INAA AND EDXRF ANALYSIS OF SOIL INFILTRATION RATE DUE TO VERTICAL MIGRATION OF LEACHATE AT UNGUWAR DOSA DUMPSITES KADUNA NORTH.

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SEPTEMBER, 2015

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DECLARATION

I declare that the work in the thesis entitled 'INAA AND EDXRF study of soil infiltration rate due to vertical migration of leachate at unguwar dosa dumpsites Kaduna north has been performed by me in the Department of Physics under supervision of Dr. Sadiq Umar and Dr. Zakari Ibrahim Yusuf. The information derived from literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any institution or university.

.... **September, 2015**

Ahmed Mohammed **Date**

P13SCPY8040

CERTIFICATION

This thesis entitled ‘ INAA and EDXRF ANALYSIS OF SOIL INFILTRATION RATE DUE TO VERTICAL MIGRRATION OF LEACHATE AT UNGUWAR DOSA DUMPSITES KADUNA NORTH’ by Ahmed Mohammed meets the regulations governing the awards of the degree of Master of Science of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

Dr. Umar Sadiq Chairman, Supervisory Committee	………………………………. Sign	…………………………………… Date
Dr. I.Y. Zakari Member, Supervisory Committee	…………………………………. Sign	……………………………………. Date
Dr. Umar Sadiq Head of Department	…………………………………. Sign	………………………………… Date
Prof A. Z. Hassan Dean, Postgraduate School	………………………………….. Sign	………………………………… Date

DEDICATION

This research work is dedicated to my beloved family

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ABSTRACT

Indiscriminate disposal of solid wastes in unauthorized places has become an increasing problem for most communities and cities in Nigeria. The two solid waste disposal sites are potentially serious sources of pollution to environment because of failure of lining system, and are situated very close to residential houses and operated haphazardly. The high pollution potential of these dumpsites is due to the fact that they usually contain almost all the types of pollutants from the source community. The contaminants can leach out through the soil, contaminating the soil itself and groundwater. In this study, six soil samples from a hole each from the two dumpsites at different depths profiles of 0, 25, 50, 100, 120 and 150cm were collected and analyzed using EDXRF and INAA with the view to elucidate: the contaminants migration due to infiltration of leachate, investigate the dynamic and rate of soil infiltration in terms of contaminants concentrations across the soil profiles, in the contaminated soil around the dumpsites at Unguwar dosa in Kaduna north area of Kaduna state. The findings revealed presence, migration and fluctuation of concentrations values in the soil profiles from top surface to the depth of 150cm. It is hoped that further research will be conducted beyond the scope of this research to underscore risk of soil contamination effect to ground water using the same techniques.

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CHAPTER ONE

INTRODUCTION

1.1 Research Background

One of the most vital and persistent public health challenges facing communities in Nigeria today is the disposal of municipal solid wastes.

Solid waste as defined by United States Environmental protection Agency (USEPA) is any useless unwanted or discarded material with insufficient liquid content to be free flowing. The non-free flowing or sticky nature of the solid waste gives rise to the accumulation of solid wastes on some habitable parts of the earth (Okoyede and Rufai, 2011).

It is also unwanted materials such as garbage, paper, plastics, and other synthetic materials, metals and wood (Encarta dictionary, 2009).

Industrialization and population increment results in challenges in the composition and quantity of waste generated. This is one of the main causes of environmental pollution and degradation in many cities of the developing world (UNIDO, 2011).

Poor waste management poses several challenges to the well-being of the city residents, particularly those living adjacent to the dumpsites due to the potential of the waste to pollute water, food sources, land, air and vegetation (Hunachew and Sandip, 2011).

In order to understand the adverse effects of solid wastes disposal, it is important to study the types and the characteristics of solid wastes present in an area. Wastes can be generally classified into three major categories according to their origin sources: Domestic or municipal, commercial or industrial and medical wastes from hospital (Sheldon and Bruce, 1993).

Medical waste are wastes contaminated with blood and tissue, sharps (needles, scalpels, and glassware), outdated and unused drugs, testing laboratories dispose of chemical wastes, and significant amounts of radioactive isotopes for diagnosis and treatment (Encarta dictionary, 2009). While,

Industrial solid wastes are usually by-product or end-product of materials from large-scale production factories and industries (Amadi and Nwankwoala, 2010).

For the purpose of this study, the concern is on municipal solid waste (MSW) which refers to the stream of garbage collected through community sanitation services (Internet).

Kaduna municipal as a result of growth and urbanization is not an exception to this environmental problem because there are about 324 solid waste sites in Kaduna metropolis (Abdullahi, 2009).

According to United Nations Environmental programme (UNEP, 2002). 0.5kg of solid waste on the average is produced per person per day. Thus, based on the 2006 census, Kaduna North with the population of 357,694 (Federal Republic of Nigeria official gazette, volume 49, number 24: ppB189 is producing about 178.874 metric tons of municipal waste and refuse daily. The entire 324 waste disposal sites are the open dump type (Abdullahi, 2009).

Waste disposal whether domestic, commercial or industrial in the world, is a problem that continues to grow with human civilization and no method so far is completely safe. Experience has shown that all forms of waste disposal have negative effects on the environment, public health and local economics (Abdul-salam, 2009).

Domestic and industrial wastes contain various substances which include radioactive materials resulting from the use of processing chemicals. Also remnants from staple foods contain traces of radioactive materials or contaminants. The disposal of these wastes in dump without adequate management exposes the population to radiation hazard. This is because people that live around, do use waste for compost and build on waste dumpsites without considering the radiological implication (Odeyemi *et al.,* 2011).

Leachate is described as the water based solution of compounds from solid wastes dumped in a landfill (Adeola *et al.*, 2011).

The generation of leachate is caused by precipitation, percolation through waste deposited in a landfill. Once in contact with decomposing solid waste, the percolating water becomes contaminated and it then flows out of the waste material (Olarewaju *et al.,* 2012).

Abdullahi, (2010) is of the understanding that, after a long time, waste that decomposed, due to combination of physical, chemical and biological processes at the landfill will make the soil become polluted and may contain large amount of heavy metals.

Heavy metals are group of elements with a mass density greater than 4.5gcm^{-3}, which tend to release electron from chemical reactions and form simple cations. In solid and liquid states they are characterized by good heat and electrical conductivity, and are glossy and opaque. They have high melting and boiling points. They are malleable with usually mono atomic pairs. The metals classified as heavy metals include: Cu, Co, Cr, Cd, Fe, Zn, Pb, Sn, Hg, Mn, Ni, Mo, V, and W (Szyczewski *et al.,* 2009).

One of the most crucial properties of metals, which differentiate them from organic pollutants, is that they are not biodegradable in the environment. As a result, they tend to persist in the various reservoirs of natural systems such as water, soils and sediments or they accumulate in biological systems, leading to an important hazard to environment and human health (Kanmani and Gandhimathi, 2012).

The severe problems associated with these toxic heavy metals are the infiltration of leachate, generated when water penetrates through the waste in the landfill into the surrounding environment, subsequent contamination of land and ground water (Kumar *et al.*, 2002).

The potential threat to ground water posed by metals contamination from municipal solid waste cannot be adequately assessed without thorough knowledge of their elemental distribution in soil and an understanding of chemical solubility and dynamics of these elements in dumpsite environment (Michael and Sheldon, 2011).

The risk of groundwater contamination by any leachate that is not caught by collection system is determined by the following factors: Depth of groundwater table, the contaminants, and the direction of groundwater flow (Papconstantinou *et al.,* 2011).

Heavy metals are natural components of the environment including soil, but they are of great concern when they are being added continuously. Refuse dumping is one of the ways in which elements are being added into soil (Okoyede and Rufai, 2011).

Municipal solid waste combustion creates solid waste called ash, which can contain any of the elements that were originally present in the waste (Internet, 2013).

Mobility of metals is based on chemical processes, which include chemical interaction with the surface or near surface environments, and the capacity to migrate within fluids after dissolution. Commonly, the more labile interaction between metal mobility and thus, higher environmental impact as a result of the impact of solid waste dump sites on soil and public health, it has become necessary to investigate the subsurface contaminants level of soil around a municipal solid waste dumpsite. The influence of the soils properties over the relative distribution of heavy metals (Lacatusu *et al.*, 1998) is better observed in the soil profile (Kabala and Singh, 2001).

Therefore, the implementation of analytical techniques (INAA and EDXRF) suitable for the determination of contaminants composition and assessment of their dynamic and migration was outlined among the objectives of this research.

The dumpsites are situated in college road and Abdullahi Bello road all in Unguwar Dosa, Kaduna North Local Government Area of Kaduna State, North Western Nigeria.

This work basically study the rate of soil infiltration across the degraded soils profile with the objectives of determining the elemental composition of the soil samples obtained from the dumpsites in the study areas. The findings will serve as a guide for the inhabitants of the dumpsites, and public in general.

1.2 Statement of the problem

i the dumpsites have been under the challenges of natural, anthropogenic and poor waste management and

ii industrial activities of the study areas with Kaduna north population of 357,694 (Abdullah, 2009) are challenges to the composition and quantity of waste generated hence,

iii the soils around the two dumpsites are polluted with chemicals due to environmentally unacceptable disposal of solid waste or failure of lining system on the two dumpsites. This can cause adverse impacts on the environment and to public health.

1.3 Justification for the Research.

i Abdullahi (2009) application of geo-physical techniques on investigation of groundwater in the same study sites shows the occurrence of fewer contaminants perhaps due to limitation of the techniques and that, the average rate of migration of leachate in vertical direction was 0.79m/month, but did not report on variation of contaminants concentration across depth interval in other to understand how soil filters the contaminants down the profiles however.,

ii Since contaminant affect the environmental qualities in and around such open dumpsites, investigating rate of soil infiltration of contaminants especially heavy metal content in dumpsite become necessary because:

iii Municipal solid waste dumpsites in the two study areas are situated within the residential houses.

iv The dumpsites are open type without lining system to prevent leachate from polluting and degrading the surface soil.

v Contaminants from the leachate can migrate through the soils profile to the home wells and boreholes thereby polluting the water and affect it quality.

vi The dumpsites are potential source of radioactive elements and dangerous gases to the soils and atmosphere.

vii The manner in which disposal sites are receiving solid waste on daily basis will continue to add heavy metals and potential toxic elements into the soils thereby raising the concentration above permissible or tolerable level.

There is therefore the need to investigate the type of metallic contaminants, their concentration across the soil profile and rate of soil infiltration on these contaminants in other to enlighten the public especially household of the residential houses around the dumpsites on the risk involved in its use of underground water close to the dumpsites and the soil itself.

1.4 *Scope of the Study*

The study involve total elemental analysis using instrumental neutron activation analysis and energy dispersive X-ray fluorescence spectrometer to investigate vertical migration of contaminants and impact of soil on contaminants concentration across the soil profile. For this study, six soil samples will be taken from a hole on each dumpsite at O, 25, 50, 100, 120 and 150cm depth interval.

1.5 *Aim and Objectives*

The research aimed at using INAA and EDXRF techniques to study rate of soil infiltration due to vertical migration of leachate across the soils profile in order to provide baseline data for continuing studies of metal soil leachability, with the following objectives in mind:

i to determine metals composition and distribution in contaminated soils.,

ii identify heavy metals amongst these metals composition.,

iii identifies the contaminants with least and highest concentrations at the top surface.,

iv investigate the group of contaminants with high concentrations and contaminant with the highest mean concentration in the two dumpsites.,

v the dynamic of these contaminants in terms of their concentrations in the soil profiles and

vi investigate the trend of these contaminants concentrations down the soils profiles.

1.6 *Study area*

1.61 *Location of the study areas*

The study areas are located at college road with co-ordinate 10^{o} 30''N and 07^{o} 25"E, both at Unguwar Dosa, Kaduna North local government area of Kaduna State in North Western Nigeria. The two solid waste dumpsites are the typical uncontrolled open solid waste facilities that have been in use for the past 25years. The dumpsites consist of heterogeneous refuse. The college road dumpsite is located within the extreme Eastern part of the Sardauna memorial college while the Abdullahi Bello dumpsites is within the residential areas that linked unguwar dosa to Kawo. Both dumpsites are accessible by a good network of roads.

1.62 *Climate and Vegetation*

The study area has a typical savannah climate with distinct wet and dry seasons. The rainy season which extend from March/April to October/November and a dry season between December and March, average annual rainfall for Kaduna is 1,272mm. Rainfall generally reaches a peak in August. Temperatures vary between less than $15^{o}C$ around December /January and $32^{0}C$ in March/April. Vegetation consists of broad leaved savannah woodland which, when well developed, may attain heights of about 15m, and may be dense enough to suppress the growth of grasses. Elsewhere the land is open to the cultivation of vegetables and other food crops as well as for grazing by animals. The topography of the study area is characterized by peneplains and extensive laterite table lands. The peneplains, which are flat footed erosion remnants are often capped by layers of indurate laterite. Generally, the landscape in the survey area is relatively flat with gentle slopes (Abdullahi, 2009).

1.63 Geomorphology

The main factors that affect the availability of surface water in Kaduna area are rainfall, temperature, evapo-transpiration, run off and seepage. The relief of the area ranges between 370 and 650m. The drainage system of Kaduna is dominated by numerous tributaries to River Kaduna. The major ones include Rafin-Guza (which is in the study area), Rigasa, Romi and Rido. The duration of flow in these streams depend on a number of factors which include: size of collecting area, the permeability of the regolith, the size of the flood plain and the gradient of land surface. These drain off into the Kaduna – Niger drainage system (Abdullahi, 2009).

CHARPTER TWO

LITERATURE REVIEW

2.1 Previous related work

Numerous reports exist in the literature on soil contamination caused by landfill (open dump) with insufficient leachate collection system and with no measures to prevent leachate from entering the soil. Soil pollution due to solid waste can be classified into Municipal, Domestic, medical waste and industrial waste (Sheldon and Bruce, 1993). For the purpose of this study, the review will focus on municipal waste comprises of all stream garbage's as a result of community sanitation and industrial waste due to by product as a result of manufacturing and mining. One of the main negative effects of solid waste from either municipal or industrial is the production and infiltration of leachate, generated when water penetrates through the waste in the dumpsite into the surrounding environment subsequently contamination of the soil and possible groundwater way.

The leachate from municipal solid waste contains high concentrations of many heavy metals such as lead, cadmium, mercury, antimony, zinc and silver. Another area of great concern is the disposal of industrial solid waste. This differ from municipal solid waste in that there are generally fewer different kinds of heavy metals, but the amount and concentrations may be orders of magnitude higher. This is particularly true for mineral based industries. Landfills and water ways are the usual recipients of industrial waste. The potential threat to soil and ground water posed by these metals is real and long-term studies of the chemical composition, elemental distribution, and leaching characteristics are essential (Sheldon and Bruce, 1993).

In these studies, EDXRF and INAA are two analytic techniques used in this soil contamination studies. However, there are scarcities of literature in the research area especially with the use of INAA and EDXRF techniques on municipal solid waste.

Instrumental neutron activation analysis was performed on water sample from a municipal solid waste disposal site in 1986 and 1987 respectively. In 1986 the average Cu values rose from 0.045mg/L to 0.13mg/L, Pb from 0.055mg/L to 0.19mg/L, Zn from 0.020mg/L to 0.24mg/L, and Fe from 0.36mg/L to 12.2mg/L. The Cadmium levels were below the detection limit of 0.02mg/L (Joachim, 1988).

Chaubey *et al.,* (2011) elemental analysis of alluvial soil samples using NAA techniques in Blue Nile basin, east gojjam Ethiopia has lead to successful determination of seventeen elements in the alluvial soil sample around research area. The result gave values of (5.5 ± 0.6ppm for Mn-56); (52.5 ± 0.3ppm for Na-24); (939.5 ± 0.3ppm for Al-28; (21.5 ± 0.6ppm for W-187); 196.5 ± 0.4ppm for Cu-64); (7.5 ± 0.8ppm for As-76); (42180 ± 0.4ppm for Xe-135); (1497.5± 0.9ppm for Ru-105); (31593.5 ± 0.5ppm for Cd-177); (770.5 ± 0.4ppm for Yb-177); (4585 ± 0.4ppm for Re-188); (l ± 0.4ppm for Ir-194); (0.06 ± 0ppm for Eu-152) and (187.5 ± 0.3ppm for Ba).

Latif *et al.,* (2004) uses instrumental neutron activation analysis for the determination of As-content in water, soil and herbal plants and Cr-content in soil of tannery industrial areas. For Cr-determination, thirty soil samples were collected at several depths of different locations from both Hazaribagh tannery area and the Tatuljhura proposed tannery area. The concentration of chromium in soil of Hagaribah tannery area, Bangladesh was determined using prompt gamma ray analysis (PGA) technique. Cr-content was found 1.45%, where 1.53% was obtained in same sample by INAA.

In Hagaribagh, the Cr-content in the range from 880 to 33550ppm was found in surface soils and it was 71-90ppm for Tatuljhura.

For Hajaribugh, the Cr-concentration decreases with the increasing of depth up to 180cm. The Cr-concentration of Tatuljhora was in the range of 50.87 to 93.63ppm, which is below the permissible level reported worldwide. The arsenic concentration in soil of Sonargam varied from 2.06 to 11.35ppm. The detection limit of As in soil is 0.91ppm. The normal level of arsenic in soil for Bangladesh is less than 3ppm, where as 5ppm arsenic containing soil can be considered toxic to sensitive crops.

Two complementary analytical techniques, epithermal (ENAA) and atomic absorption spectrometry (ASS) with flame and graphite furnace atomization were used to determine heavy metal pollution of surface soil in Thrace Region Turkey. Thirty five elements were determined. Concentrations of As, Cd, Co, Cu, Mn, Ni, Pb and Zn were determined using AAS and GFAAS, and ENAA was used for the remaining 27 elements. Results for As, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, I, In, K, Ln, Mo, Ma, Nd, Ni, Nb, Pb, Rb, Sc, Sm, Sr, Sa, Tb, Th, Ti, T, U, V and Zn are reported for the first time soils from this region. The results show that concentrations of most elements were little affected by the industrial and other anthropogenic activities performed in region. Except for distinctly higher levels of Pb, Cu, Cd and Zn in Istanbul district than median values for the Thrace region (Mahmut *et al.*, 2006).

Antoaneta *et al.,* (2011) used EDXRF and INAA techniques to determined the soil composition and pollution with heavy metals and trace elements, in the vicinity of iron and steel integrated works at Galati, Romania and to compare the elemental concentrations with the maximum values admitted by the Romanian legislation.

Soil cores representing every borough of East St Louis were analyzed using NAA and XRF for heavy metals: As, Cd, Cu, Cr, Hg, Ni, Pb, Sb, Sn, and Zn. The topsoil contained heavy metal concentrations as high as 12.5ppm Cd, 14,400ppm Cu, 1860ppm Pb, 40ppm Sb, 1130 ppm Sn, and 10,360 ppm Zn. Concentrations of Sb, Cu, and Cd were well correlated with Zn concentrations suggesting a similar primary industrial source. In a sandy loam soil from a vacated rail deport near the bank of the Mississippi River, the metals were evenly distributed down to a 38cm depth. The clay soils within a half-mile downwind of the Zn smelter and Cu products company contained elevated Cd (81ppm), Cu (340 ppm), Pb (700 ppm), and Zn (600 ppm) and displayed a systematic drop in concentration of these metals with depth (Michael and Singh, 2011).

However, leachate characterization and assessment of unsaturated zone pollution near municipal solid waste landfill at Oblogo, Accra-Ghana was investigated. The level of heavy metals of interest Cadmium, copper, chromium, iron, manganese, arsenic and zinc were measured using INAA. Cr (0.23 and 0.05mg/l), Cu (13.78 and 8.97 mg/l), Cd (0.14 and 0.20

mg/L), Mn (2.32 and 1.86mg/L), As (0.10 and 0.27mg/L) and V (2.25 and 0.99mg/L), were present in the leachate samples (Dzifa *et al.*, 2012).

Heavy metals concentration in urban soils of Fallujah city, Iraq was carried out. Twenty soil samples were collected in order to determine concentrations, spatial distribution and contamination assessment of heavy metals. The main concentrations are as follows: 235.77µg/g for Fe, 24.09µg/g for Mn, 11.59µg/g for Cr, 8.96µg/g for Ni, 5.50µg/g for Zn, 3.82µg/g for Pb, 3.43µg/g for Co, 2.01µg/g for Cu and 0.64µg/g for Cd. The mean concentration of Cu, Zn, Ni, Pb, Ni, Fe, Mn, Co and Cr did not exceed and Cd exceeds the USEPA guideline. The metal contamination in the soils was evaluated by applying EF, PLI, IPLI and GeoI. Based on EF, the urban soils in Fallujah city are extremely high enriched with Cd and Co, very high enriched with Ni and Cr and Pb, Cu and Zn exhibit significant enrichment. To IPLI values, urban soils in Fallujah are lowly polluted with heavy metals. According to GeoI, the urban soils in Falluja city are uncontaminated to slightly contaminate by Cd (Emad *et al.,* 2013).

2.2 Theory of Analytical Techniques and Solid waste Contaminants

2.2.1 *Neutron Activation Analysis (NAA)*

Neutron activation analysis was discovered in 1936 when Hevsy and Levi found that samples containing certain earth elements become highly radioactive after exposure to a source of neutrons. NAA is a very powerful analytical technique for identifying many elements present in samples of unknown composition performing both quantitative and qualitative multi-element analysis of major, minor and trace elements in samples (Chaubey *et al.,* 2011).

An isotope of atomic mass A and atomic number Z when placed in a neutron flux will, in general, absorb a neutron to become the isotope (A+1, Z). Some resulting isotopes, being unstable, will decay, emitting one or more gamma-rays with energies and half-life characteristic of the particular isotope. During irradiation the naturally occurring stable isotopes of most elements that constitute alluvial samples are transformed into radioactive isotope by neutron capture. The number of radionuclide produced in activation of a natural isotope is given by the expression:

$$N_{(A+1)} = \frac{\phi \sigma_{aA} N_{oA}}{\lambda_{(A+1)}} \left(1 - e^{-\lambda_{(A+1)} T}\right) e^{-\lambda_{(A+1)} t}$$

and the activity is $\frac{dN_{(A+1)}}{dt}$ where:

ϕ : is the neutron flux

σ_{aA} : is the neutron absorption cross-section of the original isotope

N_{oA} : is the number of nuclei of element under consideration of isotope A

$\lambda_{(A+1)}$: is the decay constant of the created isotope

T : is the irradiation time and,

t : is the time between stop of the activity and start of the counting of the activity.

The basic essentials required to carry out an analysis of soil samples by neutron activation analysis are a source of neutrons, HPGE gamma ray spectrometer coupled with MCA and printer (Chaubey *et al.*, 2011).

In the last three decades, neutron activation analysis has been found to be extremely useful in the determination of trace and minor elements in many disciplines; this includes environmental analysis application and geographical mapping, nutritional and health related studies, geological as well as material sciences. The technique is based on nuclear reaction whereby elemental content is determined by irradiating the subject sample with neutron from neutron source, creating radioactive forms of the desired element in the sample. As the sample becomes radioactive from interaction of the neutron particle source and nuclei of the element's atom, radioisotopes are formed that subsequently decay, emitting gamma ray unique in half-life and energy. This distinct energy signature provide positive identification of targeted element (S) present in the sample, while quantification is active by measuring the intensity of the emitted gamma rays that are directly proportional to the concentration of the respective element (S) in the Sample (Jatau, 2012).

Although there are several types of neutron source (reactors, accelerators, radioisotopes neutron emitters) one can use for NAA, nuclear reactors with their high fluxes of neutrons from uranium fission offer the highest available sensitivity for most element. In practice, the activities induced in an element at a time T after irradiation for time t, is given by the equation:

$$A_t = \frac{W\varepsilon\theta N_A \sigma\phi}{A} f_r\left(1-e^{-\lambda t}\right)e^{-\lambda t} \qquad \text{(IAEA, 90)}$$

$$m = A\left(ke^{-\lambda t_d}\left(1-e^{-\lambda t_I}\right)\left(1-e^{-\lambda t_c}\right)\right)^{-1}$$

$$k = z\theta N_A \sigma\varphi M^I / \lambda$$

(IAEA-TECDOC-1215, 2001)

Where A_t = measured activity in count per second (CPS)

$W = M^I$ = weight of the irradiated element in grams

ε = z = efficiency of the detector

θ = abundance of the activated nuclide

σ = isotopic activation cross section in barns (I barns = $10^{-24}cm^2$)

m = mass of particular element

ϕ = neutron flux in n/cm^{2}s

λ = decay probability

N_A= Avogadro's constant

A = atomic weight of the irradiated element

f_r = branching ratio for the x-ray of interest

t_I, t_d and t_c are time of irradiation, decay and counting respectively

NAA can generally be classified based on the neutron energy distribution, or based on the elemental detection processes involved.

2.2.2 *Thermal Neutron Activation Analysis (TNAA)*

The thermal neutron component consists of low energy neutron (energies below 0.5eV) in thermal equilibrium with atoms in the reactors moderator. In most reactors, irradiation positions, 90-95% of the neutrons that bombard a sample are thermal neutrons. In general, a one megawatt reactor has a peak thermal neutron flux of approximately 10^{13} neutrons per square centimeter per second. Thermal neutrons induce (n, gamma) reactions on target nuclei (IAEA, 1990). An NAA technique that employs only thermal neutrons to induce (n, gamma) reactions by irradiating the samples is called thermal neutron activation analysis (TNAA).

2.2.3 *Instrumental Neutron Activation Analysis (INAA)*

Is the most common form of NAA offered and utilized for individual for multi-elemental analysis (Jatau, 2012). INAA is often referred to as non-destructive NAA or as NAA without post-irradiation radiochemical separation. It is a multi-elemental method whereby γ-ray spectroscopy is applied to radioactivity measurements. INAA promises reliable analytical results, because the possible error due to contamination and element lost can be easily avoided. INAA is capable of analyzing relatively large samples varying from a several grams to several kilograms (IAEA, 1998).

INAA involve exposing the sample to a field of neutrons. This exposure causes most of the element within the sample to become radioactive. The energy of the radioactive emission allows identification of the element and intensity of the emission is proportional to the mass of that element. In INAA relative method, a known amount of sample containing unknown amount of element and known amount of standard containing a known amount of element are irradiated under same irradiation condition. For long and medium half- life irradiation, the samples and the standard are irradiated together while; short half-life irradiation, the samples and the standard are irradiated differently under same condition (Glascock, 2005). The equation used to calculate the mass of an element in the unknown sample relative to the standard is:

$$\frac{A_{sam}}{A_{std}} = \frac{m_{sam}}{m_{std}} \frac{(e^{-\lambda T_d})_{sam}}{(e^{-\lambda T_d})_{std}}$$

Where A = activity of the sample (sam) and standard (std)

m = mass of the element

λ = decay constant for the isotope and T_d = decay time

When performing short irradiation, the irradiation, decay and counting time are normally fixed the same for all samples and standard such that the time dependent factor cancels. Thus, the above equation simplifies into:

$$C_{sam} = \frac{W_{std} A_{sam}}{W_{sam} A_{std}}$$

Where C = concentration of the element and W = weight of the sample and standard.

Samples requiring short irradiation time (< 20 minutes) are expose to neutrons moderate flux densities ($< 10^{12}$ ncm^{-2} S^{-1}), and package in a virgin polyethylene vials. While samples requiring large irradiation time (hours or days), with moderate to high flux densities, are package in high purity quartz vials (Jatau, 2012).

2.2.4 *Radiochemical Neutron Activation Analysis (RNAA)*

RNAA involves a post irradiation radiochemical separation produced to isolate one or a group of element, or to eliminate interfering nuclides. Application of career and hold back career makes chemical separation much more convenient. The chemical yield can be calculated from re-determination of the added career when it is stable isotope. When the career is a radioactive one, chemical yield can be obtained directly from the sample gamma ray (IAEA, 1998).

2.2.5 *Epithermal Neutron Activation Analysis (ENAA)*

The epithermal neutron component consist of neutron (energies from 0.5eV to about 0.5MeV) which have been only partially moderated (Jatau, 2012). In ENAA, a sample is irradiated in an epithermal neutron flux by covering it with Cadmium foil or put it in a borated capsule. Some reactors provide epithermal irradiation facilities by having the irradiation position suitable surrounded by such materials. Q_o is defined as the resonance to thermal cross-section ratio. ENAA is mainly used to determine a high Q_o nuclide (s) when a low Q_o nuclide (s) is the interference. When irradiated in an epithermal neutron flux, a high Q_o nuclide like ^{114}Cd (n, γ)^{115}Cd (Q_o = 39.6) will be more activated than a low Q_o nuclide like $^{23}Na(n,\gamma)^{24}Na$ ($Q_o = 0.59$) if compared to the activation in 'normal' NAA. Consequently, a lower detection limit for Cd determination can be expected (IAEA, 1998).

2.2.6 *Prompt Gama-ray Neutron Activation Analysis (PGNAA)*

In PGNAA, the prompt γ-ray emitted during the nuclear reaction are measured. It is a non-destructive and multi-elemental method (Lindstrom *et'al.,* 1993 and Molnar *et'al.,* (1997). PGNAA may provide elemental contents and depth profiling for elements H, B, C, N, P, S Cd and some rare earth elements, especially Sm and Gd. Most of these elements either cannot, or cannot easily be determined with normal NAA, so PGNAA is a complementary method. To carry out PGNAA, a neutron beam guide and a γ-ray detector assembly are needed (IAEA, 1988).

2.2.7 *Cyclic Neutron Activation Analysis (CNAA)*

This is most frequently used in short half-life NAA. In this method, a sample is repeatedly activated, and the γ-ray spectra after each irradiation are summed (Spyrou *et al.,* 1981). The repetition can continue till the accumulated activity from long lived nuclides is too high. Cyclic NAA is used to improve the counting statistics of the peak-area of short-lived nuclides. To avoid the accumulation of the longer lived nuclide activity, this cyclic activation can be performed using a series of fresh samples: pseudo-cyclic NAA (De Silva *et al.,* 1983).

2.3 *Technical Description of NIRR-1*

The Nigerian Research Reactor-1 was installed and commissioned at the centre for energy research and training (CERT) Ahmadu Bello University Zaria in 2003. It is a miniature Neutron source reactor core, beryllium reflector, small fission chambers for detecting neutron fluxes, one central control rod and its drive mechanism, and thermocouples for measuring inlet and outlet temperatures of the coolant. There are four inner irradiation tubes connected within the beryllium annulus, two outer irradiation tubes are also connected outside the beryllium annulus. The core consists of fuel elements arranged in a fuel cage. The fuel elements are all enriched uranium-aluminum alloy extraction clad with aluminum. The beryllium annulus and lower orifice, which controls water flow through the core. The top plate of the core and annulus are spaced to form the upper orifice (Jatau, 2012).

The total number of lattice positions is 350 and the number of fuel elements is 347 and the remaining positions are filled with dummy aluminum elements. The reactor is designed to have a self-limiting power excursion characteristic. A fail-safe principle is adopted in the design of the reactor controls system. Central rod is used for regulating the power level, compensating for shutting down the reactor. The drive mechanism of control rod is mounted on the top plate of the reactor vessel. This control console consist of the reactor control system, the radiation monitoring system readouts, a monitoring panel of auxiliary system and power supply system of the console (FSAR, 2005).

There are two control modes for the reactor. In the first mode start up or shutdown of the reactor is controlled manually by the operator, in second mode; the reactor is controlled in an automatic mode. The measurement of the temperature difference between core outlet and inlet is accomplished with two alumel-chromel thermocouples. One is located at the outside of the side beryllium annulus near the core inlet orifice to measure the inlet temperature. The other one is located at the upper part of the side beryllium annulus near the core outlet temperature. Combined, these two pairs of thermocouples can monitor the temperature difference of the reactor coolant (FSAR, 2005).

The reactor core is cooled by natural convection. This was based on physics and thermal hydraulic designs calculations carried out to determine the maximum operating temperature of the fuel and the maximum temperature of cladding. The size of the upper and the lower orifices were determined to ensure efficient cooling of the core and enhance safety of the system (FSAR, 2005).

2.4 *X-ray Fluorescence Technique*

X-ray fluorescence (XRF) is a non-destructive analytical method for determining the chemical composition of all kinds of materials. The elements and their detection levels mainly depend on the spectrometer system used. Generally speaking, elements with high atomic numbers have better detection limits than lighter elements (Jatau, 2012).

2.4.1 *The X-ray Fluorescence Spectrometer*

The basic concept for all spectrometer is a source, a sample and a detection system. The source irradiates a sample. The spectrometer system can be divided into two main groups: energy dispersive system (EDXRF) and wavelength dispersive system (WDXRF).

The energy dispersive X-ray spectroscopy (EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variant of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interaction between electromagnetic radiation and matter, analyzing X-ray emitted by the matter in response to being hit with charged particle. Its characterization capabilities are due in large part of the fundamental principle that each element has a unique atomic structure allowing X-ray that are characteristic of an element's atomic structure to be identify uniquely from one another (Peter, 2006).

To stimulate the emission of characteristic X-ray from a specimen, high energy beam of charged particles such as electrons or protons, or a beam of X-ray, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy level or electron shell bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher energy shell then fills the hole, and the difference in energy between the higher- energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-ray emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, thus allows the elemental composition of the specimen to be measured (Peter, 2006).

The WDXRF spectrometer used an analyzing crystal (gas fill detector and scintillation detector) to disperse the difference energies. All radiation coming from the sample falls into the crystal. The crystal diffracts the difference energies in different direction, similar to a prism that disperses different colors in different direction.

2.5 *Heavy Metals as Pollutant from Solid waste*

Heavy metals from solid waste are artificial component of the soil profile. They cannot be degraded or destroyed. To a small extent, they enter our bodies via food, drinking water and air. Heavy metals are dangerous because they tend to bio-accumulate (killic, 2009).

The term heavy metals refer to any metallic element that has a relative high density and is toxic or poisonous even at low concentration (Lenntech, 2004).

Heavy metals is a general collective term, which applies to the group of metals and metalloids with atomic density greater than $4gcm^{-3}$ or 5 times or more, greater than water (Garbarino *et al.,* 1995 and Hawkes, 1997). However, being a heavy metal has little to do with density, but concerns chemical properties. Heavy metals include lead (Pb), cadmium (Cd), zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Copper (Cu), Iron (Fe), and the platinum group elements. Many of these metals enter the environment and remain environmental problem due to pollution properties. Most of these environmental pollutants also occur naturally through natural weathering processes e.t.c, however, published reports also indicate that solid waste release metals (Girigisu, 2011).

CHARPTER THREE

3.1 MATERIALS AND METHODS

The most suitable source of neutrons for NAA is a research reactor. This work has been carried out in the reactor engineering section of the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria. The equipment and materials used include:

- The Nigerian Research Reactor-1 (NIRR-1)
- High purity Germanium (HPGE) detector
- Winspan analytical software
- Liquid nitrogen
- Analytical balance
- Electrical oven
- Vials forces distilled water and Nitric acid.

Detailed description of the functions and use of the above materials during the research are stated in next section of this chapter.

3.2 *Sampling*

Soil sampling procedure involves the use of digger, hoe, shovel, packer, tape rule, or a standard meter rule, data recording sheet and indelible ink marker.

The first stage was to clear the refuse on surface of soil locations were sampling is to take place, until degraded soil surface was visible. These instruments were used in each of the stages to a depth of interest on the soil.

Six soil samples were collected from a hole each from the two dumpsites at different depths of 0, 25, 50, 100, 120 and 150cm respectively.

Each soil sample with the help of a packer was emptied into a black polyethylene-sampling bag, tied and labeled with a marker on a paper each inserted in the bag. The bags were double-bagged to reduce chances of cross contamination of samples. These are made to dry by direct exposure to sunlight and then taken to analytical laboratory for preparation and analysis.

3.3 *Samples preparation*

The preparation of samples was the first steps of the activation analysis and experiment, and it is extremely important to the obtaining reliable analytic results. In order to ensure the quality of analysis, the analyst should generally perform the treatment of the sample personally or at least have an overall understanding of the sample.

Conventional samples in NIRR-1 laboratory are generally classified into three categories: Biological, Geological and Environmental sample. Environmental samples are the class which the sample for this study belong and the class consists of basically soil samples. Polythene sheet are first cut from a large polythene sheet into bags of about 3cm x 4cm size and the bags sealed on three sides. The bags together with vials are washed in distilled water three times. If samples are in solid or rock form, they are crushed into powder using a mortar and agate to make them homogenous as shown bellow. Each crushed and /or grinded homogenous sample was then sub divided into two for INAA and EDXRF analyses. Therefore, in each site there was a total of twelve samples, in site A six samples for INAA was labeled: A1, A2, A3, A4, A5,A6 and the second six samples for EDXRF labeled: A11, A22, A33, A44, A55 and A66. In site B, samples for INAA were labeled: B1, B2, B3, B4, B5, B6 and samples for EDXRF labeled: B11, B22, B33, B44, B55 and B66.

Plate 3.1: Analytical weighing balance

Plate 3.2: Mortar and Agate

3.3.1 *Weighing*

An analytical weighting balance was used to measure the quantity of sample packaged for irradiation. The quantity used varies due to the activity of the material. The weighing balance was adjusted with the indicator at the middle. This was done to eliminate errors due to non stability of the balance. A polythene bag was picked using forceps and weighed. During weighing, the spatula and forceps used were cleaned using acetone (highly volatile liquid); hand gloves are changed after every measurement to avoid contamination. It is important to observe some safety precaution during sample preparation which includes avoiding physical contact with the sample.

3.3.2 *Packaging*

Using HNO_3 solution capsules, polythene films were soaked for three days in order to remove all impurities. It was washed with deionized water, after that it was dried in the oven at 60 degrees (temperature). Gloves were used in order to minimize the contamination of sample during preparation. The samples were then packaged and carefully placed inside the capsule vial using the forceps. Cotton wool was added on top before sealing with a cello tape (this is to avoid loss of samples in the irradiation channel).

For short lived irradiation, each vial contains only one sample, but for long multiple number of samples were packaged (since the maximum temperature inside the irradiation channel or sites does not exceed 50 degrees, the capsule and spacers were made-up of high density polythene materials having radiation resistance properties.

Plate 3.3: Sample and capsule vial ready for packaging

3.4 *Sample irradiation*

This is the exposure of the sample to nuclear radiation (fission reaction), when samples were bombarded with neutrons they get excited and release its characteristics (i.e. it emits gamma rays).

3.4.1 *Irradiation procedure*

Samples package in the vials were sent to the reactor irradiation sites using the rabbit system (pneumatic transfer system) after the time and the neutron flux has been determine by theoretical expression based on estimated activity of the sample. The reactor has four irradiation sites namely: $B_{1,}$ $B_{2,}$ B_3, and B_2 and B_3 are the inner irradiation sites and B_4 is the outer irradiation site. B_1 is not connected to any site.

To determine the total elemental content of a given sample two protocol were used (short and long lived). An arrangement of element with short life were determined using the short live protocol, the sample was sent to channel B_4 for either 1 minutes or 5 minutes depending on the nature and activity of the sample, while channel B_2 and B_3 are for long lived irradiation. The half- life and energy are use to determine the protocol used that is either short or long.

The rabbit system uses compressed air that is supplied by the air compressor. The sample moving to and from the irradiation site was done using the rabbit console as shown in the flow chart below

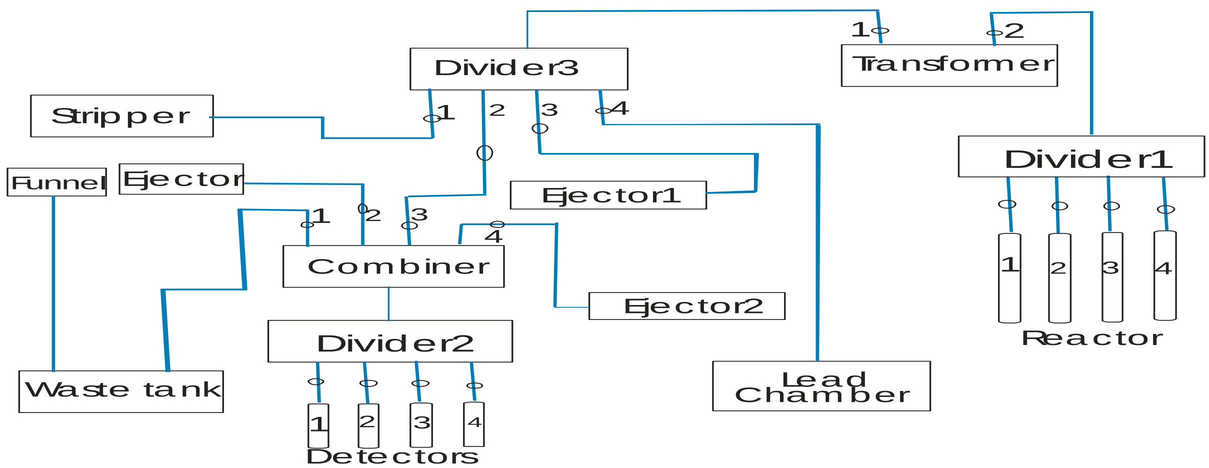

Figure 3.1: Rabbit system flow chat

3.5 *Counting and Analysis*

A high resolution gamma spectrometer was used to detect the delayed gamma rays. This is called counting. The instrument used to measure gamma rays from radioactive samples generally consists of a semi-conductor, associated electronics and a computer based multi channel analyzer (MCA computer). Most NAA laboratories operate one or more hyper pure or intrinsic germanium (HPGE) detectors which operate at liquid nitrogen temperature (77 degree Kelvin) by mounting the germanium crystal in vacuum connected to copper rod or cold finger. Gamma rays hit the detector and cause ionization of electron and holes. The detector keeps the gamma rays in different channels, using M.C.A., which sorts out gamma rays according to the energy. The detector resolution is a measure of its ability to separate closely spaced peaks in a spectrum. There are four counting regimes with two different geometries as shown below.

Table 3.1: **NIRR-1 DETECTOR COUNTING REGIMES AND GEOMETRY**

	TIME (COUNT)	SAMPLE HOLDER	IRRADIATION
First	600 seconds	Geometry H2	1 or
Short			5 minutes
Second	600 seconds	H1	1or 5 minutes
Short			
First long	1,800 seconds	H1	6 hours
Second	3,600 seconds	H1	6 hours
Long			

When samples were retrieved from the irradiation sites (i.e. for short) the gamma dose were measured to ensure it was within the safe limit for one to handle. For short lived, if the dose is around 40 μ Sv/hr the vial is open and sample placed on the detector for first count as shown in the table using the H2 (15cm) geometry, the second count however was done 3 hours after the first count. The long lived irradiation last for 6 hours after retrieving the sample. It was allowed to decay for 4 days when the measured dose was around 10 μ Sv/hr and counting the H1 (2cm) geometry. 14 days after irradiation the second counts for the samples were done using the same geometry but different time.

The measurement by gamma ray spectrometers is the determination of the number and energy of the photons emitted by the source. The peak location and the peak area in the spectra have to be determined. The peak location is a measure of the gamma energy, while the peak area is proportional to the photon emission rate. For the energy measurement the pulse height scale must be calibrated with standard reference materials of known energies and concentrations. The spectrum are saved and analyzed to generate the result using WINSPAN software.

3.6 *Sample preparation procedure for X-ray Fluorescence*

The sampling methods were employed as in 3.4 above, Small sample was analyzed, the sample was representative of the entire material, and was taken very carefully. Solid materials require only a minimum sample preparation. In many cases cleaning and polishing is sufficient. The samples for analysis were grounded using agate mortar and binder (PVC dissolved in toluene) was added to the samples, carefully mixed and pressed in a hydraulic press in pellets. The pellets were loaded in the sample chamber of the spectrometer (Jatau, 2012).

The EDXRF spectrometer used in this work was available at the X-ray Fluorescence Laboratory at the King Fahd Abdul-Aziz hospital lead poisoning centre of excellence in Gusau - Zamfara State. Manufactured march, 2013 with serial number: 502002 and model type: OS-4000. It is a portable isotopic hand held energy dispersive X-ray spectrometer for field analysis designed also for elemental analysis of a wide range of soil samples. The Innov-X Systems XRF Analyzer is powered by a replaceable Lithium Ion smart Battery. The batteries were charged an external battery charger. Batteries typically function for 4 to 8 hours, depending on usage patterns. Since the machine is multi functional, the calibration model consists of a list of elements to be analyzed, group of measured standards with assays, and calibration curves created from the standards.

3.6.1 *The procedure for creating a calibration model and running unknown standards consists of three main steps.*

1 Measured standards and enter assays.

2 Create calibration curves for each element using stored standard information.

3 Load model and analyze unknowns.

3.6.2 *Standardization procedure*

Before performing tests, it is necessary to standardize the instrument. This automated procedure involves collecting a spectrum on a known standard (Alloy 316) and comparing a variety of parameters to values stored when the instrument was calibrated at the factory.

The standardization procedure takes about 1minute. Standardization must be done any time the analyzer hardware is initiated or restarted and must be repeated if the instrument is operating for more than 4 hours. It is possible to re-standardize the instrument at any point while the soft is running. Standardization is always initiated from the Analysis screen of any Mode (Innov-X system manual, 2007).

3.7 *Qualitative and Quantitative Analysis of EDXRF*

Qualitative analyses determine which elements are present and their net intensities from the measured spectra. The quantitative analysis require net intensities (the background must be subtracted from the spectrum) to calculate the concentration of the elements present. In qualitative analysis peak search and peak match are used to find which elements are present in a sample. Peak search uses mathematical technique to find in a spectrum. Peak match determines the elements to which the peak profiles belong. This is done by comparing the position of the peaks to a database holding the positions of all the possible lines (Peter, 2006). In a situation where the peak profile overlaps, de-convolution is used to determine the area of the individual profiles (the measured spectrum is fitted to theoretical profiles). Mathematically it is formulated as finding the heights $height_p$ and $width_p$ of all the peaks profiles described by a function,

$$P_c = \sum_{\rho=1}^{energies} (R_e^m - B_e - \sum_{p=1}^{profiles} p_e(height_p, width_p))^2$$

R_e^m = is the measured intensity energy e,

B_e = is background at energy e.

In Quantitative analysis, the net intensities are converted into concentrations. The usual procedure is to calibrate the spectrometer by measuring one or more reference materials. The intensities of the elements with unknown concentration are measured, with the corresponding concentration being determined from the calibration (Peter, 2006).

Across a limited range, the intensity R, of an analytical line is linearly proportional to the concentration C, of the analyte.

$$C = D + E * R$$

Where, D and E are determined by linear regression.

However, the intensity of the analytical lines does only depend on the concentration of the originating element. It also depends on the presence and concentrations of other elements. These other elements can lead to attenuation or enhancement effects. Matrix correction model will be used to correct the absorption and enhancement effects of the other elements.

$$\mathrm{C}_i = D_i + E_i * R_i \left[1 + \sum_{j=1, j \neq e}^{n} \alpha_j * c_j \right]$$

They $\alpha^{`s}$ are numerical value that indicates how much element j attenuates or enhances the intensity of the analyte (Peter, 2006).

CHARPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULT

The field work was done during the dry season in order to obtain maximal contaminants concentration from the polluted soils around the dumpsites. Yahaya (2009) as cited by Amadi and Nwankwola,(2013) confirmed that the concentration of contaminants in soil is higher in dry season than in rainy season because more contaminants are lost in the soil due to run-off and infiltration in rainy season which are absent in dry season. Metal contamination and soil leaching varies across the soils profiles due to soil type, geology, PH e.t.c (Krishna and Govil, 2007) and their concentrations decreases across soil depths (Michael and Singh, 2011 and Latif *et al.*, 2004). However, in this present work metals are heterogeneously and evenly distributed in the soils and their concentrations fluctuate from top soil to depth of 150cm. This is evident that leaching of contaminants from top surface to the depth of 150cm has actually taken place. INAA has lead to a successful determination of twenty nine elements each from the two sites (site A and site B) as shown in table 4.1 and 4.2 respectively, while EDXRF has detected twelve similar elements on each site and additional four elements on site B also shown in tables 4.3 and 4.4 respectively.

Table 4.1: The analytical results of instrumental neutron activation analysis of six Geological samples in **site A** are presented below

ELEMENT	A1	A2	A3	A4	A5	A6	MEAN
Mg	BDL	BDL	2141 ± 503	1543 ± 460	BDL	1948 ± 534	1877.3 ± 499
Al	32990 ± 429	31300 ± 657	319780 ± 256	31420 ± 346	29900 ± 299	39820 ± 398	80868.3± 397.5
Ca	1815 ± 512	BDL	BDL	1462 ± 424	BDL	2010 ± 499	1762.3 ± 478.3
Ti	4600 ± 626	4617 ± 803	2888 ± 433	2806 ± 488	3178 ± 534	3107 ± 525	3532.7± 568.2
V	45 ± 3	4617 ± 4	45 ± 2	42 ± 3	47 ± 3	58 ± 3	809 ± 3.00
Mn	368 ± 2	427 ± 2	270 ± 2	383 ± 2	491 ± 3	426 ± 2	394.2 ± 2.17
Dy	11.4 ± 0.5	11.2 ± 0.6	5.6 ± 0.3	9.6 ± 0.5	15.2 ± 0.5	14.2 ± 0.5	11.2 ± 0.48
Na	1009 ± 4	801 ± 3	941 ± 2	854 ± 2	700 ± 1	1054 ± 2	893 ± 2.33
K	11320 ± 181	10230 ± 194	9896 ± 79	9643 ± 87	8551 ± 77	11410 ± 91	10175 ± 118.17
As	1.1 ± 0.1	1.5 ± 0.1	1.0 ± 0.1	2.8 ± 0.1	1.2 ± 0.1	6.03 ± 0.13	2.27 ± 0.11
Br	1.9 ± 0.1	1.6 ± 0.1	0.53 ± 0.09	0.9 ± 0.1	1.2 ± 0.1	0.5 ± 0.1	1.1 ± 0.10
La	80.8 ± 0.2	128.5 ± 0.3	45.8 ± 0.1	80.8 ± 0.2	63.4 ± 0.2	60.4 ± 0.2	76.6 ± 0.20
Sm	12.25 ± 0.04	23.3 ± 0.4	8.58 ± 0.03	13.68 ± 0.04	9.47 ± 0.03	11.95 ± 0.04	13.2 ± 0.10
U	9.5 ± 0.2	14.9 ± 0.3	7.26 ± 0.22	9.1 ± 0.3	7.3 ± 0.2	9.5 ± 0.2	9.59 ± 0.24
Sc	7.5 ± 0.1	7.2 ± 0.1	7.03 ± 0.06	7.1 ± 0.1	7.0 ± 0.1	7.82 ± 0.06	7.28 ± 0.09
Cr	67 ± 3	69 ± 3	57.4 ± 2.2	70 ± 3	74.4 ± 2.8	129 ± 3	77.8 ± 2.83
Fe	24110 ± 265	25670 ± 308	23490 ± 282	28300 ± 311	27300 ± 300	28690 ± 287	26260 ± 292.16
Co	10.4 ± 0.3	9.5 ± 0.4	7.2 ± 0.3	9.9 ± 0.4	12.8 ± 0.4	11.3 ± 0.3	10.18 ± 0.35
Zn	53 ± 6	50 ± 7	38.6 ± 5.6	46 ± 6	44 ± 6	54 ± 6	47.6 ± 6.10
Rb	91 ± 6	88 ± 6	83 ± 6	74 ± 5	76 ± 6	93 ± 6	84.2 ± 5.83
Sb	BDL	BDL	BDL	0.72 ± 0.07	BDL	BDL	0.72 ± 0.07
Cs	3.7 ± 0.3	4.0 ± 0.3	3.3 ± 0.4	3.6 ± 0.4	3.8 ± 0.3	4.4 ± 0.3	3.80 ± 0.33
Ba	416 ± 31	360 ± 34	386 ± 32	406 ± 30	289 ± 28	487 ± 31	390.67 ± 31.0
Eu	2.0 ± 0.2	2.1 ± 0.2	1.1 ± 0.1	2.0 ± 0.2	1.8 ± 0.2	1.9 ± 0.2	1.82 ± 0.18
Yb	8.1 ± 0.2	9.6 ± 0.2	4.8 ± 0.2	4.3 ± 0.1	4.3 ± 0.1	3.7 ± 0.1	5.8 ± 0.15
Lu	1.18 ± 0.03	1.49 ± 0.03	0.72 ± 0.02	0.79 ± 0.03	0.06 ± 0.03	0.65 ± 0.02	0.92 ± 0.03
Hf	17.9 ± 0.3	16.2 ± 0.3	13.7 ± 0.3	25.7 ± 0.4	13.01 ± 0.24	13.2 ± 0.3	16.62 ± 0.31
Ta	1.4 ± 0.2	1.8 ± 0.2	1.3 ± 0.2	2.0 ± 0.2	1.4 ± 0.2	2.8 ± 0.2	1.78 ± 0.20
Th	37.1 ± 0.3	104.0 ± 0.5	21.3 ± 0.3	37.7 ± 0.3	30.2 ± 0.3	27.2 ± 0.3	42.92 ± 0.33

All results are in ppm BDL : Below Detection Limit

Table 4.2: The analytical results of instrumental neutron activation analysis of six Geological samples I in **site B** are presented below

ELEMENT	B1	B2	B3	B4	B5	B6	MEAN
Mg	BDL	BDL	2210 ± 659	3668 ± 602	3437 ± 746	5036 ± 866	3588 ± 718.30
Al	32860 ± 362	26580 ± 239	62600 ± 1628	74740 ± 1046	95050 ± 856	95270 ± 857	64517 ± 831.30
Ca	4847 ± 810	2548 ± 525	BDL	2456 ± 675	2945 ± 677	6482 ± 1031	3856 ± 743.60
Ti	2419 ± 370	BDL	2061 ± 476	3400 ± 554	BDL	3065 ± 448	2736.3 ± 462.0
V	44.2 ± 3.1	56 ± 3	59 ± 6	46 ± 5	29 ± 4	44 ± 6	46.4 ± 4.50
Mn	327 ± 2	233 ± 1	99 ± 1	144 ±1	150 ± 1	190 ± 2	190.5 ± 1.33
Dy	4.5 ± 0.3	4.6 ± 0.3	5.6 ± 0.4	5.1 ± 0.3	6.0 ± 0.4	3.5 ± 0.4	4.88 ± 0.35
Na	2275 ± 5	2364 ± 7	3669 ± 11	5701 ± 17	9089 ± 18	15850 ± 48	649 ± 17.70
K	1452 ± 218	24260 ± 267	40830 ± 572	30780 ± 739	33410 ± 87	24010 ± 14	25790 ± 316.17
As	2.7 ± 0.2	4.6 ± 0.2	1.5 ± 0.2	1.6 ± 0.2	BDL	BDL	2.6 ± 0.20
Br	2.3 ± 0.2	2.7 ± 0.2	2.3 ± 0.2	2.9 ± 0.3	BDL	BDL	2.55 ± 0.23
La	109.8 ± 0.2	45.9 ± 0.2	52.6 ± 0.2	39.3 ± 0.2	70.3 ± 0.4	56.2 ± 0.3	62.35 ± 0.25
Sm	16.5 ± 0.1	5.65 ± 0.03	6.94 ± 0.03	5.48 ± 0.03	10.89 ± 0.04	7.27 ± 0.04	7.27 ± 0.05
U	8.6 ± 0.3	6.2 ± 0.2	5.3 ± 0.3	4.7 ± 0.4	8.7 ± 0.3	4.01 ± 0.35	6.25 ± 0.31
Sc	4.42 ± 0.05	5.02 ± 0.06	4.95 ± 0.05	6.4 ± 0.1	3.96 ± 0.04	4.9 ± 0.1	4.94 ± 0.07
Cr	56 ± 2	103 ± 3	41 ± 2	73.3 ± 2.5	19.7 ± 2.3	39.2 ± 2.1	55.4 ± 2.32
Fe	31240 ± 312	58680 ± 411	27990 ± 280	24010 ± 288	16070 ± 225	18090 ± 253	29346.7 ± 295
Co	6.04 ± 0.30	8.02 ± 0.39	9.4 ± 0.3	10.5 ± 0.3	12.9 ± 0.3	6.5 ± 0.2	8.89 ± 0.30
Zn	291 ± 10	122 ± 8	42 ± 6	40.1 ± 5.3	35.1 ± 4.6	43.5 ± 4.7	95.6 ± 6.43
Rb	90 ± 6	1446 ± 7	211 ± 6	201.7 ± 6.7	194 ± 7	168.4 ± 5.9	385.2 ± 6.43
Sb	BDL	1.5 ± 0.1	0.49 ± 0.07	BDL	BDL	0.7 ± 0.2	0.90 ± 0.12
Cs	3.2 ± 0.3	4.0 ± 0.4	5.2 ± 0.4	8.6 ± 0.4	6.5 ± 0.3	5.9 ± 0.4	0.12 ± 0.37
Ba	499 ± 40	638 ±31	1022 ± 37	788 ± 40	898 ± 45	642 ± 37	747.8 ± 38.33
Eu	1.34 ± 0.22	1.0 ± 0.2	1.3 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	1.3 ± 0.1	1.19 ± 0.14
Yb	3.1 ± 0.1	2.2 ± 0.1	2.0 ± 0.1	2.3 ± 0.3	7.9 ± 0.3	2.3 ± 0.3	3.3 ± 0.20
Lu	0.59 ± 0.02	0.42 ± 0.02	0.4 ± 0.02	0.3 ± 0.03	0.85 ± 0.03	0.23 ± 0.02	0.47 ± 0.02
Hf	12.3 ± 0.3	14.5 ± 0.3	12.4 ± 0.3	10.00 ± 0.03	5.01 ± 0.23	4.4 ± 0.2	9.77 ± 0.23
Ta	1.07 ± 0.14	1.1 ± 0.2	1.4 ± 0.2	2.1 ± 0.2	1.46 ± 0.12	1.4 ± 0.2	1.42 ± 0.18
Th	51.8 ±0.3	22.3 ± 0.3	25.0 ± 0.3	10.3 ± 02	22.5 ±0.3	7.0 ± 0.2	23.15 ± 0.27

All results are in ppm BDL : Below Detection Limit

Table 4.3: The analytical results of X-ray Fluorescence analysis of six Geological samples in **site A** are presented below

ELEMENT	A1	A2	A3	A4	A5	A6	MEAN
Ti	5657 ± 153	4830 ± 146	5084 ± 184	4973 ± 332	5287 ± 155	5289 ± 162	5186.6 ± 1132
Cr	77 ± 16	98 ± 16	64 ± 19	BDL	119 ± 17	150 ± 19	101.6 ± 87
Mn	340 ± 17	302 ± 17	242 ± 20	380 ± 40	444 ± 19	322 ± 19	338.3 ± 132
Fe	21749 ± 144	22943 ± 152	26040 ± 209	30277 ± 424	26937 ± 178	29423 ± 200	26228.3 ± 1307
Ni	38 ± 05	26 ± 05	34 ± 07	66 ± 13	31 ± 06	44 ± 06	39.8 ± 42
Cu	22 ± 03	17 ± 03	18 ± 04	BDL	13 ± 03	18 ± 04	17.6 ± 17
Zn	56 ± 03	29 ± 02	30 ± 03	31 ± 05	28 ± 02	40 ± 03	35.7 ± 18
Rb	76.9 ± 1.4	70.6 ± 1.4	74.3 ± 1.7	75 ± 03	65.4 ± 1.4	89.9 ± 1.6	75.3 ± 10.5
Zr	815 ± 06	721 ± 06	621 ± 07	1000 ± 16	714 ± 06	610 ± 06	746.8 ± 47
Ba	827 ± 125	820 ± 123	699 ± 152	1055 ± 284	839 ± 128	935 ± 136	862.5 ± 948
Pb	38 ± 02	40 ± 02	47 ± 03	58 ± 05	44 ± 02	66 ± 03	73.3 ± 17
Sr	47.1 ± 1.1	34.6 ± 01	38.6 ± 1.3	37 ± 02	31.1 ± 01	78.1 ± 1.5	44.4 ± 7.9

All results are in ppm BDL : Below Detection Limit

Table 4.4: The analytical results of X-ray Fluorescence analysis of six Geological samples in **site B** are presented below

ELEMENT	B1	B2	B3	B4	B5	B6	MEAN
Ti	4500 ± 148	4983 ± 173	3871 ± 145	4402 ±145	2560 ± 121	2754 ± 174	3845 ± 906
Cr	100 ± 17	125 ± 21	52 ± 16	55 ± 16	76 ± 15	BDL	68 ± 85
Mn	357 ± 18	204 ± 20	106 ± 15	155 ± 15	120 ± 13	85 ± 19	171.2 ± 100
Fe	32374 ± 208	54611 ± 362	30919 ±202	27937 ± 182	20196 ± 135	21480 ± 206	31252.8 ± 1295
Ni	23 ± 06	36 ± 07	43 ± 06	47 ± 06	29 ± 05	27 ± 08	34.2 ± 38
Cu	49 ± 04	36 ± 04	17 ± 04	26 ± 04	17 ±03	BDL	24.2 ± 19
Zn	328 ± 06	151 ± 04	19 ± 03	48 ± 03	42 ± 02	76 ± 04	114 ± 22
Rb	92.8 ± 1.6	145 ± 02	189 ± 02	181 ± 02	195 ±02	159 ± 03	160.3 ± 12.6
Sr	107.5 ± 1.7	127.9 ± 1.9	145.5 ± 02	115.2 ± 1.7	166 ± 02	257 ± 04	153.2 ± 13.3
Zr	511 ± 05	667 ± 06	587 ± 05	542 ± 05	210 ± 03	216 ± 05	455.8 ± 29
Ba	898 ± 127	1511 ± 153	1168 ± 130	874 ± 125	861 ± 113	556 ± 158	978 ± 806
Pb	77 ± 03	112 ± 04	64 ± 03	56 ±03	64 ± 03	67 ±04	73.3 ± 20
Cd	BDL	BDL	BDL	28 ±08	BDL	BDL	28 ± 08
Sn	BDL	110 ±15	BDL	BDL	BDL	BDL	110 ± 15
Hg	BDL	BDL	BDL	BDL	158 ± 00	BDL	158 ± 08
Ag	BDL	BDL	BDL	BDL	BDL	31 ± 10	31 ± 10

4.2 DISCUSSION

4.2.1 *INAA*

Depth wise variation of contaminants concentrations ($mgkg^{-1}$) obtained at different depth intervals of 0, 25, 50, 100, 120 and 150cm of six soil samples from a hole each from the two dumpsites were analyzed using instrumental neutron activation analysis and energy dispersive x-ray fluorescence techniques. Though the concentrations of these contaminants fluctuate from top soil to depth of 150cm in all the entire soil samples except in one sample where the concentration increases linearly across the depth intervals. It was observed that there was no much significant difference among the contaminants concentrations in the entire soil samples and depth interval except in few samples which can be attributed to either type of soil or geology of the study sites as reported by Abdullahi, (2009): application of integrated geo-physical techniques in the investigation of groundwater contamination on the same study areas. The rates of soil infiltration in terms of contaminants concentration variation or fluctuations across the depth profiles are presented in figures 4.1 - 4.86 as shown below.

Magnesium (Mg).

In site A, Mg fell below detection limit in the sample A1 (top soil), A2 and A5 respectively. Mg ranged from 1543 to 2141ppm which is higher than range of (5.0 – 175mgL^{-1}) in natural soil and (1.8862 - 42.57mgL^{-1}) in selected dumpsites in Abeokuta (Okoyede and Rufai, 2011). In figure: 1 and 4.87, a very high concentration of Mg was noticed at middle samples where detection occurs, with maximum value of Mg found in sample A3. This may be due to the fact that over the time leachates have moved downward from the top soil layer although, the first soil layer in the dumpsite is laterite and sand, sandy soils generally have large pores, absorb water rapidly and hold less leachate compared with literite and clay soil. Clay soil can take large amount of leachate due to its adhesion ability (Abdullahi, 2009). Though the values fluctuate across the depth intervals, there was no much significant variation among the Mg concentrations (figure: 4.1 and 4.87).

In site B, Mg shows similar trend with site A by not being detected in the sample B1 (top surface) and B2 respectively. An evident from samples A3, A4, A5 and A6 (fig.: 4.30 and 4.93) shows that the contaminants from top and second samples have infiltrated down since the first layer are literite and sand having high adsorption and porosity capacity (Supriyo and Govind, 2011). A very high concentration of Mg was measured with maximum value of 5036ppm as observed in sample B6. This shows continuous movement of contaminants across the soil profiles. The range in this work is higher than range in natural soil of values (5.0 – 175mgL^{-1}) and (1.8862-42.57mgL^{-1}) in selected dumpsites in Abeokuta (Okoyede and Rufai, 2011). There was no significant variation among Mg concentrations as shown in figure 4.30.

Aluminum (Al).

Aluminum is among the elements that occurred naturally with high concentrations. In site A, aluminum was found in all the samples with comparable low concentrations except in sample A3 where the concentration was observed with very high concentration, which may be due the fact that the second layer is clay sand that can absorb large amount of leachate by adhesion. Aluminum shows linear increase in concentrations from A3 up to A6. Apart for sample A3 there was no significant variation among the Aluminum concentrations as shown in figure: 4.3 and 4.87.

In site B, Aluminum was also detected with relatively large amount in all the samples except in samples A1 and A2. The low value of Aluminum in these two samples may be due to the fact that top soil layer is literite and sand having high porosity as compared to clay soil below it. The highest concentration for Aluminum was observed in sample B5 and B6 with almost the same values. The lowest and highest concentrations for Aluminum ranged from 26580 to 95270ppm. There was no significant variation among the samples except when compared with samples A1 and A2 as indicated in figure: 4.32 and 4.93.

Calcium (Ca)

Calcium fell below detection limit of 4000mgkg^{-1} (IAEA, 98) as observed in samples A2, A3 and A5 respectively. The very low concentrations or absence of contaminants in these samples may be due to the fact that leachate has moved down as evident from the bottom samples. A very high concentration was noticed in all the samples where contaminants were detected. The highest value for Ca was noticed in A6 with concentration of 2010ppm. Ca ranged from 1462 to 2010ppm, showing no significant variation among their concentrations as observed in figure: 4.5 and 4.88.

In site B, Ca fell below detection limit of 4000mgkg^{-1} in sample B1 and B3. Ca shows linear increase in concentration from B4 up to B6. The highest value of Ca in B6 is more than twice of any value in all the samples, showing that more contaminants may have infiltrated down the soil profiles. The lowest and highest values for Ca ranged from 2456ppm to 6482ppm. The comparable values shown in samples B2, B3, B4 present no significant variation among the samples (figure: 4.34 and 4.94).

Vanadium (V).

Vanadium is toxic to humans and other animals (Perez-Benito, 2006). In site A, V concentrations are measured in very small amount except in sample A2 where the highest concentration of 4617ppm was observed. The high concentration of V in this sample may be due to the fact that perhaps majority of vanadium contaminants have been trapped in clay soil of the profiles that may formed plasticity. V ranged from 45ppm to 4617ppm which is more than world range (3-500$mgkg^{-1}$) as reported by Shahabuddin *et al.*, (2010). There was no significant variation in concentrations at all with samples A1, A3, A4, A5 and A6 except in sample A2 as shown in figure: 4.4 and 4.88.

In site B, V was measured with almost equal values, the lowest and highest values for V are 29ppm and 59ppm which falls within world range: 3-500$mgkg^{-1}$(Shahabuddin *et al.*, 2010). The obtained mean for V (46.4ppm) is lower than world mean of 100$mgkg^{-1}$ (Shahabuddin *et al.*, 2010). In figure: 4.33 and 4.95, there was no much significant variation among the V concentrations in the soil samples.

Titanium (Ti).

In site A, titanium was recorded in all the samples with high concentrations. The highest concentrations were noticed in samples A1 and A2 which may be due to high clay content in literite soil. The lowest and highest concentrations for Ti are 2806ppm and 4617ppm which is within limiting values of world soil (1000 - 9000ppm) as contained is Shahabuddin *et al.*, (2010). In figures: 4.2 and 4.88, Ti shows no significant variations in concentrations among the soil samples.

In site B, Ti fell below detection limit in B2 and B5 respectively. A high concentration of Ti was recorded in all the samples with lowest and highest concentrations recorded in samples B3 and B4 (2061ppm and 3400ppm) respectively. The highest concentration in B4 may be due to clay sand in the second layer as reported by (Abdullahi, 2009). There are no significant variations among the concentrations of Ti in the soil samples (figure: 4.31 and 4.94).

Manganese (Mn).

Mn fluctuates throughout the samples and peak in sample A5. In figure: 4.6 and 4.88, Mn presents no significant variation in concentrations in the soil samples. Mn is a very important metallic redox catalyst that governs the behavior of most trace metals in soils (Shahabuddin *et al.*, (2010). The permissible range for the concentrations of Mn is from 100 - 4000mgkg^{-1} (Shahabuddin *et al.*, (2010). While in site A, Mn ranged from 270 - 491ppm. The result shows that Mn concentrations fell within its permissible range. Mn concentration range in this present work is higher than range 3.2 - 196mgkg^{-1} in Florida and lower than range 70 - 3718mgkg^{-1} in soils of Alaska, China (134 - 1740mgkg^{-1}) and Poland (83 - 1122mgkg^{-1}) as contained in Ming *et al.*, (1998).

In site B, Mn ranged from 99 - 327ppm with high concentrations recorded in samples B1, top soils that compose of literite and sand (Abdullahi, 2009). The high concentration perhaps may be due to high clay content in laterite soil. From B2 up to B6, Mn shows linear increase in concentrations with no significant variation in among the samples as presented in figure: 4.35 and 4.94. This continuous increase in concentration is an evident of more infiltration of Mn contaminants down the depth interval.

Dysprosium (Dy).

In site A, Dy fluctuate throughout the samples and peak in sample A5 with the top two samples showing comparable values. The lowest value for Dy was recorded in sample A3 as

5.6ppm and the highest concentration of Dy was 14.2ppm. Dy shows no significant variation in concentrations in all samples as seen in figure: 4. 7 and 4.92.

In site B, Dy concentrations were comparable except in sample B6 where low concentration was recorded. The lowest and highest concentrations for Dy are 3.5ppm and 6.0ppm as observed in figure: 4.36 and 4.98, Dy presents no significant variation in concentrations among all the soil samples.

Sodium (Na).

In site A, Na fluctuate through the entire samples with noticed decrease in concentration from sample A3 to A5. Na concentration is measured high in sample A6 and shows no significant variation (figure: 4.9 and 4.87). The natural range for the concentration of Na in soil is 2 – 185mgL^{-1} (Okeyode and Rufai, 2011), while at the present work Na ranged from 700-1054ppm which is much higher than natural range, and also higher than concentration range (2.4 to 4.1mgL^{-1}) for Na in dumpsites located within Ikot-Ekpene, Akwa-Ibom state though within the natural range, but much lower when compared with the result obtained in this study site A (Okeyode and Rufai, 2011).

In site B, Na shows remarkable difference among all the detected elements with relative increase in concentration from top surface to depth of 150cm. This shows that Na contaminants present continuously movement down the depth interval with a very high value recorded in sample A6 (figure 4.38 and 4.93). In this present work, Na ranged from 2275 - 15850ppm which is higher than natural range and much higher than range in dumpsite located within Ikot-Ekpene, Akwa-Ibom as mentioned above.

Potassium (K).

In site A, K is observed to show a fairly decrease in concentration from top soil down the soil profiles except in sample A6 where it peak. The minimum value for K was recorded in sample A5. K shows no significant variation in concentrations in all the soil samples as shown in figure: 4.11 and 4.87

In site B, K concentration fluctuates in the entire samples with minimum and maximum concentration recorded in sample A1 and A3. K shows no significant variation in concentrations among all the samples as presented in figure: 4.40 and 4.93.

Arsenic (As).

In site A, As fluctuate in all the entire samples with high concentration in sample A6. The high concentration is evident of migration of As contaminants. The lowest concentration of Arsenic was recorded in sample A3. The obtained range for As (1.0ppm – 6.03ppm) are within limitation value of EEA range (1-50mgkg^{-1}) in natural soil (Mahmut *et al.*, 2006) and lower than world range of 0.1 - 40mgkg^{-1} as reported by Shahabuddin *et al.*,(2010). Arsenic shows no significant variation in concentrations except in sample A6 as presented in figure: 4.8 and 4.90.

In site B, Arsenic fell below detection limit of 0.8mgkg^{-1} (IAEA, 98) in samples B5 and B6 and fluctuated in the remaining samples (figure 4.37 and 4.98). The high concentration of Arsenic was recorded in sample A2 perhaps due to clay sand in second layer of the dumpsite profile (Abdullahi, 2009). As ranged from 1.5 - 4.6ppm which is within limitation values of EEA natural soil and world range for Arsenic.

Bromine (Br)

In site A, Br was recorded high in sample A1. Br shows little decrease in concentration from top surface to sample A2 and moderate increase variation from A3 to A5 which decrease again to A6 as shown in figure: 4.10 and 4.91. Br concentration was the lowest among all the detected elements in soil of the dumpsite having minimum concentrations of 0.5ppm in sample A6.

In site B, Br fell below detection limit of 0.8mgkg^{-1}(IAEA, 98) in samples B5 and B6 respectively. Br shows comparable concentrations in samples A1, A2, A3 and A4 respectively. In figure: 4.39 and 4.98, Br shows no significant variation in concentration in the soil samples that contaminants were detected.

Lanthanum (La).

In site A, La was measured high in sample A2 with value of 128.5ppm and fluctuates in the entire samples. The high concentration of La in sample A2 may be due to clay sand in the second layer (Abdullahi, 2009). The lowest concentration of La was measured in sample A3 with a value of 45.8ppm. La shows no significant variation in all the soil samples (figure: 4.12 and 4.89).

In site B, La shows high concentration in top soil and fluctuates in the entire samples with comparable values in samples B2, B3, B4, B5 and B6 as shown figure: 4.41 and 4.95.

Samarium (Sm).

In site A, Sm shows a very high concentration in sample code A2 perhaps due to clay sand in the second layer that can take large contaminants due to adhesion. Sm concentration fluctuates in all the entire samples (figure: 4.13 and 4.92).

In site B, the highest concentration of Sm was recorded in sample code B1 and fluctuates in the entire samples. Sm shows no significant variation except in sample code B1 (figure: 4.42 and 4.98) which may be due to clay content in laterite soil in the top layer (Abdullahi, 2009).

Uranium (U).

In site A, U is measured high in sample A2 and fluctuates in the entire samples. The high value in A2 may be due to clay soil. U shows no significant variation among all the soil samples except in sample A2 (figure: 4.15 and 4.92).

In site B, U shows linear decrease in concentrations from top soil to sample A4. Samples A1 and A5 show comparable values. The lowest concentration of 4.01ppm was recorded in B6 and highest concentration of 8.7ppm was observed in B5 (figure: 4.44 and 4.96).

Scandium (Sc).

In site A, Sc in all the entire samples indicate comparable values with highest concentration in sample A6. The lowest concentration of 7.0ppm was measured in sample A5 and highest concentration of 7.82ppm was measured in sample A6 respectively. The mean of 7mgkg^{-1} exceed the mean of world soil (Shahabuddin *et al.,* (2010). The observed range in concentration of Sc (7.0 – 7.82ppm) lies within the limiting values of world natural soil (0.5 -

45mgkg $^{-1}$) (Shahabuddin *et al.,* 2010). Sc shows no significant variation in all the soil samples (figure: 4.17 and 4.90).

In site B, Sc fluctuates throughout the entire samples and peak in sample B4 with concentration of 6.4ppm. The minimum value of 3.96ppm for Sc was recorded in B5. Sc shows no significant variation in all the soil samples (figure: 4.46 and 4.96).

Chromium (Cr).

In site A, Cr show comparable values in samples A1, A2, A4 and A5 and peak in sample A6. Cr also indicates fairly increase concentration down the depth interval except in sample A3 where it depressed a little bit. The high concentration in sample A6 is an indication of continuous migration of Cr contaminants down the depth intervals (figure: 4.14 and 4.89). Cr concentrations ranged from 57.4ppm - 129ppm with a mean of 77.8ppm lower than the concentration of Cr (243ppm) in dumpsite of Addis Ababa Ethiopia that is found to be in an elevated concentration than typical concentration of MSW compost in United State (Hunachew and Sandip, 2011). Cr is used in alloys, electroplating, pigments, paint manufacture, fungicides, photography, glass and leather tanning industries. Cr is carcinogenic by inhalation and corrosive to tissues (Lin *et al.*, 2002; Aboud and Nandini, 2009).

In site B, Cr fluctuate in the entire samples indicating high value in sample B2 perhaps due to clay sand in the second layer. Cr concentrations range from 19.7ppm to 103ppm. Cr shows significant variation in all the soil samples (figure: 4.43 and 4.95).

Iron (Fe).

Fe is one of the most abundant elements in earth crust. In site A, Fe shows very high concentrations in all samples and was comparable with each other. The minimum value was recorded in top soil and maximum value in sample A6 indicating continuous movement of Fe contaminants down the soil profiles. The natural range of Fe in soil is 15 – 250mgL^{-1}, Fe in this present work ranged from 24110ppm to 28690ppm which is much above the natural range and also above the range of concentration of Fe (51.5-155mgL^{-1}) in Elelewo dumpsites Uyo (Okoyede and Rufai, 2011). Fe shows no significant variation in all the entire soil samples (figure: 4.16 and 4.87). This elevated concentration in the dumpsite may be attributed to high deposition of iron containing materials such as waste car part.

In site B, Fe present fairly decrease in concentration except in sample B2 where its concentration was measured very high almost double the second highest value in the entire soil samples. This may be attributed to the fact that the second layer in the dumpsite is clay sand (Abdullahi, 2009) that can accumulates much contaminants due to its large surface area. The lowest value was found in sample B5 and highest value in sample B2. Fe in this present work ranged from 16070ppm to 58680ppm which is above natural range of Fe in soil. With exception of sample A2, Fe shows no significant variation in concentration among the soil samples (figure: 4.45 and 4.93).

Cobalt (Co).

In site A, Co concentrations fluctuate in all the entire samples. The lowest value of 7.2ppm was recorded in sample A3 and highest value of 12.8ppm in sample A5. Co shows no significant variation of concentration in all the soil samples (figure: 4.18 and 4.92)

In site B, Co presents relative increase concentrations from top soil up to B5 indicating continuous migration of Co contaminants down the depth interval. The maximum concentration was found in sample B5 with a value of 12.9ppm and its minimum concentration at top surface with a value of 6.04ppm. Co therefore shows no significant variation in concentration except between samples B5 and B6 where there is fall in concentration (figure: 4.47 and 4.96).

Zinc (Zn).

The concentration of Zn was found to fluctuate in all the entire soil samples. These values are comparable with one another peaking in sample A6 suggesting movement of Zn contaminants down the depth profiles with no significant variation among the soil samples (figure: 4.19 and 4.89). The normal concentrations of Zn in soil ranged from 0.05 to 1.5mgL^{-1} (Okoyde and Rufai, 2011). In site A, Zn concentrations ranged from 38.6 to 54ppm which is more than normal range in soil, baseline range in Florida surface soils (0.89 – 29.6mgkg^{-1}), and less than ranges for Zn concentrations in Alaska (26 -188mgkg^{-1}), U.S (12.6 – 183mgkg^{-1}), China (28.5 – 161mgkg^{-1}) and in Poland soil (10.5 – 154.7mgkg^{-1}) and higher than concentration of Zn (0.3299 - 4.847mgL^{-1}) in selected dumpsites in Abeokuta (Okoyede and Rufai, 2011).

In site B, Zn was found with very high concentration in sample B1 probably due to clay content in laterite soil in the first layer. This very high value drops continuously up to sample B5 which then increase a little bit again in sample B6. Zn shows no significant variations except due to sample B1 (figure: 4.48 and 4.95). The lowest value of Zn was 35.1pp. The range of Zn in the present work is higher than its normal range in soil and baseline range in Florida and more than metal concentrations in Alaska soil (26-188mgkg^{-1}), U.S soil (12.6 – 183mgkg^{-1}), China soil

(28.5 – 161mgkg^{-1}) and Poland soil (10.5-154.7mgkg^{-1}) and higher than that of selected dumpsites in Abeokuta as indicated above.

Rubidium (Rb).

In site A, Rb was found with comparable concentrations in all the entire samples. The value in the top soil drop gradually up to A4 which then increases again from sample A5 and peak in sample A6 showing evident of contaminants migration down the soil profiles (figure: 4.21 and 4.89). The minimum value of 74ppm was obtained in sample A4.

In site B, Rb was found with very high concentration in sample B2 and B1 has lowest concentrations among the rest of the samples. This very high value in sample B2 may be due to clay sand in the second layer of the dumpsite that can accumulate large contaminants. With exception of sample B2, Zn shows no significant variation among the remaining soil samples (figure: 4.51 and 4.94).

Antimony (Sb)

Sb fell below detection limit of 0.2mgkg^{-1} (IAEA, 98) in all the samples except in sample A4 where the concentration was very high (figure: 4.23 and 4.91). This indicates that all contaminant have migrated down and accumulated in sample A4.

In site B, Sb shows similar pattern as in site A by falling below detection limit of 0.2mgkg^{-1} in top surface, B4 and B5 samples respectively. Sb has high concentration in sample A2. Between this value and other two values of B3 and B6 there was significant variation in their concentrations (figure: 4.52 and 4.97).

Caesium (Cs).

In site A, Cs concentrations in all the samples were high. Apart from the fact that concentrations of Cs shows no significant variation in all the soil samples, samples A3, A4, A5 and A6 presents small progressive increase in their values likewise samples A1 and A2 (figure: 4.20 and 4.90). Cs concentrations peak in sample A6 which is an evidence of continuous migration down the soil interval.

In site B, Cs concentration is high in sample B5 and shows linear increase in their concentration from top surface up to sample B5 which then decrease in small amount in sample B6 (figure: 4.49 and 4.96). This is an indication that the contaminant is moving down the soil profiles.

Barium (Ba).

For site A, Very high concentrations of Ba was presented in all the entire soils samples with no significant variation among their values (figure: 4.22 and 4.88). Ba shows a linear increase in concentrations from samples A2 up to A4 which then decrease in concentration in A5 and peak again in A6. Ba concentration ranged from 289ppm to 487ppm which is higher than baseline range in Florida (1.67 – 112mgkg^{-1}) and lower than metal (Ba) concentrations in soil of Alaska (213 – 1659mgkg^{-1}), California (197 – 1110mgkg^{-1}) and U.S (964 – 2015mgkg^{-1}).

For site B, Ba shows a high concentration in sample B3 with no significant variation among the soil samples (figure: 4.51 and 4.94). The minimum value was recorded in top soil. The first three top samples show a linear increase in their concentration down the profiles and fluctuate in the remaining three samples.

Europium (Eu).

Concentration of Eu fluctuates throughout the entire samples with comparable values except in sample A3 where the concentration was small. The minimum value of 1.1ppm for Eu was recorded in A3 and maximum value of 2.1ppm in A2. Eu shows no significant variation in concentrations (figure: 4.24 and 4.90).

In site B, the measured concentrations of Eu in all the entire samples fluctuate with no significant variation in their values (figure: 4.53 and 4.96). The lowest value of 1.0ppm was found in sample B2 and the highest value in top soil with a value of 1.34ppm.

Ytterbium (Yb)

In site A, Yb show a linear increase in concentration from sample A1 to A2 and then decreased down to A6. The increase in value noticed in the first two top soils may be attributed to the absorption capacity of literite soil in the first layer and a decrease in concentration down the profiles from sample A2 may due to accumulation in the clay soil of the second layer of the dumpsite. Samples A3, A4, A5 and A6 show comparable concentrations (figure: 4.25 and 4.90). The lowest value of 3.7ppm in sample A6 and highest value of 9.6ppm in sample A2 was measured.

In site B, Yb was detected in all the samples with comparable values except in sample B5 where a very high value was noticed. This is evidence in contaminant migration down the soil profiles. There was a decrease in concentrations from top soil down to sample A3. The lowest value of 2.0ppm for Yb was detected in sample B3 and highest value of 7.9ppm in sample B5.

With exception of sample B5 all the samples present no significant variation in their concentrations (figure: 4.54 and 4.97).

Lutetium (Lu).

For site A, concentration of Lu fluctuate throughout the entire samples. The highest and lowest values are found in samples A2 and A5 respectively (figure: 4.27 and 4.91). The high concentration of Lu in sample A2 may be due to clay soil of the second layer of the dumpsite soil that has large surface area to accumulate an amount of contaminants.

In site B, the smallest concentration of Lu (0.23ppm) was recorded in B6 and highest concentration in B5. Lu show a linear decrease in concentration from top soil down to sample B4 which increase in B5 and decrease again in B6 (figure: 4.58 and 4.97).

Hafnium,(Hf).

For site A, the concentrations of Hf fairly decrease from top soil up to sample A3 and peak in sample A4. Sample A5 and A6 are almost equal in values. The lowest value of 13.0ppm in sample A5 was measured. Apart for the high concentration measured in A4, Hf shows a systematic drop in concentration with no significant variation among them (figure: 4.29 and 4.92).

In site B, Hf show increase concentration in the first two samples and then decrease progressively from sample A2 up to A6. The highest value of 14.5ppm was measured in sample B2. Hf presents no significant variation in concentrations among the soil samples (figure: 4.56 and 4.98).

Tantalum, (Ta).

The concentration of Ta fluctuates in the entire soil samples having lowest value of 1.3ppm in sampling point A3 and highest value of 2.8ppm in sampling point A6. Ta shows no significant variation in concentration in all the soil samples (figure: 4.26 and 4.91).

In site B, Ta presents a linear increase of concentration in the first three top soil samples and a linear decrease in the last three soil samples down the depth profiles. Ta has the lowest value of 1.07ppm in top surface and highest value of 2.1ppm in sample B4. Ta shows fairly equal values in all the samples except in sample B4 (figure: 4.57 and 4.97).

Thorium (Th).

In site A, Th has a very high concentration in sample A2 and moderate and comparable values in the remaining samples. A fluctuation was seen in the first three top soil samples and a systematic linear decrease down the depth interval in the last three soil samples. The high concentration in sample A2 may be due to clay soil in the second layer of the soil dumpsite. With exception of sample A2, Th shows no significant variation in concentration in all the samples (figure: 4.28 and 4.89).

In site B, Th fluctuates throughout the soil samples. Th has lowest value of 7.0ppm in B6 and highest value of 51.8ppm in top surface. Apart for sample B1, Thorium shows no significant variation in concentration (figure: 4.55 and 4.95). The high concentration in the top soil may be due to clay content in the first soil layer of the dumpsite.

4.2.2 EDXRF

Titanium (Ti).

In site A, Ti presents a very high and comparable concentration in all the entire soil samples. The minimum and maximum values of Ti are 4830ppm found in A2 and 5657ppm in top soil. The high concentration of Ti in top soil may be due to clay content of literite soil in the first layer that can accumulate large amount of contaminants. Ti shows no significant variation in all the entire soil samples (figure: 4.59 and 4.99).

In site B, the concentrations of Ti fluctuate throughout the entire soil samples and measured high in sample A2. This high value may be due to clay content of clay soil in the second layer. The minimum concentration was recorded in sample code A5. Ti presents no significant variation in all the samples except in samples A5 and A6 where their values decreased (figure: 4.71 and 4.99c).

Chromium (Cr).

In site A, Cr concentration fell below detection limit of 1ppm (IAEA, 98) in sample A4. Cr fluctuates in all the entire samples having highest value of 150ppm in sample A6. This value is lower than maximum concentration of Cr (561ppm) in dumpsite of Addis Ababa Ethiopia (Hunachew and Sandip, 2011). Cr indicates no significant variation in concentration among the soil samples (figure: 4.61 and 4.99a).

In site B, Cr concentration fell below detection limit of 1ppm in sample A6. The lowest and highest values are 52ppm and 125ppm respectively in sample B3 and B2 respectively. Cr indicate linear increase concentration in the first two top samples down the profiles which then decrease and increase progressively again in the last three samples down the depth intervals. Cr shows no significant variation in concentration within these groups (figure: 4.73 and 4.99c).

Iron (Fe).

In site A, Fe present a systematic comparable increase in concentrations from top soil up to sample A6 except in sample A4 where high concentration of 30277ppm is noticed (figure: 4.60 and 4.99). The natural range of iron in soil is (15 – 250mgL^{-1}) (Okoyede and Rufai, 2011). Iron in site A ranged from 21749ppm in top surface to 30277ppm in sample A4.

In site B, Fe concentration increase in the first two top soil and decrease again in the next other three samples down the depth intervals and increase again in the last sample (B6). The lowest and highest value of Fe is 20196ppm in B5 and 54611ppm in B2 respectively. Fe indicates no significant variation in concentration except in sample B2 (figure: 4.72 and 4.99c).

Manganese (Mn).

In site A, Mn concentration decrease in the first three top samples and increase in next two other samples down the profiles and decrease again in the last sample A6. Mn ranged from 242 to 444ppm which is higher than natural range (1.00 – 45.00mgkL^{-1}) for Mn in soil (Okeyede and Rufai, 2011). The range in this present work is higher than baseline values in Florida (1.74 – 236mgkg^{-1}) and lower than ranges in Alaska (70 – 3718mgkg^{-1}), California (263.1-1332mgkg^{-1}), U.S (43-2532mgkg^{-1}), China (43 – 2532mgkg^{-1}) and Poland (83-1122mgkg^{-1}) (Ming *et al.*,1998). Mn was measured high in sample A5 and shows no significant variation in concentration among the entire samples (figure: 4.63 and 4.99a).

In site B, Mn concentration group into two. The first group shows a very high concentration in top soil which decreases gradually to B3 and the other group shows a decrease in concentration from B4 to B6. The lowest and highest values for Mn are 85ppm in sample B6 and 357ppm in top surface. These ranges of values are higher than natural value of Mn in soil and lower than baseline concentration in Florida, Alaska, California, U.S, China and Poland. With exception of sample B1, Mn shows no significant variation in concentration (figure: 4.75 and 4.99d).

Nickel (Ni).

In site A, Ni concentrations fluctuates throughout the entire samples showing maximum value in sample A4. This high value of Ni in sample A4 may be due to movement of the contaminant down the profiles. Apart for high value in sample A4, Ni shows no significant variation within the entire samples (figure: 4.62 and 4.99a). Ni varies from 26ppm to 66ppm which is higher than baseline range in Florida (1.70 - 48.5mgkg^{-1}) and natural range of (0 - 0.5mgL^{-1}) in soil and much higher than range (0.0896 – 0.1376mgL^{-1}) of Ni in selected dumpsites in Abeokuta (Okoyede and Rufai, 2011). The mean of 39.8ppm for Ni is higher than mean in Fallujah (8.96mgkg^{-1}), Beijing (24.0mgkg^{1}), Teresina (27.3mgkg^{-1}), Tuscany (152.3mgkg^{-1}), Baghdad (80.44mgkg^{1}) and Hawaja (152.3mgkg^{-1}).

In site B, Ni presents linear increase concentration from top soil up to sample B4 where it high value was recorded and then show some decrease in concentrations in B5 and B6 down the depth interval. There was no significant variation within the entire samples (figure: 4.74 and 4.99e). The range in this present work is higher than the natural range in soil and lower than baseline range in Florida (1.70 - 48.5mgkg^{-1}), Alaska (5.1-113mgkg^{-1}), California (6.25 - 207mgkg^{-1}).

Copper (Cu).

In site A, Cu fell below detection limit in sample A4 and measured high at top sample. The observed records show fluctuated results with no significant variation among the soil samples (figure: 4.64 and 4.99b). Cu ranged from 13ppm to 22ppm in the entire soil samples.

In site B, Cu follows similar pattern as in site A by measuring high in its concentration at top soil and fell below detection limit in sample B6. The first three top soil samples indicate gradual decrease in values and then increase in sample B4 and decrease again in sample B5. The observed variation indicate no significant variation in all its values (figure: 4.76 and 4.99e).

Zinc (Zn).

In site A, the lowest and highest values for Zn are 28ppm and 56ppm which is higher than Zn range (0.3299 – 4.847mgL^{-1}) in dumpsite of Abeokuta (Okoyede and Rufai, 2011). Zn was found to measured high at top surface and B6 respectively with comparable concentrations in middle samples (B2, B3, B4 and B5). Zn shows no significant variation in concentration within the entire soils samples (figure: 4.65 and 4.99b).

In site B, the concentrations of Zn in the entire samples fluctuate with highest value in the top soil and lowest value in sample B3. The observed variation indicates no significant variation among the samples except due to B1 and B2 (figure: 4.77 and 4.99d).

Rubidium (Rb).

In site A, Rb concentrations displayed a comparable concentration in the top four samples down the depth profiles with highest and lowest value found in samples A6 and A5 respectively. Rb shows no significant variations across the depth intervals (figure: 4.67 and 4.99a).

In site B, Rb displayed an increase concentration in the first three top samples and fluctuates in the remaining three samples down the profiles. It has minimum value of 92.8ppm in top surface and highest value of 195ppm in sample B5. The observed values indicate no significant variation (figure: 4.79 and 4.99e).

Zirconium (Zr).

In site A, Zr shows a decrease concentrations from top soil to sample A3 and peak at sample A4 which then decreases again in samples A5 and A6 (figure: 4.69 and 4.99) though the observed concentrations shows no significant variation among the soil samples.

In site B, the concentrations of Zr shows gradual drop in values from B2 to B4 and nearly equal values was recorded in B5 and B6. The highest concentration was found in sample B2. Between the top four samples and last two samples there is significant variation in concentration but not within the group of samples (figure: 4.78 and 4.99d).

Barium (Ba).

In site A, the lowest and highest values for Ba are 699ppm in A3 and 1055ppm in sample A4 respectively. Ba shows nearly equal concentrations in samples A1, A2 and A5 with highest value found in sample A4 and the lowest value in A3. The concentration in the entire soil samples shows no significant variation (figure: 4. 66 and 4.99).

In site B, the highest concentration was found in B2, nearly equal values in samples in B4 and B5 with lowest value recorded in B6. The values in the entire samples indicate no significant variation (figure: 4.80 and 4.99bc).

Lead (Pb).

In site A, with exception of sample A5 Pb present a linear increase in concentration from top to sample A6. All values show no significant variation (figure: 4.68 and 4.99b). The lowest and highest values of Pb are 38ppm in top surface and 66ppm in sample A6 which is much higher than range in natural soils (0.075 – 0.125mgL^{-1}) and higher than dumpsite range (0.4132 - 2.8137mgL^{-1}) in Abeokuta (Okoyede and Rufai, 2011).

In site B, the range of Pb is from 56ppm in sample B4 to 112ppm in sample B2 which is lower than natural range (0.075 – 0.125mgL^{-1}) in soils (Okeyode and Rufai, 2011). The highest value of Pb was found at sample B2. The last three samples down the profiles show increase concentration down the depth interval and the first three samples at the top profiles fluctuate in concentration with highest value recorded in sample B2. The observed variation in concentration is insignificant except due to sample B2 (figure: 4.82 and 4.99e).

Strontium (Sr).

In site A, Sr concentration was measure high in sample A6 and lowest in sample A5. Samples A2, A3, A4 and A5 show comparable concentrations. The very high concentration in sample A6 indicates downward migration of this contaminant (figure: 4.70 and 4.99b).

In site B, the concentrations of Sr increases from top soil down the depth intervals except in sample B4 where there was a little decrease in concentration. The highest concentrations of Sr in sample B6 indicate downward movement of the contaminant. Sr lowest and highest values are 107.5ppm in top surface and 257ppm in sample B6. The observed values show no significant variation in concentration (figure: 4.81 and 4.99d).

Cadmium (Cd), Tin (Sn), Hafnium (Hf) and Gold (Ag).

In site B, Cd, Sn, Hf and Ag fell below detection limits of 8mgkg^{-1}, 20mgkg^{-1}, 0.1mgkg^{-1}, and 2mgkg^{-1} in all the entire samples except in samples B4, B2, B5 B6. The observe variation in concentrations was insignificant (figures: 4.99f, 4.99f, 4.85, 4.99f and 4.99f respectively).

4.2.3 GENERAL DISCUSSION

4.2.3.1 *INAA*

INAA results for the collected soil samples revealed the existence of the following elements from both dumpsites: Mg, Al, Ca, Ti, V, Mn, Dy, Na, K, As, Br, La, Sm, U, Sc, Cr, Fe, Co, Zn, Rb, Sb, Cs, Ba, Eu, Yb, Lu, Hf, Ta and Th. The average concentrations of each metal are given in Table 4.1 and 4.2 respectively.

Heavy metals definition varies from discipline to discipline however, heavy metals as mentioned by some academics (Mahmut *et al.,* and Khalid *et al.,* 2006. Antoaneta and Szyczewski, 2010. Ata *et al.,* 2010, Mwegoha and Kihampa, 2010. Adu *et al.,* 2012. Emad *et al.,* and Rebecca *et al.,* 2013) confirmed that all the elements detected in each soil samples of both dumpsites are heavy metals except for few of them which includes: Dy, Mg, Yb and Lu.

Metals concentration and soil leaching fluctuates across the soil profile from the top surface up to depth of 150cm in the present studies areas. Abdullahi (2009) in the same study areas but, using geophysical approach, reported that the top soils varies in composition, color and texture and in most places they are predominantly late rite and quartz grains. An evident from analytical results showed that the two dumpsites soil revealed that elements detected are heterogeneously distributed in types and numbers, which might be due to the fact that the dumpsites are not far from each other having same source of waste.

In all the samples analyzed in this present sites **(A and B),** elements such as Al, Fe, K, Ca, Mg and Ti are found to contained high concentrations between 1000ppm to 95270ppm, in particular Al in sites A and B has highest mean concentrations of 80868.3ppm and 64517ppm respectively. Al mean concentration value in site A is comparable with 82300ppm of its world background value in soil.

Br has lowest concentrations of all the elements detected in the study **site A** with concentration of 0.5ppm and Lu with lowest concentration of 0.47ppm in **site B**.

In all the elements detected from the two sites Na show relative increase concentration from top surface to the depth of 150cm.

4.2.3.2 EDXRF

EDXRF results for the collected soil samples revealed the existence of the following elements: Ti, Cr, Fe, Mn, Ni, Cu, Zn, Rb, Zr, Ba, Pb and Sr in both sites with additional four elements: Cd, Sn, Hf and Ag in site B. The average concentrations of each metal are given in Table 4.3 and 4.4 respectively.

The same reports as in INAA above by some academics outline all the detected elements except Zr in soil samples of both dumpsites and Ag in dumpsite B are heavy metals.

The elemental concentrations fluctuate from top surface to depth of 150cm in both dumpsites.

Elements Ti, Fe, Mn, Ni, Zn, Rb, Zr, Ba, Pb and Sr were detected in all the samples, while elements Cr and Cu falls below detection limit in both samples A4 with a similar trend observed in site B in sample B6 respectively. The infiltration by rain water could be the reason.

Cu shows the least concentrations in all the samples with a value of 13ppm in sample A5 and 17ppm in samples B3 and B6 respectively.

Fe has the highest concentration among the detected elements with a value of 21749ppm and 32374ppm in dumpsite A and B respectively. The reason could be that iron is one of the most abundant elements in earth’s crust.

Cu and Ni have the least concentration at top soil with a value of 22ppm and 23ppm in sites A and B respectively.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

EDXRF and INAA were used in the multi-elemental analysis and infiltration studies in the soils around the two dumpsites at Unguwar Dosa area in Kaduna north of Kaduna state. Apart from the fact that contaminants are heterogeneously and evenly distributed our results revealed evidence of leaching in the soils profile. These contaminants fluctuate in their concentrations from top soil to depth of 150cm which is in agreement with Latif *et al.*,(2004) that metal contamination and soil leaching varies spatially across the soil profile due to soil type, geology and PH, which is supported by similar work on same soil dumpsites but, using geo-physical techniques that the soil composition varies in composition, color, texture and most places they are predominantly late rite and quartz grains (Abdullahi, 2009) however, Michael and Seldon, (2011) reported that metal displayed a systematic drop in concentration with depth. Elements Mg, Ca, Sb, Ti, As and Br could not be detected in some samples either their concentrations fall below measurable values or have been infiltrated down the profile completely. The element Na shows relative increase in concentration down the profile (table 4.2). The mean concentrations of Al (80868.3 ± 397.5ppm), Fe (26260 ± 292.16ppm), K(10175 ± 118.17ppm), Ti (3532.7 ± 568.2ppm),V(809 ± 3.0ppm) in **site A** as shown **table 4.1,** Al (64517 ± 831.3ppm), K (25790.3 ± 316.2ppm), La (62.35 ± 0.25ppm), Fe (29346.7 ± 294.8ppm), Rb (385.2 ± 6.43ppm), Sb (0.9 ± 0.12ppm) and Ba (747.8 ± 38.33ppm) in **site B** as indicated in **table 4.2**, Zr (746.8 ± 47ppm), Ba (862.5 ± 948ppm), Pb (73.3 ± 17ppm) in **site A** as observed in **table 4.3**, and Zn (114 ± 22ppm), Rb (160.3 ± 12.6ppm), Zr (455.8 ± 29ppm), Ba (978 ± 806ppm), Pb (73.3 ± 20), Cd (28 ± 08), Sn (110 ± 15), Hg (158 ± 08) and Ag (31 ± 10) in **site B** as seen in **table 4.4** are above average crustal values of respective metals (Appendix) this could be attributed to the fact that mineral dissolution and high adsorption capacity of laterite soil are responsible for the elevated mean concentration.

5.2 RECOMMENDATION

Presently there is no any pollution control method being practiced at the specific disposal sites. We strongly recommend the present dumpsites to be treated accordingly to minimize the impact of persistence of heavy metals in the area for future economical use of the land.

1. There is need to modernized the dumpsites throughout the country by providing a lining system for easy collection of leachate to solve problems of soil degradation especially in residential areas.
2. The soils in the area require application of various remediation technologies such as bioremediation and phytoremediation by growing certain plants in the area to minimize the rate of contamination and future pollution problems.
3. New modern sanitary landfill need to be developed to replace the present indiscriminate disposal method.
4. Groundwater monitoring shallow wells around the dumpsites need to be provided to understand more about the quality changes of leachate due to the waste age

5.2.1 RECOMMENDATION FOR FURTHER WORK

1. In this present work, contaminants fluctuate in concentrations from top surface to depth of 150cm, therefore further research is recommended beyond the scope of this work to elucidate the groundwater contamination in the study areas.
2. There is need to investigate home water within the surroundings of the dumpsites for heavy metals analysis.

3. An investigation into soil physicochemical parameters of the soils around the dumpsites is necessary to determine their values and understand how they affect contaminants migration.

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