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**SOIL CONTAMINATION BY RISK ELEMENTS IN AWOTAN
DUMPSITE, IBADAN IN NIGERIA**

DIPLOMA THESIS

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DECLARATION

I, NOHEEM ABIOLA TIJANI, hereby declare that except for reference to other work from different authors which have dully cited and acknowledged, this action research is the result of my effort and that it has neither in whole nor in part been presented elsewhere.

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SUPERVISOR'S DECLARATION

I hereby certify that the preparation and presentation of this thesis was supervised following the guidelines binding the supervision of Diploma thesis laid down by the Czech University of Life Sciences Prague.

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ABSTRAKT

Ukládání pevných odpadů se stává zásadním problémem v mnoha rozvojových zemích. Skládky pevných odpadů se často přeměňují na ornou půdu bez jakékoli detailní analýzy půd. Cílem této práce byla analýza obsahu rizikových prvků v půdě na skládce města Awotan v Nigérii. Obsahy rizikových prvků byly porovnány s regulačními hodnotami navrženými různými institucemi. Celkový obsah prvků v půdách ze skládky byl stanoven ve výluhu lučavkou královskou pomocí atomové absorpční spektrofotometrie. Obsahy Ti, As, Pb, Ni a Cd byly podstatně vyšší než navržené regulační hodnoty pro zemědělské půdy. Protože půdy na skládce byly silně alkalické, mnoho kovů bylo přítomno v nerozpustné formě a akumulovaly se z důvodu dlouhodobého skládkování průmyslových a domácích odpadů. Obsah rizikových prvků v půdě stoupal od povrchu s hloubkou až do 75 cm což indikuje, že některé prvky byly schopny v půdě migrovat. Ačkoli celkový obsah P, Ca, S, Mn a Na byl v půdách poměrně vysoký, půdy nebyly vhodné pro zemědělské využití, protože obsah rizikových prvků byl nad regulačními hodnotami. Ačkoli skládky mohou být plochy potenciálně zajímavé pro zemědělské využití, jejich půdy musí být nejprve analyzovány na obsah rizikových prvků.

ABSTRACT

The disposition of solid wastes has become a crucial problem in most developing countries. Solid waste disposal sites are often turned into arable fields without detail chemical analysis of their soils. This research aimed to determine the content of risk elements in soils from the dumpsite with deposition of wastes over the last 200 years, Awotan in Nigeria. The content of risk elements was compared with regulatory values as proposed by different institutions. The total content of elements in the soils from the dumpsite was determined using Aqua regia extraction followed by Atomic Absorption Spectrophotometry analysis. The contents of Ti, As, Pb, Ni, and Cd were substantially higher than the regulatory values for agricultural soils. As the soils of dumpsite were highly alkaline, many metals were present in an insoluble form and accumulated because of the long-term deposition of industrial and domestic wastes. The content of risk elements in the soil increased gradually from the surface up to the depth 75 cm indicating that some elements were able to migrate in the soil profile. Although the total content of P, Ca, S, Mn, and Na was relatively high in the soil, the dumpsite was not suitable for the agricultural production because the content of risk elements was above regulatory values. Although dumpsites can be potentially interesting areas for agricultural production, their soils must be first of all analysed for the content of risk elements.

Keywords

Atomic Absorption Spectrophotometer; Dumpsite; Industrial waste; Risk element; Total elements

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CHAPTER ONE

1. INTRODUCTION

In recent times, Nigeria produces the highest quantity of solid waste in Africa, with an annual rate of approximately 32 million tons (Amuda et al., 2014). However, in 2019, with an estimated population of about 180 million, the annual solid waste was 28 million tons, which indicate that the population growth is associated with increasing solid waste (Sowunmi, 2019). Although waste disposition is a major canker in the country, there are no detail scientific studies on the intensity of accumulated toxic elements as a result of solid waste disposal in agricultural soils.

The deposition of solid waste materials, such as polyethylene, rubbers, glasses, industrial wastes and other agrochemicals (e.g., fertilizers and pesticides) has detrimental effects on soils and water bodies (**Raman & Sathiya, 2008; Alia et al., 2013**). Generally, most of the solid wastes are deposited in a designated site referred to in this context as a dumpsite. All categories of waste; toxic or non-toxic, biodegradable or non-biodegradable, and recyclable or non-recyclable are dumped together making their management very difficult. As most of the substances mentioned above disintegrate, copious amounts of elements (e.g., Cu, Zn, As, and Cd) are released into the soil of affected areas, and subsequent release into the groundwater table (Adepoju-Bello et al., 2009; Momodu and Anyakora, 2010).

The gradual release of these elements is associated with the quantity and type of substance disposed. It is worth noting that the accumulation and subsequent leaching of these elements are further dependent on the type, physical, and chemical characteristics of the soil (**Chibuisi et al., 2009**). Nevertheless, the dispositions at dumpsite may also result from household waste from kitchen waste e.g., food residues, fuelwood, and others may also increase the elemental composition of affected areas.

Many local farmers resort to these areas as arable fields for the production of food crops for human consumption (Oyakhilomen et al, 2019). So far, what is unknown in such arable fields is ‘what extent is the elemental contents soils resulting from the deposition of both solid and domestic wastes? And whether they are conducive for the production of food crops and grasses for human and animal consumption, respectively?

Although some authors assessed the negative effects of solid waste disposition in Nigeria, these studies were limited to few elements (e.g. Pb, U, and Cd) abundant in the heavily industrialized sites of the country (Onianwa and Ajay, 2002). There is, therefore, the need for intermittent assessment of soils emanating from dumpsites as they also pose an immense danger due to the nature of disposed materials and to alert the inhabitants of likely danger.

Furthermore, landfill leachate had been implicated in environmental pollution, developmental anomalies, birth defects, surface and groundwater pollutions, and biomass reduction (Sia Su, 2008; Alloway and Ayres, 1997). This makes it important to carry out a detailed study on the effect of solid wastes disposal on soil and the long-term effect of increased population on the rate of solid waste deposition.

1.1. Aims and objectives

The objective of this work, therefore, seeks to;

- i. Identify the content of elements in the soil from an age-long dumpsite which is anthropogenically imposed
- ii. Determine the level of elements in this soil and compare it with world permissible levels and other reference values.
- iii. To provide possible inferences of this site for future cropland/arable field use.

1.2. Research Questions

- i. Which elements in the soil from the dumpsite can be termed as anthropogenic?
- ii. At what level can the content of elements be considered at the above permissible limits?
- iii. Can the soil in this site be appropriate to be used for crop production?
- iv. Can surface deposition of solid waste depositions affect the elemental composition of deeper layers of soil?
- v. What are the implications of the accumulation of specific elements in the soils from the dumpsite?

CHAPTER TWO

2. LITERATURE REVIEW

This chapter reviews all the most important literature and correlated researches about this study. It also contains all the significant researches that previously were conducted by other researchers with similar objectives. Other sources of materials reviewed were published books, thesis, journals, leaflets, online documents, and unpublished drafts.

Although natural sediments have some proportion of elements, the effect of human-induced activities can cause substantial accumulation. This chapter describes also the human aspect termed in this context as “anthropogenic elements”.

2.1. Sources of solid waste

Solid waste (SW) disposal is one of the major challenges to the environment as a whole. The composition of SW varies significantly from one country to another. Such variation depends mainly on the economic condition, waste management regulations, and industrial structures. Household or municipal wastes are usually generated from varying sources where different human activities are encountered. Several studies showed that the solid waste that is generated from the developing countries are majorly from households (55–80 %), followed by 10–30 % generated from market or commercial areas (Wangatia, 2013). The later consists of variable quantities generated from industries, streets, institutions and many others. The solid-waste composition in Ibadan comprises leaves, paper, food waste, tins, glass, and rags (Onibokun and Kumuyi, 2003). Reason being that Ibadan is located in the heart of a rich agricultural land and has a large old and unplanned sections. A comparative analysis made of the composition of solid waste from two acres of Ibadan in 1970 showed that residential land use accounted for 70.1% of the waste generated, followed by commercial land use (18.8%) and industrial land use (9.7%). Institutional and other land use accounted for 0.7% each (Ajani, 2008).

Generally, solid waste from such sources is said to be highly heterogeneous. Thus, they have variable physical and chemical characteristics that depend on their sources. The composition of SW is mostly associated with domestic waste, plastics, metals, wood, papers, rubbers, leather, batteries, textiles, inert materials, paint containers, demolishing and construction materials (Ajani, 2008; Wangatia, 2013). Solid wastes are predominantly generated from;

2.1.1. Industries

Industries are said to be one of the biggest contributors to solid waste generation. They include light and heavy manufacturing industries, fabrication plants, construction sites, canning plants, power, and chemical plants. These above mentioned industries produce solid waste in the form of housekeeping wastes, packaging wastes, food wastes, ashes, construction and demolition materials, medical wastes as well as other hazardous wastes. In heavily industrialized countries, very huge quantities of solid wastes are well accumulated within a very limited range of time. These wastes may have lasting impacts on the soil and subsequent effects on life. For example, at Khirbet Faynan, in southern Jordan, research has focused on interactions between Cu and past and present environments. On the other hand, industrial wastes which contain a significant amount of nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca), organic matter (OM) and trace elements, are considered as a great source of nutrients for plant growth (Nath et al., 2009; Uzma et al., 2016). In the ancient Roman city called Phaino, where large-scale metalworking was conducted (Pyatt et al. 2000). Hauptmann et al. (1992), studied the sedimentary ore-deposits at Faynan and concluded that this site had been exploited since the seventh millennium BC with peaks of Cu production in the Early Bronze Age, Iron Age, and Roman period. Today the site consists of between 80 and 100,000 tons of slag piles, with over 250 Cu mines and accompanying waste areas. The vegetation found within the area exhibits a high accumulation of Cu subsequently

become available to herbivores (Pyatt et al. 2000). It is still obvious that most developing countries are currently undergoing these forms of mining and metallurgy with no proper management of the aftermath of solid wastes. The study of industrial waste characteristics is quite crucial to check the effects of heavy metals on the growth of plants. Plants that were grown in heavy metal contaminated sites are known to usually accumulate higher amounts of heavy metals and contamination occurs in the food chain.

2.1.2. Agriculture

Agricultural production has increased more than three times over the last 50 years due to the expansion of soils for agricultural use; the technological impacts of the green revolution which influenced productivity; and the accelerated growth of the population (FAO, 2017c). Crop farms, orchards, vineyards, dairies, and feedlots are also sources of solid wastes. Part of the wastes they produce include agricultural wastes, pesticide containers, spoiled food, and other hazardous materials.

2.1.3. Residential discharge

Residence, also known as where people live, is a major source of solid waste. The garbage from homes includes food wastes, paper, plastics, glass, leather, metals, cardboard, yard wastes, ashes, and special wastes like bulky household items: old mattresses, tires, batteries, electronics, and used oil. Most homes have garbage bins where they can get rid of their solid wastes. Some of these wastes are being discharged in dumpsite without proper separation in developing countries.

2.2. Forms of solid waste

Biodegradable substances: The type of wastes that decompose naturally in the environment and are considered safe for the environment are known as biodegradable substances. The degradation or decomposition is said to be substances that get decayed with the aid of natural agents such as microorganisms, air, soil, water, sunlight, and ozone into the organic manure. Further, these organic matters are beneficial to the environment in some cases. These materials are mostly non-toxic to the environment and mainly include only natural substances. Plants and animals waste, even the dead plants and animals, paper, fruits, vegetables, etc. get transformed into simpler units, which further get into the soil and are used as manure, fertilizers, biogas, and compost (Hussein and Mona, 2018). They are non-pollutants, non-toxic, eco-friendly to the environment.

Non-biodegradable substances: Materials (e.g., metals, bottles, plastics, glass, poly bags, batteries, chemicals) that remain for a long period of time in the environment, without getting decomposed by any natural agents, causing harm to the environment are known as non-biodegradable substances. As these are readily available, of low cost, and convenient to use, the non-biodegradable substances are more often used. However, instead of returning to the environment, they cannot be broken down/degraded and then become hazardous to the environment. Hence regarded as toxic, pollution-causing and not considered as eco-friendly. They are usually found in dumpsites as a result of waste disposal from residential sources and industries.

Degradable and non-degradable plastics: Plastic is indispensable in contemporary daily life. The development of plastic has gone up considerably since the 1950s. In the year 2017, the world plastic production which had reached 348 million tons (Plastic Europe, 2018). Approximately 50% of plastics are used for single-use disposable products (Hopewell et al., 2009), a large amount of plastics accumulated in the environment have resulted in serious environmental problems. Plastics

are durable and inexpensive, and as a result, the levels of plastic production by humans are high. However, the chemical structure of most plastics renders them resistant to many natural processes of degradation and as a result, they go through degradation slowly. The plastics we use today are made from organic and inorganic raw materials, such as carbon, hydrogen, nitrogen, silicon, oxygen, and chloride.

The basic materials used for the production of plastics are derived from oil, coal, and natural gas. Together, these two factors have given rise to a high prominence of plastic pollution in the environment. The chemical structure of most plastics renders them indestructible by many natural processes of degradation. Therefore, they are slow to degrade. Plastics themselves contribute to approximately 10% of discarded waste. A lot kinds of plastics exist depending on their precursors and the method for their polymerization. Depending on their chemical composition, plastics and resins have varying properties related to contaminant absorption and adsorption (Seymour, 1989). Polymer degradation takes much longer as a result of saline environments. The biodegradation of plastics proceeds actively under different soil conditions according to their physical or chemical properties, because the microorganisms responsible for the degradation differ from each other and they have their optimal growth conditions in the soil.

Plastic pollution on land poses a threat to the plants and animals – which includes humans who are based on the land. Estimates of the amount of plastic concentration on land are between four and 23 times that of the ocean. The amount of plastic found on the land is greater and more concentrated than that in the water. Mismanaged plastic waste ranges from 60% in East Asia and Pacific to one percent in North America (Jambeck et al., 2015). Chlorinated plastic can release harmful chemicals into the surrounding soil, which can then seep into groundwater or to other surrounding water sources and also the ecosystem of the world. This can cause serious harm to the species that

drink from the water. During biodegradation, the organic substances are broken down employing the aid of microorganisms. Several biodegradability tests exist. The so-called “screening tests” are performed in enzymatic or aquatic conditions, and the latter can be anaerobic or aerobic. The “real-life tests” distinguish composting, soil burial and field testing (Lucas et al., 2008).

2.3. Other sources of wastes

There are different sources of toxic elements in urban soils, their loads in and around human settlements are a global concern. The release of metals into soils can persist for a very long duration due to their inability to go through microbial and chemical degradation easily (Olaniran et al., 2013; Araya et al., 2015). They enter the soils by different pathways, including 1) aerial deposition (industries, vehicles, and volcanoes), 2) paints, 3) river and irrigation waters, 4) waste utilization, 5) disposal of degraded sediments, and 6) pesticide and fertilizer application (Aguilar et al., 2013). Other sources are released by automobile, past occupational activities e.g. mining and metallurgy. Anthropogenic activities, such as industrial processing and mining, were reported as the main sources of heavy metal contamination in the environment (Xilong et al., 2005).

2.4. Soil contamination resulting from waste deposition

2.4.1. Heavy metals

Heavy metals are known to be immobile and harmless when in the solid-state but become toxic in their aqueous state. The adverse effect of heavy metals on the environment is related to their availability in soil (Adewumi and Ajibade, 2015). Heavy metal contamination in municipal solid waste (MSW) is of increasing concern, the heavy metals contained in MSW and its transformation products inhibit the beneficial use or disposal of the wastes, resulting in an increasing concern to

MSW management (Zennaro et al., 2005). García *et al.* (2005) proposed that high heavy metal levels in household waste were attributable to inorganic fractions generated by materials such as cans, metals, sand, and particles. The variation of heavy metals concentration in dumpsites is largely determined by human activities and operations that surround each. Ajayi (2005). The maximum concentration of Cu, Cd, Pb, Zn, Fe, and Mn were found in the surface soil of an automobile dumpsite. while the presence of Zn, Fe, Mn, and Pb was also said to be found in municipal dumpsite (Ibitoye et al., 2005) High concentrations of heavy metals in municipal solid waste (MSW) now dominate the outflow from most cities (Bergback *et al.*, 2001). This is a result of human activities like agricultural production, manufacturing, and industrial activities. The major reason for the presence of uncontrolled dumpsites in most localities in Nigeria is as a result of the indiscriminate deposition of the wastes, prevalently food waste, and putrescible materials. While MSW can be reused as organic fertilizer or for soil amendment after biological transformation (Manios, 2004).

Watanabe et al. (1999) reported that a high concentration of the metal (50 mg kg^{-1}) was realised in the textile, rubber, plastic, and leather fractions of the waste. Jung *et al.* (2006) pointed out that bulky and incombustible wastes contain high levels of heavy metals. Veeken and Hamelers (2002; 2003) assessed the distribution of Cd, Cu, Pb, and Zn in biowaste in the Netherlands employing particle fractionation which is based on size and density. On the other hand, García *et al.* (2005) reported that high heavy metal levels in household waste were due to inorganic fractions generated by materials such as cans, metals, sand, and particles. This led to the need to sort waste before disposition which is well implemented in developed countries but still a major issue in developing countries like Nigeria.

2.4. Common heavy metals found in Nigerian dumpsite soils

Soil, in the long run, represents a major sink and source of heavy metal ions, which is eventually incorporated in the food (Oguntimehin et al., 2005). Previous studies had been conducted on Nigerian dumpsite soils to assess their heavy metal contamination. Ihedioha et al. (2017) reported cadmium as the only heavy metal posing a high threat to the environment at the dumpsite located in Uyo, Akwa ibom. The range of heavy metals concentration found in soil was 0.7 to 558 µg/g. This results obtained indicated that these metals on dry weight basis in the soil ranged between (36.60-525.0 µg/g) Pb, (17.50-29.80 µg/g) Zn, (15.00-74.40 µg/g) Cu, (0.7-2.20 µg/g) Cd, (16.16-24.60 µg/g) Ni, and (270-558.0 µg/g) Mn (Kabiru et al., 2018). Municipal waste increases the pH, nitrogen, cation-exchange capacity, percentage base saturation and organic matter of soil (Anikwe and Nwobodo, 2001). Rajesh et al., (2006) further stated that the concentrations of heavy metals in soil, crops, and water are compared with established safe limits as this provides a basis for guiding further activities aimed at curbing excessive exposure of toxic substances (heavy metals) to human beings through control and monitoring of irrigation water and amelioration of uptake by crops.

Lead: Exposure to lead can result in a wide range of biological effects depending on the duration and level of exposure. Lead is a dangerous element, as it can accumulate in individual organism and also in the entire food chains. Lead contamination results from past use of Pb additives in gasoline, deterioration of exterior paint, emissions from smelters, battery recycling, and other industries. Lead usually occurs in mineral deposits along with other base metals, such as Zn and Cu which have been recorded to be mined on all continents except in the Antarctica (Pinho and Ladeiro, 2012). The spatial pattern of contamination by Pb depends on the history of the development of roadways, housing and industries, and is associated with inequitable chronic Pb

exposure. The high Pb content of the soil could also be attributed to exposure to vehicular emissions as well as metal plating and lubricating oils. This could also be due to the rough surfaces of the roads which increase the wearing of tyres, and also the run-offs from the roadsides. The addition of sewage sludge to agricultural soils may also add a tangible amount of lead to soil depending on the source of the sludge (Chopra et al, 2009). The most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust (Akhilesh et al., 2009). In general, plants do not absorb or accumulate Pb. However, in soils containing a high concentration of Pb, some can be taken up. Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops (e.g., squash, beans, corn, tomatoes, strawberries, and apples). Generally, it has been considered rather safe to use garden produce grown in soils with total Lead levels less than 300 ppm (Taylor et al. 2010; Dasgupta et al. 2006). The Joint FAO/ World Health Organization Expert Committee on Food Additives (JECFA) established a Provisional Tolerable Weekly Intake (PTWI) for Lead as 0.025 mg/kg/body weight (JECFA, 2004). The WHO provisional guideline of 0.01 mg/L has been enacted as the standard for drinking water (WHO, 2004)

Copper primarily can be obtained from the ores cuprite (Cu_2O), tenorite (CuO), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), covellite (CuS), chalcocite (Cu_2S), and bornite (Cu_5FeS_4). The average concentration of Cu in the Earth's crust is about 50 ppm and it is a natural element normally found at low concentrations ranging from 50 to 70 ppm in soils (Adriano 2001). However, the process of mining and smelting has been the most important anthropogenic sources of soil Cu through atmospheric and particulate emissions as well as solid and liquid wastes (Ginocchio, 2000). Copper is said to be a microelement and it is a necessary constituent of all organisms, also a component of the soil but if the copper concentration rises above the normal level, it then becomes highly toxic.

When in high doses can cause anemia, liver and kidney damage, it could also cause stomach and intestinal irritation in human through uptake from feeding on plants (Yrule, 2005). The relationship between soil-water contamination and metal uptake by plants is determined by many physical and chemical soil factors and also through the physiological properties of the crops. Soils contaminated by trace metals could cause both direct and indirect threats: direct, could be through negative effects of metals on crop growth and yield, and indirect, by altering the human food chain with a potentially negative impact on human health (Raymond and Felix, 2011). The solubility of Cu is drastically increased at pH 5.5, which is a bit close to the ideal farmland pH of 6.0–6.5. (Campbell, 2006).

Zinc: Zinc is known to be the 23rd most abundant element in the earth's crust. Sphalerite and zinc sulfide is the principal ore mineral in the world (Chesworth 1991). Zinc is added to the soil during industrial activities, such as mining of coal, steel processing, and waste combustion. As a result of this exposure, many food items contain certain concentrations of Zn which they take up from the soil. Water-soluble zinc that is located in soils can contaminate groundwater. Plants often have a certain level of Zn uptake that their system cannot handle, due to the accumulation of Zn in soils (Greany,2005). In the magmatic rocks, it ranges from 40 to 120 ppm whereas in the sedimentary rocks its contents vary from 80 to 120 ppm in argillaceous sediments and shales to only 15 to 30 ppm in sandstones and 10 to 25 ppm in limestones and dolomites (Kabata-Pendias and Pendias 2001). In agricultural soils, Zn ranges between 10 and 300 ppm and is not evenly distributed. The range of total Zn content in soils recorded in literature tends to show an overall mean of 50 to 55 ppm. Other researchers indicate that typical total Zn level in uncontaminated soils can range from 10 to 100 ppm (Smolders and Mertens, 2013). The lowest Zn levels are normally in sandy soils

and the highest are found in calcareous and organic soils. Some researchers indicate mean Zn content for worldwide soils of 64 ppm (Kabata-Pendias and Pendias 2001).

Mercury: Majority of Hg seen in soil, water, sediments, and biota excluding air is in the form HgCl_2 , $\text{Hg}(\text{OH})_2$, HgS , or the organomercuric compound methylmercury (CH_3Hg^+ , MeHg), with other organo-mercuries (i.e. dimethylmercury and phenylmercury) existing in small fractions. Mercury exists naturally in the Earth's crust and soils, with average concentrations usually not exceeding 0.07 ppm and 1.1 ppm respectively (Kabata-Pendias 2011). The main source of mercury is the Sulphide ore cinnabar, mercury (II) forms strong complexes with both organic and inorganic ligands, making it very soluble in oxidized aquatic systems (Alysson and Fabio, 2014) which a high concentration of it could be of effect to the groundwater.

2.5. Other elements

Trace metals (like chromium) distributed indirectly at low concentrations through anthropogenic activities could be toxic. Other elements needed as nutrients usually found on dumpsite soils are calcium, potassium, magnesium, phosphorus and sodium. However, many organizations have used different analytical approaches to estimate the required content of elements suitable for most agricultural soils. Although this is a conventional scale, many regional contents of elements in the soil have been conducted (see Table 1 for details of regulatory values for elements in most soils).

Table 1 International Agricultural Standards of elements contents in the soil. a- according to Nigerian standard (adopted from Osunkiyesi et al., 2014)

REGULATORY VALUES					
S/N	PARAMETER	UNITS	A	(DPR,2002)	WHO (1996)
1	P	mg/kg	>7	-	-
2	K	mg/kg	>80	-	-
3	Cu	mg/kg	100	36	80
4	Hg	mg/kg	1	-	-
5	Cd	mg/kg	1	0.8	0.02
6	Cr	mg/kg	100	100	77.1
7	As	mg/kg	30	-	-
8	Pb	mg/kg	500	85	50
9	Fe	mg/kg	NGVS	5000	-
10	Mn	mg/kg	500	-	-
11	Ni	mg/kg	20	35	35
12	Zn	mg/kg	250	146	50

2.6. Effects of solid waste deposition in the ecosystem

The soil is a primary recipient of solid wastes. Millions of tons of these wastes are derived from varieties of sources: domestic, industrial, and agricultural, find their way into the soil. These wastes end up interacting with the soil system thereby changing the biological, physical, and chemical properties. The accumulation of contaminants is aided by the capability of the soil to bind them with organic substances or clay minerals. Their accumulation has multiple impacts on the usability and functions of soil in the ecosystem (Nielsen, 1997). MSW components such as food residual

and plastic have different environmental risks on heavy metal leaching. As all kinds of MSW components gathering into a landfill site, heavy metals in them converged and became a new artificial sink. Heavy metal absorption is governed by soil characteristics such as the pH and organic matter content (Salt et al., 1996). The contamination of soil with heavy metals is particularly problematic because they are not degraded in soil. Heavy metals in soil cannot be permanently eliminated. At best, they can be locally reduced by redistribution in the ecosystem or removed from circulation by immobilizations (Bakar et al., 1994). This could have several consequences depending on the level and the type of heavy metals present. Metals are commonly associated with municipal wastes. Toxic metals including arsenic can cause a large number of different damaging effects, for example, skin cancer, bladder, lung, and kidney cancers; perhaps other internal tumors, vascular disease, hypertension, and diabetes (Chen et al., 2007). Several studies have indicated the public health and environmental importance of assessing the cumulative health risks that are associated with multi-pathway exposure to heavy metals within the vicinity of municipal solid waste dumpsites (Li et al., 2017). Nowadays, heavy metal pollution from landfills has attracted increasing attention but their source analysis has heretofore been widely neglected. The lack of knowledge about the heavy metal source in MSW not only limits our insights into environmental risk evaluation but also restricts our understanding of policymaking on separation, collection, and sustainable management.

The volume and structure of waste comprise the vital data required for the development and improvement of waste management structures (Beigl et al., 2008). The increased urban waste in various compositions follows the population pressure, economic development, municipal expansion, improvement of people's living (Li, et al 2007) and changing lifestyle of urban population (Gutberlet, 2017). From all indications, the urban growth process is not going to halt

in the coming years. It is therefore important that society found a way to maximize the associated benefits while managing the environmental deteriorating effect through the implementation of sustainable solid waste policies (Kwakwa et al., 2018).

Poor waste management could lead to serious environmental problems such as groundwater pollution and explosion in landfill areas in addition to the unpleasant odours (Mor *et al.*, 2006). More than 90% of total MSW volume is disposed of speciously in open dumps, creating environmental and community health issues. Solid wastes are a main and unavoidable outcome of development and urbanization and have risen as a genuine environmental danger. Growth in most municipal population and the ways of life are moving the attribute of solid waste management in developing nations from a limited risk to a worldwide network issue. Environmental policies regarding solid waste deposition. The management of MSW is a key concern for municipal societies all over the world due to the mounting waste production rates and dwindling waste processing limits as well as growing environmental and health concerns. Anthropogenic activities, such as mining and industrial processing, were recorded as the main sources of heavy metal contamination in the environment (Xilong et al., 2005)

In the past, many researchers proposed inexact optimization techniques for managing uncertainties in ecological management schemes.

2.7. Potential health impacts of soil contamination

Metals cause physiological disorders in soils as absorption through the root system consequently mitigates plant growth and deprives it of vigor (Moustakas et al., 1994). Waste carries different metals which are then transported to plants in different ways (Voutsas et al., 1996). Depending on the tendency of the contaminants they end up either in water held in the soil or leached to the

underground water. Contaminants like Cd, Ni, Cu, Pb, and Zn can alter the soil chemistry and have an impact on the organisms and plants depending on the soil for nutrition (Shaylor et al., 2009).

According to Zhang et al. (2008), studies on the distribution and occurrence of heavy metals in MSW could assist policymakers and management authorities in eliminating the major contaminant sources.

Heavy metals can be transferred to the ecosystem components such as underground water or crops, and can thus affect human health through the water supply and food web. The research findings have shown that the metals concentrations in dumpsites are high and potentially carcinogenic. The risks however varied with the type of metal, level of contamination, season, medium contaminated and age of human exposure to risk.

2.8. Challenges of Solid Waste Management in Nigeria

Most Nigerian cities are often characterized by the public provision of urban infrastructure facilities. These facilities, such as water supply, sewerage, drainage, access roads, solid waste disposal, and collection are usually of poor quality. The administrative structure and financing arrangements of the Nigerian government are pointers to the problem of solid waste management. The three tiers of government in Nigeria are often involved in one way or another in the provision of necessary services in the country's major urban areas. Constitutionally, some of these services fall within the statutory function of one tier of government or another. For instance, the 1989 federal constitution assigned to city councils the responsibility for the construction and maintenance of some categories of roads, for street drainages, for the installation of street lighting and the provision of refuse services. In practice, the state government sometimes steps in to complement the efforts of municipal councils, particularly in those cities that are state/regional capitals. As a result, the responsibilities for waste services varies between Nigerian cities. The

poor state of SWM in Nigeria is also characterized by poor financing of public waste services provision. The annual average financial resources allocated to sewerage, drainage and refuse services by all the states in Nigeria fell from US\$ 163 million between 1981 and 1985 to only US\$ 1.8 million between 2005 and 2010. It was difficult to determine the amount allocated exclusively to solid waste services (Ogu, 2000). This was because the national development plan documents 67 *Journal of Sustainable Development Studies* that were consulted did not disaggregate the allocation to each category. However, public funds for waste services are not usually enough, considering the many expanding cities in the country (Amuda et al., 2014).

CHAPTER THREE

3. METHODOLOGY

3.1. Study area description

The study site Awotan dumpsite (map coordinates, 7°27'41" N 3°50'52" E; Figure 1), is located in Ibadan, Oyo state at approximately 128 km NE of Lagos and 345 km SW of Abuja, the federal capital of Nigeria, The dumpsite has been in existence since 1829.



Figure 1 Map of Nigeria showing the location of the studied dumpsite in Awotan, Ibadan in Oyo state.

The Awotan dumpsite covers an area of approximately 25 ha. The population of the whole area was estimated at 3,552,000 (Owoeye, 2020). Materials commonly deposited on the site are

predominantly domestic waste (polyethylene bags, kitchen waste), industrial waste from nearby industries (waste from paints and herbicides; Figures 2 and 3). Like other parts of Nigeria, Ibadan experiences two local climates; rainy and dry (harmattan) seasons. The rainy season runs from March to October and the dry season is from November to February. The average annual precipitation is approximately 1311 mm. The temperature in Ibadan ranges from 21°C and 35°C in the rainy and dry seasons, respectively. The soil in the study site is characterized by reddish lixisol on Igneous and metamorphic rock (Precambrian Basement Complex; MacDonald et al, 2005). The average waste generation per capita per day in Ibadan is about 0.3 kg. The waste generation in Ibadan can be estimated at 279,289,934 kg/year (307,864 tons per year).



Figure 2. Solid waste deposition at Awotan dumpsite, Nigeria, a) collection of plastic materials, b) evidence of domestic waste disposition c) the dumpsite showing discolored plant species (Siam and milkweeds) which indicate the lack of major plant elements and d) aerial view showing a heap of different wastes.



Figure 3 Solid waste deposition at Awotan dumpsite, predominantly from domestic activities.

3.2. Sampling design

Specific sampling design was conducted to cover the variability of soil samples in the site. The excavations were conducted based on a judgmental sampling technique (Shennan, 1992). The

whole area of the dumpsite was visually divided into four equal quadrants. Bulk soil samples were taken from upper 0-25, 25-50, and 50-75 cm soil layers from each quadrant after removal of surface litters. In all, four excavated pits were sampled - pit A, B, C, and D (see Figure 3). In each excavated pit, six soil samples (2 soil samples \times 3 layers) were collected according to the analyzed soil layers.



Figure 4 The soil profile of, a) upper 25 cm b) 25-50 cm, and c) 50-75 cm layers of the sampled dumpsite.

3.3. Soil sampling

All 24 soil samples were air-dried and subsequently, oven-dried at 40°C for 24 hours. Soil samples were ground in a porcelain mortar and passed through a 2-mm sieve after the removal of living roots and debris for homogenization.

3.4. Particle size distribution

Of all the soil samples, 10 g each from each layer was analyzed to determine the percentage particle sizes. The analysis of particle size distribution of soil samples from the four excavated pits were determined using 2 (very coarse sand), 1 (coarse sand), 0.5 (medium sand), and 0.25 (fine sand) mm sieves (sieve analysis) and compared.

3.5. Soil chemical analysis

Total contents of P, Ca, Mn, S, Cu, Na, Zn, Si, Ti, Pb, Ni, Cl, Th, U, Cd, Co, Al, and Fe were pertinent in this study as they were above the detection limit in all the soil samples. Digestion was done as follows; 50 ml soil sample was measured into a conical flask and 10 ml of concentrated nitric acid (HNO₃) was added. The mixture was heated in the fume cupboard at 120 °C for approximately 20 minutes to near dryness and was allowed to cool and then filtered (using Whatman filter papers 125 mm Ø Cat No. 1001125) before being transferred into a standard flask and then made up to 50 ml with distilled water.

The digested solutions were analyzed for the presence of the studied elements using AAS (Atomic Absorption Spectrophotometer (AAS) Type: S4 AA System, Nc: 942340030042). The pH (H₂O) of all the soil samples was obtained from a 1:1 ratio (soil-water) in two replicates using Voltcraft PH-100 ATC pH meter (pH 212) produced by I & CS spol s r.o., Czech Republic.

3.6. Data analysis

There was relatively homogeneity of variance among data for all analyzed soil samples. To evaluate the differences in particle size, pH as well as elemental contents between analyzed soil samples in all layers (0-25, 25-50, and 50-75 cm), one-way ANOVA was used. We used ANOVA

as there was the normality of data using the Shapiro-Wilk W test. In the case of significant ANOVA, a *post-hoc* comparison using the Tukey HSD test was applied to identify significant differences between soil particle sizes, pH, and content of elements among the layers of soil in all sampled locations. To evaluate the relationship between the content of different elements correlation analysis was used (Pearson correlation). All statistical analyses were performed using STATISTICA 13.4 program (www.statistica.oi).

CHAPTER FOUR

4. RESULTS

4.1. Soil physical characteristics and particle size distribution

The soil texture in the dumpsite is mostly characterized by sandy loam and at a 25-50 cm layer, clay particles were recorded. The soil is mostly coarse, sticky, and plastic. Generally, there were 18.6, 11.7, 43, 21, and 5.3% of skeleton grains, very coarse, coarse, medium, and fine sands, respectively (Table 1). The highest fraction of soil particles was recorded in the coarse soil particles followed by medium sand particles, skeleton grains, very coarse, and the least in fine sand.

Table 2 Texture, consistency, and particle size distribution of soil samples from all analyzed pits in the studied dumpsite

Sampled location	layers [cm]	Texture ^a	Consistency	Particle size distribution [%]				
				≥2 mm	<2-1 mm	<1-0.5 mm	<0.5-0.25 mm	<0.25 mm
Pit A	0-25	SL	Coarse sl. sticky + sl. Plastic	19.4	11.5	41.9	18.2	8.1
	25-50	SL	Sl. Coarse, sticky + sl. Plastic	17.6	11	45	19.9	6.0
	50-75	SL	Sl. Coarse, sticky + sl. Plastic	14.9	11.9	44.1	20.7	8.1
Pit B	0-25	SL	Coarse sl. sticky + sl. Plastic	21.1	12.1	43.8	16.9	5.6
	25-50	SL + C	Coarse, sticky + plastic	18.7	10	40.9	20	10
	50-75	SL	Sl. Coarse, sticky + sl. Plastic	16.2	11.6	43.4	20.4	8.0
Pit C	0-25	SL	Coarse sl. sticky + sl. Plastic	21.4	10.9	41.6	19.9	6.0
	25-50	SL	Sl. Coarse, sticky + sl. Plastic	20.7	10.9	40.6	19.0	8.1
	50-75	SL	Sl. Coarse, sticky + sl. Plastic	17.1	12	42.7	20	8.0
Pit D	0-25	SL	Coarse sl. sticky + sl. Plastic	19.7	12.5	44.3	18.0	5.2
	25-50	SL + C	Coarse, sticky + plastic	18.1	12	40.2	17.2	12.3
	50-75	SL	Sl. Coarse, sticky + sl. Plastic	16.8	10.9	43.7	23.0	5.3
Mean				18.6	11.7	43	21.0	5.3

Abbreviations, ^a- Soil texture according to Jahn et al (2006), SL- sandy loam, C-clay, sl- slightly.

4.2. Soil chemical properties

There was a basic reaction ranging from 9.1 to 10.7 in all analyzed soil samples in all the depth of the studied pits (Table 2). Except for 25-50 cm soil layers in all the pits, there was a significant difference in the pH of the 0-25 and 50-75 cm soil layers in all the pits. There were significant differences difference between the contents of Ca, Mn, S, Cu, Na, Zn, Si, Ti, As, Pb, Ni, Cl, Cd, and Al and vice versa in the case of contents of P, Th, U, Co, and Fe in the 0-25 cm layers of all analyzed pits (see Tables 2 and 3).

Table 3 The pH and total content (mean \pm SD) of P, Ca, Mn, S, Cu, Na, Zn, and Si from excavated pits of the studied dumpsite. F and p-values were obtained using one-way ANOVA. Using Tukey HSD post-hoc test mean values with the same letter were significantly not different.

Sampled location	layers [cm]	pH [H ₂ O]	P [g kg ⁻¹]	Ca [mg kg ⁻¹]	Mn [mg kg ⁻¹]	S [mg kg ⁻¹]	Cu [mg kg ⁻¹]	Na [mg kg ⁻¹]	Zn [mg kg ⁻¹]	Si [mg kg ⁻¹]
Pit A	0-25	9.1 \pm 0.1 ^a	2.5 \pm 0.06 ^a	3200 \pm 120 ^a	621 \pm 17.7 ^a	13.9 \pm 0.1 ^a	968 \pm 21.2 ^a	280 \pm 3.0 ^a	606 \pm 0 ^a	27.2 \pm 0.5 ^a
	25-50	9.8 \pm 0.03 ^a	1.9 \pm 0.004 ^a	3222 \pm 149 ^a	630 \pm 29.0 ^a	13 \pm 0.1 ^a	967.9 \pm 2.9 ^a	297 \pm 3.4 ^a	714 \pm 8.4 ^a	27.8 \pm 1.1 ^a
	50-75	10.0 \pm 0.1 ^a	1.9 \pm 0.008 ^a	3241 \pm 127 ^a	635 \pm 13.4 ^a	11.5 \pm 0.07 ^a	971 \pm 1.4 ^a	320 \pm 0.02 ^a	820 \pm 2.1 ^a	27.9 \pm 0.1 ^a
Pit B	0-25	9.4 \pm 0.0 ^a	2.1 \pm 0.007 ^a	3215 \pm 134 ^b	745 \pm 2.8 ^b	15.7 \pm 0.5 ^b	950 \pm 2.1 ^a	200 \pm 0.0 ^b	717 \pm 8.4 ^b	28.6 \pm 0.6 ^a
	25-50	9.8 \pm 0.04 ^a	1.9 \pm 0.0 ^a	3218 \pm 50 ^a	582 \pm 18.4	12.7 \pm 0.1 ^a	964 \pm 1.8 ^a	200 \pm 0.2 ^b	798 \pm 1.4 ^b	29.9 \pm 0.2 ^a
	50-75	10.2 \pm 0.1 ^a	1.6 \pm 0.0 ^b	3280 \pm 57 ^b	497 \pm 139 ^b	10.6 \pm 0.1 ^a	979 \pm 1.6 ^a	202 \pm 0.1 ^b	892 \pm 0.7 ^b	32.4 \pm 3.3 ^b
Pit C	0-25	10.0 \pm 0.1 ^b	1.9 \pm 0.0 ^a	3210 \pm 71 ^b	398 \pm 5.0 ^c	14.2 \pm 0.1 ^a	986 \pm 2.3 ^b	289 \pm 0.8 ^c	780 \pm 1.4 ^c	35.4 \pm 0.1 ^b
	25-50	10.2 \pm 0.3 ^a	1.8 \pm 0.0 ^a	3395 \pm 196 ^b	384 \pm 43.1 ^c	12.3 \pm 0.2 ^a	992 \pm 1.4 ^b	297 \pm 0.6 ^a	850 \pm 5.6 ^c	35.7 \pm 0.8 ^b
	50-75	10.8 \pm 0.04 ^b	1.7 \pm 0.0 ^{ab}	3407 \pm 290 ^c	380 \pm 20.1 ^c	10.6 \pm 0.2 ^a	996 \pm 1.2 ^c	332 \pm 1.4 ^c	860 \pm 3.5 ^c	35.5 \pm 0.4 ^c
Pit D	0-25	9.3 \pm 0.1 ^a	2.2 \pm 0.007 ^a	3200 \pm 35 ^a	450 \pm 0.7 ^d	13.8 \pm 0.07 ^a	923 \pm 1.6 ^c	280 \pm 4.4 ^d	663.5 \pm 0.7 ^d	36.2 \pm 0.7 ^b
	25-50	9.7 \pm 0.1 ^a	2.0 \pm 0.007 ^a	3210 \pm 37 ^c	331 \pm 11.3 ^d	10.7 \pm 0.2 ^b	943 \pm 4.2 ^b	283 \pm 0.8 ^b	755 \pm 3.5 ^d	35.7 \pm 1.0 ^b
	50-75	10.7 \pm 0.3 ^b	1.5 \pm 0.007 ^b	3257 \pm 137 ^d	344 \pm 25.5 ^d	9.5 \pm 0.1 ^b	953 \pm 3.5 ^d	285 \pm 0.2 ^d	756 \pm 7.1 ^d	35.7 \pm 1.0 ^c
Position (F & p-values)	0-25	16.6, *	1.5, NS	712.1, ***	589.0, ***	16.6, *	12.6, *	0.019, ***	593.0, ***	135.8, ***
	25-50	4.0, NS	5.5, NS	0.024, ***	0.042, **	53.2, **	103.2, ***	1375, ***	229.1, ***	46.1, **
	50-75	7.6, *	22.6, **	3735.0, ***	6.6, *	59.3, **	137.4, ***	5247.0, ***	404.1, ***	8.7, *
Interaction (F & p-values)		17.5, ***	4.9, *	8135, **	18.9, ***	130.7, ***	21.4, ***	2703, **	645.1, ***	21.1, ***

SD indicates standard deviation, *-p<0.05, **-p<0.01, ***- p<0.001

Table 4 Total content (mean \pm SD) of Ti, Pb, Ni, Cl, Th, U, Cd, Co, Al, and Fe from excavated pits of the studied dumpsite. F and p-values were obtained using one-way ANOVA. Using Tukey HSD post-hoc test mean values with the same letter were significantly not different.

Sampled location	Depth [cm]	Ti [mg kg ⁻¹]	As [mg kg ⁻¹]	Pb [mg kg ⁻¹]	Ni [mg kg ⁻¹]	Cl [mg kg ⁻¹]	Th [mg kg ⁻¹]	U [mg kg ⁻¹]	Cd [mg kg ⁻¹]	Co [mg kg ⁻¹]	Al [g kg ⁻¹]	Fe [g kg ⁻¹]
Pit A	0-25	3142 \pm 7.8 ^a	243 \pm 1.1 ^a	94 \pm 6.4 ^a	17 \pm 0.0 ^a	2400 \pm 1.4 ^a	272.9 \pm 3.5 ^a	14 \pm 0.5 ^a	4.7 \pm 0.0 ^a	12.1 \pm 0 ^a	86 \pm 0.0 ^a	223 \pm 1.5 ^a
	25-50	2841 \pm 147.8 ^a	235 \pm 4.5 ^a	93 \pm 11.3 ^a	21 \pm 0.2 ^a	2390 \pm 5.9 ^a	293.6 \pm 4.6 ^a	25 \pm 0.2 ^a	4.6 \pm 0.01 ^a	12.4 \pm 0.13 ^a	87 \pm 0.1 ^a	237 \pm 0.7 ^a
	50-75	3167 \pm 119.5 ^a	283 \pm 2.7 ^a	120 \pm 1.4 ^a	34 \pm 1.6 ^a	2568 \pm 9.1 ^a	242.5 \pm 4.5 ^a	11 \pm 0.6 ^a	4.9 \pm 0.02 ^a	13 \pm 0.16 ^a	89 \pm 0.0 ^a	256 \pm 1.5 ^a
Pit B	0-25	3282 \pm 306.2 ^b	231 \pm 0.9 ^b	77 \pm 3.5 ^b	17 \pm 0.0 ^a	2402 \pm 4.5 ^a	277.4 \pm 3.1 ^a	15 \pm 2.1 ^a	4.8 \pm 0.0 ^a	12.1 \pm 0 ^a	64 \pm 0.4 ^b	240 \pm 1.0 ^a
	25-50	3299 \pm 169.0 ^a	239 \pm 1.6 ^a	80 \pm 1.4 ^a	22 \pm 0.3 ^a	2400 \pm 2.3 ^a	290.0 \pm 0.7 ^a	25 \pm 0.7 ^a	4.6 \pm 0.02 ^a	12.0 \pm 0 ^a	69 \pm 0.1 ^b	266 \pm 1.5 ^a
	50-75	3912 \pm 1130.0 ^b	271 \pm 1.3 ^b	102 \pm 5.7 ^b	35.4 \pm 0.4 ^a	2580 \pm 1.0 ^b	247.2 \pm 8.5 ^a	11 \pm 0.1 ^a	5.3 \pm 0.1 ^{ac}	13.0 \pm 0.10 ^a	68 \pm 0.1 ^b	276 \pm 1.6 ^a
Pit C	0-25	5038 \pm 295.6 ^c	364 \pm 0.3 ^c	103 \pm 5.7 ^c	24 \pm 0.0 ^b	2413 \pm 3.9 ^b	279.3 \pm 5.7 ^a	14 \pm 1.1 ^a	10.6 \pm 0.5 ^b	12.4 \pm 0 ^a	68 \pm 0.2 ^b	254 \pm 1.5 ^a
	25-50	4731 \pm 29.7 ^{bb}	373 \pm 5.4 ^b	120 \pm 1.4 ^b	24 \pm 0.4 ^b	2589 \pm 0.8 ^b	291.6 \pm 1.5 ^a	25 \pm 0.6 ^a	11.2 \pm 0.2 ^b	13.9 \pm 0.01 ^b	80 \pm 0.0 ^a	258 \pm 2.5 ^a
	50-75	4826 \pm 176.8 ^b	417 \pm 7 ^c	128 \pm 0.0 ^b	39 \pm 0.1 ^b	2609 \pm 0.1 ^a	240.5 \pm 1.8 ^a	12 \pm 1.5 ^a	15.2 \pm 0.1 ^b	14.6 \pm 0.04 ^b	88 \pm 0.1 ^a	280 \pm 2.2 ^a
Pit D	0-25	4746 \pm 70.7 ^d	262 \pm 0.6 ^d	80 \pm 1.4 ^b	25 \pm 0.0 ^b	2401 \pm 2.6 ^a	276.8 \pm 2.1 ^a	15 \pm 2.3 ^a	4.9 \pm 0.0 ^a	12.1 \pm 0 ^a	67 \pm 0.0 ^b	261 \pm 2.1 ^a
	25-50	4715 \pm 112.4 ^b	278 \pm 0.9 ^b	102 \pm 5.7 ^a	22 \pm 0.1 ^a	2397 \pm 1.3 ^a	290.2 \pm 0.2 ^a	25 \pm 0.6 ^a	5.4 \pm 0.14 ^a	12.6 \pm 0.1 ^{ab}	85 \pm 0.2 ^a	272 \pm 1.6 ^a
	50-75	5096.5 \pm 48.8	344 \pm 2.1 ^d	103 \pm 2.1 ^c	34 \pm 0.6 ^a	2580 \pm 1.4 ^b	241.1 \pm 2.8 ^a	11.3 \pm 0.5 ^a	6.1 \pm 0.1 ^{ac}	13 \pm 0.01 ^a	87 \pm 0.3 ^a	283 \pm 2.0 ^a
Position (F & p-values)	0-25	41.2, **	0.0012, ***	19.5, **	163.2, ***	0.7, *	1.0, NS	0.2, NS	270.1, ***	0.2, NS	43.1, **	2.1, NS
	25-50	118.4, ***	630.7, ***	13.7, *	36.9, **	1759, ***	0.9, NS	0.5, NS	1479.0, ***	242.9, ***	61.2, **	1.6, NS
	50-75	4.7, NS	575.2, ***	34.9, **	15.5, *	27.7, **	0.7, NS	0.3, NS	4961.0, ***	173.2, ***	89.8, ***	0.9, NS
Interaction (F & p-values)		11.5, ***	816.6, ***	25.4, ***	510.2, ***	1770, **	58.7, ***	56.5, ***	864, ***	314, ***	66.6, ***	2.4, NS

SD indicates standard deviation, * - p<0.05, ** - p<0.01, *** - p<0.001

Except for the total contents of P, Th, U, and Fe, there were significant differences between the total contents of Ca, Mn, S, Cu, Na, Zn, Si, Ti, As, Pb, Ni, Cl, Co, Cd, and Al in the 25-50 cm soil layer of all the studied pits. Again, the total contents of P, Ca, Mn, S, Cu, Na, Zn, Si, As, Pb, Ni, Cl, Cd, and Al were significantly different in the 50-75 cm soil layers of all the pits except for Ti, Th, U, and Fe. There was generally, a significant difference in all the studied elements in all the pits except for the total content of Fe. The highest contents of total Ca, Cu, Zn, Si, Ti, As, Pb, Ni, Cl, Cd, Co, Al, and Fe were recorded in the 50-75 cm soil layers in all the studied pits compared to the 0-25 and 25-50 cm soil layers. There were relatively higher contents of all the studied elements in the 25-50 cm soil layer in comparison to the 0-25 cm soil layer (Tables 2 and 3).

The total P content ranged from 1.5 to 2.5 (in g kg⁻¹) was recorded in pit A and pit D, respectively. The content of total Ca was lowest (3200 mg kg⁻¹) in pit A and the highest content (3407 mg kg⁻¹) was recorded in pit C, respectively. The total Mn content ranged from 331 mg kg⁻¹ in pit D to 745 mg kg⁻¹ in pit C. The lowest (9.5 mg kg⁻¹) total S content was recorded in pit D and the highest (15.7 mg kg⁻¹) in pit B. Total Cu content was lowest (922 mg kg⁻¹) in Pit D and highest (978 mg kg⁻¹) in pit B. The total Zn content was lowest (606 mg kg⁻¹) in pit A and highest (891 mg kg⁻¹) in pit B. The content of total Na ranged from 200 to 332 in-pit A and pit C, respectively. A range from 27.2 to 36.2% of total Si was recorded in pit A and D, respectively (see Table 2).

Additionally, the content of Ti ranged from 3142 to 5096 mg kg⁻¹ in pits A and D. The lowest (231 mg kg⁻¹) As content was in Pit A and the highest (417 mg kg⁻¹) in Pit C. The lowest (77 mg kg⁻¹) Pb content was in Pit B and D and highest (128 mg kg⁻¹) in Pit C. Again, the lowest (17 mg kg⁻¹) content of Ni was in Pits A, B, and C and the highest (35 mg kg⁻¹) in Pit B. The content of Cl was lowest (2391 mg kg⁻¹) in Pit A and highest (2590 mg kg⁻¹) in Pit C. Additionally, the lowest (241 mg kg⁻¹) Th content as recorded in Pit D and the highest (294 mg kg⁻¹) in Pit A. The lowest

(11 mg kg⁻¹) content of U was in Pit B and the highest (25.2 mg kg⁻¹) in Pit D. The content of Cd was lowest (4.6 mg kg⁻¹) in Pit B and the highest (15.2 mg kg⁻¹) in Pit C. In addition, content of Co was lowest (12 mg kg⁻¹) in Pit B and the highest (14.6 mg kg⁻¹) in Pit C. The lowest (in mg kg⁻¹) Al (64), and Fe (223) contents were observed in Pits B and A, respectively. The highest content of (in mg kg⁻¹) Al (8.9), and Fe (28.3) were recorded in pits A, and D, respectively (see Table 3). Except for the content of P and Th, there was a positive correlation between pH and content of Pb, As, Cd, Co, and Na. There was a positive correlation between As and Pb, Ca and Pb, Ca and Zn, and Ca and Si contrast to a negative correlation between P and Ni, P and As, P and Cu, and P and Ca (Figures 4-7).

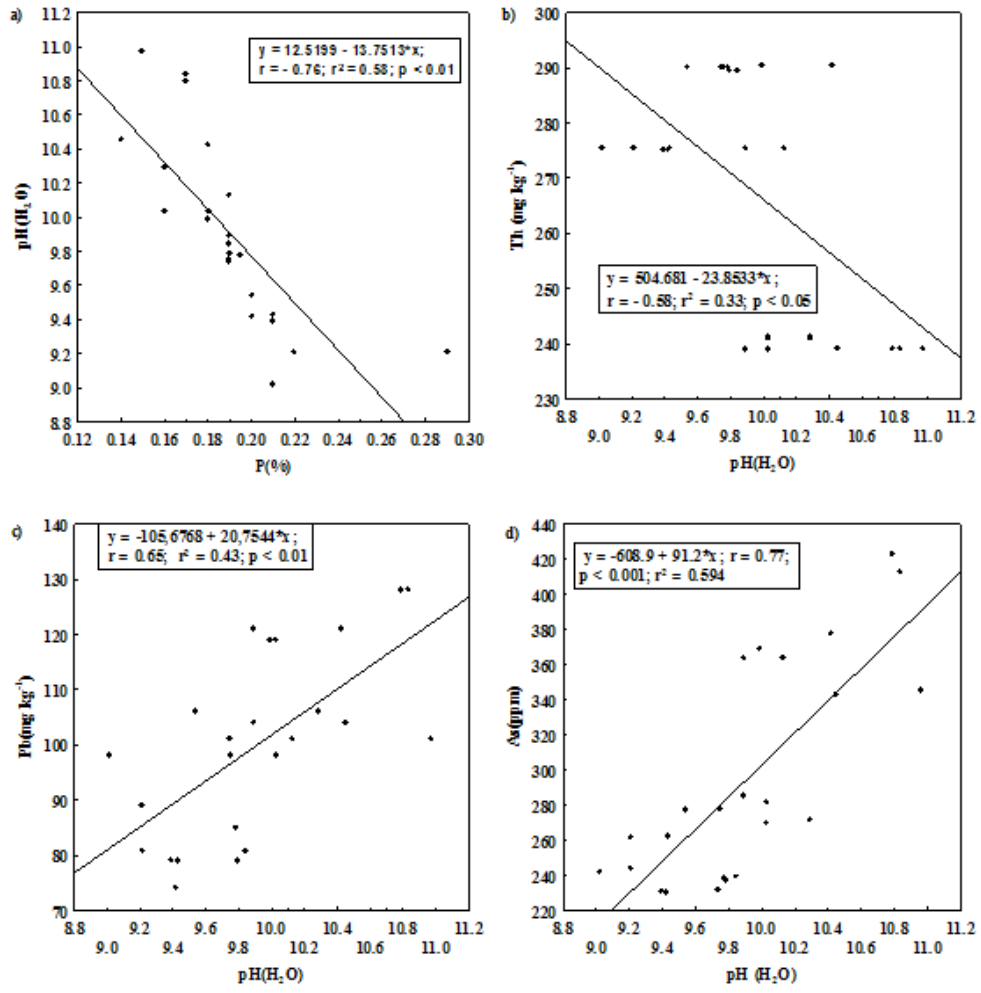


Figure 5 Relationship between, pH (H₂O) and P (a), Th (b), Pb (c) and As (d).

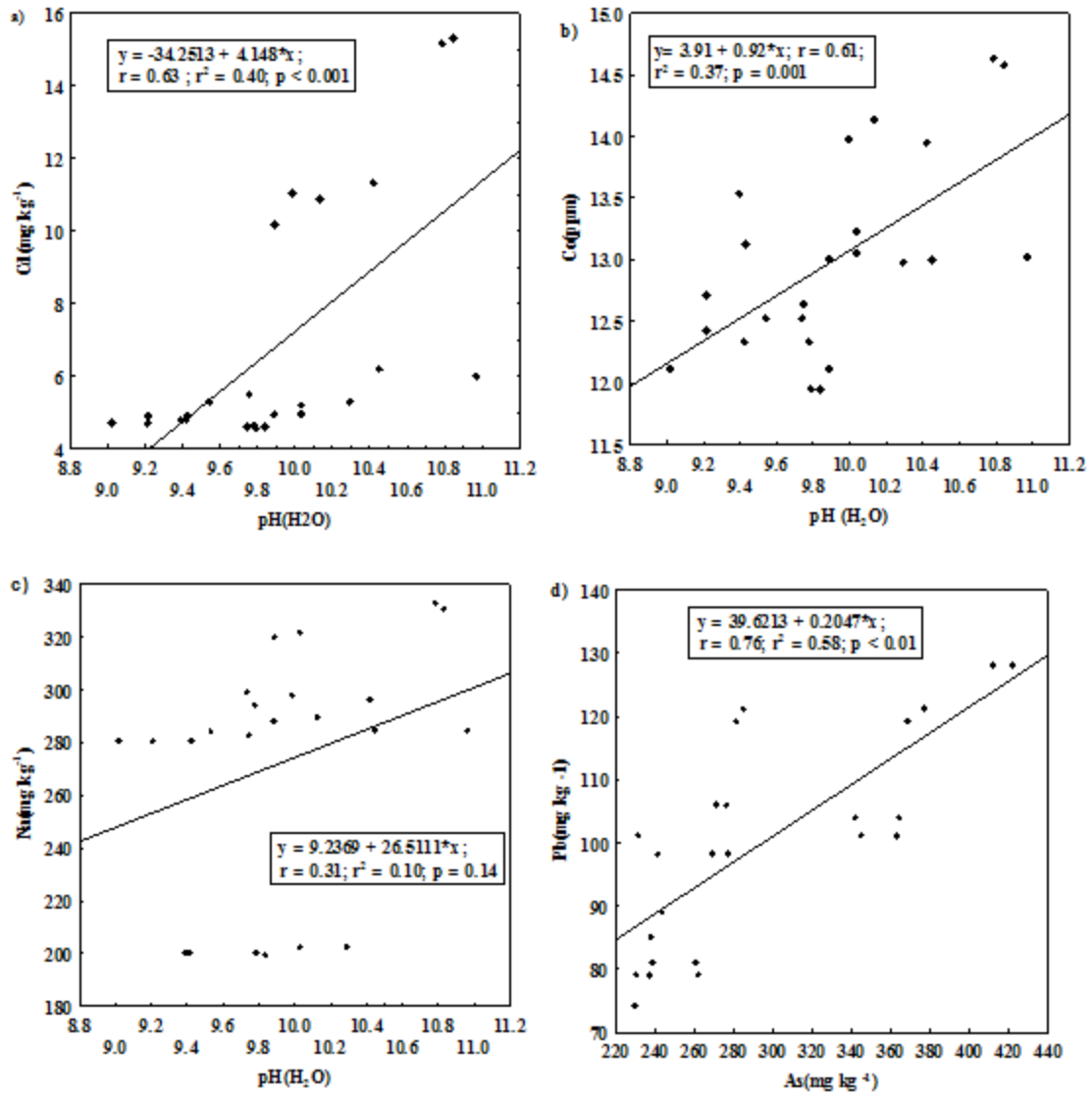


Figure 6 Relationship between, pH (H₂O) and Cd (a), Co (b), Ni (c) and between As and Pb (d).

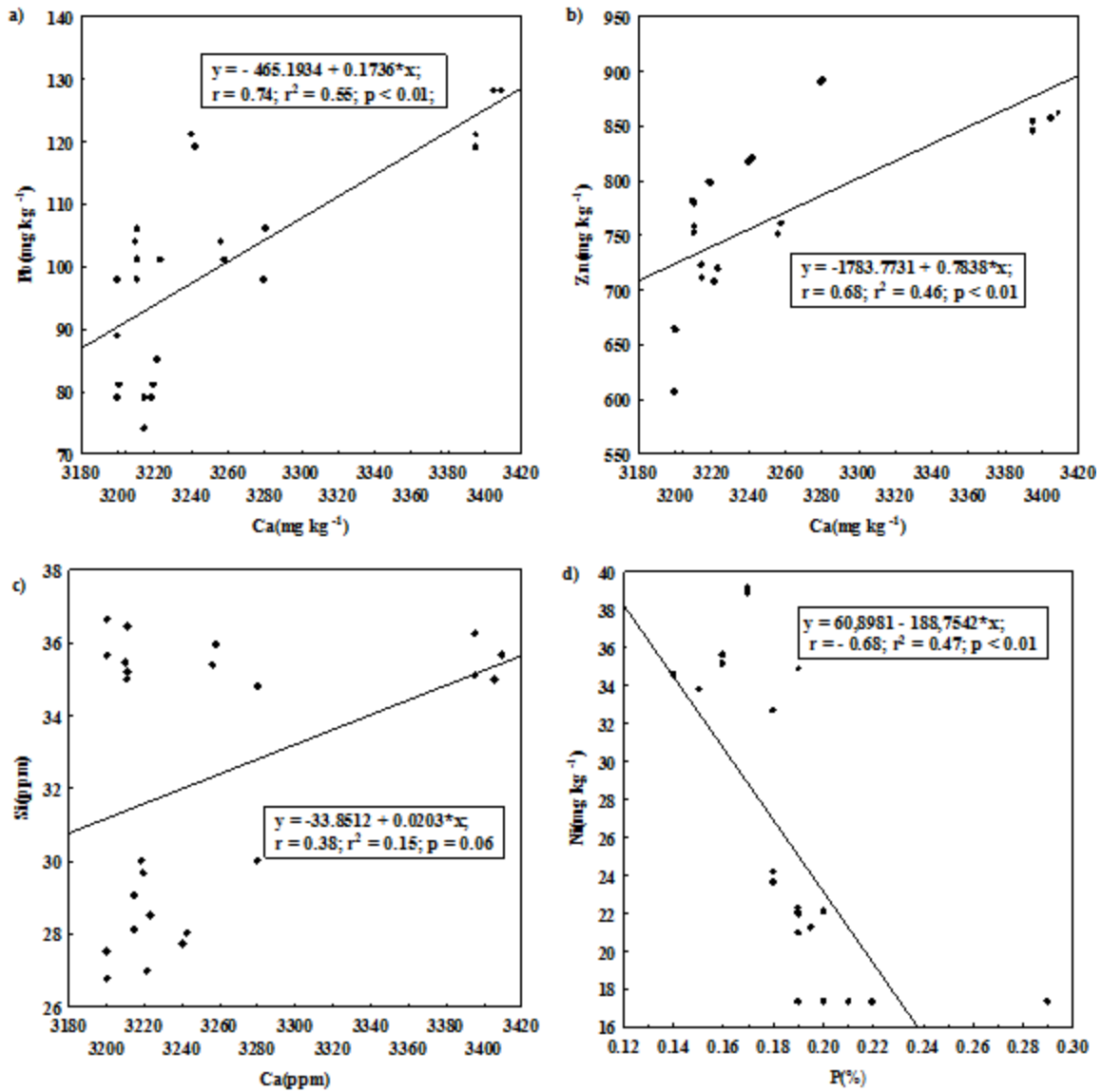


Figure 7 Relationship between Ca and Pb (a), Ca and Zn (b), Ca and Si (c) and P and Ni(d).

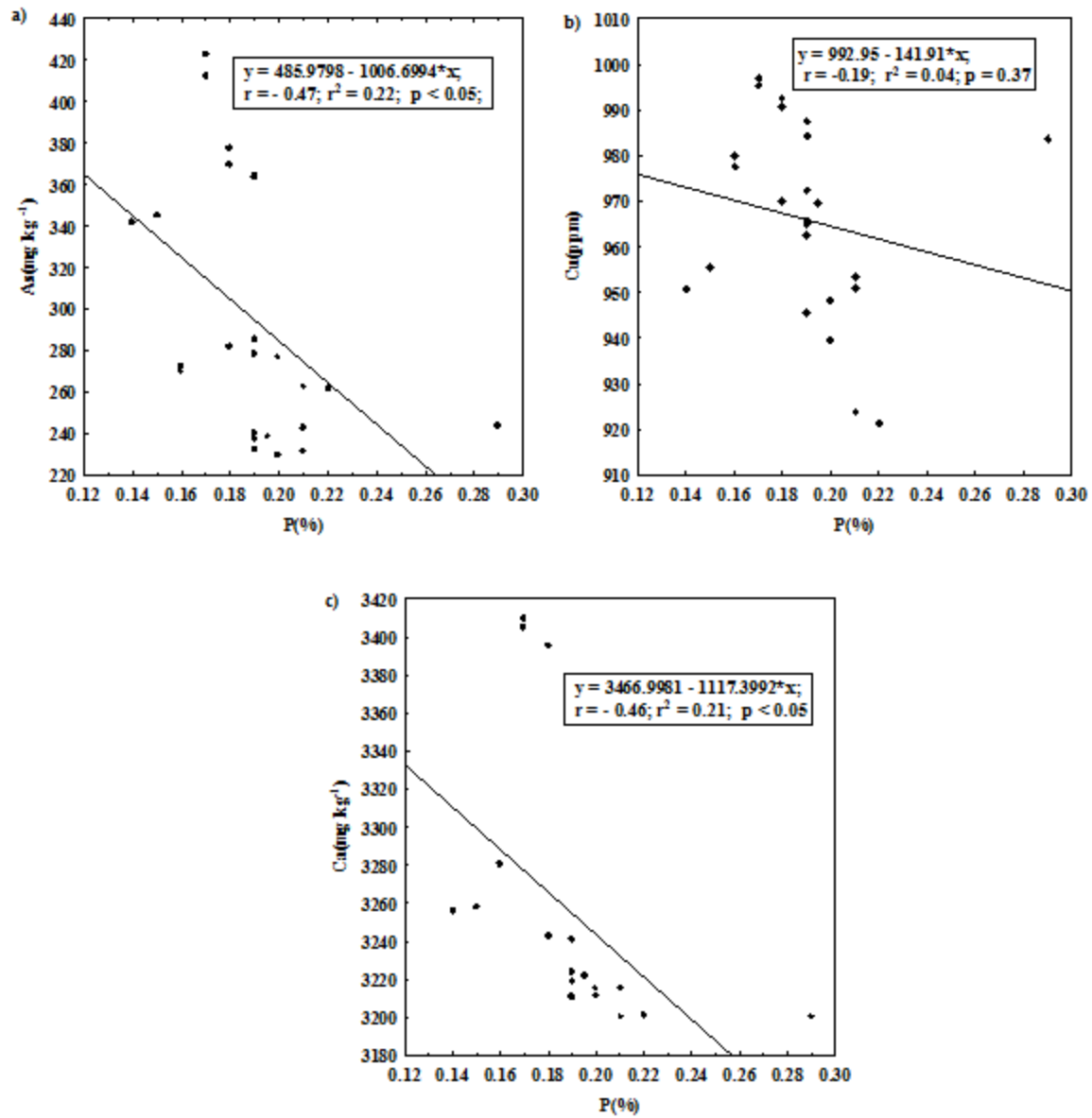


Figure 8 Relationship between P and As (a), Cu (b), and Ca (c).

CHAPTER FIVE

5. DISCUSSION

The main message of this study was that the long-term disposition of solid waste generated from homes and industries resulted in the substantial accumulation of risk and other metallic elements (Cu, Zn, Ti, As, Pb, Cd) in the soil. The effect of the accumulation is still visible even after several decades of banning the disposition of the waste mentioned above. This message is important as it solved the question of 'at what level and how long can the effects of solid waste deposition affect the soil elemental contents with potentially toxic elements. Also, most abandoned dumpsites in Nigeria are often used as arable fields for the cultivation of crops especially vegetables without detail soil chemical analysis. Although there was the surface disposition of the solid waste, the effect on the soil could be detrimental identified from the accumulation of the studied risk elements in the subsoil layers.

The fraction of coarse particles in the studied soil was approximately 90% higher than the fine particles. Besides, there was a relatively high fraction of skeleton grains indicating that most of the studied elements leached into the lower layers of the soil. This is confirmed by the accumulation of some risk elements (Ti, As, Pb, and Cd) in the 25-50 and 50-75 cm soil layers of this study.

Notably, the pH of the soil in all the analyzed layers of the soil was basic (9.1-10.8), which influenced the content of some elements such as P, even though such sites are noted of the high accumulation of P due to the disposition of organic waste (Osunkiyesi et al., 2014). This basic soil reaction can also be attributed to the local geology of the site. The content of P, Ca, Mn, S, Fe, Al, and Si in all the analyzed pits were relatively within the recorded range in most Agricultural soil (Alloway, 2008). The content of these elements could contribute to the proper growth of arable crops and other higher plants, yet, the content of other risk elements may subsequently be

accumulated. The content of both Al and Si respected their natural content in the local geology. However, there was a marginal accumulation of the contents of P, Ca, Mn, S, Fe, Al, and Si from the upper soil layers to the 50-75 cm layers in all the analyzed pits.

Although Cu and Zn are important microelements needed in plant growth, the content of Cu and Zn exceeded the threshold level in most Agricultural soil - 100 mg kg^{-1} for Cu and 300 mg kg^{-1} for Zn (Alloway, 2008). The accumulation of both elements can result from the disposition of waste from metallurgical activities such as smelting and illegal mining activities that once thrived in the area before the abolishment of waste deposition (Liao et al., 2008). The sources of this accumulation are confirmed based on the slags of Cu in the dumpsite. There was a substantial accumulation of both Cu and Zn in the soil from the dumpsite. Comparing the Cu content to permissible limits in the soil by WHO, Cu content was 8 times greater (WHO, 1996). The accumulation increased with increasing depth. The direct negative effects of plant-Cu uptake lead to poor growth rate and low yield. Copper acts as a cofactor for numerous enzymes and plays a major role in the central nervous system development. However, a high dose in the human food chain through ingestion leads to neurological disorders such as Aceruloplasminemia, Alzheimer, Amyotrophic lateral sclerosis, and Huntington diseases (Desai and Kaler, 2008). Residents and workers of ancient Cu mining and smelting center in Wadi Faynan in southern Jordan may have been exposed to Cu and Pb through inhalation and ingestion of airborne particulates, ingestion from trophic-level accumulation of cations (from food) and the drinking of contaminated water. This was confirmed by chemical analysis of skeletons of copper miners, which indicates significant heavy metal loads with values of Cu at 55 ppm and Pb 375 ppm (Pyatt and Grattan 2001).

Also, the content of Zn was 3- 4.7 times greater than the permissible limit according to WHO and another reference level such as DPR (2002). Zinc content in natural soil represents the chemical composition of the parent rock and the extent of weathering processes (Chesworth, 1991). In the magmatic rocks, it ranges from 40 to 120 ppm whereas in the sedimentary rocks its contents vary from 80 to 120 ppm in argillaceous sediments and shales to only 15 to 30 ppm in sandstones and 10 to 25 ppm in limestones and dolomites (Kabata-Pendias and Pendias, 2001). In agricultural soils, Zn range between 10 and 300 ppm and is not uniformly distributed. The range of total Zn content in soils reported in literature tends to show an overall mean of 50 to 55 ppm. Other researchers indicate that typical total Zn contents in uncontaminated soils can range from 10 to 100 ppm (Mertens and Smolders, 2013). The lowest Zn values are normally in sandy soils and the highest in calcareous and organic soils. Some researchers indicate mean Zn content for worldwide soils of 64 ppm (Kabata-Pendias and Pendias, 2001).

Spatial and multivariate analysis of 800 years of mining and smelting in Kutná Hora, Czechia, revealed a list of metal contaminants. However, the increased content of Zn was ascribed to the processing and smelting which Zn was prominent. (Horák and Hejzman, 2016). Some of the identified elements.

Content of Pb was 1.5 to 2.5 times greater in the dumpsite in comparison permissible limit according to WHO (1996) and DPR (2002). However, in the 50-75 cm layers, Pb content was significantly higher in comparison to values obtained by DPR (2002). The risk of Pb poisoning in the food chain is elevated as the soil increases in Pb concentration. Meanwhile, at above 300 ppm of Pb content in the soil, most of the risk is deposited on plants rather than root-plant uptake (Rosen 2002). However, in soil tested of high Pb concentration, there is a high possibility of plant uptake.

Leafy vegetables and surface of root crops have the highest tendency for the accumulation of Pb as the fruiting part and fruit crop does not readily accumulate.

Similarly, the content of As, Cd was significantly greater in comparison to values by proposed DPR and WHO. It must be highlighted here that these metals are considered mobile under common thermodynamic soil conditions and could easily pollute the groundwater. The content of the metal significantly correlated with high pH values indicating the increasing pH caused by the disposition of solid waste there could still increase the tendency of metal contamination. We can conclude that the pH of the soil in the study site was favorable to retain the risk elements. The higher accumulation of these elements is a direct result of intensive and long-term deposition of solid waste for approximately 200 years. However, the effect of past disposition of other domestic waste contributed to this accumulation. The real surprise was the comparatively lower content of P and was due to the effect of higher pH which makes them form complexes with other elements. The reliable indicator of past disposition (anthropogenic) in this sense was the risk elements that form significantly positive correlations with the pH, not in the case of P which is very persistent in anthropic soils.

In the past decades, many dumpsites in Nigeria are turned in to arable fields for the cultivation of predominantly vegetables. These sites are considered very rich in plant nutrients and may consequently produce the required yield. Although this can partly be true, the recent industrialization and the spill of oil has rendered many soils in the country highly contaminated with risk and other metals.

This work forms part of the maiden research revealing the states of dumpsite soil and their long-term effect on soil and potential uptake by plants.

CHAPTER SIX

6. CONCLUSIONS

The comparative elemental analysis of dumpsite soils and other reference levels indicated that long-term disposition of solid and other forms of waste resulted in substantial accumulation of risk (Ti, As, Pb, and Cd) and other metals (Cu and Zn) which subsequently resulted in soil contamination. The intensity of the contamination is supported by the gradual leaching of the elements mentioned above in the deeper layers of the soil. The high leaching of elements is complemented by the high proportion of very coarse sand particles.

The enrichment factor showed that Cu, Zn, Cd, As, and Pb are essentially from the anthropogenic source while Fe, Al, P, Ca, and Na may originate from natural and anthropogenic sources.

There is a growing concern about the gradual build-up of toxic metals in the dumpsites as a greater percentage is in the mobile fractions. These will become available to plants or groundwater over geological time scale where they are biomagnified. The information on the potentially available trace metals, as opposed to estimated total metals, may be useful in designing remediation programs for contaminated sites and future agricultural use. It provides information on the relationship between contaminants and the environment. It is recommended that the government should consider a basement treatment for dumpsites before use. This will provide sorption surfaces for pollutants and prevent groundwater contamination.

In conclusion, the enrichment of soils as a result of the disposition of solid waste in dumpsite is highly unsuitable for arable fields due to the subsequent uptake of the risk elements by plants. Therefore, thorough soil chemical analyses are encouraged in such sites.

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Difference types of solid waste in the dumpsite.