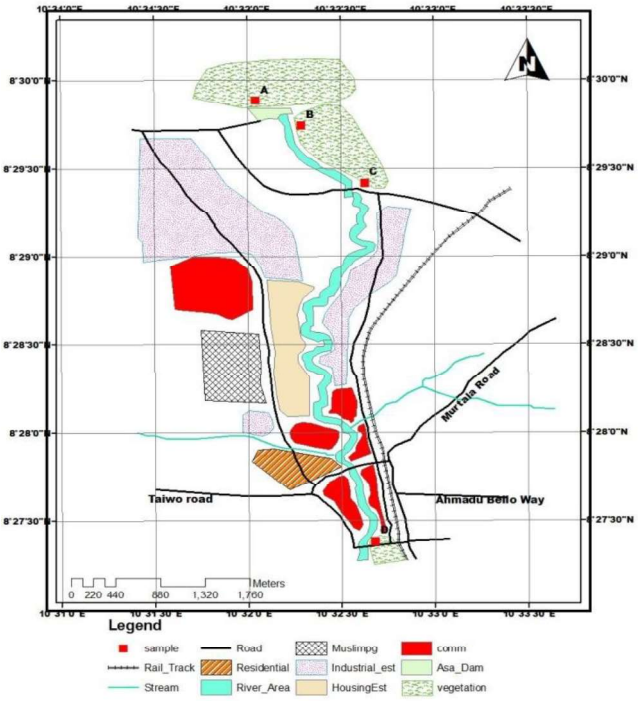



**Figure: 1 Map showing the sampling locations**

### 2.3 Sample Treatment, Analysis and Sample Characterisation

Some 2 g of soil samples were oven dried at about 105°C for 24 hours. The samples were cooled, pulverized, mixed thoroughly to achieve homogeneity and sieved through 2.0 mm International Standard sieve. All equipments used were cleaned before the experiment.

The soil samples were digested with a mixed acid $HClO_3$, HCl and $HNO_3$ and heated up under reflex. On cooling, the digested sample was transferred into 50 ml volumetric flask and made up to mark with distilled water. The digested samples were analysed for five heavy metals (Fe, Cu, Mn, Pb and Zn) using Atomic Absorption Spectrophotometer, AAS (Model 210VGP). The results obtained were compared with FAO/WHO guidelines for metals in soil (Table 1). The concentrations of the metals were then characterised using the Degree of Contamination (Cd), Modified Degree of Contamination (mCd), Pollution Load Index (PLI) and Geoaccumulation Index ($I_{geo}$) methods.

Table 1: FAO/WHO guidelines for metals in soil

| Metals (mg/kg) | FAO/WHO |
|---|---|
| Cu | 30 |
| Fe | 48 |
| Zn | 60 |
| Mn | - |
| Pb | 2 |

#### 2.3.1 Enrichment Factor (EF)

The enrichment factor (EF) is based on the standardization of a tested element against a reference one. An enrichment factor (EF), was known for investigating the origin of elements in the atmosphere, precipitation, or seawater, but in recent time it is applied to the study of soils, lake sediments, and other environmental materials (Loska *et al.*, 2004). While EF value less than one indicate that the source is nature, greater than one indicates that the element is of anthropogenic origin (Ololade, 2014). In this study, it is applied to assess the probable source of the heavy metals in soils as well as the degree of pollution (Feng *et al.*, 2004; Valdés *et al.,* 2005). Though, Mn, Al and Fe are some of the most commonly used reference elements, Fe was preferred as the geochemical normalizer because of its conservative nature during diagenesis and because of its abundance in Nigeria soils (Loska *et al.,* 1997; Ololade 2014). EF is computed using the equation reported by Rubio *et al* (2000) *as*;

$$EF = \left(\frac{X}{Fe}\right)_{soil} / \left(\frac{X}{Fe}\right)_{background} \quad (1)$$

Where $\left(\frac{X}{Fe}\right)_{soil}$ is the ratio of heavy metal (X) to Fe in the soil of contaminated sites, and $\left(\frac{X}{Fe}\right)_{background}$ is the ratio of heavy metal (X) to Fe in the soil of control site. The result is interpreted as shown in table 2.

Table 2. Contamination Categories based on Enrichment Factor

| EF | Enrichment Factor Classification |
|---|---|
| $EF < 1$ | no enrichment |
| 1≤EF<3 | minor enrichment |
| 3≤EF<5 | moderate enrichment |
| 5≤EF<10 | moderately severe enrichment |
| 10≤EF>25 | severe enrichment |
| 25≤EF>50 | very severe enrichmen |
| EF > 50 | extremely severe enrichment |

**Source:** Ololade, 2014

#### 2.3.2 Contamination Factor (CF) and Degree of Contamination (Cd)

**Contamination Factor (CF)**

This was applied to the study of heavy metals in the soils to obtain factors which is not only needed for the soil classification (Table 1) but also for further estimation of Cd, mCd, and PLI. In applying it, five samples were averaged to produce a mean pollutant concentration which was then divided by the background (control), as

proposed by Hakanson (1980). It was computed using the equation below (Equation 2)

$$Cf = \frac{CmSample}{CmBackground\ (ControlSample)} \quad (2)$$

Where:
Cm sample is the concentration of a given metal at contaminated location
Cm Background is the concentration of an element in the background soil sample

There seems not to be a distinctive difference between enrichment factor and contamination factor in terms of computation but interpretation of the obtained value for the two differ slightly as EF tends to reveal source of pollution. Since some of the earlier works argued that EFs do not provide a reliable indication of the degree of human contribution, further indices need to be employed (Sucharovà *et al.,* 2012)

### 2.3.3 The Degree of Contamination (Cd)

This gives the summation of all contamination factor (Cf) at a particular location (Abrahim and Parker, 2007). It is aimed at providing a measure of the degree of overall contamination in a sampling site. The computation was done using the formula below (equation 3) and the obtained value was classified based on the categories shown in Table 3

$$Cd = \sum_{i=1}^{N} Cfi \quad (3)$$

Where; N is the number of element analysed
Cf is contamination factor

Table 3. The Contamination factor & degree of contamination classification

| Cf classes | Cf and Cd terminology | Cd classes |
|---|---|---|
| $Cf < 1$ | Low Cf (indicate low contamination) & low Cd | $Cd < 8$ |
| $1 \leq Cf < 3$ | Moderate Cf & Cd | $8 \leq Cd < 16$ |
| $3 \leq Cf < 6$ | Considerable Cf & Cd | $16 \leq Cd < 32$ |
| $Cf \geq 6$ | Very high Cf & Cd | $Cd \geq 32$ |

**Source:** Loska et al. (2004)

### 2.3.4 Modified Degree of Contamination (mCd)

The degree of contamination modified formula is generalized by defining the degree of contamination (mCd) as the sum of all the contamination factors (Cf) for a given set of location divided by the number of analysed pollutants. The modification of Hakanson formula for Cd was done by Abrahim and Parker (2008) (equation 4). The obtained value was used for the classification of soil using the table below (Table 4)

$$mCd = \frac{i}{N}\sum_{i=1}^{N} Cfi \quad (4)$$

Where N is the number of element analysed
Cf is contamination factor

Table 4. Modified degree of contamination classification & description contamination

| mCd | Modified degree of contamination |
|---|---|
| $mCd < 1.5$ | Nil to very low degree of contamination |
| $1.5 \leq mCd < 2$ | Low degree of contamination |
| $2 \leq mCd < 4$ | Moderate degree of contamination |
| $4 \leq mCd < 8$ | High degree of contamination |
| $8 \leq mCd < 16$ | Very high degree of contamination |
| $mCd \geq 32$ | Extremely high degree of contamination |

**Source:** Loska *et al.* (2004)

### 2.3.5 Pollution Load Index (PLI)

Pollution Load Index (PLI) gives an estimate of the number of times by which metals content of soil exceeds the background (Ololade, 2014). It is defined as contamination factor (CF) of each of the considered metals in reference to the value of the control sample (Angulo, 1996). PLI was computed using equation 4 as proposed by Tomlinson *et al,* (1980).

$$PLI = (Cf_1 \times Cf_2 \times Cf_3 \times \cdots\cdots Cf_N)^{\frac{1}{N}} \quad (5)$$

Where N is the number of metal under consideration
When PLI<1 denote perfection
PLI=1 means that only the baseline of pollutants are present
PLI>1 indicates deterioration of site quality.

### 2.3.6 Geoaccumulation Index ($I_{geo}$)

This enables the assessment of contamination level of the metal in soil, by comparing the current levels of metals concentration and the background (control) concentration (Sucharova, 2012). The method assesses the degree of metal pollution in term of seven enrichment classes and factor 1.5 is introduced to minimise the effect of possible variations in the sediments (equation 6). The obtained value was classified based on the categories shown in Table 5

$$I_{geo} = \mathrm{Log}_2\left(\frac{Cmsample}{1.5 \times Cmbackground}\right) \quad (6)$$

Table 5. Geoaccumulation index classification

| Value | Class | Description |
|---|---|---|
| $I_{geo} > 5$ | 6 | Extremely contaminated |
| $4 < I_{geo} \leq 5$ | 5 | Strong to extremely contaminated |
| $3 < I_{geo} \leq 4$ | 4 | Strong contaminated |
| $2 < I_{geo} \leq 3$ | 3 | Moderately to strong contaminated |
| $1 < I_{geo} \leq 2$ | 2 | Moderately contaminated |
| $0 < I_{geo} \leq 1$ | 1 | Uncontaminated to moderately |
| $I_{geo} <= 0$ | 0 | Uncontaminated |

**Source:** Huu et al., 2010; Syed *et al.,*2012

### 2.3.7 Statistical Analysis

In establishing the relationship between the heavy metals contents of samples from each of the locations under

consideration and within the samples, descriptive Analysis, ANOVA and Duncan Multiple Test was employed using SPSS 16.0 version

## 3.0 RESULTS AND DISCUSSIONS

### 3.1 Heavy metals concentration

Heavy metals concentrations of Asa river catchment soil samples were assessed across four locations. The mean concentrations of Mn at 1st, 2nd, 3rd and 4th location were 0.001 mgkg$^{-1}$, 7.90 mgkg$^{-1}$, 15.30 mgkg$^{-1}$ and 10.00 mgkg$^{-1}$ respectively (Fig. 1). The result showed that the highest mean concentration was recorded at the 3rd location, while the lowest was at 1st location. The variations in Mn between 1st location (control) and other sampling locations were statistically different at 5 %. The highest mean value of Mn obtained for soil (15.30 mgkg$^{-1}$) in this study was not up to the lowest value (218.1 mgkg$^{-1}$) recorded for sediment of the same river by Adekola and Eletta (2007) indicating the river as a probable source of pollution to the soil. This also agrees with the finding of Ibrahim *et al*. (2013) who opined that the concentration of Mn in Asa River is above the WHO standard. This high level of the metal reported for the sediment and water of the river were associated with indiscriminate discharge of effluents and wastes that are rich in Mn into the river. Thus, the river water could be polluting the soil either through the base flow or its application for irrigation

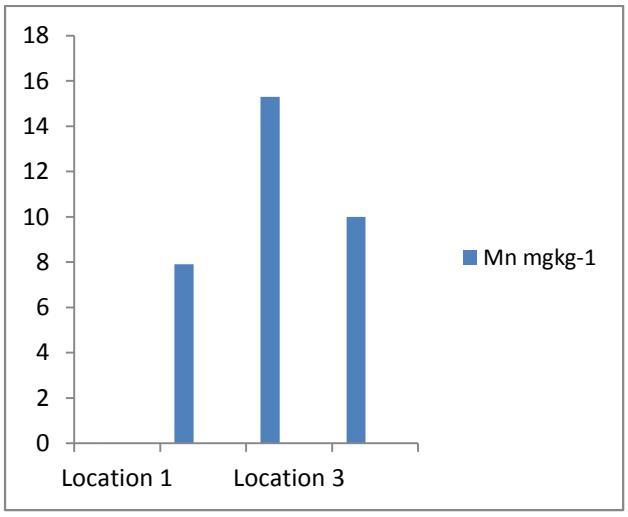



Fig. 1: Mean concentration of Mn across the locations

The mean concentrations of Fe at 1st, 2nd, 3rd and 4th location were 1400 mgkg$^{-1}$, 1594 mgkg$^{-1}$, 1570 mgkg$^{-1}$ and 1216 mgkg$^{-1}$ respectively (Fig 2). The highest concentration of Fe was at the 2nd location (1594 mgkg$^{-1}$) and the lowest concentration was at 4th location (1216 mgkg$^{-1}$), meaning that the 4th location as a mean value lower than that of the control.

This suggests that though, anthropogenic input cannot be overlooked, Fe content of the soils seems to depend largely on the natural factor. This result is supported by the earlier findings which claimed that Nigeria soil especially that of Ilorin areas are characterized with iron-rich (Ololade, 2014; Adekola and Eletta, 2007). Though, the values obtained in all the locations are above the recommended value for soil, it is not of health concerned.

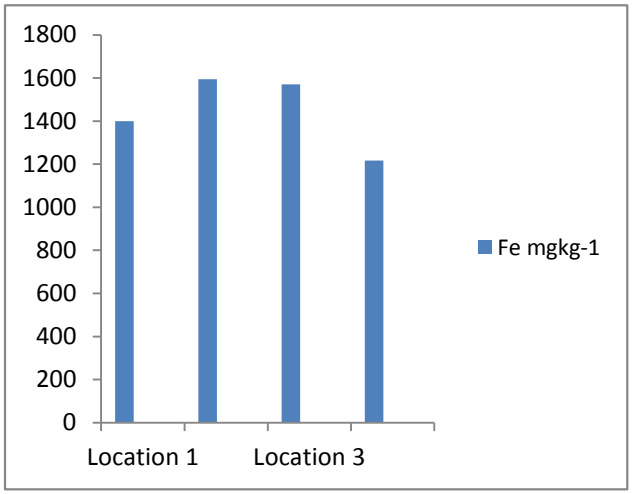



Fig. 2: Mean concentration of Fe across the locations

The mean concentrations of Cu in soil at 1st, 2nd, 3rd and 4th locations were 0.001 mgkg$^{-1}$, 150.00 mgkg$^{-1}$, 10.00 mgkg$^{-1}$ and 50 mgkg$^{-1}$ respectively (Fig. 3). This metal was found to exhibit high concentrations at second to fourth locations and has least concentration at the first location. The high concentration of Cu at second to fourth locations could be attributed to the waste (liquid and solid) discharge into the river by the industries along its bank. This consequently impact negatively on the catchment soils either through direct usage of the river for irrigation or the through base flow. It could also be due to application of agrochemicals or direct discharge of wastes that are rich in Cu into the soils, as some values noted the for soil in this study are higher than what was reported for sediment of the same river by Adekola and Eletta (2007). The concentration of Cu was though lower than the established limits (30 mgkg$^{-1}$) by WHO and FAO at the first and third location, it is higher at the second and fourth locations. The variations in Cu content of the catchment soils between 1st location and other sampling locations were statistically different at 5 %.

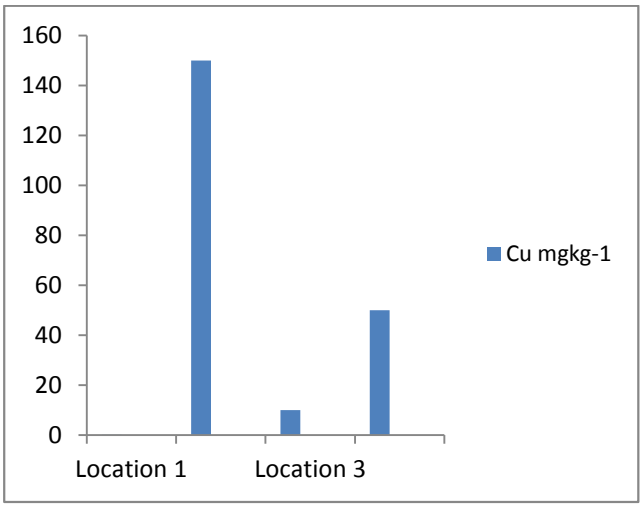



Fig. 3: Mean concentration of Cu

The mean concentrations of Zn at 1st, 2nd, 3rd and 4th locations were 13.00 mgkg,-1 36.50 mgkg-1, 33.90 mgkg-1 and 15.20 mgkg-1 respectively (Fig 4). The highest mean concentration was obtained at 2nd location and the least mean concentration was obtained at the 1st location. The presence of Zn at the second to fourth locations could be linked to the high availability of the metal in the river and sediment which find its way to the soil through mobility or the usage of water for irrigation (Adekola and Eletta, 2007). The value obtained at the 1st location was close to that recorded at the 4th location suggesting agricultural practice as a probable pollution source, as the soil at the 1st location was not under industrial influence

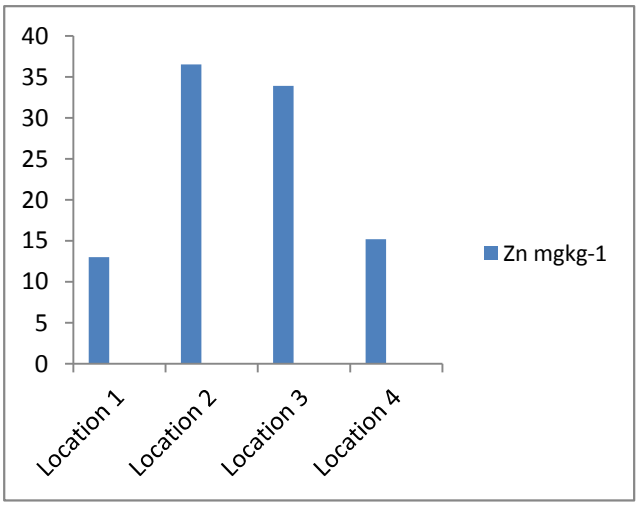
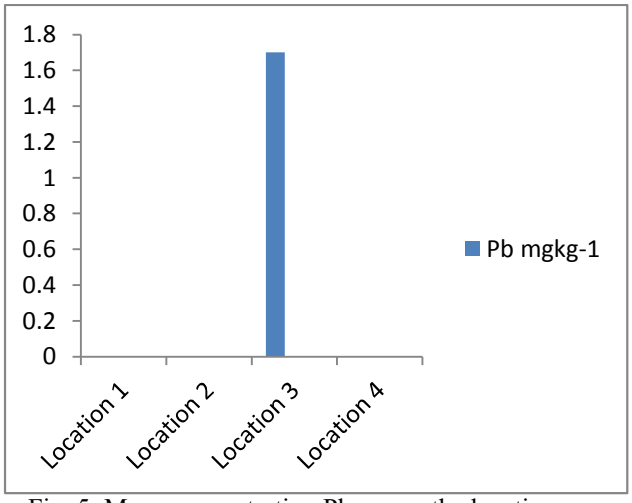



Fig. 4 Bar chart showing mean concentration Zn

The respective mean concentrations of Pb at 1st, 2nd, 3rd and 4th locations were 0.001 mgkg-1, 0.002 mgkg-1, 1.70 mgkg-1 and 0.003 mgkg-1(Fig. 5). The highest concentration was recorded at third location and the lowest at first location. The high level of Pb concentration at third location could be attributed to anthropogenic activities around the location. Earlier works claimed presence of low concentration of Pb in the river (Ahaneku and Animashaun, 2013)




Fig, 5: Mean concentration Pb across the locations

### 3.2 Index Classification of Heavy Metals in Soils

The classification of heavy metal concentrations in the soil was done using the Enrichment Factor (EF), Contamination Factor (CF), Degree of Contamination (Cd), Modified Degree of Contamination (mCd), Pollution Load Index (PLI) and Geoaccumulation Index (Igeo).

The enrichment factors in the second to fourth location ranged from 8921 - 131,797 for Cu, 6941 – 13649 for Mn, 1.757 – 1517 for Pb and 1.346 – 3.460 for Zn (Table 6). Virtually the values of all the metals suggested man's influence, considering the submission of Hernandez *et al.* (2003) that EF values ranging between 0.5 and 2 signify natural processes as the source of occurrence of the metal, while values greater than 2 are associated with anthropogenic contribution. This implies that only the Pb (in the 2nd location) and Zn (in the 4th location) were from natural sources. No value reported for 1st location as it serves as the reference point.

Table 6. Showing the Enrichment factor for the locations

| Location | Cu | Mn | Pb | Zn |
|---|---|---|---|---|
| 1st location | | | | |
| 2nd location | 131,797 | 6941 | 1.757 | 2.466 |
| 3rd location | 8921 | 13649 | 1517 | 3.460 |
| 4th location | 57589 | 11518 | 3.46 | 1.346 |

The 1st location has a Contamination Factor (Cf) of 1, which was used as the basis for comparison and the contamination factors for other locations were determined in reference to it. The results obtained showed that the 2nd location was moderately contaminated with Fe (1.14), Pb (2.00) and Zn (2.81) while Cu (1500) and Mn (790) ranged very high. At 3rd location, Fe with 1.12 and Zn with 2.61 fall in moderate Cf class while Cu (1000), Mn (1530), and Pb (170) have very high Cf (Table 7). The obtained contamination factor for Fe (0.87) at the 4th location showed that it has a low Cf. Zn (1.17) and Pb (3.0) have a moderate Cf, while Cu (5000) and Mn (1000) have a very high Cf .

Table 7. showing the $C_f$, for the locations

| Location | Fe | Cu | Mn | Pb | Zn | mCd |
|---|---|---|---|---|---|---|
| 1st location | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| 2nd location | 1.14 | 1500 | 790 | 2.0 | 2.81 | 3159 |
| 3rd location | 1.12 | 1000 | 1530 | 170 | 2.61 | 541 |
| 4th location | 0.87 | 5000 | 1000 | 3.0 | 1.17 | 1201 |

While Cf showed the contribution of each of the metals at each location, Degree of Contamination (Cd) gives a reflection of all the metals at a particular location. At first location, the obtained value was 5 indicating a low degree of contamination. This suggests low influence of human activities on the location. The 2nd, 3rd and 4th locations with respective Cd value of 15796, 2704 and 6005 indicate a very high degree of contamination. The wide variation between the control and other locations suggest anthropogenic input.

The value of the modified degree of contamination (mCd) for the first location was 1.00 which showed that the location can be classified into "nil to very low degree of contamination", while the second, third and fourth locations with respective values of 3159, 541 and 1201 fall into the class of "ultra high degree of contamination". The high degree of contamination at these locations further confirmed the results and classification with Cd.

The value obtained for Pollution Load Index (PLI) at the first location was 1.00 indicating the baseline of pollutants while the 2nd, 3rd and 4th locations with 38, 60 and 27 respectively implied site quality deterioration.

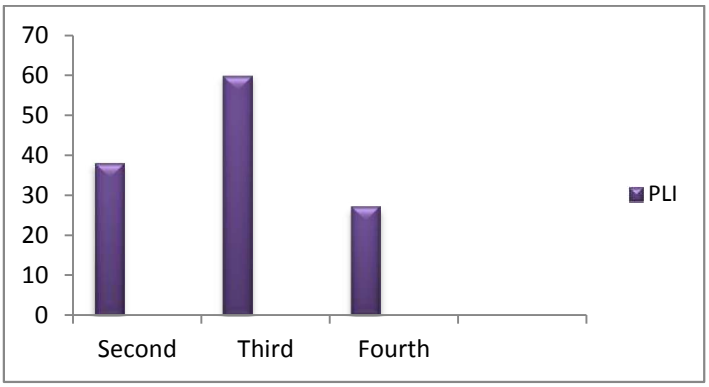



Fig. 6: Pollution Load Index

From table 8 the negative Igeo values found in table are the result of relatively low levels of contamination for some metals in soil sample. Based on this Igeo classification, Asa river soil can be classed on average as uncontamination to an extremely contaminated.

Table 8: Classification based on geoaccumulation index.

| Location | Fe | Cu | Mn | Pb | Zn |
|---|---|---|---|---|---|
| 1St location | -0.58 | -0.58 | -0.58 | -0.58 | 0.58 |
| 2nd location | -0.40 | 13.30 | 9.00 | 0.41 | 0.88 |
| 3rd location | -0.42 | 9.38 | 10.00 | 6.82 | 0.80 |
| 4th location | -0.40 | 11.70 | 9.38 | 1.00 | -0.36 |

## 4.0 CONCLUSION

Catchment soils of Asa River were assessed. Though, concentrations of the heavy metals were below the level recommended by FAO/WHO (except for Fe), there is a significant difference between the control sample and other sampling locations. The high values and significant variations in the concentrations of the heavy metals in 2nd to 4th locations suggest pollution status of the soil as compared to the reference location. Thus, there is need for soil analysis for heavy metal content before planting on the soils. This was also reflected in the results of the indices which showed probable influence of anthropogenic activities, hence caution should be taken in its usage for farming edible phytoplant.

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