Assessment of Heavy Metals; Lead (Pb), Cadmium (Cd) and Mercury (Hg) Concentration in Amaenyi Dumpsite Awka

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Abstract- The study investigated Assessment of heavy metals; lead (pb), cadmium (cd) and mercury (hg) concentration/load in Amaenyi Dumpsite Awka. The sample was collected and analysed digested and analysed in the laboratory. The Analysis of the samples shows that the samples contain heavy metals such as cadmium, mercury, and lead and high in concentration. This concentration of the heavy metal is higher than W.H.O approved limited of heavy metal in soil samples. Therefore, the study recommended that Designated places should be used as dumpsites and indiscriminate marking of dumpsites be discouraged. Dumpsites should be treated before use especially for cultivation and people living around these dumpsites should stop farming on or around them as well as designated places should be used as dumpsites.

Indexed Terms- Heavy Metal and Dumpsites

I. INTRODUCTION

1.1 Background of the study

The proper wastes disposal has been a serious problem in Awka and most cities in Nigeria. In Nigeria, leachates from refuse dumpsites constitute a source of heavy metal pollution to both soil and aquatic environment (Obaliagbon & Olowojoba, 2006). In some cases, waste are dumped recklessly with no regards to the environmental implications, while in some dumpsites, waste is burnt in the open and ashes abandoned at the sites. The burning of waste gets rid of the organic materials and oxidizes the metals, leaving the ash richer in metal contents. After the process of oxidation and corrosion, these metals will dissolved in rain water and leached into the soil from where they are picked up by growing plants, thereby entering the food chain. Improper wastes management methods also pilot the contamination of underground water, while most of the metals are being washed away by runoff into streams and rivers thus contaminating the marine environment. Consequently, these metals accumulate in fish and other organisms (aquatic), hence posing a health threat to the consumers (Njojju & Ayoka, 2006).

Amongst all the classes of pollution, solid wastes pose the greatest threat to life, since, it has the potential of polluting the terrestrial, aquatic and aerial environment. Land pollution by component of refuse such as heavy metals has been of great concern in the last decades because of their health hazards to man and other organisms when accumulated with a biological system (Adekunle *et al.,* 2012). Recent studies have also reviewed that waste dumpsite can transfer significant levels of these toxic and persistent metals into the soil environment. And eventually these metals are taken up by plant part and transfer same into the food chain. Consequently, higher soil heavy metals concentration can result in higher levels of uptake by plants. Although, the rate of metal uptake by crop plants could be influenced by factors such as metal species, plants species, plant age and plant part. In Awka metropolis, most of the dumpsites are used as fertile soils for the cultivation of some fruits and vegetables. Some farmers collect the decomposed parts of the dumpsites and apply to their farms as manure. These cultivated plants take up these heavy metals either as mobile ion in the soil solution through their roots or through their leaves thereby making it unfit for human consumption (Uzoho & Oti, 2006).

Heavy metals are metals with a density at least five times that of water. Heavy metal is the term commonly adopted as a group name for the metals which are associated with pollution and toxicity. They may also include some elements which are very essential for living organisms at low concentrations. Among these heavy metals some have been found to be of serious hazard to plants and animals and have listed by the European Commission to include;

As, Cd, Cr, Cu, Pb, Hg, Ni, Al and Zn. Heavy metals are stable elements that cannot be metabolized by the body, as such they are passed up in the food chain to human beings (Bioaccumulation). The most common and harmful heavy metals are Al, As, Cd, Cu, Pb, Hg and Ni etc. Heavy metals in general have no basic function in the body and can be highly toxic. They are present in drinking water, food and countless human-made chemicals and products (Jekin, 1989).

In the last 50 years, human infection by heavy metals had risen dramatically; this is as a result of an exponential increase in the use of heavy metals in industrial processes and other human activities. Pollution of the environment by heavy metals results mainly from these activities. For example, refuse dumping, agricultural activities, industrial activities among others. The presence of heavy metals in the environment especially in food materials poses a serious threat to both health and socio-economic wellbeing of man and his environment. With the knowledge that waste dumps are potential sources of heavy metals contamination, it is believed that there would be heavy metals contamination in residential and commercial areas in urban areas (Jekin, 1989).

1.2 Statement of problem

The environment has over the years faced adverse natural and anthropologenic challenges including overpopulation, rapid loss of biodiversity, global warming and waste management. Urban managers in developing countries, in particular, face an enormous array of problems. Some of the most important ones are poor housing, unemployment, land degradation, and waste management with the range of problems requiring immediate attention constantly increasing. In the midst of new initiatives and uncertain solutions to all of these and several other demanding situations, the quality of the environment is deteriorating. Environmental pollution from solid waste land filing (SWL) is of major concern to both environmental scientists and individual citizens. SWL inevitably generates chemicals or pollutants that reach their surroundings, such as soil, groundwater resources, and even the ambient air, because of environmentally unacceptable disposal of solid waste, or failure of lining system in the dumpsites. It is feared that some of the adverse consequences are the noticed increase in disease incidence especially cancer, kidney infection and damage, as well as problems of the cardiovascular system and gastroenteritis (Agbozu et al., 2001; Rajappa et al., 2010). The practice of dumping of refuse and wastes is common in both the old urban areas and the new-urban areas adjoining those (Bhaskar et al., 2010). Efficient waste management requires provision of well selected, designed and operated sanitary landfills. Due to the importance of good water quality, monitoring of pollutants has become imperative. Increasing amount of MSW emanating from residential, commercial and industrial areas, together with changing nature of waste over time, have led to the degradation of the quality of the environment. Municipal Solid Waste (MSW) disposal in Nigeria is particularly a growing problem in urban areas such as Awka, Onitsha, Lagos, Aba and Port Harcourt. Environmental sound management and increasing difficulty in treating organic waste is of major concern in these cities. Waste management planning, operation and maintenance strategies and systems for the management of materials for which there is no further use for a particular purpose at a specific time, can be approached in four ways namely; source reduction, recycling and composting, waste to energy conversion facilities and landfills. Landfills, most of which are open and uncontrolled dumpsites, are the most common waste disposal systems in Nigeria. Most of these waste landfills are improperly designed due to their low capital investment, thus allowing for environmental pollution in those areas. The health risk and the effect on the quality of livelihood cause by this practice calls for comprehensive approach to the assessment of the impact of waste dumpsites on the environment. Most researchers depend on the hydro chemical and geochemical analysis (Khanal, 2007), in determining the level of environmental impact caused by this practice. These analyses depends on samples which are picked from selected location from the sites hence may not give true picture of the overall level of pollution in the areas. This study therefore seeks to determine the environmental impact caused to communities around solid waste dumpsite in the Awka Metropolis.

1.3 Significant of study

The benefits of heavy metal tests are important to recognize as their value is immeasurable when heavy metal exposure is suspected. Toxic metals cause serious damage within the body and can affect every organ system causing and/or contributing to brain, nervous system, immune system, cardiovascular and hormone problems. Heavy metal analysis is excellent for all around assessment of past exposure to heavy metals. Blood testing is worthwhile forcing exposure to various metals like lead and mercury, and urine testing is best used as a base line prior to heavy metal detoxification or as a way to track metal excretion when undergoing heavy metal detoxification therapy. The benefits of heavy metal tests unfortunately are not regularly appreciated by traditional medicine practitioner, but are often seen as a vital tool in the practices of integrative medical doctors.

1.4 Aims and Objectives of the Study

In line with the study problem, this study is aimed at the following:

Aim: To access the level of heavy metal (Lead, Cadmium and Mecury) pollution in dumpsite of Amaenyi Awka.

Objectives;

- Determination of the level of soil pollution around the waste dump site and the community where they are sited.
- Determination of the level and extent of ground water pollution in the catchment area of the dumpsite.
- Using my findings to produce a model for disposing of solid waste in similar environment.
- To suggest possible ways of managing or reclaiming contaminated soil.

1.5 Scope of the Study

The scope of this study is wide, ranging from collection of sample, digestion, determination of pH and the use of Atomic Absorption Spectrophotometer (AAS) to determine the concentration heavy metals (Lead, Cadmium and Mecury).

1.6 Limitation of the Study

The data of this project work focuses only on the concentration of heavy metals ((Lead, Cadmium and Mecury) in a dumpsite of Amaeyi-Awka in Anambra state, Nigeria.

II. LITERATURE REVIEW

2.1 Solid Waste

In any human society, bulk solid waste is produced as a bye product of normal and fundamental activities of living. These wastes can be as rudimentary as food scraps, ash from fires, and excreta from humans and animals. In a modern, highly industrialized society, however the waste goes much beyond the fundamental materials both in quantity and variety. The amount of waste produced by intensive agriculture and modern industry activities are staggering, to say nothing of waste generated by ordinary citizens in a wealthy consumer-oriented urban setting (Alan, 2006).

We use the word waste with some hesitation. Almost any substance that is discarded, and is therefore designated as waste, can also be thought of as a potential resource. Throughout human history, societies have found ways in which to use waste-organic residues as fertilizers, animal dung as fuel, inert materials as landfill. In the present era too, there is effort to discover new uses for materials that have served their primary purpose. This has given rise to a concept of refuse recycling. Alongside these efforts are ones to minimize the production of waste by products so that a reduced quantity of residual materials remains to be discarded.

With or without the reduction/refuse/recycling efforts, some solid materials that must be discarded are inevitably an end product of many activities (Alan, 2006).

2.2 Significant of study

Solid waste materials are disposed of on land. The solid waste covers a wide range of types – everything from animal manures, to municipal garbage to waste steel from automobiles, to mine tailings. The waste materials inevitably interact chemically and physically with environmental components but the time scale over which such reactions occur may be short or long depending on the type of materials and their degree of exposure. Disposal of waste can also be done by incineration (burning the refuse), compositing, land filling, open dump system etc (Adekunle *et al.,* 2012). The dumping of these refuse have introduced many substances in our environment which possess threat to our society e.g. heavy metals.

2.3 Behaviour of Inorganic (Heavy Metals) Contamination in the Soil

The most prevalent group of element in the sub soils is the transition metals otherwise called heavy metals. Examples include Copper (Cu), Iron (Fe), Manganese (Mn), Zinc (Zn), Mercury (Hg), Arsenic (As), Lead (Pb), Nickel (Ni), etc. These metals may occur in soil due to industrial or from refuse dumps.

2.4 Lead (Pb)

Lead is a soft heavy metallic element. It was one of the nine chemical elements known and used in the ancient world. Throughout history it has been widely employed in arts and architecture and in modern times it has been used in making printer typefaces and reaction shields. It is used as element in lead storage batteries, solder, plumbing, cable covering is also recognized. It is used in interior paints. It causes serious hazards because lead is highly toxic if improperly handled (Wajahat *et al.,* 2006). Lead in the solid is bought into solution either by digesting it with hydrochloric acid solution. The extract is used to determine the element using Atomic Absorption Spectroscopy (AAS). The element has a wave length of 280mm.

Lead can cause severe health effects at relatively low levels of exposure. It is found in organic and inorganic forms. Inorganic lead affects typically the nervous system (CNS), peripheral nervous system (PNS), haematopoietic, renal, cardiovascular and reproductive system. Organic lead toxicity tends to predominantly affect the central nervous system. Inorganic lead enter the body by way of ingestion or inhalation, for adult only about 10% of the ingested dose is absorbed in contrast, children may absorb as much as 50% of an ingested dose.

Lead affects the production of blood cells, kidneys and behaviour. It passes the placenta and can damage the foetal nervous system, increasing the risk for premature birth, or low birth weight and size babies or it can induce miscarriage. Nutritional deficiencies increase the risk for lead absorption and toxicity (Wajahat *et al.,* 2006).

2.5 mercury

The metallic mercury is a naturally occurring metal which is a shiny silver-white, odourless liquid and becomes colourless and odourless gas when heated. Mercury is very toxic and exceedingly bioaccumulative. Its presence adversely affects the marine environment and hence many studies are directed towards the distribution of mercury in water environment. Major sources of mercury pollution include anthropogenic activities such as agriculture, municipal wastewater discharges, mining, incineration, and discharges of industrial wastewater (Chen *et al.*, 2012).

Mercury exists mainly in three forms: metallic elements, inorganic salts and organic compounds, each of which possesses different toxicity and bioavailability. These forms of mercury are present widely in water resources such as lakes, rivers and oceans where they are taken up by the microorganisms and get transformed into methyl mercury within the microorganism, eventually undergoing biomagnifications causing significant disturbance to aquatic lives. Consumption of this contaminated aquatic animal is the major route of human exposure to methyl mercury. Mercury is extensively used in thermometers, barometers, pyrometers, hydrometers, mercury arc lamps, fluorescent lamps and as a catalyst. It is also being used in pulp and paper industries, as a component of batteries and in dental preparations such as amalgams (Trasande *et al.*, 2005).

2.6 Chromium (Cr)

The only Chromium compound of practical importance is chromites, a slack spinal of the idealized composition FeCr2O4 in practice it contains varying amount of MgO, Al_2O_3 and SiO2 major producers of chromites include South Africa, Russia, Albania etc. Since 1990, the production of chromites has doubled roughly every decade, reaching 2.6million tones, in

1984; chromium was more rarely as the mineral crocoites ($PbCrO_4$) and minor amounts minerals.

The greater part of chromites are produced by heating with coal to give ferrochrome used in the manufacture of alloy steels, pure chromium metal for use in iron is produced by reduction of Cr_2O_3. Less than 15% of the ore is transformed into chromium compounds, principally chromates, dichromate chromium oxide, chromium (III) oxide etc. Chromium is toxic in high concentration to both plants and animals. It causes perforation, bronchogenic, carcinoma etc. Chromium poisoning causes skin disorder and liver damage. Chromium has a wavelength of 357nm (Ndiokwere, 2005).

2.7 Cadmium

Cadmium is a white shining but tarnishes able metal, similar in several characteristics to Zinc and Tin. Cadmium is not found to a great extent in nature, its presence in the earth crust is estimated to range between 0.15 to 0.11mg/g (67th element in order of abundance), with a Zn/Cd ratio around 250:1 (the ratio depends strictly on the nature of rocks).

Cadmium can be present as a result of volcanic emission and release from the vegetation. It is not essential to plant growth, but under certain conditions can accumulate in some plants to level that are hazardous to animals and humans. Some sewage sludge contains enough cadmium to encourage accumulation. The chemistry of cadmium reaction in the soil is not well understood, but it is known that the uptake of this element is generally reduced by organic matter, silicate clay, and hydrous oxides of iron and aluminium and poor soil aerations. Cadmium uptake is high in acids soils and is reduced when the soil is limed. This element has a wavelength of 228mm.

It is a hazardous air pollutant which enters plants and animals from soil and water thus entering products cadmium has an inhibitory effect on antioxidant processes, it interacts with sulphuric group of essential enzymes. Chronic exposure to cadmium is associated with a wide range of diseases, including heart disease, anaemia, skeletal weakening depressed immune system responses. At extreme levels it causes an illness called Tai – “itai” disease characterized by brittle bones and intense pain (Connell & Miller, 2006).

2.8 Nickel (Ni)

Nickel is widely used in consumer products like buttons, zips, coins, dental braces, orthodontic application (appliances used in the treatment of problems concerning the teeth and jaws) household appliances tools, artificial joints, jewellery, batteries, hair spray etc. Nickel occurs naturally in metal refineries and municipal solid waste incinerators release nickel needed by the human body to produce red blood cells, however, in excessive amounts can become mildly toxic. Short term over exposure can cause some health problems, but long term exposure can lead to decrease of body weight, heart and liver damage and skin irritation. The EPA does not currently regulate nickel levels in drinking water. Nickel can accumulate in aquatic lives, but its presence is not magnified along food chains (Connell & Miller, 2006).

2.9 Arsenic (As)

Arsenic occurs naturally in the environment on the earth crust, it is an essential element that becomes toxic when ingested at high levels, arsenic is combined with other elements such as oxygen, chlorine and sulphur to form inorganic arsenic compounds. Arsenic enters the environment primarily from air pollution and by seeping into the soil and ground water from hazardous waste dumps.

Arsenic gains access to the water environment through mining operations the use of arsenical insecticides and from the combustion of fossil fuels. Arsenic compounds including lead and calcium arsenates and copper aceto-arsenic have been extensively used as pesticides and after many years of application may accumulate in soils to levels that become hazardous. Arsenic toxicity varies with several factors including concentration rate of absorption and the chemical form ingested.

Some toxic effects of arsenic poisoning are gastrointestinal complaints, diarrhoea, constipation, gastrointestinal disturbances, loss of appetite and weight. Exposure to arsenic at low levels for extended periods of time can cause a discordant of skin and the appearance of small corns or warts. Exposure to high levels of arsenic can lead to death (Connell & Miller, 2006)

2.10 Aluminium (Al)

Aluminium was classified as a non-heavy metal but has been recently discovered to be a heavy metal. Everyone is exposed to low levels of aluminium from the atmosphere and water since acid rain usually dissolves the aluminium in the soil and rocks. High levels can affect respiratory and nervous systems and the bones. Aluminium has been found in at least 489 of the 1416 (34%) national priorities list sites identified by the environmental protection agency (EPA) (David, 1989). At neutral or alkaline pH values aluminium is not a problem for plants, however in acid soil a form of aluminium ($Al3+$) is solubilized into a soil solution that is quite toxic to plant roots.

Aluminium toxicity limits crop production on acid soil. When soil becomes acidic, the toxic aluminium damages roots system, which greatly reduces yields (Connell & Miller, 2006).

2.11 Exposure of Human to Heavy Metals

Since the industrial revolution, the production of heavy metals such as lead, zinc etc. has increased exponentially, production of this metals has increase nearly 10 – fold with emissions rising in tandem, once emitted, metals can reside in the environment for hundreds of years or more human beings may be exposed to these metals through the food chain after the food has been contaminated. Heavy metals have been used in a variety of ways for at least two millennia, for example, lead has been used in plumbing and lead arsenate has been used to control insects in apple orchards. Lead was added to wine to improve its taste and mercury was used to alleviate teething pair in infants, many metals are essential to life and only become toxic when exposures to life become excessive. (i.e. exceed some threshold for the introduction of adverse effect) (Nwajei *et al.,* 2007).

Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage and even death in some instances of exposure to high concentrations. Despite abundant evidence of these deleterious health effects, exposure to heavy metals continues and may increase in the absence of concerted policy actions. Exposures to unhealthy elements remain common throughout both developed and developing countries. Unlike most chemicals for which health impacts of low level dose are still uncertain, exposure of lead even at low level is highly toxic. The natures of biological response to metal exposures are direct consequences of exposure and are defined through dose-effect relationship (Ademoroti, 1996).

2.12 Bioaccumulation of Heavy Metals in Living System

The word environment and society where we live have made bodily contamination impossible to ignore – through eating, smoking, breathing, skin absorption and every day exposure to limitless products and chemicals made and used by human, contaminants find their way into the body. Over time these heavy metals, toxic chemicals and residues, plagues and other unnatural intruder continue to slowly accumulate. If the body natural detoxification pathways (such as blood lymph and cerebral spinal fluid) cannot eliminate them faster that they enter the body, the build-up can eventually reach toxic levels.

"Bioaccumulation of metals is the process whereby organisms stored up metals from the surrounding medium into their tissues by chelating process". It is the product of equilibrium between the concentration of the metal in organisms, environment and the rate of ingestion and excretion, for example inorganic mercury present in product like pesticide, insecticides, fungicides etc. usually deposit in water to form sediments. These chemicals may be absorbed by Aquatic organisms and the organisms are eventually eaten up by fish, the fish are caught and eaten by man, as such the chemicals may bio-accumulate in man on exposure for a long time. The consequence of this may result to various ailments which may sometime life threatening (Osuj & Onojake, 2004).

2.13 Natural Chelating Agents

The word, chelates, means to grab onto something. Thus chelating agents are substances that have a strong ability to grab onto metals and dislodge them from the tissues so they can be removed. The human body has its own cleansing mechanism utilizing chelating agents. Each cell in the body manufactures its own chelating agents such as cysteine, histidine, glutathione and other metallothioneins designed to remove heavy metals and other toxins.

These chelating agents involved in natural chelation are amino acids. Our bodies can only synthesize these amino acids from a sufficient amount of dietary protein. For example, our bodies synthesize cysteine from the amino acid methionine found in garlic and onions. Additionally, sugars, lipids (i.e. fat) and other proteins can act as chelating agents. As we age, our cells produceless and less of these chelating agents. So, over our lifetime, supplementation becomes increasingly important to remove heavy metals and other toxins from our bodies. For instance, older adults should greatly increase their supplementation of these chelating agents from plants, clay and fermented foods. Therefore an increased dietary intake of plant and animal proteins is highly recommended to keep natural chelation going otherwise the body may be exposure to toxins ingested.

2.14 Review of Related works

Umoh & Etim (2013) reports that the concentration of metals in soils at the decomposed biodegradable waste dumpsite and 100m away (control site) from dumpsite indicate that there is a relative increase in the concentration of heavy metal at dumpsites compared to those in soils 100m away (control site) from the dumpsite. This is in agreement with the results obtained from similar a study by Amusan *et al.,* (2005). This could be attributed to the availability of metals containing wastes at dumpsite which are eventually leached into the underlying soils. The metals considered in this study include the metals which are micro-nutrient such as iron, zinc and copper and the non-essential/toxic heavy metal which are toxic to plant when present in the soil at concentrations above tolerance level. These elements are highly needed by plants for their normal growth. From the results obtained, the concentration of lead at dumpsites ranged from 9.46 mg/kg to 18.83mg/kg and for – the control sites it ranged from 5.21 mg/kg to 7.53mg/kg showing that both the dumpsites and control sites had normal range of 2-200mg/kg (Ebong *et al.,* 2008). Comparing values at dumpsites with that at control sites, the higher concentration of lead at dumpsites could be attributed to the decomposition of lead containing wastes.

Ebong *et al.,* 2008. Also reported that plants growing at dumpsite soil accumulates considerably high heavy metal content than those in normal soil and the concentration of heavy metal on this soil can easily increase beyond tolerance level causing serious problems along the food chain.

From similar work reported by Dara (2010), the major source of lead pollution is industrial source. Thus, any nearby industry that disposes lead as one of its wastes can also influence the concentration of lead in that environment. According to Aluko *et al.,*(2003) the mean concentration of lead in soil at Ibadan dumpsite also ranged from 1.34mg/g to 1.693mg/g. But since lead is a cumulative pollutant (Dara, 2010) the pollution of soil by lead remains a very serious problems that should be given much attention by environmental chemists in collaboration with government agencies. Also, effort should be made to educate the public on the health effect of this metal when ingested in excess. Such effects which includes: damage of the brain, kidney, miscarriage in pregnant women and damage of sperm production organ in male (Sabine and Wendy, 2009).The standard and accepted level of iron in soil ranges between 100-700mg/kg (Ebong *et al*., 2008). From this study, the dumpsite at Udua Adan Market recorded the highest level of iron (23.47mg/kg) while the dumpsites at Ukam Street recorded the least level of iron (18.06mg/kg). The five dumpsites analysed for iron ranged between (18.06 to 23.47) mg/kg which fell far below the accepted range of iron in soil. At the control site, the concentration also ranged between (8.24 to 11.72) mg/kg, which is much far below the accepted range of iron in soil. But levels iron recorded was higher than the levels of all the metals analysed. This indicates the importance of iron to humans.

According to WHO (1984), the deficiency of iron in man can cause weak muscular coordination, vomiting, diarrhoea and other serious health defects. Comparing this with the result obtained by Akaeze (2009), Elelenwo (of Rivers State) dumpsite had concentration of iron range between (10,300 - 31,000) ppm which falls within accepted level. But from studies carried out by Udeme (2001) for soil along Abak/Ikot Ekpene Road, in Uyo metropolis,

Akwa-Ibom State Nigeria, using different methods at different sample location revealed results that are comparable to the one obtained in this study. Eddy *et al.*, (2004) suggested that different sample location revealed results that are comparable to the one obtained in this study. Eddy *et al.*, (2004) suggested that any pollution of the environment by iron cannot be conclusively linked to waste materials alone but other natural sources of iron must be taken into consideration. From the authors' point of view: despite the fact that iron is a micro nutrient, it should be properly monitored to maintain its concentration in the accepted range to avoid health defect caused by the deficiency or excess amount of it

Cadmium is classified as a soft acid, preferentially complexing with sulphides (Moore, 2006). Its accepted range in soil as stated by Ebong *et al.*, (2008) is (0.01 - 300) mg/kg. The result obtained showed that the cadmium level at dumpsite and control site, both fall below accepted range of the metal in soil. From the analytical result, it was found that the range of cadmium at dumpsite within the study area falls between (0.09 to 0.42) mg/kg and that of its control site falls between (0.04 to 0.08) mg/kg. Cadmium was listed by EPA (1991) as one of the 129 priority pollutants and among the 25 hazardous substances. Ingestion of high level of cadmium severely irritates the stomach leading to vomiting and diarrhoea. Cadmium and its compounds are known human carcinogens and smokers get exposed to significant amount of cadmium than non-smokers. Other effects associated with cadmium include damage of lungs, fragile bones and kidney disease (Sabine and Wendy, 2009). Thus, should be able to attract the attention of environmental chemists, Government agencies and other private bodies.

The concentration of zinc in soils was obtained to range between(13.82 to 17.26) mg/kg for dumpsites and (6.32 to 8.15) mg/kg for the control sites. It could be seen that this falls within the accepted standard for the dumpsites but slightly deviate for the control sites. Control sites for kent Street, Udua Adan market and Ukam Street were specifically found to fall out of the accepted range of zincs in soil which is (10 - 300) mg/kg. According to Odukoya *et al.*, (2000), the range of zinc obtained from Abeokuta dumpsites was 100.80 to 226.00 mg/kg, while its control sample range was found to be (51.25 to 71.43) mg/kg which falls within the accepted range. This variation could be attributed to the fact that categories of waste introduce to such dumpsites have high concentration of zinc. Also from the concentration of zinc in the two control soil samples can be high due to some environmental factors. This was confirmed by Dara (1993). Zinc is required in human nutrient for normal functioning of the body. The deficiency of zinc in man can lead to impaired growth, low energy balance and low protein intake. While excessive intake of zinc from plants can lead to vomiting, dehydration, electrolyte imbalance, abdominal pain, and lack of muscular co-ordination (Udosen, 2000). The natural range of concentration of copper in soil is (2-100) mg/kg (Ebong *et al.*, 2008) the concentration range between (6.68 to 11.4)mg/kg and (2.06 to 5.61) mg/kg for dumpsite and control site respectively of the study area. Both the dumpsites and control sites concentration of copper within the study area falls within the accepted standard range. There is no deleterious effect of copper resulting from its deficiency or excess amount. According to Dara (1993) the high concentration of copper at the dumpsite might be attributed to biodegradable waste introducing metallic copper into the soil. World Health Organization (1984) stated that, the injection of copper can lead to severe muscular irritation, nausea, vomiting, diarrhea, intestinal cramps, severe gastrointestinal irritation, and other dangerous health defects. For the general results obtained from this study, the top layer (0-15cm depth) of the soil was employed in the research since earlier studies by Nyangababo and Hamya (1986) indicated the top soil layers as better indicators of metallic burdens. From the study (Umoh & Etim, 2013), he observed that since none of the heavy metals analysed was higher than the accepted standard, there was no hazard associated with the high concentration of the metals analyzed but the concentrations of all the heavy metals analysed at dumpsites were higher than the values at the control sites which might not be unconnected with the rate or level of leaching in the soil. An evidence of this relative increase in concentrations of metals in soils at dumpsites compared to those 100m away from dumpsites shows that the concentration of heavy metal in soil at dumpsite is directly proportional to its concentration distance away from dumpsite provided porosity is constant. Thus dumpsites have a significant impact in the environment which could be positive or negative. This means that there should be a kind of measure taken in order to safely dispose of our refuse to prevent the general public from being exposed to unnecessary hazards. Hence, residential areas should be sited a reasonable distance away from dumpsite especially when the need for drilling bore hole for town water supply arises, environmental impact assessment is highly recommended. Effort should also be made to discourage the practice of cultivation at dumpsite soil (Ebong *et al*., 2008) since plants growing at dumpsite soil bio accumulate considerably high heavy metal content than those in normal soil and the concentration of heavy metal on this soil can easily increase beyond tolerance level causing serious problems along the food chain. Thus the need to test for the physicochemical parameters of waste and the concentration of heavy metals in waste before dumping in a different study remains an outstanding area which should be focused on (Umoh & Etim, 2013). Ideriah *et al.*, (2005) studied the levels of some heavy metals in soils around designated municipal solid waste dumpsite and a control site within Port Harcourt and its environs. The soil samples were randomly collected and analyzed for As, Cd, Cu, Cr, Ni and Pb. Levels from the waste dumpsite were higher than those from the control site. Soils around the waste dump were also contaminated as a result of continuous dispersion of heavy metals from the waste dump by run-off water, wind and scavengers. The difference in the mean concentrations of metals between the main dump and outside the dump were not significant ($P>0.05$) in the wet season but were found to be significant ($P<0.05$) in the dry season. The concentrations of the metals in soils in both seasons ranged from 0.50 g/g to 20.5 g/g for As, 0.20 g/g to 13.0 g/g for Cd, 0.50 g/g to 100.0 g/g for Cr, 2.50 g/g to 910.0 g/g for Cu, 0.50 g/g to 34.0 g/g for Ni and 1.0 g/g to 127.5 g/g for Pb. The difference observed in the concentrations of Cd, Cu and Pb in both seasons are statistically not significant ($p > 0.05$ Pb) while the seasonal variations in the concentrations of As, Cr, and Ni show signification difference ($P<0.05$). Cd, Cr, and Cu showed positive correlation with distances across the waste dump ($r = 0.9236, 0.9338, 0.3586$ respectively). The mean concentrations of Cd and Cu in the soils from the waste dumpsite are sufficiently high to cause environmental concern as their concentrations exceeded tolerable limits (Ideriah *et al.*, 2005).

III. MATERIALS AND METHODS

3.1 Apparatus and Equipment

Sampling is carried out with a number of tools, depending upon the purpose for which sampling is done and the nature of the sample.

Equipment/apparatus used for the collection of samples in this research work as well as those used for preparation of the samples include:

- Matchet
- Meter rule
- Polyethene bags
- Trowel
- 100ml volumetric flask
- 50ml beakers
- pH meter
- 100ml measuring cylinder
- Filter paper
- Chemical weighing balance
- Fume cupboard
- Hot plate
- Mesh sieve (2mm)

3.2 Reagents

- Distilled water
- Standard buffer solution pH 4.0 & 9.2
- Aqua regia
- Concentrated HCl
- Concentrated HNO3

3.3 Sample Collection

Soil samples were collected from the four cardinal points of the dump site (i.e east, west, north and south). These samples were obtained at the depth of 5cm – 10 cm by the use of matchet for digging; trowel for fetching and the meter rule for measurement, the samples collected were packaged in a neat/dried polyethene bags and were labelled prior to shipment to the laboratory for preparation and analysis.

3.4 Sample Preparation

The soil samples were oven-dried to remove all the moisture contents. The samples were grinded after drying and sieved through a 2mm mesh sieve and the coarse particles were discarded. The powdered form were then stored for digestion and subsequent analysis.

3.5 Determination of pH (physio-chemical analysis)

The pH meter was calibrated using a standard buffer solution of PH 4.0 and 9.2. The pH was determined with soil to water ratio to be 1:2.5 i.e 10 g of soil to 25 mm of distilled water.

3.5.1 Method

10 g of 2 mm sieved, air dried soil was put into a 50 mL plastic beaker and 25mL of distilled water was added and the mixture was stirred for several times for 2mins. The soil suspension was then allowed to stand for another 2mins more undisturbed. The electrode was then immersed into the beaker but it was prevented from touching the bottom of the beaker. The pH reading was taken after 30 secs, so a as to allow steady reading (Carter, 1993). The experiment was repeated for all the eight (8) samples.

3.6 Sample Digestion

3.6.1 Method

Conventional aqua regia (i.e. solution of HCl & HNO3 with ratio of 3:1) digestion was employed. This was performed in 50ml glass beaker covered with watch glasses. A well-mixed sample of 3g was digested in 12ml of aqua regia on a hot plate for 2h at 1000C. After evaporation to near dryness, the sample was diluted with 20ml of 2% (with H2O) nitric acid and transferred into a 100ml volumetric flask after filtering through a filter paper and diluted to 100ml with distilled water. The extract where then taken for subsequent analysis of heavy metals (Chen, 2008).

3.7 Determination of Trace Metals (Pb, Cd, and Hg) Using Atomic Absorption Spectrophotometer

3.7.1 Method

Atomic absorption spectroscopy is based on the ability of an "excited" atom of an element to absorb energy from wavelength of light of the same frequency as the element. This creates a decrease in the initial signal energy and this difference is proportional to the concentration.

Each element has its own series of specific characteristics for sensitivity; noise and linearity define the range in which calibration curve will be accurate.

The optical system is set up with a hollow cathode lamp for element of interest (analyte). With the appropriate slit and wavelength selected for the element. A solution of a known concentration of the analyte (standard) is aspirated and the absorbance reading is rational to the standard and a sample concentration is interpolated from the intensity of the reading.

Atomic Absorption Spectrophotometer (AAS) has various models but for this analysis the buck model 210 VGP systems was used. This model has the advantages over other models because it operates in three (3) modes: direct measurement deuterium background correction (dz) and variable giant pulse correction (gp). The two correction modes allow the chemist to analyse samples that have complex or "dirty" matrices; which would normally give significant interference in the analytical determination (Ajayi & Kamson, 2007).

Finally, *t*he concentration of heavy metals Pb, Cd, and Hg in the top soil samples were analyzed using an AAS (Atomic absorption spectroscopy) successfully.

3.7.2 Method of Data Analysis

The values for each metal tested were subjected to two way analysis of variance (ANOVA) to determine the level of significance at 0.05%. Least significant difference ($LSD_{0.05}$) was tested to ascertain the sample with the highest concentration of heavy metal.

IV. RESULTS

Table 4.1: Concentration of Heavy Metals in Samples and WHO Approved Limit

Heavy Metals(ppm)	SpA	Sp B	SpC	Sp D	WHO Limit (ppm)
Cadmium	0.033	1.052	0.286	0.078	0.005
Mercury	0.122	0.062	0.078	0.033	0.001
Lead	0.115	0.005	0.039	0.211	0.01

Table 4.1 shows that the concentration of cadmium in sample A is 0.033ppm, sample B is 1.052 ppm, 0.286 for sample C and 0.078ppm for sample D. The concentrations of these metals are higher than the

0.005ppm world health approved limit for cadmium. Mercury concentration in sample A is 0.122ppm, 0.062ppm in sample B, 0.078ppm for sample C and 0.033ppm for sample D. this sample concentration is also higer than 0.001ppm approved W.H.O limit. Lead concentration in sample A, B, C and D are 0.115ppm, 0.005ppm, 0.039ppm and 0.211ppm respectively. As compared with W.H.O standard, the concentration is higher than the approved W.H.O standard. This result implies that the samples have high heavy metal concentration and may have significant negative impact.

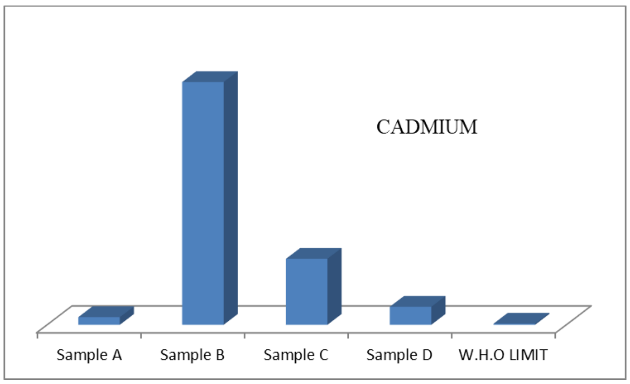

Fig 1: Comparison of Cadmium Concentration in Samples with W.H.O Standard.

Fig 1 shows that Sample B have high concentration of cadmium followed by sample C, D and lest in sample A. From the graph, W.H.O approved Standard is far less than the concentrations of the samples.

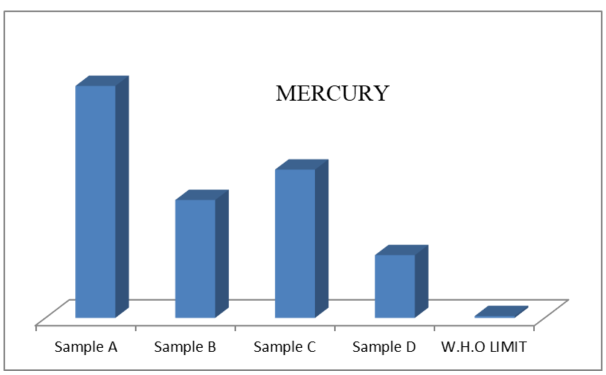

Fig 2: Comparison of Mercury Concentration in Samples with W.H.O standard.

Fig 2 shows that the concentration of mercury in sample A in higher than that of sample C following by sample B and D. This means that the concentration of sample in respect of mercury is on the high concentration than others. Comparing the concentrations of mercury in the sample with W.H.O standard, it is clear that the concentration of heavy metal in the samples are high than that of W.H.O approved standard.

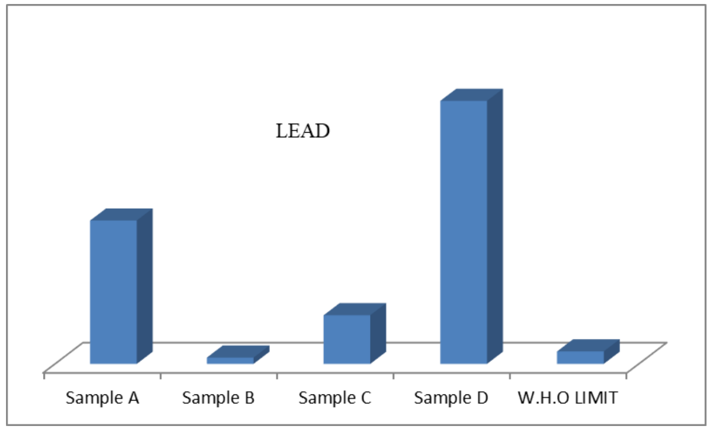

Fig 1: Comparison of lead Concentration in samples with W.H.O standard.

The concentration of heavy metal in sample D is greater than that of sample A, followed by sample c and least in sample B. Heavy concentration in the sample A, C and D is above W.H.O approved standard expect for sample B. therefore, sample B can be said to be within the approved standard of W.H.O.

Table A: Two way analysis of variance (ANOVA)

Source of Variation	DF	SS	MS	F	P
Sample	3	0.158	0.0527	0.583	0.648
Metal	2	0.208	0.104	1.154	0.377
Residual	6	0.542	0.0903		
Total	11	0.908	0.0826		

0.05% Level of significance.

Table A indicates that at P = 0.0648 and P= 0.377 there is no significant difference in the concentration of heavy metals present in the samples. Therefore, it can be concluded that the concentration of heavy metal present in the sample can have an impact on the environment.

CONCLUSION

The study investigates concentrations of heavy metals,(lead, cadmium and mercury) in waste dumpsite of Amaenyi Awka. Findings of this study showed that the dumpsite of Amaenyi Awka contains heavy metals such as cadmium, mercury, lead among others. The concentrations of heavy metals in the samples were observed to be very high in concentration as compared to W.H.O approve limit. This implies that the waste dump area is not safe for human as well as some crop cultivation as this may interfere with some physiological functioning of the plant. This finding disagree with the finding of Eddy *et al.*, (2004) suggested that any pollution of the environment by iron cannot be conclusively linked to waste materials alone but other natural sources of iron must be taken into consideration. From the authors' point of view: despite the fact that iron is a micro nutrient, it should be properly monitored to maintain its concentration in the accepted range to avoid health defect caused by the deficiency or excess amount of it. The finding also agree with the finding of Dara (1993) who reported that high concentration of copper at the dumpsite might be attributed to biodegradable waste introducing metallic copper into the soil

RECOMMENDATION

The most effective way to reduce/eliminate the impact of these heavy metals on the environment is to develop and implement an effective waste management plan.

Based on the finding of the study, it is recommended that designated places should be used as dumpsites and not indiscriminate marking of dumpsites as it is the case.

Dumpsites should be treated before use especially for cultivation. Also the people living around these dumpsites should stop farming on or around them.

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Furthermore, Waste dump should be recycled to control heavy metal pollution level and government should try to make policies that will prevent indiscriminate dumping of waste by making Plans to identify the materials and wastes at a particular site and try to manage it.

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