ASSESSMENT OF SOME HEAVY METALS AND ORGANIC CONTAMINANTS LEVEL AROUND SOME SELECTED HOSPITALS AND MUNICIPAL DUMPSITES IN KADUNA METROPOLIS, NIGERIA

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M.Sc/Sci/34033/2012-2013

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA

IN PARTIAL FULFILMENT FOR THE AWARD OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY

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NIGERIA

NOVEMBER, 2016

Abstract

This study was designed to assess the levels of some selected heavy metals and identify organic contaminants from soil collected from hospitals dumpsites and incinerator ash within Kaduna metropolis. Samples (soil and ash) were collected from three medical and one municipal dumpsite between the hours of 8am and 11am, when disposal activities are high. The mean concentrations of some heavy metals (Pb, Cu, Zn, Cd and Fe) were determined in both seasons by atomic absorption spectrophotometry while organic contaminants were identified by gas chromatography-mass spectrometry. Data of heavy metals collected were analyzed using ANOVA to conduct a test of significance; pollution index to assess environmental risk and Pearson's correlation to determine relationship between parameters. The result showed the order of relative abundance as Fe>Zn>Cu>Pb>Cd. Saint Gerard catholic hospital dump soil contained more heavy metal concentration due to its high contents of sharps as waste while the municipal dump soil has the highest mean concentration of cadmium. The result also indicated a decreasing pattern in the mean concentrations of the heavy metals vertically down the soil depths. Seasonal variation shows high concentrations of heavy metals during the dry season than the wet season. Heavy metals were not destroyed by incineration and their concentrations depend on the amount of metals in the waste. The result from GC-MS showed some organic pollutants that have strong health implications. The pollution index showed that the municipal dump soil is severely polluted with cadmium and it is, therefore not recommended for agricultural activities. The pollution levels of the heavy metals decreased in the order Cd>Fe>Pb>Cu>Zn. Strong positive correlation ($P>0.01$) was recorded between Pb and Cu and between Fe and Zn. Cadmium has a positive correlation ($P>0.05$) with Cu and Pb. The studied physicochemical parameters in soil samples showed poorly sorted soil with sand fraction generally high in all samples. Alkaline pH,

ranging from 7.1 to 9.8 was observed while low soil organic matter was recorded (ranging from 0.28 to 2.25%) from sampling sites. The level of the studied metals in all the dump soils and ashes were within tolerable limit by WHO, FEPA and US EPA but could be of an environmental concern with continues dumping of medical wastes.

CHAPTER ONE

1.0 INTRODUCTION

1.1 Hospital and Municipal Solid Waste

A modern hospital is a complex, multi-disciplinary system which consumes thousands of items for delivery of medical care and is a part of the physical environment (Chandra, 1999). It is place where patients' health problems are diagnosed, analyzed and treated. During these activities, generation of solid waste is unavoidable.

The medical waste tracking act of United State defines medical waste as "any solid waste'' that is generated in the diagnosis, treatment, or immunization of human beings or animals, in research pertaining thereto, or in the production or testing of biological and the animal waste from slaughter houses or any other establishment (US.EPA, 1988).

World health organization (WHO) defines hospital waste as the total waste stream from a health care or research facility that includes both potential risk wastes and non-risk waste materials. WHO (1999) states that 85% of hospital wastes are actually non-hazardous, whereas 10% are infectious and 5% are non- infectious but they are included in hazardous waste.

The world health organization has classified medical waste into seven categories:

i. General waste: This is largely composed of domestic or house hold type of waste. It is non-hazardous to human beings, e.g. kitchen waste, packaging material, wrappers and plastics.
ii. Pathological waste: This consists of tissue, organ, body part, human fetus, blood and body fluid. This constitutes hazardous waste.

iii. Infectious waste: The waste which contain pathogens in sufficient concentration or quantity that could cause diseases. It is also hazardous.

iv. Sharps: Waste materials which could cause the person handling it, a cut or puncture of skin, e.g. needles, broken glass, saws, nails, blades and scalpels.

v. Pharmaceutical waste: This includes pharmaceutical products, drugs and chemicals that have been returned from wards, have been spilled, are outdated, or contaminated.

vi. Chemical waste: This comprises discarded solid, liquid and gaseous chemicals, e.g. cleaning, housekeeping and disinfecting products.

vii. Radioactive waste: It includes solid, liquid and gaseous waste that is contaminated with radionuclide generated from *in-vitro* analysis of body tissue and fluid, *in-vivo* body organ imaging and tumor localization and therapeutic procedures (WHO, 2002).

Most medical waste constitutes a small fraction of municipal solid waste and if not properly handled could be hazardous. Municipal solid waste (MSW) normally termed as ‘‘garbage’’ or ‘‘trash’’ is an inevitable byproduct of human activity. It is usually generated from human settlements, small industries and commercial activities (Singh *et al*., 2011). An additional source of waste that finds its way to MSW is the waste from hospitals and clinics. When medical risk wastes are mixed with MSW, they pose a threat to human health and they may also have long term effect on environment (Pattnaik and Reddy, 2009). Municipal waste dumping sites are designated places set aside for waste disposal. Depending on a city’s level of waste management, such waste may be dumped in an uncontrolled manner, segregated for recycling purposes, or simply burnt.

The growth of the medical sector around the world combined with an increase in the use of disposable medical products has contributed to the large amount of medical waste generated. The

proper collection and disposal of this waste is of great importance as it can directly or indirectly have health risk impact on the public and environment (Babanyara *et al.*, 2013).

1.2 Justification

It is ironic that the healthcare delivery system, which is established to provide treatment and safeguard the health of the people against illnesses, becomes a source of infection and means of spreading diseases in the process of medical treatment. Modern hospitals and research centers use a wide variety of drugs including antibiotics, cytotoxics, corrosive chemicals, radioactive substances, which ultimately become part of hospital waste. These generate different types of infectious and/or hazardous medical waste that poses enormous risk to patients, healthcare providers, waste pickers, and the community at large, if their disposal is not urgently and scientifically managed.

Most hospitals in Kaduna State, Nigeria are built close to residential areas and have their temporary dumpsites within their vicinity. This creates health challenges to the immediate communities via air, soil and water contamination. This research will create awareness amongst the hospital personnel in health-care units on the need to segregate medical wastes before disposing and the danger of improper disposal of hospital waste. This will further provide awareness on the need to always carryout research on the pollution level of medical dumpsite soil, plants and underground water within the vicinity.

1.3 Statement of Problem

Disposal of medical waste is of a growing environmental concern in the developing world. The problem is growing with an ever-increasing number of hospitals, clinics and diagnostics laboratories

universally. In developing countries such as Nigeria, where health concern is competing with limited resources, medical wastes have not received sufficient attention and the priority it deserves. The notion that disposal of waste is the responsibility of the government authorities has not enabled waste generators to appreciate the negative impact of improper waste disposal (Ngwuluka *et al*., 2009).

The main environmental problem associated with the disposal sites is the potential risk posed to the soil. Since the waste will be disposed directly on the surface of the soil, a number of contaminants including heavy metals readily penetrate and eventually contaminate the soil and percolate to the ground water.

1.4 Aim and Objectives

The aim of this research is to determine the levels of some heavy metals and organic contaminants at hospital and municipal dumpsites soil and incinerator ash within Kaduna metropolis, Nigeria. This aim was actualized via the following objectives:

i. Determination of physicochemical parameters such as pH, % organic carbon, electrical conductivity and particle size distribution of dumpsite soil.
ii. Determination of the concentration of some heavy metals, present in the soil and incinerator ash during wet and dry seasons.
iii. Identification of organic contaminants, present in the dumpsite soil and incinerator ash.
iv. Determination of pollution levels of the various hospitals dump soils for agricultural activity using pollution index analysis.
v. Determination of the relationship between the heavy metals and physicochemical parameters using Pearson's correlation matrix.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Hospital Waste

Open dumping of municipal solid waste has hazardous impact on environmental soils and vegetation (Syeda *et al.,* 2013). Many factors which control the mobility of heavy metals in soils profile

include soil pH, soil texture, type of clay minerals, percentage of organic matter, cation and anion exchange capacity, soil drainage and amount of rainfall. (Covelo *et al.,* 2007). Significant modifications were observed in the soil properties of the dumping sites of study. Soils at the disposal sites showed high pH, TDS and EC regime in comparison to control sites. The pH at disposal site was 8.75 while control site 8.65. Percentage of sand and silt were lower at control site than disposal site. The mean value of Pb was 67.06 ug g^{-1} and 133.32 ug g^{-1} at control and disposal sites respectively. The mean value of cadmium was high at control site and low at disposal site. Relatively high organic matter with an average mean value of 1.54 was found at open dump sites contributing to an increase in pH also. This is mainly due to release of exchangeable cation during mineralization of organic matter (Woomer *et al.*, 1994, Anikwe and Nwobodo, 2002).

The use of disinfectants and drugs which are discarded through sinks, normally lead to pollution of water bodies. Organic pollutants in hospital waste water and food samples within Ahmadu Bello University Teaching Hospital, (ABUTH) showed the presence of methylene chloride, xylene, butylated hydroxytoluene, octadecanoic acid and tetradecene. Methylene chloride was obtained in waste water sample in minute quantity (0.725 ppm), which is far below its toxicity level of 200 ppm when exposed continuously for 2-3 hours. Xylene was detected in waste water and food samples. The research carried out by the international agency for research on cancer and USEPA, 2009, found out that high level of xylene (200 ppm) causes increase number of death of unborn babies in womb of pregnant mothers, decrease in weight of foetus and delayed in skeletal development of young children. The concentration of butylated hydroxytoluene determined were 0.204, 0.059, 0.051 and 0.592 ppm in the waste water and food samples. It produced hyperactivity in small children at concentration above 100 ppm. Inhalation of octadecanoic acid may cause irritation to the respiratory tract with symptoms such as

coughing, sore throat, difficulty in breathing and chest pain in concentration greater than 100 ppm (Wyasu and Kure, 2012).

Hospital waste dumps and incinerator ash contain heavy metals which influence the immediate receiving environment. Heavy metals concentrations in ash, dump soils and crop samples in this environment (ABUTH) showed the order of relative abundance as Fe>Pb>Mn>Cr>Cd. Of all the metals analysed in dump soils, iron had highest mean concentration of 0.807 mg/kg for both dry and wet seasons while nickel showed the lowest mean concentration of 0.40 mg/kg for wet and 0.038mg/kg for dry season. Lead had the highest mean concentration of 0.38 4mg/kg of the entire metals analysed in ash samples while cadmium showed the lowest mean concentration of 0.002 mg/kg during dry season to 0.005 mg/kg for wet season. For crop samples, tomatoes had the highest iron mean concentration of 0.467 mg/kg among all the food crop analysed while Guava had the lowest mean concentration of cobalt 0.009 and 0.016 mg/kg for both wet and dry seasons (Sunday and Agbaje, 2012). The results for the heavy metals are in line with the report of Dempsery and Oppett, 1993, that heavy metals are not destroyed by incineration but is simply concentrated in the remaining ashes or released to the environment via stack emission. The concentrations of heavy metals in the ashes are dependent on the amounts of these metals in the waste being incinerated.

The presence of oragnic contaminants in hospital waste dump soils and incinrator ash poses serious health risk to human and the environment through the soil and crops (Sunday and Agbaje, 2012). The dump soils obtained from hospital dump waste on analysis were found to contain 1,2-benzenedicarboxylic acid, n-hexadecanoic acid, octadecanoic acid and diethyl phthalate while the grown crops contained p-xylene, ethylbenzene and butylated hydroxytoluene in addition. Benzenedicarboxylic acid is used in blood storage bag, tubing and other devices.

High exposure can occur to individual receiving blood transfusion, undergoing major surgery or undergoing kidney dialysis. Environmental health and safety commission USA report showed that the injection of octadecanoic acid in food causes intestinal obstruction and irritation of gastro-intestinal tract. Diethyl phthalate are used as plasticizers and solvents in cosmetics and medical devices; chronic organ toxicity including histopathological effects in liver and kidney is the most common effect of diethyl phthalate (Osterhout, 2010). Butylated hydroxytoluene is a lipophilic (fat soluble) organic compound that is primarily used as an antioxidant food additive, as well as inn cosmetic, pharmaceutical and emblaming fluid (Benjamin, 1986). It is linked to causing cancer when exposed to food.

Assessment of heavy metals bioavailability in dumpsites around Zaria metroplis was carried out to investigate the chemical fractionation, mobility and bioavailability of Cd, Cu, Mn, Pb and Zn in refuse waste soils. Lead and cadmium were found to be in the mobile phase of the samples indicating that the metals are potentially more bioavailable to the environment than the other metals. The mean of the total extractable metals in the samples analysed for Cd, Cu, Mn, Pb and Zn ranged from 25.86 to 95.71, 170 to 446.43, 141.92 to 423.22, 399 to 739.10 and 122.45 to 511.57 mg/kg. Overall, the order of mobility and bioavailabilty of the metals is Cd>Pb>Zn>Mn>Cu. The dumpsites are alkaline in nature with pH ranging from 7.80 to 9.21. The total mean percentage of organic matter ranged from 2.63 to 6.10 % which is high based on the classification of soil organic matter given by Enwezor *et al.,* 1988. The electrical conductivity of the refuse waste soils also ranged from 0.42 to 4.0 $mscm^{-}$. This high range was as a result of metal scraps which are constituents of refuse dumpsites (Uba *et al.,* 2008).

The distribution of mean concentration of elements present in soils of abandoned waste dumpsite revealed lead had the highest concentration (133.74 ± 10.60 mg/kg) while calcium the

least concentration ,2.08 ± 0.12 mg/kg (Okoronkwo *et al.*, 2006). The results on physicochemical analysis of the soils showed that mean percentage of sand, silt and clay were 75.01±2.31, 12.87±0.93 and 10.45±1.47 respectively while the mean of pH was 6.81±0.01. Soils samples with high sand and low clay content have high pollutant leading potential (Nyles and Ray, 1999). It was deduced that the underground water in this dumpsite could suffer from pollution. Most plants and soil microorganisms thrive best in soils with pH between 6 and 7.5 (Isirimah *et al.*, 2003). The toxic elements in these soils were also examined for dependency upon some soil factors through correlation analysis. Sand organic matter and effective cation exchange capacity correlated significantly and positively with lead and cadmium indicating that these factors largely control the concentration of these elements in the soils (Okoronkwo *et al.*, 2006).

The study of trace metals in hospital waste incinerator ash showed a wide variation in concentration due to initial waste composition, design of incinerator and operating condition (Ranjan *et al.*, 2004). The ashes were collected from four hospitals, one municipal waste incinerator and two R and D laboratory incinerators. The concentration of trace elements vary according to the location of incinerator. The concentration of zinc was observed to be higher in hospitals and municipal samples, probably due to burning of teeth, bone and plastic materials. The concentration of zinc and lead, 320 to 7000ppm and 8.35 to 375ppm respectively were found to be very high in comparision to other metals due to burning of plastic products (Ranjan *et al.*, 2004).

2.2 Impact of Open Dumping Sites on the Environment

Open dumping is the improper disposal of any waste including household trash, garbage, tyres, barrels, demolition/construction waste, appliances, shingles, pipes, metals or any material which will rust, rot or burns (Foday *et al.,* 2013).

Open dumped waste has serious dual implications for both the environment and the quality of life. Dumped waste contaminates both soil and water. This occurs when rain water seeps through dumped waste and mixes with substances within the waste and forms a substance known as leachate. Leachate released from waste sites also poses a high risk to groundwater and surface water if it is not properly managed (Akinbile and Yusuff, 2011). Dumpsites also make the surrounding areas prone to flooding as the different components of waste can block drains, creeks and cul-verts (United Nations Environment Programme, 2005). In an attempt to combat illegal dumping and mitigate its effects, residents in rural areas burn sites, this however, has a direct impact on the environment because fires cause severe erosion due to burning of trees which limits vegetation growth. Small animals such as birds are also affected as they die from feeding on materials from waste sites and by being stuck in debris (Project Green Sweep, 2011).

The presence of open dumpsites can cause serious health problems for nearby residents as it is an ideal breeding ground for disease vectors such as rats and mosquitoes (US EPA, 1998). These areas become sources of contamination due to the incubation and proliferation of flies, mosquitoes and rodents. They in turn are disease transmitters that affect population's health, which has its organic defenses in a formative and creative state. This said situation produces gastrointestinal, dermatogical, respiratory, genetic and several other kinds of infectious disease. Health care waste and other medical waste disposed in dumpsite mixed with domestic waste increases the risk of infection with hepatitis B and HIV (Foday *et al.,* 2013).

The occurrence of illegal dump sites does not only affects health and the environment but also the quality of life. According to Madava (2001), open dumpsites have adverse effects on the basic human rights of people with regards to the in standard of living. This is because hazardous wastes are prospective pollutants of the biophysical and human environment. The presence of dumpsites does not

only deteriorate the quality of the environment but also breaches human rights as it has an impact on community pride. More often than not, the sight and smell that emerge from open dumpsites are unpleasant and diminished land value. Open dumpsites that mostly constitute of flammable substances and gases are vulnerable to fires. This not only has an impact on the aesthetic appeal of landscapes but it also diminishes the value of surrounding properties significantly, forcing residents to vacate their homes to further places (US EPA, 1998).

2.3 Health and Environmental Effect of Metals

2.3.1 Lead

Lead is a persistent and cumulative toxicant that affects multiple body systems and is particularly harmful to young children. In the body, it is distributed to the brain, liver, kidney and bones. It is stored in the teeth and bones, where it accumulates over time. Human exposure is usually assessed through the measurement of lead in blood. W.H.O, (2016) has identified lead as one of ten chemicals of major public health concern, needing action by member states to protect health of workers, children and women of reproductive age (WHO, 2016). Exposure to lead can result in a wide range of biological effects, depending on its level, duration and timing. It is toxic and its effects may range from enzymes inhibition and anaemia to disorders of the nervous, immune and reproductive systems, impaired kidney and cardiovascular functions and even death. These effects occur over a broad range of doses (IPCS, 1995).

Impaired neurodevelopment in children is one of its most critical effects and may result from exposure *in utero* and during early childhood. Lead accumulates in the skeleton and its mobilization from bones during pregnancy and lactation causes exposure to fetuses and breast fed infants. Children exposures to it are linked to lower intelligent quotient, behavioural effect and learning disabilities (WHO/UNECE, 2007). Lead poisoning could cause abdominal pain, loss of appetite, insomnia and

constipation. Severe kidney as well as brain damage has been reported on long term exposure (Momodu and Anyakora.C, 2010). It is very toxic and has very chronic health implications even at very low concentration; ingestion of lead could cause mental cases in children (Huges *et al.,* 1980). Its effect is cumulative and long term exposure has been noted to cause serious health hazard, which include inhibition of the synthesis of hemoglobin and also adversely affect the central and peripheral nervous system as well as the kidney (Bhata, 2002).

2.3.2 Zinc

Zinc as a trace element has indispensible role in human health and diseases. It has been insufficiently recognized by a number of experts as an important public health issue, especially in developing countries. Zinc deficiency results in dysfunction of both humoral and cell-mediated immunity and increases the susceptibility to infection, disturbance in nucleic acid metabolism and protein synthesis (Davi *et al.,* 2014). When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Its shortages can cause birth defects. Although humans can handle proportionally large concentrations of it, too much of this element can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders.

Zinc is extra ordinarily useful in biological systems. It is involved in many biochemical processes that support life and required for a host of physiological functions including normal immune-function, sexual function, neuro sensory function such as cognition and vision. Numerous proteins, enzymes and transcription factors depend on zinc for their function. It plays specific and important catalytic, co-catalytic and structural roles in enzyme molecules and in many other proteins and bio-membrane. The acute effects of zinc are usually the result of short-term, high dose exposure and depend strongly on the

point of contact. Chronic somatic effects tend to be associated with low-dose exposure over an extended period of time. Skin contact with zinc powders or concentrated solutions can result in severe corrosive effects including ulceration, blistering and permanent scarring (Jerome, 2007).

2.3.3 Copper

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Because it is released both naturally and through human activity it is very widespread in the environment. It is often found near mines, industrial settings, landfills and waste disposals. Most of its compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually such compounds occur in the environment after release through application in agriculture (US EPA, 2006).

Copper is an essential element in human health, and health effects can result from both deficiencies and over exposures. It has little toxicity, but its soluble salts are poisonous, low levels of copper are essential for maintaining good health. Extremely high levels of exposure can cause harmful effects such as skin allergies, irritation of the nose, mouth and eyes, nausea, diarrhea, vomiting and stomach cramps. Long period of exposure can result in kidney and liver damage. It may decrease fertility in adults (ATSDR, 2004). Effects of copper deficiency can include anaemia, low numbers of white blood cells, osteoporosis in infants and children, and defects in connective tissue leading to skeletal problems (IRIS, 1998).

2.3.4 Iron

Iron can be found in meat, whole meal products, potatoes and vegetables. It has an essential role as a constituent of enzymes, such as cytochromes and catalase, and of oxygen-transporting proteins, such as haemoglobin and myoglobin. It is an essential part of hemoglobin; the red coloring agent of the blood that transports oxygen through our bodies. From acients times, man has recognized

the special role of iron in health and disease. It had early medicinal uses by Egyptians and Romans in treating chlorosis (green disease), a condition often resulting from iron deficiency. Its deficiency can exist with or without anaemia. Even mild and moderate forms of iron deficiency anaemia can be associated with functional impairments affecting cognitive development, immunity mechanisms and work capacity. The deficiency also reduces learning ability and is associated with increased rates of morbidity (Nazanin *et al*., 2014).

Globally, anaemia is one of the most prevalent nutritional deficiency diseases. Iron deficiency is one possible cause of anaemia. Such deficiency is not necessarily cause by an inadequate dietary intake of iron or reduced dietary availability of iron. Other causes include impaired absorption and increased blood losses due to menstruation or gastrointestinal blood loss caused by gastro intestinal disease. Since iron is required for oxidative energy production, it is proposed that anaemia (irrespective of its cause) and iron deficiency affect work capacity by two separate mechanisms. Anaemia reduces the oxygen transport capacity of the circulation, which impairs aerobic endurance capacity and energetic efficiency of muscles (iron and health, 2010).

2.3.5 Cadmium

Cadmium is a toxic metal that occurs naturally in the environment. Human are exposed to it mostly through plant-derived food. There is safe margin of cadmium exposure and the need to lower human exposure is desperate. It produces a number of health problems and is a known carcinogen (Taylor, 1997). An exposure to significantly higher cadmium levels occurs when people smoke. Tobacco smoke transports it into the lungs. Blood will transport it through the rest of the body where it can increase effects by potentiating cadmium that is already present from its-rich food. Other high exposures can occur with people who live near hazardous waste sites or factories that release the metal

into the air and people that work in the metal refinery industry. When people take-in such metal, it can severely damage their lungs. This may even cause death. It is first transported to the liver through the blood. There, it is bonded to proteins to form complexes that are transported to the kidneys. The metal accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body. (US EPA, 2006)

Cadmium adversely affects several important enzymes. It can also cause painful osteomalacia (bone disease) and destruction to red blood cell. It is believed that much of the physiological action of cadmium arises from its chemical similarity to zinc (Miller and Miller, 2002). It is a very mobile heavy metal in the environment. It is easily taken up by plants and transferred to their particular organs (Kabata-pendias and Pendias, 2011). Cadmium can have a destructive effect on the cell membrane plasma in the roots of sensitive plants, limiting the uptake of water and micro-elements (Obata *et al.,* 1996). Acute exposure of its fumes may cause flu-like symptoms including chills, fever and muscle ache. Sometimes referred to as 'the cadmium blue' symptom may resolve after a week if there is no respiratory damage, inhaling cadmium-laden dust quickly leads to respiratory tract and kidney problems which can be fatal (Taylor, 1997).

2.4 Persistent Organic Pollutants

Persistent organic pollutants (POPs) are toxic chemical substances which are highly persistent and bio-accumulative. Due to their chemical properties, they pose a global threat to human health and the environment. POPs are organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation (WFPHA, 2000). They are characterized by their solubility is water, leading to their bioaccumulation in fatty tissues. They are also semi-volatile, enabling them to move long distances in the atmosphere before deposition occurs. They may exist, both natural and anthropogenic. Those noted with

persistence and bio-accumulative characteristics include the first generation organochlorine insecticides such as dieldrin, DDT, toxaphene and chlordane and several industrial chemical products or byproducts including polychlorinated biphenyls (PCBs), dibenzo-p-dioxans (dioxins) and dibenzo-p-furans (furans). Many of these compounds have been or continue to be used in large quantities and, due to their environmental persistence, have the ability to bio-accumulate and bio-magnify. Some of these compounds such as PCBs may persist in the environment for periods of years and may bio-concentrate by factors of up to 70,000 fold (WFPHA, 2000).

Persistent organic pollutants are highly hazardous chemical pollutants that pose serious global threats. Four common features characterize all POPs. They are highly toxic and therefore have the potential to cause harm to human and the ecosystem. They are lasting for years or even decades before degrading into less dangerous form. This means they resist biological, chemical and physiological degradation. They are subject to long-ranged transport, that is they travel long distances and cause harmful contamination at locations far distant from where the chemical originally entered the environment. Lastly, POPs bioaccumulation in fatty tissue. They easily dissolve in fats and accumulate in the tissues to concentrations much higher than the concentrations in the surrounding environment. Persistent organic pollutants cause numerous human diseases, illness and disorders. As carcinogens, they have been shown to cause breast and pancreatic cancer, soft tissue sarcoma, non-Hodgkins lymphoma and adult onset leukemia. They negatively impact the reproductive system as well, causing abnormal sperm, miscarriages pre-term delivery, low birth weight, shortened lactation period and menstruation complications (Bileton *et al*., 2012).

2.5 Effects of Organic Pollutants on Human Health

The greatest part of human exposure to the twelve persistence organic pollutants (POP) is attributed to the ingestion of food. Contamination of food may occur through environmental pollution in the air, water and soil, or through the previous use or un-authorized use of pesticides on food crops.

The health effects of POPs are generally subtle and can be triggered at extraordinary low concentrations. The latency period for POPs may be very long, between exposure and outcome in the exposed individual, in some cases effects occurring in future generations. Exposure to POPs can be associated with the following health effects in humans:

a. Immune system biochemical alterations
b. A shortened period of lactation in nursing mothers
c. Neurobehavioral impairment including learning disorders, reduced performance on standard tests, and attention deficits
d. Diabetes
e. Cancer

The acute exposure to high-dose results from accidental fires or explosions involving electrical capacitors or other PCB-containing equipment, or high dose food contamination while mid-level chronic exposure is predominantly due to the occupational exposure. Chronic, low-dose exposure is characteristic for the general population world-wide as a consequence of the existing global background levels of POPs with variations due to diet, geography, and level of industrial pollution. Low level and population-wide effects are more difficult to study. People are exposed to multiple POPs during their lifetime and most people today carry detectable levels of a number of POPs in their body (Parivesh, 2001)

2.6 Principle of Atomic Absorption Spectroscopy

Atomic absorption spectrometry is an analytical method based on the absorption of ultraviolet or visible light by gaseous atoms. The sample containing metallic compound is converted into atomic vapor by spraying the sample solution into the flame. Some of these gaseous metal atoms may be excited but much larger number of the gaseous metal will normally remain in the ground state. These ground state atoms are capable of absorbing radiant energy of their own specific resonance wavelength.

Hence, if light of the resonance wavelength is passed through the flame containing the atom, that part of the light will be absorbed. The extent of absorption is proportional to the number of the ground state atoms present in the flame. The great advantage of the method over other procedures is its high degree of freedom from interference from its environment i.e. by the presence of other elements (Vogel, 1996).

Table 2.1 Operating condition used for the spectrometer (Instrumentation).

Element	Wavelength (nm)	Band pass	Flame type	Uptake time
Lead	283.00	0.5nm	Air/Acetylene	4 seconds
Cadmium	228.80	0.5nm	Air/Acetylene	4 seconds
Zinc	213	0.5nm	Air/Acetylene	4 seconds
Copper	324.80	0.5nm	Air/Acetylene	4 seconds
Iron	248.30	0.5nm	Air/Acetylene	4 seconds

(Vogel, 1996)

2.7 Principle of GC-MS

Gas chromatography mass spectrometry (GC/MS) is an instrumental technique, comprising a gas chromatograph (GC) coupled to a mass spectrometer (MS), by which complex mixtures of chemicals may be separated, identified and quantified. This makes it ideal for the analysis of the hundreds of relatively low molecular weight compounds found in environmental materials. In order for a compound to be analyzed by GC/MS it must be sufficiently volatile and thermally stable. In addition, functionalized compounds may require chemical modification, prior to analysis, to eliminate undesirable adsorption

effects that would otherwise affect the quality of the data obtained. Samples are usually analyzed as organic solutions consequently materials of interest (e.g. soils, sediments, tissues etc.) need to be solvent extracted and the extract subjected to various 'wet chemical' techniques before GC/MS analysis is possible (Gary, 2004).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Description of Sampling Sites

Soils and ash samples from dumpsites and incinerators were collected from four major locations in Kaduna metropolis, Nigeria. Soil samples were collected from three hospital dumpsites and one municipal dumpsite (control). The medical dumpsites are located within the hospitals vicinity while the municipal dumpsite is at the entrance of a community. Two of the hospitals have well managed incinerator while the third hospital does not.

The names and locations of the sampling sites are as follows:

1. 44 Nigerian Army Reference Hospital Kaduna (NARHK): This is a military hospital located in Camilla barrack, adjacent to Sir Kashim Ibrahim House (Government House) Tudun-wada Kaduna. It was initially meant for military personnel and their families but now made available to the public because of increase in medical needs. The hospital has two incinerators and a temporary dumpsite.
2. Saint Gerard Catholic Hospital Kaduna (SGCHK): This is a Christian missionary hospital located in Kakuri region of Kaduna metropolis. It is a modern hospital with standard equipment and training school. SGCHK was established to meet the medical challenges of the community without religion discrimination. In the hospital is a well-managed incinerator and temporary dumpsite.
3. Yusuf Dan-tsoho Memorial Hospital Kaduna (YDMHK): This is a general hospital managed by the state government and is located opposite Federal Polytechnic Tudun-Wada Kaduna. Being a public hospital, YDMHK has poor waste management system and has no incinerator.

4. Municipal dumpsite: This is temporary dumpsite located at Farin-gida community Mando Kaduna. Residents in this community dispose their waste in temporary dumpsite within the vicinity and the wastes are cleared by government service truck once in two weeks. The map indicating the location of the dumpsites and incinerators is shown in Figure 3.1.

3.2 Sample Collection, Treatment and Preservation

Soil and ash samples were collected from the four dumpsites and two incinerators in wet and dry season. At dumpsites, soil samples were collected randomly from different spots at 0-5cm and 5-10cm depths. The collected soil sub-samples were thoroughly mixed, pooled together to make a composite of each soil sample at different depths. Ash samples were collected at three points in the incinerators before mixing homogenously. Sixteen soil samples and four ash samples are collected in both seasons.

The dumpsite soils and incinerator ash were collected from each site with the aid of clean stainless steel spoon which has been washed with soap and rinsed with distilled water after each sampling. Immediately the soil samples were collected, they were isolated and packaged in neatly labelled black polythene bags that had been washed and rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metals and organic residue before taken to the laboratory.

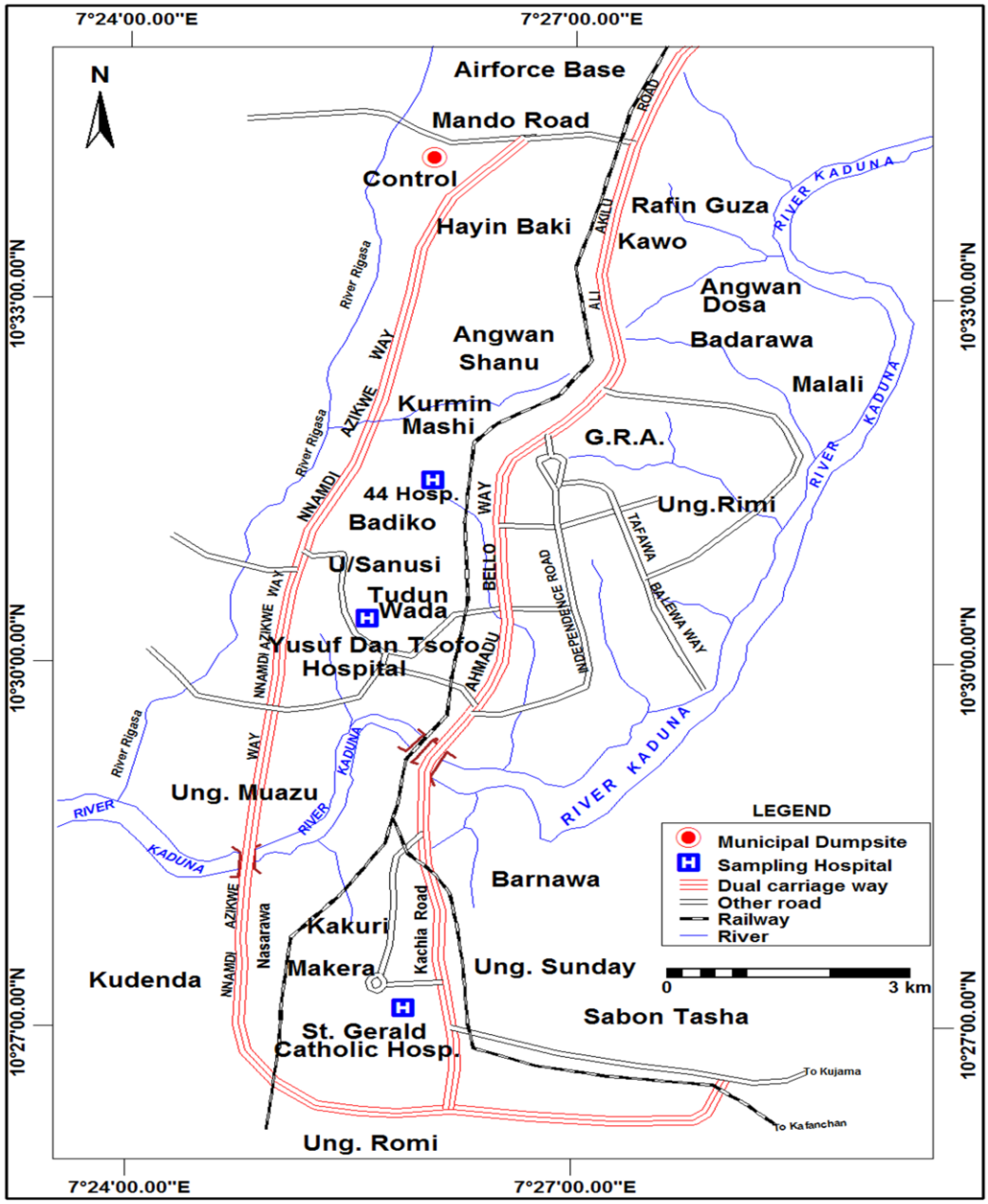


Fig 3.1: Map of the study area and sampling locations in Kaduna municipal

3.3 Determination of Soil pH

An accurate weight (0.5 g) of air-dried soil was weighed into a plastic sample bottle and 2.5 cm^3 of de-ionized water was measured into the plastic sample bottle. The bottle was placed on a mechanical shaker and was allowed to shake for an hour. The suspension was stirred and Hanna pH meter (which has been calibrated with buffer 7) immersed into the soil suspension. Reading was taken after 30 seconds. The electrode was carefully removed from the suspension and was rinsed with distilled water in a separate beaker before been dried with a tissue (Rayment and Higginson, 1992).

3.4 Determination of Organic Carbon in Soil (1934)

In the quantitative determination of soil organic matter, usually the organic carbon content is determined or measured and not the total carbon content of the soils. The soil organic matter content may then be obtained by multiplying the organic carbon concentration by a factor that varies from 1.724 to 2.0 (Tan, 1996). In ordinary routine research, Walkley–Black rapid titration method which measures only the decomposed fraction of soil organic matter is used; in this wet combustion method, the soil is digested with K2Cr2O7 and H2SO4 making use of the heat of dilution of H2SO4. The excess of Chromic acid, not reduced by the soil organic matter is determined by titration with standard FeSO4.7H2O.

The organic matter of the soil samples was determined by the method of Walkley and Black wet combustion method. A portion (1g) of the soil sample, (passed 0.5 mm sieve) was weighed into 250 cm^3 conical flask. Then 10 cm^3 of 0.17M $K_2Cr_2O_7$ solution was measured into the flask and the soil was dispersed by swirling gently. Concentrated H_2SO_4 (20cm^3) was added rapidly by the used of an automatic pipette, and the stream was directed into the suspension. Gentle continuous swirling of the flask was maintained until the soil and the reagents were mixed and more vigorous swirling was maintained for a minute. The flask was rotated again and allowed to stand on a white tile for 30 minutes; 100 $cm^3$of distilled water was added after standing for 30 minutes. Three to four drops of ferroin (1, 10-

Phenathroline Ferrous Sulfate complex) indicator was added and titration was done with 0.5M $FeSO_4$ solution. As the end point was approached, the titrand took on a greenish cast and then changed to dark green. At this point the titrant was added with care until the color changed sharply from green to red on reflected light against a white background.

The results were calculated according to the following formula:

$$\text{Organic Carbon in soil (\%)} \quad \frac{(\text{Me } K_2Cr_2O_7 - \text{Me } FeSO_4 \text{ X } 0.003 \text{ X } 100 \text{ X F}) \ldots\ldots\ldots 3.1}{\text{Mass (g) of soil (dried soil)}}$$

where F = correction factor (1.33) and

Me = Molarity of titrant/titrand x volume of solution used

$$\%\ \text{organic matter (OM) in soil} = \%\ \text{organic carbon x } 1.729 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

3.5 Determination of Soil Particle Size Distribution (Bauyocos hydrometer method, 1951)

A portion (50g) of 2 mm sieved soil was weighed into a 250 cm^3 plastic beaker. Then 100 cm^3 of 50% of sodium hexametophosphate (calgon) solution was added to the soil mixture and stirred with glass rod. Distil water (100cm^3) was added to the mixture, stirred and allowed to stand for 30 minutes. With occasional stirring, it was transferred to a 250 cm^3 plastic container and shaken on mechanical shaker for 10 minutes and then into 1000 cm^3 measuring cylinder and made up to mark with distilled water. Before the hydrometer reading was taken, the suspension in the cylinder was mixed vigorously using a long handle plunger making sure that the soil at the bottom was thoroughly disturbed. Hydrometer readings at 40 seconds and 2hours were taken. The hydrometer was then removed and the temperature of suspension was recorded with a thermometer. A blank consisting of 100 cm^3 of 50% of sodium hexametophosphate (calgon) solution, was diluted to 1000 cm^3 in a measuring cylinder and hydrometer and temperature readings taken.

The corrected hydrometer readings C (g/l) were obtained by subtracting the blank reading R(g/l) from the hydrometer readings in soil suspension R(g/l) and adding 0.36 (g/l) for every degree above 20^{o}C.

Calculations

Temperature correction factor, T (may be different for each reading):

T = (Observed temperature - 20°C) X 0.36

$$\% \text{ Clay} = \frac{(\text{corrected 2 hours reading} - \text{blank})\text{X } 100}{\text{weight of soil taken}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.3$$

$$\% \text{ Silt} = \frac{(\text{corrected 40 seconds reading} - \text{blank})\text{X } 100}{\text{Weight of soil taken}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 34$$

$$\% \text{ Silt} = 100 - (\% \text{ silt} + \% \text{ clay}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.5$$

$$\text{Corrected reading } \left(\frac{\text{g}}{\text{l}}\right) = \text{R} - \text{RL} + (0.36\text{T}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.6$$

R = hydrometer readings of soil suspension

RL = Blank readings

0.36 g/l is added to soil suspension reading for every degree above 20^{o}C

3.6 Determination of Soil Electrical Conductivity

To determine soil electrical conductivity, soil paste filtrates were prepared by mixing equal weight of soil sample and distil water in 250 cm^3 plastic bottle. The mixture was shaken for an hour with mechanical shaker then filtered through what man No 42. A portion (0.7456g) of potassium chloride was dissolved in water and made up to 1000cm^3 with distilled water. The electrode of the electrical conductor meter was rinsed with distil water and calibrated with standard potassium chloride prepared

(0.01M at 25^0C, reference EC equal 1.413 ds/m). The electrode was then inserted into the filtrate and reading taken.

3.7 Digestion of Sample for Atomic Absorption Spectroscopy Analysis

Soil samples from each dumpsite were separately homogenized and air-dried in circulating air in the oven of 30^oC to a constant weight and passed through a 2 mm sieve. Soil sample of 1.0 g was placed in 100 ml beaker. Following Shriadah procedure (1999), $3cm^3$ of 30% hydrogen peroxide was added to the soil sample. This was left to stand for 60 minutes until the vigorous reaction ceased. Thereafter, 75 cm^3 of 0.5M solution of HCl was added and the content heated gently at low heat on hot plate for 2 hours. The digest was then filtered into 50 cm^3 standard flasks. Duplicate digestion of each sample and control was carried out. Quantitation of metallic content of digested samples was carried out with Atomic absorption spectrophotometer.

3.8 Extraction of Organic Compounds for GC-MS Analysis

Liquid-liquid solvent extraction was used to extract the organic compound present in the soil and ash samples. A portion (2.0g each) of the samples were measured carefully and placed in a beaker and chloroform was added; the mixture was then shaken vigorously and allowed to settle for an hour before they were separated from the extracting solvent using 2 mm sieve. They were carefully poured into a clean container that had been washed and rinsed with soap and distil water (Burton and Patterson, 1979). Extracts were taken to National Research Institute for Chemical Technology Zaria (NARICT) for organic pollutants analysis

3.9 Analysis of Results

The data obtained in this study were subjected to analysis of variance (one-way ANOVA), to conduct a test of significance at $p<0.05$ between pairs of data (both one tail and two tail analysis) using

SPSS. The student t-test was also conducted to determine the significant level of the variation of the metals with time of the year.

The data were further subjected to pollution index analysis and Pearson's correlation matrix to assess the environmental risk caused by the contaminated soils and the relationship among heavy metals and physicochemical parameters respectively.

The pollution index can be estimated by using the following formula.

$$\mathrm{Pi} = \frac{\mathrm{Ci}}{\mathrm{Si}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.7$$

where *Pi* is an environmental quality index for heavy metal i, Ci is the heavy metal content in a soil sample (mg/kg), Si is the permitted standard of the same metal (mg/kg). If $Pi > 1$, the soil sample is classed to be polluted, while $Pi \leq 1$ suggests unpolluted soil (Li and Xu, 2003).



Plate 3.1: Saint Gerard Catholic Hospital Kaduna temporary dumpsite



Plate 3.2: Saint Gerard Catholic Hospital Kaduna incinerator side view



Plate 3.3: Yusuf Dan-tsoho Memorial Hospital Kaduna temporary dumpsite

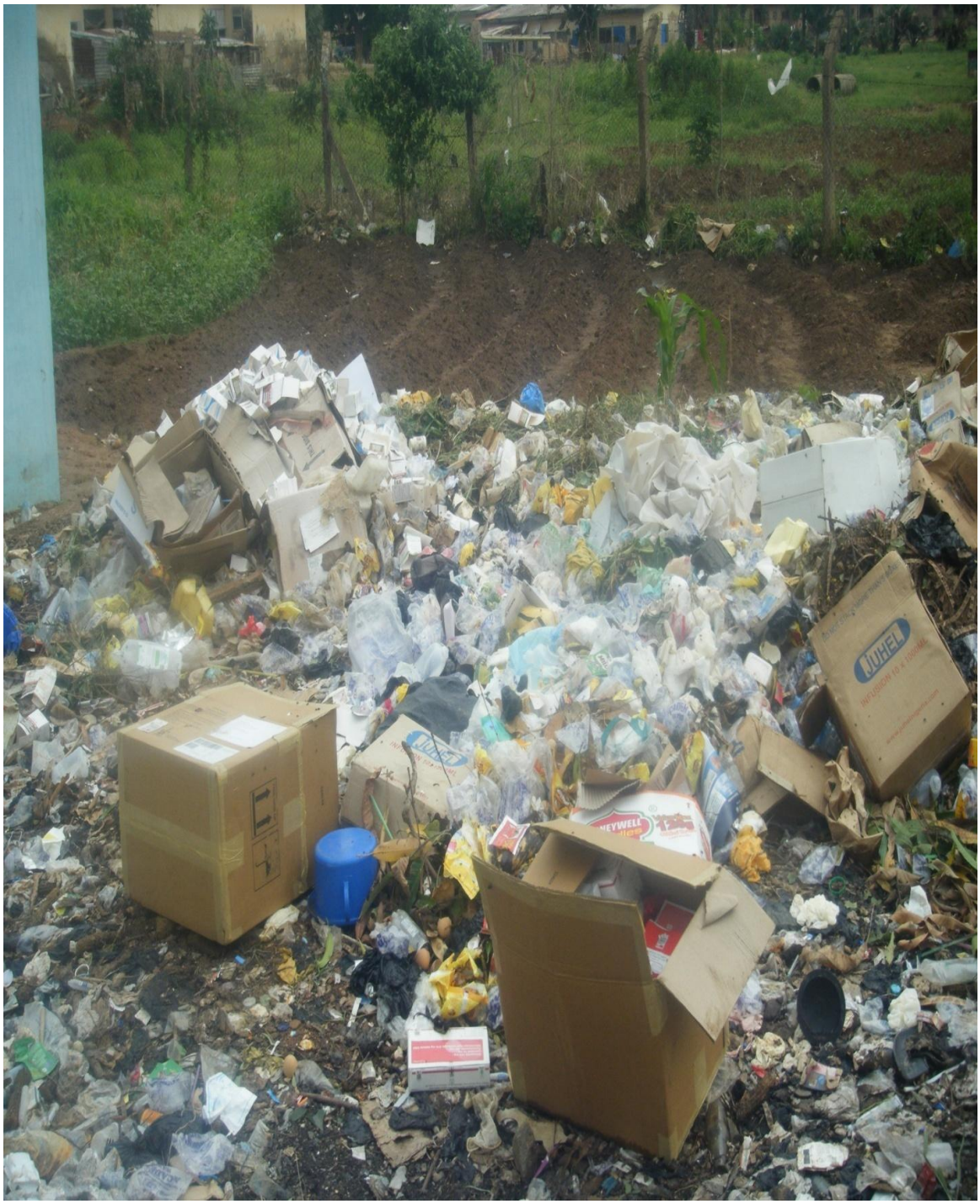


Plate 3.4: 44 Nigerian Army Reference Hospital Kaduna temporary dumpsite



Plate 3.5: 44 Nigerian Army Reference Hospital incinerator side view

3.10 Preparation of Standard Solutions for AAS

Respective stock solutions of the metals of interest were prepared from their matrix compounds and intermediate solutions produced with serial dilution techniques for AAS.

a. Lead stock solution

An accurate weight (0.1599g) of lead nitrate, $Pb(NO_3)_2$ was dissolved in $20cm^3$ of 1% v/v HNO_3, and made up to $1000cm^3$ in a volumetric flask with distilled water. A working concentration of 2, 4, 6, 8 ppm was prepared by diluting 2, 4, 6 and 8 cm^3 of the stock solution respectively to a 1000 cm^3 mark in a volumetric flask.

b. Iron stock solution

An accurate known weight (5.1579g) of ammonium ferrous sulphate, $Fe(NH_4)_2(SO_4)_2.6H_2O$ was dissolved in water. This was made up to $1000cm^3$ in a volumetric flask with distilled water. A working concentration of 1, 2, 3, 6 ppm was prepared by diluting 1, 2, 3 and 6 cm^3 of the stock solution respectively to a 1000 cm^3 mark in a volumetric flask.

c. Copper stock solution

An accurate weight (3.05g) of copper trioxonitrate, $Cu(NO_3)_2$ was dissolved in $50cm^3$ of 2M trioxonitrate(V) acid and was made up to $1000cm^3$ in a volumetric flask with distilled water. A working concentration of 2, 4, 6, 8 ppm was prepared by diluting 2, 4, 6 and 8 cm^3 of the stock solution respectively to a 1000 cm^3 mark in a volumetric flask.

d. Cadmium stock solution

An accurate weight (2.059g) of hydrated cadmium sulphate, $CdSO_4.H_2O$ was dissolved in distilled water and made up to $1000cm^3$.A working concentration of 0.25, 0.50, 1.0, 2.0

and 4.0 ppm was prepared by diluting 0.25, 0.50, 1.0, 2.0 and 4.0 cm^3 of the stock solution respectively to a 1000 cm^3 mark in a volumetric flask.

e. Zinc stock solution

An accurate weight (1.000g) of zinc was dissolved in 30cm^3 of 0.5M trioxonitrate(V) acid, and made up to 1000cm^3 in a volumetric flask with distilled water. A working concentration of 2, 4, 6, 8 ppm was prepared by diluting 2, 4, 6 and 8 cm^3 of the stock solution respectively to a 1000 cm^3 mark in a volumetric flask.

4.0 RESULTS

4.1 Physicochemical Parameters of Soil Samples

The results for the physicochemical parameters of the various dump soils studied are presented in Tables 4.1 and 4.2. The results showed that the dumpsites soils were alkaline in nature. The pH of the dump soils ranged from 7.1±0.1 (YDMHK) to 8.8±0.1 (Municipal) and from 7.8±0.1 (YDMHK) to 9.4±0.1 (Municipal) during wet and dry season respectively. The soil organic matter (OM) for dump soils analysed ranged from 0.35 to 2.25% and from 0.28 to 2.25% in wet and dry season respectively.

The results obtained for soil particle size distribution across the sampling sites showed fractions of sand, silt and clay in the dump soils. In wet season, the ranges of the fractions recorded were: Sand% (63.63, NARHK) to (74.30, YDMHK), silt% (10.10, Municipal) to (13.65, NARHK) and clay% (15.43, YDMHK) to (22.72, NARHK) while the ranges of fractions recorded during the dry season were: Sand% (71.40, SGCHK) to (78.10, YDMHK), silt% (8.00, YDMHK) to (14.29, NARHK) and clay% (13.90, YDMHK) to (21.43, NARHK). The soil classes of the dumpsites were sand-clay loam and sand-loam base on textural triangle.

The electrical conductivities recorded across the sampling sites ranged from 2.57±0.19, (NARHK) to 331±6.08 $mscm^{-}$ (municipal) and 1.37±0.04 (NARHK) to 80.1±1.39 $mscm^{-}$, (municipal) in wet and dry season respectively.

Table 4.1: Soil properties of Hospitals and Municipal dumpsites (wet season)

Sample sites	pH	Organic matter	Sand%	Silt%	Clay%	Soil Class	EC (ms/cm)	
44 Nigerian Army Hospital	8.0±0.1	1.90±0.04	63.63	13.65	22.72	Sand-clay loam	2.57±0.19	Reference
Saint Gerard hospital	7.3±0.2	1.45±0.03	70.90	13.50	15.60	Sand- loam	2.63±0.03	Catholic
Yusuf Dan-tsoho Hospital	7.1±0.1	0.35±0.01	74.30	10.27	15.43	Sand- loam	3.66±0.65	Memorial
Municipal	8.8±0.1	2.25±0.04	72.70	10.10	17.20	Sand- loam	331±6.08	

Table 4.2: Soil properties of Hospitals and Municipal dumpsites (dry season)

Sample sites	pH	Organic matter	Sand%	Silt%	Clay%	Soil Class	EC (ms/cm)	
44 Nigerian Army Hospital	8.5±0.1	1.75±0.02	64.29	14.29	21.43	Sand-clay loam	1.37±0.04	Reference
Saint Gerard hospital	8.2±0.2	1.35±0.02	71.40	13.20	15.40	Sand- loam	2.56±0.04	Catholic
Yusuf Dan-tsoho Hospital	7.8±0.1	0.28±0.02	78.10	8.00	13.90	Sand- loam	2.40±0.03	Memorial
Municipal	9.4±0.1	2.18±0.01	75.40	8.56	16.04	Sand- loam	80.1±1.39	

4.2 Heavy Metals

4.2.1 Hospital dump soil

The statistical results for the studied hospital dumpsites and municipal site for dump soils and ash samples are presented in Tables 4.3 to 4.7.

The results obtained for selected heavy metals at Nigerian Army Reference Hospital dump soils were recorded in season and depth, with concentrations of Cu as 0.312±0.001 (wet, 0-5cm), 0.342±0.002 (dry, 0-5cm), 0.148±0.002 (wet, 5-10cm) and 0.154±0.001 (dry, 5-10cm) while that of Pb were 0.168±0.001 (wet, 0-5cm), 0.173±0.002 (dry, 0-5cm), 0.129±0.0002 (wet, 5-10cm) and 0.132±0.003 (dry, 5-10cm). The mean concentrations of Zn recorded at NARHK dump soils were 0.179±0.0002 (wet, 0-5cm), 0.796±0.006 (dry, 0-5cm), 0.103±0.0004 (wet, 5-10cm) and 0.708±0.006 (dry, 5-10cm) while that of Cd were 0.034±0.0002 (wet, 0-5cm), 0.037±0.0002 (dry, 0-5cm), 0.018±0.0001 (wet, 5-10cm) and 0.023±0.0002 (dry, 5-10cm). Also the results showed the mean concentrations of Fe recorded as 0.076±0.0001 (wet, 0-5cm), 1.047±0.002 (dry, 0-5cm), 0.069±0.0003 (wet, 5-10cm) and 1.017±0.007 (dry, 5-10cm).

Saint Gerard Catholic Hospital dump soils analyzed for selected heavy metals recorded that the mean concentrations of Cu were 0.487±0.001 (wet, 0-5cm), 0.481±0.002 (dry, 0-5cm), 0.435±0.001 (wet, 5-10cm) and 0.438±0.0003 (dry, 5-10cm) while that of Pb were 0.136±0.003 (wet, 0-5cm), 0.147±0.001 (dry, 0-5cm), 0.135±0.0001 (wet, 5-10cm) and 0.137±0.0003 (dry, 5-10cm). The mean concentrations of Zn were 0.292±0.0003 (wet, 0-5cm), 0.697±0.002 (dry, 0-5cm), 0.292±0.001 (wet, 5-10cm) and 0.689±0.001 (dry, 5-10cm) while the concentrations of Cd were 0.022±0.001 (wet, 0-5cm), 0.023±0.001 (dry, 0-5cm), 0.020±0.001 (wet, 5-10cm) and 0.022±0.002 (dry, 5-10cm). The results also recorded the mean concentrations of Fe as 0.144±0.001 (wet, 0-5cm), 1.106±0.002 (dry, 0-5cm), 0.121±0.0004 (wet, 5-10cm) and 1.095±0.001 (dry, 5-10cm).

At Yusuf Dan-tsoho Memorial Hospital, the mean concentrations of Cu recorded were 0.178±0.0001 (wet, 0-5cm), 0.178±0.0003 (dry, 0-5cm), 0.089±0.0002 (wet, 5-10cm) and 0.090±0.0002 (dry, 5-10cm) while that of Pb were 0.048±0.0004 (wet, 0-5cm), 0.065±0.001 (dry, 0-5cm), 0.033±0.001 (wet, 5-10cm) and 0.064±0.0002 (dry, 5-10cm). Likewise, the mean concentrations of Zn at YDMHK dump soils were 0.084±0.001 (wet, 0-5cm), 0.548±0.0004 (dry, 0-5cm), 0.042±0.001 (wet, 5-10cm) and 0.439±0.002 (dry, 5-10cm) while that of Cd were 0.015±0.0002 (wet, 0-5cm), 0.015±0.0003 (dry, 0-5cm), 0.006±0.0003 (wet, 5-10cm) and 0.013±0.0003 (dry, 5-10cm). Furthermore, the concentrations of Fe were found to be 0.123±0.0004 (wet, 0-5cm), 1.078±0.001 (dry, 0-5cm), 0.108±0.0003 (wet, 5-10cm) and 1.056±0.002 (dry, 5-10cm).

The mean concentrations of cadmium in municipal dump soils were found to be 0.176±0.0003 (wet, 0-5cm), 0.177±0.0002 (dry, 0-5cm), 0.108±0.001 (wet, 5-10cm) and 0.175±0.0003 (dry, 5-10cm) while for Pb were 0.033±0.0002 (wet, 0-5cm), 0.035±0.0003 (dry, 0-5cm), 0.022±0.0003 (wet, 5-10cm) and 0.029±0.0003 (dry, 5-10cm). Also at the municipal dump soils, the results recorded the concentrations of Zn as 0.060±0.0003 (wet, 0-5cm), 0.589±0.0003 (dry, 0-5cm), 0.057±0.0003 (wet, 5-10cm) and 0.528±0.0003 (dry, 5-10cm) while that of Cd as 0.047±0.0002 (wet, 0-5cm), 0.047±0.0004 (dry, 0-5cm), 0.007±0.0004 (wet, 5-10cm) and 0.042±0.002 (dry, 5-10cm). The mean concentrations of Fe were recorded as 0.055±0.0003 (wet, 0-5cm), 1.038±0.0004 (dry, 0-5cm), 0.051±0.0002 (wet, 5-10cm) and 1.021±0.002 (dry, 5-10cm).

Table 4.3: Level of heavy metals (mg/kg) in Nigerian Army Reference Hospital Kaduna dump soil during the wet and dry seasons at 0-5cm and 5-10cm depth

Metal/Season	Wet (0-5cm)	Dry (0-5cm)	Wet (5-10cm)	Dry (5-10cm)
Cu	0.312±0.001^{z}	0.342±0.002^{z}	0.148±0.002^{z}	0.154±0.0001^{z}
Pb	0.168±0.001^{z}	0.173±0.002^{z}	0.129±0.0002^{z}	0.132±0.003^{z}
Zn	0.179±0.0002^{z}	0.796±0.006^{z}	0.103±0.0004^{z}	0.708±0.006^{z}
Cd	0.034±0.0002^{z}	0.037±0.0002^{z}	0.018±0.0001^{z}	0.023±0.0002^{z}
Fe	0.076±0.0001^{y}	1.047±0.002^{z}	0.069±0.0003^{y}	1.017±0.007^{z}

Values with different superscript across the row for wet and dry season pairs are significantly different ($p<0.05$).

Values are mean ± SD

Mean sample size = 3.14

Table 4.4: Level of heavy metals (mg/kg) in Saint Gerard Catholic Hospital Kaduna dump soil during the wet and dry seasons at 0-5cm and 5-10cm depth

Metal/Season	Wet (0-5cm)	Dry (0-5cm)	Wet (5-10cm)	Dry (5-10cm)
Cu	0.478±0.001^{z}	0.481±0.002^{z}	0.435±0.001^{z}	0.438±0.0003^{z}
Pb	0.136±0.003^{z}	0.147±0.001^{z}	0.135±0.0001^{z}	0.137±0.0003^{z}
Zn	0.292±0.0003^{z}	0.697±0.002^{z}	0.292±0.001^{z}	0.689±0.001^{z}
Cd	0.022±0.001^{z}	0.023±0.001^{z}	0.020±0.001^{z}	0.022±0.002^{z}
Fe	0.144±0.001^{y}	1.106±0.004^{z}	0.121±0.0004^{y}	1.095±0.001^{z}

Values with different superscript across the row for wet and dry season pairs are significantly different ($p<0.05$).

Values are mean ± SD

Mean sample size = 3.14

Table 4.5: Level of heavy metals (mg/kg) in Yusuf Dan-tsoho Memorial Hospital Kaduna dump soil during the wet and dry seasons at 0-5cm and 5-10cm depth

Metal/Season	Wet (0-5cm)	Dry (0-5cm)	Wet (5-10cm)	Dry (5-10cm)
Cu	0.178±0.0001^{z}	0.178±0.0003^{z}	0.089±0.0002^{z}	0.090±0.0002^{z}
Pb	0.048±0.0004^{z}	0.065±0.001^{z}	0.033±0.001^{z}	0.064±0.0002^{z}
Zn	0.084±0.001^{z}	0.548±0.0004^{z}	0.042±0.001^{z}	0.439±0.002^{z}
Cd	0.015±0.0002^{z}	0.015±0.0003^{z}	0.006±0.0003^{z}	0.013±0.0003^{z}
Fe	0.123±0.0004^{y}	1.078±0.001^{z}	0.108±0.0003^{y}	1.056±0.002^{z}

Values with different superscript across the row for wet and dry season pairs are significantly different ($p<0.05$).

Values are mean ± SD

Mean sample size = 3.14

Table 4.6: Level of heavy metals (mg/kg) in Municipal dump soil at Mando Kaduna during the wet and dry seasons at 0-5cm and 5-10cm depth

Metal/Season	Wet (0-5cm)	Dry (0-5cm)	Wet (5-10cm)	Dry (5-10cm)
Cu	0.176±0.0003^{z}	0.177±0.0002^{z}	0.108±0.001^{z}	0.175±0.0003^{z}
Pb	0.033±0.0002^{z}	0.035±0.0003^{z}	0.022±0.0003^{z}	0.029±0.0003^{z}
Zn	0.060±0.0003^{z}	0.589±0.0003^{z}	0.057±0.0003^{z}	0.528±0.0003^{z}
Cd	0.047±0.0002^{z}	0.047±0.0004^{z}	0.007±0.0004^{z}	0.042±0.002^{z}
Fe	0.055±0.0003^{y}	1.038±0.0004^{z}	0.051±0.0002^{y}	1.021±0.002^{z}

Values with different superscript across the row for wet and dry season pairs are significantly different ($p<0.05$).

Values are mean ± SD

Mean sample size =

4.2.2 Incinerator ash

Table 4.7: Level of heavy metals (mg/kg) in incinerator Ash samples of Nigerian Army Reference Hospital and Saint Gerard Catholic Hospital during the wet and dry seasons

	NARHK		SGCHK	
Metal/Season	**Wet**	**Dry**	**Wet**	**Dry**
Cu	0.207±0.0002^{z}	0.643±0.002^{z}	0.037±0.0002^{z}	0.437±0.001^{z}
Pb	0.109±0.0004^{z}	0.164±0.002^{z}	0.074±0.0003^{z}	0.095±0.0003^{z}
Zn	0.042±0.0004^{z}	0.862±0.004^{z}	0.355±0.0004^{z}	0.885±0.002^{z}
Cd	0.003±0.0002^{z}	0.024±0.0003^{z}	0.010±0.0002^{z}	0.025±0.002^{z}
Fe	0.031±0.0003^{z}	1.056±0.0002^{y}	0.073±0.0003^{z}	1.034±0.004^{y}

Values with different superscript across the row for wet and dry season pairs are significantly different ($p<0.05$).
Values are mean ± SD
Mean sample size = 3.14

The concentrations of the selected heavy metals analysed in hospital incinerator ash samples were recorded in season. The mean concentrations of Cu were found to be 0.207±0.002 (wet, NARHK), 0.037±0.0002 (wet, SGCHK), 0.643±0.002 (dry, NARHK) and 0.437±0.001 (dry, SGCHK) while that of Pb were 0.109±0.0004 (wet, NARHK), 0.074±0.0003 (wet, SGCHK), 0.164±0.002 (dry, NARHK) and 0.095±0.0003 (dry, SGCHK). The mean concentrations of Zn recorded in the ash samples were 0.042±0.0004 (wet, NARHK), 0.355±0.0004 (wet, SGCHK), 0.862±0.004 (dry, NARHK) and 0.885±0.002 (dry, SGCHK) while that of Cd were found to be 0.003±0.0002 (wet, NARHK), 0.010±0.0002 (wet, SGCHK), 0.024±0.0003 (dry, NARHK) and 0.025±0.002 (dry, SGCHK). The concentrations of Fe in the ash samples were recorded as 0.031±0.0003 (wet, NARHK), 0.073±0.0003 (wet, SGCHK), 1.056±0.0002 (dry, NARHK) and 1.034±0.004 (dry, SGCHK).

4.3 Organic Contaminants

The organic contaminants identified are shown in Table 4.8. D-limonene was identified at Nigerian army reference hospital and Saint Gerard Catholic hospital Kaduna dump soil and ash. n-Hexadecanoic acid is one common organic contaminant found in most dumpsites. It was obtained in four of the six studied sites including the municipal site.

The analysis also identified 2,3,6,7- tetramethyl octane in Saint Gerard Catholic hospital dumpsites (soil and ash) and methyl octanoate in Yusuf Dan-tsoho memorial hospital dump soil, as well as Saint Gerard Catholic hospital ash and dump soil. Benzenecarboxylic acid and 9-octadecenamide were identified in the municipal dump soils. Nigerian Army reference hospital incinerator ash contained 11-octadecenoic, methyl ester.

Table 4.8: Organic Contaminants Identified at the Studied Sites
(Spectra are in appendices 21-32)

Sampling Sites	Organic Contaminants
Nigeria Army Reference Hospital Kaduna (Soil)	d-limonene n-hexadecanoic acid 2,9-dimethyldecane
Nigeria Army Reference Hospital Kaduna (Ash)	d-limonene n-hexadecanoic acid 11- octadecenoic, methyl ester
Saint Gerard Catholic Hospital Kaduna (Soil)	d-limonene Methyl octanoate 2,3,6,7-tetramethyl octane
Saint Gerard Catholic Hospital Kaduna (Ash)	d-limonene Methyl octanoate 1,3-cyclopentadiene 2,3,6,7-tetramethyl octane
Yusuf Dan-tsoho Memorial Hospital Kaduna (Soil)	Methyl octanoate n-hexadecanoic acid
Municipal dump soil	n-hexadecanoic acid 9-octadecenamide Benzenecarboxylic acid

4.4 Pollution Index

Table 4.9: Environmental quality index (*Pi*) of heavy metals in dump soils at 0-5cm depth during wet season

Sample sites (soil)	Cu	Pb	Zn	Cd	Fe
Nigerian Army Reference Hospital Kaduna	0.208	1.677	0.012	3.430	0.252
Saint Gerard Catholic Hospital Kaduna	0.318	1.362	0.019	2.150	0.480
Yusuf Dan-tsoho Memorial Hospital Kaduna	0.119	0.484	0.005	1.480	0.411
Municipal	0.117	0.333	0.004	4.670	0.182
Standard (Li and Xu, 2003)	>1.000	>1.000	>1.000	>1.000	>1.000

Table 4.10: Environmental quality index (*Pi*) of heavy metals in dump soils at 0-5cm depth during dry season

Sample sites (soil)	Cu	Pb	Zn	Cd	Fe	
Nigerian Army Reference Hospital Kaduna	0.228	1.731	0.053	3.720	3.491	
Saint Gerard Catholic Kaduna	0.321	1.473	0.046	2.270	3.687	Hospital
Yusuf Dan-tsoho Memorial Hospital Kaduna	0.118	0.646	0.037	1.520	3.592	
Municipal	0.118	0.352	0.039	4.730	3.460	
Standard (Li and Xu, 2003)	>1.000	>1.000	>1.000	>1.000	>1.000	

The environmental quality index (*Pi*) assessed during wet and dry season using single index method are presented in Tables 4.9 and 4.10. From the assessment, pollution index range for Cu, Pb, Zn, Cd and Fe across the sampling sites during the wet season were from 0.117 (municipal) to 0.318 (SGCHK), 0.333 (municipal) to 1.677 (NARHK), 0.004 (municipal) to 0.019 (SGCHK), 1.480 (YDMHK) to 4.670 (municipal) and 0.182 (municipal) to 0.480 (SGCHK) respectively.

The assessment of selected heavy metals pollution levels also recorded the pollution range of Cu, Pb, Zn, Cd and Fe across the sampling sites during the dry season as 0.118 (YDMHK and municipal) to 0.321 (SGCHK), 0.352 (municipal) to 1.731 (NARHK), 0.037 (YDMHK) to 0.053 (NARHK), 1.520 (YDMHK) to 4.730 (municipal) and 3.460 (municipal) to 3.687 (SGCHK) respectively.

4.5 Correlation Analysis

Pearson's correlation analysis was performed among the heavy metals, pH, soil organic matter and electrical conductivity of all the soil samples. The level of significance ($P \leq 0.05$ and $P \leq 0.01$) of heavy metals and parameters correlation for samples were determined and results given in Tables 4.11 to 4.14 above**.**

The correlated analysis of heavy metals concentrations and selected physicochemical parameters values obtained from Nigerian army reference hospital dump soils showed the correlated values between Cu and Pb, Zn, Cd, Fe, pH, OM and EC as (r=0.999**), (r=0.234), (r=0.978*), (r=0.122), (r=-0.061), (r=0.738) and (r=-0.617) respectively. The correlated values between Pb and Zn, Cd, Fe, pH, OM and EC were recorded as (r=0.241), (r=0.984), (r=0.129), (r=-0.087), (r=0.754) and (r=-0.583) respectively. There were also correlated values between Zn and Cd, Fe, pH, OM and EC, which were recorded as (r=0.380), (r=0.994*), (r=-0.882), (r=0.771) and (r=0.109) respectively.

Saint Gerard catholic hospital dump soils recorded correlated values between Cu and Pb, Zn, Cd, Fe, pH, OM and EC as (r=0.636), (r=0.085), (r=0.697), (r=0.091), (r=-0.919), (r=0.881) and (r=0.791) respectively while between Pb and Zn, Cd, Fe, pH, OM and EC were recorded as (r=0.712), (r=0.889), (r=0.709), (r=-0.344), (r=0.201) and (r=0.219) respectively. There were also correlated values between Fe and pH, OM and EC which were recorded as (r=0.053), (r=-0.359) and (r=0.018) respectively. Likewise, there were correlations obtained between pH and OM and EC which were given as (r=-0.934) and (r=-0.960).

The Pearson's correlated analysis of heavy metals concentrations and selected physicochemical parameters values obtained from Yusuf Dan-tsoho memorial hospital dump soils showed the correlated values between Cu and Pb, Zn, Cd, Fe, pH, OM and EC as (r=0.314), (r=0.176), (r=0.710), (r=0.023), (r=-0.373), (r=0.264) and (r=0.398) respectively. The correlated values obtained between Pb and Zn, Cd, Fe, pH, OM and EC were given as (r=0.924), (r=0828), (r=0.914), (r=-0.373), (r=0.428) and (r=0.397) respectively. The analysis also gave the correlations between Cd and Fe, pH, OM and EC which were recorded as (r=0.537), (r=-0.702), (r=0.686) and (r=0.726) respectively and between Fe and pH, OM and EC as (r=-0.004), (r=0.089) and (r=0.025) respectively. Furthermore, correlations were obtained between pH and OM and EC which were given as (r=0.990**) and (r=-0.999**) while between OM and EC as (r=0.988*).

Table 4.11: Pearson's correlation coefficient of heavy metals and some physicochemical parameters for Nigerian Army Reference Hospital dump soil.

Metal/parameter	Cu	Pb	Zn	Cd	Fe	pH	OM	EC
Cu	1							
Pb	0.999**	1						
Zn	0.234	0.241	1					
Cd	0.978*	0.984*	0.380	1				
Fe	0.122	0.129	0.994**	0.273	1			
pH	-0.061	-0.087	-0.882	-0.260	-0.889	1		
OM	0.738	0.754	0.771	0.856	0.698	-0.718	1	
EC	-0.617	-0.583	0.109	-0.462	0.075	-0.526	-0.090	1

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

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

Table 4.12: Pearson's correlation coefficient of heavy metals and some physicochemical parameters for Saint Gerard Catholic Hospital dump soil.

Metal/parameter	Cu	Pb	Zn	Cd	Fe	pH	OM	EC
Cu	1							
Pb	0.636	1						
Zn	0.085	0.712	1					
Cd	0.697	0.899	0.772	1				
Fe	0.091	0.709	1.000**	0.777	1			
pH	-0.919	-0.344	0.065	-0.555	0.053	1		
OM	0.881	0.201	-0.367	0.304	-0.359	-0.934	1	
EC	0.791	0.219	0.003	0.533	0.018	-0.960*	0.806	1

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

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

Table 4.13: Pearson's correlation coefficient of heavy metals and some physicochemical parameters for Yusuf Dan-tsoho Memorial Hospital dump soil

Metal/parameter	Cu	Pb	Zn	Cd	Fe	pH	OM	EC
Cu	1							
Pb	0.314	1						
Zn	0.176	0.924	1					
Cd	0.710	0.828	0.601	1				
Fe	0.023	0.914	0.985*	0.537	1			
pH	-0.373	-0.373	0.008	-0.702	-0.004	1		
OM	0.264	0.428	0.056	0.686	0.089	0.990**	1	
EC	0.398	0.397	0.017	0.726	0.025	-0.999**	0.988*	1

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

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

Table 4.14: Pearson's correlation coefficient of heavy metals and some physicochemical parameters for Municipal dumpsite soil.

Metal/parameter	Cu	Pb	Zn	Cd	Fe	pH	OM	EC
Cu	1							
Pb	0.902	1						
Zn	0.580	0.475	1					
Cd	0.994**	0.943	0.540	1				
Fe	0.580	0.443	0.997**	0.532	1			
pH	-0.875	-0.687	-0.174	-0.857	-0.217	1		
OM	0.731	0.830	-0.069	0.786	-0.091	0.781	1	
EC	-0.850	-0.741	-0.079	-0.854	-0.090	-0.979*	0.888	1

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

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

At the municipal dumpsite, the correlation analysis between the concentrations of heavy metals and physicochemical parameters showed correlated values such as between Cu and Pb, Zn, Cd, Fe, pH, OM and EC recorded as (r=0.902), (r=0.580), (r=0.994**), (r=0.580), (r=-0.875), (r=0.731) and (r=-0.850) respectively. The analysis also obtained correlated values between Pb and Zn, Cd, Fe, pH, OM and EC recorded as (r=0.475), (r=0.943), (r=0.443), (r=-0.687), (r=0.830) and (r=-0.741) respectively. Similarly, correlations were recorded between Zn and Cd, Fe, pH, OM and EC as (r=0.540), (r=0.997**), (r=-0.174), (r=-0.069) and (r=-0.079) respectively and between Cd and Fe, pH, OM and EC were given as (r=0.532), (r=-0.857), (r=0.786) and (r=-0.854) respectively. There were correlated values also recorded between pH and OM and EC which were given as (r=0.781) and (r=-0.979*).

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physicochemical Parameters

The physicochemical properties of the dump soils recorded that the pH of the dump soils recorded were slightly alkaline in nature with Yusuf Dan-tsofo memorial hospital and Municipal dump soils having the lowest and highest pH values respectively across the seasons. This suggests that the dumpsites were alkaline in nature. According Isirimah *et al.,* (2003), most plants and soil microorganisms thrive best in soils of pH between 6 and 7.5. Soil pH generally has a major contribution in the metal bioavailability, toxicity and leaching capability into the surrounding areas (Chimuka *et al.,* 2005).

Soil organic matter (SOM) for dump soils were low based on the classification of soil organic matter given by Enwezor *et al.,* (1998). The organic matter in the soil samples varied significantly with municipal dump soils containing the highest amount of organic matter, which may be responsible for increase in the soil pH as compared to other dump soils. This observation was supported by Oyedele *et al.,* (2008), who reported that dump sites had significantly higher pH regime and soil organic matter as compared to the control soil. Ayolagha and Onwugbuta (2001) also demonstrated that high organic matter (>2.0%) in soils is conducive for heavy metal chelation formation. Higher organic matter content in municipal dump site soil may be due to decomposition and composting processes of the animals waste, plants/vegetable matter and polymer or plastic materials and also washed away agricultural chemicals (pesticides, insecticides and herbicides) that passed through the dump site before entering the main river from the farms and town (Alloway and Ayres, 1997).

The physicochemical properties of the dump soils showed poorly sorted soils with sand fractions generally high in all the samples. From soil textural triangle, the dump soils from 44 Nigerian Army Reference Hospital belong to sand-clay loam texture while others belong to sand-loam texture class. The clay fractions were low across the soil samples. According to Nyles and Ray (1999), soil samples with high sand and low clay fractions have high pollutant leaching potentials. It could therefore be deduced

that the underground water in these dump sites could suffer from pollution. Though the soils of the dumpsites predominantly contained high sand fractions (>63.0%) that allows high permeability of water and leacheates, the textural class (loamy sand) may be suitable for sanitary landfills (Loughry, 1973). The soils from the 44 Nigerian army reference hospital dumpsite consisted of moderately high clay fractions thus they exhibit plasticity and encourage surface water flooding and pollution. This clayey texture of the dump soils also favours low permeability of water and leacheates (Ahn, 1993).

The electrical conductivity of the dump soils were higher at municipal dumpsite compared to the medical dumpsites. The high electrical conductivity value of municipal dump soil may be attributed to the presence of higher percentage organic matter, which retains much higher positively charged ions. The presence of these ions in the moisture filled soil pores will enhance soil electrical conductivity (Badmus *et al.,* 2014). These values are in close range with the values reported by Osakwe *et al.,* (2008), Ovasogie and Omoruyi (2007), Isirimah (1987) but comparatively lower than the values reported by Gupta and Pant (1983) and Tukura *et al.,*(2007). This may be due to the increase in the concentration of some soluble salts in the soil.

5.2 Soil Heavy Metal Concentration

The results obtained for the concentrations of the heavy metal across the sampling sites varied considerably. This variation showed that Saint Gerard Catholic hospital dump soil contained more concentrations of heavy metals than other sites due to the types of medical waste deposited. The municipal site has the least mean concentrations of heavy metals while cadmium has the lowest value.

Nigerian Army reference hospital dump soils recorded the highest mean concentration of Pb among all the sampling sites in both season. The concentrations of Cu obtained were higher than other metals analysed in NARHK dump soils during dry and wet season. The results also showed that Saint Gerard catholic hospital dump soils contained the highest mean concentration of Cu among all the sampling sites while Yusuf Dan-tsoho memorial hospital recorded the least concentration of Cu. The concentrations of Cd during dry and wet season at YDMHK showed no significant difference. The municipal dump soils recorded the highest concentrations of Cd in both season than any other sampling sites. The mean concentrations of Cu in both seasons were higher than other metals analyzed in municipal dump soils. It (municipal) also recorded the least concentrations of Pb among the studied metals in its dump soil.

The results also showed a decreasing pattern in the mean concentrations of the heavy metals vertically down the soil depths. The concentrations of all heavy metals at depth of 0-5cm (top-soil) were higher than those found at the depth of 5-10cm (sub-depth). It can be assumed that the sub-soil is considerably less influenced by soil-forming process and anthropogenic input than the top soil. Seasonally, the mean concentrations of metals obtained across the dumpsites showed high values of metals in dry season compared to wet season. This might be due to the run off effect that is capable of removing heavy metals from the dump sites and the effect of rainfall which may facilitate the dilution of soil solution during the wet season.

Previous studies showed that surface soils are better indicator of metallic burden and metal concentration decreases horizontally away from the dumpsite. According to Sunday *et al.,* (2012), the concentrations of heavy metals decrease vertically down the depth and horizontally away from dumpsites. Seasonal variation has no significant effect on concentrations of heavy metals at dumpsites. Heavy metal concentrations at different depths across the sampled sites showed significant variation,

this trend may be correlated with the soil properties that influence heavy metal availability in different depth. The relationship between heavy metals and the depth obey exponential distribution (Jintao *et a*l., 2011). The high concentrations of heavy metals during dry season can be attributed to dumping and burning of wastes as a common practice at the dumping site. This and more intense evaporation in the dry season makes soil solution more concentrated than in wet season (Brady, 1984).

The student t-test showed that there is no significant difference in the concentrations of the heavy metals (except iron) in both seasons. The concentrations of the heavy metals in all the studied dump soils are within permissible limits set by the standard regulatory bodies (US EPA, 1993, FEPA, 1999 and WHO, 1996) for agricultural soil. Even though these heavy metal concentrations fell below the critical permissible concentration level, it seems that their persistence in the soils of the dump site may lead to increase uptake of these heavy metals by plants. Klock *et al.,* (1984) reported that plants can also accumulate relatively large amounts of these elements by foliar absorption.

The accumulation of heavy metals can degrade soil quality, reduce crop yield and the quality of agricultural products, and thus negatively impact the health of human, animals, and the ecosystem (Nagajyoti et al. 2010)

5.3 Incinerator Ash

The concentrations of heavy metals varied with regard to the location of incinerator. Zinc concentration is high in both incinerators ash samples, probably due to burning of teeth, bones and plastics material. The results recorded high concentrations of heavy metals in ash during dry season and more concentrations at Saint Gerard catholic hospital. The high concentration of Pb in NARHK incinerator ash samples may be due to burning considerable amount of plastic. Heavy metals are not destroyed by incineration but simply concentrated in the remaining ashes or released to the environment via stack emission (Ranjan *et al*., 2004). The concentrations of heavy metals in the ashes are dependent on the amount of metals in the wastes being incinerated. Heavy metals can remain in

their original form during incineration or may react to form new compounds such as metal oxides, chlorides or fluorides (Dempsey and Oppelt 1993). Student t-test for the result showed that there is no significant difference in the concentration of all the metals analysed for both the wet and dry season. The concentrations of heavy metals in the ash samples are above US EPA (1993) permissible limit.

5.4 Organic Pollutants in Soil and Ash Samples

D-limonene was identified in Nigeria army reference hospital dump soils and incinerator ash sample and Saint Gerard catholic hospital incinerator ash sample. It is a colorless cleansing liquid used as a reagent and solvent in organic synthesis. In medical treatment, d-limonene has been used to dissolve retained cholesterol gallstone post-operatively (IARC 1993), it is used as an additive to systems for transdermal application of medicines to increase the penetration of active substance (Karlberg and Lindell, 1993).

According to Osterhout (2013), n-hexadecanoic acid consumption in foods when contaminated with other toxic impurities may cause cancer and neurotoxicity. n-hexadecanoic acid enters the soil through chemical waste (soaps, cosmetics and release agent). It is slightly hazardous in case of skin contact, eyes contact or ingested into the body system but acts as an anticancer drug (Harada *et al.,* 2002).

Waste at Saint Gerard Catholic hospital incinerator ash contained 1,3-cyclopentadiene which is a colorless liquid with unpleasant odor. It is used as a starter compound in the manufacturing of resins and in organic synthesis as a starting material for synthetic prostaglandins, chlorinated insecticides and formation of sandwich compounds by chelation. Long term exposure may damage the liver and kidneys (ICSC. 2004).

The analysis recorded that benzenecarboxylic acid and octadecenamide were identified in the municipal dump soil. Report showed medical devices constitute a special, but significant source of exposure to benzenecarboxylic acid. It is used in blood storage bags, tubing and other devices. High exposures can occur to individuals receiving blood transfusion, undergoing surgery, or undergoing kidney dialysis. Recently, it has been suggested that benzenecarboxylic acid may contribute to the occurrence of the ''testicular dysgenesis syndrome'' in humans, that is testicular germ cell cancer, cryptorchidism and low sperm count (Mahood *et al*., 2007). This implies that the municipal dumpsite might contain medical waste disposed by health centers in the community. Octadecenamide can cause irritation of the skin, eyes and respiratory tract. It could also have lasting effect on aquatic organism when ingested or absorbed.

Yusuf Dan-tsoho memorial hospital dump soils and Saint Gerard catholic hospital dump soil and incinerator ash samples on analysis identified the presence of methyl octanoate. Methyl octanoate causes breathing difficulties when inhaled and symptoms of overexposure may be headache, dizziness, tiredness, nausea and vomiting (Acros organic, 2015).

5.5 Assessment of Pollution Index

Assessment of soil pollution becomes difficult when contaminants belong to different sources and their products are variably distributed. From the calculated pollution indices of the heavy metal in medical wastes, the pollution levels of the heavy metal decreased in the order of Cd>Fe>Pb>Cu>Zn. According to Li and Xu (2003), pollution index (P_i) > 1, means the sample is polluted. The dump soil from Yusuf Dan-tsoho memorial hospital had the lowest mean values of pollution indices of heavy metal in general. High pollution indices for Cd, Fe and Pb were observed in virtually all the dumpsites notwithstanding the season (except Fe metal at wet season). The pollution index results showed that NARHK and SGCHK dump soils are polluted with Pb while all the dumpsites are polluted with Fe (dry

season) and Cd. Based on environmental quality index, municipal dump soil is severely polluted with Cd in both season and not recommended for agricultural use. Cadmium is a non-essential element of human health with a high biological toxicity; it mainly accumulated in the surface soil which enters the body mainly through the digestive system.

5.6 Correlation

The correlation results obtained at Nigerian army reference hospital dumpsite recorded a strong positive correlation ($P<0.01$) of Pb with Cu, and between Fe and Zn. It also recorded a positive correlation ($P<0.05$) of Cd with Cu and Pb. Yusuf Dan-tsoho memorial hospital dump soil showed a strong correlation of pH with electrical conductivity and organic matter while the municipal dump soil had a strong positive correlation between Cd and Cu. The strong positive correlation implies that correlated values are directly proportional while negative correlation implies inverse proportionality.

CHAPTER SIX

6.0 SUMMARY AND CONCLUSION

6.1 Summary

The physicochemical parameters analysed across the sampling sites showed that the dump soils were alkaline in nature. The soil organic matter recorded at the dump soils were low based on the classification of soil organic matter given by Enwezor *et al.,* (1998). The dump soils were poorly sorted with high sand fraction and low clay fraction. NARHK belong to sand-clay loam texture while others belong to sand-loam. The electrical conductivity of the dump soils were higher at municipal dumpsite compared to the medical dumpsites.

The hospitals and municipal dumpsites used in this study showed the presence of some heavy metals at concentrations below permissible limit and organic pollutants. The results of heavy metals concentrations obtained showed no significant difference in the wet and dry seasons except for iron, with high values in dry season. The results for metals analysis showed the following order of relative abundance as Fe>Zn>Cu>Pb>Cd for wet and dry seasons except for the municipal site where Cd comes before Pb , due to high plastic waste at municipal dumpsite.

Nigeria Army reference hospital dump soil had the highest mean concentration of lead among all the dump soil samples in both seasons. The concentrations of copper were higher than other metals analysed in Nigeria Army reference hospital dump soil while cadmium had the least concentrations in both seasons. Saint Gerard catholic hospital dump soil had the highest mean concentration of copper among all the dump soil samples in both seasons. Yusuf Dan-tsoho memorial hospital had the lowest concentrations of copper among all the dump soils. The highest mean concentrations of cadmium were in municipal dump soils compared to other dump sites due to high plastic waste.

Organic pollutants observed in the dumpsites are n-hexadecanoic acid, 2,9 dimethydecane, D-limonene, benzenecarboxylic acid, methyl octanoate, 1,3-cyclopetandiene and octadecenamide . D-limonene and n-hexadecanoic acid were identified in most dump soils while benzenecarboxylic acid and octadecenamide at municipal dump soil.

The pollution load index at the sampling sites showed that NARHK and SGCHK were polluted with Pb while all the dumpsites were polluted with Fe (during dry season) and Cd. The municipal dump soil had the highest pollution index of Cd while SGCHK had the highest pollution index of Fe.

6.2 Conclusion

The study showed the presence of the analyzed heavy metals at significant levels across the sampling points. The levels of heavy metals were noted to be affected by change in season and depth of soil. The concentrations were found to be higher in the dry season as well as 0-5cm depth. The results also showed that the soils were not polluted by pollutants (except Cd at municipal site) and not harmful for agricultural purposes. All values recorded were within the accepted limits of US EPA, FEPA and WHO respectively. Organic contaminants were also identified across the sampling sites.

6.3 Recommendations

Based on the observations and experience from this work, the following recommendations were drawn:

a. This research work should be carried out from time to time so as to monitor the amount of heavy metals and organic contaminants released into the soil to avoid accumulation due to leachate migration and food chain transfer.

b. The organic matter content, pH, conductivity and available heavy metals on open dump sites are greatly affected by the quantity of wastes dumped. Much more attention is needed for solid waste management to reduce the risk from heavy metal pollution.

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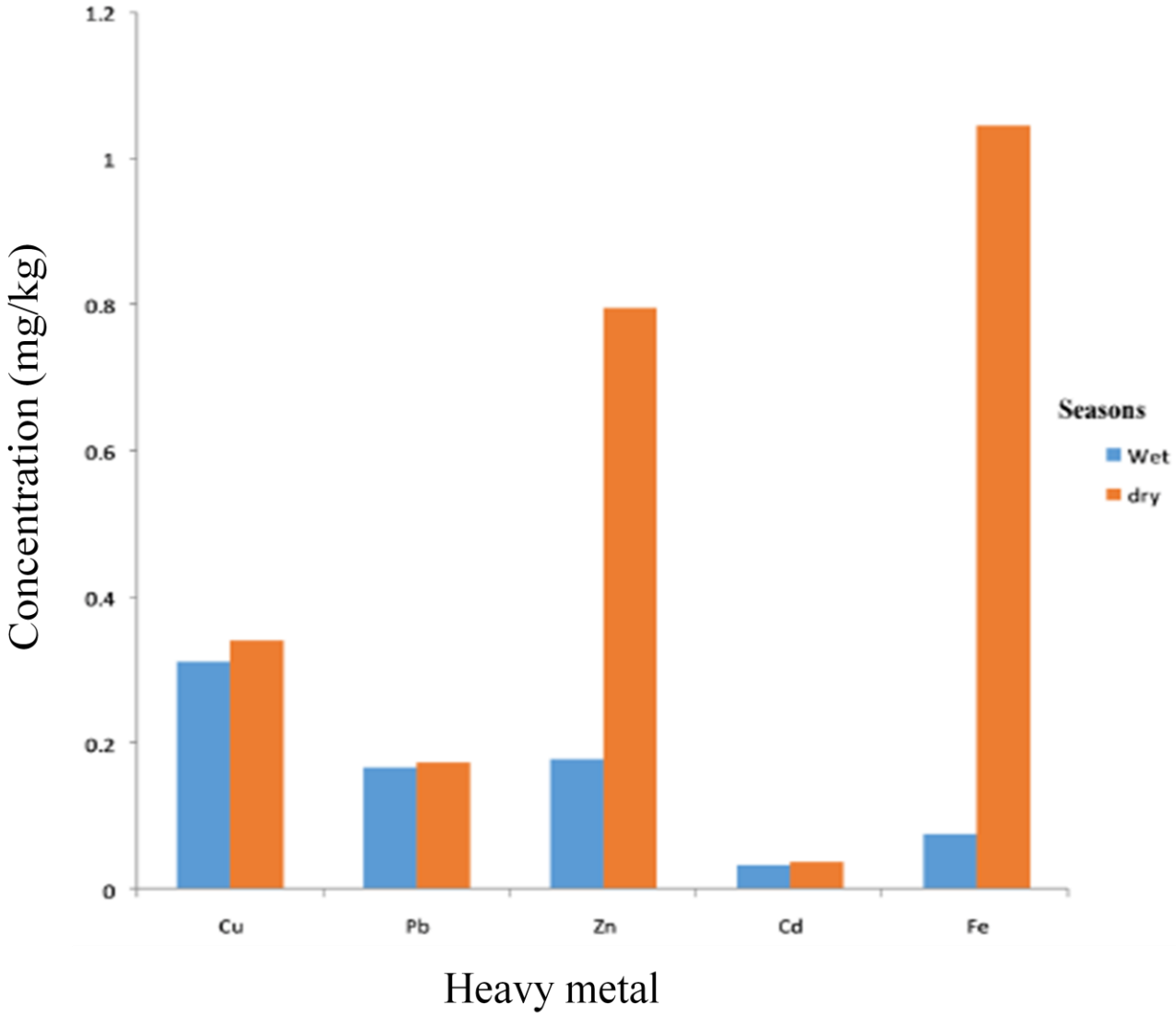
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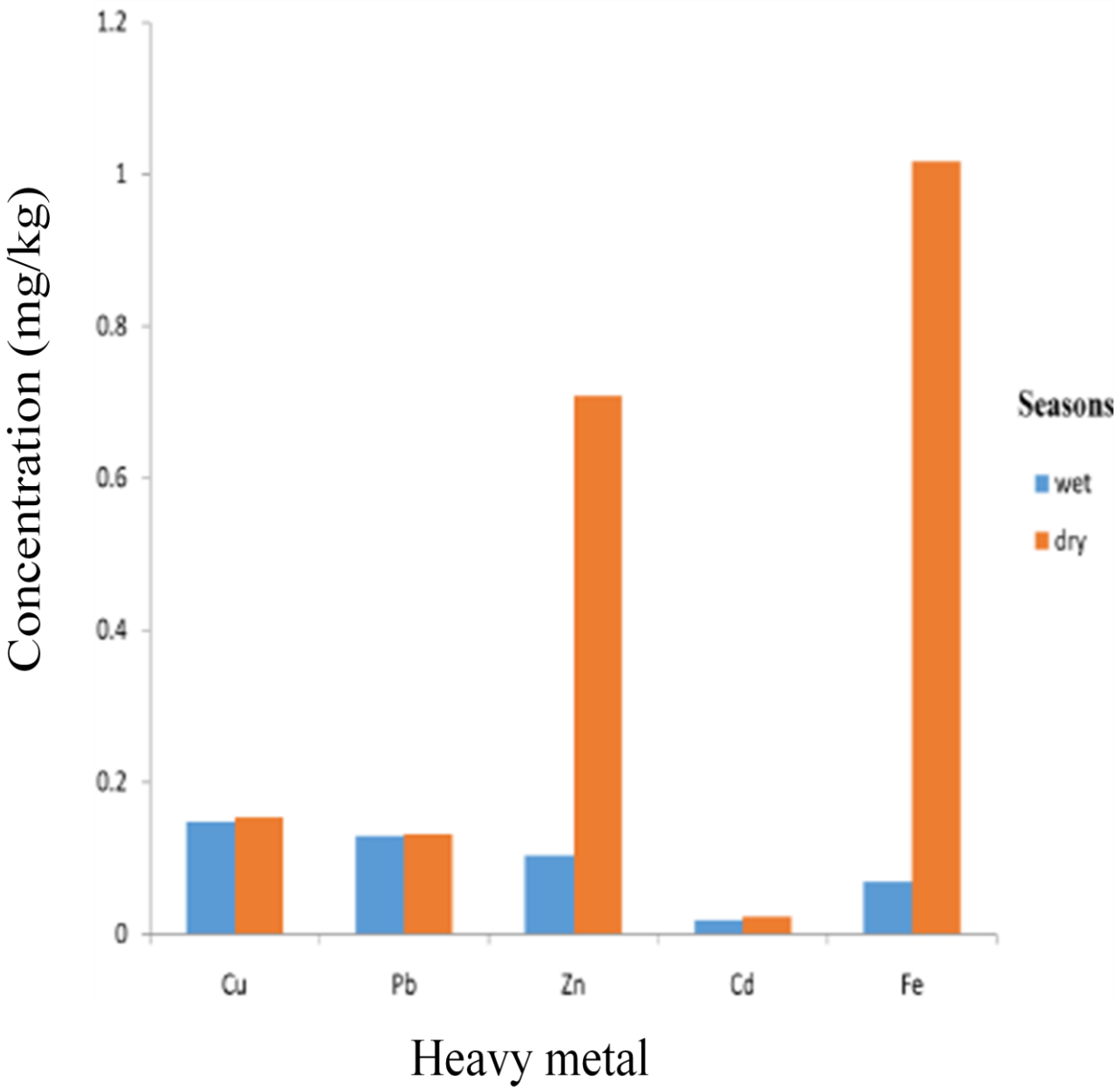
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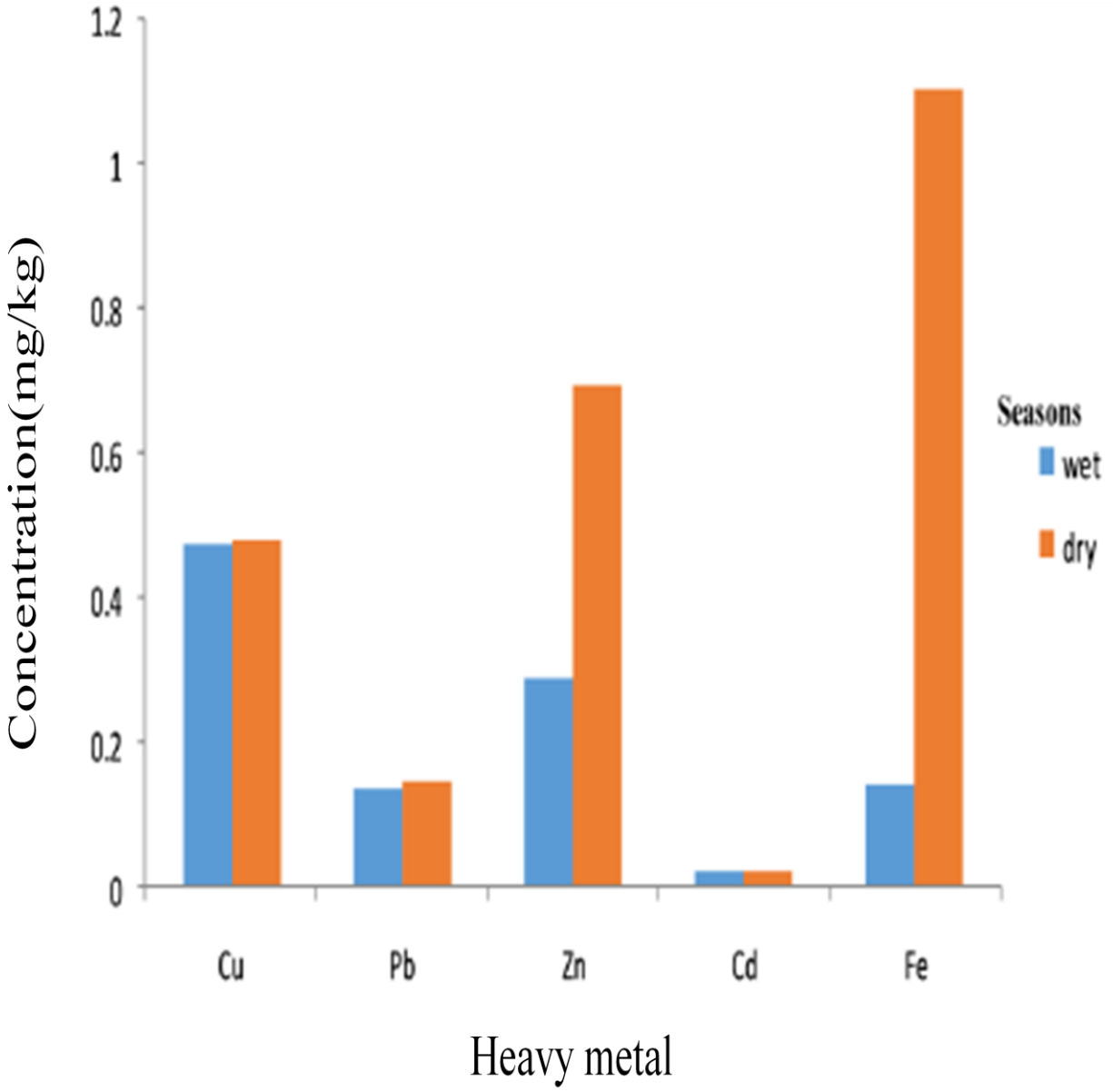
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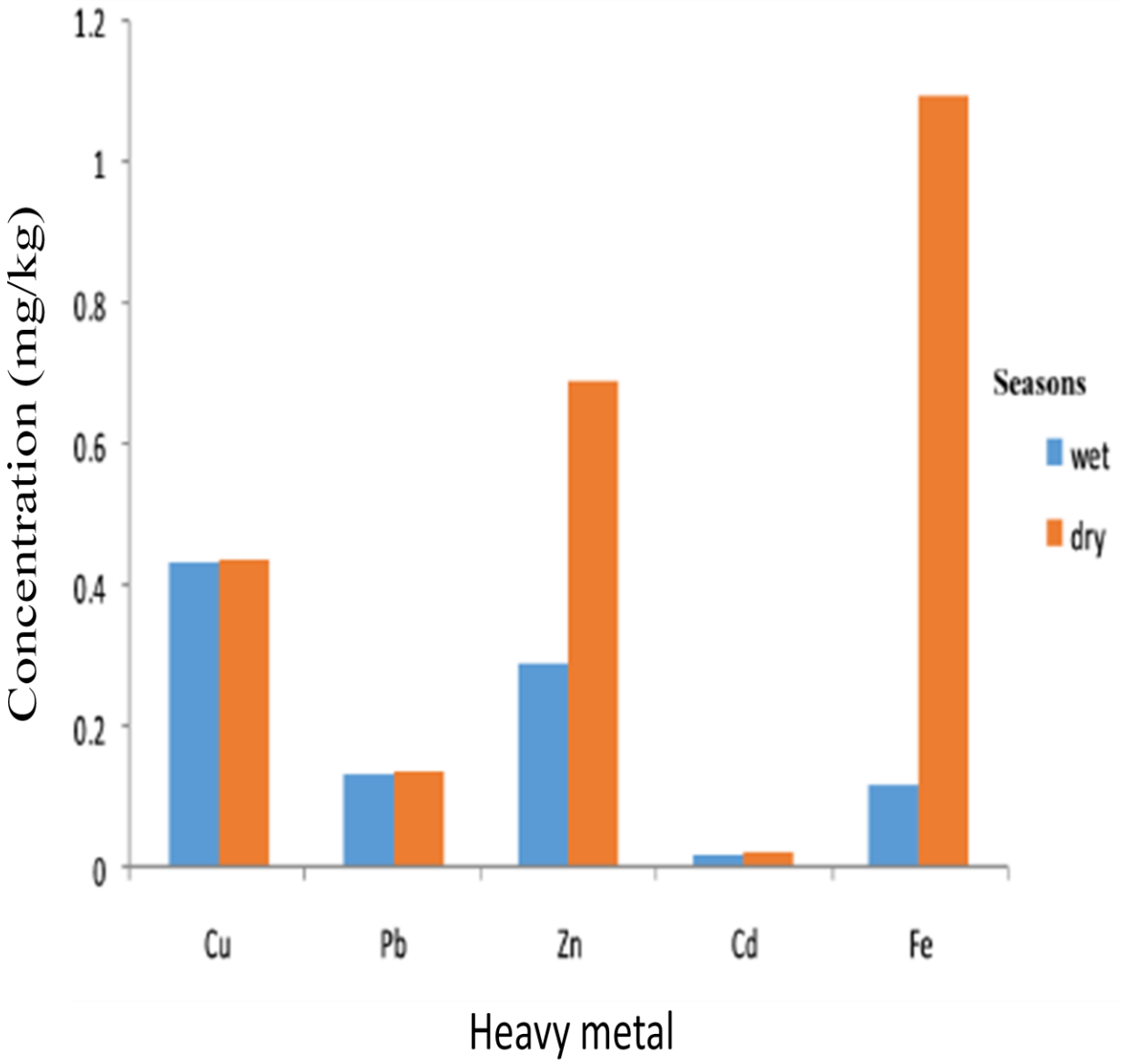
Appendix 1: Concentration of heavy metals in 44 Nigerian Army Reference Hospital Kaduna dump soil in both seasons at 0-5cm depth



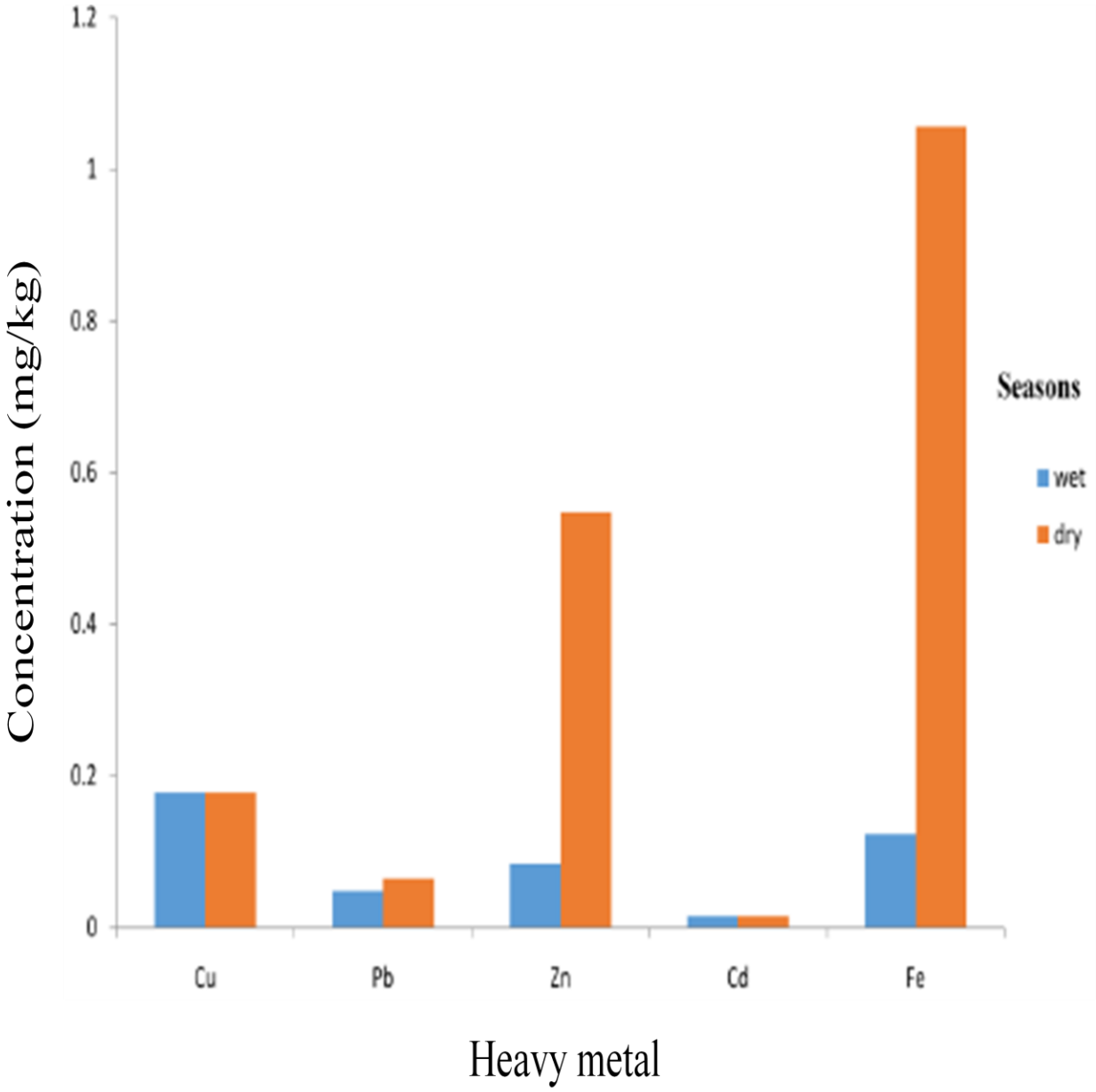
Appendix 2: Concentration of heavy metals in 44 Nigerian Army Reference Hospital Kaduna dump soil in both seasons at 5-10cm depth



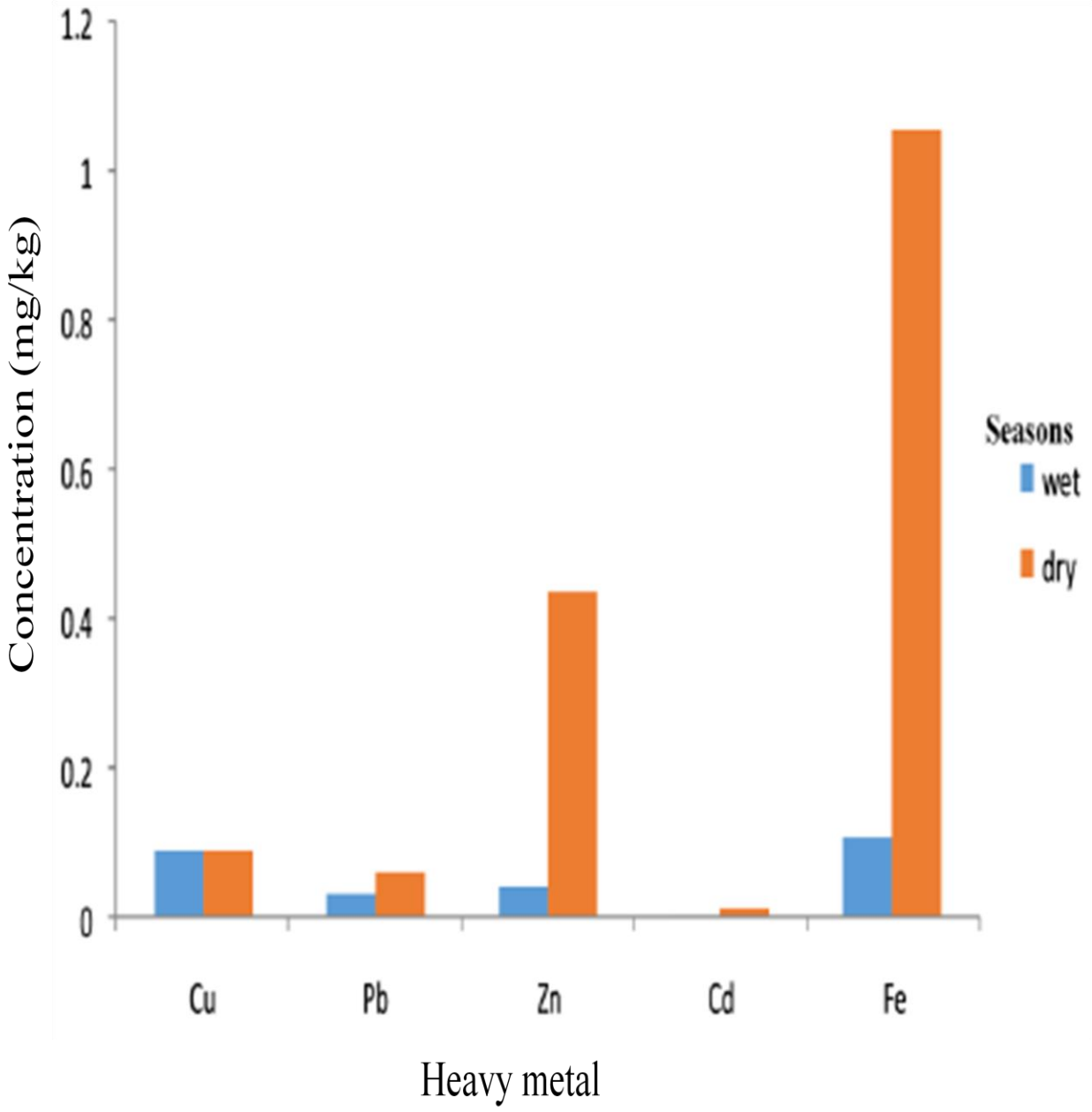
Appendix 3: Concentration of heavy metals in Saint Gerard Catholic Hospital Kaduna dump soil in both seasons at 0-5cm depth



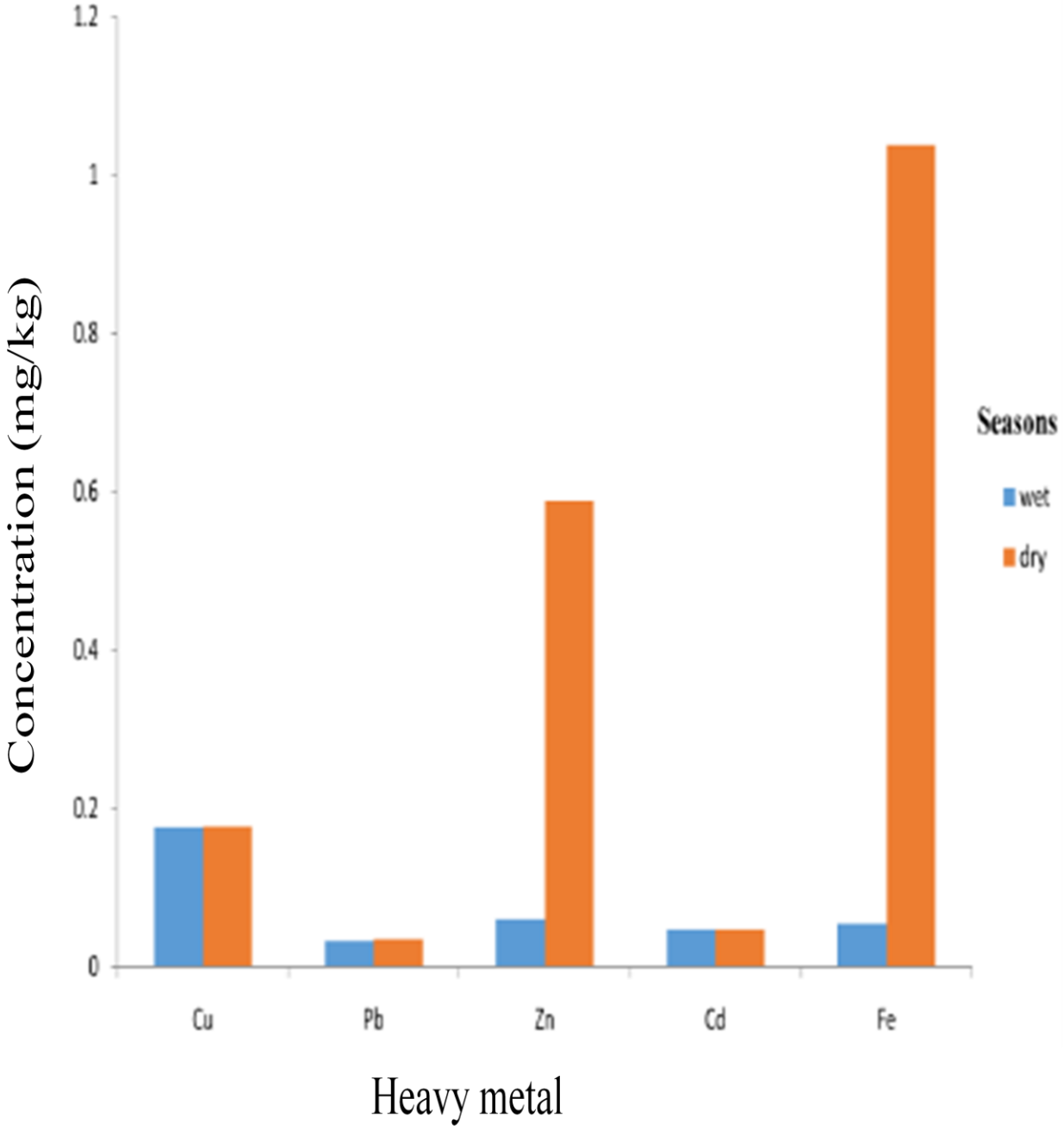
Appendix 4: Concentration of heavy metals in Saint Gerard Catholic Hospital Kaduna dump soil in both seasons at 5-10cm depth



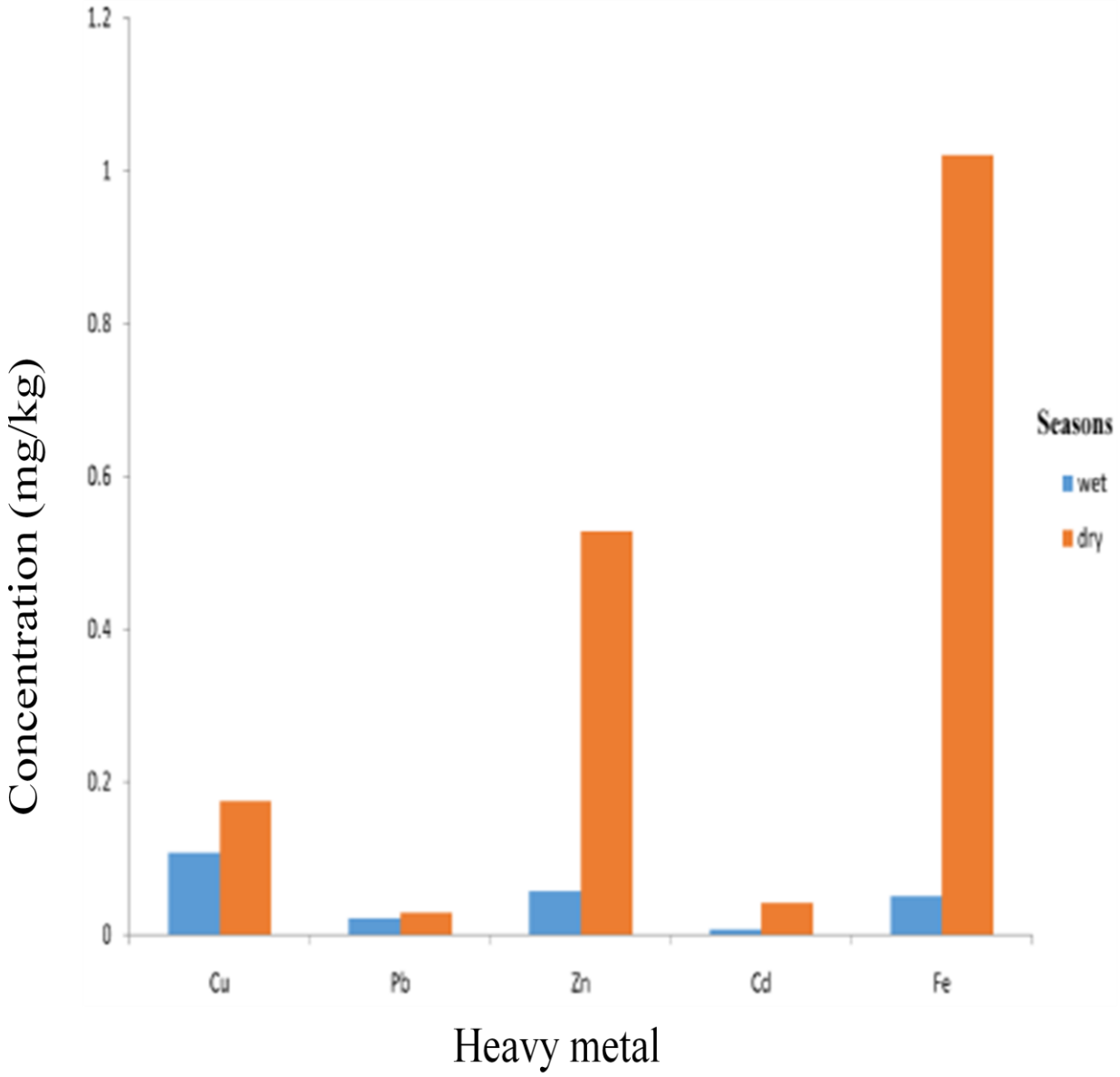
Appendix 5: Concentration of heavy metals in Yusuf Dan-tsoho Memorial Hospital Kaduna dump soil in both seasons at 0-5cm depth



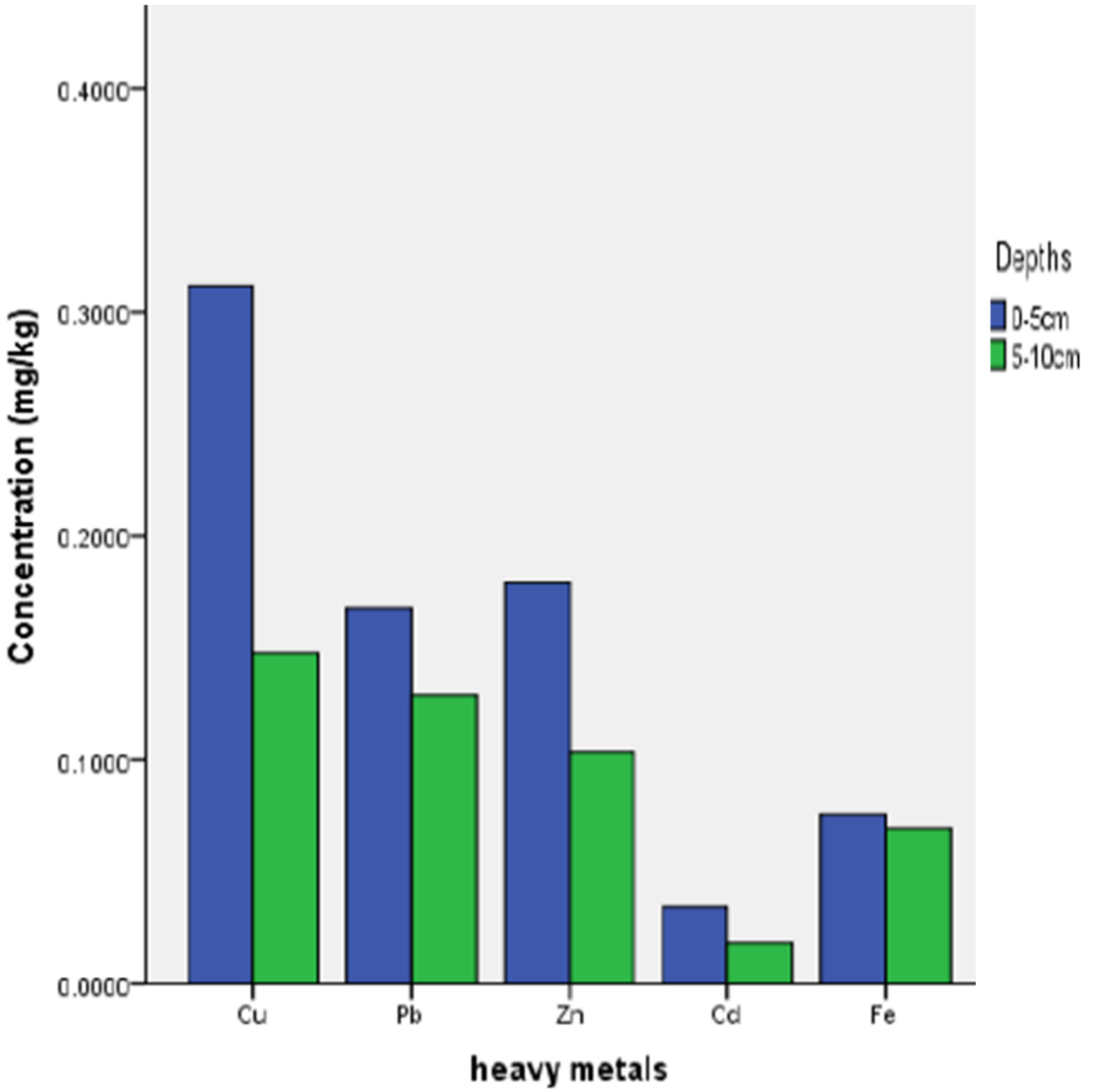
Appendix 6: Concentration of heavy metals in Yusuf Dan-tsofo Memorial Hospital Kaduna dump soil in both seasons at 5-10cm depth



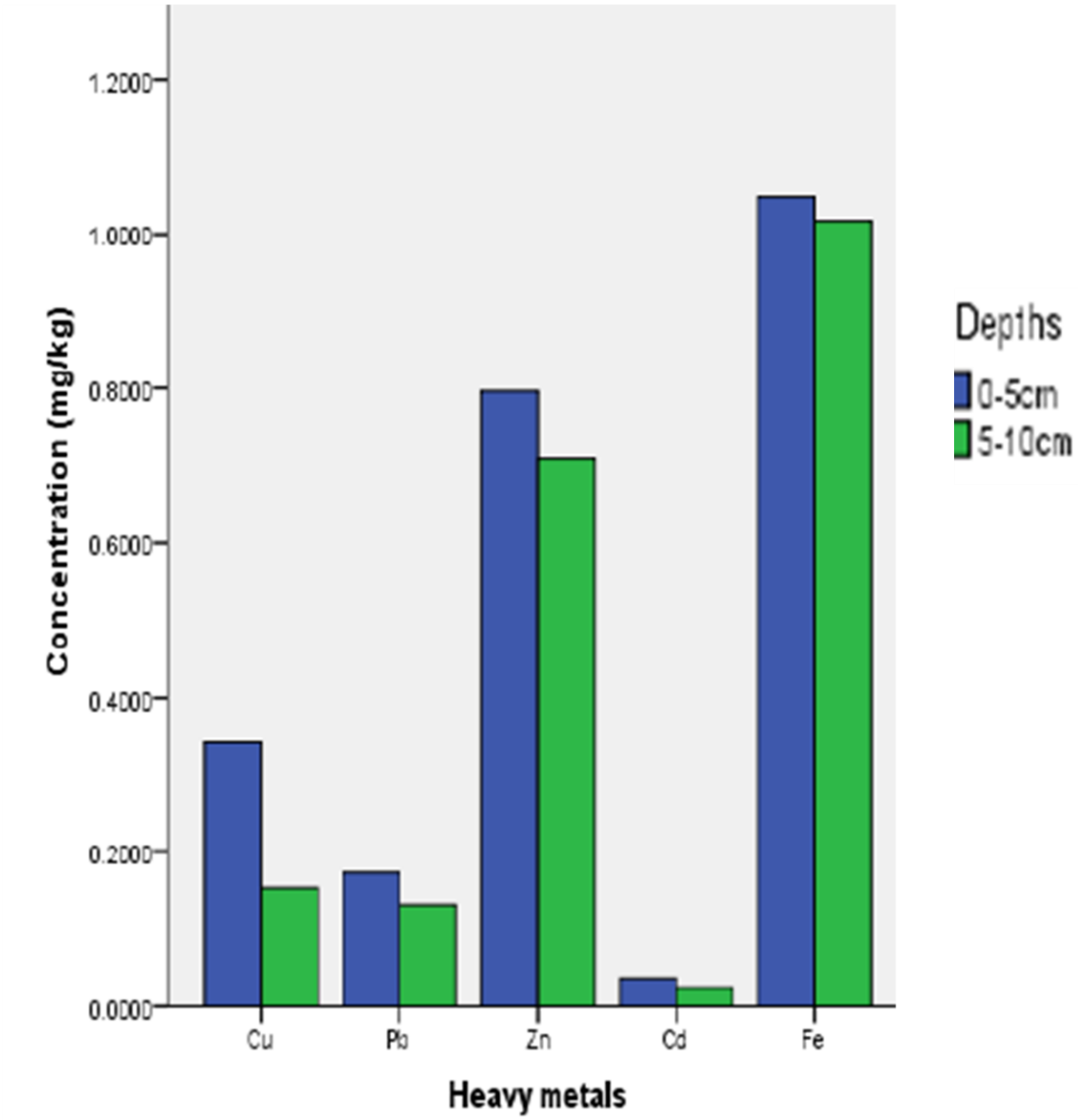
Appendix 7: Concentration of heavy metals in Municipal dump soil in both seasons at 0-5cm depth



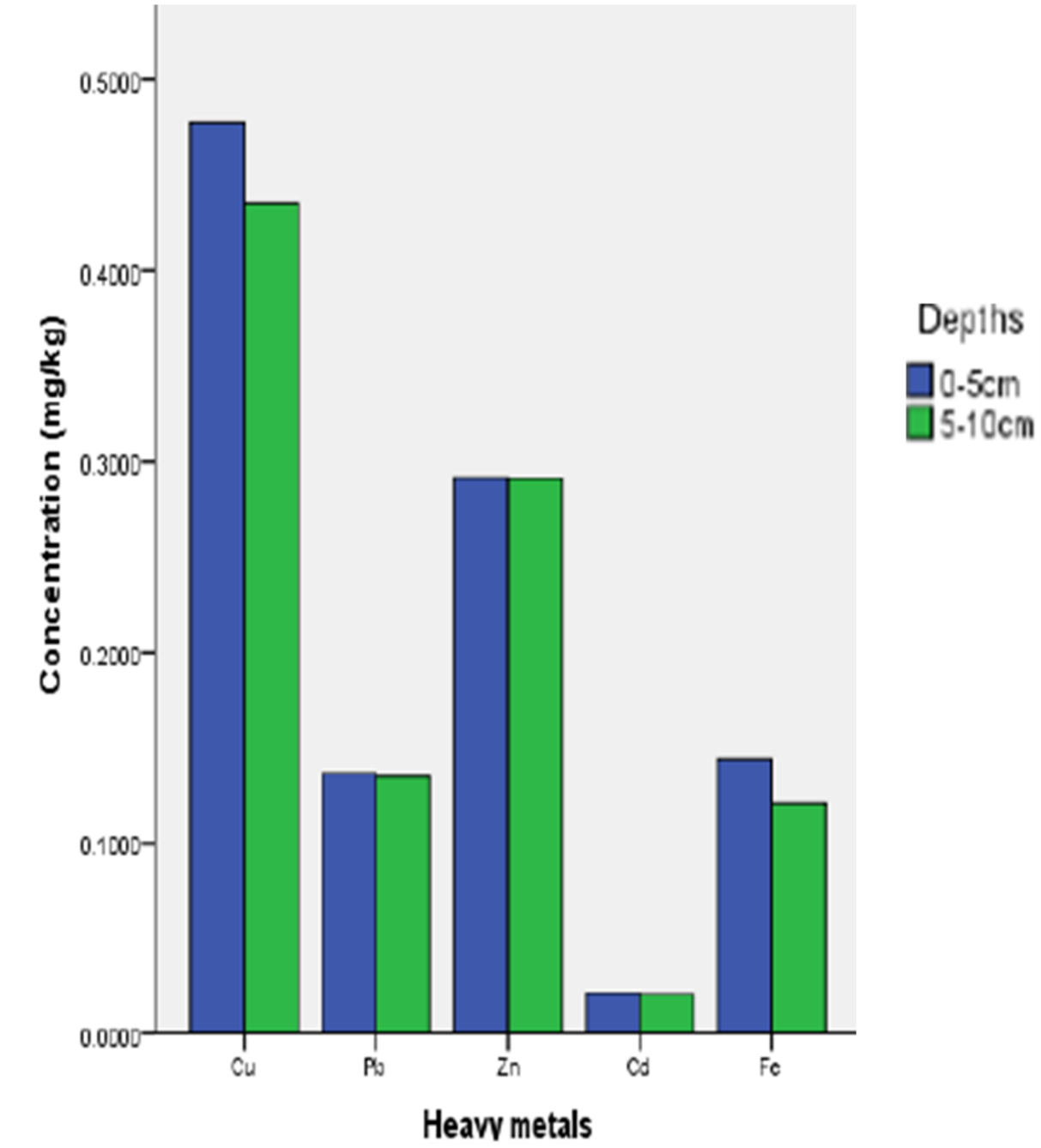
Appendix 8: Concentration of heavy metals in Municipal dump soil in both seasons at 5-10cm depth



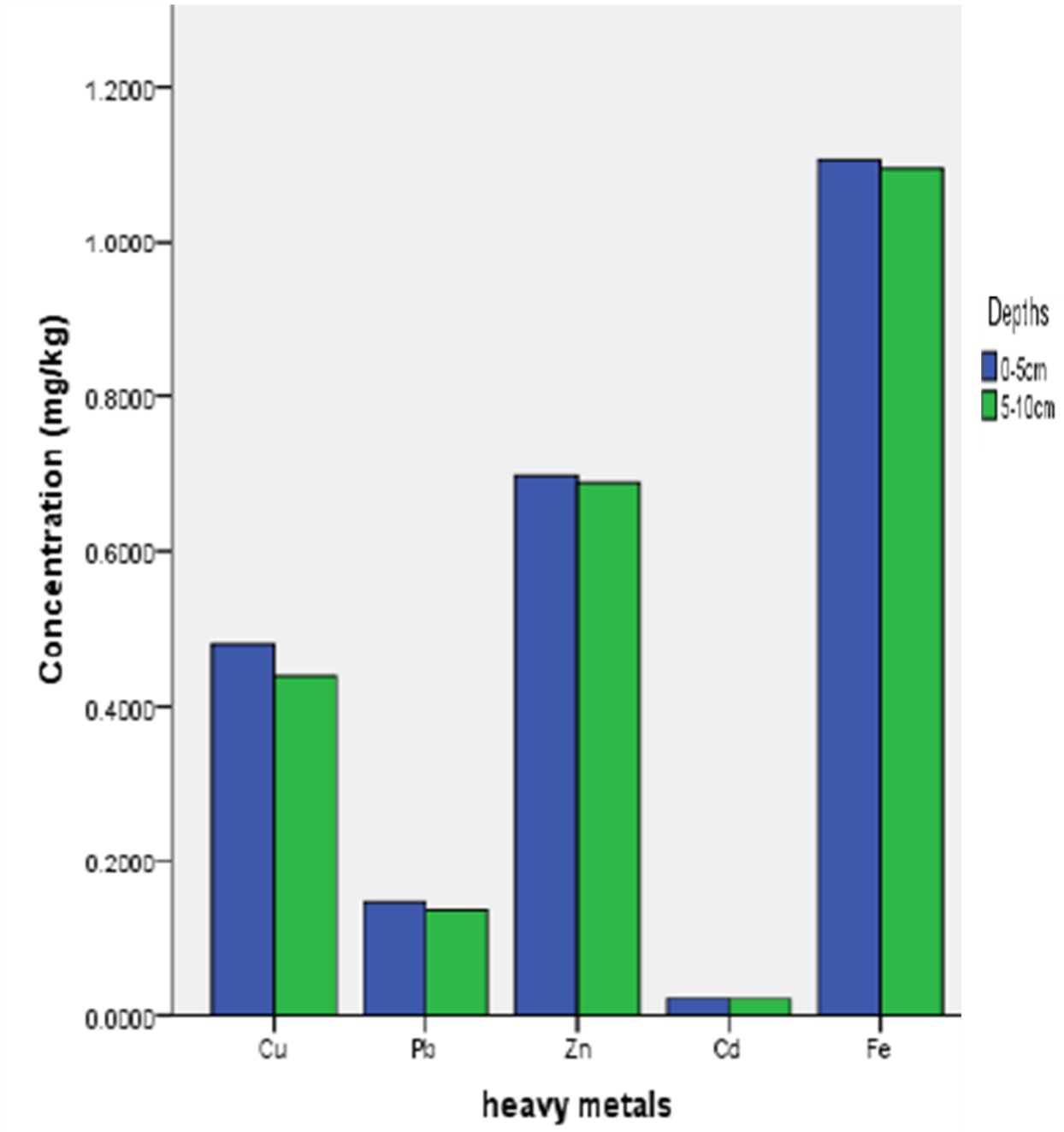
Appendix 9: Concentration of heavy metals in 44 Nigerian Army Reference Hospital Kaduna dump soil during wet season



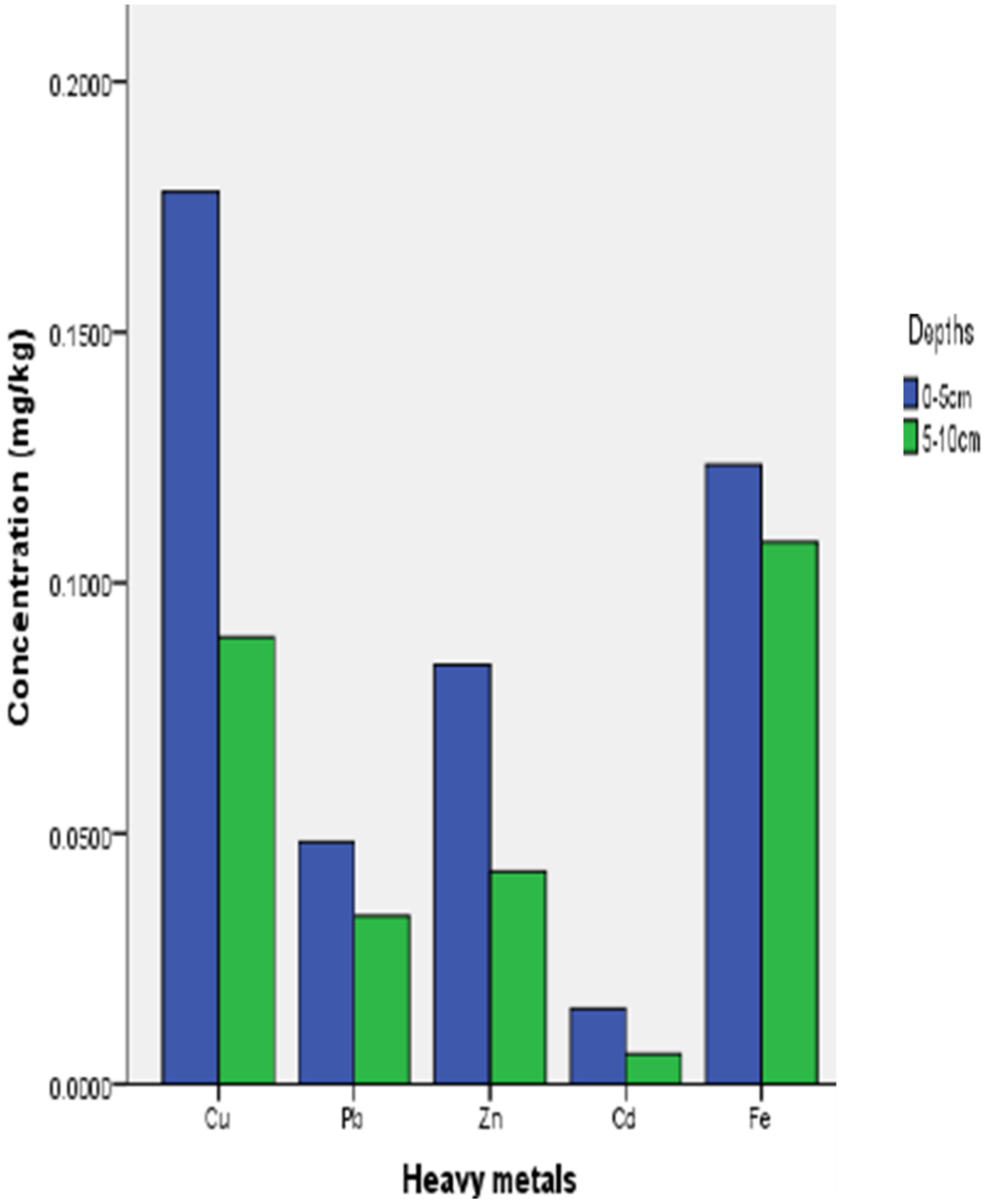
Appendix 10: Concentration of heavy metals in 44 Nigerian Army Reference Hospital Kaduna dump soil during dry season



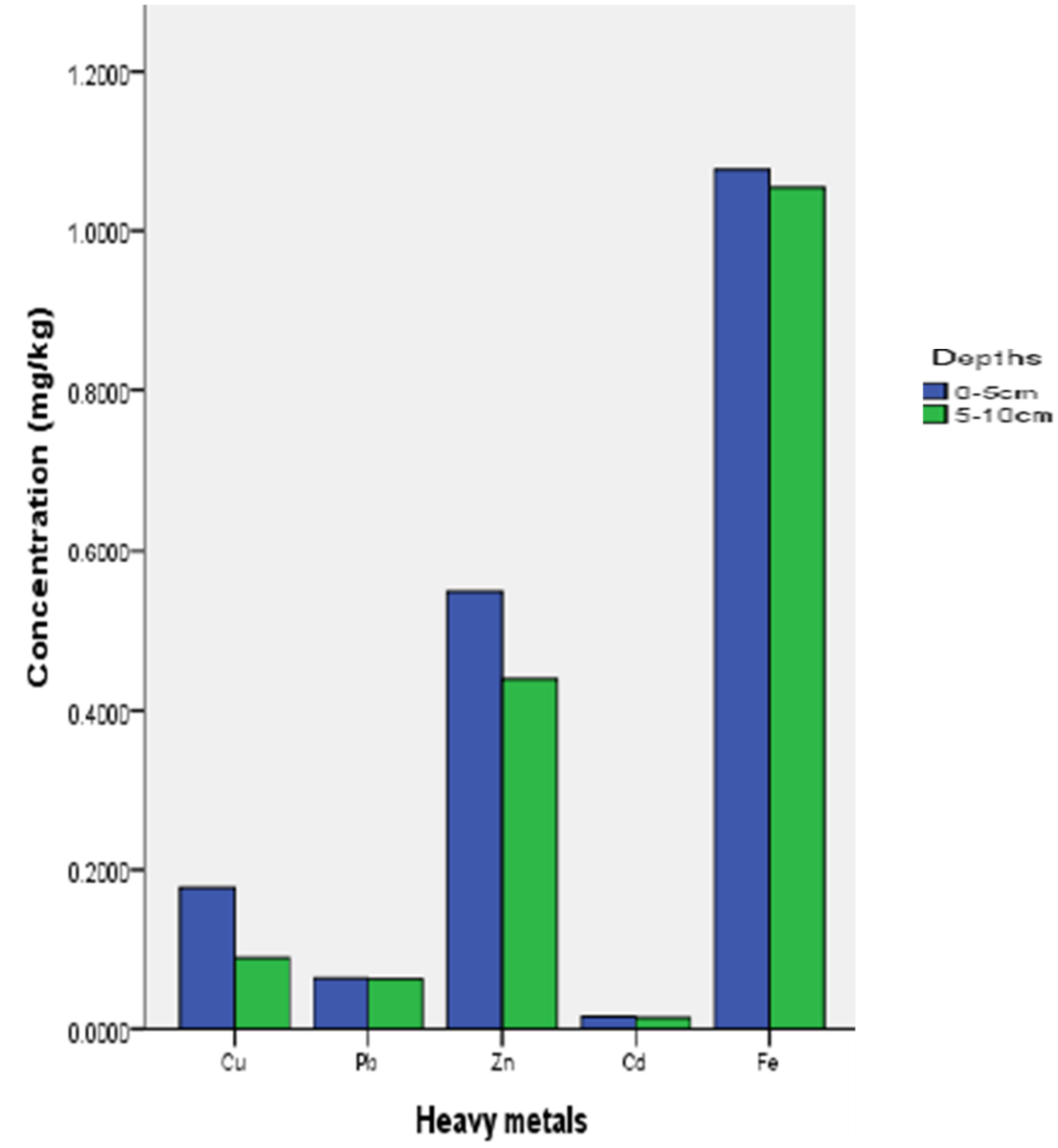
Appendix 11: Concentration of heavy metals in Saint Gerard Catholic Hospital Kaduna dump soil during wet season



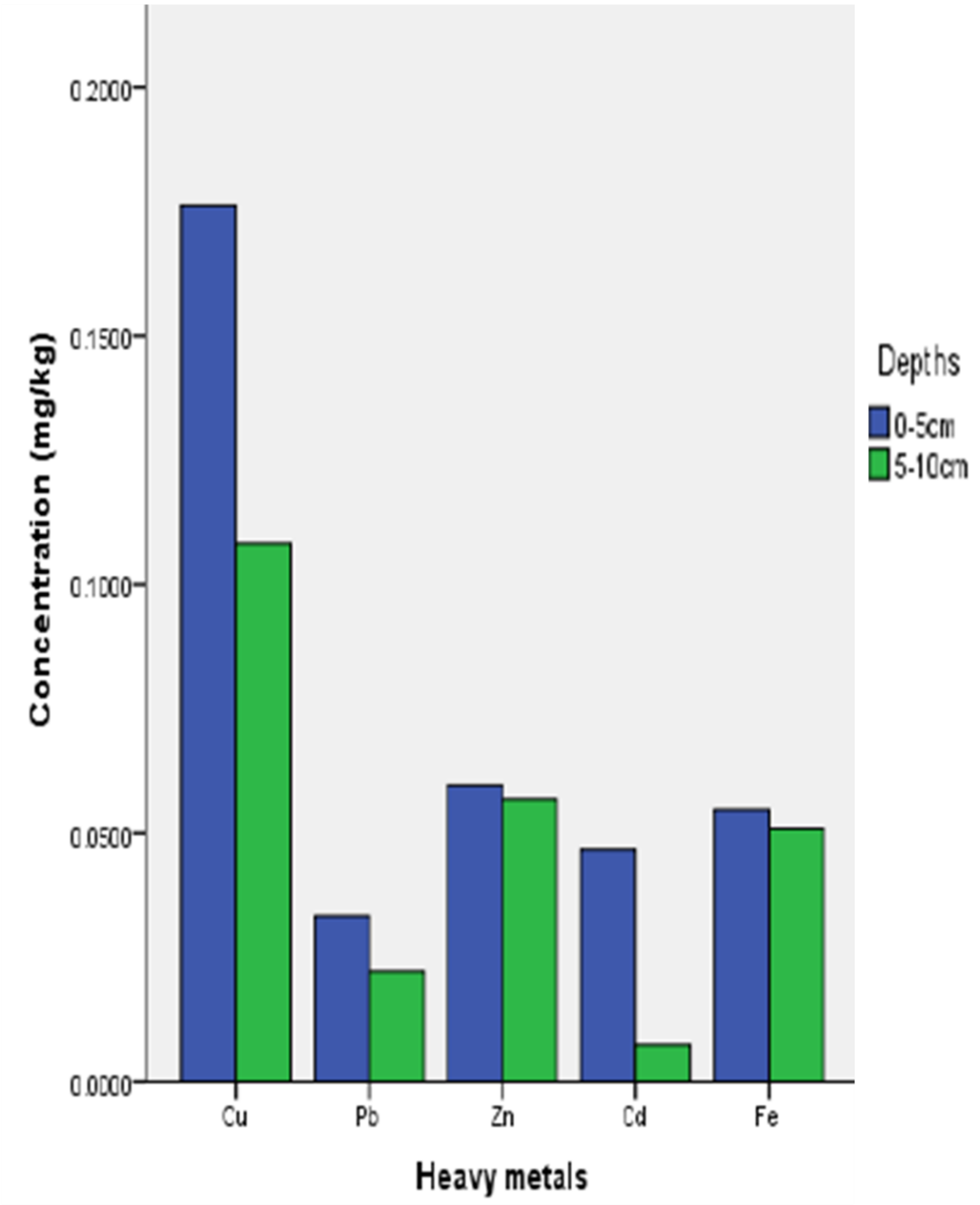
Appendix 12: Concentration of heavy metals in Saint Gerard Catholic Hospital Kaduna dump soil during dry season



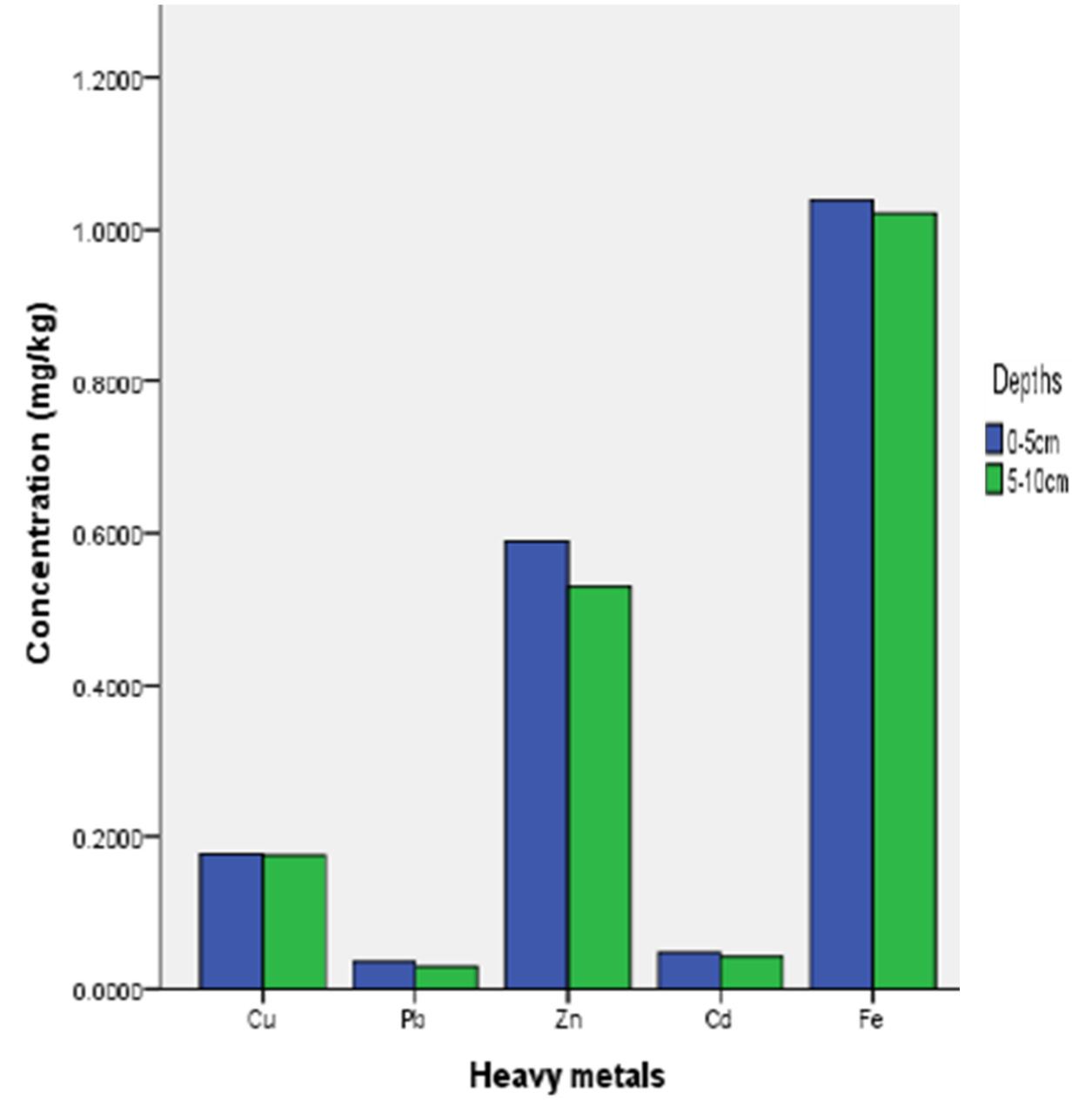
Appendix 13: Concentration of heavy metals in Yusuf Dan-tsoho Memorial Hospital Kaduna dump soil during wet season



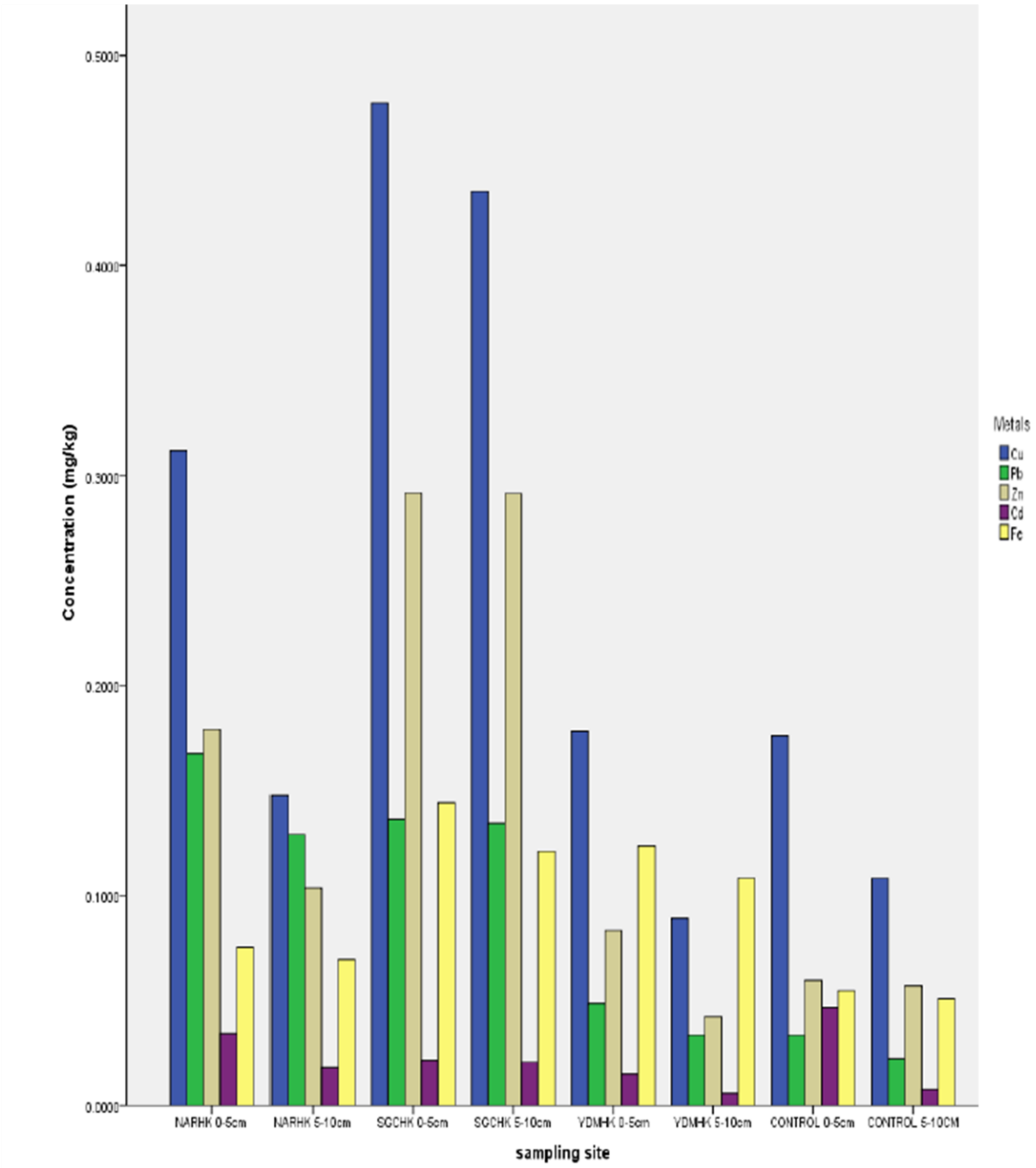
Appendix 14: Concentration of heavy metals in Yusuf Dan-tsoho memorial Hospital Kaduna dump soil during dry season



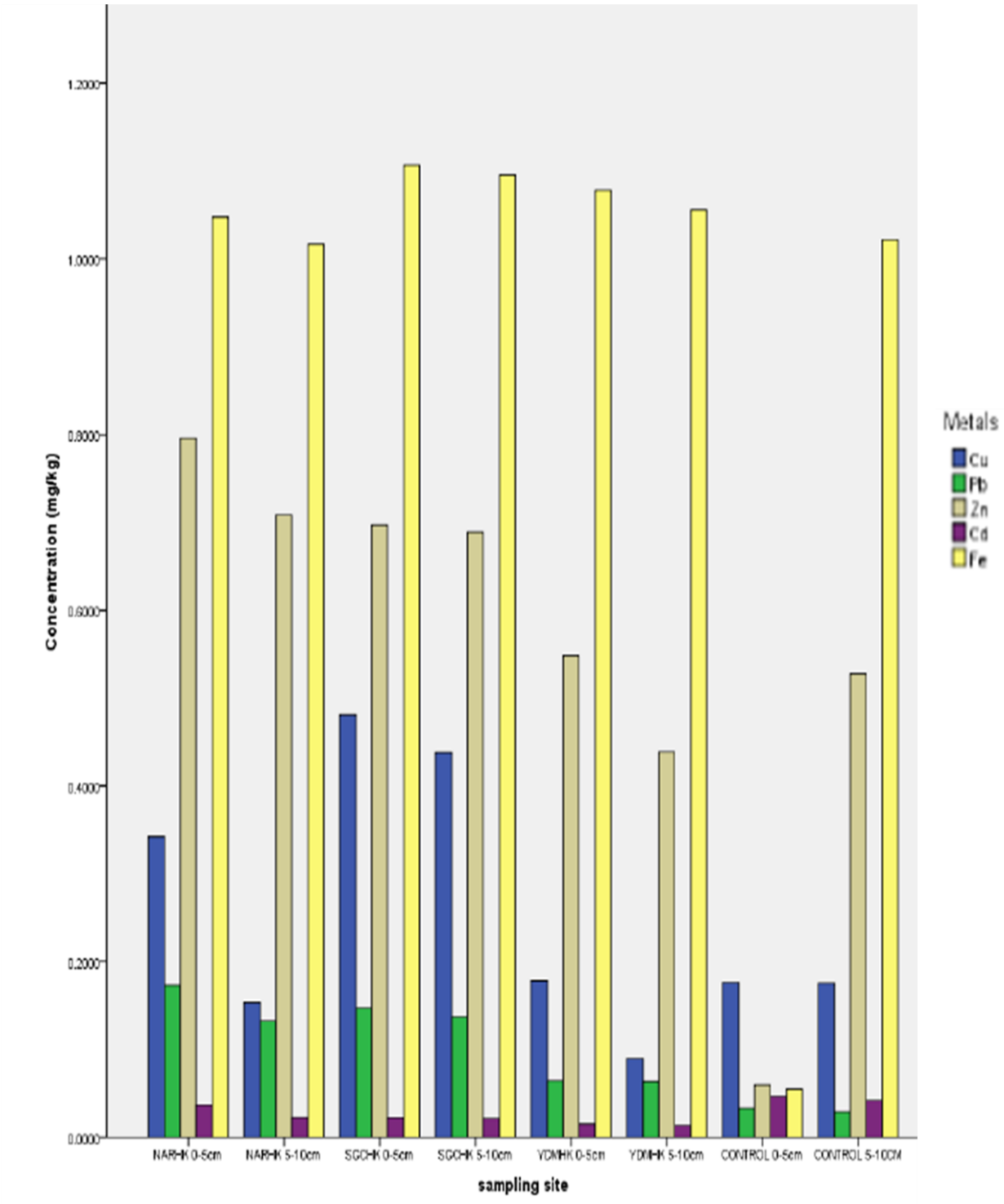
Appendix 15: Concentration of heavy metals in Municipal dump soil during wet season



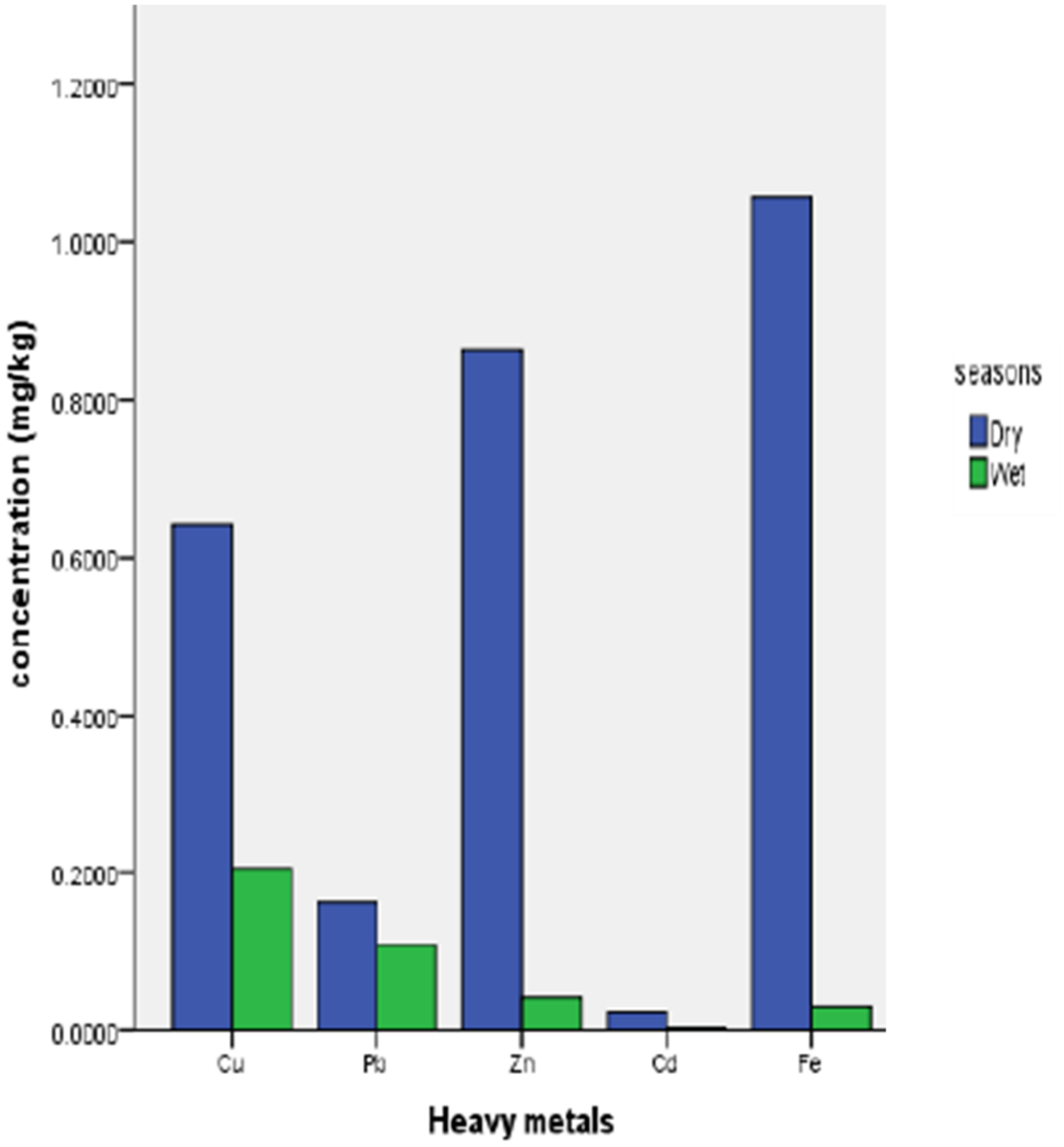
Appendix 16: Concentration of heavy metals in Municipal dump soil during dry season



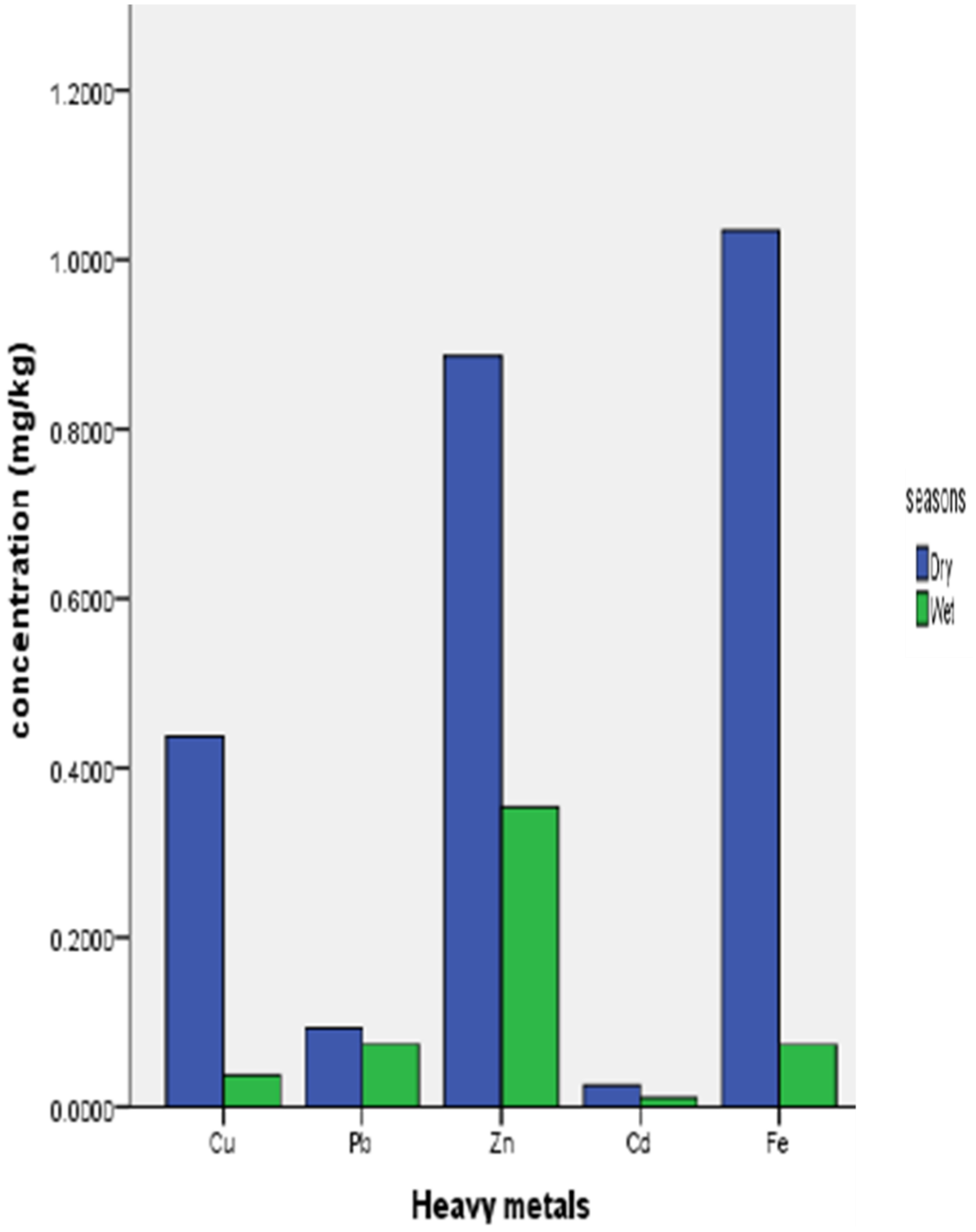
Appendix 17: Metal concentrations in dump soils of sampling sites during wet season



Appendix 18: Metal concentrations in dump soil of sampling sites during dry season



Appendix 19: Concentration of heavy metals in 44 Nigerian Army Reference Hospital Kaduna incinerator Ash for wet and dry season

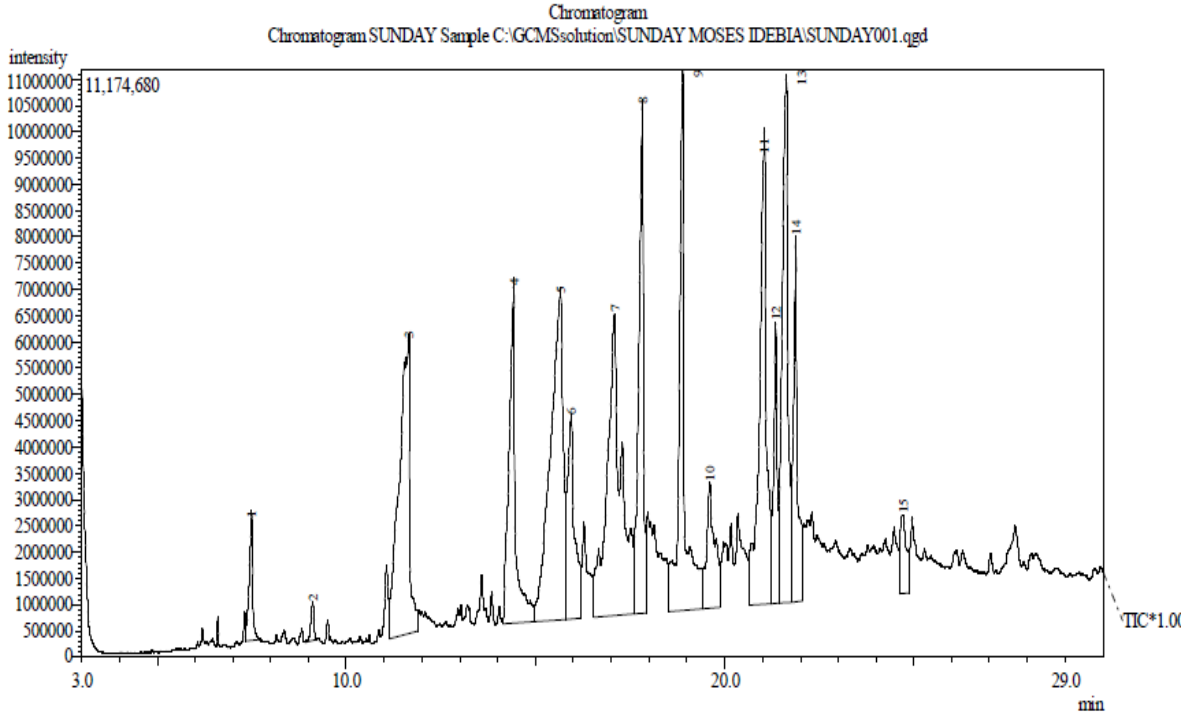


Appendix 20: Concentration of heavy metals in Saint Gerard Catholic Hospital Kaduna incinerator Ash for wet and dry season

GCMS-QP2010 PLUS
SHIMADZU,JAPAN

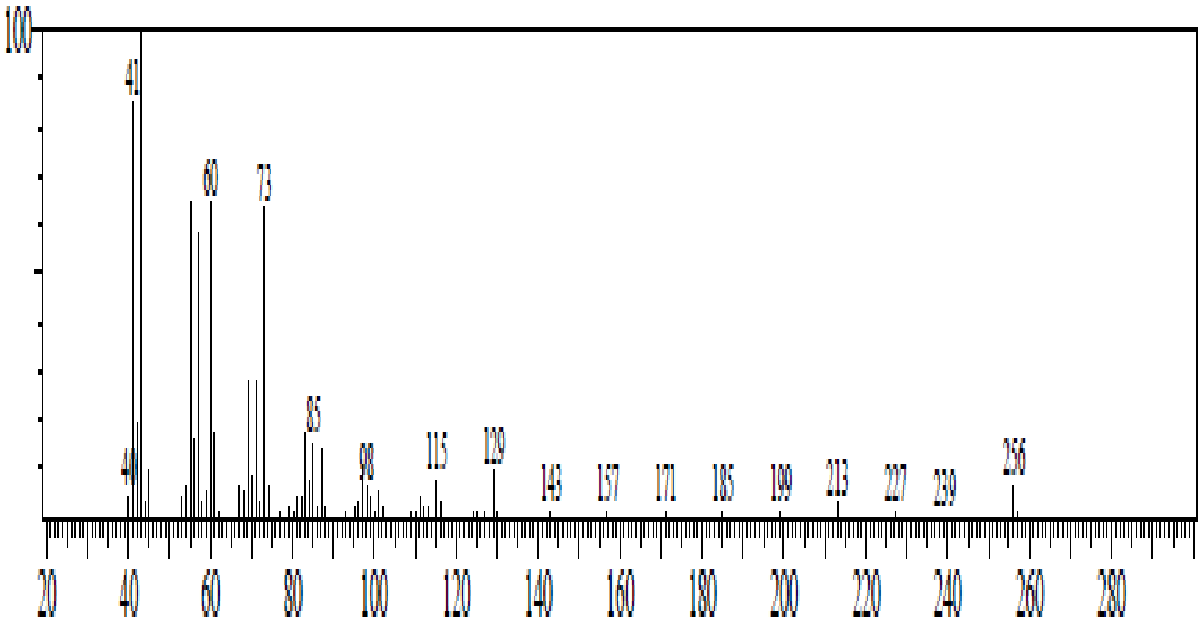
NARICT, ZARIA
GCMS ANALYSIS

SUNDAY MOSES I(SAMPLE -CONTROL SOIL)

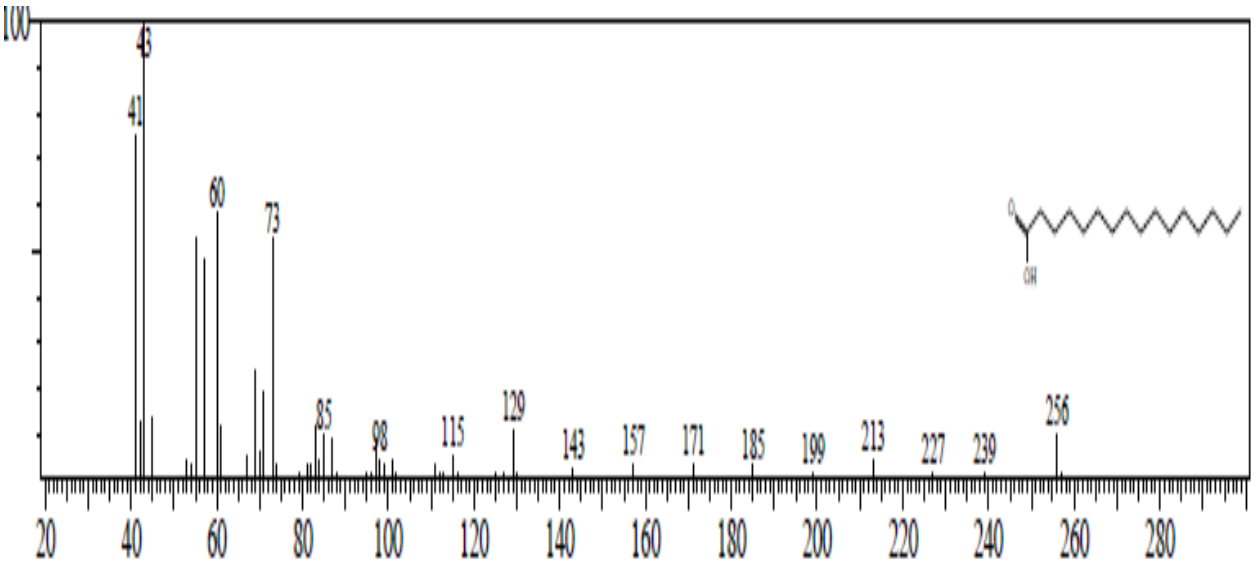


Appendix 21: GC/MS Chromatogram of Municipal dump soil

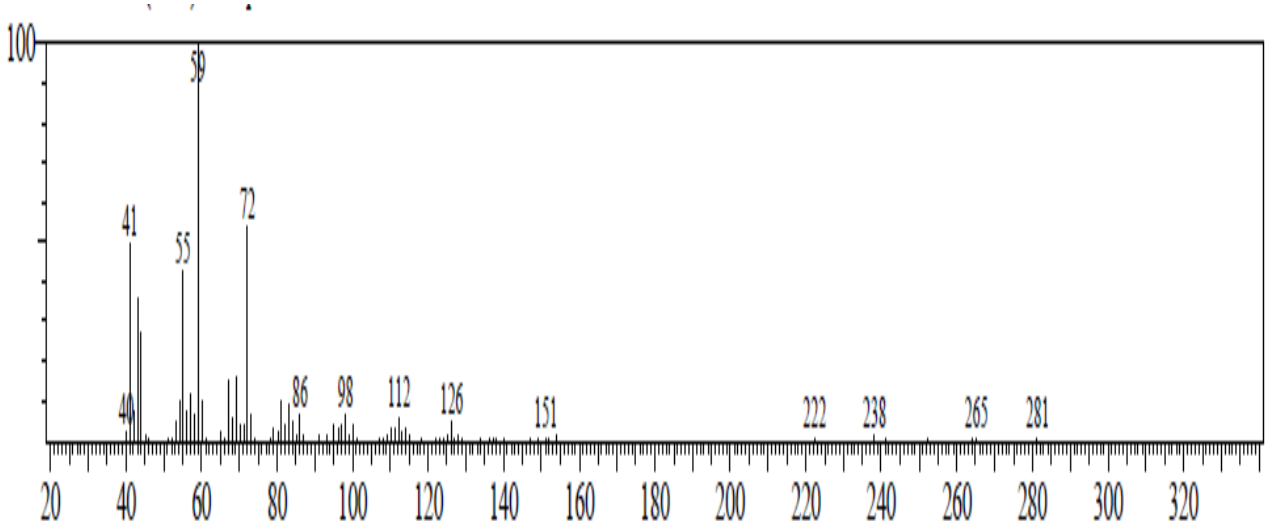
Appendix 22: GC/MS spectra of Municipal dump soil



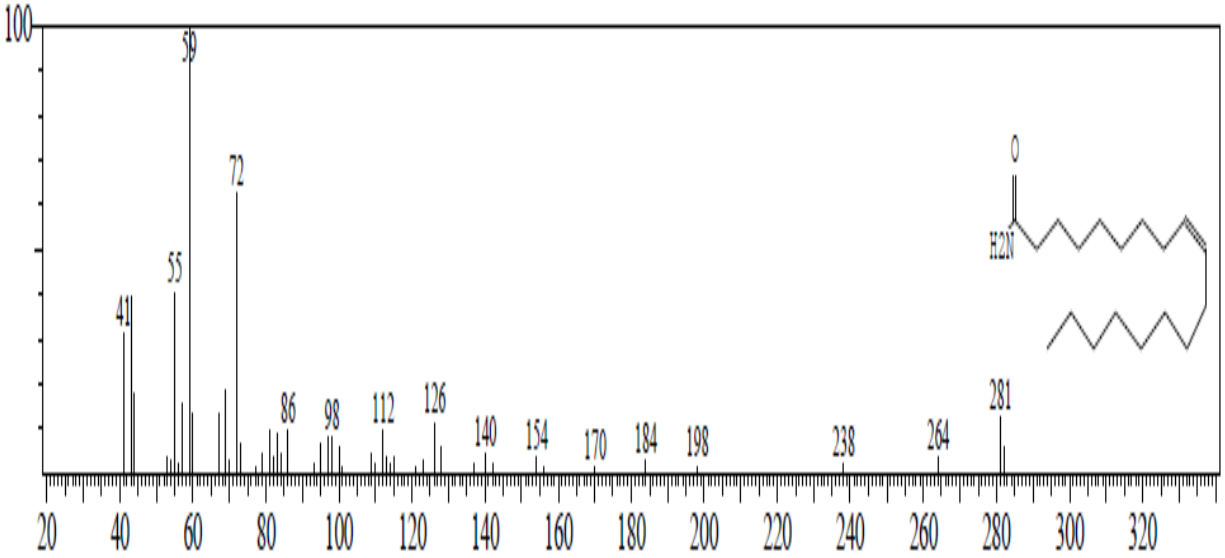
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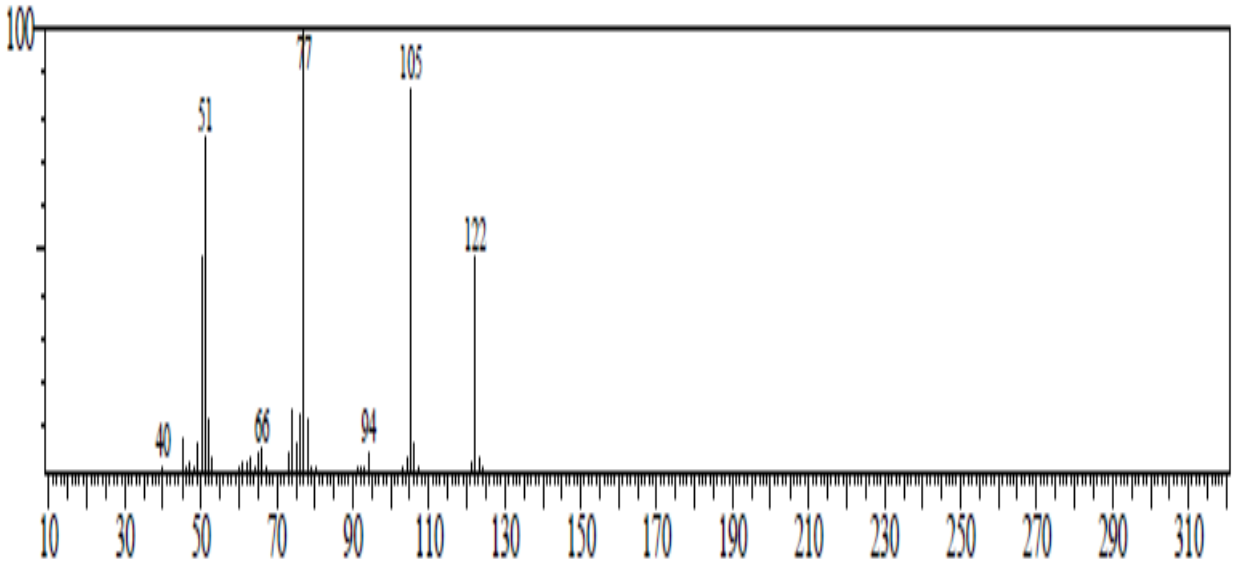
n-Hexadecanoic acid



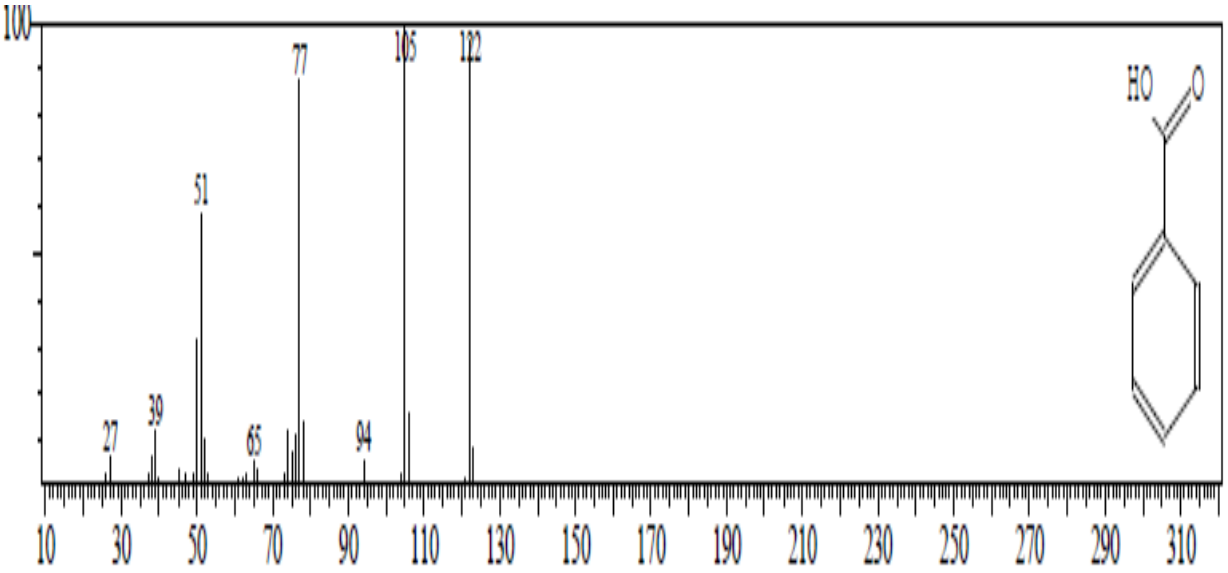
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9-octadecenamide



(Text file) 1348 (7.490mins)

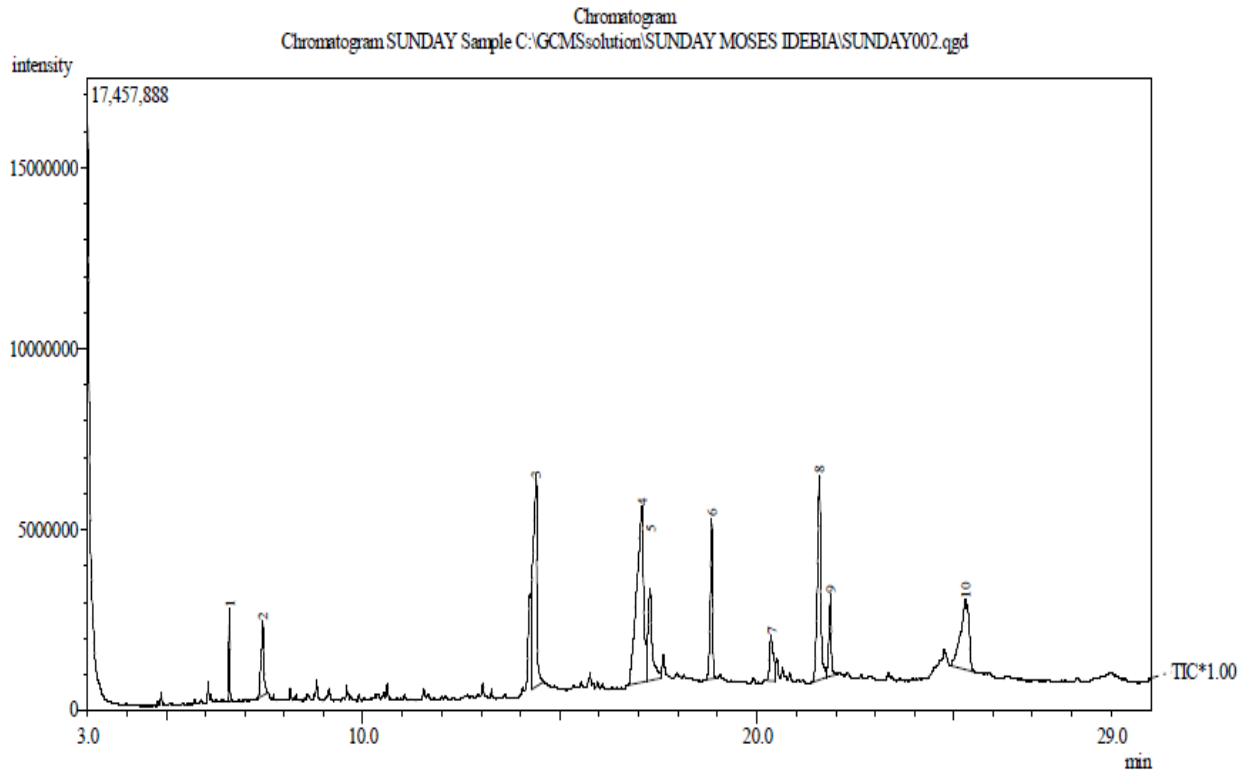


Benzenecaboxylic acid

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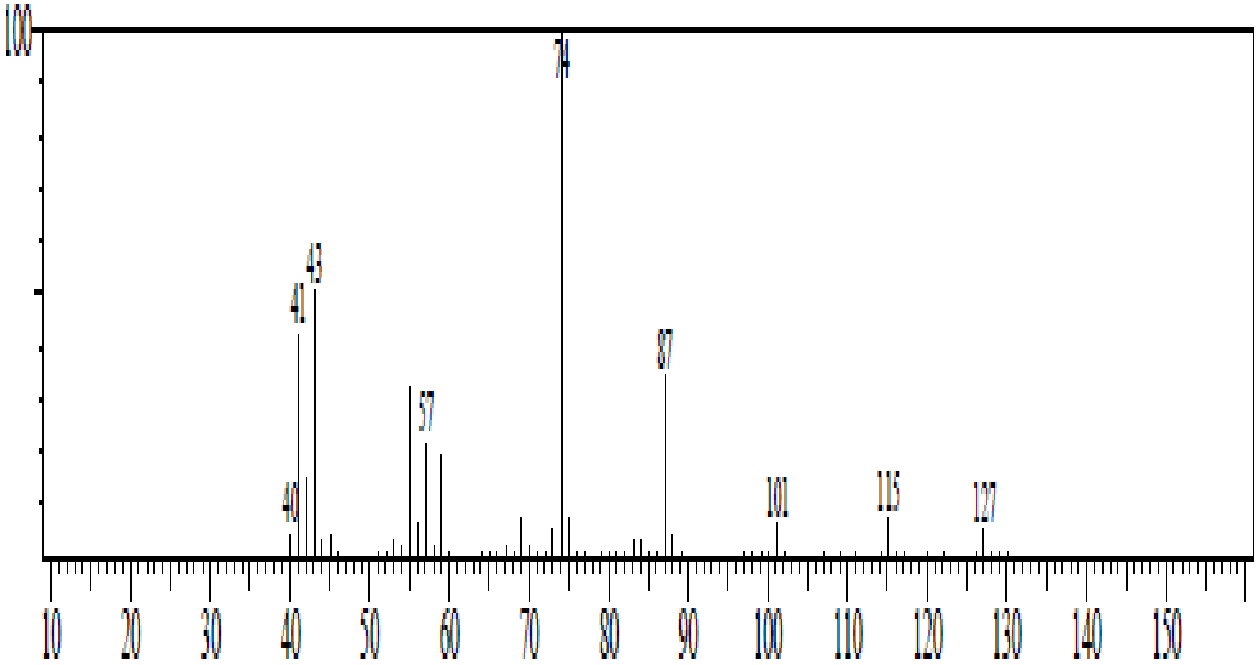
NARICT, ZARIA
GCMS ANALYSIS

SUNDAY MOSES I(SAMPLE -YDMH SOIL)

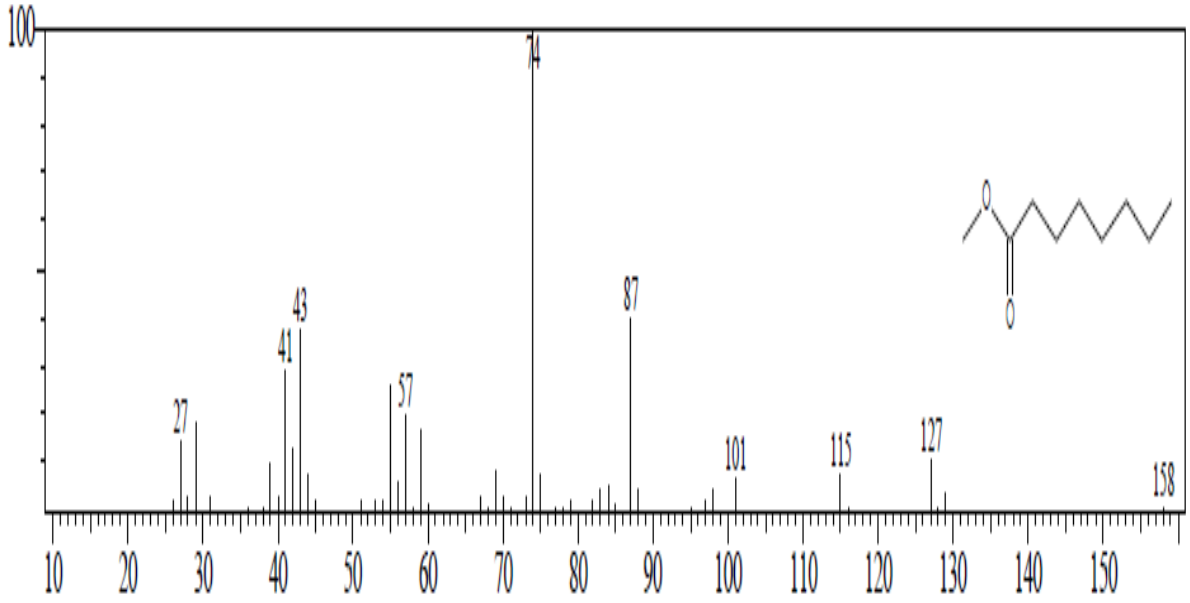


Appendix 23: GC/MS Chromatogram of Yusuf Dan-tsoho Memorial hospital dump soil

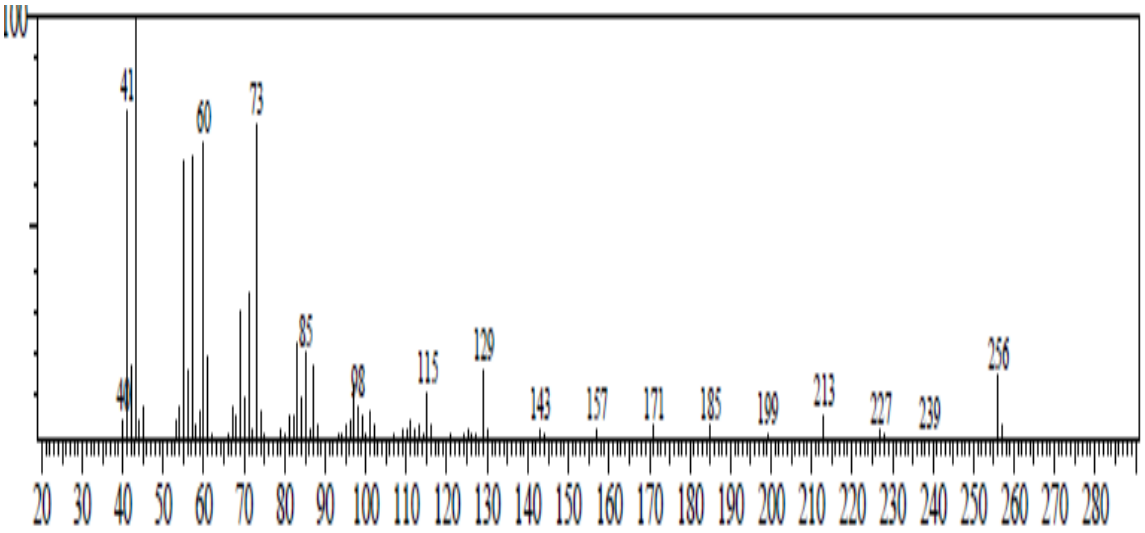
Appendix 24: GC/MS spectra of Yusuf Dan-tsoho memorial dump soil



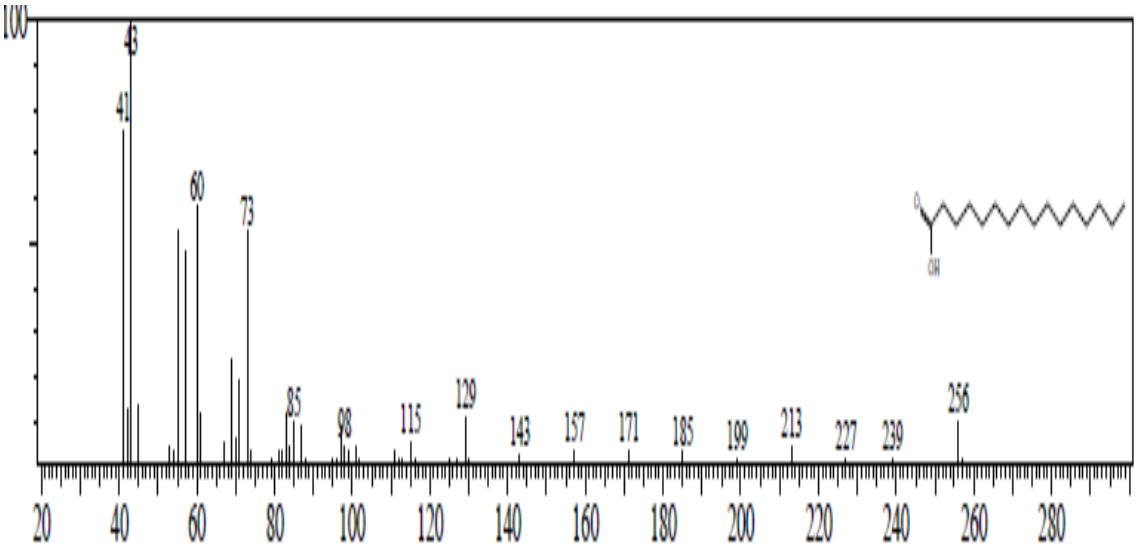
(Text file) scan 1083 (6.607mins)



Methyl octanoate



(Text file) scan 3416 (14.383 mins)

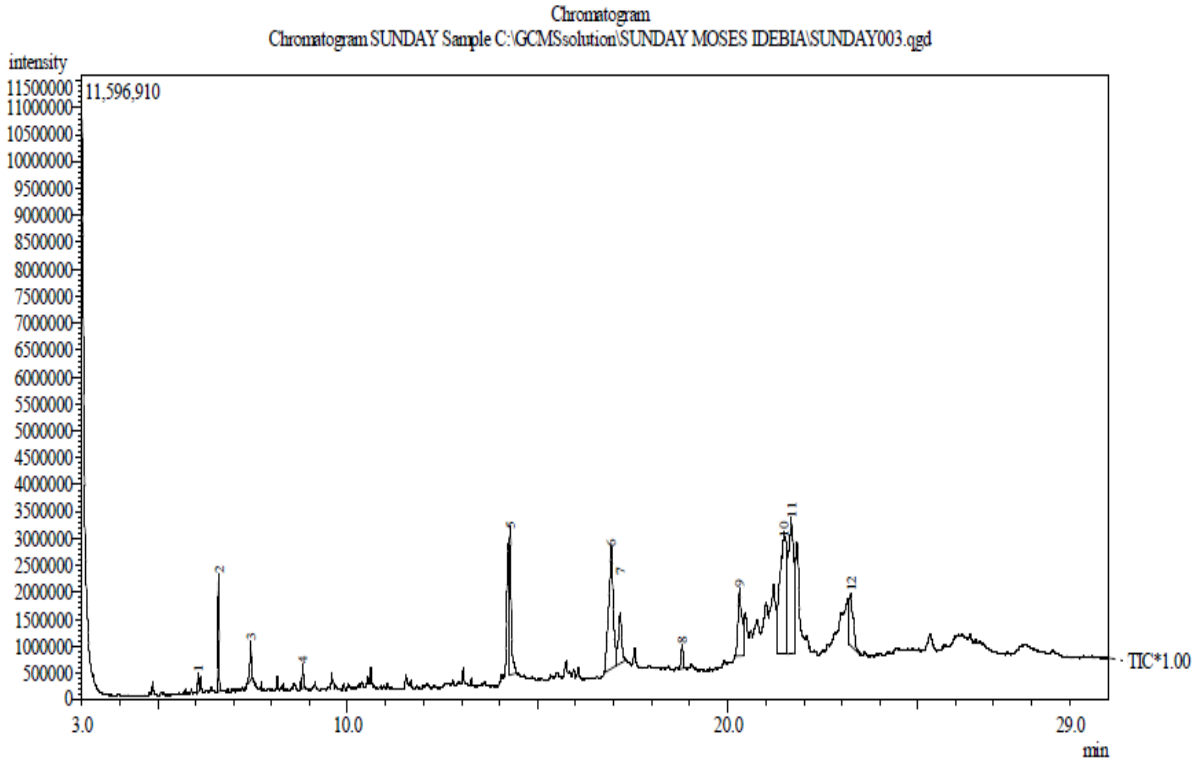


n-Hexadecanoic acid

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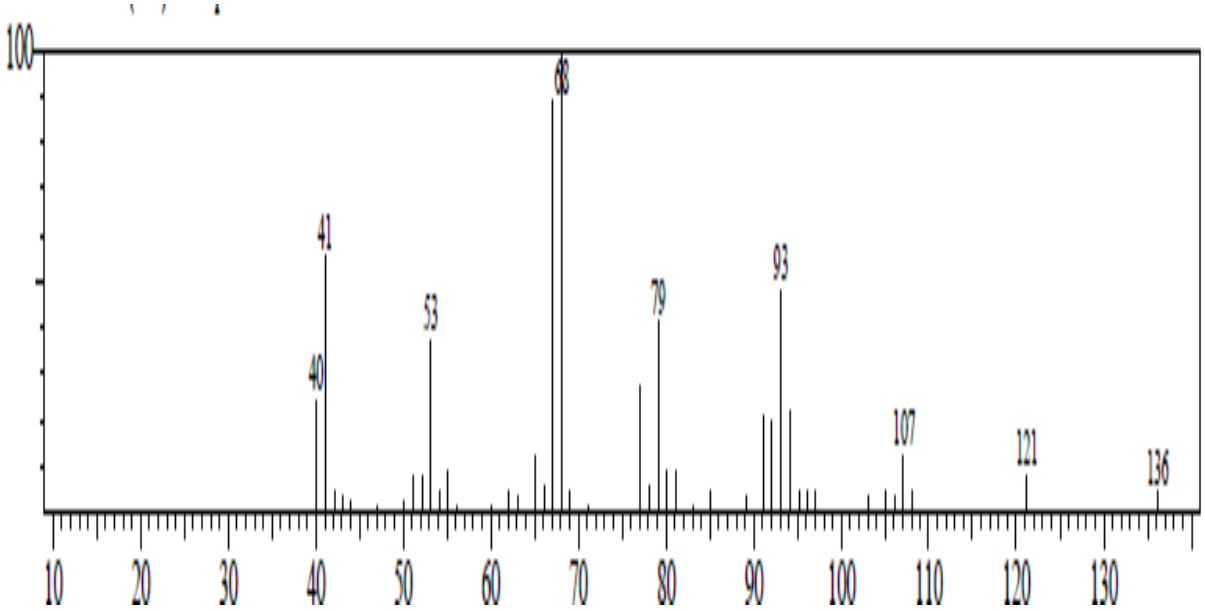
NARICT, ZARIA
GCMS ANALYSIS

SUNDAY MOSES I(SAMPLE -44 NARHK SOIL)

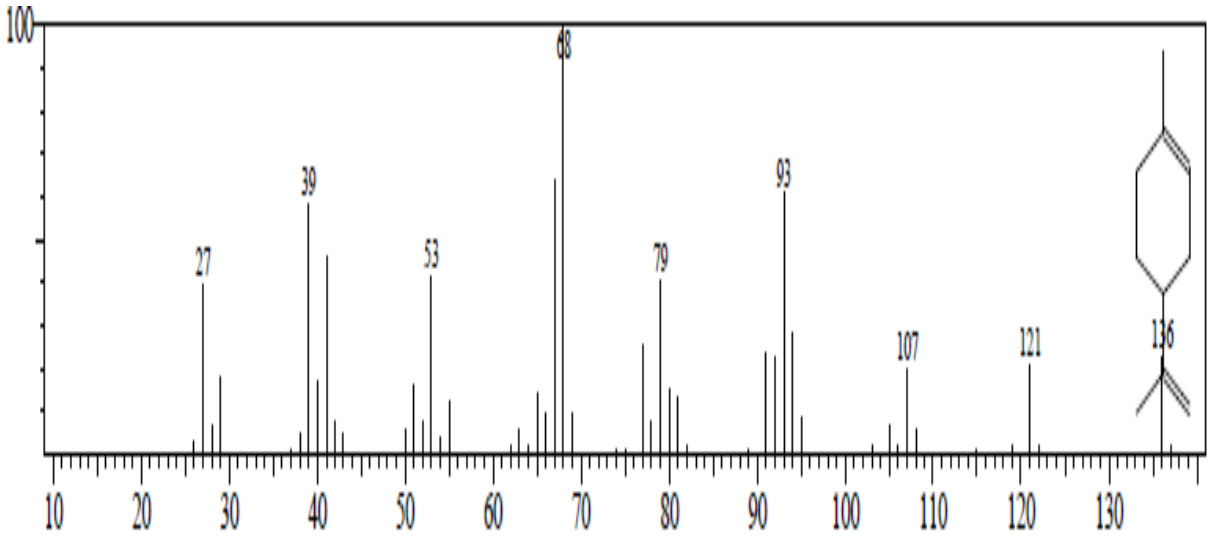


Appendix 25: GC/MS Chromatogram of 44 Nigerian Army Reference Hospital dump soil

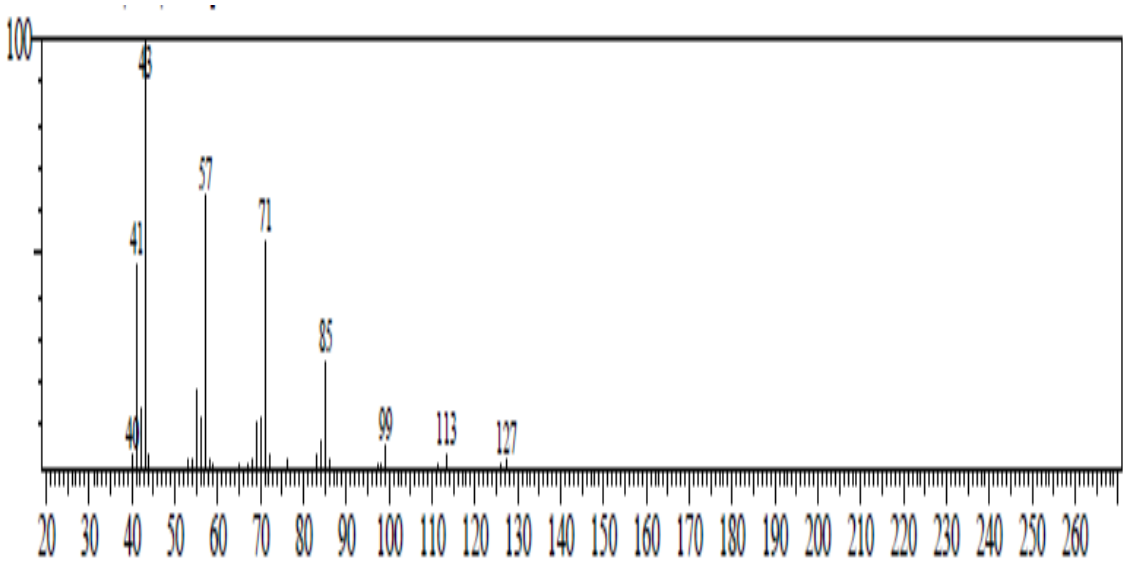
Appendix 26: GC/MS spectra of 44 Nigerian Army Reference Hospital dump soil



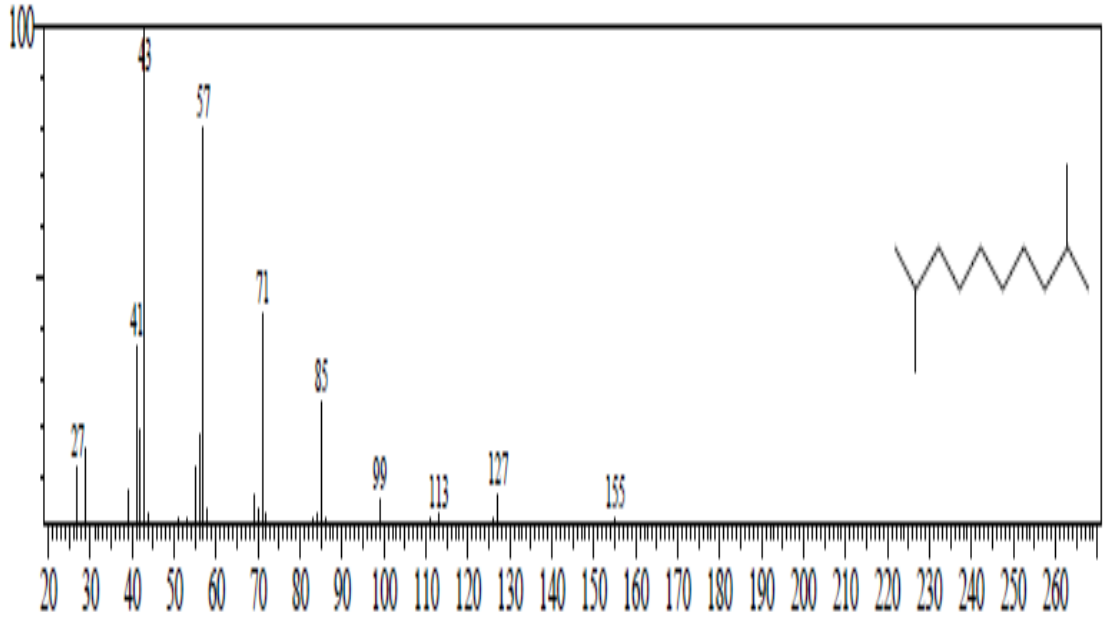
(Text file) scan 922 (6.070 mins)



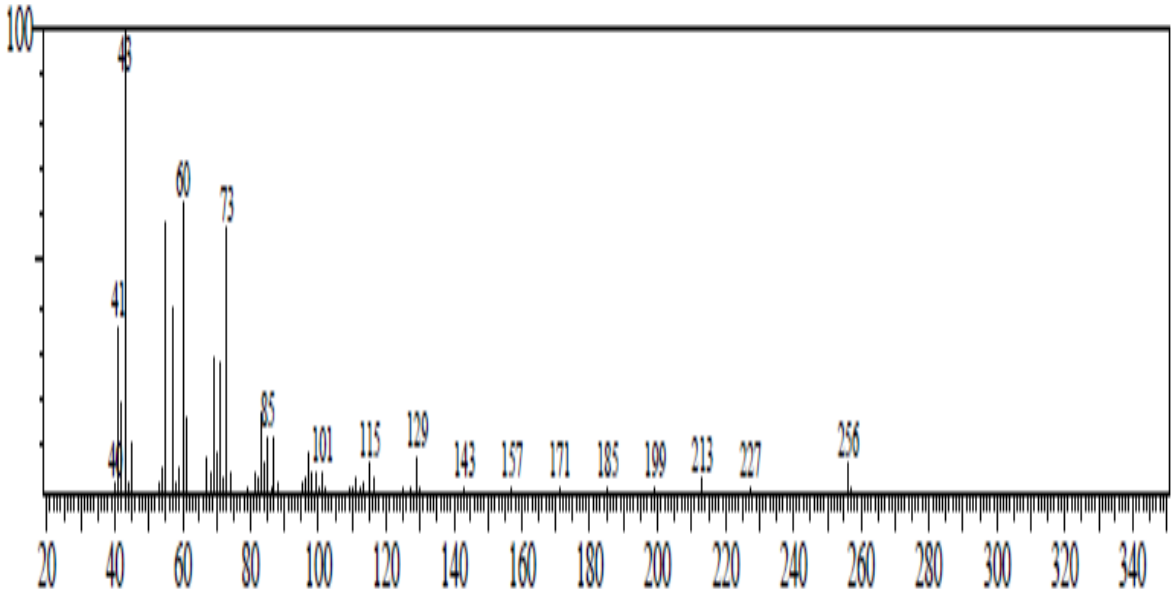
D-limonene



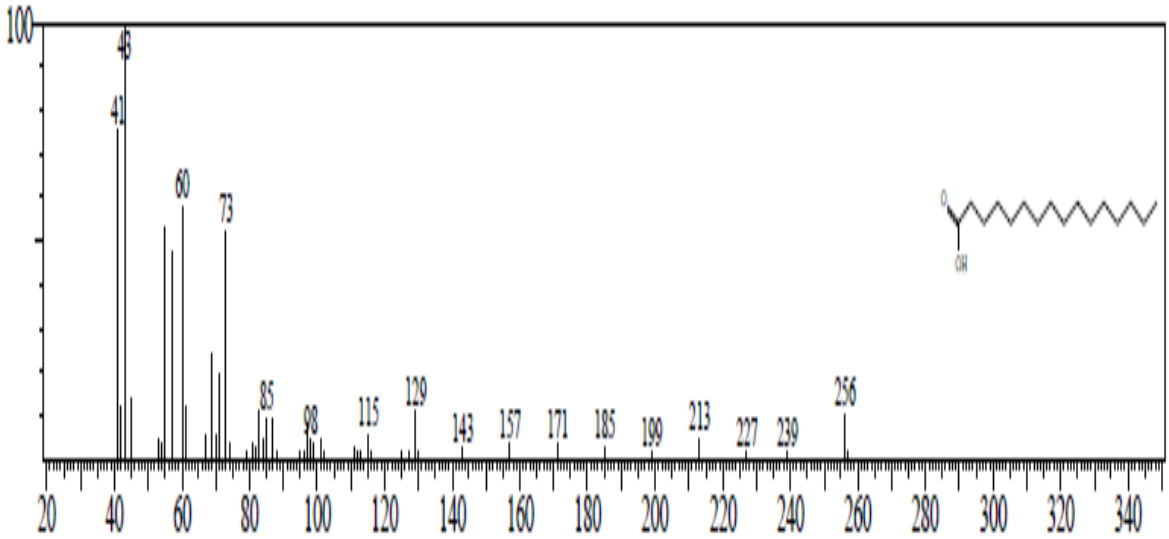
(Text file) scan 1336 (7.450 mins)



2,9 – dimethyl decane



(Text file) scan 3382 (14.270 mins)

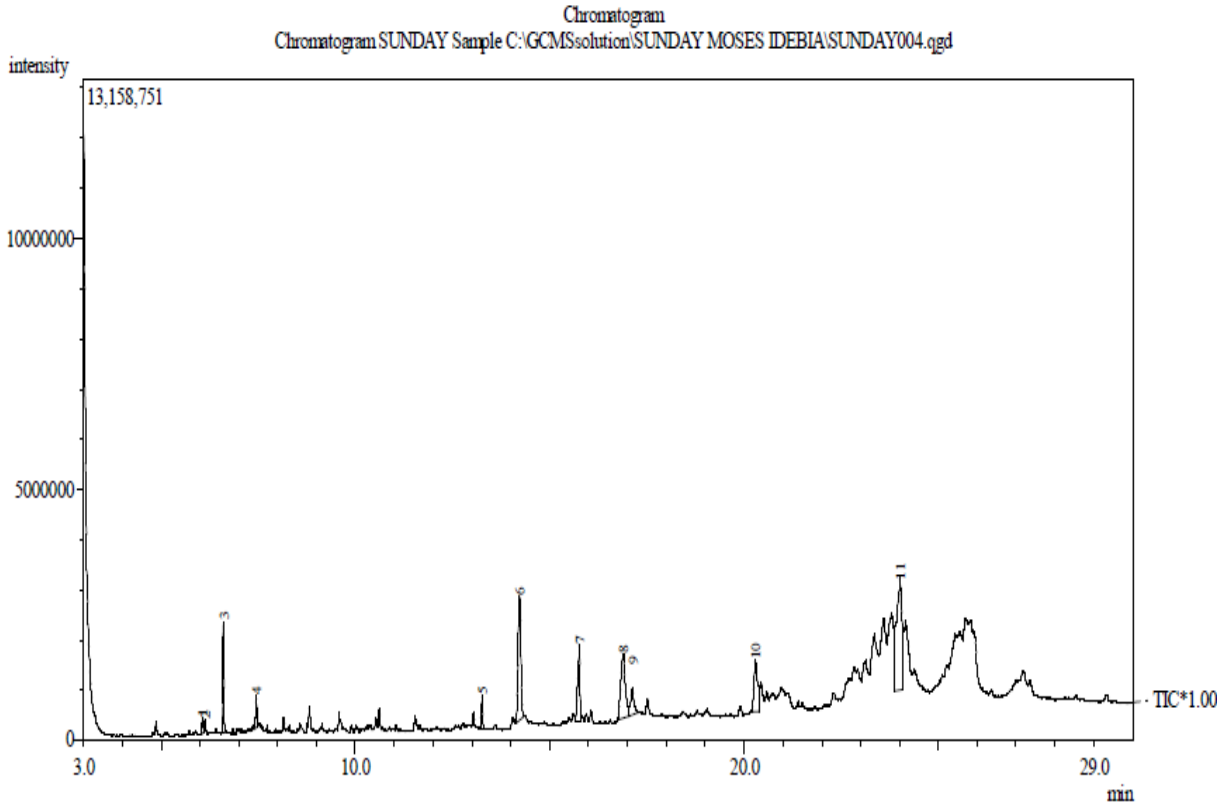


n-Hexadecanoic acid

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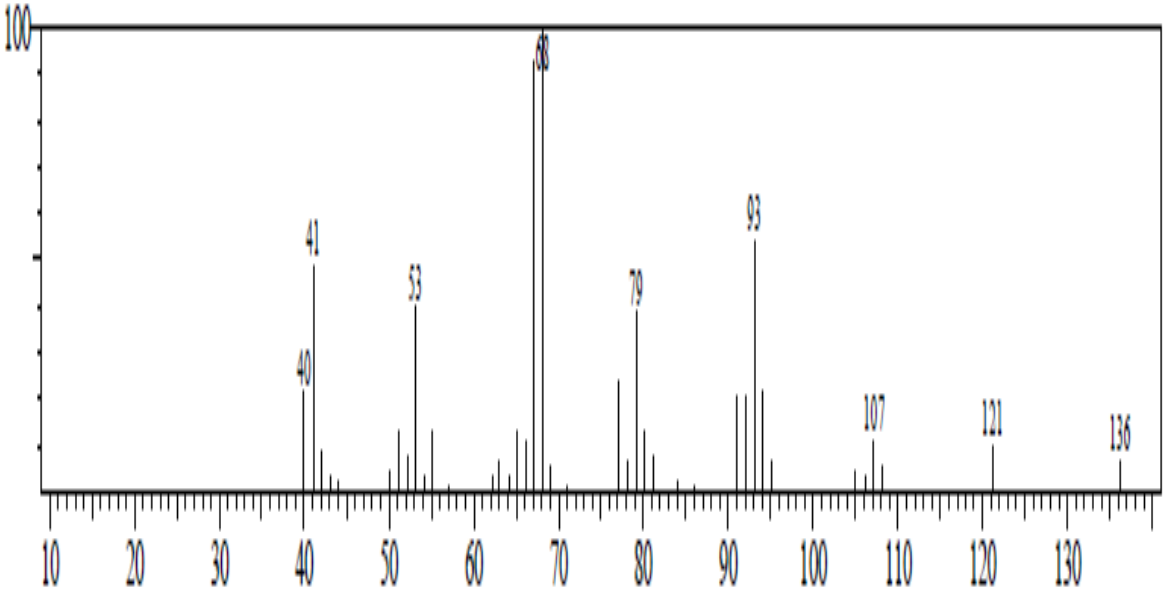
NARICT, ZARIA
GCMS ANALYSIS

SUNDAY MOSES I(SAMPLE -44 NARHK ASH)

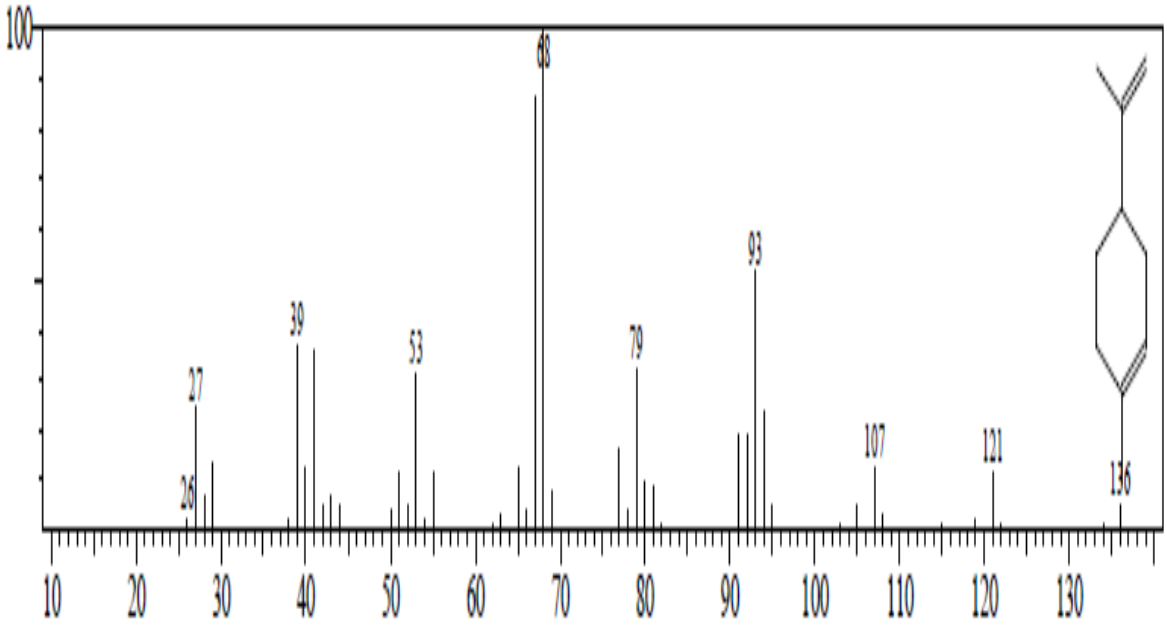


Appendix 27: GC/MS Chromatogram of 44 Nigerian Army Reference Hospital Ash

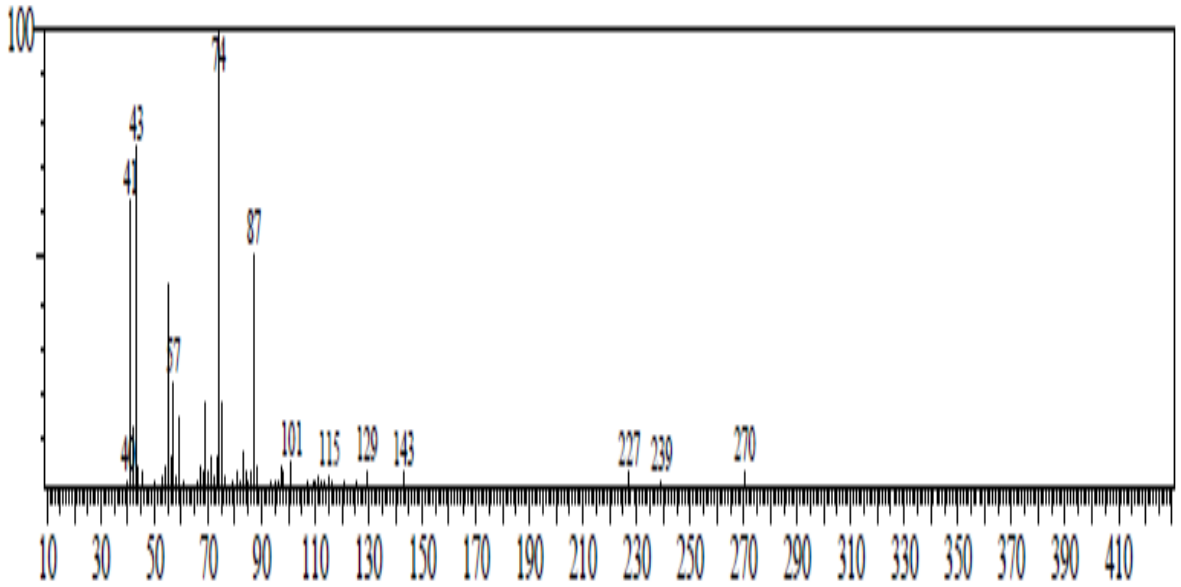
Appendix 28: GC/MS spectra of 44 Nigerian Army Reference Hospital Ash



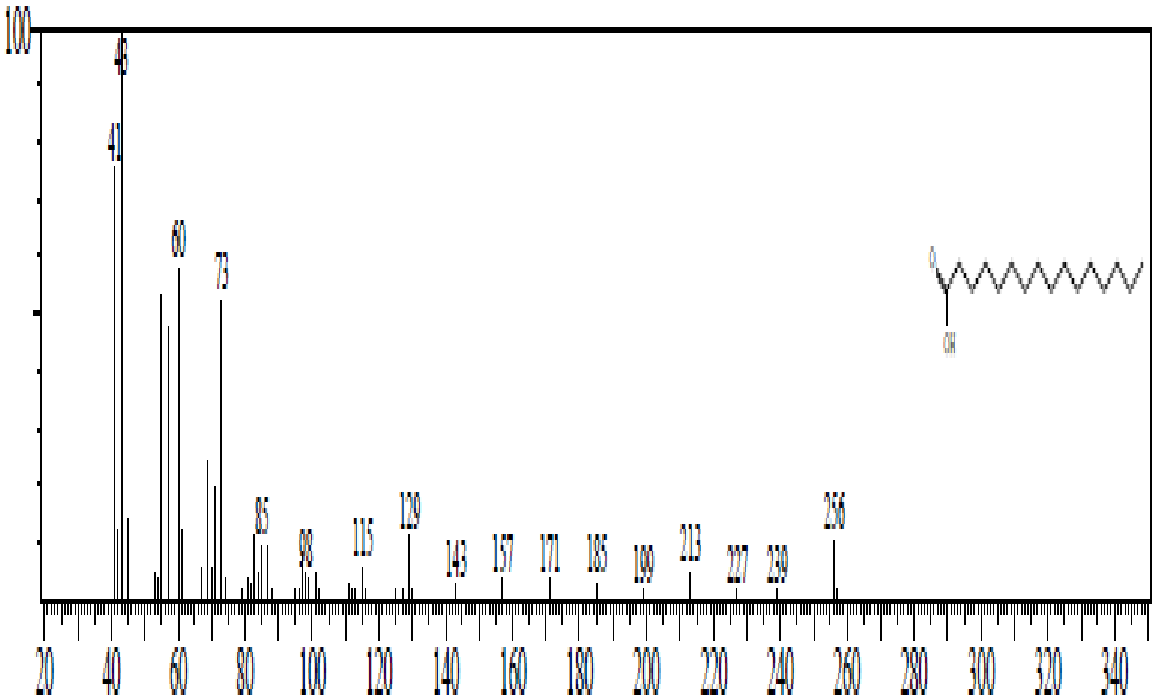
(Text file) scan 922 (6.070 mins)



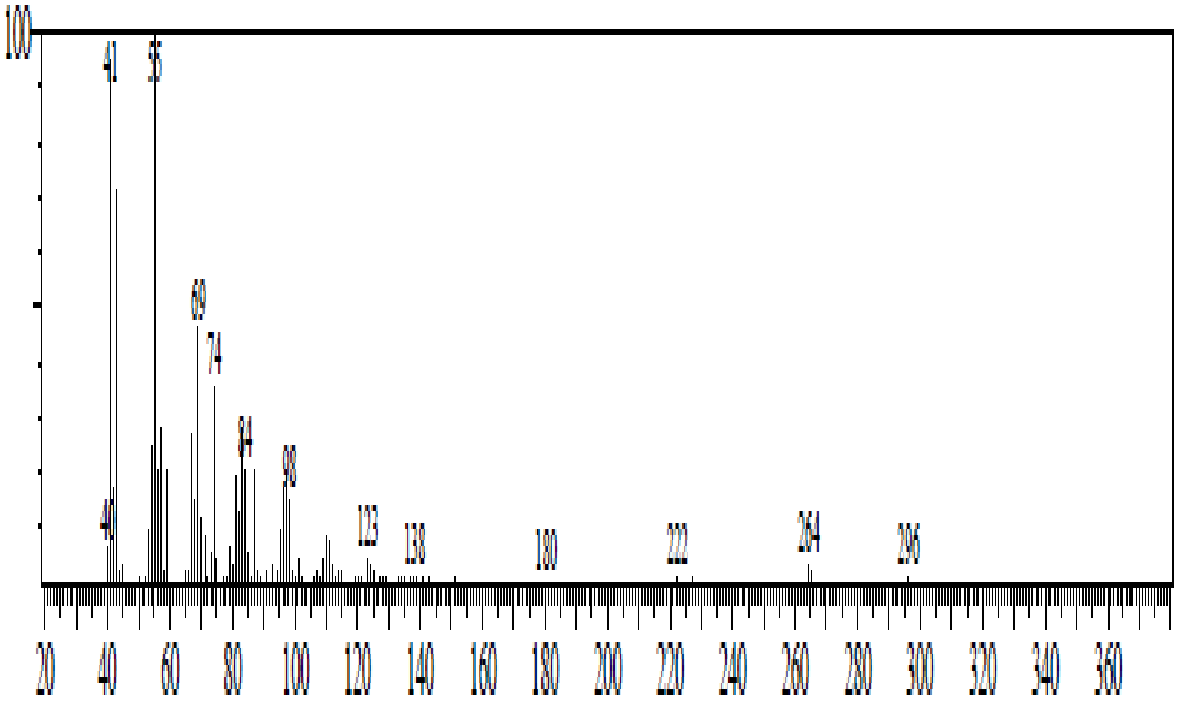
D-limonene



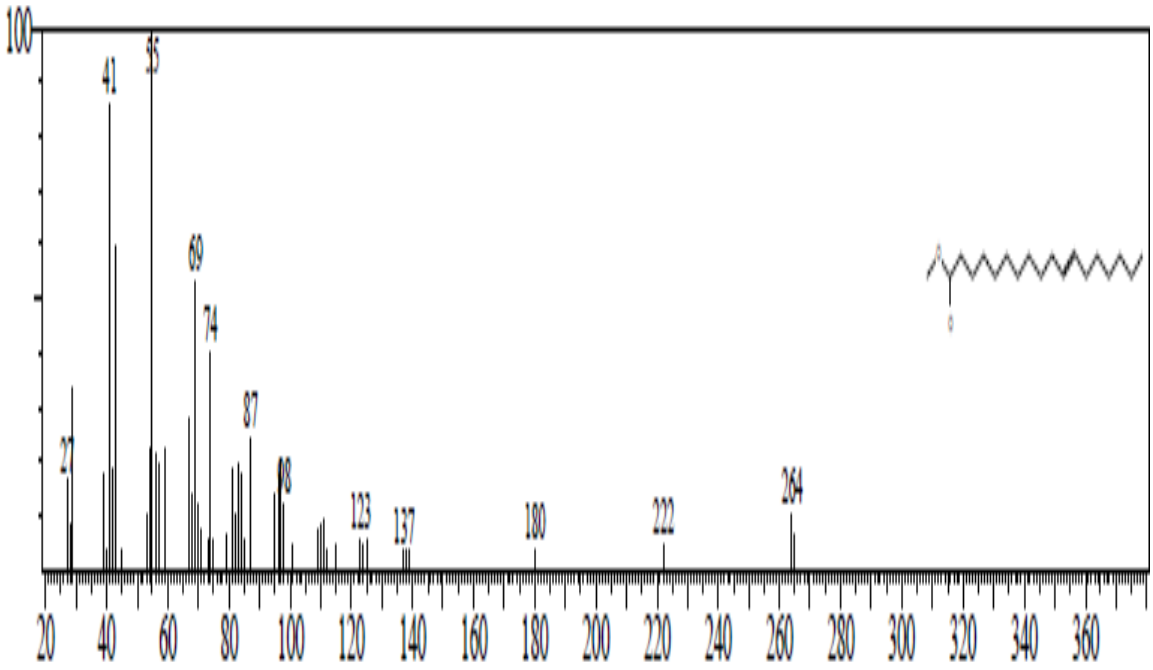
(Text file) scan 3078 (13.257 mins)



n- Hexadecanoic acid



(Text file) scan 3829 (15.760 mins)

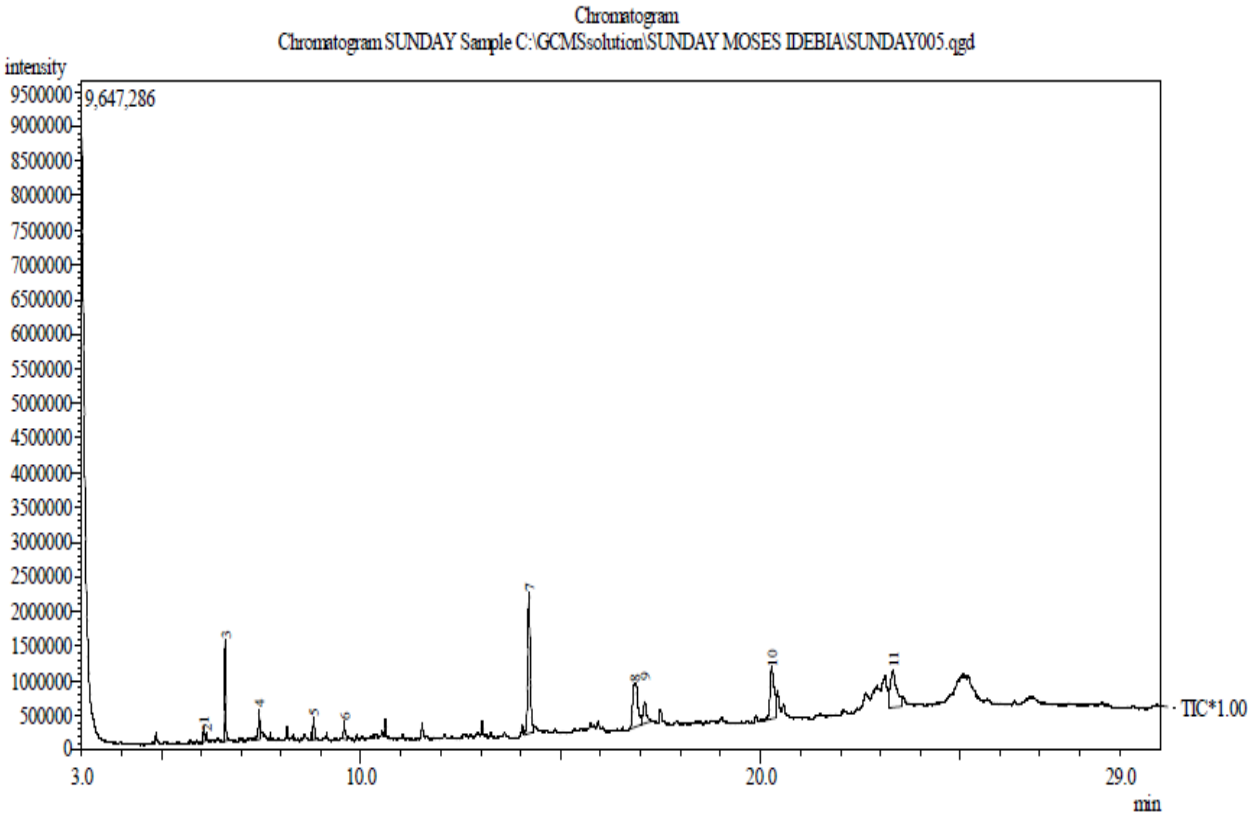


Octadecenoic acid

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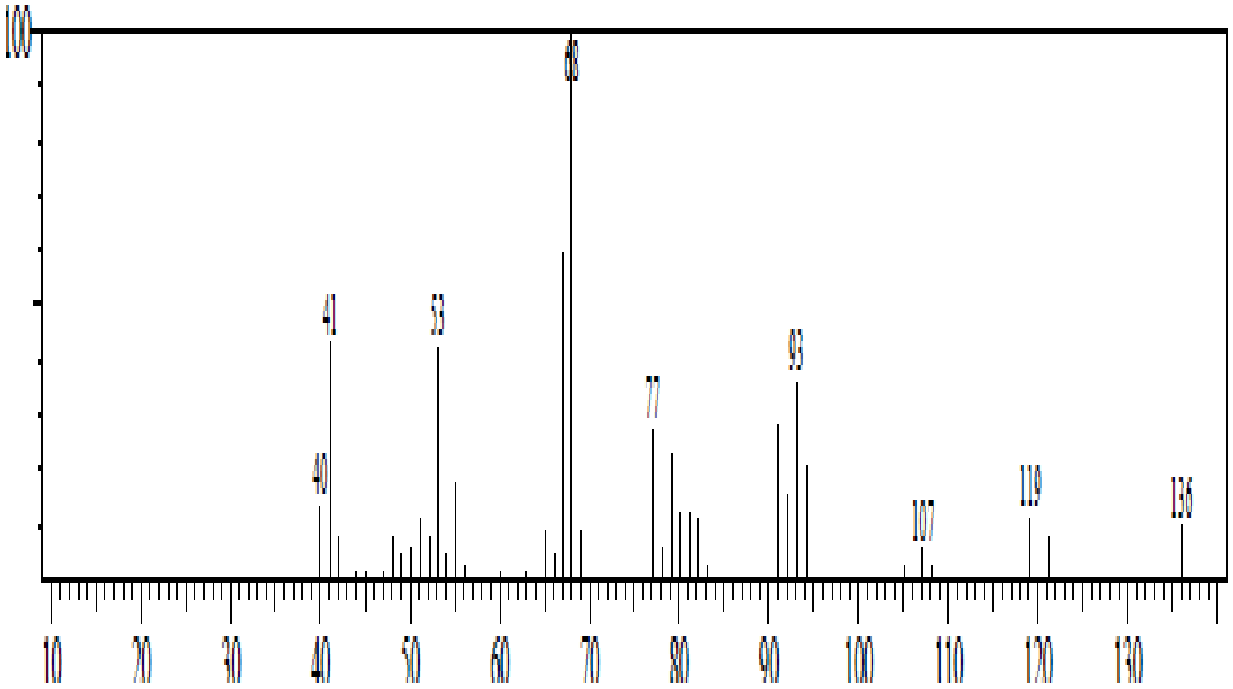
NARICT, ZARIA
GCMS ANALYSIS

SUNDAY MOSES I(SAMPLE -ST. GERARD SOIL)

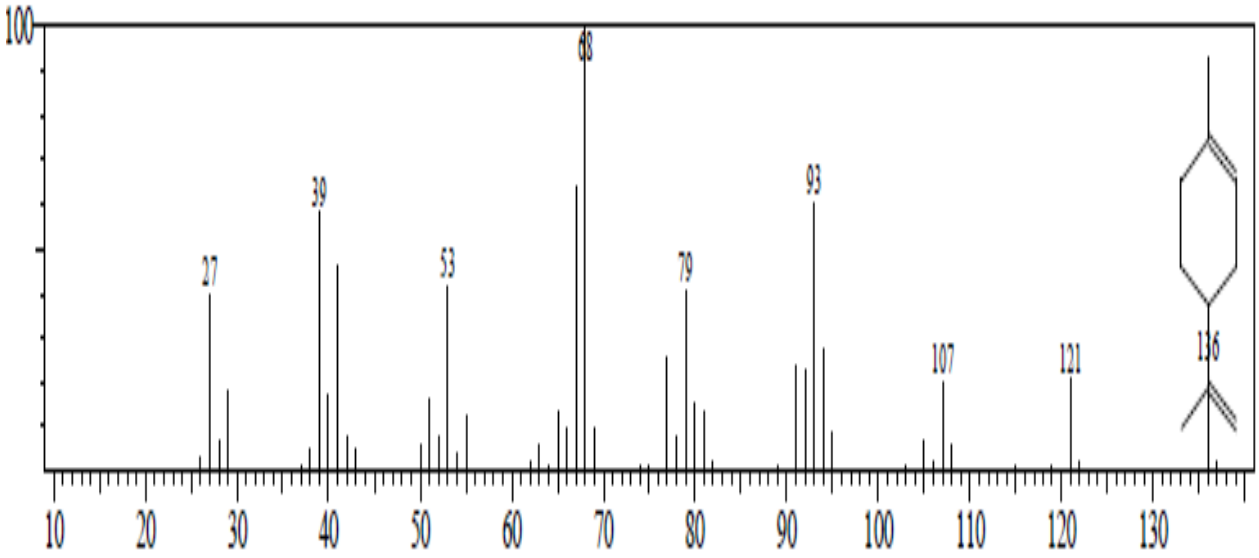


Appendix 29: GC/MS Chromatogram of Saint Gerard Catholic Hospital dump soil

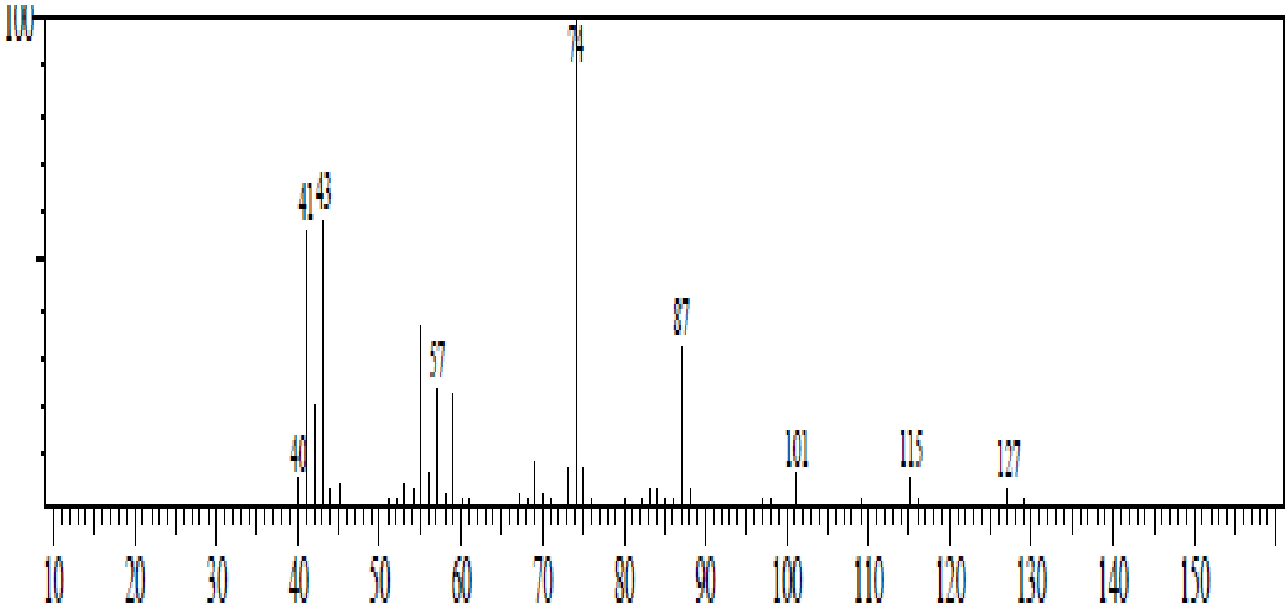
Appendix 30: GC/MS spectra of Saint Gerard Catholic Hospital dump soil



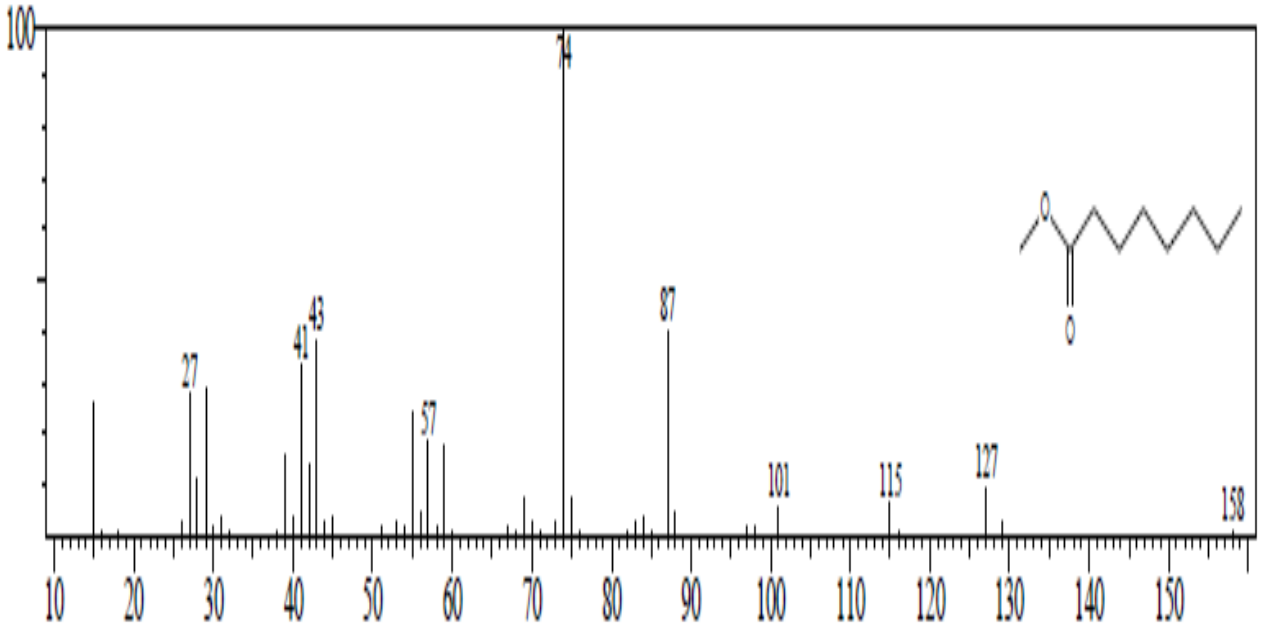
(Text file) scan 921 (6.067 mins)



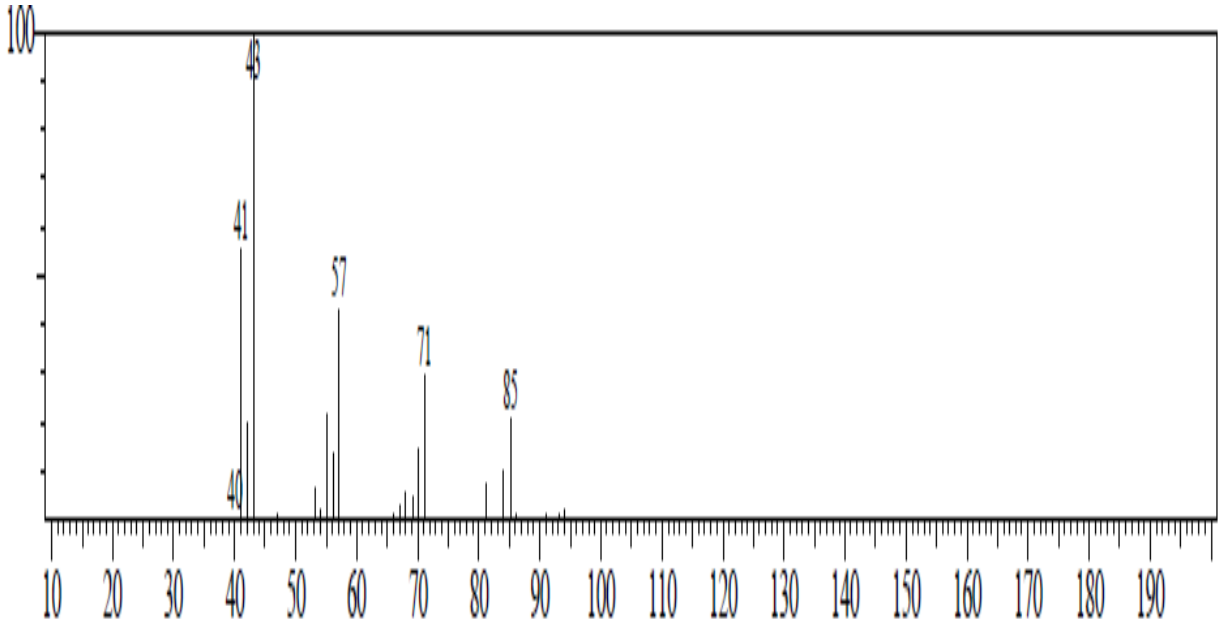
D-limonene



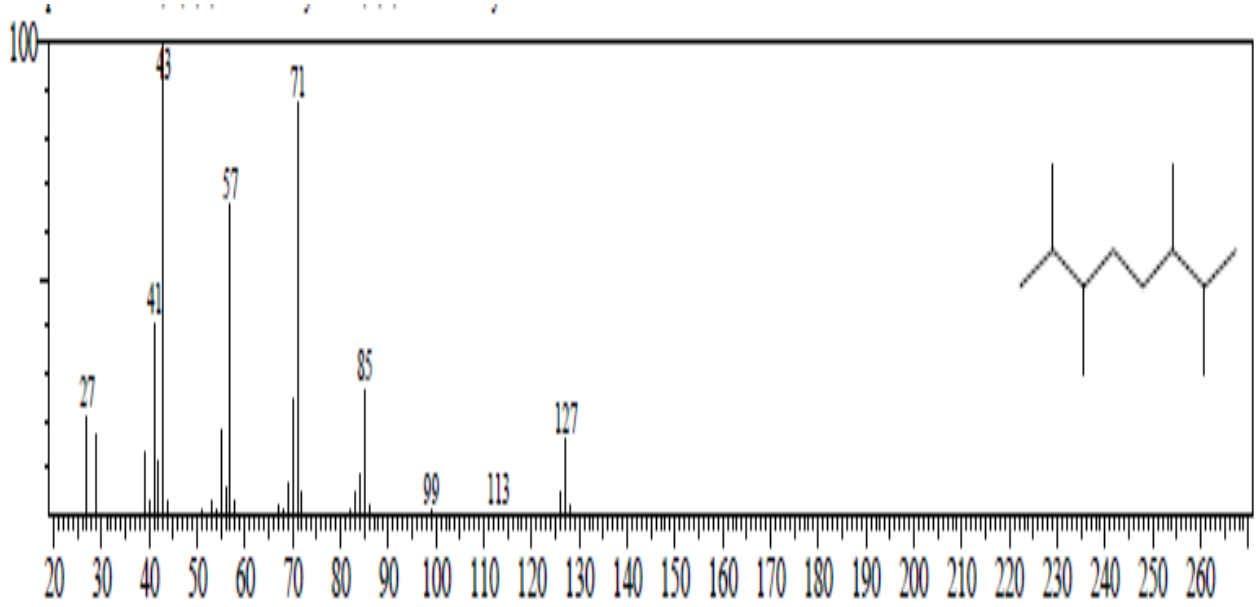
(Text file) scan 1082 (6.063 mins)



Methyl octanoate



(Text file) scan 938 (6.123 mins)

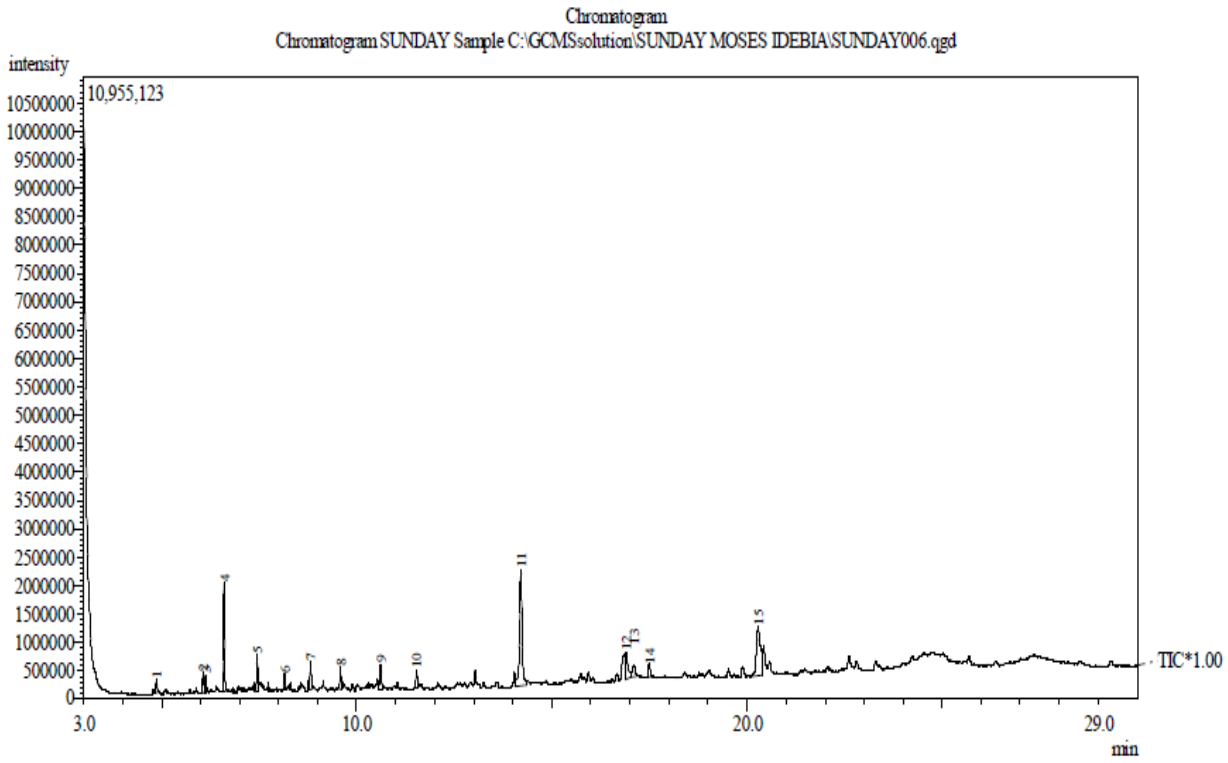


Octane 2,3,6,7- tetramethyl

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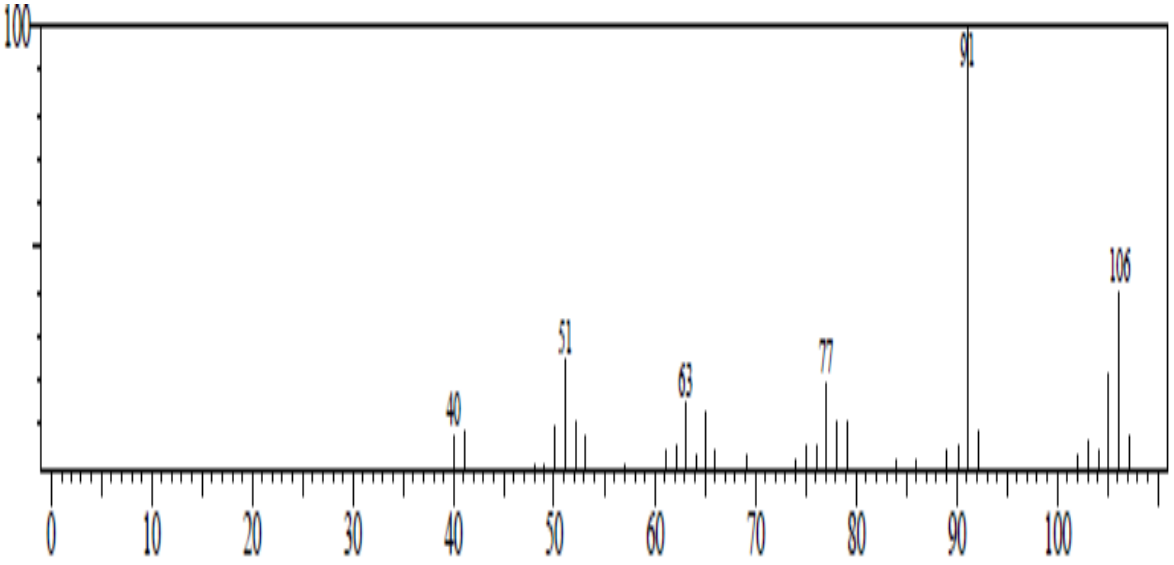
NARICT, ZARIA
GCMS ANALYSIS

SUNDAY MOSES I(SAMPLE -ST. GERARD ASH)

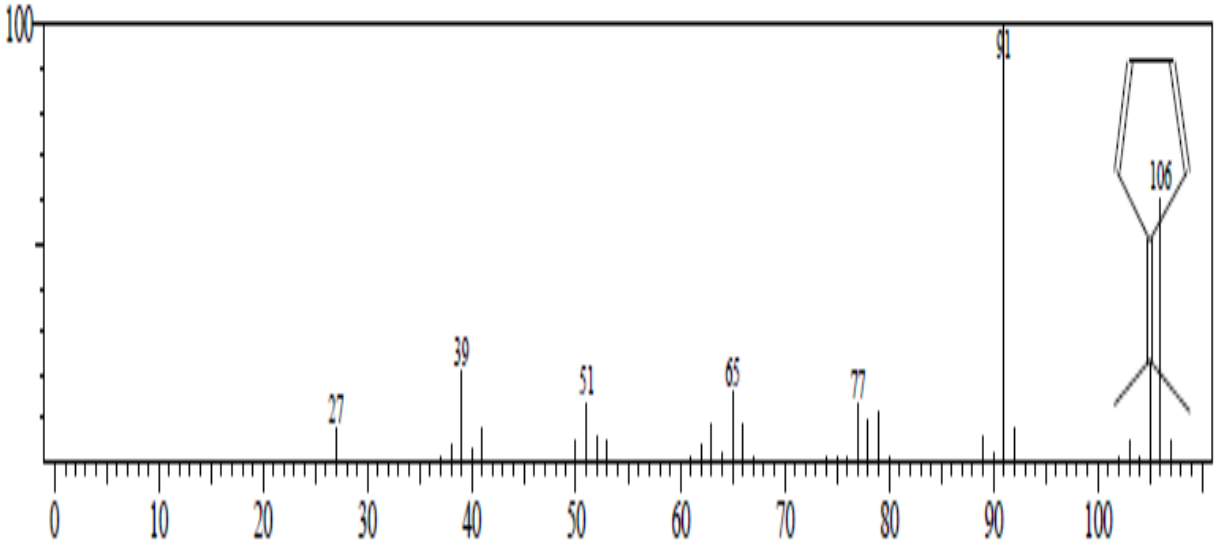


Appendix 31: GC/MS Chromatogram of Saint Gerard Catholic Hospital Ash

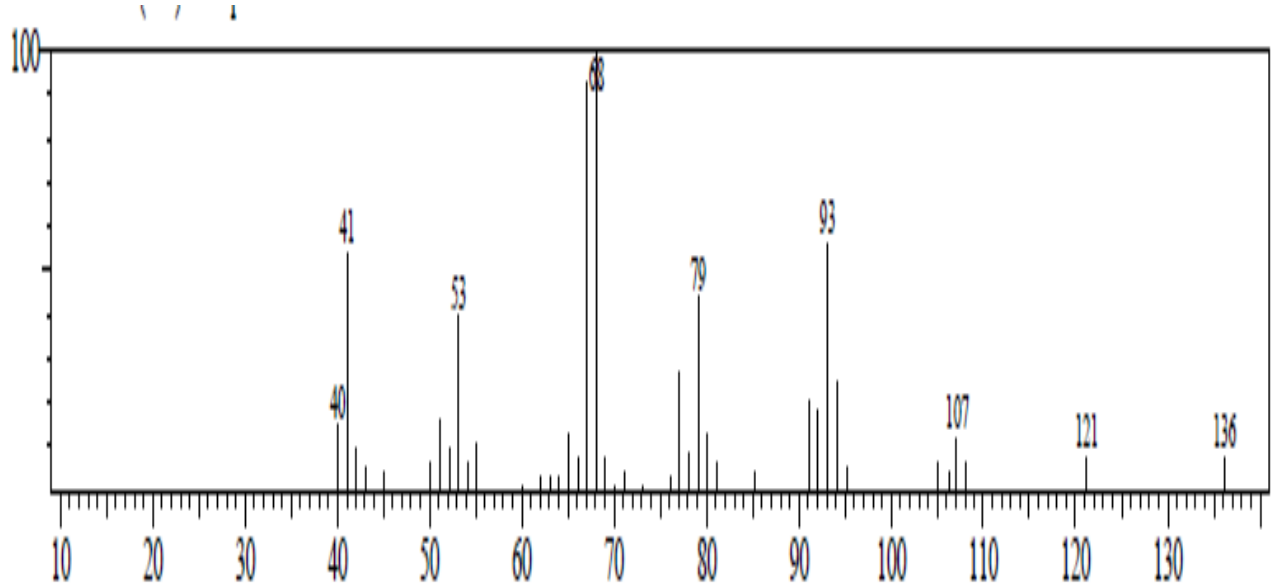
Appendix 32: GC/MS spectra of Saint Gerard Catholic Hospital Ash



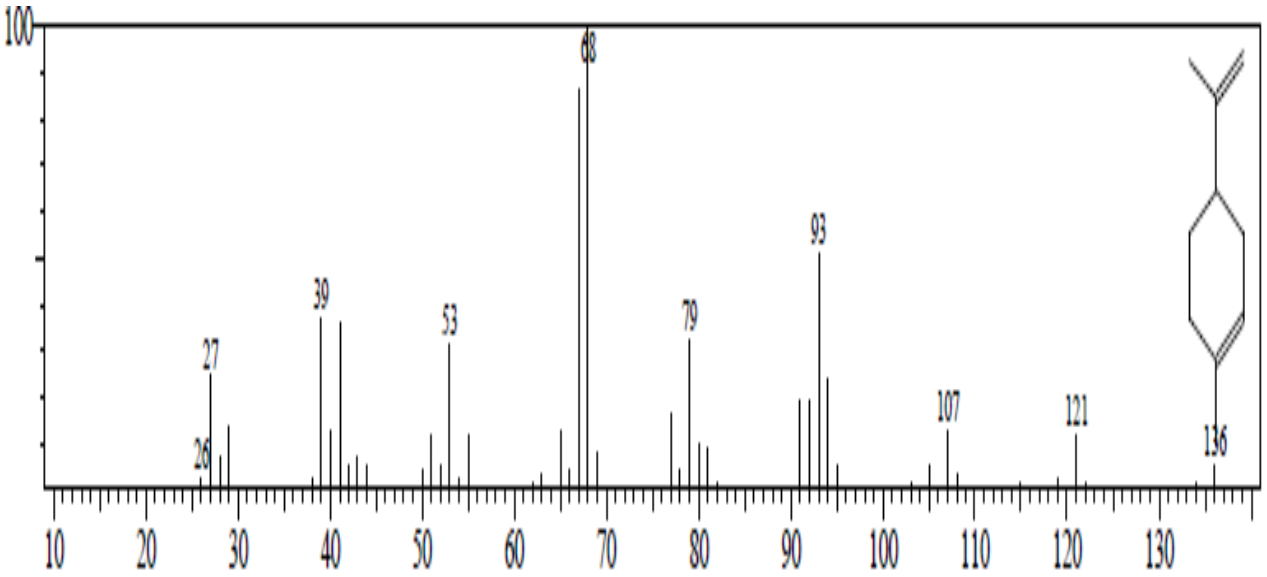
(Text file) scan 561 (4.867 mins)



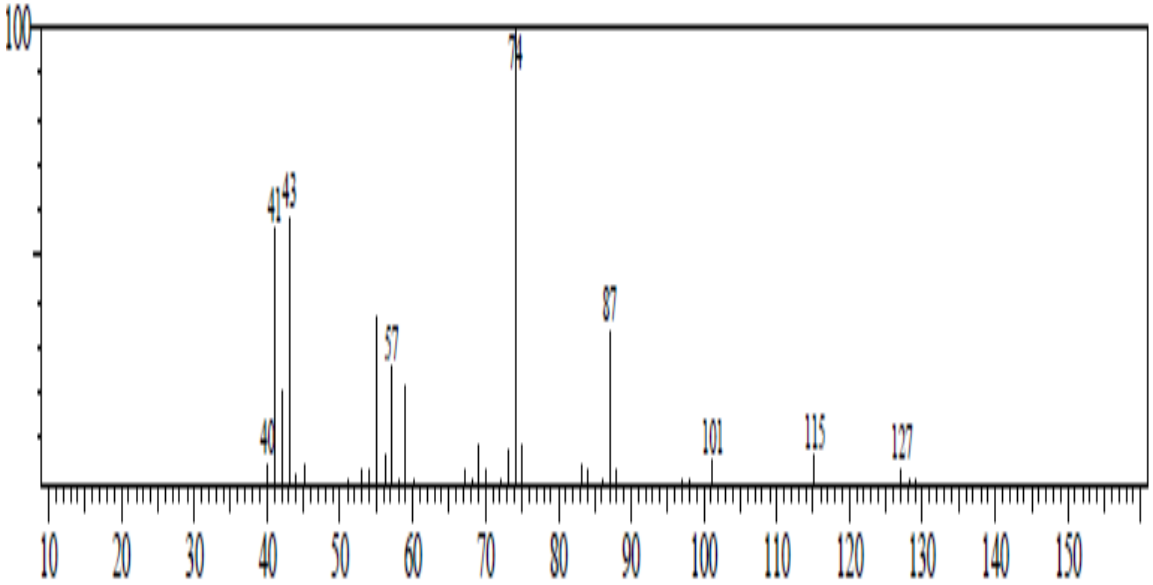
1,3 – cyclopentadiene



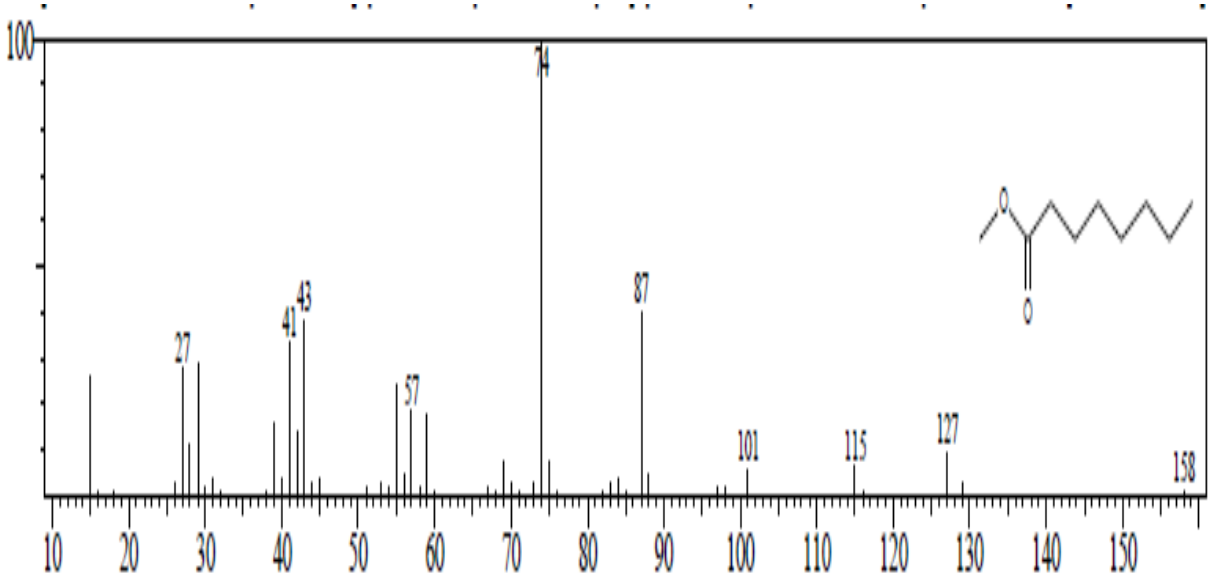
(Text file) scan 921 (6.067 mins)



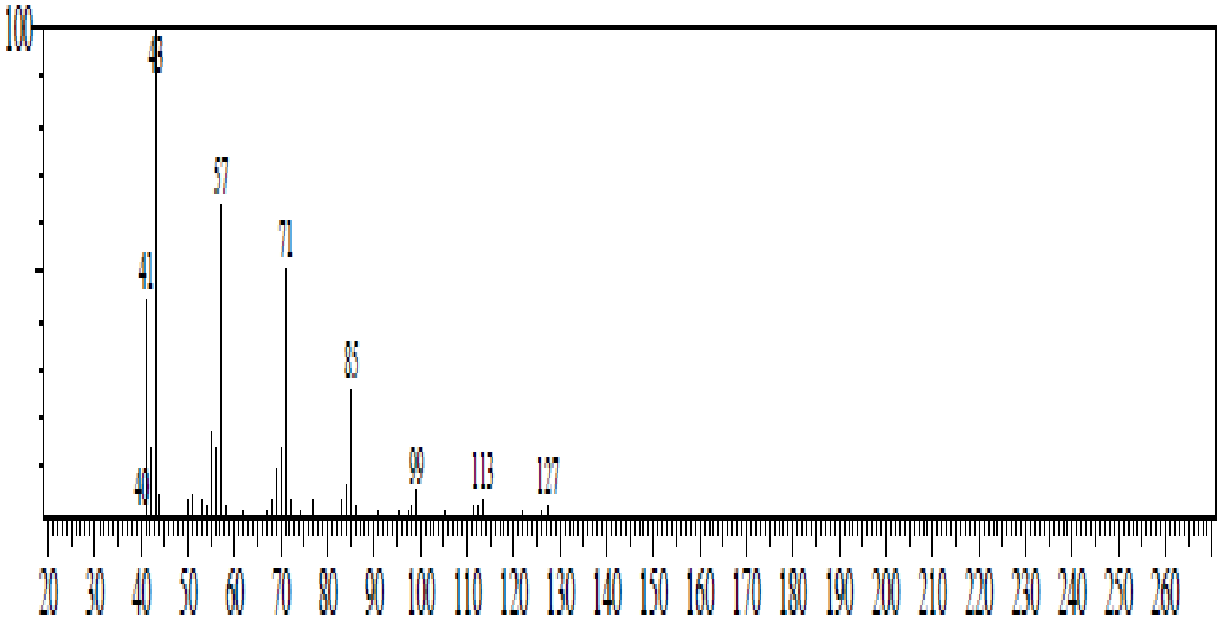
D-limonene



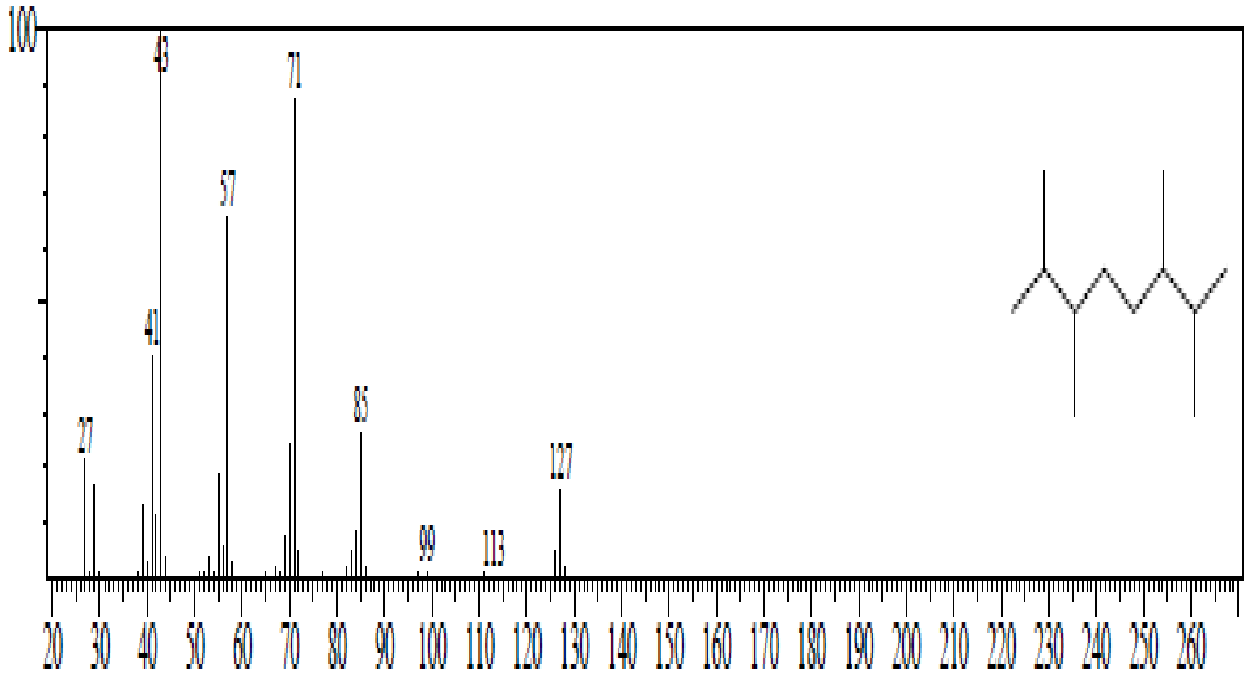
(Text file) scan 1082 (6.603 mins)



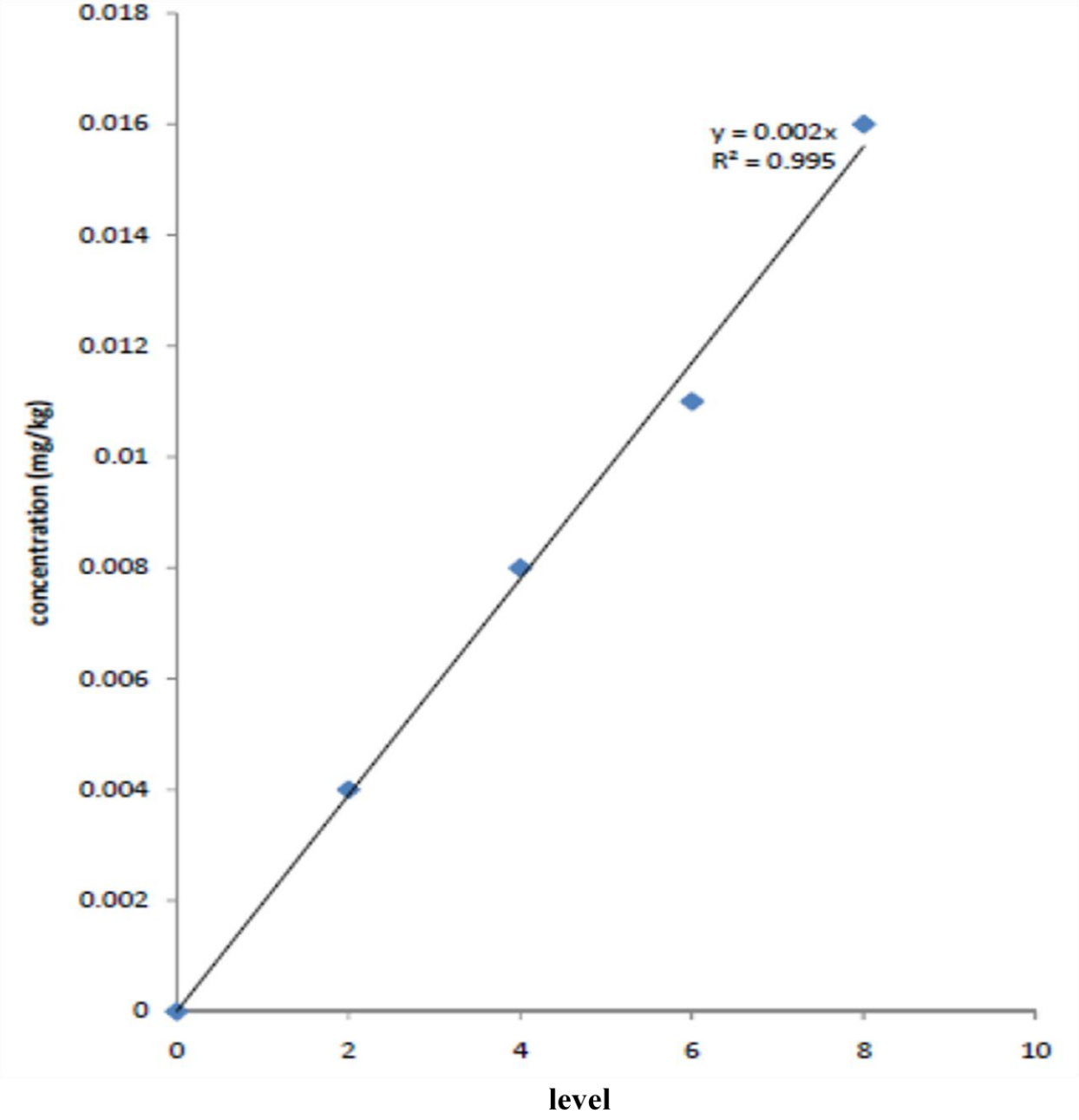
Methyl octanoate



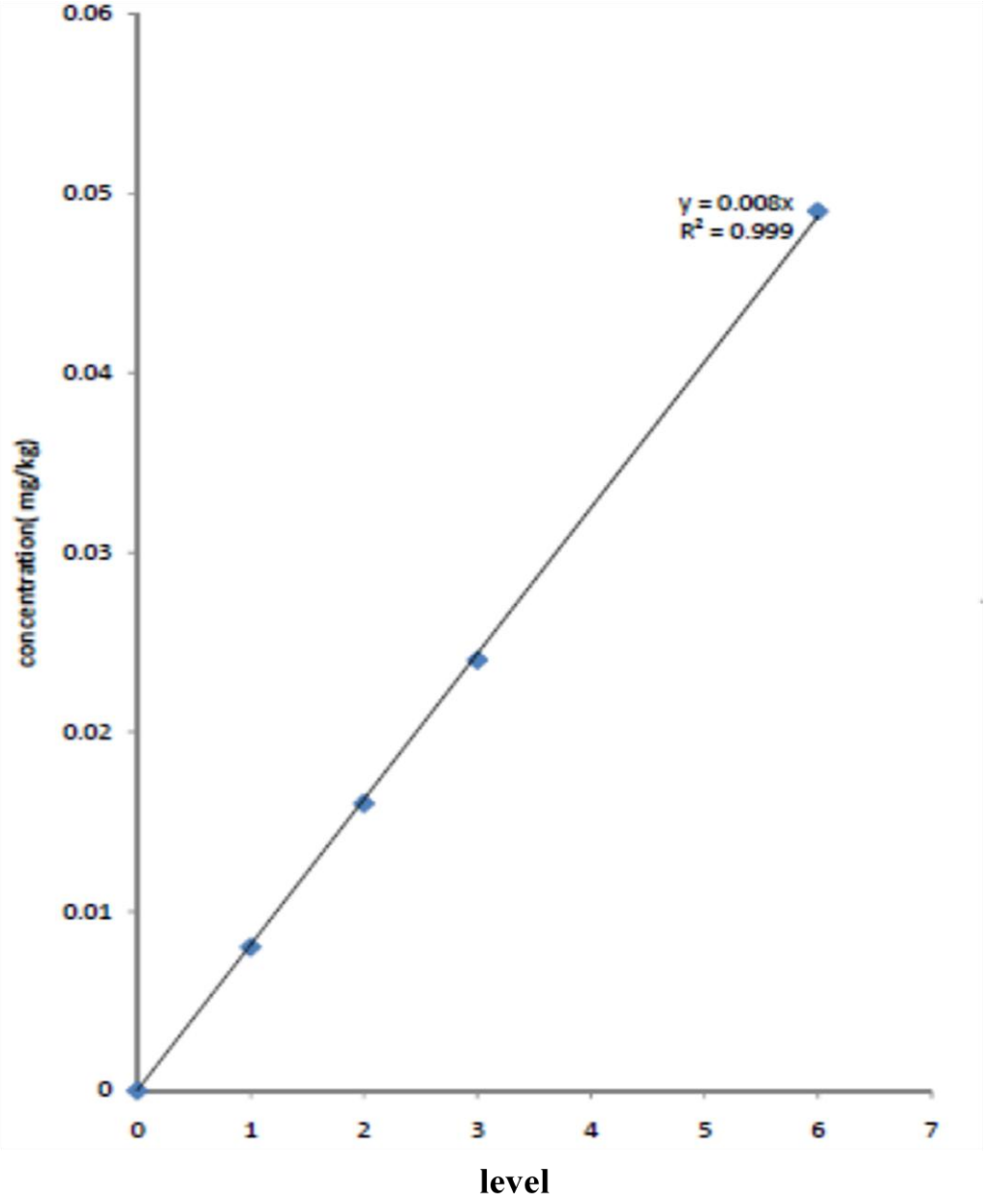
(Text file) scan 1337 (7.453 mins)



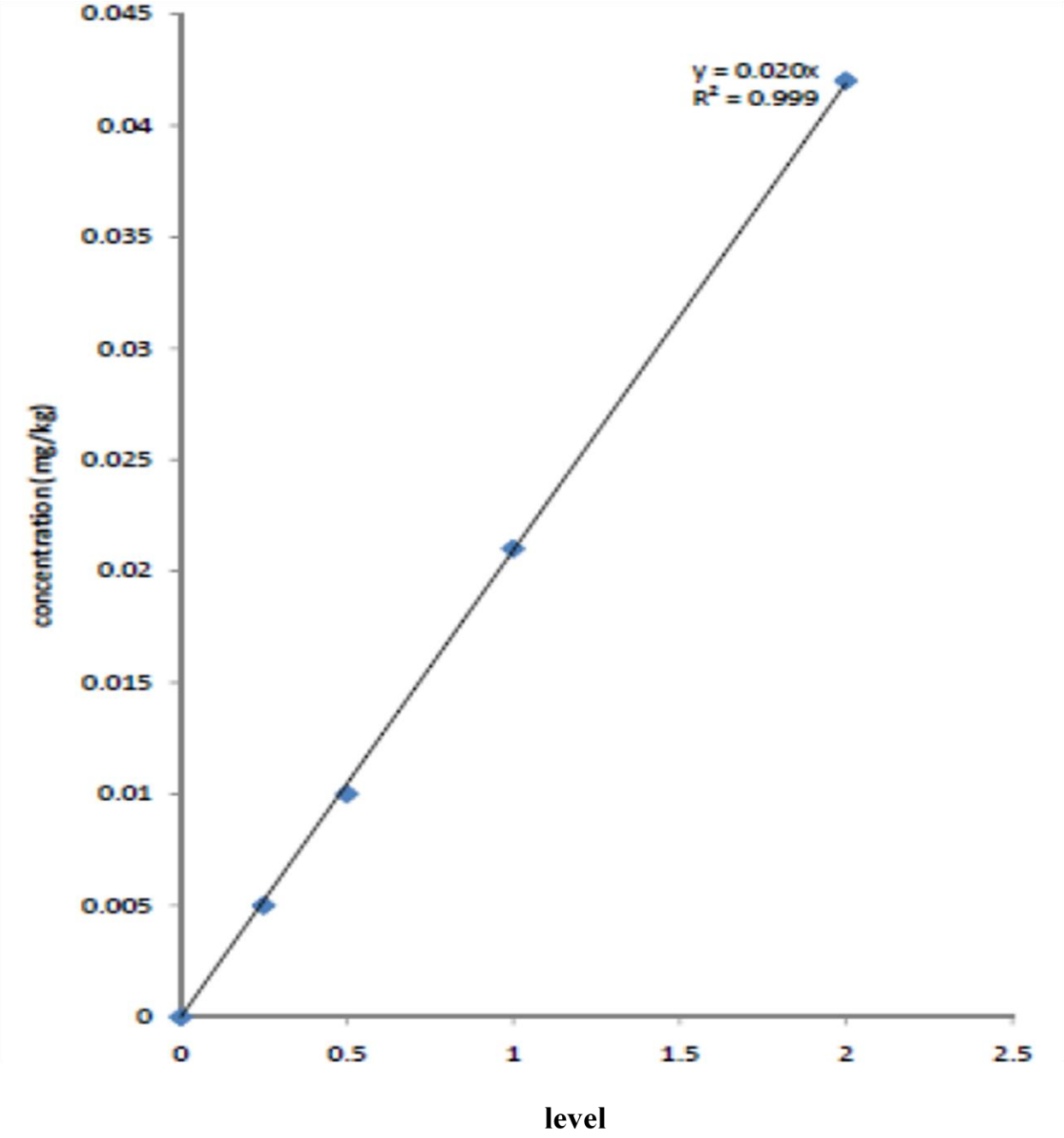
Octane 2,3,6,7 –tetramethyl



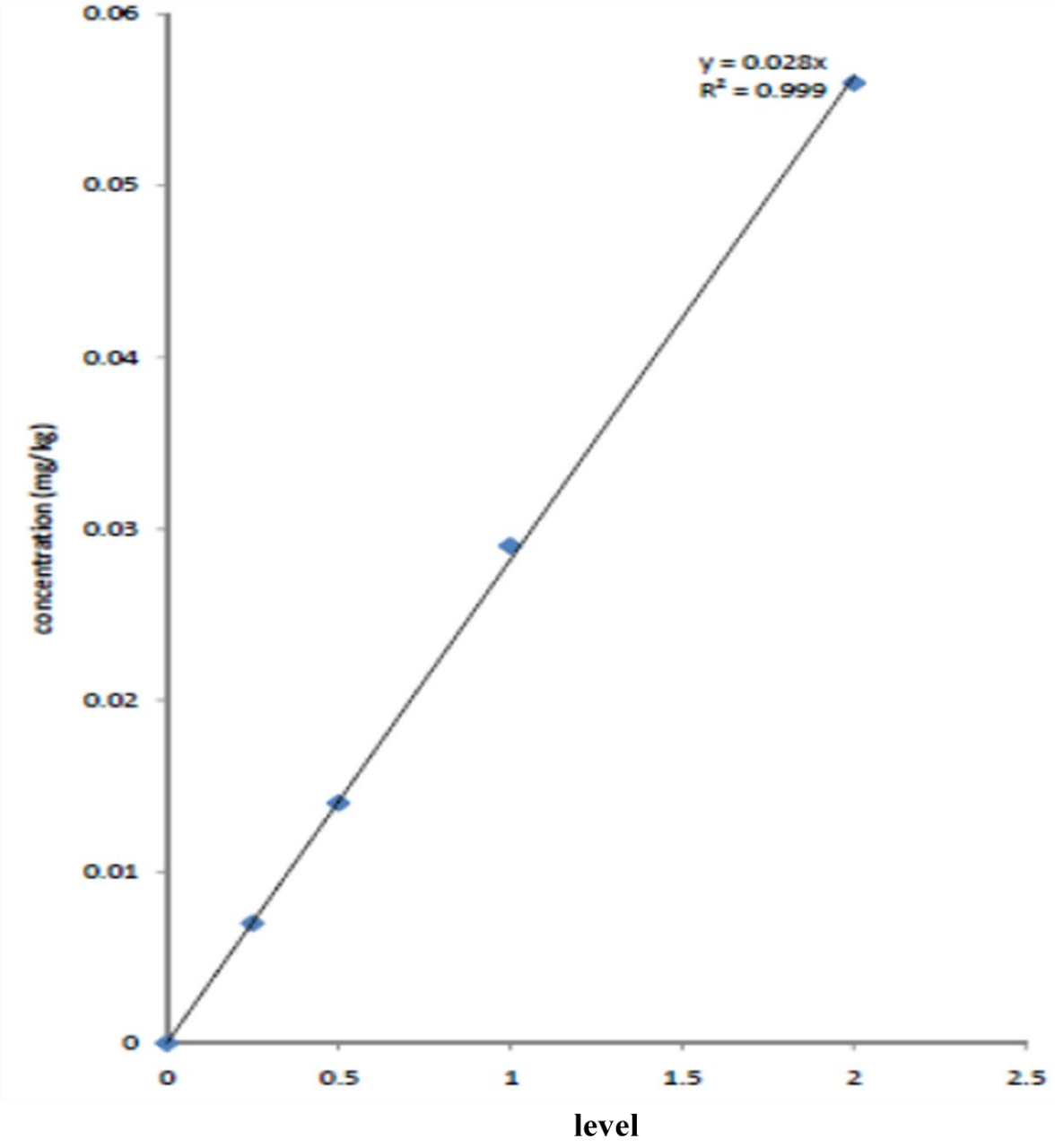
Appendix 33: Calibration curve for standard lead metal



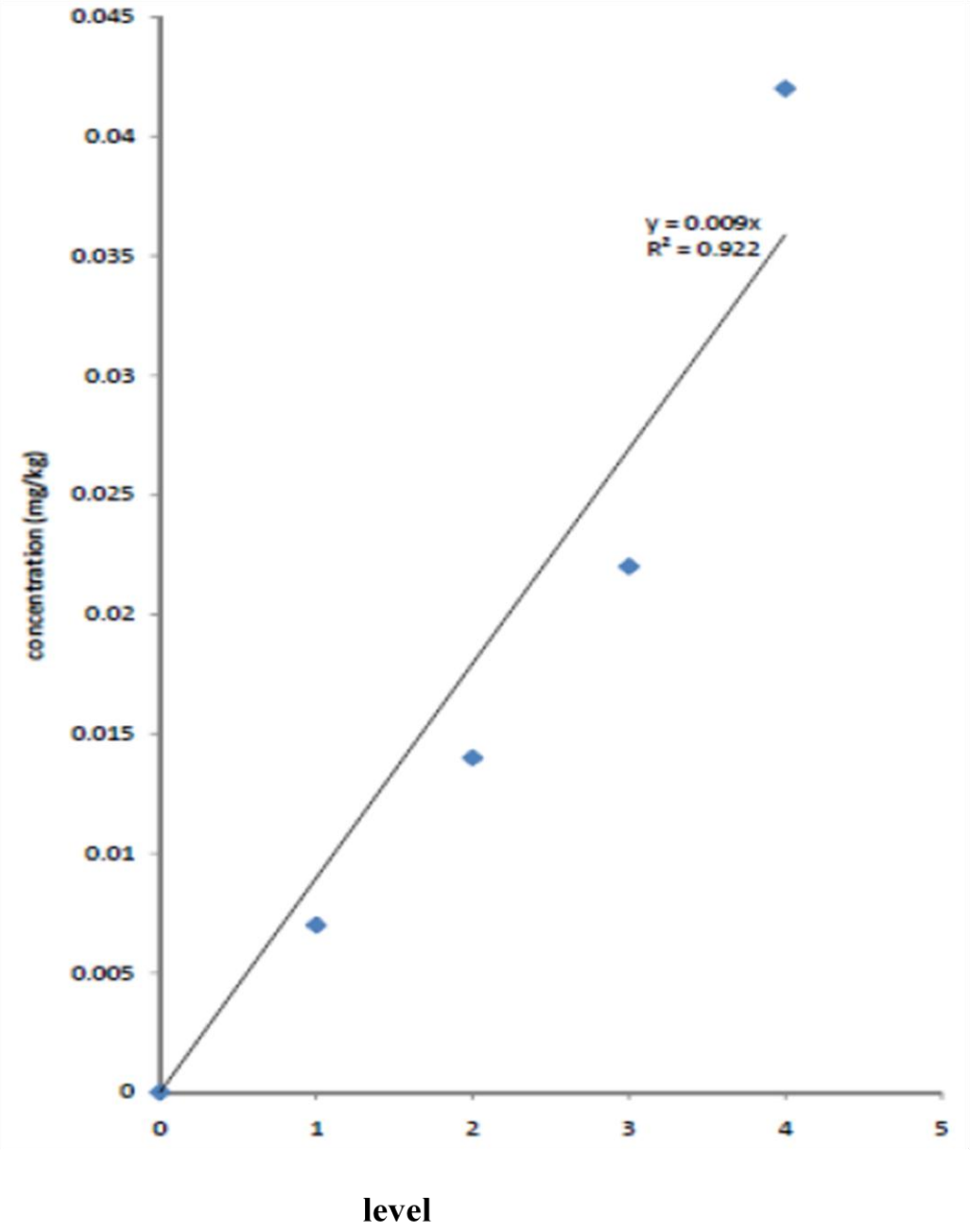
Appendix 34: Calibration curve for standard iron metal



Appendix 35: Calibration curve for standard cadmium metal



Appendix 36: Calibration curve for standard copper metal



Appendix 37: Calibration curve for standard zinc metal

Metal	Highest permissible level	Maximum permissible level
Pb	0.05	0.1
Cd	0.005	0.01
Zn	5.0	15.0
Cu	0.05	1.5
Fe	0.1	0.3
Cr	0.02	0.05
Ni	0.5	6.5

Appendix 38: World Health permissible limits for some heavy metals in mg/kg (Ekpete *et al.*2013)



3 Particle Size (Hydrometer)

Appendix 39: Textural Triangle