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Geochemical study of heavy metals in samples from dumpsites at Onitsha, Anambra Basin, Southeastern Nigeria

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Abstract

Core (0-60cm) samples were collected from selected dumpsites at Onitsha and control site at Awka, Nigeria. Physiochemical parameters (particle size distribution, cation exchange capacity (CEC), pH, Organic Matter (OM in %)) and heavy metals (Lead (Pb), Copper (Cu), Zinc (Zn), Chromium (Cr), Nickel (Ni), Aluminium (Al), Cobalt (Co), Molybdenium (Mo), Cadmium (Cd), Manganese (Mn) and Silicon (Si)) were analyzed using standard methods. The result of the physiochemical analysis shows that the samples were generally sandy with acidic pH values (4.89-6.24); OM ranged from 5.693-27.71%; CEC ranged from 0.072-0.62(Cmol/kg). Comparatively, DS 5 (Obosi) has the highest levels of these heavy metals followed by DS 2 (Woliwo). The order is Bida < Okpoko <Obosi 1 < Woliwo < Obosi 2. The levels of these heavy metals were above the control values. They were equally above national and international guidelines. Enrichment Factor (EF) values varied between no enrichment to extremely severe enrichment. Pollution load index (PLI) indicated that all the sampled sites were polluted while the ecological risk of heavy metals varied between low contamination to high contamination. The prevailing indiscriminate disposal of wastes occasioned by nonexistence of appropriate disposal facilities is the direct cause of the situation. Proactive measures and regular environmental monitoring must be taken to minimize further deterioration as the contaminants pose serious deleterious effects on human and soil organisms.

Keywords: Heavy Metals; Dumpsites; Enrichment Factors; Pollution Load Index; Potential Ecological Risk Index

1. Introduction

Onitsha is well known for commercial activities as well as an ecclesiastical and administrative center. Lying on the eastern bank of the Niger River, just south of its confluence with the Anambra River, Onitsha and its environs constitute one rapidly urbanizing region that has witnessed a dramatic growth in industrial and commercial activities in the last four to five decades. This has led to increase in the city's population through natural births and migration, as well as a consistent increase in commercial, industrial and administrative activities. Although there are benefits inherent in urbanization, according to Chen (2007), a rapidly evolving urban area risks environmental degradation because urbanization directly contributes to waste generation. Unscientific waste management results in health hazards and urban environmental degradation. Onitsha serves as a center for the production and sale of local goods and services. It also provides a market for the sale of foreign goods and is reputed to host the largest market in sub-Saharan Africa which has greatly increased the pulse of commercial and industrial activities in the city in recent times (Ezeabasili *et al.,* 2014). In the study area, like many other developing cities, more metal-containing wastes are constantly being released into the environment as a result of industrial activities such as tire retreading, saw-milling, auto-servicing, printing and soft/alcoholic drink bottling and refuse incinerators (Adamu and Nganje, 2010). As a metropolitan city brimming with industrial and commercial activities, numerous dumpsites abound and all these may be having harmful

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effects on the environment. In other words, indiscriminate disposal of waste occasioned by development and expansion are having visibly negative footprints on the environment (Edet *et al.,* 2014). Soil being an important environmental medium, is unavoidably exposed to the negative impacts of urbanization. Besides acting as a medium for plant growth or waste disposal, the soil also serves as a transmitter of many pollutants to surface water, groundwater, atmosphere and food (Adamu and Nganje, 2010). The level of potentially harmful substances that gain access to the soil as a result of human activities is quite significant. The non-biodegradable nature and long-biological half-lives of toxic elements are the reasons for the extensive and grave nature of its contamination (Radha et al., 1997). The content and distribution of harmful heavy metals in soils is dependent on many factors including human activity, geology and weathering (Martinez 2003). Soil is the component of the natural environment in which most of these pollutants accumulate.

Since accumulation of heavy metals poses serious threats to human health and soil micro-organisms, it is therefore necessary to carry out an evaluation of the concentrations and distribution of heavy metals in soils within some selected dumpsites in Onitsha, Anambra Basin, Southeastern Nigeria.

1.1. Description of the study area

1.1.1. Location and Geology

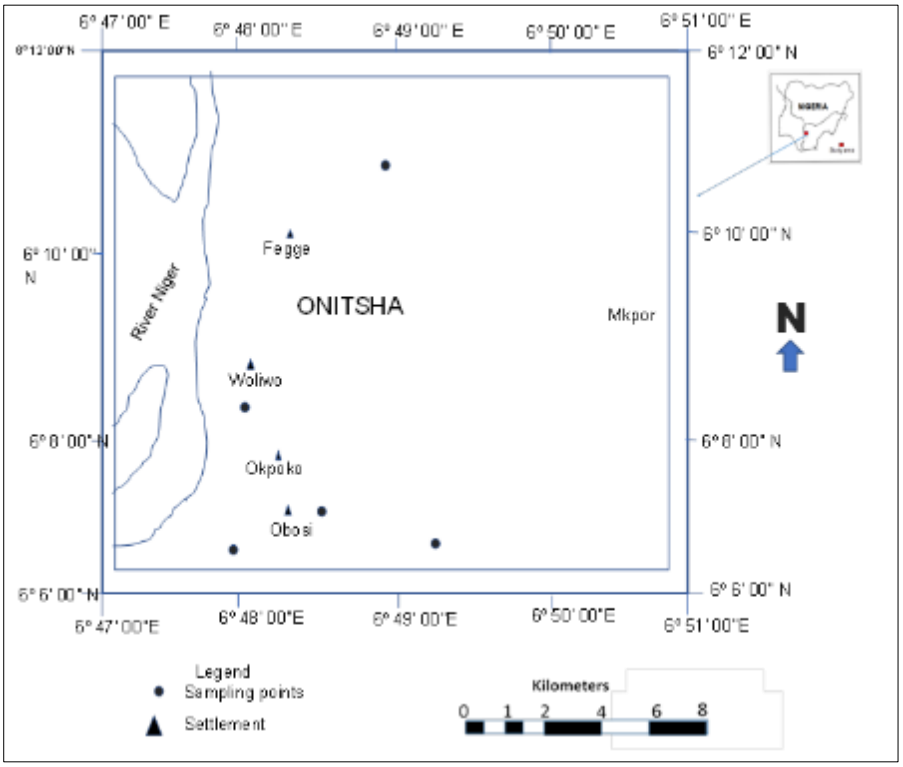

Figure 1 Location map of the study area showing some settlements and sample collection points (Drawn using Corel Draw)

The study area lies between Latitudes 6^0 05' 56" and 6^0 12' 02"N, and Longitudes 6^0 46' 0" and 6^0 52' 30" E (fig. 1). The main geologic units within the study area include Ameki Formation (Nanka Sand), Asaba-Ogwashi Formation and Benin Formation (Coastal Plain Sand) (figure 2). The Ameki Formation was classified by Simpson (1955) into two lithological groups viz: the lower part which consists of fine to coarse grain sandstones and intercalations of calcareous shales and thin shelly limestone and upper part which comprise coarse, cross-bedded sandstone with bands of fine, grey-green sandstone and fine – grained fossiliferous sandstone with thin limestone bands. The age of the formation has been considered to be either early Eocene (Reyment, 1965) or early middle Eocene (Adegoke, 1969). The depositional environment of the Ameki Formation has been interpreted based on the faunal content. Nwajide (1979) and Arua (1986) suggested environment that ranged from nearshore to intertidal and subtidal zones. The Ameki Formation underlies the Imo shale (Paleocene) which conformably overlies the Nsukka Formation (Reyment, 1965). The Ogwashi–Asaba Formation is also represented within the Palaeocene Anambra Basin (Oboh – Ikuenobe et al., 2005). This Formation, also called the Lignite "series", is characterized by widely differing lithologies comprising alternation of clays, sands, grits and lignites (Dessauvagie and Fayose, 1970; Whiteman, 1982; Parkinson, 1907). Reyment (1965)

recommended Oligocene–Miocene age for this formation. The Ogwashi–Asaba Formation is a surface lateral equivalent of the Agbada Formation which occurs in the subsurface of the Niger Delta (Short and Stauble, 1967; Assez, 1989; Akpoborie et al., 2011). The Benin Formation (Coastal Plain Sand) consists of alternating sequence of gravel, sand, clay and alluvium which are derived from the adjoining Precambrian basement and cretaceous rocks (Short and Stauble, 1967). The age is upper Miocene–Recent (Short and Stauble, 1967; Kogbe, 1976).

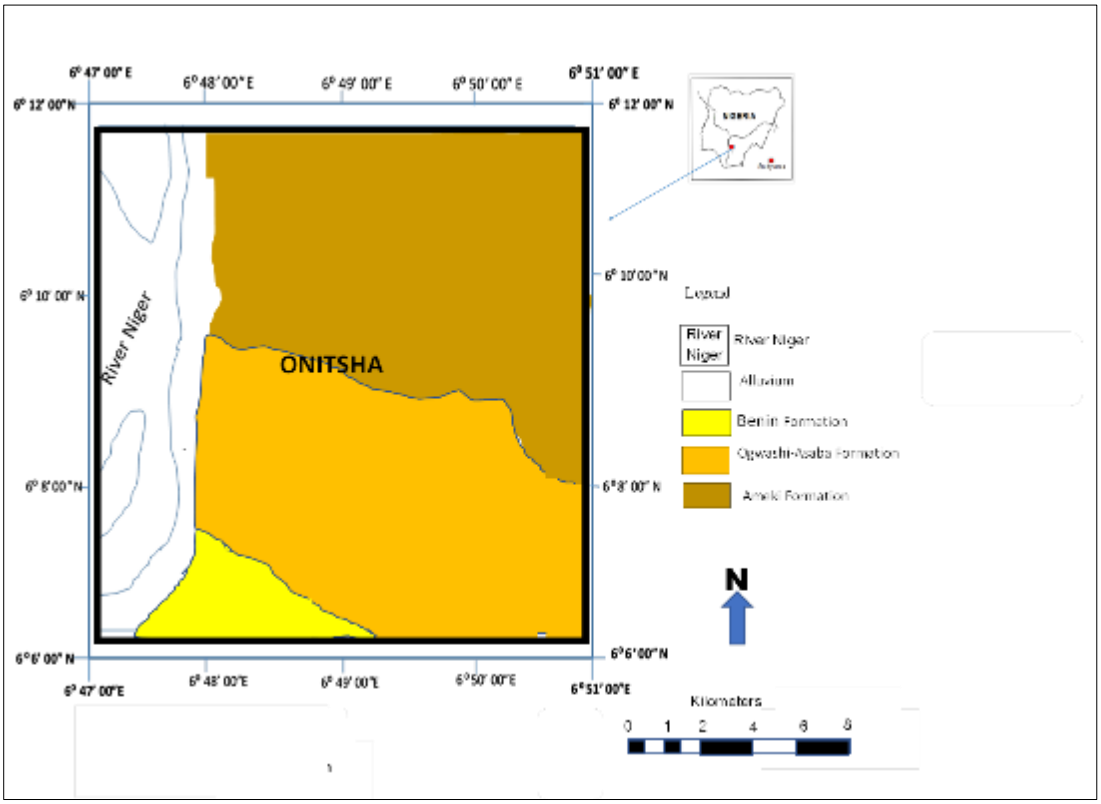

Figure 2 The geologic map of the study area

2. Review of literature

Urban soil geochemistry is of global concern due to its interest on issues that impact on the health of city dwellers. This has led to numerous studies, both local and international, in this field. Research by Sani et al. (2012) focused on the physico-chemical parameters of soil in some selected dumpsites in Zaria and its environs were assessed using standard field measurements and laboratory procedures. This was to assess the impact of these dumpsites on the soil quality within the study area. All the parameters considered in the research (pH, conductivity, moisture content, OM (%) and CEC) showed higher mean values in the dumpsites than in the control site.

Odigie et al. (2011) worked on the distribution of heavy metals in soils of Port Harcourt and its environs using standard field and laboratory methods. The geochemical analysis showed the vertical and horizontal distributions to be higher than the background values. The Igeo values for Pb, Cd, and As indicate low-level contamination while Zn and V show medium-level contamination. The sources of contamination were attributed to urbanized anthropogenic activities.

In a study by Nwankwoala and Ememu (2018) titled Contamination Indices and Heavy Metal Concentrations in Soils in Okpoko, Southeastern Nigeria, soil quality in Okpoko was assessed. All the assessed heavy metal concentrations were above the control sample levels. Assessment of anthropogenic influences on the soil quality in the area with the control site as the baseline was accomplished using soil quality models including Contamination Index (CI), Pollution Load Index (PLI), Modified Contamination Degree (mCD), Geo-accumulation Index (Igeo), and Nemelov Integrated Pollution Index (NIPI) which show that the soils are heavily polluted.

Karkarna and Matazu (2021) worked on the evaluation of heavy metals pollution around Kano municipal solid waste dumpsites, Kano State, Nigeria using single and integrated pollution indices. Forty-two soil samples were collected at a depth of 0 – 15cm (top soils) and 15-30cm (sub-surface soil) from seven municipal solid waste dumpsites of Kano

metropolis using circular plot method. The samples were analyzed with Flame atomic absorption spectrophotometer to determine the heavy metal concentration. The results indicated that concentrations of heavy metals of soil samples from dumpsites in Kano Metropolis were within limits of European Union (2002) standards. The results also revealed that the calculated CF and Er documented that investigated soil samples are uncontaminated with Zn, Pb, Cd, Cr and Pb and Ni. The pollution load index (PLI) was less than unity (<1) showing that there was minimum pollution in the studied dumpsite. The potential ecological risk showed that soil samples were in the class of low contaminated with the studied heavy metals.

Anzene, S. J. (2019) worked on the determination of Heavy metals in waste dumpsites in Lafia town and environs. In this study, ten (10) samples were obtained from the five different zones within Lafia town and environs using standard field and laboratory procedures (Atomic Absorption Spectrophotometer). The analysis revealed that the mean concentrations of Pb, Cd, Zn and Se exceeded their WHO/FAO guidelines and geochemical backgrounds reported in the literature. Pb and Zn were observed in all the sites, Cd and Se were detected in only 3 to 4 out of the 10 sites assessed. The concentrations of As, Cr, Fe, Cu, Mn Ni Ba, Co were within tolerable limits and therefore pose no risk. The study revealed that these metals originated from both natural and anthropogenic sources.

Agbaji et al. (2015) assessed the heavy metals level of soil in Kakuri industrial area of Kaduna, Nigeria using Mini Pal 4 version in PW 4030 X–ray spectrometer. The result was compared with the control soil sample and the environmental soil guidelines. It was revealed that the location was considerably polluted with heavy metals but below the intervention/alert level provided by the environmental protection agency (DPR, 2002). Soil pollution assessment by means of Cf and Igeo indices confirmed the soils are uncontaminated. The result also showed that heavy metal availability and distribution pattern varies with the nature of industrial activities and this was indicated by the wide range of concentration values observed in virtually all the heavy metals in the soils analyzed across the sample locations.

Fong et al. (2008) investigated the distribution and possible sources of heavy metals in urban soils within Kuala Terengganu town. The results revealed that Fe, Mn and Al originated from the parent materials while Cu, Cd, Pb and Zn were from anthropogenic input from vehicular traffic and metal corrosion. The result also suggested that Pb, Cd and Zn were found to be significantly enriched which supports anthropogenic origin. Similarly, a study was undertaken by Assah et al. (2005) to assess the heavy metal concentrations and distribution in surface soils of Bassa industrial zone 1, Douala, Cameroun. This was to assess the quality of surface soils in the area. It revealed that the area was highly polluted with Pb, Zn, Cu, Co, Sb and to a lesser extent with Ag, Cd, Fe, Mn, Mo and Ni. Chang and Broadbent (1981) worked on the adverse impact of heavy metals on soil microbial activities, biochemical processes and the decomposition of organic matter. The study found that high levels of some heavy metals (Cu, Zn) can be toxic to soil micro-organisms thereby killing and reducing soil microbial population. This would then reduce microbial induced reactions and the rate of biodegradation of soil organic matter which, in turn, results in the reduction of soil fertility of the affected area.

Xie et al. (2016) studied the effects of heavy metals pollution on soil microbial diversity and Bermudagrass genetic variation in Hunan Province, Central China. The sampling sites consisted of two separate field sites including polluted and un-polluted (control) sites. The concentration of some heavy metals (Cd, Pb, and Zn) in the soils and plants was analyzed by flame atomic absorption spectrophotometry (AAS, Z-5300). The result indicated that all the polluted soils (Liuyang, Zhuzhou, Xiangtan, and Yueyang) contained extremely high Pb and Cd concentrations, which were one to two orders of magnitude higher than those in un-polluted soils. Bermudagrass collected from the polluted sites contained a higher level of heavy metals (Cd and Pb) than those from the un-polluted sites.

Shehu-Alimi et al., (2020) assessed the Physicochemical and Heavy Metals Characteristics of Soil from three Major dumpsites in Ilorin Metropolis, North-Central Nigeria to assess the major contaminants in some municipal waste disposal sites and the prospective impact to the surrounding domestic water supply source as well as the impact on the health of the people in the city. This was carried out by studying various physico-chemical parameters of soil which were collected from three municipal dump locations namely; Ita-Amodu, Sawmill garage and Kuntu areas in Ilorin metropolis, Kwara State Nigeria. The geochemistry of the dumpsites was studied with respect to important parameters such as pH, electrical conductivity, temperature, sulphates, chlorides, nitrates, moisture content, organic matter and heavy metals having the following constituents present in its composition- Cadmium (Cd), Lead (Pb), Zinc (Zn), Iron (Fe), and Copper (Cu). The study revealed that the three different soils samples: “(A) Ita-Amodu”, “(B) Sawmill Garage”, and “(C) Kuntu”) have pH of 7.1, 7.2 and 6.8, respectively. Temperature of 24.2, 26.4, and 28.0oC, Organic matter compositions of 0.95%, 0.73%, and 1.14%. The Moisture contents were 3.93%, 2.89%, and 3.48% respectively. The chloride contents of the samples were found to be 31.76 mg/L, 48.98 mg/L, and 91.63 mg/L, while nitrates were found to be 0.10 mg/L, 0.06, mg/L and 0.23 mg/L, with sulphate values of 1.96 mg/L, 2.35 mg/L, and 2.14 mg/L. The conductivities were 1.79 µs/cm, 2.23µs/cm, and 1.15 µs/cm respectively. Heavy metal analysis from the waste soil were

found to contained copper (Cu) - 0.03 mg/L, 0.028 mg/L, and 0.031 mg/L, zinc (Zn) - 0.04, mg/L 0.009 mg/L, and 0.066 mg/L), cadmium (Cd) - 0.516 mg/L, 0.62, mg/L and 0.048 mg/L), Lead (Pb) - 0.063 mg/L, 0.07 mg/L, and 0.056 mg/L), and iron (Fe) - 0.518 mg/L, 0.62 mg/L, and 0.190 mg/L.

Ghrefat et al., (2021) worked on the assessment of heavy metal contamination in the soils of the Gulf of Aqaba (Northwestern Saudi Arabia): Integration of geochemical, remote sensing, GIS, and statistical data. Rock and soil sample geochemical analysis was conducted to investigate the extent and causes of soil contamination in the Gulf of Aqaba region in NW Saudi Arabia. The inductively coupled plasma mass spectrometry was used to determine the concentrations of Pb, Zn, Cu, Co, Cr, Mn, Fe, Hg, Mo, and Cd in 23 soil samples and 25 samples from granitic and Cenozoic marine sedimentary formations. The geochemical results have been integrated with remote sensing, GIS, and statistical analysis to assess the severity of soil pollution in the area. The concentrations of heavy metals (ppm) in the collected soil samples were as follows: Fe (2259.70), Mn (101.85), Zn (20.15), Pb (10.74), Cr (8.67), Cu (6.10), Co (1.35), Mo (0.69), Hg (0.30), and Cd (0.17). A significant variation in the mean metal concentrations was observed for the rock samples. The correlation analysis results showed that different degrees of positive and negative relationships exist among different metals in the area. Two factors (PC1 and PC2) were identified using the principal component analysis (PCA) and were responsible for about 60% of the total variance in the data. The studied metals were separated and classified into two factors based on their geochemical features and source. In contrast, the hierarchical cluster analysis grouped the identified metals into different groups based on the similarity of their characteristics. The principal component (PC2) applied to the Sentinel-2A image classified the land cover in the area into three classes: vegetation, barren rocks, and urban area. The enrichment factor shows a relatively higher percentage of enriched Mo; however, the indices of geo-accumulation and potential ecological risk generally reveal no substantial metallic contamination in the study area. The main sources of soil contamination with metals are rock-weathering processes and various agricultural works that are widely practiced in the area.

Umoh and Etim (2013) worked on the determination of heavy metal contents from dumpsites within Ikot Ekpene, Akwa Ibom State, South-South Nigeria Using standard methods and procedures. The study discovered that elemental composition of Pb, Fe, Cd, Zn and Cu in the top soil samples (0-15cm) from some selected dumpsites and 100m away from the dumpsites within Ikot Ekpene town in Akwa Ibom State, Nigeria, were measured and determined using Atomic Absorption Spectrophotometer. At dumpsites, the concentrations of lead, iron, cadmium, zinc and copper ranged from 9.466 to 18.83 mg/kg, 18.06 to 23.47 mg/kg, 0.10 to 0.42 mg/kg, 13.82 to 17.26 mg/kg and 6.68 to 11.04 mg/kg respectively, while at control sites (100m away from dumpsites) the concentrations ranged from 5.21-7.53 mg/kg, 8.24-11.72 mg/kg, 0.04-0.08 mg/kg, 6.32-8.15 mg/kg and 2.06-5.61 mg/kg respectively. The concentrations of metals in soils at the decomposed biodegradable wastes dumpsites were higher than those at the control sites. It was observed that the concentrations of these metals in some sampling points were below accepted limit while others were within the accepted limit. Thus, no marked deleterious effect on the soil resulting from excess amount of these metals was detected. Highlights on good maintenance and improvement in the quality of soil in this area was suggested.

Kuok and Zhu (2022) assessed the levels of heavy metals in the soil of illegal open dumpsites in Malaysia using standard field procedures and laboratory methods. The soil heavy metal concentrations were found to be as follows: Al (24.67-142.20 mg/kg), Cd (< 0.01-0.083 mg/kg), Cu (0.10-14.99 mg/kg), Fe (11.20-241.77 mg/kg), Mn (0.09-22.60 mg/kg), Ni (0.02- 0.77 mg/kg), and Zn (0.14-35.03 mg/kg). All the heavy metals have been detected at all the sampling points except that the Cd levels at some sampling points were below the detection limit. The levels of heavy metals varied spatially and temporally, though higher Cd, Cu, Fe, Mn, Ni, and Zn were detected consistently at two sampling points of the dumpsite receiving municipal waste. This could be linked to the electrical and electronic waste at the dumpsite. This study concluded that though the levels of heavy metals in the soil did not constitute soil contamination, however, it is important to control illegal dumping activities to reduce the associated health and safety concerns, such as infestation of vermin, fire, physical hazards, and odor.

3. Materials and methods

Field procedure: Prior to the actual sampling activities, a reconnaissance survey was undertaken in order to identify possible sampling points and assess background information, site conditions and historical data. The reconnaissance survey was also used to identify variable possible routes, assess the topography, geology and traffic volume as well as economic land use (commercial and industrial activities) patterns within the study area. The sampling points were selected based on the information gathered during this reconnaissance survey.

During sampling (two weeks after the reconnaissance), surface soil samples were collected at the depth of 0 - 60cm within the vicinity of five (5) major dumpsites within the city using soil auger from the locations shown in figure 1. One

soil sample was also collected from an undeveloped plot of land with minimal human activities at Awka to serve as control.

The instruments used for collecting the soil samples were a T- shaped manual soil auger, hand trowel and pre-labelled sampling bags. At each sampling location, the auger was decontaminated by cleaning the blades with white handkerchief soaked with methylated spirit and drilled into the soil in an anti-clockwise direction. When it penetrated the soil up to the pre-marked 60cm depth, it was brought out in a clockwise direction. The soil samples that stacked to the auger screw were collected using a decontaminated hand trowel before putting them separately into pre-labeled polyethylene bags. The control sample was collected at a similar depth in an undeveloped plot of land with a very low volume of traffic and no industrial activities at Awka and labelled as 'Control'. All the samples were preserved in an ice box to minimize degradation. The metal spades of the soil auger and the hand trowel were cleaned with methylated spirit in between sample collection points in order to eliminate cross-contamination. In total, six samples were taken in a big ice box to the laboratory for various analyses.

3.1. Laboratory Procedure: Sample Preparation, Digestion and Analysis

The collected soil samples were air-dried at room temperature for sixteen days to remove excess moisture. The soil samples were also disaggregated to facilitate quick drying. At the end of the drying period, the soil samples were crushed in a porcelain mortar with a pestle and thoroughly mixed (homogenized). The mortar and pestle were cleansed with methylated spirit using white handkerchief after crushing each sample to prevent cross contamination of samples.

The crushed soil samples were sieved through a 2.0mm sieve made of stainless steel in order to remove stones, pebbles and plant debris. Some portions of the individual sieved soil samples were further pulverized to a fine powder and passed through a 0.5mm sieve for analyzing organic carbon and total metal content. Mechanical analyses were made using serial sieves. The sieved samples were properly stored as sub- sample for the determination of various parameters. The digestion of soil samples was carried out by weighing approximately 2.0g of the soil sample into a crucible and heating it at a temperature of 5500C for 3hours to get rid of the organic portion of the sample before being removed and allowed to cool. After cooling, it was emptied into a 100ml beaker and 20ml of 20% H_2SO_4 was added, heated on a hating mantle and boiled vigorously for five minutes before being brought down and allowed to cool. It was made up to 50ml with distilled water before being filtered into a sample container for elemental analysis using Atomic adsorption spectrophotometer.

The prepared samples were analyzed for metal concentrations using Varian AA240 Atomic Absorption Spectrophotometer (AAS) at Springboard Research Laboratory, Udoka Housing Estate, Awka in Anambra State, Nigeria. Analysis for ten (10) metals namely: Lead (Pb), Copper (Cu), Zinc (Zn), Chromium (Cr), Nickel (Ni), Cobalt (Co), Molybdenium (Mo), Cadmium (Cd), Manganese (Mn) and Silicon (Si)) were carried out in the digested soil samples.

3.2. Particle size analysis

Approximately 50g of the sample was weighed into a 250ml beaker and 200ml of distilled water was added and the mixture was vigorously stirred and allowed to stand for 10mins for sedimentation to take place. At the end of the 10mins, the water was siphoned and the process was repeated four times to wash the sample before 25ml of 25% hexametaphosphate was added and the mixture was allowed to stand till the next day. On the next day, the mixture was siphoned through a 75mm sieve and the sieved particles and the sieved liquid was dried using an oven before being allowed to cool and the following calculations made:

$$\%\text{Silt} = \frac{\text{wt of beaker} + \text{dried residue}}{\text{Wt. of sample}} \times 100 \ldots\ldots\ldots (1)$$

$$\%\text{Silt} = \frac{(\text{wt of beaker} + \text{dried residue}) - \text{wt of empty beaker}}{\text{Wt. of sample}} \times 100 \ldots\ldots\ldots (2)$$

$$\%\text{Clay} = 100 - (\%\text{Silt} + \%\text{Sand}) \ldots\ldots\ldots (3)$$

3.3. Loss on Ignition (LOI)

The organic matter content (OM) of the soil samples was estimated from LOI. Approximately 2g of the sample was weighed into a crucible and dried in the oven at 1050C for 1hr before it was brought down and allowed to cool before the weight was recorded using an electric weighing balance. Then it was transferred into a muffle furnace and heated at 360°C for 3hrs. At the end of 3hrs, it was brought down and allowed to cool in a desiccator and the weight was recorded before the following calculations were made:

$$\text{LOI (\%)} = \frac{(\text{wt. at } 105^0\text{C}) - (\text{wt. at } 360^0\text{C})}{\text{wt. at } 105^0\text{C}} \text{X } 100 \quad \ldots\ldots\ldots\ldots (4)$$

3.4. Soil pH determination

Soil pH was determined using a PH meter with glass electrode. Approximately 1g of air-dried and sieved soil sample was measured into a beaker and 10ml of distilled water was added to it. The suspension was stirred continuously for 30mins and allowed to stand for about 1hour. The digital pH meter was plugged, switched on and calibrated with a known buffer solution (buffer 7). After calibration, the pH electrode was dipped into the beaker containing the suspension and the reading was taken once the digital display became stable. The electrode was rinsed with deionized water between samples.

Cation exchange capacity (CEC)

Approximately 1g of the sample was weighed into a 100ml beaker and 10ml of 1mol of potassium chloride (KCl) was added. The mixture was allowed to stand for 30mins before being filtered. The filtrate was analyzed for Mg, K, Ca and Na using AAS.

Then the concentration levels of these cations were converted from parts per million (ppm) to Cmol/kg using the following formulae:

$$\text{Mg(ppm)} \div 120 = \text{Mg (Cmol/kg)} \quad \ldots\ldots\ldots (6)$$

$$\text{K(ppm)} \div 390 = \text{K (Cmol/kg)} \quad \ldots\ldots\ldots\ldots (7)$$

$$\text{Ca(ppm)} \div 200 = \text{Ca (Cmol/kg)} \quad \ldots\ldots\ldots\ldots (8)$$

$$\text{Finally, the Cmol/kg results of Mg + K + Ca = CEC} \quad \ldots\ldots\ldots (9)$$

3.5. Quality control/assurance

As part of quality control/assurance, measures were taken to check for background contamination and to ensure reliability of data. Series of standard metal solutions in the optimum concentration range were prepared. The reference solutions were prepared daily by diluting the single stock element solutions with water containing 1.5ml concentrated nitric acid/litre. A calibration blank was prepared using all the reagents except for the metal stock solutions. Calibration curve for each metal was prepared by plotting the absorbance of standards versus their concentrations. Moreover, blank samples were analyzed after five samples. Duplicate analyses were performed on all samples using certified methods and the analytical results reported on a dry weight basis. Precision and accuracy of analyzed metals were checked against standard reference material for every heavy metal.

3.6. Statistical analysis of data

3.6.1. Microsoft Office Excel and SPSS Statistics were the statistical method of data used in this work

Microsoft Office Excel was used for statistical analysis (range, mean, standard deviation (SD) and coefficient of variation (CV)). Moreover, several pollution indices (EF, PLI and ERI) were calculated to determine the level of heavy metal contamination in soil samples from the facilities. SPSS Statistics was employed to estimate the extent of interrelation between the heavy metals. Descriptive statistics were employed to summarize the general trend in the data set and to identify main features of the parameters investigated. Bar Charts were used to analyze the concentrations of the physiochemical parameters and heavy metals in order to obtain and compare their pictorial representations. The respective concentrations were compared with various national and international guidelines so as to ascertain the quality status of soils within the study area. Moreover, several pollution indices were calculated to determine the level of heavy metal contamination in soil samples from the facilities.

3.6.2. Pollution Indices

The pollution indicators employed to evaluate the level of contamination in the soils within the study area include: enrichment factor (EF), Pollution Load Index (PLI) and Potential ecological risk index (Eri).

3.6.3. Enrichment Factor (EF)

The Enrichment Factor (EF) is applied in differentiating between metals that accumulate due to human activities from those that accumulate due to geogenic or natural processes. To evaluate the magnitude of contaminants in the environment, Enrichment Factors (EF) were computed relative to the abundance of species in source material to that found in the Earth's crust. Silicon (Si) is chosen as the element of normalization because natural sources vastly dominate its input. The following equation proposed by Simex and Helz (1981) was used:

$$EF = (C_M/C_{Si})\text{sample} / (C_M C_{Si})Background \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

Where, $(C_M/C_{Si})_{sample}$ is the ratio of concentration of measured heavy metal (C_M) to that of Si (C_{Si}) in the soil sample and $(C_M/C_{Si})_{Background}$ is the same reference ratio in the Earth. The five contamination categories recognized and interpreted as suggested by Birch (2003), adopted by Ololade (2014) and equally used in this research are as follows:

- EF < 1 indicates no enrichment,
- EF 1 < 3 indicates minor enrichment
- EF between 3 < 5 show moderate enrichment
- EF between 5 < 10 denotes moderately severe enrichment
- EF between 10 < 25 denotes severe enrichment
- EF between 25 < 50 denotes very severe enrichment
- EF ≥ 50 refers to extremely severe enrichment

3.7. Pollution Load Index (PLI)

The extent of pollution in the studied soils by heavy metals has been assessed with the aid of the pollution load index (PLI) proposed by Tomlinson et al. (1980).

PLI provides a simple, comparative means for assessing pollution status of an area.

The PLI is proposed as a standardized system for detecting pollution which permits a comparison of pollution levels between different sites and at different times.

The PLI for a single site is the nth root of n number multiplying the contamination factors (CF values) together:

$$\text{PLI} = (CF_1 CF_2 CF_3 \times \ldots CF_N)^{\frac{1}{N}} \ldots\ldots\ldots\ldots\ldots (12)$$

Where CF = contamination factor, n = number of metals at a given site

PLI value > 1 indicates pollution of the site while <1 implies that the site is unpolluted

3.8. Potential Ecological Risk Index (Eri)

The ecological risk index evaluates the toxicity of elements in sediments/soils (Hakanson, 1980; Xu et al., 2008). It is calculated as shown follows:

$$ER^i = TR^i \text{ X } C_f^i \ldots\ldots\ldots (13)$$

Where,

Tr = Toxicity coefficient of each metal

C_f^i [Contamination Factor] = Ci/Bi

[Where Ci = measured conc. of pollutants and Bi= level of geological background. The average compositions of the metals in the control sample were used as background values for the metals].

If Er is less than 40, it implies low contamination risk

If Er falls between 40 – 80, it implies moderate contamination risk

If Er falls between 80 –160, it implies considerable contamination risk

If Er falls between 160 – 320, it implies high

Standard values of Tr are Cd=30, Co=5, Cu=5, Ni=5, Pb=5, Cr=2, Zn=5 (Hakanson, 1980; Xu et al., 2008).

4. Results and Discussions

4.1. Physiochemical Parameters

The physiochemical parameters (table 2 and fig 3) show that the percentage sand fraction range between 46.24 – 54.93% with a mean±sd value of 51.27±3.76%. The silt fraction also has a mean±sd value of 21.62±1.51% and ranges from 19.38 - 23.48% while the clay fraction ranges from 21.59 – 31.38% with an average value of 27.10±4.25%. The control sample has 39.96% sand, 37.49% silt and 22.55% clay. The samples were found to be generally sandy loam in majority of the study areas. Due to the fact that soil texture plays a key role in mobility of metals in the soil, the sandy nature of the soil in the study area could aid the infiltration of contaminants. This could increase the pollution pathway for contaminants (Nwankwoala and Ememu, 2018). This also implies that the soil, being coarse-textured, will have low sorption capacity for ions (Osakwe, 2012) as well as low supply of nutrients and moisture unlike fine-textured soils that have sufficient water holding capacity, good aeration and high supply of nutrients. The mean±sd of soil pH in the dumpsites was 5.16±0.03 and range between 5.12 - 5.21. The control sample equally showed an acidic pH of 5.33. These data show that the surface soils from these facilities as well as the control site were strongly acidic. The optimum pH range for most agricultural soils is between 5.5 - 7.5 (Nwankwoala and Ememu, 2018). This was taken as the normal pH range for ordinary soils that support plant and microorganisms (Anegbe et al., 2016).

Table 1 Physiochemical parameters of the samples from the dumpsites

Site	%sand	%silt	%Clay	pH	CEC (Cmol/kg)	OM (%)
Control	39.96	37.49	22.55	5.33	0.56	11.73
DS 1	54.93	21.48	23.59	5.17	0.14	12.12
DS 2	49.13	21.39	29.48	5.12	0.15	12.71
DS 3	46.24	22.38	31.38	5.14	0.21	27.71
DS 4	51.14	19.38	29.48	5.14	0.17	10.71
DS 5	54.93	23.48	21.59	5.21	0.62	11.21
Min	46.24	19.38	21.59	5.12	0.14	10.71
Max	54.93	23.48	31.38	5.21	0.62	27.71
Mean	51.27	21.62	27.10	5.16	0.26	14.89
SD	3.76	1.51	4.25	0.04	0.20	7.21

In other words, a low pH (less than 5) is harmful to plant growth, not because of the acidity itself, but because of imbalances in nutrient levels. Phosphate is poorly available, and aluminum and/or manganese may be present in toxic concentrations. In the current study, the recorded pH values which were below 5.7 clearly shows that the soil samples were polluted. These values suggest that heavy metals availability for uptake by plants is high in the sample soils. Low pH values recorded from these sites could be as a result of the decomposition of organic matter that releases carbon (iv) oxide which reacts with water to form carbonic acid which eventually reduces soil pH (Osakwe and Okolie, 2015). It could also be attributed to the burning of wastes in the dumpsites. The organic matter content (%) of the samples

ranges from 10.71 – 27.71% with an average value of 14.89±7.2%. It was higher than 11.3% that is reported from the control sample. The occurrence of organic matter has a substantial effect on the mobility and bioavailability of heavy metals (Agbaji et al., 2015). It has also been stated that about 50% of the total heavy metals in organic rich soils are retained with organic substances (Smagunova et al., 2004) but these values across the locations does not give an indication of a high tendency of heavy metals availability and retention in the samples. The Cation Exchange Capacity (CEC) values of the samples range from 0.14 – 0.62 Cmol/kg with a mean±sd value of 0.26±0.2 Cmol/kg. The CEC of the control soil sample was 0.56 Cmol/kg which implies higher CEC level at the control site. The observed minor differences in values of CEC in the samples may be due to negligible differences in the amount of organic matter and clay in the samples. The decline in CEC of the studied soil samples over that of the control sample may be a reflection of nutrient depleting wastes (Ololade, 2014). It could also be due to displacement by toxic metals which are indirectly introduced to the soil system through indiscriminate disposal of wastes and other pollutants. The CEC of soil can regulate the mobility of metals in soils and increase as pH increases (Pam et. al., 2016).

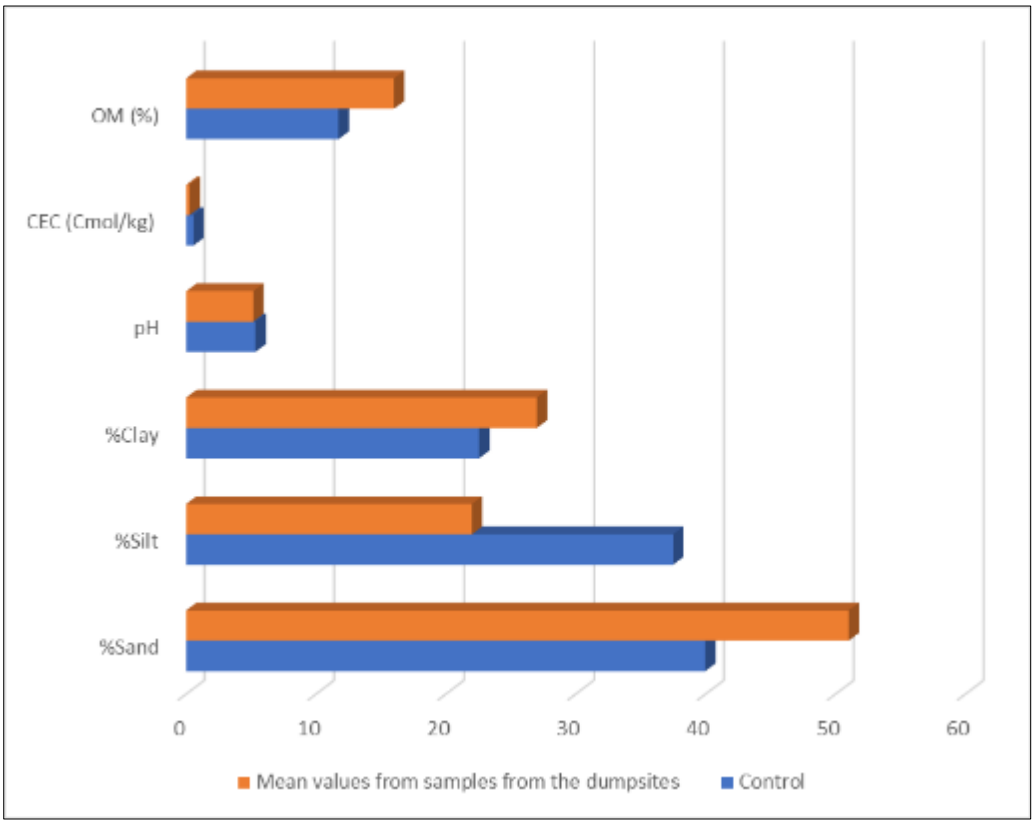

Figure 3 Pictorial comparison of the physiochemical parameters of dumpsite samples with that of the control (generated using Corel Draw)

4.2. Total heavy metal concentrations in the dumpsites

Atomic Absorption Spectrophotometer (AAS) analysis results for the collected samples show the presence of Pb, Cu, Zn, Cr, Ni, Co, Mo, Cd, Mn and Si in all the samples (Table 2) and discussed below. The pictorial comparison is also shown in figure 4.

Pb in the samples from the dumpsites has a mean±sd value of 4.368±2.04mg/kg and range from 0.86 – 6.06mg/kg. The average Pb concentration in the samples is above the control sample value of 0.4mg/ kg but below the general mean abundance values of 17 - 30mg/kg according to Rose, et al, (1979), 20 mg/kg value of average composition of Shales (Turekian & Wedepohl, 1961), the EPA (1995) Ecological Screening Value of 30.2 mg/kg and the Dutch Soil Quality Standard (MHSPE, 1994) target and intervention values of 85 and 530 mg/kg respectively. It is also below the critical level of 300 mg/kg stipulated by FAO/WHO (2002) and 85 mg/kg recommended by the DPR (2002). Coefficient of variation (CV) of heavy metals can suggest the interference degree of human activities to environmental media (Han et al., 2006; Zhang et al., 2007). In other words, environmental media that is strongly affected by human activities may produce a higher coefficient of variation. According to the classification of variation of heavy metals by Aweto (1982), low variation is CV≤ 20%; moderate variability is 20-50% while C.V. ≥ 50 % is considered high variability. Pb with a CV

value of 47% has a high variability rating in the dumpsites. This high variability rating is an indication of relatively enhanced and uniform external influence on this heavy metal and the likely homogeneity of its concentration in the dumpsites. Pb is closely associated with metropolitan waste disposal. Therefore, the level of Pb in the dumpsites could be attributed to the burning of different electronic wastes in the dumpsites. It could also be from atmospheric deposition derived from combustion of gasoline.

Cu has a range of 0.27 - 24.79 mg/kg with a mean±sd value of 11.49±10.69 mg/kg and highly variable (93%) in the studied surface soil samples. The high variability is an indication of a high external/anthropogenic influence on the availability of Cu in the samples. an indication of relatively uniform external influence on this heavy metal and the likely homogeneity of its concentration throughout the study area. The average Cu level is above the control value of 0.16 mg/kg but within the normal range of 5.00 - 20.00 mg/kg required for normal plant growth (Bowen, 1979). However, it's below the general mean abundance value of 20-50 (Rose, et al. 1979), average composition of Shales according to Turekian & Wedepohl, (1961) which is 45 mg/kg, 18.7 mg/kg stipulated by the EPA (1995), the Dutch Soil Quality Standard target and intervention values of 36 and 190 mg/kg respectively, and the permissible limit of 36 mg/kg set by FAO/WHO (1996) and DPR (2002). The solubility of Cu is governed by the pH and redox conditions (Iwegbue et al., 2013). In the pH range of 5.4 - 6.5, Cu is distinctly more soluble under oxidizing conditions than reducing conditions (Bhattacharya et al., 2002). Cu concentrations are increasing in the soil samples from the dumpsites when compared with the concentration in control sample and according to Chindah, et al., (2004), Cu is also closely associated with municipal wastes disposal. Possible sources of Cu within the dumpsites are from Cu pipes and wires in the dumpsites (Adegoke et al., 2009) and also past atmospheric deposition derived from combustion of gasoline.

Zn concentrations range from 4.53 - 59.82 mg/kg with mean±sd value of 24.0±20.95 mg/kg. The high variability rating (87%) is as a result of external influence. In the control sample, the concentration of Zn was 2.05 mg/kg.

The solubility of Zn is governed by the pH and redox conditions (Iwegbue, 2013). In the pH range of 5.4-6.5 as within the range recorded in this study, Zn is distinctly more soluble under oxidizing conditions than reducing conditions (Bhattacharya et al., 2002). Zn level is above the control sample level (2.05 mg/kg). It is below the stipulated range given by Rose et al., (1979) which is 36 – 100mg/kg as the general mean abundance. Also, it is below the target concentration value of 50 mg/kg and 140mg/kg set by WHO (1996) and DPR- EGASPIN (2002) respectively; 95 mg/kg value of average composition of Shales (Turekian & Wedepohl, 1961), the EPA (1995) Ecological Screening Value of 124 mg/kg and the Dutch Soil Quality Standard (MHSPE, 1994) values of 140 and 720 mg/kg for target and intervention values respectively. According to Chindah et al., (2004), Zn is also closely associated with municipal wastes disposal. The presence of Zn in the soil at the different dumpsites could be credited to the disposal of dry cells in the municipal waste, the burning of electronic waste materials containing alloys of brass and bronze, empty cans of fungicides, pigments and pesticides as well as the disposal of metallic objects containing galvanizing steel and iron in the dumpsites.

The levels of Cr observed in the dumpsites range from 2.5 – 18.95 mg/kg. The mean±sd is 6.73±6.58 mg/kg and the variability rating of 98%. This variability rating is an indication that human activities have a high input in the observed level of this heavy metal in the dumpsites. The recorded values are above the concentration of 0.25 mg/kg in the control sample but below the general mean abundance range of 40 - 50 mg/kg according to Rose et al., (1979); the EPA (1995) Ecological Screening Value of 52.3 mg/kg; average composition of Shales according to Turekian & Wedepohl (1961) which is 90 mg/kg; the Dutch Soil Quality Standard (MHSPE, 1994) target and intervention values of 100 and 380 mg/kg respectively, and the WHO (1996) permissible limit of 54 mg/kg. In spite of these, there is Cr enrichment in the dumpsites as indicated by the difference in the control value and the value recorded at the samples. The possible sources of Cr in the dumpsites include discarded metallic alloys, pigments and paints manufacture industries, used containers for fungicides, wastes from photographers, glass industries and wastes from leather tanning industries found within the study area.

Ni has a range of 0.81 – 12.12 mg/kg with a mean±sd value of 3.61±4.86 mg/kg. These values are above the background value of 0.66 mg/kg but below the Dutch Soil Quality Standard target and intervention values of 35 and 210 mg/kg respectively, the EPA (1995) Ecological Screening Values 15.9 mg/kg, the average composition of Shales according to Turekian & Wedepohl (1961) which is 68 mg/kg and the WHO/FAO (2001) permissible limit of 50 mg/kg for soils. There is profound Ni enrichment in the samples within the study area as shown by the coefficient of variability value of 135%. This indicates highly variable anthropogenic sources of Ni within the area under study. Ni enrichment could be from the nickel-containing wastes such as batteries, welding and electronic products (Amadi and Nwankwoala, 2013). Cd concentrations range from 1.11 - 2.12 mg/kg with mean±sd value of 0.716±0.84 mg/kg. Cd also has a high variability rating of 117% which is an indication of high external influence on the observed concentrations on the samples. The recorded average Cd level was lower than the permissible limit of 3 mg/kg (WHO/FAO, 2001) but above the global average in surface soil which is 0.53 (Jones and Jarvis, 1981), general mean abundance range of 0.1 - 0.5 mg/kg (Rose

et al., 1979) and the average composition of Shales according to Turekian & Wedepohl (1961) which is 0.3 mg/kg. The Cd level is below the EPA (1995) Ecological Screening Value of 1.00 mg/kg; WHO (1996) and DPR (2002) stipulated value of 0.8 mg/kg. It is also below the Dutch Soil Quality Standard (MHSPE, 1994) target value of 0.8 mg/kg and intervention value of 12 mg/kg.

Cd is used as an anticorrosive on steel. Cd sulfide is also commonly used as pigments in plastics, batteries and in various electronic components. When these are no longer usable, they are thrown into the dump as waste. During decomposition, the Cd component is leached into the surrounding soil and over time gets accumulated in the soil (Amadi and Nwankwoala, 2013).

Mn ranged from 9.62 - 31.114 mg/kg with an average value of 15.76± 483 mg/kg and a high variability rating of 3065%. The Mn concentration in the control sample was 9.62 mg/kg while the DPR (2002) stipulated a maximum value for Mn is 850 mg/kg for Mn in soil.

Si ranged from 7.55 – 16.35 mg/kg with an average value of 9.71±3.75 mg/kg and a high variability rating of 39%. According to Basile-Doelsch (2006), the second most abundant element in the crust is Si. The chemical weathering of silicate-bearing minerals is the ultimate source of dissolved Si which contributes to continental soil formation (Basile-Doelsch, 2006).

Co concentrations range from 0.2 – 9.75 mg/kg with a mean±sd value of 3.32±4.13 mg/kg and a variability rating of 124% which is an indication of highly variable anthropogenic sources. The measured concentrations of Co were higher than the control level of 0.06 mg/kg and the acceptable range of 3 mg/kg for uncontaminated soil (WHO/FAO, 2003). This signifies enrichment of Co in the dumpsites which could have resulted from different sources such as atmospheric deposition of cobalt-containing dust as well as from alloys for steels and electroplating-generated wastes disposed at the dumpsites (Chinda et al., 2004).

Mo has a range of 0.12 - 0.39 mg/kg with a mean±sd value of 0.25±0.1 mg/kg and high variability rating of 40%. The measured concentrations of Mo are higher than the control level of 0.015 mg/kg but below the acceptable range of 4 mg/kg for uncontaminated soil (WHO, 2003). This implies that there is enrichment of Mo in the dumpsites and this could have resulted from different sources including atmospheric deposition of Mo containing dust. Metal concentrations in the control sample were generally lower than what was detected in dumpsite soil samples by over one hundred orders of magnitude in some metals, which may be explained by the negative effects of waste burning activities at the dumpsites.

Table 2 Heavy metals concentrations (Mg/kg) across the dumpsites and the control

Facility	**Pb**	**Cu**	**Zn**	**Cr**	**Ni**	**Co**	**Mo**	**Cd**	**Mn**	**Si**
CONTROL	0.4	0.16	2.05	0.25	0.66	0.06	0.015	0.04	9.62	6.13
DS 1	5.23	13.21	19.18	4.66	3.19	0.36	0.21	0.12	14.04	7.55
DS 2	6.06	17.98	16.95	4.62	1.1	5.2	0.12	0.42	9.62	8.12
DS 3	4.47	1.02	19.5	3.5	0.82	1.1	0.27	0.81	13.59	8.88
DS 4	0.86	0.27	4.53	2.5	0.81	0.2	0.25	0.11	10.97	7.64
DS 5	5.22	24.79	59.82	18.39	12.12	9.75	0.39	2.12	30.58	16.35
Min	0.86	0.27	4.53	2.5	0.81	0.2	0.12	0.11	9.62	7.55
Max	6.06	24.79	59.82	18.39	12.12	9.75	0.39	2.12	10.97	16.35
Mean	4.37	11.45	23.99	6.73	3.61	3.32	0.25	0.72	15.79	9.71
SD	2.04	10.69	20.95	6.58	4.86	4.13	0.1	0.84	483.08	3.75
CV	47	93	87	98	135	124	40	117	3065	39

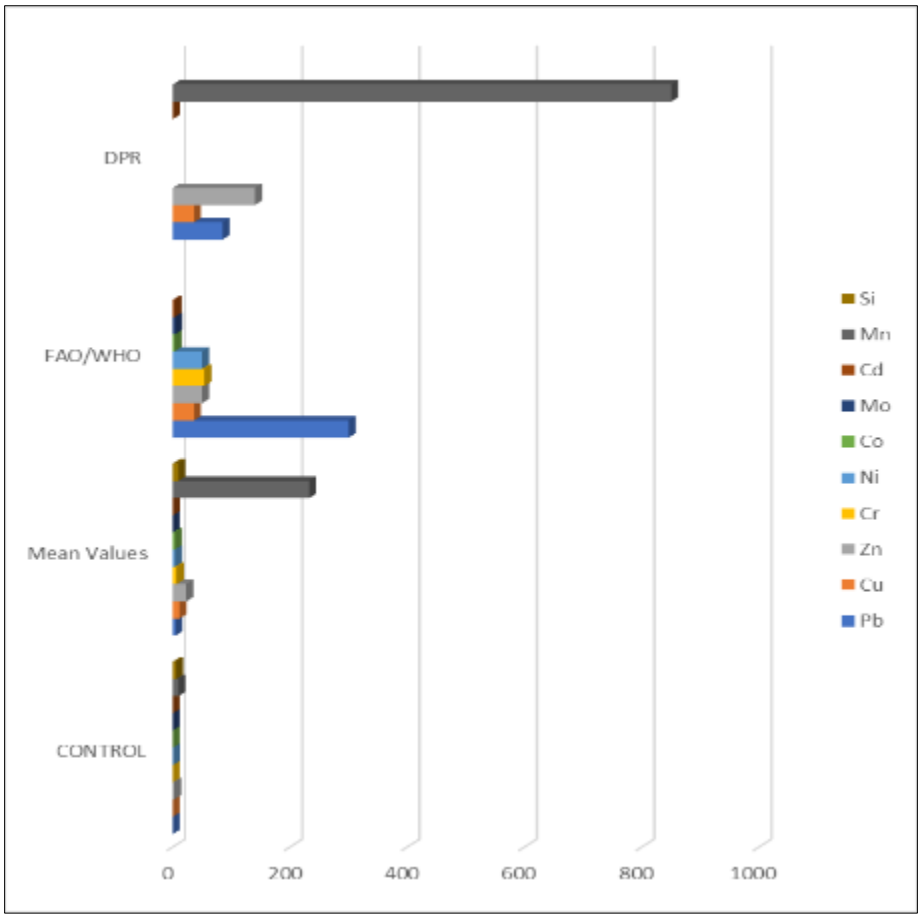

Figure 4 Comparison of heavy metals concentrations in the dumpsites with the control, WHO and DPR values (generated using Corel Draw)

4.3. Soil quality assessment

Quantitative appraisal of soil quality in the dumpsites were carried out by means of indices such as Enrichment Factor (EF), Pollution Load Index (PLI) and Potential Ecological Risk Index (PERI). They are discussed appropriately below.

Enrichment Factor

The calculated Enrichment Factors (EF) shown in Table 3 indicate that there is Pb enrichment in all the dumpsites. Pb enrichment was minor (<1) in DS 4 but moderate (3<5) in DS 5. It was moderately severe (5<10) in DS 3 but severe in DS 1 and DS 2. Cu enrichment was minor in DS 4, moderate in DS 3 but extremely severe in Ds 1, DS 2 and DS 5. On the other hand, Zn has a moderately severe enrichment in DS 1, DS 2 and DS 2 but severe enrichment in DS 5. The enrichment of Zn was minor in DS 4. There was no Cr enrichment (<1) in DS 4 but it was moderately severe in DS 3, severe in DS 1 and DS 2. Cr enrichment in DS 5 is very severe. Cd enrichment was minor in DS 1 and DS 4. It was moderately severe in DS 2 but severe in DS 3 and DS 5. There was no Ni enrichment in DS 3 and DS 4. Ni enrichment was minor in DS 2, moderate in DS 1 but moderately severe in DS 5. In the same vein, there was no enrichment of Co in DS 4 but it has a minor enrichment in DS 2, moderately severe enrichment in DS 1, severe enrichment in DS 3 and extremely severe in DS 5. Mo has a moderate enrichment in DS 3 but moderately severe enrichment in DS 1, DS 2, DS 4 and DS 5. There is no Mn enrichment in all the samples except in DS 1 and DS 5 where it was Minor.

4.3.1. Pollution Load Index (PLI)

The extent of pollution in the study area by heavy metals has been assessed with the aid of the pollution load index (PLI) as proposed by Tomlinson *et al*. (1980). The Pollution Load Indices (PLI) of the sites in this study is presented in Table 4. It shows that the PLI of the study area ranges from 4.3 – 26.18. This is an indication that the study area is polluted.

4.3.2. Ecological Risk Index (Er^i)

The results as shown in Table 5 indicate that the potential ecological risks of the heavy metals within the study area were mainly posed by Cd, Cu and Co. The Er^i contribution to the RIs of these heavy metals were 39%, 26% and 20% respectively, while the contributions of Pb, Zn, Cr and Ni were only 3.99, 4.28, 2.830, 3.94 and 2.0% respectively. Based on these calculations, the order of the single ratio of the tested heavy metals in the study area for the total potential ecological hazard is Ni<Cr<Zn<Pb<Co<Cu<Cd. This analysis also shows that in the study area, the Er^i of all the heavy metals range from low to high ecological risk.

4.3.3. Correlation Analysis of Soil Heavy Metals, pH and OM (%)

In this study, the raw data was used in calculating the correlation coefficient between the heavy metals, pH and OM (%) using the IBM SPSS as shown in table 6. The result of the analysis show that the heavy metals show both negative and positive relationships. Some of the heavy metals are significantly correlated with each other as well as the pH and organic matter (O.M). Pb shows a strong positive correlation (>+0.7) with Cu (+0.711) indicating that Pb and Cu have the same source(s) in the sample soils. These significant positive correlations between heavy metals imply that the sources of these metals are related to common anthropogenic rather than geogenic inputs. On the other hand, there is some observed weak positive correlations (<0.5) between Pb and Zn (0.481), Cr (0.356), Co (0.307), Cd (0.499), Si (0.34) and the organic matter content (0.271). These small positive correlation values signify that the presence of local high concentration for metal by possible contamination does not unavoidably show high values for other metals. Moreover, there is a strong negative correlation between Pb and pH (-0.962) and weak correlation between Pb and Mn (-0.166). Cu shows a strong positive correlation with Zn (+0.768), Cr (+0.779), Co (+0.754) and Cd (+0.854). Moderate positive correlations (0.5-0.7) exist between Cu and Si (0.603) and OM (0.662) indicating moderate anthropogenic influence. There is a strong negative correlation between cu and pH (-0.577). Zn has a strong positive correlation with Cr (+0.927), Cd (+0.897), Mn (+0.734), Si (+0.952) and OM (+0.966) but with a strong negative correlation with pH (-0.505). Cr shows a strong positive correlation with Co (+0.987), Cd (+0.897), Mn (+0.746), Si (+0.933), and OM (+0.980). Also, Zn has a strong negative correlation with pH (-0.345). Cr has a strong positive correlation with Co (+0.987), Cd (+0.897), Mn (+0.746), si (+0.933) and OM (+0.980). However, it has a strong negative correlation with pH (-0.345). Strong positive correlation was observed between Ni and Cd (-0.824), Ni and Mn (+0.775), Ni and Si (+0.885), Ni and OM (+0.955).

Table 3 Tabular presentation of the calculated EF of heavy metals in the dumpsites

Facility	Pb	Cu	Zn	Cr	Ni	Co	Mo	Cd	Mn	Si
DS 1	10.62	67.03	7.6	15.13	3.92	4.87	5.41	2.44	1.18	
DS 2	11.44	84.83	6.24	13.95	1.26	2.52	5.54	7.93	0.75	
DS 3	7.71	4.4	6.57	9.66	0.86	12.66	3.22	14.1	0.98	
DS 4	1.73	1.35	1.77	0.8	0.08	0.8	8.02	2.81	0.91	
DS 5	4.89	58.1	10.94	27.59	6.88	60.93	8.75	19.87	1.2	

Table 4 Tabular presentation of the PLI of the dumpsites

SITE	PLI	RATING
DS 1	7.27	Polluted
DS 2	9.16	Polluted
DS 3	6.62	Polluted
DS 4	4.3	Polluted
DS 5	26.18	Polluted

Ni and pH have a weak negative correlation (-0.306). Co has a strong positive correlation with Si (+0.865) and OM (+0.878) but a weak negative correlation with pH (-0.411). Mo shows strong positive correlation values of +0.796 with Si and +0.82 with OM. Cd shows a strong positive correlation (0.978) with OM and a weak negative correlation with pH

0.391 while Mn and OM also has a weak negative correlation (-0.293).Generally, the detected small positive correlation values between heavy metals show that the appearance of local high concentration for a particular metal by possible contamination does not automatically show high values for other metals while the negative correlations indicate that they have different source(s) of contamination in the environment.

Table 5 PERI of the different heavy metals across the dumpsites

	Pb	**Cu**	**Zn**	**Cr**	**Ni**	**Co**	**Mo**	**Cd**	**Mn**	**Si**
Tri	5	5	5	2	5	5		30	-	
DS 1	65.38	412.81	46.78	37.28	24.17	30.00	-	90.00	-	-
DS 2	75.75	561.88	41.34	36.96	8.33	433.33	-	315.00	-	-
DS 3	55.88	31.88	47.56	28.00	6.21	91.67	-	607.50	-	-
DS 4	10.75	8.44	11.05	20.00	6.14	16.67	-	82.50	-	-
DS 5	65.25	774.69	145.90	147.12	91.82	812.50	-	1590.00	-	-
Total	273.00	1789.69	292.63	269.36	136.67	1384.17	-	2685.00	-	-
%	4.00	26.20	4.28	3.94	2.00	20.26	-	39.31	-	-

Table 6 Correlation table of the heavy metals from the dumpsites

	Pb	**Cu**	**Zn**	**Cr**	**Ni**	**Co**	**Mo**	**Cd**	**Mn**	**Si**
Pb	1	-.183	.355	.215	-.494	-.728	.308	.464	.084	.096
Cu		1	-.576	.580	.202	-.005	.528	-.572	.205	.146
Zn			1	-.087	.392	-.242	-.355	.958*	.448	.361
Cr				1	.354	-.738	.911*	.115	.794	.828
Ni					1	.080	-.026	.348	.749	.653
Co						1	-.771	-.487	-.599	-.682
Mo							1	-.108	.511	.613
Cd								1	.576	.537
Mn									1	.976**
Si										1

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

4.3.4. Environmental implications

Anthropogenic input of these potential pollutants leads to severe soil contamination which poses serious health concern for human; harmfully affects plant vigor, animal health, microbial processes and overall soil health as summarized below. There is also the likelihood of surface and groundwater contamination. In human, the major pathways of exposure to these potential pollutants include ingestion, inhalation and dermal contact but the effects from all the pathways are the same.

Pb exposure causes mental retardation, high blood pressure, fertility problems in men, miscarriage in women, developmental delay and damage to nervous system in children (Oyeleke *et al.,* 2016). According to Needleman et al. (1990), exposure to Pb also impairs physical and mental development as well as elevate hearing threshold and reduces serum levels of vitamin D.

Cr is associated with allergic dermatitis in humans (Scragg, 2006). Exposure to Cr has also shown to cause mutagenic, carcinogenic and teratogenic effects on humans (Chokor, 2016). Zn exposure can result in gastrointestinal irritation and

interference of physiological processes. High level of Zn adversely affects plant health (Chokor, 2016). Extreme Zn intake in human aggravates Cu deficiency (Hurley and Keen, 1979). It can also interrupt microbial activity in soils, as it harmfully influences the activity of microorganisms and earthworms and as a result, retards the breakdown of organic matter.

Ni compounds that are released to the environment will adsorb on soil particles and become immobile as a result (Oyeleke *et al.,* 2016). However, in acidic soils such as the ones within the study area, Ni becomes more mobile and often leaches down to the groundwater (Chokor, 2016). Microorganisms can also suffer from growth decline owing to the presence of Ni. The most common harmful health effect of nickel in humans is an allergic reaction or skin rash (dermatitis or eczema). Nickel inhalation can also cause asthma attacks. Cd is another non-essential element for biota growth and development which is known to cause renal, prostate and ovarian cancers (Hartwig, 1998). Cd ingestion of any substantial amount also causes immediate poisoning, damage to the liver and the kidneys (Fasanya – Odewumi *et al.,* 1998) while ingestion in excess causes 'Itai – Itai', a disease that results in soft bones, shrinking body and death (Chorkor, 2016; Kazantzis, 2004) and hypertension (Adamu and Nganje, 2010). Mn is poisonous at high concentrations. The harmful effect in humans is always related with severe psychiatric disorder resembling schizophrenia, followed by permanently crippling neurological disorder clinically similar to Parkinson's disease (Klaassen, 2001; Chorkor, 2016). Mn has also been reported to impede synthesis of chlorophyll by obstructive Iron processes causing chlorosis and necrotic lesions on old leaves, dark brown or red necrotic spots and accretion of small particles of MnO_2 in epidermal cells of leaves or stems, drying leaf tips, and stunted roots (Clairmont *et al.,* 1986). On the other hand, exposure to high levels of Co results in lung and heart diseases and dermatitis (Olajide and Saeed, 2015).

Though Cu is a vital element, it may be injurious at high concentration. Cu restricts fatty acid and protein metabolism and inhibits respiration and nitrogen fixation process in plants (Chorkor, 2016; Konstantinidis *et al.,* 2003; Fernandez and Henrigues, 1991). Excessive dietary copper intake in mammals causes nausea, vomiting and diarrhea. It also causes pathological changes in brain tissue (Pizzarro *et al.,* 1999). Copper accumulates in the liver, kidney, cornea, and brain (Davis *et al.,* 2000). The accumulation of Cu in the brain leads to trauma and eventual death (Varela–Nallar *et al.,* 2006). A number of studies have investigated the toxicity of Mo following inhalation exposure. Decreases in lung function, dyspnea, and cough were reported in workers exposed to fine or ultrafine Mo dust.

Since several of the studied heavy metals are considered probable human carcinogens, therefore, the findings of this work should be a public health concern.

5. Conclusion

This research has been able to establish that surface soils within the area of study have been negatively impacted and degraded by these toxic elements which resulted from location of dumpsites in unapproved sites. In the developed world like the United States of America, the Environmental Protection Agency (EPA) identifies the most serious hazardous waste sites in the nation. These sites are then placed on the National Priorities List (NPL) and are targeted for long-term federal clean-up activities. Nigeria should adopt this method because these heavy metals are harmful not only to the residents but also to the flora and fauna and can also alter the ecology of the area. This study will help in no small measures to create awareness about the inherent dangers associated with non-scientific method of handling wastes and also complement other literatures/reference materials on urban soil geochemistry. It is recommended that sanitary landfills should be provided at different parts of the commercial city of Onitsha, Anambra State in the Southeastern part of Nigeria.

Compliance with ethical standards

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No conflict of interest to be disclosed.

Statement of informed consent

The authors have no competing interests to declare that are relevant to the content of this article

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