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Soil Pollution, Degree of Contamination, Enrichment Factor, Principal Component Analysis, Heavy Metal

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# **Profiling heavy metal distribution and contamination in soil of old power generation station in Lagos, Nigeria**

## Adebola A. Adeyi<sup>1, 2, \*</sup>, Nelson Torto<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Ibadan, Ibadan, Nigeria <sup>2</sup>Chemistry Department, Rhodes University, Grahamstown, South Africa

## **Email address**

bolaoketola@yahoo.com (A. A. Adeyi), n.torto@ru.ac.za (N. Torto)

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### Abstract

The extent of heavy metal contamination of soil of the old power generation station in Lagos was assessed. The concentrations of heavy metals in the soil samples collected were analyzed using ICP-OES after acid digestion. Principal component and correlation coefficient were used to identify the possible sources of pollution. There was a great variation in the concentrations of the metals in both surface and subsurface soil. The order of heavy metal concentrations in the surface soil was: Fe>Zn>Pb>Mn>Cu>Cr>Cd>Ni>Co while Zn, Cd, and Cu were not detected at most depths. Obvious accumulation of some of these metals was indicated in the surface soil. Soil contamination was assessed on the basis of enrichment factor (EF), contamination factor (CF) and degree of contamination. Thus, a potential pollution risk may exist, which might contribute to heavy metal loading of the Lagos Lagoon.

## **1. Introduction**

Soils composed of mineral constituents, organic matter (humus), living organisms, air and water, are of vital importance to human health and well-being. Contamination of soil by heavy metal is the most serious environmental challenge as it poses significant implications to human health (Dang et al., 2002; Obiajunwa et al., 2002). Soils in urban environments are often highly variable in composition due to a wide variety of human influences, and typically contain higher loading of contaminants than those from rural settings due to the higher density of anthropogenic activities in urbanized areas (Davidson et al., 2006). Concentrations of toxic metals in the environment have increased significantly as a direct result of human activities through emissions from industrial plants, thermal power stations, waste disposal, soil amendments, and vehicle, traffic and road infrastructures. Generally, the distribution of heavy metals is influenced by the nature of the parent material, climatic condition, and their relative mobility depending on soil parameters such as mineralogy, texture and classification of soil (Krishna and Govil, 2007). Heavy metals do not degrade but remain in the environment for a long time even after the removal of the pollution sources

Different human activities have resulted in an increase in quantity of contaminants

discharged into the environment. For most heavy metals (e.g., Pb, Cu, Zn and Hg), anthropogenic sources contribute more to pollution than natural sources (Bilos et al., 2001) with various impacts on human health and the environment. Mn, Co, Cu, Pb, and Zn are initiators or promoters of carcinogenic activity in animals (Nriagu, 1988; Lu et al., 2010). Arsenic can affect the gastrointestinal tract, respiratory tract, skin, liver, cardiovascular, hematopoietic and nervous system (Al Rmalli et al., 2005) and can cause black foot disease and cancer risk for skin and various viscera, including lung, bladder, kidney and liver (Duker et al., 2005) while Hg can damage nervous system (Walcek et al., 2003).

Methods of multivariate analysis have been widely used in environmental investigations to identify pollution sources and to apportion natural versus anthropogenic contribution (Facchinelli et al., 2001; Luo et al., 2007). Principal component analysis (PCA) and Cluster analysis (CA) are the most common multivariate statistical methods used in environmental studies (Han et al., 2006; Lu et al., 2010; González-Pérez et al., 2008; Zheng et al., 2008; Tahri et al., 2005). CA classifies a set of observation into two or more mutually exclusive unknown groups based on a combination of internal variables. CA is often coupled with PCA to check results and to group individual parameters and variables (Facchinelli et al., 2001). The purpose of CA is to discover a system of organizing observations, where a number of groups/variables share observed properties. A dendrogram is the most commonly used method of summarizing hierarchical clustering (Lu et al., 2010). PCA is widely used to reduce data and to extract a smaller number of independent factors (principal components) for analyzing relationships among observed variables (Han et al., 2006). The correlation matrix describe the dispersion of the original variables and extract the eigenvalues and eigenvectors (Chen et al., 2007; Astel et al., 2008). An eigenvector is a list of coefficient multiplying the original correlated variables to obtain new uncorrelated (orthogonal) principal components, which are linear weighted combination of the original variables (Chen et al., 2007, Lu et al., 2010). PCA can reduce the number of correlated variables to a smaller set of orthogonal factors, making it easier to interpret a given multidimensional system by displaying the correlation among the original variables. Principal components are those whose Eigenvalues exceed 1.

This study thus investigated the distribution and contamination of heavy metals in soil of the old power generation station, Ijora, Lagos. In this work, the soil contamination was assessed to ascertain their lithogenic or anthropogenic origin using various indices such as enrichment factor (EF), contamination factor (CF), degree of contamination (DC), and principal component analysis (PCA).

## 2. Material and Methods

#### 2.1. The Study Area

Ijora power generation and transmission station was established in 1921 and power generation/transmission stopped in 1978. There is a transformer repair workshop at the site, which has been in existence since 1921. Though, power generation and transmission has stopped at the station, it has been fully converted to transformer repair station for the country since 1985. The Latitude/Longitude Coordinates are  $6^{\circ}$  27 59.83 N;  $3^{\circ}$  22 35.45 E (North) and 6<sup>°</sup> 27 57.49 N; 3<sup>°</sup> 22 35.43 E (South), respectively. Figure 1 shows the base map of the site while Figure 2 is the geological map of Lagos (Jones and Hockey, 1964). There is a drain, which channeled its content directly into the Lagos Lagoon. The geology of the area is sedimentary based on the geology of Lagos and the climate fall within the humid tropical climate characterized by high temperature as a result of proximity of the equator. Two climatic seasons, rainy and dry are experienced in Lagos.

#### 2.2. Soil Sampling

A total of seven surface and thirty-five subsurface soil samples from the four boreholes drilled were collected at different depth. Grab soil samples were collected at each depth from the four boreholes (labeled as #1, #2, #3, #4). Borehole diameter varied from 250 mm to 150 mm, depending on the ground condition. The four boreholes were drilled from 0 m to depth of 4.5 m, 5.6 m, 4.5 m and 5.5 m, respectively. The drilling depth for each borehole was chosen to terminate at a significant clay stratum that underlay a sandy rich stratum. Samples were collected from 0 m to the final depth at almost regular interval when no defined soil change boundary exists. Soil samples were collected from a 1.5 m split-core. After each use, the core was steam washed and dried to avoid cross-contamination. The samples were collected from within the central part, which had no contact with the auger. The samples were collected directly into a polythene bag and labeled appropriately for onward transportation to the laboratory immediately after sampling. Sampling points are shown in Figure 1. Control sample (surface soil) was also collected from a rural community, Lalupon in Ibadan.



Fig 1. Base map of the study area.



Fig 2. Geological Map of Lagos.

#### 2.3. Soil Preparation and Analysis

In the laboratory, the samples were air dried at room temperature and passed through a 2 mm nylon sieve. Soil pH was measured in milliQ water (1:2.5 w/v) using a calibrated electrode (Jenway model 3510) pH meter. Approximately, 10 g each of the soil samples were shaken with 25 ml of milliQ water and left to stand for 2 hours, the pH of the suspension was then measured. Samples for metal analysis were digested in open vessels. About 1 g each of the dried and sieved samples were digested with 20 ml of 2 M nitric acid and the digestate make up to 50 ml with milliQ water after filteration. The resulting solutions were analyzed for heavy metals using Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP-OES) (Thermo Electron iCAP 6000 series). All the reagents used were analytical grade and milliQ water was used throughout. To check the analytical quality, reagent blank and duplicate determination were carried out. Blank determination was carried out and the level of the metals was below the detection limit of the instrument in all cases. Contamination was prevented during sampling and analysis. 20% duplicate determination was carried out and the result was not more than 10% for all the metals. Calibration standards were also analyzed at the end of each run to ensure that drift did not occur.

#### 2.4. Enrichment Factor (EF)

The enrichment factor is calculated by comparing the concentration of a test element with that of a reference element (Liu et al., 2005). In this study, the value of the enrichment factor was calculated using modified formula based on the equation suggested by Buat-Menard and Chesselet (1979). The most common reference elements are Sc, Mn, Ti, Al, and Fe (Quevauviller et al., 1989; Schiff and Weisberg 1999; Sutherland, 2000). According to Sutherland (2000), five contamination categories are generally recognized on the basis of the enrichment factor. These are:

| EF < 2     | Deficiency to mineral enrichment |
|------------|----------------------------------|
| EF = 2-5   | Moderate enrichment              |
| EF = 5-20  | Significant enrichment           |
| EF = 20-40 | Very high enrichment             |
| EF > 40    | Extremely high enrichment        |

Enrichment factor was determined using the formula;

$$EF = (C_{n \text{ (sample)}} / C_{ref \text{ (sample)}}) / (B_{n \text{ (background)}} / B_{ref \text{ (background)}})$$

Where,

 $C_{n \text{ (sample)}}$  is the concentration of the examined element in the study site,  $C_{ref \text{ (sample)}}$  is the concentration of the

reference element in the study site,  $B_n$  (background) is the concentration of the examined element in the control sample, and  $B_{ref}$  (background) is the concentration of the reference element in the control sample. In this study, Fe was used as the reference element, and the value obtained from the control sample was used as the reference value.

# 2.5. Contamination Factor (CF) and Degree of Contamination (DC)

The contamination factor and the degree of contamination were used by Hakanson (1980) to assess soil contamination through comparison of the concentration in the surface layer to background value (Liu et al., 2005). CF was defined according to four categories as follows:

| $C_{f}^{i} < 1$             | Low contamination factor          |
|-----------------------------|-----------------------------------|
| $1 \le C_{\rm f}^{\ i} < 3$ | Moderate contamination factor     |
| $3 \le C_{\rm f}^{\ i} < 6$ | Considerable contamination factor |
| $6 \le C_f^i$               | Very high contamination factor    |

DC is the sum of the contamination factors of all the elements examined. According to Hakanson (1980),

Cd < 9: low degree of contamination

 $9 \le Cd < 18$ : moderate degree of contamination

 $18 \le Cd < 36$ : considerable degree of contamination

 $Cd \ge 36$ : very high degree of contamination, indicating serious anthropogenic pollution.

Concentration factor and degree of contamination were calculated using the formulae

Concentration factor,  $C_{f}^{i} = C_{0-1}^{i} / C_{n}^{i}$ 

Overall degree of contamination, mDC =  $\sum_{i=n}^{i=n} C_{f}^{i}$ 

Where,

 $C_f$  = contamination factor;  $C_{0-1}^i$  = mean concentration of each metal in the soil;  $C_n^i$  = baseline or background value (concentration of each metal in the control sample was used); n = number of analyzed elements; i = ith element (or pollutants). The modified formula of CF was used as there is no established background value of heavy metals for the country.

In this study, a simplified approach to risk assessment

based on comparison of the measured level of contamination in the soil of the study site with the background value from the control sample was adopted.

#### 2.6. Statistical Analysis

To identify the relationship among pH and heavy metals in the soil and their sources, Pearson's correlation coefficient and Principal Component Analysis (PCA) were performed using Statistical Package for the Social Sciences (SPSS) software packages 13.0 for windows and Microsoft Office Excel (2007). The correlation coefficient measures the strength of inter-relationship between two parameters while PCA identify possible sources. Shakery et al. (2010) however concluded that statistical methods are strong tools for monitoring current environmental quality of industrial soils in terms of heavy metal accumulation and predicting future soil contamination.

## **3. Results and Discussion**

#### 3.1. Soil pH and Total Metal Concentration

The pH of the surface soil ranged from 6.26-7.03 with an average of 6.64±0.3 while subsurface soil samples collected at different depth in the four boreholes ranged from 6.20-7.71. Heavy metals are natural component of soil but their concentrations can be increased by human activities and then become a pollution concern. Some trace elements are required for healthy growth of organisms, but concentrations exceeding threshold can be toxic (Wade et al., 2008). Heavy metal concentrations in the surface and subsurface soil samples are presented in Tables 1 and 2, respectively. The range of metal concentrations in the surface soil are 44.3-557 mg/kg Pb; ND-3540 mg/kg Zn; ND-9300 mg/kg Fe; ND-20.4 mg/kg Cd; 29.7-61.6 mg/kg Mn; 11.5-27.4 mg/kg Cr; 0.82-3.18 mg/kg Co; 1.40-9.85 mg/kg Ni and 1.13-48.5 mg/kg Cu while in the subsurface soil, the range are 0.08-79.6 mg/kg Pb; ND-0.18 mg/kg Cd; ND-45.9 mg/kg Zn; 0.23-40.1 mg/kg Mn; ND-9180 mg/kg Fe; 1.46-18.7 mg/kg Cr; ND-39.1 mg/kg Co; 0.10-5.77 mg/kg Ni; and ND-2.06 mg/kg Cu, respectively.

| Table 1. Descri | ptive statistics.  | heavy metal    | concentrations       | (mg/kg) | and pH o     | of surface soil | of the old   | power s | generation station.   |
|-----------------|--------------------|----------------|----------------------|---------|--------------|-----------------|--------------|---------|-----------------------|
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| Sampling<br>points | рН        | Pb       | Ni        | Cr        | Cu        | Со        | Cd      | Zn      | Mn        | Fe      |
|--------------------|-----------|----------|-----------|-----------|-----------|-----------|---------|---------|-----------|---------|
| 1                  | 6.91      | 557      | 9.85      | 27.4      | 48.5      | 3.18      | 20.4    | 3540    | 61.6      | ND      |
| 2                  | 6.70      | 44.9     | 1.40      | 12.9      | 1.13      | 0.85      | 0.05    | ND      | 41.8      | 8500    |
| 3                  | 6.65      | 71.8     | 2.07      | 24.7      | 4.31      | 1.22      | ND      | 289     | 53.8      | ND      |
| 4                  | 6.27      | 77.5     | 2.03      | 11.5      | 18.9      | 0.93      | 0.03    | 1020    | 36.4      | 6110    |
| 5                  | 6.26      | 44.3     | 1.81      | 14.2      | 5.32      | 0.82      | 0.11    | ND      | 33.4      | 9300    |
| 6                  | 7.03      | 94.2     | 1.82      | 14.2      | 3.24      | 1.46      | 0.01    | 112     | 29.7      | 7560    |
| 7                  | 6.65      | 76.1     | 1.43      | 13.6      | 2.61      | 1.13      | 0.01    | 46.0    | 36.1      | 6760    |
| Average            | 6.64      | 138      | 2.91      | 16.9      | 12.0      | 1.37      | 2.94    | 715     | 41.8      | 5460    |
| Median             | 6.65      | 76.1     | 1.82      | 14.2      | 4.31      | 1.13      | 0.03    | 112     | 36.4      | 6760    |
| Range              | 6.26-7.03 | 44.3-557 | 1.40-9.85 | 11.5-27.4 | 1.13-48.5 | 0.82-3.18 | ND-20.4 | ND-3540 | 29.7-61.6 | ND-9300 |
| Skewness           | -0.23     | 2.59     | 2.60      | 1.20      | 2.09      | 2.26      | 2.65    | 2.27    | 0.99      | -0.92   |
| Kurtosis           | -1.02     | 6.79     | 6.84      | -0.51     | 4.32      | 5.38      | 7.00    | 5.25    | -0.27     | -1.05   |

Note: ND = Non-detectable

Table 2. Heavy metal concentrations (mg/kg) and pH of subsurface soil of the old power generation station.

| Borehole<br>No | Depth (m) | рН       | Pb        | Ni       | Cr            | Cu      | Со      | Cd      | Zn      | Mn            | Fe          |
|----------------|-----------|----------|-----------|----------|---------------|---------|---------|---------|---------|---------------|-------------|
| #1             | 0-0.25    | 6.53     | 24.9      | 3.30     | 15.3          | 0.79    | 11.9    | ND      | ND      | 35.9          | 8680        |
|                | 1.50      | 6.31     | 42.4      | 0.88     | 10.7          | ND      | 0.45    | ND      | ND      | 6.32          | 7880        |
|                | 2.00      | 6.38     | 10.9      | 0.11     | 3.60          | ND      | 0.07    | 0.01    | ND      | 1.07          | 2490        |
|                | 2.29      | 6.49     | 3.74      | 0.10     | 3.26          | ND      | ND      | ND      | ND      | 0.90          | 2330        |
|                | 2.40      | 6.49     | 12.4      | 0.57     | 6.55          | ND      | 0.01    | 0.08    | ND      | 2.33          | 4110        |
|                | 2.48      | 6.54     | 52.0      | 0.12     | 1.46          | ND      | ND      | ND      | ND      | 0.44          | 783         |
| #2             | 0-0.35    | 6.61     | 38.3      | 1.16     | 16.4          | 1.09    | 0.54    | ND      | ND      | 31.9          | 7140        |
|                | 0.8-1.0   | 6.76     | 37.6      | 1.37     | 18.4          | 1.05    | 0.67    | ND      | ND      | 40.1          | 9100        |
|                | 1.5-1.8   | 7.41     | 27.9      | 1.41     | 15.0          | 0.30    | 0.20    | ND      | ND      | 14.8          | 9180        |
|                | 2.0-2.5   | 7.54     | 25.8      | 1.32     | 6.20          | 0.22    | 0.09    | ND      | 35.0    | 7.91          | 2430        |
|                | 2.5-3.0   | 7.57     | 20.6      | 4.13     | 11.0          | 0.24    | 0.45    | ND      | ND      | 7.04          | 6300        |
|                | 3.0-4.0   | 7.37     | 4.68      | 0.19     | 2.96          | ND      | ND      | ND      | ND      | 0.75          | 4200        |
|                | 4.0-4.5   | 7.25     | 7.05      | 0.45     | 7.08          | ND      | 0.13    | ND      | ND      | 1.50          | 3750        |
|                | 4.5-5.25  | 6.99     | 7.84      | 0.27     | 8.34          | ND      | 0.11    | ND      | ND      | 0.84          | 4880        |
|                | 5.25-5.6  | 6.64     | 21.3      | 2.06     | 5.70          | ND      | ND      | ND      | ND      | 0.23          | 3670        |
| #3             | 0.0-0.25  | 7.02     | 1.71      | 1.62     | 16.5          | 1.47    | 39.1    | 0.08    | 45.9    | 24.8          | 6860        |
|                | 0.8-1.0   | 7.15     | 0.25      | 1.96     | 7.02          | ND      | 0.51    | ND      | ND      | 5.05          | 4240        |
|                | 1.5-1.8   | 6.81     | 0.32      | 0.63     | 12.6          | ND      | 0.08    | ND      | ND      | 4.73          | 6080        |
|                | 2.0-2.3   | 6.67     | 0.21      | 0.95     | 6.89          | ND      | 0.05    | 0.01    | ND      | 1.97          | 3810        |
|                | 2.5-3.0   | 6.59     | 0.14      | 5.77     | 4.03          | ND      | ND      | ND      | ND      | 1.21          | 1890        |
|                | 3.0       | 6.49     | 0.08      | 0.31     | 5.67          | ND      | ND      | ND      | ND      | 1.53          | 3130        |
|                | 3.0-4.0   | 6.71     | 0.43      | 0.42     | 5.74          | ND      | ND      | 0.18    | ND      | 1.37          | 3110        |
|                | 4.0-4.5   | 6.84     | 0.46      | 0.25     | 10.6          | ND      | ND      | ND      | ND      | 1.00          | 6050        |
|                | 4.5       | 6.2      | 0.16      | 0.41     | 18.7          | ND      | ND      | ND      | ND      | 0.99          | 5050        |
| #4             | 0.0-0.35  | 6.66     | 64.1      | 1.16     | 14.3          | 2.06    | 0.14    | ND      | ND      | 29.8          | 5790        |
|                | 0.8-1.0   | 7.56     | 79.6      | 1.77     | 14.7          | 1.64    | 0.60    | ND      | ND      | 33.0          | 7230        |
|                | 1.5-1.8   | 7.71     | 25.6      | 2.44     | 11.0          | 0.21    | 0.65    | ND      | ND      | 7.35          | 5650        |
|                | 2.0-2.5   | 7.44     | 11.9      | 0.55     | 8.72          | ND      | 0.14    | ND      | ND      | 0.71          | 3980        |
|                | 2.5-3.0   | 7.07     | 9.20      | 0.16     | 7.12          | ND      | 0.14    | ND      | ND      | 2.68          | ND          |
|                | 3.0-4.0   | 6.81     | 8.89      | 0.30     | 9.39          | ND      | ND      | ND      | ND      | 2.72          | 4860        |
|                | 4.0-4.5   | 7.03     | 10.60     | 0.27     | 10.9          | ND      | 0.01    | ND      | ND      | 2.30          | 5820        |
| Range          |           | 6.2-7.71 | 0.08-79.6 | 0.1-5.77 | 1.46-<br>18.7 | ND-2.06 | ND-39.1 | ND-0.18 | ND-45.9 | 0.23-<br>40.1 | ND-<br>9180 |

Note: ND = Non-detectable

Highest concentration of the metals was obtained in the surface soil in most of the sampling points. Elements with a potential risk of pollution are Pb, Cd, and Zn. Fe has the highest concentration in both surface and subsurface soil while Cu, Cd and Zn showed a non-homogeneous distribution. In the surface soil, Co, Ni and Cd have the lowest average concentrations while in the subsurface soil, Cd have the lowest concentration. The order of average concentration of the metals in the surface and subsurface soil are;

Surface soil: Fe > Zn > Pb > Mn > Cu > Cr > Cd > Ni > Co; and

Subsurface soil: Fe > Pb > Zn > Mn > Co> Cr > Ni > Cu > Cd.

There was a great variation in the metal concentrations in both surface and subsurface soil with depth. The low value of Ni, Cu, and Cd at the site suggested that little contamination has occurred. Though, the values exceed the concentration in an unpolluted soil. Cd can travel long distance in the atmosphere and then deposited unto surface soil and water, which can result in elevated Cd level even in remote locations (Shevchenko et al., 2003). Cd occurs in the earth crust at an abundance of 0.1-0.5 ppm and commonly associated with Zn, Pb, and Cu ores. Cd mobility in soil depends on several factors including the pH of the soil and the availability of organic matter. Generally, Cd will bind strongly to organic matter and this will immobilize cadmium (Autier and White, 2004). Low pH favours the accumulation of Cd in soil (Kirkham, 2006) and tends to be more available at this pH (acidic) (Elinder, 1992). However, immobilized cadmium is available to plant and can easily enters the food supply. Top soil concentration is often more than twice as high as subsoil level due to atmospheric fallout and contamination (Pierce et al., 1982), which is the trend observed in this study. The mean value in the surface soil exceed the calculated worldwide mean in non-polluted soil (0.53 mg/kg) reported for Cd (Kabata-Pendias and Pendias, 2001). Concentration above 0.5 mg/kg could reflect the influence of human activity (McBride, 1994). Human activity can contribute to increased Cd level as a result of urban and industrial activities and/or agricultural practices (Adriano, 2001).

In most depth, the concentrations of Cu, Cd and Zn were non-detectable but high in the surface soil. This showed that these metals have little migration tendency and mobility within the soil depth. Copper's movement in soil is determined by a host of physical and chemical interactions of copper with the soil components. In general, copper will adsorb to organic matter, carbonate minerals, clay minerals, or hydrous iron and manganese oxides (Tyler and McBride, 1982). The concentration of Copper was found to be low in the study area. The normal threshold value prescribed in soil is 30 mg/kg and copper normally accumulate in the surface horizon, a phenomenon explained by the bioaccumulation of the metal and recent anthropogenic source (Kabata-Pendias, 2004; Gowd et al., 2010). Thus, the surface sampling point 1 has a concentration (48.5 mg/kg) which is above this normal threshold value. Thus, copper is however, characterized by the so called point source of contamination (Gowd et al., 2010).

Zinc belongs to a group of trace metals, which are essential for the growth of humans, animals and plants and is potentially dangerous to the biosphere when present in high concentration. The main sources of pollution are industries and the use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides in agriculture (Romic and Romic, 2003). Zinc does not volatilize from soil and soil pH limits the mobilization of Zn. The mobility of this metal in soil depends on the solubility of the speciated form of the element and on soil properties such as cation exchange capacity, pH, redox potential, and chemical species present in soil (EPA, 1980). Mobility of Zn increases at lower soil pH under oxidizing condition and at a lower cation exchange capacity (Bergkvist et al., 1989). Movement towards the groundwater is expected to be slow unless Zn is applied to soil in soluble form (such as in agricultural applications) or accompanied by corrosive substances (such as in mine tailings) (EPA, 1980). The normal threshold value prescribed in soil is 200 mg/kg (Gowd et al., 2010). The average zinc concentration obtained in this study was 715 mg/kg in the surface soil and non-detectable in all the four boreholes except in boreholes #2 (2.0-2.5 m) and #3 (0.0-0.25 m) with concentrations of 35.0 mg/kg and 45.9 mg/kg, respectively.

The highest Pb concentration was found at depth 0.8-1.0 m in borehole #4, which was closer to the canal that discharges directly into the Lagos Lagoon and also opposite point 1 of the surface sampling points, which have the highest concentration (557 mg/kg). Lead has a long residence time in soil due to its relatively low solubility. Because it is strongly adsorbed to soil, it is generally retained in the upper layer of the soil and does not leach appreciably into the subsoil and groundwater (EPA, 2001). Baseline Pb values for surface soil on the global scale have been estimated to be 25 mg/kg; levels above this suggest an anthropogenic influence (Wong and Li, 2004). Lead is released from smelting, motor-vehicle exhaust fumes and from corrosion of lead pipes (Kumar et al., 2005). The average concentration in the surface soil obtained in this study was 138 mg/kg while the range in the boreholes are 3.74-52.0 mg/kg in # 1, 4.68-38.0 mg/kg in # 2, 0.08-1.71 mg/kg in # 3, and 8.89-79.6 mg/kg in # 4. These shows that there is significant lead contamination at the site.

Other persistent and toxic metals such as Cr and Mn showed significant concentrations in both surface and subsurface soil. Cr showed highest concentration (18.7 mg/kg) at 4.5 m in borehole #3 while the highest Mn concentration (40.1 mg/kg) was found at 0.8-1.0 m in borehole #2. The mobility of chromium in soil is dependent upon the speciation of the metal, which is a function of the redox potential and the pH of the soil. In most soils, it will be present predominantly in the chromium (III) oxidation state. This form has very low mobility and low reactivity, resulting in low mobility in the environment (Robson, 2003). Chromium level in the study area ranged from 11.5-27.4 mg/kg in the surface soil, with an average of 16.9 mg/kg; and 1.46-18.7 mg/kg in the subsurface soil. The normal range of chromium in soil is 100 mg/kg (Wedepohl, 1995) and the concentration in both surface and subsurface soil samples was below this reported normal value. The range of Mn in the surface soil is 29.7-61.6 mg/kg. Manganese mobility in soil is extremely sensitive to soil conditions such as acidity, wetness, organic matter content, biological activity etc. The solubility of soil manganese is thus controlled by redox potential and soil pH, where low pH or low redox potential favour the reduction of insoluble manganese oxides resulting in increased manganese mobility. At soil pH above 6, manganese form bonds with organic matter, oxides and silicates whereby its solubility decreases. Manganese availability and solubility is thus generally low at high pH and high organic matter content, while in acid soils with low organic matter content its availability is high. The solubility of manganese is also high in anaerobic condition at pH above 6, as well as in aerobic condition at pH below 5.5 (Kabata-Pendias and Pendias 2001; McBride 1994).

Heavy metal concentrations in the surface and subsurface soils in this study was also compared with the control sample collected at a rural community, Lalupon in Ibadan and some typical values in rural and urban soils around the world. The concentrations of Pb, Zn and Cd in the surface soil were above the values reported by Bowen (1979) (Table 3). Also, the average metal concentrations in both the surface and subsurface soil were higher than the values obtained from the control sample except Mn whose concentration (58.7 mg/kg) was higher than that obtained in the study site; and Cu whose concentration was higher than the concentration obtained in the subsurface soil. High concentration of Mn in the control sample may be attributed to the crustal materials. There are no background and baseline data on toxic metals for the country. Metal concentrations in the study site when compared to the control sample suggested that anthropogenic inputs have occurred over the years.

### **3.2. Descriptive Statistics**

As confirmed by the skewness (Table 1), metal concentrations in the surface soil were characterized by large variability, with positively skewed frequency distributions except pH and Fe in the surface soil, which showed negative skewness. Also, flat distribution was indicated by pH, Cr, Mn and Fe as shown by the kurtosis of the surface soil while Pb, Ni, Cu, Co, Cd and Zn data are peaked, relative to normal distribution. This is common for heavy metal because they usually have low concentration in the environment so that the presence of a point source of contamination may cause a sharp increase in local concentration, thus exceeding the threshold values (Sollitto et al., 2009).

Table 3. Comparison of mean concentrations (mg/kg) of metals in this study with the control sample and typical soil values

|                              | Pb   | Zn   | Cd   | Fe     | Cu   | Cr   | Ni   | Mn   | Co   |
|------------------------------|------|------|------|--------|------|------|------|------|------|
| Surface soil (this study)    | 138  | 715  | 2.94 | 5,460  | 12.0 | 16.9 | 2.91 | 41.8 | 1.37 |
| Subsurface soil (this study) | 17.3 | 2.53 | 0.01 | 4,760  | 0.28 | 9.35 | 1.14 | 8.58 | 1.76 |
| Control site (0-15cm)        | 9.12 | ND   | ND   | 2,550  | 4.57 | 4.83 | 0.57 | 58.7 | 0.53 |
| Rural–urban                  |      |      |      |        |      |      |      |      |      |
| Soils average (Bowen, 1979)  | 35   | 90   | 0.35 | 40,000 | 30   | 70   | -    | -    | -    |

#### 3.3. Contribution of Particular Metals to the Contamination of Soil in the Study Site

To describe the contamination of these metals in the soil, different parameters were used, which include enrichment factor, contamination factor and degree of contamination. The enrichment factor was calculated to evaluate anthropogenic influence of the studied metals. The result shows that the EF value for Pb in the surface soil was enriched significantly when compared with the background level as shown in Table 4. The EF values for Cr, Cu, and Co < 2 showed deficiency to mineral enrichment while Ni also showed moderate enrichment based on Sutherland (2000) classification. EF for Zn, Cd and Mn (EF = 0) indicated that these metals was not influenced by anthropogenic activity. Generally, an EF value of about 1 suggests that a given metal may be entirely from crustal material or a natural weathering process (Zhang and Liu, 2002), which was the case for Fe in this site with EF = 1. Nevertheless, a slight positive deviation of EF value from unity may not arise from anthropogenic activity, for the natural difference in elemental composition between pristine sediment and the reference Earth's crust used in EF calculation could also cause this (Gao et al., 2008). An EF value of >1.5 suggests that a significant portion of a given metal is delivered from non-crustal material, or non-natural weathering process, and then anthropogenic sources become an important contributor (Feng et al., 2004). At this site, the highest EF value was recorded for Pb while Ni and Cr have an EF > 1.5 suggesting possible soil contamination due to anthropogenic activity. The EF< 1.5 was obtained for Cu, Cd, Zn, Mn and Co.

Pb has the highest CF value (15.1) while Ni, Cr and Cu followed suit. Cd, Zn and Mn have the lowest CF of 0 as shown in Table 4. The calculated CF value showed that there was heavy metal contamination in the soil and Pb, Ni, and Cr contamination is apparent. The degree of contamination (DC) in the study site is 31.1. This value revealed a considerable degree of contamination, which might be attributed to the previous and ongoing activities at the site. Also, possible contamination by Pb, Ni and Cr might reveal their common source and sink in the study site.

#### 3.4. Correlation of Heavy Metal Concentration

Correlation coefficient of the metals with pH is presented in Table 5. Significant correlation exists between Pb, versus Zn, Ni, Cu, Co and Cd at 0.01 levels (2-tailed). Cr also showed a strong positive correlation with Mn ( $r^2 = 0.91$ ). Cr and Mn did not show significant correlation with all the other metals except Fe, where there is strong negative correlation between them at the 0.01 level (2-tailed). This indicates that Pb and Ni might originate from similar pollution source, which is different from source of Fe and Mn, which might be said to be rock-derived and mainly from natural origin. Also, there is no significant correlation between pH and all the metals.

Table 4. Contamination factor (CF) and enrichment factor (EF).

| Metals | EF   | CF   |
|--------|------|------|
| Pb     | 7.07 | 15.1 |
| Ni     | 2.38 | 5.11 |
| Cr     | 1.63 | 3.50 |
| Cu     | 1.23 | 2.63 |
| Co     | 1.21 | 2.58 |
| Cd     | 0    | 0    |
| Zn     | 0    | 0    |
| Fe     | 1.0  | 2.14 |
| Mn     | 0    | 0    |
| Total  | 14.5 | 31.6 |

#### **3.5. Principal Component Analysis (PCA)**

PCA was used to investigate the multivariate structure of the data and to highlight the possible trend. PCA was applied to identify the sources of heavy metal in the surface soil by applying Varimax rotation with Kaiser Normalization. Varimax rotation was conducted to minimize the number of variables influencing each factor thus facilitating the interpretation of the result. Eigenvalues were extracted from the correlation matrix; the number of significant factors and the percentage variance explained by each of them were calculated. Table 6 and Table 7 summarize the PCA loading of the metals in the surface and subsurface soil, eigenvalue of each principal component (PC), total variance explained as well as the cumulative variance. Two principal components were extracted for the surface soil, which explained 100% variance. The first factor (PC 1) was responsible for 77.8% of the total variance and was best represented by pH, Pb, Cr, Co, Mn and Fe while the second factor (PC 2) explained 22.2% total variance and was dominated by pH, Ni, Cr, Cu, Cd, Fe and Zn. Three principal components were also extracted for

the subsurface soil, which explained 69.9% of the total variance. PC 1 was responsible for 38.9% of the total variance and was dominated by Pb, Cr, Cu, Mn and Fe while PC 2 explained 19.1% variance and was loaded heavily on Co, Cd, and Zn. PC 3 was best represented by pH and Ni, which accounted for 11.9% of the total variance.

Table 5. Correlation coefficient between heavy metals and pH in the surface soil of the study area.

|    | Pb   | Ni      | Cu      | Со           | Cd      | Zn           | Cr          | Mn          | Fe       | pН     |
|----|------|---------|---------|--------------|---------|--------------|-------------|-------------|----------|--------|
| Pb | 1.00 | 0.994** | 0.941** | 0.980**      | 0.995** | 0.966**      | 0.730       | 0.732       | -0.644   | 0.453  |
| Ni |      | 1.00    | 0.952** | 0.964**      | 0.996** | $0.972^{**}$ | 0.752       | $0.759^{*}$ | -0.657   | 0.387  |
| Cu |      |         | 1.00    | $0.878^{**}$ | 0.938** | 0.993**      | 0.615       | 0.674       | -0.607   | 0.187  |
| Co |      |         |         | 1.00         | 0.961** | 0.916**      | $0.770^{*}$ | 0.712       | -0.682   | 0.593  |
| Cd |      |         |         |              | 1.00    | $0.960^{**}$ | 0.726       | 0.747       | -0.619   | 0.408  |
| Zn |      |         |         |              |         | 1.00         | 0.675       | 0.731       | -0.662   | 0.279  |
| Cr |      |         |         |              |         |              | 1.00        | 0.912**     | -0.912** | 0.415  |
| Mn |      |         |         |              |         |              |             | 1.00-       | -0.894** | 0.288  |
| Fe |      |         |         |              |         |              |             |             | 1.00     | -0.327 |
| pН |      |         |         |              |         |              |             |             |          | 1.00   |
|    |      |         |         |              |         |              |             |             |          |        |

\*\* Correlation is significant at the 0.01 level (2-tailed); \* Correlation is significant at the 0.05 level (2-tailed)

Table 6. Principal component loadings of the surface soil.

| Variable             | PC 1  | PC 2   |
|----------------------|-------|--------|
| pН                   | 0.83  | -0.56  |
| Pb                   | 1.00  | -0.004 |
| Ni                   | 0.24  | 0.97   |
| Cr                   | 0.62  | -0.79  |
| Cu                   | -0.40 | 0.92   |
| Со                   | 0.90  | -0.44  |
| Cd                   | -0.44 | 0.90   |
| Zn                   | -0.38 | 0.93   |
| Mn                   | -0.99 | 0.11   |
| Fe                   | 0.86  | -0.51  |
| Eigenvalues          | 7.78  | 2.22   |
| % Variance explained | 77.8  | 22.2   |
| % Cumulative         | 77.8  | 100.0  |

Extraction method: principal component analysis; Rotation method: Varimax with Kaiser Normalization.

Figures in italics indicate absolute values greater than 0.5

Table 7. Principal component loadings of the subsurface soil.

|                       | Component |        |        |  |  |  |
|-----------------------|-----------|--------|--------|--|--|--|
| rarameter             | 1         | 2      | 3      |  |  |  |
| pН                    | 0.003     | 0.046  | 0.833  |  |  |  |
| Lead (Pb)             | 0.699     | -0.307 | 0.159  |  |  |  |
| Nickel (Ni)           | 0.209     | 0.050  | 0.604  |  |  |  |
| Chromium (Cr)         | 0.843     | 0.136  | 0.040  |  |  |  |
| Copper (Cu)           | 0.862     | 0.238  | 0.109  |  |  |  |
| Cobalt (Co)           | 0.276     | 0.880  | 0.076  |  |  |  |
| Cadmium (Cd)          | -0.103    | 0.597  | -0.389 |  |  |  |
| Zinc (Zn)             | 0.052     | 0.850  | 0.273  |  |  |  |
| Manganese (Mn)        | 0.932     | 0.135  | 0.104  |  |  |  |
| Iron (Fe)             | 0.806     | 0.027  | 0.106  |  |  |  |
| Eigenvalues           | 3.894     | 1.908  | 1.188  |  |  |  |
| % Variance Explained  | 38.944    | 19.084 | 11.884 |  |  |  |
| % Cumulative Variance | 38.944    | 58.028 | 69.912 |  |  |  |

Extraction Method: Principal Component Analysis, Rotation Method: Varimax with Kaiser Normalization. Bold figures indicate values > 0.5.

#### 4. Conclusion

Ijora power station which was a power generation and transmission facility in Nigeria until 1985, when it was converted to transformer repair station can be said to be contaminated with metals. Toxic metal concentration was higher on the surface with some metal mobility, which was not significant in Zn. Fe concentration was the highest in the surface soil while Zn and Pb concentrations followed suit. Concentrations of Zn, Cu and Cd were below the detection limit of the instrument at most depth in the boreholes. This investigation revealed obvious accumulation of the metals except Mn as their concentrations in both the surface and subsurface soil was lower than the values obtained from the control site. According to the contamination factor, Pb displayed very high contamination while Ni and Cr displayed considerable contamination. Enrichment factor was used to identify the lithogenic or anthropogenic origin of the metals. Pb, Ni and Cr were shown to be mainly from anthropogenic sources. The result of the PCA allowed the reduction of the original data matrix from the surface soil to two important PCs explaining total variance of 100% while it is 69.9% in the subsurface soil. Because of the direct linkage of this site to the Lagos Lagoon, there is need for proper control measures to prevent risk due to exposure of organisms including man around the site to toxic metals, which can lead to accumulation through the food chain. Also, high concentration of toxic metals in the environment induces an increase in their concentration in groundwater.

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