Health Risk Assessment of Heavy Metals in Water and Soil Samples around Mechanic Workshops in Ibadan Main City, Oyo State, Nigeria.

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Certification

This is to certify that this Thesis was written by Adeola Ebenezer Olalekan with Matric Number LCU/PG000463 of the Department of Chemistry, Faculty of Basic Medical Sciences, Lead City University, Ibadan Oyo State, for the award of Master of Science (MSc.) in Environmental and Analytical Chemistry, and that this work has not been previously submitted.

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Dedication

This research is dedicated to God Almighty, who is my source and my strength.

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I give all the Glory, Honour and Adoration to God for his sustenance and provision throughout this period of study.

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Abstract

Heavy metal contamination due to activities in auto-mechanic workshops is of public health concern. In most cities in Nigeria, auto-mechanic workshops are often sited close to residential areas and inhabitants are often exposed to possible health risks arising from heavy metals exposure.

This study investigated the physicochemical parameters such as pH, Total Dissolved Solids (TDS), Electrical conductivity, total hardness and concentrations of selected heavy metals (Cu, Cr, Ni, Cd, Mn, Co and Pb) in water and soil samples using standard analytical methods. Samples were collected around some randomly selected auto-mechanic workshops across Ibadan North Local Government (IBNLG) and Ibadan North-East Local Government (IBNELG) Areas of Ibadan.

A total of 82 samples comprising 60 soil samples, 20 hand-dug Wells and two (2) control sites were collected from twenty (20) selected auto-mechanic workshops based on the absence of other industries and the presence of dug Wells. Composited (top soil and subsoil) soil samples in three locations and water samples from hand-dug well (0-50 m) around the workshops were collected between October and November 2019. Values obtained were subjected to descriptive (Mean ± SD), correlation statistical analyses and also compared with World Health Organization (WHO) standards and the controls.

The pH ranged from 8.18 to 8.40, TDS from 73 to 394 mg L^{-1}, Conductivity from 148 to 790 mg L^{-1} and Total Hardness from 295 to 300 µS cm^{-1}. Also, the concentrations of Cu, Cr, Ni, Mn and Pb in water samples ranged from ND-1.85, ND-4.13, ND-0.02, 0.02-0.38 and ND-0.84 mg L^{-1} respectively. Similarly, the concentrations of Cd, Cr, Ni, Cu, Co, Pb and Mn in soil samples ranged from ND to 0.15 to 1.86, 0.04 to 0.37, 0.01 to 2.47, ND to 0.79, 0.81 to 32.6 and 0.10 to 8.73 mg kg^{-1} respectively. Based on the result of this study, carcinogenic and non-carcinogenic risk factor over a lifetime of exposure through contaminated water and soil are below the tolerable value of lifetime carcinogenic risk set by USEPA (10^{-5}), indicating that the contact with the soil might not pose carcinogenic and non-carcinogenic risk.

Keywords: Heavy metal, auto-mechanic workshop, Health Risk, Carcinogenic.

Word Count: 292

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List of Abbreviations

Abbreviation		Meaning
AAS	–	Atomic Absorption Spectrophotometer
IBN	–	Ibadan North
IBNE	–	Ibadan North-East
LGA	-	Local government Area
HM	–	Heavy metals
HQ	–	Health quotient indices
WHO	–	World Health Organization
IARC	–	International Agency for Research on Cancer
USEPA	–	United States Environmental Protection Agency
DI	-	Daily Intake
EDI	-	Estimated Daily Intake

Chapter One

Introduction

1.1 Background to the Study

Environmental pollution is a unique problem of industrialized countries and has now become a global problem, especially in developing countries. Industrialization and other anthropogenic activities had contributed immensely towards the pollution of the environment, with the constant release of pollutants especially heavy metals[1]. The global increase in industrialization and urbanization has led to the discharge of effluents laden with heavy metals, resulting in environmental pollution[2]. The problem is more severe in countries where there is an indiscriminate discharge of untreated sewage arising from domestic and industrial wastes containing a varying degree of pollutants, wastewater from animal husbandry and drainage of irrigated lands and runoff[3].

Industrialization is a major source of waste generation leading to heavy metals contamination in soil. Heavy metals in soil have generated serious concern because of their widespread sources, toxicity, non-biodegradable properties, accumulative behaviours as well as some varied negative effects it has on soil quality, biota, ecosystem and groundwater pollution. Heavy metal contamination in soils, sediments, sludge, water and food products is global. It has a serious environmental concern both in developed and underdeveloped countries especially the potential health and ecological risk associated with such contamination[4].

The soil serves as a long-term reservoir for heavy metals such as Pb, Cd, Zn, Cu and Ni. Heavy metals such as Cu and Zn in the soil are essential trace elements for plants and animals, but excessive concentrations through external additions can destroy the overall soil fertility, and hence agricultural productivity. These heavy metals are toxic at soil concentrations above the normal level[2]. Heavy metal pollution is considered a global problem due to its toxic behaviour even at low concentrations. At higher dosages, heavy metals form free radicals which cause oxidative stress. Their accumulation, mobility and toxicity are influenced by the soil characteristics and environmental factors[5]. Heavy metal contamination has different sources which may include chemical industries, agricultural activities (such as fertilizer application), vehicular traffic, industrial plants, power generation facilities, residential oil burning, waste incineration, construction and demolition activities e.t.c. Due to the characteristics of heavy metals such as bio-accumulation, stability and toxicity, these contaminants are considered hazardous pollutants in the environment because exposure to these toxic heavy metals is associated with many chronic diseases and can cause a wide variety of health problems[6]. Additionally, the epidemiological study also showed that the non-biodegradable nature of heavy metal is a serious concern in exposure assessments[7].

One of the major sources that contributed to the increase in heavy metal concentrations of the ecosystems in Nigeria is automobile workshop activities[4]. These auto mechanic workshops are found in clusters of open fields in urban towns and cities[8]. Automobile service and repair workshops are the largest small-scale producers of hazardous waste. They generate different types of waste during their day-to-day operations. These include spent oil and other fluids, dirty shop rags, used parts, asbestos from brake pads and solvents used for cleaning engine parts. All of which are expensive to dispose of, and sometimes hazardous. The most toxic waste commonly generated in auto mechanic workshops is from the solvents used to clean different automobile parts. Many of the chemicals that make up the solvents are extremely dangerous to humans and the environment[9]. If not well handled, these chemicals can find their way into the air we breathe, the water we drink, soil, lakes and streams[10]. Many parts cleaners and solvents are dangerous to the health of the workers within these workshops. This is because used oil may contain components such as lead, cadmium, barium and other potentially toxic metals. Contaminations caused by heavy metals have generated a great concern due to their toxicity and accumulative characteristics[11].

Wastes obtained from automobile workshops and their activities include used lubricating oils, hydraulic fluids, damaged parts, packaging materials, metal scraps, used batteries, cans stripped oil sludge, and gasoline paint. There is a daily increase in the massive movement of vehicles into Nigeria since the late 1990s. Even with the recent ban on cars manufactured over ten years by the Federal Government, illegal movement of vehicles with a lifespan of more than ten years into the country has increased the numbers of vehicles on the roads, activities of automobile repairs and subsequently the number and amount of pollutants in the environment[12]. Since there are no proper policies as regards the areas where automobile repair workshops should be situated, most automobile mechanics site their workshops in populated residential areas especially in the heart of the cities in most areas[13]. Automobile wastes are usually generated after the repair, maintenance and servicing of motor vehicles, heavy-duty machines and other engines. The discharge of automobile waste into the environment can have harmful effects on organisms and the environment because it contains oxidative products, distributed via sediments and metallic particles produced from machine wear, organic and inorganic chemicals used in oil additives and metals present in fuels and transferred to the crankcase during the combustion process[14]. Considerable amounts of heavy metals such as Pb, Zn, Cu, Cr, Ni, and Cd are present in automobile wastes. Wearing and tearing of engines introduced these pollutants into the oil, which then pose great risks to human and environmental health [14]. The leakage of leachates from these materials is a great threat to water sources such as groundwater. Unfortunately, information on the impact of auto mechanics' activities on the ecosystem is still very scarce. In many sites contaminated by auto-mechanic wastes in Nigeria and other developing countries, the existence of toxic heavy metals poses a serious threat to the environment. The importance of trace elements in soil chemistry has increasingly become a global concern, especially as the soil is an important constituent of the rural and urban environments[10].

Certain lubricating oils usually contain heavy metals as additives, and gasoline does not decompose in the soil. Some of them have been listed as priority pollutants by the United States Environmental Protection Agency (USEPA). Currently, there are few technologies available to treat these mixed wastes, such as soil cleaning and bioremediation[15]. The soil has a load of heavy metals, and this might be because of natural reasons or particles size and not necessarily because of man-made influence. It is therefore hard to figure out how much of the metal in the soil comes from nature or human activities because both add metals to the soil[16].

1.2 Statement of the Problem

Automobile waste such as engine oil, grease, hydraulics, petrol, transmission fluid, power steering fluid, brake fluid, antifreeze solvents, degreasers and solid wastes (like metals and plastics) generated during repairs are deposited and disposed of directly on the floor of the auto mechanic shops. By this improper disposal method, the liquid wastes are absorbed into the ground while the solid wastes are buried over time with consistent disposal. These wastes have high constituents of heavy metals which are capable of contaminating groundwater and soil nutrient. Usually, the solid wastes decay releasing heavy metals and other harmful substances into the soil and water body. This study investigates the influence of waste from auto-mechanic workshops on the concentration and distribution of heavy metals in groundwater and soil around the study area.

1.3 Aim and Objectives of the Study

This study aims to investigate the physicochemical and heavy metal loads of soil and groundwater samples from twenty (20) automobile workshops within Ibadan North and Ibadan North East Local Government Areas of Ibadan, Oyo State, Nigeria.

The objectives of the study were to:

1. Assess the physicochemical characteristic of groundwater sources.
2. Determine the elemental (Cu, Cr, Ni, Cd, Mn, Co and Pb) concentrations in the soil samples from selected automobile workshops in Ibadan, Oyo state.
3. Assess the level of contamination of soil and water samples.
4. Assess the health risk associated with these metals heavy metals.

1.4 Research Rationale

Auto-mechanic workplaces are frequently located near residential communities in many major towns across Nigeria. This proximity can have a negative impact on the ecosystem and human health by contaminating soil, surface water, and groundwater. The many operations done in these vehicle workshops, such as engine repairs, brake system maintenance, and oil changes, are known to cause and contribute considerably to the increase of heavy metals in the environment. Welding, battery repair, and spent oil disposal are frequent in these workshops, adding to the potential environmental impact.

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Chapter Two

Literature Review

2.1 Environmental Pollution

Environmental pollution remains one of the most challenging burdens in the world due to the indiscriminate dumping of waste that arises from industrial processes such as automobile waste into the soil in and around automobile workshops. Environmental pollution being a unique problem of industrialized countries has now become the problem of the developing countries in the process of industrialization[1]. Human activities create a vast amount of various wastes and pollutants, the release of these materials into the environment sometimes causes serious health problems. Waste is any substance for which no direct use is envisaged but which is transferred for processing, dumping, elimination by incineration or other methods of disposal[2]. Due to the process of urbanization and industrialization, a large number and amount of pollutants have been continuously introduced into the ecosystem[3].

In Nigeria, landfill leachate is another major source of heavy metal pollution mostly to the soil and water system. In most cases, wastes are dumped at will without considering environmental impact[4]. Among all the categories of wastes that pose the greatest threat to life, due to the potential to pollute the land, water and air environment, in recent decades, heavy metals have become a major problem due to their health hazards to humans and other organisms when accumulated in their biological systems[5].

The solubility and absorption of pollutants in the soil matrix occurs in the gastrointestinal tract and intestinal membranes[6]. Industrialization has been identified as an important source of waste that causes soil to be polluted by heavy metals. Elevated levels of heavy metals in soil are of serious concern because of their widespread sources, toxicity, non-biodegradable properties, accumulative behaviours as Well as some other negative effects it has on soil quality, biota, ecosystem and groundwater pollution. Heavy metal contamination is referred to as the introduction of toxic metals in soil, sediments, sludge, water, etc as a result of anthropogenic influences and this may result in the deterioration of the environment[7]. The exposure and effect of heavy metals on human health depend upon several factors, such as the route of exposure, age, and distribution in humans[8]. The route of exposure includes inhalation of soil dust, incidental ingestion, and dermal contact[9,10]. One of the most important routes of exposure related to contaminated soil is accidental ingestion, which poses a high risk to human health. Accidental intake, especially among children, involves hand-to-mouth transfer during outdoor activities in urban environments[1011].

Heavy metal pollution is a global phenomenon, but the associated ecological and health risks are still not a priority issue for Nigerian authorities[12]. Today in Nigeria, the use of groundwater has become the driving force for development because the government cannot meet the growing water demand. Therefore, residents have to look for alternatives such as groundwater, shallow Wells and boreholes. The quality of these groundwater sources is affected by the environmental characteristics of the water flowing to the groundwater saturated zone[13]. Thus, the heavy metals discharged by industries, traffic, municipal wastes, and hazardous waste sites as Well as from fertilizers for agricultural purposes and accidental oil spillages from tankers will lead to a steady increase in pollution of groundwater. Therefore, it is necessary to assess the quality of groundwater sources. The World Health Organization has set the maximum levels for heavy metals contaminants in water.

2.2 Automobiles in Nigeria

An automobile is a machine whose ultimate design function is to transport people and goods. It is also called a motor vehicle[14]. It is a self-propelled vehicle that is used to transport passengers and goods on land, such as cars, buses, trucks, articulated vehicles, etc. It is also a kind of transport equipment unit composed of a frame to support the bodywork and certain power to man, such as moving people and goods from one place to another[15]. The Nigerian economic recession dating back to the 1980s led to the adoption of Structural Adjustment Programs (SAPs), which encouraged the large-scale import of used cars into Nigeria[15]. The low purchasing power of the middle class makes second-hand cars the only solution because most Nigerian cities do not have organized public transportation[13]. Similarly, in Nigeria, the consequences of currency devaluation led to the import of used cars. Since then, as the purchase of used cars has become cheaper, the number of cars imported into the country has increased year by year.

Nigeria imports a large number of used cars, and repairs require manual (unregulated) activities. Automobile parts include mechanical parts, electronic and electrical equipment, polymers and other parts that may contain toxic substances, such as automobile crankshafts, engine blocks and connecting rods, which contain steel, chromium, nickel, titanium, and copper while switches, batteries, headlamp bulbs, brake light, data tapes, floppy disk, power supply boxes, car stereo equipment etc. are sources of cadmium, chromium and nickel[16]. When these vehicles are of age and break down, they pose a threat to the environment and public health. When trying to repair these vehicles, artisans at the workshop are exposed to heavy metal pollution in the paint dust of abandoned cars in various subtle ways, such as touching workshop tools, shaking hands, body hugs, exchanging personal items, inhaling and touching micro air suspensions in the workshop. Most of these workshops are located on busy but congested roads in Nigeria, interspersed with other commercial activities, making it possible for humans to come into contact with heavy metals through paint dust. However, this comes at the expense of the environment, as they have been found to pollute the air through incomplete combustion emissions from old engines, such as carbon oxides (COx). Nitrogen (NOx), sulfur (SOx), etc.

2.2.1 Automobiles Repair in Nigeria

The rapid import and influx of "used" vehicles have led to an increase in many auto repair shops across the country[15]. In Nigeria's major cities and towns, a common practice is to allocate a very large portion of land to small groups of auto machinery companies and designate them as villages, where they open workshops and repair shops to provide services to the public[3]. A typical city in a developing country like Nigeria usually has a large number of auto repair shops in proportion to its population and activities. In addition to the organized collection of places, some individual workshops have also been observed in some remote areas of these cities. The increase in car repair and workshop activities in Nigeria is due to the increasing demand for personal vehicles, most of which are used "Tokunbo" vehicles. These have played a significant role in soil pollution problems in most cities[17]. The auto-mechanic villages (AMVs) are frequently cited in shanties, which are often characterized by poverty, overpopulation, and a low level of education. It has been reported that their literacy level contributes to pollution and environmental degradation in these areas due to the information and knowledge gap[18]. Over the past 20 years, environmental pollution caused by the release of potentially hazardous metals from auto mechanic workshops has increased significantly in most cities in Nigeria. This can be attributed to the significant increase in the number of cars and the promotion of economic activities, as Well as economic growth and increased traffic activities in machinery and sites[19].

The increase in cars and urbanization in cities and towns around the world has led to an exponential increase in pollution with traffic being the main cause of pollution[20].

Imported second-hand cars may be the reason for the high rate of car repair activities in the country, thus greatly exacerbating the soil pollution problem in most cities[21]. It is particularly important to study the distribution, enrichment and accumulation of heavy metals in the soil within auto mechanic workshops, especially in developing countries such as Nigeria, due to the unprofessional and illegal waste disposal methods and the evaluation of the possible impact of human factors on groundwater quality[17].

Increasing the number of cars on any country road means increased traffic-related problems like road congestion, increased ambient air temperature due to heat from the engine and exhausts combustion, delayed time of movement, and traffic emission pollution. Gaseous pollutants from automobiles such as carbon (IV) oxide (CO_2), carbon monoxide (CO), methane (CH_4), sulfur (IV) oxide (SO_2), and nitrogen (IV) dioxide (NO_2) and particulate aerosols were reported in Nigeria above ambient level[15].

In addition to auto repair shops, other places such as parking lots and highways are also susceptible to contamination by metals such as lead, cadmium, copper, zinc, and nickel. These metals are generally used as primary or secondary additives for gasoline and automobiles lubricants. With these, the accumulation of more and more metals in these environments cannot be overemphasized. Most worrisome are the workers that are occupationally exposed to substances containing toxic metals and are unaware of their side effects. in addition to other negative effects on health and the environment, some elevated levels of these metals can deplete the blood antioxidants**Error! Bookmark not defined.**.

Another emerging issue related to automobiles is the increasing amount of car waste, which is due to the large number of used cars imported into Nigeria, coupled with the lack of appropriate legislation on the service life of cars imported into the country. This became everyone's business, and the result was that old, shaky and worn cars were scattered in Nigeria's environment. Climatic factors such as acid rain, humidity (dew), and sunlight affect these cars as they corrode, degrade, and decompose, releasing toxic chemicals into the environment. This in addition to other factors constitutes environmental and public health issues[15]**Error! Bookmark not defined.**.

Cars and other vehicular maintenance and repair are some human activities related to environmental pollution[22]. Auto repair and service shops are the largest generators of small-scale hazardous waste. Many different types of waste are generated in the daily operation of auto repair shops[23]. Automobile repair workshops are facilities where automobiles are usually operated in semi-stationary or stationary modes[24]. The pollution load caused by their activities varies with the size of the service area, the nature of the activity, the skills of the artisans, and the types of tools and equipment used. However, the types of waste observed appear to be roughly the same, including solid waste, liquid effluent, and gaseous matter. Pollution arising from an automobile workshop where repairs, maintenance and servicing of automobiles are carried out has generated great concern because debris can reduce soil quality and threaten human health[22]. Therefore, the management of automobile waste is one of the most difficult environmental problems of this century[25]. There is little attention in the vicinity of auto repair shops, and these places are also susceptible to pollution from gasoline-burning leaks, lubricating oil leaks and other chemical inputs in automobile operations[23].

Relevant waste products produced by auto repair shops include liquid waste such as waste oil, oil and grease, battery acid, gasoline, and wastewater used in welding and cleaning processes.

Gaseous waste includes combustible gases (CHx), sulfur compounds (SOx), nitrogen compounds (NOx), carbon oxides (COx), volatile metal vapours, etc[22]. The waste generated by automobile repair workshops can be divided into (i) maintenance and material handling waste, including empty drums and containers (ii) solvents used for maintenance, cleaning and paint dilution (iii) waste heat transfer fluid (iv) waste lubricating oil (vii)) Waste hydraulic oil (vi) Extracted oily sludge (vii) Waste blasting media and (viii) Wastewater. These wastes include gasoline, fats, oils, suspended solids, organic solvents and discarded auto parts, and contain heavy metals that are phytotoxic to plants and harmful to animals[26]. Most of these wastes are dumped on the ground. In addition to heavy metal pollution of the soil by automobile waste, they may also cause soil acidification. Heavy metals themselves are toxic. Unlike other pollutants, they are not biodegradable and undergo global ecological cycles. In addition, the rapid accidental migration of heavy metals can lead to environmental disasters, threatening human health and Well-being by poisoning water and food[27].

Engine oil generally contains chemical additives, which can include amines, phenols, benzene, calcium, zinc, barium, magnesium, phosphorus, sulfur, and lead. Waste lubricating oil, also known as waste motor oil, is generally obtained after subsequent repairs and discharges of cars and generator engines. Nigeria has more than 87 million litres of waste lubricating oil every year, but not enough attention is paid to its proper disposal[28]. Since the current waste management is not good, the habit of spraying used oil and other car debris on the ground can cause further soil pollution and other environmental pollution[29].

2.2.2 Classification of Automobiles

Different standards and potential pollutants were used to classify automobiles while reviewing the environmental and public health impacts of automobile waste and transportation in Nigeria, used as follows[13]:

(1) Based on Load or Capacity

Automobiles can be classified based on the load or their capacity. Heavy-duty tyransport Vehicle (HTV) or heavy-duty motor vehicle (HMV), which carries heavy objects, large mass and large volume. For example, tractors, heavy trucks, etc. They also have light transport vehicles (LTV) or light motor vehicles (LMV), which can transport light items and are smaller in size (such as cars).

(2) Based on Wheels

Automobiles can be two-wheeled vehicles (TWV) (e.g., scooters, motorcycles), three-wheeled vehicles (TWV) (e.g., auto rickshaw), four-wheeled vehicles (FWV) (e.g., cars, buses, jeeps, trucks etc.), six-wheeled vehicles (SWV), etc., depending on the conveyor design.

(3) Based on Fuel Used

In this category, we have petrol vehicles, diesel vehicles, electric vehicles, which use a battery to drive (forklift, battery truck and electric car), steam vehicles (e.g., steam engine boat), and gas vehicles (i.e., vehicles that use liquefied petroleum gas and compressed natural gas).

(4) Based on Purpose

They can be divided into passenger vehicles, cargo vehicles and other special-purpose vehicles (such as armoured vehicles, ambulances, etc.).

(5) Based on Transmission

Automobiles could be: Vehicles with a manual transmission.

Semiautomatic transmission system: They are designed in a way that makes it easy to change the manual transmission ratio through the clutch pedal.

Automatic transmission system: These automobiles do not need to change gears manually, but can automatically change the gear ratio when moving.

(6) Based on the Drive

This classification is based on the position of the steering wheel. They could be Left-hand drive, right-hand drive and fluid units (vehicles that use torque converters (such as fluid flywheels)).

(7) Based on the Suspension System

This can be classified into three systems, which includes:

i. Independent Suspension: This system allows the wheels to be raised and lowered vertically without affecting the opposite wheels[30].

ii. Dependent suspension: It has a beam (a simple frame axis) or drive shaft, where the wheels are parallel to each other and perpendicular to the shaft.

iii. Semi-dependent system: In this system, the movement of one wheel does not affect the other wheel, but they are not firmly connected, such as a rear suspension with a rotating beam[31].

2.2.3 Components of an Automobile

Since the 17th century, various attempts were made to design and manufacture practical and operable automobiles. Making the vehicle movable was achieved by combining the various parts to form an automobile. Automobiles have six major components, which include:

(1) The Body Structure or Frame

This is the chassis that carries the engine, wheels, braking system, steering, etc. It serves as the major mounting bracket for all components. Other body parts include engine hood (engine cover), bumper, hood screen, trunk lid, fender, top plate, radiator core bracket, grille, luggage rack, rim and hub cover, spoiler, fuel tank door, luggage compartment, etc[13].

(2) The Transmission System

This system helps to transmit engine power to the rear wheels through the gearbox to obtain different transmission ratios. Due to the gears in the gearbox, the speed and torque of the wheels will vary with the speed and torque of the engine. They include clutch components (clutch linings, clutch forks, clutch plates, clutch fans, clutch cables, clutch hoses, clutch shafts, clutch springs and clutch pedals), gear sets (i.e. gear shift lever knob, gear pumps, gear rings, gear couplings and gearboxes, including idlers, joints, master cylinders, bearings, countershafts or output shafts, pinions and gear sets), propellers or driveshafts, rear axle shafts, transaxle housings, differentials gears (i.e. star gears, differential seals and spring, pinion gears, differential flanges and differential clutches), speedometer transmission assembly (i.e. transmission gears, transmission seals and transmission springs), flywheel teeth ring, shift valve, reducer or governor, wheels and torque converter[31]

(3) The Internal Engine System

This part of the automobile is designed as an engine, where the chemical energy of the fuel is converted into mechanical energy by burning with air (in the combustion chamber). The internal motor provides the power transmitted by the drive system to the wheels through a clutch or hydraulic coupling[32].

The system is divided into three parts:

Engine parts, including engine block, engine shock absorber, shock absorber, fan belt, piston pin, piston (ie piston pin, crankshaft pin, piston pin brush and piston ring), engine valve, harmonic balancer, accessory belt, gasoline engine, camshaft bearing, camshaft bracket, camshaft lock plate, camshaft push rod and camshaft phaser, air duct, connecting rod bearing and bolt, crankshaft, crankshaft Case, crankshaft pulley, crankshaft oil seal, distributor, transmission belt, cylinder head (with cylinder gasket and cylinder head cover parts), rocker arm, rocker arm cover, starter motor (starter ring and sprocket), blower, turbine booster Compressor and supercharger, radiator parts (radiator, radiator) gasket, radiator pressure cover, overflow tank, thermostat, radiator bolt), water tank parts (water tank, water pump, pump pad and water pipe) , oil system (oil filter, oil pan, oil cushion, oil pipe, oil pump and oil trainer) and spring valves and valve seals[33].

Exhaust system, including exhaust pipe, heat shield, exhaust clamp and bracket, exhaust flange gasket, catalytic converter, resonator and isolation ring etc.

Fuel system, including air filter, carburettor, fuel cap, fuel cell components, fuel distributor, fuel filter and its seal, fuel pump, fuel injector and gasket, fuel pressure regulator, fuel rail, etc[34].

(4) The Control System (suspension, steering, and brake systems)

This controls the arms, shock absorbers, shafts, spindles, springs (air springs, leaf springs, parabolic springs, ball joints, rubber and springs), tires, power steering assemblies, steering arms, steering boxes, steering wheels, steering assembly column, steering shaft, steering rack (rack and pinion), king pin, steering pump, strut, cam arm, handle, link arm, short shaft, steering rod, tie rod, connecting rod foot, horizontal tie rods, suspension links and bolts, idler arms, beam shafts, swing shafts, wheel alignment, trailing arms, automatic braking systems, anti-lock braking systems (ABS), brake fluid, brake linings, discs brake, drum brake, adjusting wheel, anchor, hydraulic oil, hydraulic brake, inboard brake, vacuum booster, dual circuit brake system, metering valve and combination valve, wheel cylinder, wheel bolt, roller brake, p brake Support paint, brake disc, brake lever (handle), brake piston, master cylinder, brake shoe, brake hose, brake caliper pin, brake pad and bracket[35].

(5) The Auxiliaries

This part of the car consists of all electrical and electronic components and battery systems. They include audio/video equipment (i.e., antenna and cable assemblies, radio media players, video players, tuners, speakers), voltage regulators, alternators, meters (such as ammeters, odometers, pressure gauges, hydrometers, pressure gauge, speedometer, water meter). Thermometer, pressure gauge, fuel gauge, vacuum gauge, tire pressure gauge, etc.), thermostat, ignition box, ignition coil, spark wire, distributor cover, electronic time controller, instrument, remote control lock, engine compartment, starting system (Solenoid valve) starter, door switch, ignition switch, switch cover, glow plug and starter motor), lighting (bulbs, interior lights and lights, headlights, fog lights, dealers, turn signal control, license plate lights and bulbs), Sensors (airbag sensor), coolant temperature sensor, throttle position sensor, crankshaft and camshaft position sensor, fuel pressure and automatic transmission speed sensor), GPS navigation/navigation equipment system, central locking system, battery system (battery Box battery) a battery cable, battery monitoring system, battery plate and battery cover), sulfuric acid and distilled water.

(6) Automobile Interiors

Dashboards, secret compartments or traps, car seats, seat belts, seat covers, armrests, headrests, headrests, carpets and floor materials, infant and toddler seats and benches.

(7) Miscellaneous Components and Accessories

These are small accessories in automobiles. They include air conditioning systems (air conditioning clutches, compressors, hoses, relays, valves, coolers, suction hoses, air tanks, condenser filters, and cabin filters), bearings (i.e., grooved ball bearings, roller bearings). bearings) Bearings, roller bearings, sleeve bearings, slide bearings, needle bearings and wheel bearings), hoses (fuel vapour hoses, high-pressure hoses and radiator hoses), ribbons and sheets, airbags, cables of speedometer, phone numbers, rubber (extrusion moulding), bolts, nuts (flanges) and hex nuts), fasteners, split or split pins, rivets, drag chains, dynamic seals, gaskets, centre consoles, glove boxes, gaskets, hood and trunk release cables, as Well as paint and sun visors[13].

2.2.4 Chemical Constituents

A large number of chemical materials such as iron, aluminum, plastics, steel, glass, rubber, petroleum products, copper, steel, etc are used to build automobiles and their components. These materials are used to create everything from small parts such as dashboard needles and cables to large parts like engine blocks or transmission gears. Due to the high demand for cars and technological advancement, suitable materials have been used to produce auto parts that are durable and serve automotive purposes. Some of the chemical constituents of various auto parts are as follows:

2.2.5 Environmental Impact Associated with Automobile Repair Workshops

Due to poverty and the urgent need to own vehicles to facilitate movement, ageing vehicles still attract customers from the Nigerian middle class and those at the bottom of the class of the economy. A large number of these automobiles are taken to auto repair shops for maintenance and renovation. Considering public health concerns, auto workshops are important because they are held in a hostile environment, and the workshop workers lack a safe and hygienic lifestyle (they do not wash their hands to eat, they wear dirty and contaminated workshop clothes for a long time). However, it is a hive of activities because it has become a source of employment for some informal sector workers, such as car repairs, servicing and refurbishing, car parts cleaning, car washes, pumps and tire repairs, automobile electricians, wheel balancing and positioning, sale and services of oil, sale of spare parts, water and food supply, etc. In addition to aesthetic pollution, auto repair shops have also made significant contributions to environmental and public health discourse.

Several literatures have reported that the activities of automobile workshops are sources of pollutants such as heavy metals, benzene, nitrobenzene, petroleum fumes, particulate matter, etc to the environment, and have negatively affected surface and underground water and adjacent farmlands. In major Nigerian cities, there are clusters of auto repair shops on the main roads, which include unregulated activities such as auto-mechanics and panel beaters. A large area of land that could have been cultivated is occupied and polluted. The drainage system is blocked by waste generated in their workshops, heavy metals, used oil and toxic gases are released into the environment, neighbouring farmland and food crops, which can be contaminated by heavy metals and toxic substances. The exposed artisans were identified as high-risk groups for cardiovascular and pulmonary diseases[36].

2.2.6 Automobile Wastes

The waste generated by the activities of the automobile workshop can be divided into (i) maintenance and material handling waste (ii) solvents used for maintenance, cleaning and dilution of paint (iii) Waste heat transfer fluids (iv) Used lubricant (vii) Used hydraulic oil (vi) Pickled mud (vii) Used blasting medium and (viii) Wastewater. These wastes, including gasoline, oils, grease, organic solvents, suspended solids, and discarded car parts, all contain heavy metals that are phytotoxic to plants and harmful to animals[36]. Most of these wastes are dumped on the ground. In addition to heavy metal pollution of the soil by car waste, they may also cause soil acidification. Heavy metals themselves are toxic, and unlike other pollutants, they are not biodegradable[37]. In addition, the rapid and accidental mobilization of heavy metals can lead to environmental disasters, threatening human health and Well-being by poisoning water and food[27].

The list of some components of automobiles and are summarized in Table 2.1 below:

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Table 2.1: Some major parts and Chemical component components of automobiles

S/n	Major parts of automobile	Chemical component
1	Body	iron, carbon, aluminium, magnessium, silicon
2.	Chasis	Al- Mg alloy
3.	Trunk	Fiber glass composite or nitrile rubber
4.	Door panel	Carbon, iron, steel or aluminium
5.	Window screen	Glass made from Kevlar glass (polyparaxylylenediamine), K_2O, MgO, Al_2O_3 Polymethylmethacrylate
6.	Rim	Aluminum/Magnesium
7.	Radiator cores and tanks	Copper, zinc and steel alloy
8.	Tires and tubes	Elastomer, oil, resin, carbon black, steel, silica and styrene-butadiene rubber (SBR))
9.	Wheels	Al, Mg, Si, Cu
10.	Glass	SiO_2
11.	Sun visor	Made from substrates of polypropylene
12.	Racks	Al alloys
13.	Rivets	Al alloys, steel, Cu, fe, Ni
14.	Batter, battery case, plates and connectors	Nickel, Cadmium, lead, HDPE
15.	Pumps and valves	Copper, Cobalt, Beryllium, Aluminium

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Table 2.1: Some major parts and Chemical component components of automobiles (cont'd)

S/n	Major parts of automobile	Chemical component
16.	Automotive exhaust system components	Chromium, Silicon, manganese, iron, nickel zinc, copper and magnesium
17.	Engine block	Carbon, silicon, manganese, iron, nickel, zinc, copper, magnesium
18.	Engine cylinder	Cast iron and Al alloy
19.	Wheel cover	Plastics
20.	Radiator	Aluminium sheets
21.	Axles	Chromium, molybdenum
22.	Pinion, and steering column	Stainless steel and aluminium
23.	Steering arms	Carbon iron, and chromium
24.	Spring and suspension coil	iron, manganese, silicon, phosphorus, vanadium, nickel, chromium, tin, zinc, aluminum, and carbon
25.	Gear assembly system	Copper, zinc and steel
26.	Clutch assembly	Copper, tin and phosphorus

2.3 Heavy Metals

Heavy metals are defined as metals with a density greater than 5 g cm^{-3} [39,40]. They are elements with an atomic weight between 63.546 and 200.590 and a density greater than 4.0 (that is, the density is at least 5 times that of water)[41]. Their appearance in bodies of water could be of natural origin (as minerals from erosion in sediments, leaching products from mineral deposits and volcanic extrusion) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic wastewater, dredging of seaports and inland waterways). Some metals (such as calcium, magnesium, potassium, and sodium) are essential to sustain life, and they must be present to maintain normal bodily functions[42]. Additionally, small amounts of elements like cobalt, copper, iron, manganese, molybdenum, and zinc are required as catalysts for enzymatic activity[43], but excessive exposure to heavy metals can become toxic.

Heavy metals have an antagonistic effect, destroying trace elements in the body, inhibiting and competing with proteins and enzymes for binding sites, and also damaging the immune system. Depending on the characteristics and amount of metals ingested, they can cause serious health effects and present different symptoms[44]. They produce toxicity by forming complexes with proteins, involving groups such as carboxylic acid (–COOH), amine (–NH_2) and thiol (–SH) groups. These modified biomolecules can no longer function normally as expected, therefore causing cell dysfunction or death. When metals are attached to these groups, they can inactivate important enzyme systems or affect the structure of proteins, which is related to the catalytic properties of enzymes. This type of toxin can also lead to the formation of free radicals, which are dangerous chemicals that can cause the oxidation of biological molecules[45].

Of the 90 natural elements, 53 are considered heavy metals, and some are of biological importance. According to their solubility under physiological conditions, 17 kinds of heavy metals can be used in biological cells, which are important for the flora and fauna in various ecosystems. After the ingestion process, these pollutants will become bioavailable and be absorbed into the blood[46].

Heavy metals are significant environmental pollutants, their pollution refers to the situation where the content of these elements in environmental media is higher than the maximum permissible concentration, which is potentially harmful to biological life in these places[3]. The availability of heavy metals in the soil depends on natural processes, especially lithology and soil formation, but also on human factors, such as mining, fossil fuel combustion, municipal waste treatment, soil runoff, metallurgical industry, marine activities, phosphate fertilizer application, effluent from sewage treatment plants and municipal solid waste dumps[33]**Error! Bookmark not defined.**. There are many sources of heavy metals, but human economical activities like coal mining, metal ore mining, chemical manufacturing, oil mining and refining, power generation, metal smelting, metal refining, and electroplating, and to some extent, domestic sewage is the principal source[47].

Metal is persistent pollutants, which can bio-magnify in the food chain, causing more and more harm to humans and wild animals. Therefore, assessing the amounts of pollutants in different components of the ecosystem has become an important task to prevent natural life and public health risks. The most common heavy metals that humans are exposed to are aluminum, arsenic, cadmium, lead, and mercury[33]. Aluminum is related to Alzheimer's and Parkinson's disease, aging and Alzheimer's disease. Exposure to arsenic can cause diseases or symptoms such as cancer, abdominal pain, and skin damage. Exposure to cadmium can cause kidney damage and high blood pressure. Lead is an exchangeable poison and may be a human carcinogen, and the toxicity of mercury can cause mental disorders and speech, hearing, vision and movement disorders[47]. In addition, lead and mercury can lead to the development of auto-immunity, in which case a person's immune system will attack one's own cells, leading to joint diseases and diseases of the kidneys, circulatory system and neurons. At higher concentrations, lead and mercury can cause brain damage, which could not be easily reversed[33].

Some heavy metals are essential for maintaining human metabolism, however, many heavy metals can be toxic at higher concentrations because they tend to bioaccumulate in the human body, making them dangerous and posing a great risk to health and environmental safety[48]. With the rapid development of industrialization and the economy, heavy metals continue to enter the environment through different channels: the application of herbicides, fertilizers and pesticides on agricultural land, irrigation, river runoff, atmospheric deposition and sources. They also come from industrial activities such as metal mining, electroplating, by-product production, refining and rehabilitation. Heavy metal contamination in soil, sediment, sludge, water and food has become a serious environmental problem in developed and underdeveloped countries, especially the potential health and ecological risks associated with such contamination[7]. Imported second-hand cars may be the reason for the high rate of auto repair activities in the country and thus have a significant impact on soil pollution problems in most cities. This is due to the short service life of vehicles; therefore, in most cities, they are easily thrown on the side of the road. Metal from this source seeps into the ground in the form of rust. Other sources, such as oil used to clean machine parts during servicing, grease used for lubrication, scrap metal, and used batteries, waste that is arbitrarily discarded on the earth by automotive engineers due to ignorance and inefficient regulatory mechanisms to control such disposal[49]. Some heavy metals such as Cu, Ni and Zn are necessary for plants and animals at very low concentrations. They are components of enzymes, structural proteins, and pigments, and also help maintain the ion balance of cells[3].

2.4 Soil

Soil is an organic or stony material whose surfaces on planets and similar celestial bodies have been altered by biological, chemical and/or physical factors. It is a generally loose layer of mineral and organic materials that are affected by physical, chemical and biological processes on the planet's surface, generally containing liquids, gases and biota and supporting plants[49]. This means that organic mineral materials are a key component of the soil, while liquids, gases, biota and plants are often indispensable factors. Soil is the natural system for plant growth. It is also defined as a natural body made up of layers (layers of soil) made up of weathered minerals, organic materials, air and water. It is the end product of the integral influence of the climate, the topography, the organisms (flora, fauna and humans) on the parent material (rocks and primitive minerals) over time. Therefore, the soil is different from its original material in terms of texture, structure, consistency, colour chemical, biological and physical properties[50]. Soil is a biologically active and porous medium developed in the upper layer of the earth's crust. It is one of the main substrates of life on earth, as a reservoir for water and nutrients, a medium for filtering and decomposing toxic waste, and a participant in circulation and other elements throughout the global ecosystem[51]. The soil can be contaminated by the accumulation of heavy metals and metalloids. This can happen through rapidly expanding industrial areas, mine tailings, high metal waste disposal, and discharge of leaded gasoline and paint. Other possible applications on land include chemical fertilizers, animal manure, sewage sludge, pesticides, sewage irrigation, carbon residues, petrochemical spills, and atmospheric deposition[51]. Metals from these sources enter the soil matrix and are absorbed by plants, and their amounts can adversely affect the people or animals that eat these plants[21].

Soil is the main reservoir of heavy metals in the atmosphere, the hydrosphere and biota, which is why it plays a fundamental role in the entire metal cycle in nature[52]. Heavy metal pollutants in the environment will eventually settle in the soil as some form of low solubility compounds (such as pyrite) or will be adsorbed on the surface reaction phases, such as iron and manganese oxides[3]. Heavy metals in soil represent a potential threat to the environment and can harm human health through multiple absorption routes, such as direct ingestion, skin contact, diet through the soil chain- food, inhalation and oral intake[53]. Due to the high degree of human activities in urban areas, heavy metal concentrations in the soil in these areas are higher than in areas with fewer human activities (such as rural areas)[54]. Topsoil is an important part of the urban environment. Heavy metal contamination on the soil surface is vital for human health because fine particles on the soil surface can be widely dispersed by environmental factors such as rain and wind[55]. The damage to human health is due to the high frequency of exposure to heavy metals, which is mainly divided into carcinogenic effects and non-carcinogenic effects[56].

Soil has many functions, including supporting plant growth by providing a medium for plant roots, providing essential nutrients for plants, and controlling the fate of water in the hydrological system. Soil also serves as a circulatory system of nature, providing habitats for a large number of organisms, and as an engineering method in an ecosystem built by humans. Due to the extensive human activities brought about by industrialization, the soil ecosystem is often saturated with heavy metals[57]. Heavy metals represent a set of inorganic chemical hazards, which when released into the soil environment pose an increasingly serious threat to the environment and public health due to their accumulation and persistence in the food chain**Error! Bookmark**

not defined.. Soil is the main sink for heavy metals released into the environment by human activities. Unlike organic pollutants that are oxidized to carbon (IV) oxide through the action of microorganisms, most metals will not undergo microbial or chemical degradation, and their total concentration in the soil has a duration of time, which becomes longer after its introduction. However, changes in its chemical form (speciation) and bioavailability are possible[51]. In many countries, contamination by heavy metals (HM), total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) is widespread. Pollution caused by the treatment of used motor oil is one of Nigeria's environmental problems and is more common than contamination from crude oil[58]. Soil surfaces contaminated by heavy metals can cause carcinogenic and non-carcinogenic health hazards[59].

2.5 Water

Water is considered an important substance in the environment. The sustainable development of the world's social and economic conditions depends on the availability of water resources. The development of industry, agriculture and domestic activities requires water of adequate quality and quantity. As the main result of population growth, the demand for water for households and agricultural and industrial consumption is increasing considerably. This has led to the overuse of underground water resources as the main source of water supply. Water is a compound with specific chemical properties that can dissolve various compounds or keep them in suspension. The contamination of underground water resources is a serious environmental problem[60].

In recent years, research into water pollution by heavy metals (HM) has become a major focus of environmental scientists [61]. The presence of heavy metals in the host rock of aquifers in the natural environment is one of the major problems, which can cause metalloids and metals to pollute water bodies. The quality of drinking water and irrigation water is adversely affected by high concentration heavy metal contamination caused by man (such as mining, wastewater, irrigation, industrial and agricultural activities) and resources natural (such as bedrock erosion and volcanic eruption processes)[62]. When heavy metals come into contact with surface and groundwater, they can cause pollution and reduce water quality, leading to deterioration of drinking water and irrigation water supplies[61]**Error! Bookmark not defined.**.

Heavy metals in water can come from natural sources (weathering and erosion of bedrock and mineral deposits) and man-made sources (mining, industry, sewage irrigation and agricultural activities)[63]. Among the pollutants that affect water resources, heavy metals have received more attention due to their high toxicity at low concentrations[64]. Heavy metals in water can exist as a colloidal, particulate, or dissolved form. Heavy metals such as iron, copper, cobalt, molybdenum, manganese, and zinc are helpful to the body, but in low doses they can catalyze enzyme activity[6561]. However, they are toxic in high doses[66], and high concentrations of other metals such as cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb) are considered highly toxic to humans and aquatic life[62]. The indiscriminate location of groups of auto-mechanic workshops (commonly known as mechanic villages) is a common feature of urban and rural communities in Nigeria. These sites are the center of various activities, including repairs, panel beating, and painting of these vintage and second-hand cars.

Metals are unique environmental pollutants because they are ubiquitous in different environmental matrices. Metals are concentrated and transformed into various products via some man-made processes. These processes often result in concentrations of different chemicals that are much higher than those naturally found in the environment. Environmental pollution caused by heavy metals is a serious event that affects soil, air, food, and organisms in aquatic ecosystems[13]. These pollutants infiltrate the groundwater through the soil, and eventually transport from there to the surface water.

2.6 Heavy Metal Pollution and Distribution

2.6.1 Distribution in Atmosphere

Heavy metals are transferred and accumulated into the atmosphere through dry and wet sediments. The surface soil and surface water then pollute the ecological environment through certain biochemical effects, and finally transfer to animals and plants, and then transfer to the human body. On the other hand, heavy metals enter the atmosphere through industrial combustion gases, mining, automobile exhaust gases, dust, etc., and enter the human body through human respiration[67]. Heavy metals in the atmosphere are easily enriched and absorbed with particulate matter (PM, PM 10 or PM 2.5). The different chemical nature of heavy metals in atmospheric particles largely determines the possible toxic effects of the heavy metals contained in the atmosphere. The distribution of chemical forms of the different heavy metals is quite different and heavy metals in different regions have different shapes. Therefore, studying the heavy metal content in atmospheric particles and their temporal and spatial distribution characteristics is very important for environmental monitoring and related analyzes[66].

2.6.2 Distribution of Heavy Metal Pollution in Water

Heavy metals have long-term, hidden and difficult characteristics to decompose, and is one of the important contaminants in surface water, with high toxicity in water. Heavy metal contaminants are generally distributed in surface water, interstitial water and sediments. The weight of heavy metals in the sediment of the river is higher than that of the surface, and the heavy metal content of the downstream river is greater than that of the river above. Heavy metal in the water area is ultimately stored in river deposits, and the possible sources of retention of pollutants of air pollutants are stored beyond heavy metals in rivers. The excess content and distribution of heavy metals in water and sediments are particularly important for the transplant material and the transfer of energy in the downstream regions. The use of systematic sampling to understand the characteristics of spatial distribution, sources and possible health effects is very important to reduce human exposure and control potential risks[68]. Heavy metals from various sources enter the rivers in various ways, and finally flow to lakes and reservoirs. It also brings great threats to the ecological environment and human health of the basin. Therefore, in recent years, the lake, rivers and estuary are important to examine heavy metals in the water area.

Gao et al.[69] studied the pollution of trace metals in sediments and organisms in the Bohai Sea and found that the concentration of trace metals is very high in the coastal areas, which occurred mostly in estuaries. However, scholars have assessed the level of heavy metal pollution in water bodies such as rivers and lakes in different parts of the world. For example, Li et al.[70] collated the concentrations of twelve heavy metals, dissolved in rivers and lakes around the world from published papers. The result from the study (from 1970 to 2017) showed that the amounts of cadmium, chromium, copper, nickel, manganese and iron in the rivers and lakes of the world showed an increase, and the contents of lead and zinc showed a downward trend. In addition, mining and manufacturing are always considered a source of relevant metal contamination for rivers and leaks from the lake. Heavy metals concentrated in sediments according to environmental changes are "time bomb", aquatic collection and basins[71]. Besides, mining activities have long been related to deteriorating water and sediment quality. The pollution and spatial distribution of heavy metals in the sediments and surface of the Mustafaq Malpas River in the world's largest borate basin in Turkey was evaluated and possible sources of contaminations were identified[72]. It was found that although chromium, arsenic, and cadmium exist naturally, mining accelerates their existence in river sediments, and the content of chromium has a potential negative impact on biota.

2.6.3 Distribution of Heavy Metal Pollution in Soil

Heavy metals in soil show a complex spatial variability under the action of several sources of contamination and indicate changes in soil spatial properties. Heavy metals can reflect the source and strength of heavy metal contamination to some extent. Therefore, scientific research on the composition and spatial distribution of heavy metals in the soil is a prerequisite to prevent and administer soil pollution and early soil risk alert, which attracts professionals and attention A academics. Currently, one of the most effective methods to examine the distribution characteristics and change of changes in heavy metals in soil is the geographical structure[67]. The geographical hygienic method is to form regional data by spatial interpolation, which provides an impartial estimate to study the spatial distribution of heavy metals in the soil and can cause the pollution law to some extent.

2.7 Effect, Source and Transport of Heavy Metals in Soil

2.7.1 Lead

Lead is a naturally occurring metal. It is soft and whitish in colour, with a low melting point, and is corrosion-resistant. The atmosphere contains a large proportion of lead particles caused by emissions. The natural concentration of lead in the atmosphere is estimated to be in the range of 5.0×10^{-5} µg m^{-3}. The urban concentration is around 0.5 µg m^{-3}, with annual average concentrations of 3 µg m^{-3} or higher in cities with heavy traffic[73].

The mining, smelting and processing of lead and lead-containing metal ores are the most significant stationary sources of lead emissions. Furthermore, incinerators, power plants, industries and households burning of lead-containing waste added to the concentrations of lead in the atmosphere. Vehicle traffic is the most significant source of atmospheric lead in many urban areas, accounting for 90 % of lead emissions into the atmosphere due to widespread use of alkylated lead compounds as additives[74].

Because of its unique physical properties, lead is used in a variety of products. Water distribution systems commonly use lead pipes or solder, which can contaminate drinking water. Lead-containing paint and lead-contaminated dust are still the main sources of human exposure in some countries. Electronic circuit boards and lead-acid batteries will pollute all environmental media during their production, disposal and incineration. In polymer, some lead compounds are utilized as stabilizers. Other lead-containing products include; food cans, glassware, tires, lead-lined cables, ammunition and cosmetics, etc., all of these are sources of lead in the environment[75].

Lead is a cumulative toxin that can produce multiple systemic toxicities even at a very low exposure level[76]. Lead is the most common environmental pollutant in soil. Unlike other metals, lead has no biological effects and is potentially toxic to microorganisms[77]. Its excessive accumulation in the body is always harmful[76]. Lead is a potent multi-organ poison and occupational exposure to lead is associated with a significant decrease in semen quality.

Prolonged exposure to lead can affect the central nervous system, causing seizures, coma, memory loss, and even death. Long-term exposure of children to lead can also cause diminished mental ability[78]. Presence blood lead levels below10 μmg/dL are considered acceptable, but recent studies have shown that lead can have toxicological effects even at exposure levels lower than previously expected[79].

Additionally, lead exposure can cause seizures, mental retardation, and behavioral disturbances in humans. The human body is exposed to heavy metals mainly through three ways, namely inhalation, ingestion, and skin absorption. All of this happens in countless places, including auto repair shops. Generally, toxic metals can cause enzymes to inactivate and damage cells by acting as anti-metabolites or by forming precipitates or chelates with essential metabolites[58]. Lead is a highly toxic and carcinogenic metal that can cause chronic health risks, such as headaches, irritability, abdominal pain, nerve damage, kidney damage, blood pressure, lung cancer, stomach cancer, and glaucoma. As children are more prone to its toxicity, their exposure to high levels of metals can lead to serious health problems, such as behavioral disturbances, decreased memory and decreased understanding, and prolonged exposure can lead to anemia[61].

Generally speaking, lead has little mobility in soil. Under most natural conditions, the rate of leaching of lead compounds from soil to groundwater through downward movement is very slow, due to clay, silt, iron and manganese oxides, and organic matter from soil can combine lead and other metals[80]. Additionally, soil pH, humic acid content, and organic matter content affect lead content and mobility in soil. Erosion of lead-containing soil particles will also bring lead to surface water. Lead can form complexes with dissolved humus materials, especially in aquatic environments (strong bond strength, limiting usability). It is attached to colloidal particles, such as solid iron oxide particles (which has a strong binding force and lower mobility than free ions when obtained in this form) or solid particles of clay or dead organic matter[81].

2.7.2 Cadmium

Cadmium is a silvery-white soft metal, generally combined with other elements. The Registry of Toxic Substances and Diseases has identified that the burning of fossil fuels (such as coal or oil) and the burning of municipal waste as the world's most important sources of cadmium into the atmosphere and other environmental media[82]. Other sources of cadmium include; agricultural processes (such as fertilizer application, pesticides application) industrial waste treatment, rechargeable batteries, cleaning agents and refined petroleum products[51]. Cadmium is harmful when inhaled and swallowed and can cause acute and chronic poisoning in humans. Its half-life is very long and it accumulates in the kidneys, lungs and liver. It is very toxic and can even destroy biological systems, even at very low concentrations than most toxic metals. Studies have shown that the low environmental exposure to cadmium currently found in industrialized countries can cause subtle kidney effects, leading to a significant increase in the excretion of microbial proteins in the urine[13].

Prolonged exposure can cause ulcers and perforations of the nasal septum, lowered lung function, chronic bronchitis, pneumonia, and other respiratory effects. Cadmium can have chronic and acute health effects on organisms. It has been identified as an occupational health hazard that can cause a notorious pain caused by ingestion of products contaminated with cadmium[8183]. Studies have shown that the kidneys and bones are the most severely affected human systems, although recent studies have also reported cancers with excessive risk and low-level environmental exposure[83]. In most dietary exposures, the kidney is the most affected organ. Cadmium can cause kidney damage due to the absorption dysfunction of the proximal tubules. This can lead to end-stage renal disease (ESRD) and death due to high and long-term exposure. Experimental data on humans and animals indicate that cadmium can cause cancer in humans[61].

Prolonged exposure to cadmium has been shown to cause bone disease characterized by multiple fractures and dislocation of bones in the skeleton, with serious pain in the affected individuals[84]. International Agency for Research on Cancer has categorized cadmium as a human carcinogen (group I) because of sufficient evidence for carcinogenicity in humans and experimental animals, while the European Commission has classified some cadmium compounds as possibly carcinogenic[85].

The California Environmental Protection Agency (CalEPA) has established a reference exposure level of 1.0×10^{-5} mg m^{-3} of cadmium based on the human body's effects on the kidneys and respiratory system. The CalEPA reference exposure level is equal to or lower than the concentration at which adverse health effects are unlikely to occur[86].

Cadmium in soil environment is mainly controlled by pH value. Under acidic conditions, the solubility of cadmium increases, and soil colloids, hydrated oxides and organic matter have little adsorption of cadmium. The adsorption or precipitation of cadmium on soil solids occurs when the pH value is greater than 6, which reduces the concentration of dissolved cadmium in the soil. The mobility and bioavailability of cadmium depend on the characteristics of the soil[81].

2.7.3 Nickel

Nickel content in soil varies with the geology of the area and human intervention. The typical nickel concentration in the soil is between 4 and 80 ppm. Nickel can be found in rivers and waterways due to natural soil weathering and anthropogenic emissions and runoff. This nickel accumulates in the deposits. The column migration experiments of Liao and Selim[87] show that Ni mobility is strongly hindered, tailing or slowly release during the leaching process. Their results show that Ni is very immobile. The mobility of nickel is controlled by soil adsorbing substances in soil and other factors; therefore, the uptake of nickel by the soil is site-specific. Soil properties, such as particle size distribution, texture, organic matter, pH value, the nature and amount of clay minerals, and the degree of flow of groundwater, all affect the retention and release of metals underground. Human exposure to nickel causes a varying degree of pathological effects, but the adverse effects on health depend on the route of exposure (inhalation, oral or skin) and the classification into systemic, immunological, neurological, reproductive and developmental distorting effects or carcinogenicity after acute (one day), sub-chronic (10 to 100 days) and chronic (100 days and above) exposure periods. The kidney is the organ where nickel accumulates, but bronchiolitis, alveolar congestion, alveolar cell hyperplasia, and luminal congestion do occur[88].

2.7.4 Chromium

Chromium is a hard, steel-grey metal that is highly resistant to oxidation, even at high temperatures. It does not occur naturally in the form of elements. It is obtained as a primary mineral product in the form of the mineral chromite $Fe[Cr_2O_4]$. The main sources of chromium contamination include emissions from the electroplating process and the disposal of waste containing chromium[89].

Environmental sources of chromium include airborne transfers from chemical plants and incinerators, cement dust, contaminated landfills, sewage from chemical plants, erosion of asbestos coatings, erosion of catalytic converters and asbestos brake pavement dust, tobacco smoke, and topsoil and rocks. Occupational sources include chrome alloy manufacturing, chrome plating, antifreeze, cement, etc. Chromium is used in all three basic industries: metallurgy, chemical, and refractory materials (heat resistant applications). These industries are the most important industrial sources of chromium in the atmosphere[90].

Reports revealed that when chromium compounds are inhaled, they can irritate the respiratory tract, causing respiratory tract irritation, airway obstruction, and lung, nasal, or sinus cancer. The dose, length of exposure, and the specific compound involved can determine the harmful health effects of chromium. Chromium skin contact has been shown to cause allergic and irritant contact dermatitis[91]. Chromium (Cr) compounds are very toxic to plants. It affects the physiological processes involved in seed germination[92]. The ability of a seed to germinate in chromium-containing media depends on its level of tolerance to this metal[93].

Chromium can be transported to surface water in its soluble or precipitated form through surface runoff. The soluble and unabsorbed chromium complex can be leached from the soil into the groundwater. The mobility of chromium depends on the adsorption characteristics of the soil, including clay content, mineral oxide content (at pH less than 5) and the solubility is low when the pH is higher than 5, due to the formation of $Cr(OH)_3$. Generally, the leaching of Cr increases with the increase of soil pH. However, most of the Cr released into natural water is related to particles and eventually deposited in sediments[89].

2.7.5 Cobalt

Cobalt contents on the earth's surface vary considerably. This element does not exist in its free form except in meteorites. Cobalt is most often present in the form of arsenide and sulfide. The most important cobalt minerals are cobaltate CoAsS, linnaet Co_3S_4 smaltyn $CoAs_2$ and karrolit $CuCo_2S_4$. The source of cobalt contamination (except industrial waste) is the combustion of cobalt-containing substance. Cobalt can appear at an oxidation level of -1 to +4, but in nature, it generally appears as the divalent cation Co^{2+} (cobalt compound)[94].

Cobalt has beneficial and harmful effects on human health. It is beneficial for humans because it is part of vitamin B12 and is essential for maintaining human health. It is also used to treat anemia and increase the production of red blood cells in healthy people, but only at very high exposure levels. However, adverse health effects can occur at very high concentrations. Serious effects on the lungs have been reported, including asthma, pneumonia and wheezing, which in some cases can lead to death. Exposure to radioactive cobalt can be very dangerous to health. It causes a decrease in the number of white blood cells, which reduces resistance to infections. Other effects could be changes in the genetic material of cells, which can lead to the development of certain types of cancer. Although cobalt is essential for life, a small amount is enough[95].

2.8 Automobile workshops and their contribution to environmental pollution

A considerable amount of heavy metals such as lead, zinc, copper, chromium, nickel and cadmium, are present in automobile waste. These enter the soil due to engine wear. Compared to new oil, used oil contains a high proportion of other aromatic and aliphatic hydrocarbons, nitrogen, sulfur compounds and other metals[96]. Heavy metals, such as cadmium (Cd), chromium (Cr), copper (Cu), manganese (Mn), lead (Pb), zinc (Zn), and nickel (Ni) are often included as additives in some oils and gasoline. Some of them have been classified as priority pollutants by the US Environmental Protection Agency Currently, there are few technologies available to treat these mixed wastes, such as soil cleaning and bioremediation[95].

Automobile waste also includes used oils (oil used for cleaning engine parts during maintenance), scraps of metals, and used batteries. They are treated indiscriminately by artisans, and then pollute the earth and other environmental media. Due to the low solubility of used oil, once discarded, the oil tends to seep into soil and sediments and poses a threat to groundwater [97]. In many sites contaminated by auto-mechanic sites in Nigeria and other developing countries, the coexistence of hydrocarbons and toxic heavy metals poses a great threat to the environment[98].

The World Health Organization (WHO) standard for drinking water, pollution load index (PLI) and contamination factor (Cf) indicate that the soil around the sites for automobile waste has varying degrees of heavy metal pollution, ranging from mild to serious pollution[99]. They concluded that the water surrounding the automobile waste market is unsuitable for domestic use. Used (waste) automobile oil contains oxidation products, sediment, water, and metal particles produced by machine wear, used batteries, oil additives, and organic and inorganic chemicals used in metals. Migration of these materials into the water body poses a threat to groundwater[94].

A study on the role that auto repair shops played on heavy metals in soil and groundwater in the metropolis of Ibadan showed that the daily activities of auto repair shops considerably increased the content of heavy metals in soil in the area and lowered groundwater quality[100].

The degree of soil contamination near the automobile repair workshops in Warri, Delta State, Nigeria was evaluated so as to determine the estimated impact of contamination on soil quality[96]. The results showed that the soil was moderately (5.42) to slightly acidic (6.41). The zinc pollution in the soil is very serious, the lead pollution index is 0.11 and the copper pollution index is 2.57, which suggested moderate pollution. The contamination factor (CF) of all the metals in the soil is greater than 6, which indicates that the level of contamination is very high. The degree of contamination is 163.25, which indicates that the degree of contamination is very high. The value of the pollutant load index obtained for n = 3 (metal) is 5.47, which indicates that the soil has a very strong disturbance. The obtained TPH pollution coefficient ranges from 41.88 to 47.27. The soil is classified as excessively contaminated by petroleum hydrocarbons. At the level of P = .05, there is a significant difference between the control and the contaminated soil. The affected soil may adversely affect the soil quality and terrestrial organisms within and outside the auto-mobile repair shop.

2.9 Pollution Status Evaluation

Various indices, such as the contamination/pollution index (C/P), contamination factor (CF), degree of contamination (DC), pollution load index (PLI) can be used to determine the pollution status of soil and/or sediments[96].

2.9.1 Health Risks Assessment

Heavy metals have gotten a lot of attention due to their toxicity. Heavy metals are also necessary for human survival and Wellness in some cases. However, for these heavy metals (essential or toxic), the health hazard requirements must consider the toxicity of overexposure. Contamination of the environment by heavy metals represents a significant risk to human health, but this is not only explained by its metal content. Health risk assessment is an effective method to quantitatively determine the risks of various pollutants to human health through different routes of exposure. To investigate the health risks caused by pollutants, it is necessary to understand the bioavailability of pollutants in the soil[59].

Risk assessment in environmental science is a model used to determine the estimation and quantification of the adverse health effects of pollutants in various environmental media. It includes four basic steps: hazard identification, exposure assessment, dose response assessment, and risk characterization[96].

The hazard identification step involves identifying the contaminants and their potential effects on human health. This is done by determining the level of trace metals in the water and the soil matrix in the environment. Exposure assessment determines the ways in which humans can be exposed to toxic substances. It can be oral, inhalation or skin contact with the source of the pollutant. It is a function of the daily intake, for a particular route. Various methods have been proposed to estimate the potential risks of heavy metals to human health. Risk can be divided into carcinogenic and non-carcinogenic. The United States Environmental Protection Agency (USEPA) divides the health risk assessment into four steps:

i. Hazard identification,
ii. Dose-response assessment,

iii. Exposure assessment, and

iv. Risk characterization[101,102]

2.10 Primary Exposures

Workers were exposed to many solvents, adhesives, resins, polycyclic aromatic hydrocarbons, and heavy metals when working in automobile workshops. Hazards and risks depend on the type of exposure, time, route of exposure, intensity, and personal susceptibility. The main risks are as follows.

2.10.1 Benzene

Benzene is a component of gasoline and a known carcinogen [103]. Due to its carcinogenicity, its exposure is strictly regulated and monitored around the world. Different studies have indicated that its exposure can damage biomolecules, micronuclei, DNA chain breaks and chromosomal aberrations[104].

2.10.2 Lead

Exposure to lead is a very common feature among auto repair shops. This represents 0.9% of the global health burden and the most affected populations are developing countries. For decades, the health hazards of lead have been recognized globally[95]. Lead poisoning was prevalent in the American automobile industry as early as 1924. Occupational exposure is the main cause of lead poisoning among adults, which have adverse effects on the health of workers and their immediate families. Artisans working in auto industries can also pass on lead content to their families and their environment through their clothes (wears). Automotive workers who are exposed to lead include battery manufacturers and repairers, panel beaters, painters, and radiator repairers. Reports showed that lead poisoning and death due to ingestion and inhalation of petrol are common among auto-mobile repair workers. It was also revealed that auto-mobile repair artisans will also absorb gasoline and use it to wash their hands, which will cause tetraethyl lead to be absorbed through the mucous membranes, and the inorganic lead in the exhaust gas will cause blood levels to rise[105].

2.10.3 Polyaromatic Hydrocarbons (PAHs)

The International Agency for Research on Cancer (IARC) has classified certain PAHs as human carcinogens, especially for workers who continue to inhale the smoke, vapour and mist of used gasoline engine oil. Polycyclic aromatic hydrocarbons (PAH) are Well-known mutagens, teratogens and endocrine disruptors. They are mainly formed during the incomplete combustion of organic materials and are also released during industrial activities[106]. Polyaromatic Hydrocarbons having three or more rings are responsible for 70% carcinogenicity. Other health effects associated with short-term and long-term exposure to crude oil or petroleum include tumors, blood diseases, reproductive problems, slowed growth, morphological problems, and nephrotoxicity[107].

2.11 Occupational Health Hazards

While working in various workshops, auto mechanic workers will encounter a variety of occupational health risks, which vary depending on the type of work they perform. Some conventional hazards are accidental, physical, chemical, biological, and ergonomic. Detailed information is as follows.

2.11.1 Accident Hazards

These include risk of falling, danger of injury, crushed toes, eye injury, electric shock, musculoskeletal disease, burns, acute musculoskeletal injury, burns, brazing, brazing operations and brazing. Other accidental hazards include carbon monoxide poisoning, fires and explosions, cuts, abrasions, punctures, tire breaks, and steam-powered pressure washer accidents[108].

2.11.2 Physical Hazards

Different examples of physical hazards in auto mechanic workshops include exposure to infrared, ultraviolet, microwave and radio frequency radiation. Continued use of power hand tools can cause arm vibration and, if used continuously, can cause white finger syndrome. Exposure to excessive noise and exposure to excessive heat or cold are also examples of physical hazards[108].

2.11.3 Chemical Hazards

Contact with lubricants, brake fluids, used gasoline; degreasers, adhesives, asbestos, detergents, paints, solvents, antifreezes and epoxy resins can cause serious health hazards for workers. Exposure to asbestos during brake drum cleaning and body spray can cause asbestos is and mesothelioma. Exposure to benzene, toluene, ethylene, and xylene (BTEX) has been reported to cause hematological changes. Inhalation of diesel exhaust gases, nitrogen oxides and inhalable particulates, and ingestion of adhesives can increase the risk of brain injury, acute irritation of the eyes and mucous membranes, headache, dyspnea, and chest tightness[109].

2.11.4 Biological Hazards

These are also called biohazards. Biological materials that pose a threat to humans refer to biological materials that pose a threat to living organisms, primarily human health. These are the dangers that living organisms cause during work in the workshop. Commonly used adhesives can promote the growth and contamination of microorganisms and these microorganisms can cause infection among workers who come in contact with the adhesive[109].

2.11.5 Ergonomic

An ergonomic hazard is a physical factor that can cause harm to workers on the job. The main factors related to the work environment are repetitive motion, lifting and carrying heavy objects, improper body posture, height of the work station, task design, and manual handling. The result is an acute musculoskeletal injury, namely, hernia, spinal pressure, strain and pain, disc rupture, and tendon rupture and many more[108].

2.11.6 Socio-psychological and Organizational Factors

Auto repair shop workers face psychosocial risks, such as stress caused by working long hours under time pressure, carpal tunnel, and traumatic injuries caused by repeated work schedules. When performing repairs and maintenance tasks, their main role is to use their senses, experience and electronic instruments to investigate problems immediately and quickly. Their work could be to fix or repair single or multiple interconnected parts. The auto mobile workers are known to suck oils using a tube through the mouth, which can easily expose them to dangers. They also come into contact with fuel when cleaning different parts of the vehicle. Exposure to automotive gasoline most likely occur while inhaling its vapours at workshops by smelling, washing, degreasing mechanical engine repair works while fixing of atomizer and diesel oil pump, pistons rings etc[110].

2.12 Analytical Procedures for Heavy Metal Analysis

Heavy metals pose a major threat to living organisms and natural ecosystems, even if the content in the environment is low. As a powerful tracer for monitoring the impact of human activities, efficient and accurate detection of heavy metals hidden in the environment is a necessary prerequisite for pollution assessment and prevention. In recent decades, heavy metal detection technology has also shown a trend of automation, intelligence, completeness, accuracy and rapid detection. The most widely used detection methods include:

i. Inductively Coupled Plasma Mass Spectrometry/Atomic Emission Spectrometry (ICP-MS/AES)
ii. Atomic Absorption Spectroscopy (AAS)
iii. Atomic Fluorescence Spectrophotometry (AFS)
iv. Laser-induced breakdown spectrometry (LIBS), etc[111].

2.12.1 Inductively Coupled Plasma Mass Spectrometry/Atomic or Optical Emission Spectrometer (ICP-MS/AES/OES)

In optical emission spectrometry (OES) the sample is exposed to a of high-energy source, such as inductively coupled plasma (ICP). At temperatures of 5000 to 10000 K, elements emit light of a spectrum being characteristic for each element. This emitted light is collected by photomultipliers or LEDs. Since the intensity of the emitted light is directly proportional to the concentration of the element in the sample, it can be quantified by calibration. Modern ICP-OES instruments may analyze up to 70 elements in one step. Since Inductively coupled plasma–optical emission spectrometry (ICP-OES) is a multi-element method, it is ideal for scanning liquid samples in order to obtain general information about the inorganic composition of the sample under study. The sample requirement is higher than for GFAAS (1–2 mL). The detection limits for ICP-OES are higher than those obtained by GFAAS and other atomic absorption spectroscopic techniques. The time per sample required using ICP-OES is much lower than for GFAA.

Another analytical method uses the radiation of an ICP source: by exposing a sample to the high temperatures of the plasmas, not only light is emitted but ions are also formed. These can be analyzed by a mass spectrometer (MS). Mass spectrometry can be used for the quantification of atoms or molecules by using differences in the mass-to-charge ratio (m/z) of ionized atoms or molecules to separate each other. Almost all elements of the periodic table can be analyzed in one analysis step with very low detection limits by using ICP-MS. The ICPMS has the following features:

i. High sensitivity analysis
ii. Lower detection limits for most elements (ppt or ppb range)

iii. Simultaneous analysis of multiple elements

iv. Wide dynamic range

v. Isotope composition.

The disadvantage of ICPMS is the high operating cost because it uses a large amount of argon gas and is very sensitive to the high concentration of salt present in the digestion solution or in the sweat and saliva extraction solution, which causes interference in the measurement. Therefore, ICPMS is mainly used for wastewater analysis. The determination of isotopes and their percentages in natural fibers provides information on their origin[112].

Inductively coupled plasma mass spectrometry can be considered one of the leading technologies in the field of elemental analysis, focusing on the determination of ultra-trace metals and metalloids in various types of samples. The specific working principle is as follows: first, the sample is pretreated. The non-aqueous phase is prepared in the form of an aqueous solution through acidification or microwave digestion. After the aqueous solution sample is atomized into an aerosol, the aerosol enters the ICP with the inert gas, and evaporates, atomizes, and ionizes under the action of the high-temperature plasma. The ionized elements enter into the vacuum mass spectrometer and pass the quality screening. The separator completes the separation of element ions. Inductively coupled plasma mass spectrometry has the advantages of high sensitivity, wide linear range, strong anti-interference, good reproducibility, low limit of detection (LOD), etc. Lagerström et al. proposed an automatic online extraction and flow injection ICPMS method for the simultaneous determination of Mn, Fe, Co, Ni, Cu, and Zn in high sea water samples. However, ICPMS usually cannot directly determine trace metal ions in environmental samples. The matrix interference and low concentration of metal ions in the sample make the direct determination of ICPMS very difficult. In order to improve the sensitivity of trace metal determination, pre-concentration and separation are necessary[113]. The various extraction methods commonly used include solid-phase micro-extraction, solid-phase extraction, dispersion liquid-liquid micro-extraction for the separation and pre-concentration of trace heavy metals in environmental samples[111]. $Fe_3O_4.SiO_2$ composite was prepared[114] and developed a novel method of magnetic solid-phase extraction-ICP-MS, which has been successfully applied to the determination of trace rare earth elements in different samples. In addition, the combination of ICPMS and other technologies will make up for the deficiencies of ICPMS in the analysis of some materials, and will become a research hotspot in the field of analysis. The online analysis technology of laser ablation (LA) and ICP-MS has the advantages of simple sample preparation, no need for sample digestion and less pollution, and can be used to analyze solid samples. Using Laser Ablation ICP Time of Flight Mass Spectrometry (LA-ICP-TOF-MS) solid samples can be analyzed. Figure 2.1 shows a simple schematic of an LA-ICP-MS system; the interaction between laser pulses and solid materials is a complicated process. At present, technologies that can be combined with ICP-MS also include high-performance liquid chromatography (HPLC), gas chromatography (GC), ion chromatography (IC), hydride generation (HG), isotope dilution (ID), capillary electrophoresis (CE), AFS, AAS, etc. ICP-AES is the primary method for multi-element determination of major, minor, and trace elements. With the development of science and technology, the ICPAES spectrometer has made significant progress in sensitivity, analysis efficiency, automation, and speed of analysis. Both ICPAES and ICPMS instruments are equipped with nebulizers and spray chambers to introduce samples into the plasma. ICP AES has been widely used to detect heavy metal elements in soil[115].

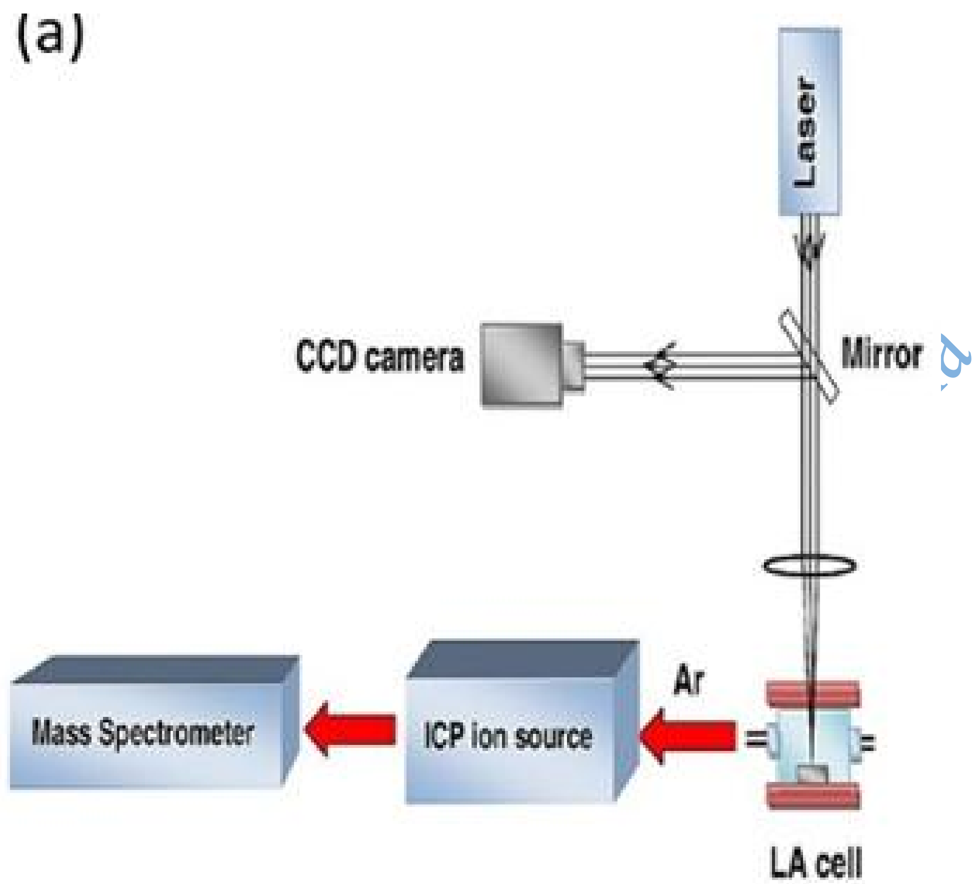

Figure 2.1 Schematic diagram of Inductively Coupled Plasma Mass Spectrometre (ICP-MS)

2.12.2 Atomic Absorption Spectrometry (AAS)

This technique was first used in the 1950s, as an instrumental analysis method for qualitative and quantitative analysis of elements, which to be measured according to the essential characteristics of characteristic spectral lines and different spectral line attenuation degrees[112].

AAS involves the atomization and determination by flame sources to form free atoms which can absorb radiation at discrete wavelengths. Each wavelength corresponds to a single element and the width of an absorption line, measured in picometers (pm) to give the technique its elemental selectivity. The amount of energy absorbed is proportional to the concentration of determinants in the sample when the Beer-Lambert Law is applied. Atomic absorption spectrometry (AAS) is mostly used to determine trace and ultra-trace elements in different samples. In this technique, a beam of light passes through the sample, and depending on the concentration of the element, a certain amount of light is absorbed. The concentration of the element can be calculated by comparing the intensity of the original beam of light before and after passing through the sample. Since each element absorbs light of different wavelength, the AAS instruments have a varying source of light for each element. Commonly, AAS is a technique for the determination of only one single element per analysis. The advantage is that this analytical technique permits the determination of elements in very low mass concentrations (measured in mg L^{-1})[115]. Depending on the expected mass concentration range and the amount of sample available, the analysis can be carried out by flame AAS (FAAS) or Graphite AAS (GFAAS). First, a little milliliter sample capacity (ML) is required, and only a small number of samples (10-30 ml) are required for the latter. Therefore, GFAAS allows a much lower detection limit than FAAS. In addition, GFAAS can concentrate the analyte by pipetting into the sample in the graphite tube. When changing the speed of the autosampler device, it is possible to minimize the effects of physical interference with a greater viscosity of solutions, such as saliva and sweat solution. In order to avoid chemical inferences, chemical modifiers may be applied[112].

AAS is composed mainly of five parts, which include sharp line light source, atomization system, spectroscopic system, power supply synchronization system, and detection system. A sharp line light source is a resonant line that emits the element to be measured. The main function of the atomization system is to provide energy to produce atomization, evaporation, drying, atomization and generate the basic atomic vapour. The spectroscopic system can separate the resonant lines of measured elements from adjacent spectral lines. The energy synchronization modulation system converts an optical signal into an electrical signal and shows the absorbance. The detection system eliminates the interference of the background emissions and is used to improve the signal-to-noise ratio, and prolong lamp life. According to reports, atomization systems, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF-AAS), and hydride generation atomic absorption spectrometry (HG-AAS) have distinct characteristics. FAAS can analyze more than 30 elements, and the detection limit (LOD) can reach μg cm^{-3} having a relative error of less than 1%.

GF-AAS can analyze more than 70 elements and provide energy by electricity, which is more sensitive than FAAS. In a report, different acid combinations to evaluate six methods of digestion of GFAA and recommend the most appropriate digestion method to determine five heavy metals in tea samples[116]. HG-AAS is suitable for determining As, Sb, Bi, Ge, Sn, Pb, Se, Te, and other elements. The automatic management of the analysis processes can be achieved, and there is an excellent effect on the monitoring of the contamination of the trace elements[117]. Currently, AAS has several advantages in the determination of factors, such as solid selectivity, high precision, the extensive scope of analysis and strong anti-interference capabilities. It is not only used to determine trace, trace, and even ultra-trace elements but also for its stable spectral line. However, AAS has the disadvantage of changing the lamp from the light source when the element is determined and the multiple elements cannot be analyzed simultaneously. In this stage, the use of AAS for environmental monitoring of the soil must be an essential part of ecological and environmental protection[111]. Kashem et al.[118] used AAS to determine the content of heavy metals in soil, which has a more extensive measurement range than that of ultraviolet spectrophotometer, and its accuracy reaches mmol L^{-1}.

2.12.3 Atomic Fluorescence Spectrometry (AFS)

Atomic fluorescence spectroscopy is a fast-developing analytical technique for the detection of heavy metals. It is based on the excitation of atoms of the element to be tested in the vapour state by radiation at a certain wavelength, to produce atomic fluorescence. The intensity of atomic fluorescence is directly proportional to the concentration. According to the fluorescence intensity the elements in the soil can be effectively determined. AFS can be divided into two types: dispersive and non-dispersive. AFS is similar to AAS, but the light source and other components are not in a straight line, but at right angle of 90° to avoid the influence of the radiation emitted by the excitation light source on the fluorescent detection signal atoms. It has the advantages of both atomic emission and atomic absorption[119]. However, its disadvantages are that its application scope is not wide enough, and only 11 elements are used, such as As, Hg, and Se. Therefore, the promotion and application of AFS in heavy metal detection research is still a hot research topic for analysts. The earliest application of AFS is the determination of trace elements in soil, coal, rocks, river sediments and various minerals. With the further development of this technology, researchers have conducted more in-depth research on AFS. At present, the applicable fields include agriculture, food, medicine, hygiene and epidemic prevention, environment and many more. Tao et al.[120] designed a UV digital micromirror spectrometer (Figure 2.2), which uses digital micromirror devices as spatial light modulators, gratings as spectroscopes, and photomultiplier tubes as detectors for dispersive atomic fluorescence spectrometry. Mao et al.[121] used a new dielectric barrier discharge reactor (DBDR) to capture/release As and coupled with Hg-AFS for detection. An analytical method for ultra-trace arsenic in real samples was established, with the limit of detection as low as 1.0 ng L^{-1}. In order to adapt to the situation of heavy metal monitoring in the environment and to effectively give play to the characteristics of AFS. An atomic fluorescence heavy metal monitoring instrument suitable for online monitoring requirements researched and designed and was applied to the online analysis of environmental water samples, with satisfactory results, providing a more reliable and practical means for online monitoring of heavy metals[122].

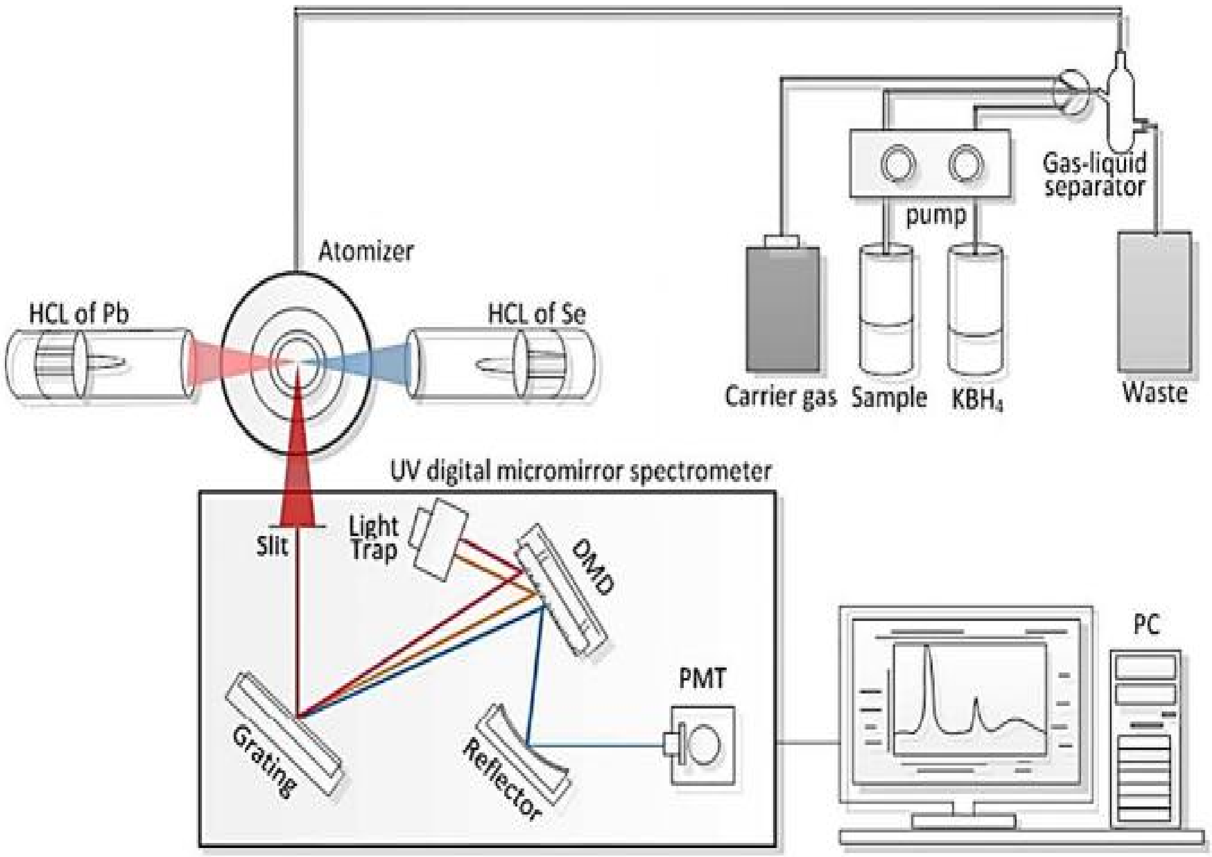

Figure 2.2: Experimental setup of UV digital micrometre spectrometer for dispersive Atomic Fluorescence Spectrometer (AFS).

2.12.4 Laser-Induced Breakdown Spectrometry (LIBS)

LIBS is a fast, universal, and non-contact atomic spectroscopy technology, which can provide qualitative and quantitative analysis information for almost any sample in an almost non-destructive manner without any substantial sample preparation[111]. It is a powerful analysis technology in the field of environmental quality control. It shows excellent results in detecting heavy metals in the atmosphere, water and soil. Its technology has been used to measure harmful aerosols since 1980. However, compared to the analysis of solids or gases, LIBS directly analyzes the liquids with the worst detection limit and lower precision. This is because laser-induced plasma generated in the middle of a large amount of liquid has a tendency to explode[123]. Its experimental device is shown in Figure 2.3 below. LIBS can also be used for non-contact optical field detection in harsh environment[124]. This technology uses a laser to emit a high-energy laser, which is focused directly on the surface of the sample through a focusing lens, and induces the sample to generate transient plasma. The content and composition of the elements in the sample can be obtained by analyzing the intensity of distribution of the plasma and the wavelength of the emission spectrum. Compared to mature spectral analysis methods such as AAS and ICPMS, LIBS needs to be improved in terms of detection precision and sensitivity. After decades of development, LIBS instrument technology continues to improve, and then some technologies such as nanosecond LIBS, femtosecond LIBS, polarization resolution LIBS, double-pulse LIBS, multi-pulse LIBS have appeared[125]. Although some types of samples can achieve excellent LIBS results without any sample processing, the application of LIBS has been expanded through the use of sample preparation techniques and its analytical performance is comparable to that of XRF, ICPOES, and ICPMS.

LIBS has two detection techniques: one is to focus the laser on the enrichment filter, which can detect the lowest concentration of substances in the aerosol; the other is to use the laser directly Focusing on the aerosol for detection, it has a higher detection limit than the former.[126]. Järvinen et al.[127] uses LIBS technology to detect trace metal elements Ni, Pb, Zn in water. This technology can use high-sensitivity instruments for online monitoring of industrial wastewater. The liquid to solid conversion and sample concentration can be used to increase the detection limit. In recent years, researchers have done a lot of comparative studies on the measurement of heavy metals in soil by different LIBS techniques. Barbafieri[128] developed a LIBS detector, which was used to identify the Pb content of three contaminated lands in the field, and compared the calibration results with the results of the AAS method. The determination coefficient of the two is greater than 0.71. Some scholars also use the existing LIBS technology combined with other methods and technologies to improve the detection accuracy of elements and the detection limits of LIBS instruments.

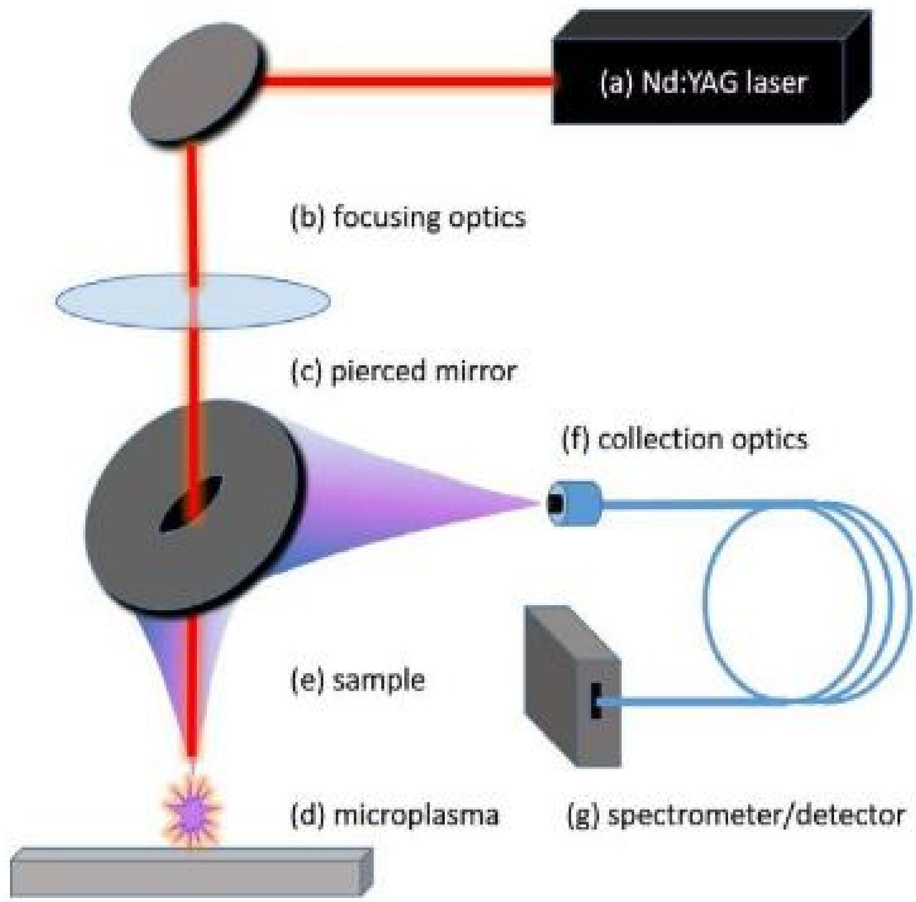

Figure 2.3: Schematic diagram of Laser-Induced Breakdown Spectrometer (LIBS) experimental setup

2.13 Comparison of Common Heavy Metal Detection Methods

The appropriate selection of heavy metal detection methods is the key to find out the heavy metal contamination. The advantages and disadvantages of ICP-MS/AES, AAS, AFS, and LIBS are summarized, as shown in Table 2.2.

In general, ICP-AES and ICP-MS are ideal analytical methods and are routine analytical methods that must be set up in laboratories. Both methods have better detection limits, wide linear ranges and can be used for the simultaneous determination of multiple elements[125]. However, the spectral interference of ICP-MS is smaller than that of ICP-OES, and isotopes can also be analyzed. If the laboratory chooses ICP-AES instead of ICP-MS, the laboratory should be equipped with AAS. This configuration can meet the needs of general laboratories for primary, secondary, and trace component analyses. However, it needs to rely on large and expensive instruments [127]and equipment, which is only suitable for laboratory testing, complicated to operate, and the reagents used are easy to cause environmental pollution.

The introduction of LIBS can realize fast detection and real-time monitoring. However, further improvements are needed to reduce interference, improve spectrum stability, precision and sensitivity, and adapt to detection under various conditions. According to the concentration of the element to be tested in the test solution, if one to three elements are measured in each sample, and the concentration of the element is less than the ppb level, and it can meet the requirements of the element to be tested, AAS is the most suitable. If there are five to twenty elements in each sample and the content is sub-ppm to %, ICPAES is the most suitable. If each sample needs to measure more than 4 elements of sub-ppb and ppb, and the number of samples is quite large, ICPMS is more suitable[127].

AFS has advantages in detecting specific elements. However, due to its obvious fluorescence quenching effect and weak anti-stray light interference ability, its application range is not wide enough. These methods have their own advantages and disadvantages. Traditional laboratory methods can be combined with technology to achieve complementary advantages. If a suitable detection method is choosing based on the actual needs, the best detection results can be achieved[111].

Table 2.2: Comparison of heavy metals analytical testing technologies

	ICP-MS	ICP-OES	AAS	AFS	LIBS
Detection limits	$10^{-15} – 10^{12}$	10^{9}	$10^{-12} – 10^{-9}$	10^{9}	$10^{-12} – 10^{-6}$
Detection sensitivity	Maximum	Low	High	High	Low
Analyzable elements	>80	>70	>30/70	>11	>70
Linear range	8 – 9	4 – 6	2 – 3	3 -5	2 -5
Relative standard deviation (%)	0.5 -3	4-6	2 – 3	3 – 5	2 – 5
Isotope analysis	Yes	No	Yes	No	No
Simultaneous analysis of elements	Multiple	Multiple	Single	Multiple	Multiple
Time of analysis	All elements (2 – 6 minutes/sample)	5–30 elements per minutes per sample	3–4 minutes per sample	6-10 minutes/sample	Several seconds/sample
Running costs	High	Upper middle	Medium	Medium	Low

Table 2.3: Comparison of Heavy Metals Analytical Testing Technologies (cont'd)

Method	Advantages	Disadvantages
ICP-MS	Less spectral interference than ICP-OES; Wide linear range; Better detection limit; High sensitivity; It can be used for simultaneous analysis of multiple elements and determination of isotopes	High cost; Samples generally must be converted into solution; Limits of detection can actually be as much as 50 times worse due to poor salt tolerance; Some light elements (such as S, Ca, Fe, K, Se) have serious interference in ICP-MS
ICP-OES	Simultaneous multi- element analysis; It is the most mature in terms of automation Low relative standard deviation	Higher equipment operating costs; Samples generally need to be pre-converted to solution; General-purpose pneumatic nebulizer has low nebulization efficiency; Large argon consumption of working gas.
AAS	Good selectivity; Strong anti-interference ability; Fast and and convenient operation; Wide range of analysis	Analysis of multiple elements requires changing lamp sources; Inability to detect elements whose resonance lines are in the vacuum UV region; Narrow range of standard curves; Interference problems arising from the complexity of some sample matrices are not easy to solve
AFS	It has simple emission line; Higher sensitivity is than AAS; Low interference	Significant fluorescence burst effect; Weak resistance to scattered light interference
LIBS	Can be applied directly to any sample phase; Minimal sample preparation is needed; Does not damage the sample; Real-time detection; Fast and easy to operate; Low cost	Unstable spectrum; High limit of detection; Insufficient precision; Large matrix effect; Laser scattering easily interferences with the detection of samples

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Chapter Three

Methodology

3.1 Description of Study Area

Twenty (20) auto-mechanic workshops were selected randomly across two local government areas in Ibadan (Ibadan North Local Government (IBN) and Ibadan North-East Local Government (IBNE)), Oyo State (Figure 3.1). Ibadan North Local Government Area (LGA) covers a large expanse of land with an area of about 420 km^2. It is heavily populated with an estimated population of 856,986 People. Ibadan North is located between latitude 7º 38'N to 7° 44´ N and longitude 3º 88' E and 3° 95´E. The climate of these areas is characterized by a dry season (mostly, November to March) and a rainy season (April to October), with strong winds and occasional storms. Its maximum and minimum temperatures are 26.46 ºC and 21.42 ºC, respectively, and the relative humidity is 74.55%, while its average annual rainfall is 1420.06 mm[1].

Ibadan North-East Local Government Area, of Oyo State, is geographically located within latitude 7º36'28" N and 7º39'4"N and longitude 3º93'69" E and 3º94'7"E, with an area of approximately 17.88 km^2 and has an average temperature of 28 ºC. The average humidity level of the area is 61 % while the total annual precipitation of the LGA is 2100 mm of rainfall. It has a small land area, but it is one of the most populous local governments in Ibadan. The 2006 National Census (NPC, 2007) has a total population of 330,399 people in the local government area of Northeast Ibadan. It is a commercial centre characterized by various economic activities such as markets, transportation systems and some industrial services[2].

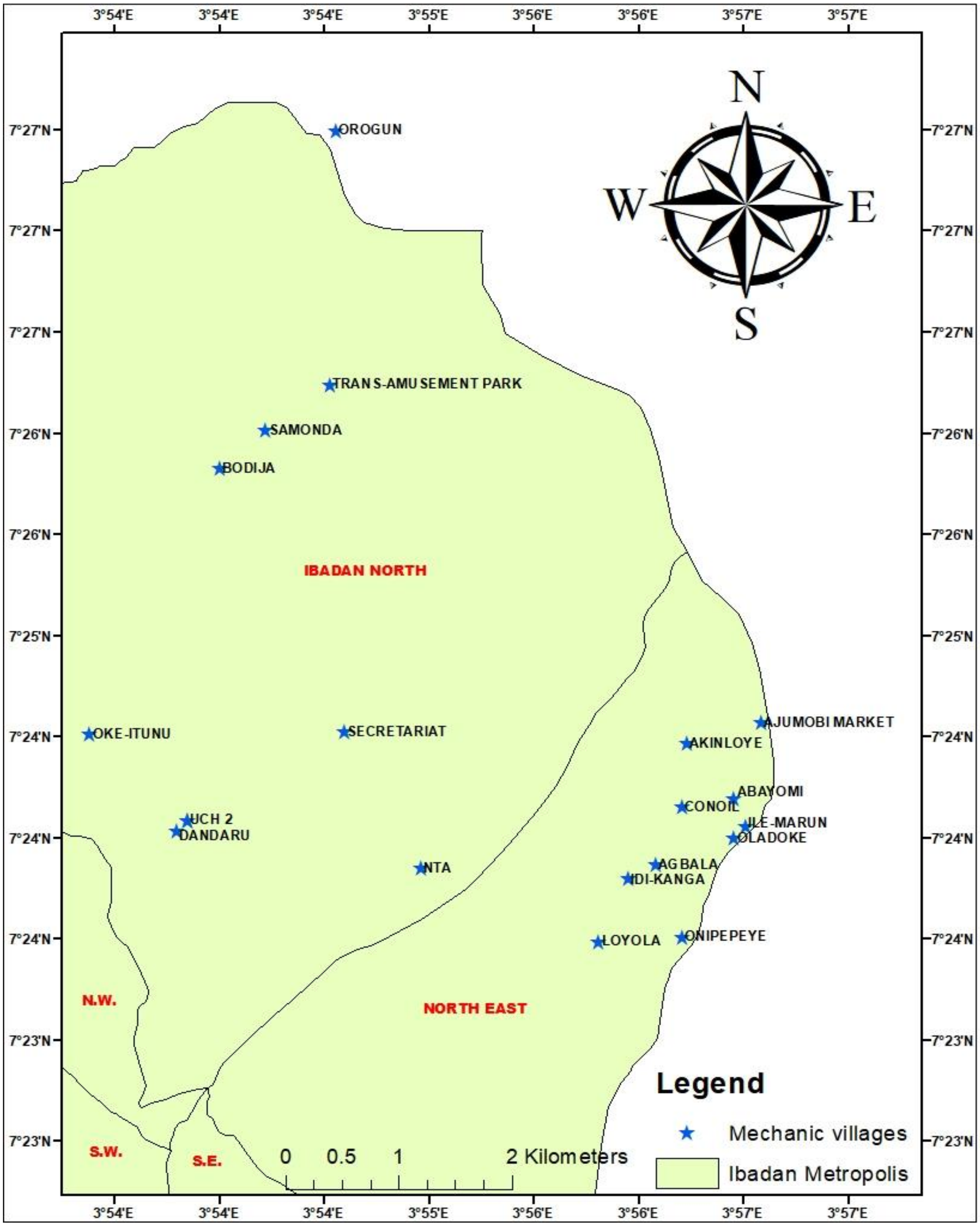

Figure 3.1: Map of Study Area showing Sampling Points

3.2 Sampling and Sample Preparation

Twenty auto-mechanic workshops were investigated using a Simple Random Sampling method based on the following criteria: Number of years of operation (≥ 5years), Absence of other industries within the locations, Availability of groundwater and Nature of activities carried out within the workshops. Samples (soil and water) were collected in triplicate from different locations (Table 3.1 and Table 3.2) within Ibadan North Local Government and Ibadan North-East Local Government Areas of Oyo State (Figure 3.1). A residential area (Sagbe-Extension) where industries and mechanic activities were absent served as control.

3.2.1 Soil Sampling

Grab samples of soil were obtained in triplicates at each site at different depths of 0-15; 15-30; 30-45; and 45-60 cm, using a depth calibrated soil auger and then composited. The samples were immediately placed in a fresh plastic bag and tightly sealed. All the samples were transported to the laboratory for preparation and analysis

3.2.2 Soil Samples Preparation

The soil samples were placed on a flat surface and air-dried at room temperature in the laboratory. After drying, the samples were pulverized using a pestle and mortar to break the large lumps and to homogenize the soil particles and then sieved using a 2 mm sieve.

3.2.3 Water Sampling

Water samples were obtained from hand-dug Wells from each selected site following the standard water sampling procedure[3]. Each sample was directly collected into a pre-washed 1 L plastic bottle, with the cap securely tightened. Water (Well) and control samples were collected in triplicates from each Well. After collection, the samples were acidified with 5 mL concentrated nitric acid on site and transported to the laboratory and preserved in the refrigerator. The laboratory analysis commenced the same day.

Table 3.1: Sampling sites in Ibadan North Local Government Area

Locations	Latitude	Longitude
Secretariat	N7º 24’31.334”	E3º 54’35.722”
Bodija	N7º 25’49.57”	E3º 53’59.999”
Samonda	N7º 26’0.791”	E3º 54’13.175”
Trans Amusement Park	N7º 26’14.399”	E3º 54’31.543”
Orogun	N7° 27'29.743"	E3°54'33.236"
NTA	N7° 23' 51.0036"	E3° 54' 57.5526"
Oke-Itunu	N7° 24' 30.7974"	E3° 53' 22.812"
UCH1	N7° 24' 2.8512"	E3° 53' 56.1114"
UCH2	N7° 24' 5.1876"	E3° 53' 50.7192"
Dandaru	N7° 24' 2.0442"	E3° 53' 47.6088"

Table 3.2: Sampling sites in Ibadan North-East Local Government Area

Locations	Latitude	Longitude
Loyola	N7° 23' 29.1588"	E3° 55' 48.4386"
Ajumobi market	N7° 24' 34.0632"	E3° 56' 34.8252"
Akinloye	N7° 24' 28.047"	E3° 56' 13.5774"
Conoil	N7° 24' 9.0108"	E3° 56' 12.246"
Agbala	N7° 23' 51.8748"	E3° 56' 4.8012"
Idi-Kanga	N7° 23' 47.9652"	E3° 55' 56.7906"
Ile-Marun	N7° 24' 3.2106"	E3° 56' 30.4974"
Abayomi	N7° 24' 11.4768"	E3° 56' 27.2682"
Oladoke	N7° 23' 59.7408"	E3° 56' 27.2466"
Onipepeye	N7° 23' 30.5262"	E3° 56' 12.4254"

3.3 Soil Analysis

3.3.1 Digestion and Elemental Analysis of Soil Samples

The soil samples were digested using aqua regia, a mixture of hydrochloric acid (HCl) and nitric acid (HNO_3) in ratios of 3:1 respectively. Soil samples (1 g) were weighed into Well-labelled crucibles and 15 ml of aqua regia was added to each crucible and heated to near dryness, then 10 ml of distilled water was added and heated till it boils. The extract was then allowed to cool, filtered and make up to mark with distilled water in a 25 mL volumetric flask.

Blank samples were also prepared by subjecting distilled water into the same processes as the water samples.

3.4 Water Analysis

The pH of the water sample was done immediately with a calibrated Jenway Model 3510 pH/mV/Temperature Meter.

3.4.1 Physico-chemical Analysis

Physicochemical analyses were performed using standard international procedures. The parameters determined include pH, total dissolved solids, electrical conductivity and total hardness.

3.4.1.1 pH

The pH values of the Well samples and control sample were determined using a portable pH meter (Jenway Model 3510). The water sample was vigorously stirred using a clean glass stirring rod and 50 ml of each sample was poured into a glass beaker using the watch glass as a cover. The sample was allowed to stand (for temperature stabilization). Stirring was occasionally done while waiting. The pH meter was standardized using standard solutions (pH 4, 7, and 9). The pH meter electrode was immersed into the water sample and allowed to stabilize in the sample before the reading was made. After each reading, the electrode was well rinsed with distilled water and then dabbed lightly with tissues to remove any film formed on the electrode[4]. The procedure was repeated for other samples and their respective pH values were recorded in triplicates.

3.4.1.2 Total Dissolved Solids (TDS)

The Total Dissolved Solids (TDS) of Well water and control samples were determined using the standard gravimetric method by USEPA. A cleaned beaker was oven-dried at a temperature of 105℃, then transferred to a desiccator and allowed to cool to room temperature. The beaker was then weighed to a constant weight. Fifty millimeters (50 mL) of a Well-mixed water sample was filtered into the weighed beaker, heated, and evaporated at a temperature of 105 ℃ to dryness on a steam bath. The dried sample was cooled in a desiccator and weighed. Drying and weighing between the weight of the empty beaker and the beaker with its contents is the weight of the dry residue[5]. The Total Dissolved Solids in mg L^{-1} was computed as follows:

$$\text{TDS (mg L}^{-1}) = \frac{\text{wt. of dry residue (mg)}}{\text{Vol. of sample (mL)}} \times 1000 \text{ -------------------------- (1)}$$

3.4.1.3 Electrical Conductivity

The electrical conductivity was measured by dipping the electrode of the portable meter (Jenway Model 3510) into each water sample. The corresponding readings were taken after stabilization and the probe of the conductivity meter was rinsed with deionized water after each reading. The conductivity meter was calibrated using a 0.01 M KCl solution and measurement was done in triplicate.

3.4.1.4 Total Hardness

A Well-mixed water sample of 50 mL was put into a conical flask using a pipette, to which 1ml of ammonia /ammonium chloride buffer of pH 10 and 2-3 drops of Eriochrome Black -T indicator were added. The mixture was titrated against standard 0.01M EDTA until the wine red colour of the solution turned pale blue as the endpoint.

Total hardness (mg/L) = (T) (1000) / V

Where, T = Volume of titrant

V = Volume of sample

3.4.2 Digestion and Elemental Analysis of Water Samples

The heavy metals concentrations of the water samples were determined by digesting 50 mL of water sample with a mixture of hydrochloric acid (HCl) and nitric acid (HNO_3) in a ratio 3:1 respectively. The digest was filtered into a 25 mL standard flask, made up to the mark with deionized water, and stored in a nitric acid pre-washed polyethylene bottle in the refrigerator before chemical analysis. The water extracts were analyzed for metals (Cu, Cr, Ni, Cd, Mn, Co, and Pb) by atomic absorption spectrophotometer (Buck Scientific model 210). Triplicate samples were analyzed, and the average of the results taken[3].

3.5 Quality Assurance (QA)/Quality Control (QC)

Quality assurance (QA)/control (QC) protocol prescribed by the U. S Environmental Protection Agency (EPA) for metal analysis was used, which included reagent blanks, and replicate samples. To control the analytical procedure, the precision of the analytical results was estimated by replicate analysis. All laboratory equipment used for analysis was from Pyrex, washed with 0.1 N HNO_3, rinsed twice with distilled water and placed in a clean environment until dry. All plastic containers were washed with double distilled water and then soaked overnight in 1 M HNO_3, and all reagents used were of analytical grade (BDH, Merk).

The method validation for the elemental determination was conducted via recovery experiments. This was done by multi-element spiking.

3.6 Health Risk Assessment

The human health risk assessment of heavy metals in the soil and water of the automobile workshops was examined for non-carcinogenic risks to humans. The methods used for the health risk assessment were based on the guidelines and Exposure Factors Handbook of the US Environmental Protection Agency[6].

The risks associated with oral ingestion of heavy metal at the automobile workshops were calculated as the daily intake of the metal, non-cancer hazard quotient, and total chronic hazard index.

$$\text{Daily intake (DI) (mg/kg/day)} = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (2)$$

C means the heavy metal concentration at the sampling points

IR = Ingestion rate (1L for children, and 2 L for adults)

EF = Exposure frequency (365 days/year)

ED = Exposure period (24 years for adult, 6 years for children)

BW = Body weight (70 kg for adults, 15 kg for children)

AT = Average time for non-carcinogens (ED × 365 days)[7].

The non-carcinogenic and carcinogenic effects of heavy metals were assessed using the hazard quotient (HQ), hazard index (HI) and carcinogenic risk (CR) methods.

The hazard quotient (HQ) is the ratio of the average daily dosage (DI) of heavy metal to its reference dose (RfD) (mg/kg day) for the same exposure pathway.

i.e. $$HQ = \frac{DI}{RfD} \quad (3)$$

RfD is the maximum daily dosage of metal from a certain exposure pathway that is thought not to cause a meaningful risk of adverse consequences to sensitive persons over their life for both children and adults. If the DI is less than the RFD, HQ ≤ 1, it is considered that there will be no adverse health effects, whereas if the DI exceeds the RfD, HQ >1, it is likely that there will be adverse health effects[6].

The hazard index (HI) is the sum of HQ and the means of the total risk of a non-carcinogenic element via different exposure pathways for a single element. If the value of HI<1, no risk of non-carcinogenic effects is believed to occur, whereas HI > 1 indicated a probability of adverse health effects and probability increases with the increase of HI values.

The HI was calculated as follows:

$$HI = \sum HQ_i = \sum \frac{ADI_i}{RfD_i} \quad (4)$$

Table 3.3: Definition and reference value of some parameters for health risk assessment of heavy metals in soil

Factor	Definition	Unit	Value	
			Children	Adults
C_{soil}	Heavy metal concentration in soil	mg/kg	-	-
IngR	Ingestion rate of soil	mg/day	200	100
EF	Exposure frequency	days/year	365	365
ED	Exposure duration	Years	6	24
BW	Bodyweight of the exposed individual	kg	15	70
AT	Average time	Days	365ED	365ED
PEF	Particle emission factor	m^3/kg	1.36×10^9	1.36×10^9
SA	Exposed skin surface area	cm^2	1600	4350
AF	Skin adherence factor	mg/cm day	0.2	0.7
ABF	Dermal absorption factor	No unit	0.001	0.001

Source[8]

Table 3.4: Definition and reference value of some parameters for health risk assessment of heavy metals in water

Parameters	Unit	Adult	Children
Heavy metal concentration (C_W)	$\mu g\ L^{-1}$		
Daily average intake (DI)	L/day	2.2	1.1
Exposure frequency (EF)	Days/year	365	365
Exposure duration (ED)	Year	70	6
Body weight (BW)	Kg	70	15
ABS	All	0.001	0.001
Average time (AT)	Days	25550	2190

Source[9]

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Chapter Four

Results and Discussion of Findings

4.1 Physico-Chemical Analysis of Water Samples

The water samples from the selected auto-mechanic workshops from the two Local Government Areas varied in appearance from colourless to slightly brown and the temperature of the water samples was within acceptable limits for groundwater quality. Table 4.2 summarized the result of the pH, TDS, conductivity and hardness of water samples collected from ten (10) auto-mechanic workshops in Ibadan North Local Government Area in Ibadan, Oyo State. The result showed that the pH of the water samples was within the WHO permissible range of 6.50-9.50 and was in the alkaline region with values ranging from 8.31 ± 0.02 to 8.39 ± 0.02. The pH values from all the sampling sites were higher and significantly different from that of the control (Table 4.1), indicating the impact of the different activities in these auto-mechanical workshops on the quality of water sources. The non-significance difference in the pH values among the ten auto-mechanic workshops in Ibadan North Local Government also corroborated the impact of the activities at these sites. These pH values were also higher than those reported by Oloruntoba and Ogunbunmi[1].

Although the TDS values ranged from 73 ± 1.5 mg L^{-1} to 329 ± 0.6 mg L^{-1} and were within the WHO permissible limits of 500 mg L^{-1} values at Idi kanga and Orogun were higher and significantly different from the control sample[1]. The TDS result showed that 60% of total samples had similar values to those reported by Oloruntoba and Ogunbunmi[1]. Aside from Samonda, Idi kanga, and Orogun, the TDS values for other sampling sites were not significantly different from each other (Table 4.1), suggesting similarity in activities at these auto-mechanic workshops.

Table 4.1: Physico-Chemical parameters of water samples in Ibadan North Local Government Area of Ibadan

Location	pH	TDS	Conductivity	Hardness
Idi kanga	8.36 ± 0.03^{a}	309 ± 1.1^{a}	620 ± 0.6^{a}	299 ± 0.3^{a}
UCH1	8.34 ± 0.02^{a}	163 ± 1.2^{c}	328 ± 0.1^{c}	299 ± 0.2^{a}
NTA	8.31 ± 0.02^{a}	93 ± 0.6^{e}	184 ± 0.6^{g}	298 ± 0.1^{a}
Oke-Itunu	8.37 ± 0.03^{a}	174 ± 0.6^{c}	348 ± 0.1^{c}	299 ± 0.2^{a}
Secretariat	8.29 ± 0.02^{a}	133 ± 1.2^{cd}	268 ± 0.2^{d}	297 ± 0.1^{a}
Orogun	8.33 ± 0.02^{a}	329 ± 0.6^{a}	658 ± 0.2^{a}	299 ± 0.3^{a}
UCH2	8.31 ± 0.02^{a}	118 ± 1.2^{d}	238 ± 0.3^{e}	297 ± 0.3^{a}
Samonda	8.39 ± 0.02^{a}	73 ± 1.5^{f}	148 ± 0.6^{h}	299 ± 0.3^{a}
Bodija	8.35 ± 0.04^{a}	138 ± 1.5^{c}	278 ± 0.2^{d}	300 ± 0.5^{a}
Dandaru	8.32 ± 0.03^{a}	102 ± 2.1^{d}	208 ± 0.3^{f}	298 ± 0.1^{a}
*Control	6.57 ± 0.2^{b}	238 ± 2.0^{b}	471 ± 5.6^{b}	209 ± 2.0^{b}
WHO	6.50-9.50	500	300	-

Values are Mean ± SD, n = 3. Means with the same superscript alphabet(s) along column are not significantly different ($P > 0.05$) Means with different superscript alphabet(s) along the same column are significantly different ($P < 0.05$).

Similarly, the conductivity and water hardness ranged from 148 ± 0.6 to 620 ± 0.6 μS cm^{-1} and 297 ± 0.1 to 300 ± 0.5 mg L^{-1} respectively. The conductivity result showed that 40% of total samples had values greater than the WHO permissible limits of 300 μS cm^{-1} while 20% had values that were significantly greater than the control sample. These conductivity values were higher than those reported by Oloruntoba and Ogunbunmi[1]. Likewise, the Total Hardness values were higher and significantly different from that of the control but similar throughout all the sampling locations.

Similarly, Table 4.2 summarized the result of the pH, TDS, conductivity and hardness of water samples collected from ten (10) auto-mechanic workshops in Ibadan North East Local Government Area in Ibadan, Oyo State. Also, the result showed that the pH of the Well samples from the selected auto-mechanic workshops in Ibadan North East Local Government Area were in the alkaline region and ranged from 8.20 ± 0.08 to 8.40 ± 0.03. Although these pH values were within the WHO permissible range of 6.50 to 9.50, they were all significantly higher and different from the control. This significant difference is probably due to the activities in the selected auto-mechanic workshops. These pH values were also higher than those reported by Oloruntoba and Ogunbunmi[1]. The pH is a significant factor in the mobility of ions such as heavy metals in the environment medium, these ions tend to form insoluble complexes at high pH values. The total dissolved solids (TDS) values ranged from 103 ± 2.6 mg L^{-1} to 393 ± 2.6 mg L^{-1} and were within the WHO permissible limits of 500 mg L^{-1} for domestic use[1].

Table 4.2: Physico-Chemical parameters of water samples in Ibadan North East Local Government Area of Ibadan

Location	pH	TDS	Conductivity	Hardness
Loyola	8.25 ± 0.05^{a}	247 ± 2.6^{c}	509 ± 1.0^{c}	296 ± 0.2^{a}
Ajumobi Mkt	8.40 ± 0.03^{a}	181 ± 1.2^{d}	363 ± 3.6^{d}	300 ± 0.6^{a}
Akinloye	8.38 ± 0.06^{a}	306 ± 2.0^{b}	$609 \pm 8.2a^{b}$	300 ± 0.2^{a}
Conoil	8.33 ± 0.05^{a}	393 ± 2.6^{a}	790 ± 1.0^{a}	299 ± 0.3^{a}
Agbala	8.18 ± 0.15^{a}	247 ± 2.0^{c}	511 ± 3.2^{c}	295 ± 0.4^{a}
Idi-Kanga	8.37 ± 0.04^{a}	122 ± 3.2^{ef}	242 ± 2.1^{f}	299 ± 0.3^{a}
Ile Marun	8.34 ± 0.07^{a}	$152 \pm 1.5d^{e}$	303 ± 2.1^{e}	299 ± 0.5^{a}
Abayomi	8.29 ± 0.05^{a}	258 ± 1.5^{c}	540 ± 1.5^{bc}	298 ± 0.5^{a}
Oladoke	8.20 ± 0.08^{a}	103 ± 2.6^{f}	210 ± 1.5^{g}	295 ± 0.4^{a}
Onipepeye	8.26 ± 0.05^{a}	301 ± 2.1^{b}	602 ± 3.2^{b}	296 ± 0.6^{a}
*Control	6.57 ± 0.2^{b}	238 ± 2.0^{c}	471 ± 5.6^{d}	209 ± 2.0^{b}
WHO	6.50-9.50	500	300	-

Values are Mean ± SD, n = 3. Means with the same superscript alphabet(s) along column are not significantly different ($P > 0.05$) Means with different superscript alphabet(s) along the same column are significantly different ($P < 0.05$).

Consequently, 60% of the Well samples from the selected auto-mechanic workshops in Ibadan North East Local Government Area were higher and significantly different from the control (238 ± 2.0 mg L^{-1}). This result is similar to that obtained from Ibadan North Local Government Area but higher than the values reported by Oloruntoba and Ogunbunmi[1].

The conductivity ranged between 210 ± 1.5 µS cm^{-1} and 790 ± 1.0 µS cm^{-1} while hardness ranged from 295 ± 0.4 to 300 ± 0.6 mg L^{-1}. The conductivity values for 80% of the Well samples were above the WHO permissible limits of 300 µS cm^{-1} while Well samples at Idi-Kanga (242 ± 2.1 µS cm^{-1}) and Oladoke (210 ± 1.5 µS cm^{-1}) were within the WHO permissible limits[2]. This data showed that 80% of the Wells observed were unsafe for domestic use such as drinking. The taste of water could also be affected when conductivity is high[3].

According to 1993 guidelines proposed by WHO for drinking-water quality, no health-based guideline value for total hardness was proposed, although hardness above approximately 200 mg L^{-1} may cause scale deposition in the distribution system[2].

4.2 Elemental Analysis

Water and soil samples from twenty (20) auto-mechanic workshops from Ibadan North and Ibadan North East Local Government Areas of Ibadan were analyzed for seven elements namely; Cu, Cr, Ni, Cd, Mn, Co and Pb. The mean concentrations (Mean ± SD) of heavy metals (Cu, Cr, Ni, Cd, Mn, Co and Pb) in water and soil samples from the selected auto-mechanic workshops within the two Local Government Area of Oyo State Nigeria are presented in Table 4.3 to Table 4.6. Cobalt and Cd were not detected in the all the water samples from all the locations investigated, hence they were excluded from Table 4.3 and Table 4.4.

For the soil analysis, Cd was not detected in locations within Ibadan North East Local Government, and was only detected at two locations within Ibadan North.

4.2.1 Concentrations of Heavy metals in water samples from IBN Local Government Area

Table 4.3 summarized the concentrations of Cu, Cr, Ni, Mn and Pb in Well water samples collected from ten (10) randomly selected auto-mechanic workshops from Ibadan North Local Government Area of Oyo State. The concentrations of Cd and Co were below the detection limits, hence they were excluded from Table 4.3.

The concentrations of Cr ranged from 0.16 ± 0.48 to 1.63 ± 0.14 mg L^{-1} and 60 % of the Well samples had Cr concentrations above the WHO drinking water limit of 0.05 mg L^{-1} while the concentrations of Cr in the remaining 40 % and the control samples were below the limit of detection. The concentrations of Cr at Orogun, NTA, Oke-Itunu, UCH1, UCH2 and Dandaru were significantly higher than the control indicating the impact of the various activities at these auto-mechanic workshops. The average concentrations of Cr measured were above the WHO permissible limits of 0.05 mg L^{-1}), but similar trend was obtained by Agagnehu and Gabbineb in their study[4]. Dandaru sampling site recorded the highest concentration (1.634 ± 0.137 mg L^{-1}), while the concentrations of Cr in other sites investigated occur in decreasing order of UCH1 (1.468 ± 0.117 mg L^{-1}) < UCH 2 (1.007 ± 0.196 mg L^{-1}) < Oke-itunu (0.608 ± 0.099 mg L^{-1}) < NTA (0.276 ± 0.108 mg L^{-1}) < Orogun sampling site (0.156 ± 0.477 mg L^{-1}).

Similarly, the concentrations of Cu obtained from 50% of the sampled locations in IBN ranged from 0.01 ± 0.01 to 0.09 ± 0.02 mg L^{-1}, while the concentrations of Cu in the remaining 50% of the sampled locations were below detection limits. All Cu concentrations were below the permissible limit of 2.0 mg L^{-1} set for Cu in drinking water by WHO. This suggested that the consumption of water poses no danger as far as the intake of copper is concerned[5]. The highest and the lowest concentration of Cu were obtained from the sampling sites around secretariat (0.09 ± 0.02 mg L^{-1}) and Oke-Itunu (0.01 ± 0.01 mg L^{-1}) respectively. The secretariat sampling location was characterized by activities such as panel beating, rewiring and engine repairs, while Oke-Itunu had lesser activities compared with other locations.

Table 4.3: Heavy metal concentrations in water samples from automobile workshops in Ibadan North Local Government Area

Locations	Cu	Cr	Ni	Mn	Pb
Secretariat	0.09 ± 0.02^{cd}	ND	0.02 ± 0.003^{b}	**0.21 ± 0.02^{b}**	ND
Bodija	ND	ND	0.02 ± 0.003^{b}	**0.21 ± 0.02^{b}**	ND
Trans	ND	ND	0.02 ± 0.003^{b}	**0.38 ± 0.04^{b}**	ND
Samonda	ND	ND	0.01 ± 0.004^{b}	**0.20 ± 0.02^{b}**	**0.42 ± 0.11^{b}**
Orogun	0.07 ± 0.01^{cd}	**0.16 ± 0.48^{a}**	0.01 ± 0.004^{b}	**0.35 ± 0.03^{b}**	**0.20 ± 0.20^{a}**
NTA	0.02 ± 0.003^{b}	**0.28 ± 0.11^{a}**	0.01 ± 0.004^{b}	**0.24 ± 0.02^{b}**	**0.28 ± 0.28^{a}**
Oke-Itunu	0.01 ± 0.01^{b}	**0.61 ± 0.10^{b}**	0.01 ± 0.003^{b}	**0.28 ± 0.02^{b}**	**0.46 ± 0.46^{b}**
UCH1	ND	**1.01 ± 0.20^{b}**	0.002 ± 0.003^{a}	**0.19 ± 0.01^{b}**	**0.24 ± 0.04^{a}**
UCH2	0.02 ± 0.01^{b}	**1.47 ± 0.12^{b}**	0.004 ± 0.003^{a}	**0.22 ± 0.02^{b}**	**0.17 ± 0.17^{a}**
Dandaru	ND	**1.63 ± 0.14^{b}**	0.01 ± 0.002^{b}	**0.24 ± 0.02^{b}**	**0.18 ± 0.18^{a}**
Control	0.002 ± 0.0003^{a}	ND	ND	0.07 ± 0.003^{a}	ND
*WHO 2011	2.0	0.05	0.02	0.10	0.10

Values are in mg L^{-1} (Mean ± SD, n = 3). Means with the same superscript alphabet(s) along column are not significantly different ($P > 0.05$) Means with different superscript alphabet(s) along the same column are significantly different ($P < 0.05$). *ND (values are below detection limit). * World Health OrganizationGuidelines for Drinking-water Quality.

Nickel concentrations in water samples from the selected auto-mechanic workshops ranged from 0.004 to 0.02 mg L^{-1}, but the concentration at the control site was below the detection limit. The concentrations of some Ni measured were within the permissible limits of 0.02 mg L^{-1} by WHO, while some had the same value with WHO. Nickel has different types of effects on the immune system; hence exposure may lead to adverse hypersensitivity reactions[6]. It can thus be concluded that the auto-mechanic activities within the sampling sites of the LGA are responsible for the presence of Ni in the groundwater because Ni is an indicator of petroleum-based pollution[78]. Manganese concentrations ranged from 0.193 to 0.384 mg L^{-1}, while the concentrations of Pb ranged from 0.173 to 0.455 mg L^{-1}. The concentrations of Mn and Pb in water samples collected from auto-mechanic workshops within IBN were all above the permissible limits of 0.1 mg L^{-1} for both metals. This suggested a possible threat to the lives of both adults and children using the water. The decreasing order of concentration in the water samples from IBN was Cu < Ni < Pb < Cr < Mn.

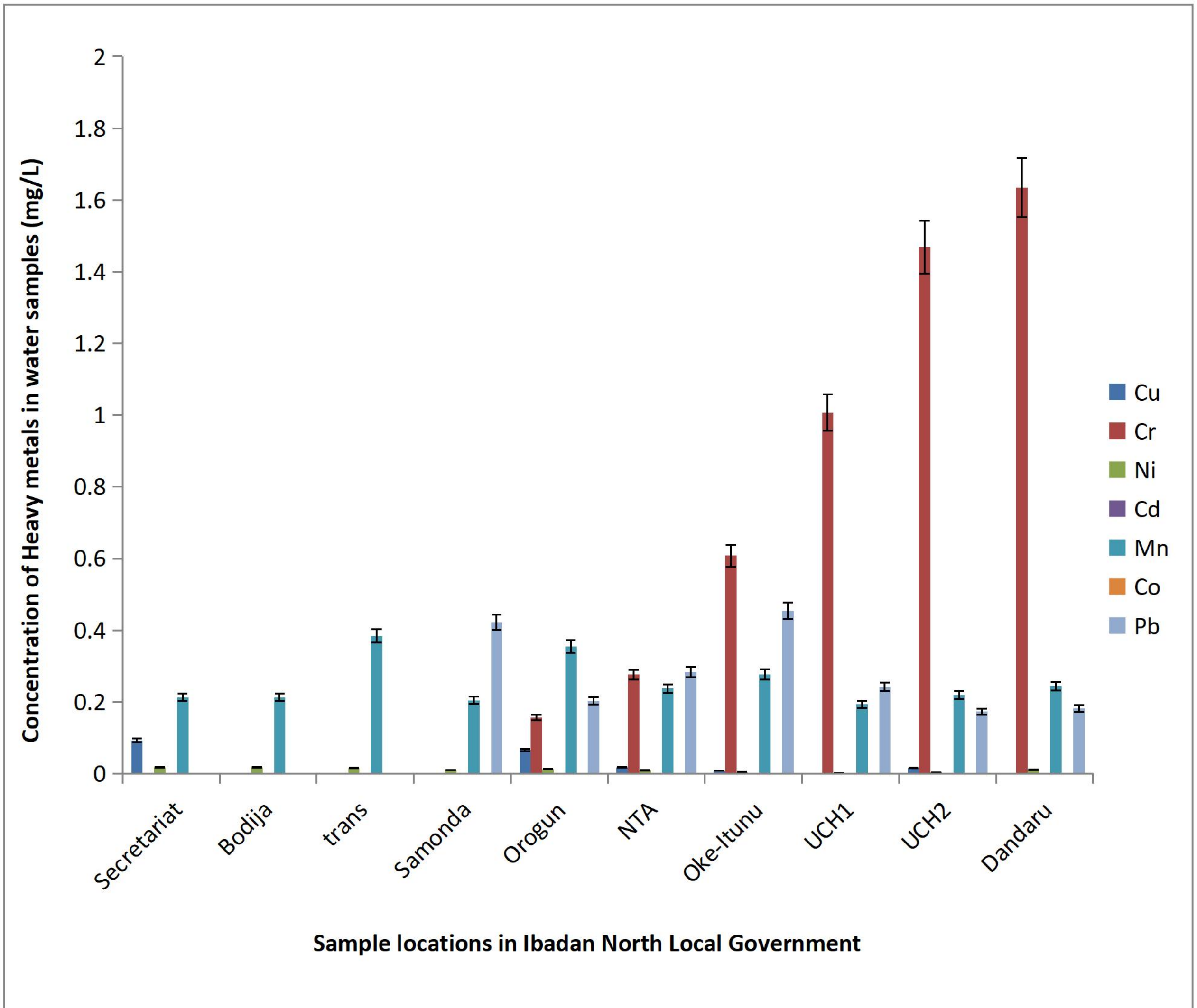

Figure 4.1: Distribution of Heavy metals in water samples in selected auto mechanic workshop within Ibadan North Local Government Area.

4.2.2 Concentrations of Heavy metals in water samples from IBNE Local Government Area

The concentrations of Cu, Cr, Ni, Mn and Pb obtained from water samples from selected automobile workshops within Ibadan North-East Local Government Area of Oyo State are presented in Table 4.4 and the distribution is shown in Figure 4.2.

Cadmium and Co were not detected in all the samples analyzed. The mean concentration of studied heavy metals in water samples from IBNE was in decreasing order of Ni $<$ Mn $<$ Pb $<$ Cr $<$ Cu. Copper concentrations were below detection limits in eight (8) out of the ten (10) sites sampled. The concentrations of Cu in the two locations ranged from 0.002 to 1.85 mg L^{-1}. Loyola sampling site had the highest concentration of Cu (1.85 ± 0.04 mg L^{-1}), and Conoil had the lowest concentration of Cu. The results further revealed that the concentrations of copper obtained from the auto-mechanic sites were above that obtained from the control site.

The concentration of Cr from selected auto-mechanic sites within IBNE ranged from 0.01 to 4.13 mg L^{-1}. These values were above both the control site value and the WHO maximum permissible limits of 0.05 mg L^{-1}.

The average Ni concentrations in water samples ranged from 0.001 to 0.01 mg L^{-1} and are below the WHO permissible limit of 0.02 mg L^{-1}. Similarly, average Mn concentrations in water samples ranged from 0.02 to 0.38 mg L^{-1}. The results obtained showed that only four (4) locations recorded Mn concentrations below the maximum permissible limit of 0.1 mg L^{-1}, while Pb ranged from 0.12 and 0.84 mg L^{-1}[7]. The values followed the same trend as was obtained for IBN, which also gave results above the permissible limits (0.1 mg L^{-1}).

Table 4.4: Heavy metal concentrations in water samples in automobile workshops in Ibadan North East Local Government Area

Locations	Cu	Cr	Ni	Mn	Pb
Loyola	1.85 ± 0.04[c]	**2.09 ± 0.11[c]**	0.01 ± 0.003[b]	**0.23 ± 0.03[b]**	**0.84 ± 0.10[b]**
Ajumobi Mkt	ND	**2.76 ± 0.11[c]**	0.002 ± 0.002[a]	**0.20 ± 0.01[b]**	**0.12 ± 0.12[a]**
Akinloye	ND	**3.25 ± 0.18[c]**	0.002 ± 0.001[a]	**0.34 ± 0.03[b]**	**0.16 ± 0.16[a]**
Conoil	0.03 ± 0.01[b]	**3.73 ± 0.29[c]**	ND	**0.38 ± 0.03[b]**	ND
Agbala	ND	**3.89 ± 0.18[c]**	0.001 ± 0.01[a]	**0.20 ± 0.02[b]**	ND
Idi-Kanga	ND	**4.13 ± 0.02[c]**	ND	**0.22 ± 0.02[b]**	ND
Ile Marun	ND	0.01 ± 0.12[a]	ND	0.02 ± 0.01[a]	ND
Abayomi	ND	**0.31 ± 0.13[a]**	ND	0.04 ± 0.02[a]	ND
Oladoke	ND	**0.90 ± 0.22[b]**	ND	0.02 ± 0.01[a]	ND
Onipepeye	ND	**1.10 ± 0.26[b]**	ND	0.02 ± 0.01[a]	ND
Control	0.002 ± 0.0003[a]	ND	ND	0.07 ± 0.003[a]	ND
WHO	2.0	0.05	0.02	0.10	0.10

Values are in mg L^{-1} (Mean ± SD, n = 3). Means with the same superscript alphabet(s) along column are not significantly different ($P > 0.05$) Means with different superscript alphabet(s) along the same column are significantly different ($P < 0.05$). *ND (values are below detection limit). *World Health Organization Guidelines for Drinking-water Quality**Error! Bookmark not defined.**.

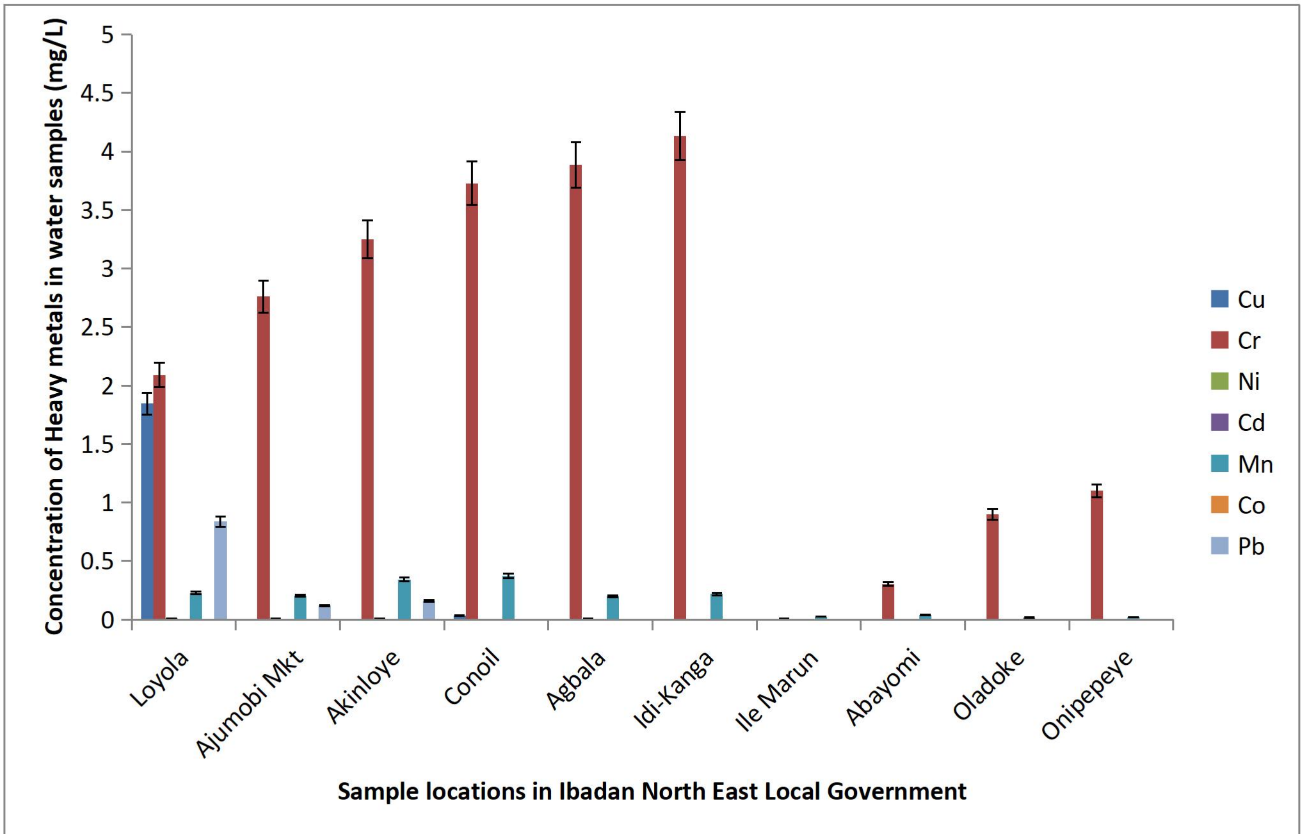

Figure 4.2: Distribution of heavy metals in water samples in selected auto mechanic workshop within Ibadan North East Local Government Area.

The results obtained from the analysis of water in all the sites investigated had a significant impact on the drinking water quality. The higher concentration of heavy metals studied in the work suggested that the activities carried out in these sites are contributing immensely environmental hazards in these locations. More worrisome is the hazardous nature of most of these elements in water. An increasing release of these substances into groundwater, presents very serious problem.

4.2.3: Concentrations of Heavy metals in Soil samples from IBN Local Government Area

The average concentrations of Cd, Cr, Ni, Cu, Co, Pb and Mn in soil samples collected from ten (10) automobile workshops within Ibadan North Local Government Area of Oyo State are presented in Table 4.5 and distribution shown in Figure 4.3. The average concentrations of selected heavy metals in soil samples in IBN exhibited a decreasing order of Pb > Mn > Cr > Ni > Co > Cu > Cd. Although, the average concentrations of Cd, Cr, Ni, Cu, Co, Pb and Mn in soil samples in automobile workshops within IBN were all below the permissible limits, they were above values obtained for control.

Out of the ten (10) automobile workshops investigated, 80% of the Cd concentrations were below the detection limit, and the remaining 20% Cd concentration ranged from 0.03 to 0.147 mg kg^{-1}. These results were below both the concentration of the control site and the maximum permissible limit of 0.80 mg kg^{-1} set by WHO. Likewise, the average Cu concentrations in soil samples in automobile workshops within IBN ranged from 0.013 to 1.118 mg kg^{-1}. The results obtained are below the permissible limit (35.0 mg kg^{-1}) set by WHO. Highest concentration of 0.330 ± 0.08 mg kg^{-1} was obtained from the sampling site around NTA, which is far below the permissible limits, therefore suggesting no threat associated with copper when the individuals within the sites come in contact with the soil samples.

Other investigated heavy metals ranged as follows; Co (0.013 to 0.353 mg kg^{-1}), Cr (0.147 to 1.862 mg kg^{-1}), Ni (0.082 to 0.330 mg kg^{-1}), Mn (0.104 to 8.731 mg kg^{-1}) and Pb (0.814 to 32.610 mg kg^{-1}). The concentrations of these heavy metals are within the various limits (12, 20, 35, 85 and 100 for Mn, Co, Ni, Pb and Cr respectively) set by WHO[9].

Table 4.5: Heavy metal concentrations in soil samples in automobile workshops in Ibadan North Local Government Area

Location	Cd	Cr	Ni	Cu	Co	Pb	Mn
Secretariat	ND	1.73 ± 0.01^{c}	0.08 ± 0.03^{a}	0.12 ± 0.10^{a}	0.06 ± 0.06^{b}	0.81 ± 0.35^{a}	0.10 ± 0.02^{a}
Bodija	ND	1.19 ± 1.09^{c}	0.08 ± 0.00^{a}	0.01 ± 0.00^{a}	0.35 ± 0.12^{bc}	3.88 ± 0.14^{b}	8.73 ± 0.50^{e}
TAP	ND	0.15 ± 0.00^{a}	0.10 ± 0.00^{a}	0.05 ± 0.04^{a}	0.001 ± 0.00^{a}	2.35 ± 0.19^{b}	3.17 ± 0.10^{c}
Samonda	0.15 ± 0.12^{a}	0.48 ± 0.05^{a}	0.04 ± 0.01^{a}	0.11 ± 0.10^{ab}	0.06 ± 0.06^{b}	1.11 ± 1.11^{a}	3.46 ± 0.17^{c}
Orogun	ND	1.05 ± 0.09^{c}	0.09 ± 0.01^{a}	0.03 ± 0.02^{a}	0.11 ± 0.00^{b}	1.50 ± 0.00^{a}	5.24 ± 0.04^{c}
NTA	ND	1.30 ± 0.09^{c}	0.33 ± 0.08^{b}	0.03 ± 0.01^{a}	0.12 ± 0.01^{b}	23.3 ± 19^{c}	3.98 ± 0.07^{c}
Oke-Itunu	ND	1.86 ± 0.09^{c}	0.14 ± 0.04	0.03 ± 0.00^{a}	0.10 ± 0.00^{b}	3.42 ± 2.30^{b}	6.81 ± 0.78^{c}
UCH1	0.03 ± 0.02^{b}	0.18 ± 0.03^{a}	0.12 ± 0.04^{a}	0.04 ± 0.00^{a}	0.24 ± 0.02^{b}	4.56 ± 0.8^{b}	5.62 ± 0.65^{cd}
UCH2	ND	0.61 ± 0.16^{ab}	0.22 ± 0.01^{ab}	0.02 ± 0.01^{a}	0.22 ± 0.01^{b}	32.6 ± 5.40^{d}	5.78 ± 0.79^{cd}
Dandaru	ND	1.07 ± 0.09^{c}	0.09 ± 0.07^{a}	0.01 ± 0.00^{a}	ND	1.84 ± 0.68^{a}	1.09 ± 0.02^{b}
Control	ND	ND	ND	0.002 ± 0.001	ND	ND	0.04 ± 0.001
WHO	0.8	100	35	36	20	85	12

Values are in mg L^{-1} (Mean ± SD, n = 3). Means with the same superscript alphabet(s) along column are not significantly different ($P > 0.05$) Means with different superscript alphabet(s) along the same column are significantly different ($P < 0.05$). *ND (values are below detection limit). * WHO = Maximum permissible limits (WHO, 2011). **World Health OrganizationGuidelines for Drinking-water Quality*[2]. *TAP = Trans Amusement Park

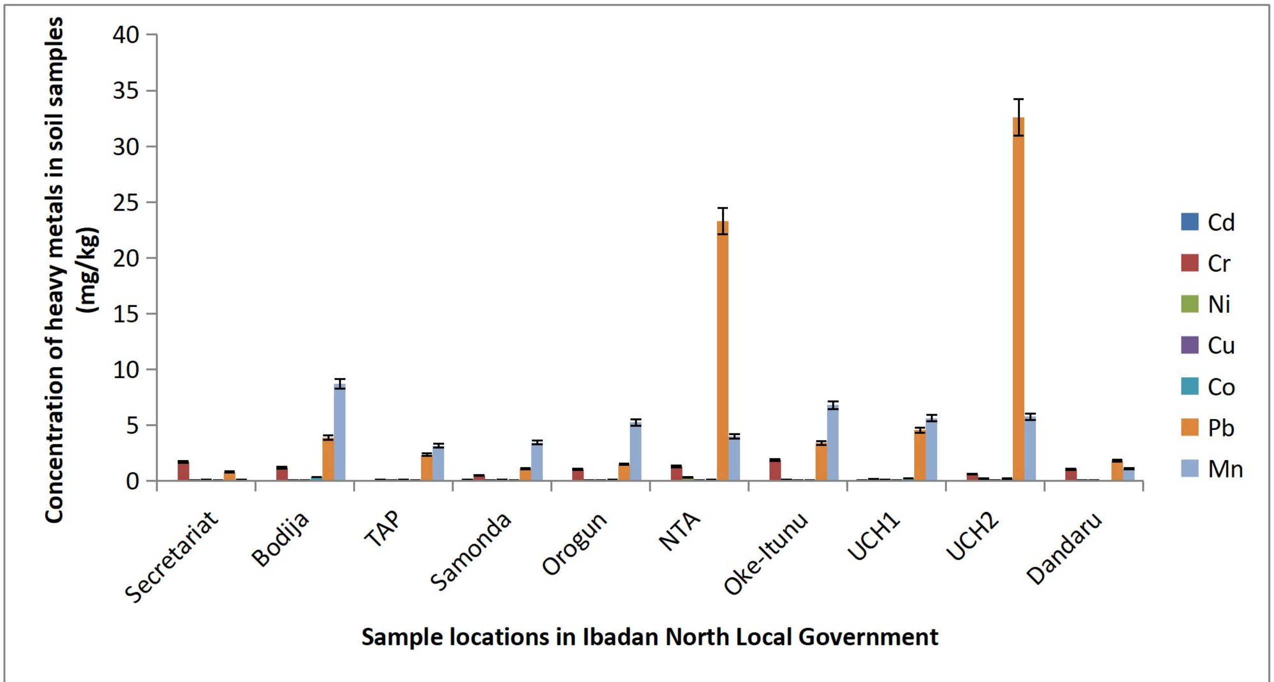

Figure 4.3: Distribution of heavy metal in soil samples in selected auto mechanic workshop within Ibadan North Local Government Area.

4.2.4: Concentrations of Heavy metals in Soil samples from IBNE Local Government Area

Similar to the results obtained from IBN, all the heavy metals are within permissible limits[10]. The average concentrations of Cr, Ni, Cu, Co, Pb and Mn in automobile workshop soil samples within Ibadan North-East local Government Area of Oyo State are presented in Table 4.6 and the distribution shown in Figure 4.4. Cadmium concentration was below the limit of detection across all studied sites. The average concentrations of the selected heavy metals in the soil samples within IBNE was in the decreasing order of Pb < Mn < Cu < Cr < Co < Ni.

The average concentration of Pb, followed by Mn were the highest across all the automobile workshops. The concentrations of Cu, Co, Cr, Ni, Mn and Pb in soil samples ranged from 0.015 ± 0.01 to 2.470 ± 2.32; 0.070 ± 0.01 to 0.790 ± 0.54, 0.302 ± 0.18 to 1.135 ± 0.24, 0.093 ± 0.02 to 0.373 ± 0.19, 1.263 ± 0.87 to 6.811 ± 0.79 and 0.569 ± 0.08 to 23.347 ± 15.3 mg kg^{-1} respectively. Similarily, the concentrations of Cd, Cr, Ni, Cu, Co, Pb and Mn in the samples are below the WHO permissible limit 0.8, 100, 35, 36, 20, 85 and 12 mg kg^{-1} respectively.

Studies[1] revealed that if the concentrations of these heavy metals are accumulated over time, they could cause various health effects such as gastro-intestinal disease, neurological disorder, carcinogenicity, kidney malfunctioning etc, caused by Cu, Pb, Cd, and Cr respectively.

Table 4.6: Heavy metal concentrations in soil samples in automobile workshops in Ibadan North Local East Government Area

Location	Cr	Ni	Cu	Co	Pb	Mn
Loyola	0.85 ± 0.08^{a}	0.17 ± 0.01^{a}	0.09 ± 0.00^{a}	0.30 ± 0.01^{b}	19.1 ± 5.06^{d}	2.44 ± 0.17^{b}
Ajumobi Mkt	0.66 ± 0.11^{a}	0.37 ± 0.19^{b}	2.46 ± 0.02^{c}	0.36 ± 0.09^{b}	3.32 ± 0.74^{b}	3.01 ± 0.14^{c}
Akinloye	0.88 ± 0.12^{a}	0.13 ± 0.01^{a}	1.47 ± 0.00^{c}	ND	23.36 ± 15.3^{d}	1.26 ± 0.87^{b}
Conoil	1.10 ± 0.06^{a}	0.11 ± 0.04^{a}	0.06 ± 0.01^{a}	0.08 ± 0.05^{a}	0.57 ± 0.08^{a}	1.48 ± 0.08^{b}
Agbala	0.30 ± 0.18^{a}	0.14 ± 0.03^{a}	0.45 ± 0.05^{b}	0.19 ± 0.01^{a}	6.01 ± 0.62^{c}	3.44 ± 0.24^{c}
Idi-Kanga	0.74 ± 0.08^{a}	0.09 ± 0.02^{a}	0.61 ± 0.00^{b}	0.79 ± 0.54^{c}	1.30 ± 0.12^{a}	2.62 ± 0.08^{b}
Ile Marun	0.79 ± 0.03^{a}	0.17 ± 0.02^{a}	2.36 ± 2.14^{c}	0.19 ± 0.01^{a}	3.48 ± 0.23^{b}	2.42 ± 0.14^{b}
Abayomi	1.06 ± 0.30^{a}	0.20 ± 0.05^{a}	2.47 ± 2.32^{c}	0.26 ± 0.05^{ab}	2.67 ± 1.14^{b}	4.57 ± 0.79^{c}
Oladoke	0.77 ± 0.39^{a}	0.17 ± 0.09^{a}	1.20 ± 1.14^{c}	0.18 ± 0.03^{a}	6.74 ± 4.54^{c}	6.81 ± 0.79^{d}
Onipepeye	1.14 ± 0.24^{a}	0.10 ± 0.01^{a}	0.02 ± 0.01^{a}	0.07 ± 0.01^{a}	1.56 ± 0.39^{a}	4.84 ± 0.26^{c}
Control	ND	ND	0.02 ± 0.01^{a}	ND	ND	0.44 ± 0.01^{a}
WHO	100	35	36	20	85	12

Values are in mg L^{-1} (Mean ± SD, n = 3). Means with the same superscript alphabet(s) along column are not significantly different (P>0.05) Means with different superscript alphabet(s) along the same column are significantly different (P<0.05). *ND (values are below detection limit). *WHO = Maximum permissible limits (WHO, 2011). **World Health OrganizationGuidelines for Drinking-water Quality*[2].

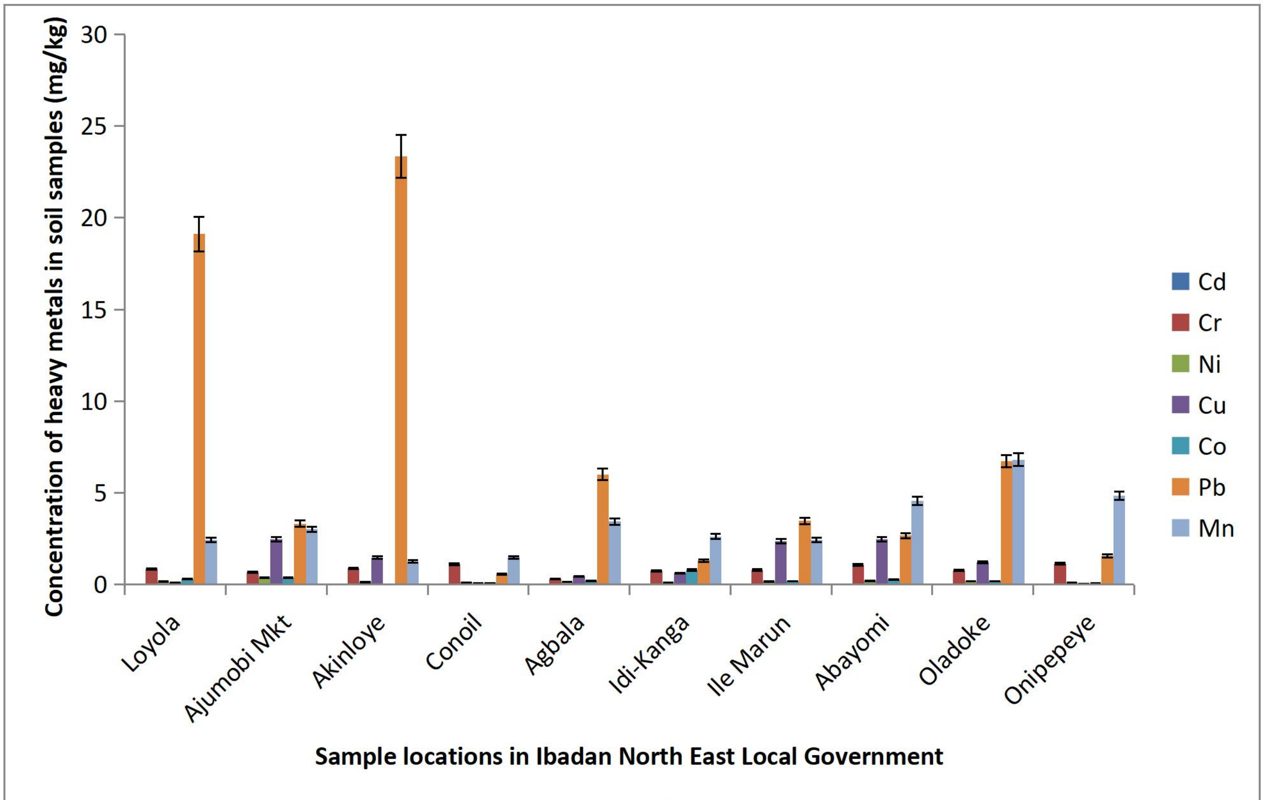

Figure 4.4: Distribution of heavy metal in soil samples in selected auto mechanic workshop within Ibadan North East Local Government Area.

4.3 Statistical Analysis

A summary result of the Pearson's correlation coefficient (PCC) analyses performed using SPSS package (v20) at 95% confidence limit ($p < 0.05$) to determine relationships between the heavy metals in groundwater and soil are presented in Tables 4.7 to 4.10.

4.3.1 Correlation Matrix of Heavy Metals in Groundwater in IBN and IBNE LGAs

The result of correlation of heavy metals in water samples in IBN presented in Table 4.7 showed that there is weak correlation (correlation coefficients lie between 0.10 – 0.39)[11] between Cu and Ni (0.36), Cu and Mn (0.11), Ni and Mn (0.32) and Cr and Pb (0.18), indicating that they were likely contributed simultaneously (closely associated). Co and Cd were not correlated because a constant value was obtained (i.e. not detected) in the samples analysed.

Table 4.7: Correlation Matrix of Heavy Metals in Water Samples in Locations within IBN

	Cu	Cr	Ni	Mn	Pb
Cu	1				
Cr	-0.32	1			
Ni	0.36	-0.64	1		
Mn	0.11	-0.27	0.32	1	
Pb	-0.30	0.18	-0.69	-0.18	1

In IBNE, all the heavy metals analyzed gave positive correlation values as shown in Table 4.8 (except Cu-Cr). Very strong correlation was obtained for Ni-Pb > Cu-Pb > Cu-Ni with correlation coefficients of 0.997, 0.974, 0.964 respectively. Cr-Mn produced a strong relationship ($r = 0.840$), while a low correlation was observed for Ni-Mn > Pb-Mn > Cu-Mn, with r values 0.276, 0.261, and 0.167 respectively. Similar to samples in IBN, Co and Cd were not detected in the samples analyzed from IBNE, thus could not be correlated.

Table 4.8: Correlation matrix of heavy metals in water samples in locations within IBNE

	Cu	Cr	Ni	Mn	Pb
Cu	1				
Cr	-0.02	1			
Ni	0.96	0.06	1		
Mn	0.17	0.84	0.28	1	
Pb	0.97	0.03	0.99	0.26	1

4.3.2 Pearson Correlation Matrix of Heavy Metals in Soil Samples in IBN and IBNE

The correlation matrix of heavy metals in soil samples are summarized in Table 4.9 and 4.10. In IBN, a strong relationship exists between the heavy metals in the order Ni-Pb > Co-Mn, with coefficients of 0.847 and 0.794 respectively. Cd-Cu, produces a moderate relationship (0.580) while Co-Pb (0.315), Pb-Mn (0.208), and Ni-Co (0.164), were weakly correlated.

Table 4.9: Correlation matrix of heavy metals in soils around automobile workshops in IBN LGA

	Cd	Cr	Ni	Cu	Co	Pb	Mn
Cd	1						
Cr	-0.376	1					
Ni	-0.378	0.144	1				
Cu	0.580	0.007	-0.412	1			
Co	-0.133	-0.047	0.164	-0.410	1		
Pb	-0.224	-0.080	0.847	-0.351	0.315	1	
Mn	-0.094	-0.038	0.134	-0.562	0.794	0.208	1

In IBNE, no strong correlation was obtained. A moderate correlation of (0.666) was observed Ni-Cu. Other results showed insignificant relationship. These results suggesedt that these heavy metals in the soil could be originating from similar sources

Table 4.10: Correlation matrix of heavy metals in soils around automobile workshops in IBNE LGA

	Cr	Ni	Cu	Co	Pb	Mn
Cr	1					
Ni	-0.241	1				
Cu	-0.088	0.666	1			
Co	-0.281	0.098	0.039	1		
Pb	-0.089	-0.069	-0.075	-0.295	1	
Mn	-0.001	0.103	0.076	-0.026	-0.323	1

4.4 Health Risk Assessment

4.4.1 Non- Carcinogenic Risk Assessment of the Intake of Water

The non-carcinogenic risk was calculated as the hazard quotient (HQ).

4.4.1.1 Estimate Daily Intake (EDI)

The non-carcinogenic risk assessment of the studied heavy metals at IBN and IBNE across different age groups (children and adults) is presented in Tables 4.11 and Table 4.12 respectively.

The estimated daily intake through water ingestion was calculated according to the modified equation:

$$\textbf{EDI} = \frac{C \times DI \times ABS \times EF \times ED}{BW \times AT} \qquad (1)$$

where Cw (in µg L^{-1}) is the heavy metals concentration in water, ABS (no unit) is the dermal absorption factor, DI (in L/day) is the daily average intake of water in the area, EF (in days/ year) represents the annual exposure frequency, ED (in years) is exposure duration, BW (in kg/person) is bodyweight, and AT (in days) is the average time

The Estimated daily intake (EDI) of the studied metals obtained at IBN showed Cr as the highest dose in both children and adults with EDI of 1.20×10^{-4} $mg^{-1}kg^{-1}day^{-1}$ and 5.13×10^{-5} $mg^{-1}kg^{-1}day^{-1}$ respectively. Results obtained for other metals in children was in order Pb > Mn > Cu > Ni with EDIs 3.34×10^{-5}, 02.81×10^{-5}, 8.19×10^{-6} and 1.34×10^{-6} $mg^{-1}kg^{-1}day^{-1}$ respectively.

Daily intake of the studied heavy metals from groundwater in adults was in order Cr > Pb > Mn > Cu > Ni with of 5.13×10^{-5}, 1.43×10^{-5}, 1.21×10^{-5}, 3.51×10^{-6} and 5.76×10^{-7} $mg^{-1}kg^{-1}day^{-1}$ respectively.

Cu recorded the highest dosage for both children and adults in the automobile workshop at Secretariat with daily intake (EDI) of 8.19 $\times 10^{-6}$ and 3.51 $\times 10^{-6}$ $mg^{-1}kg^{-1}day^{-1}$ respectively. Cr highest dosage was obtained at Dandaru (1.20 $\times 10^{-4}$ and 5.13 $\times 10^{-5}$ $mg^{-1}kg^{-1}day^{-1}$ for children and adults respectively). Ni highest dosage was at the Secreatariat mechanic village (1.34 $\times 10^{-6}$ and 5.76 $\times 10^{-7}$ for children and adults respectively). Auto-mechanic workshop situated opposite Trans Amusement park recorded most dose of Mn (2.81 $\times 10^{-5}$ and 1.21 $\times 10^{-5}$ for children and adults respectively).

Pb highest value was obtained from Oke-itunu site (3.34 $\times 10^{-5}$ and 1.43 $\times 10^{-5}$ for children and adults respectively).

The estimated daily intake (EDI) of the studied metals obtained at IBNE followed the same trend as the result obtained from IBN where Cr showed the highest in both children and adults with EDI of 2.98 $\times 10^{-4}$ $mg^{-1}kg^{-1}day^{-1}$ and 1.28 $\times 10^{-4}$ $mg^{-1}kg^{-1}day^{-1}$ respectively. Results obtained for the intake of other heavy metals studied was in the order Cu> Pb > Mn > Ni with EDIs 1.35 $\times 10^{-4}$, 6.13 $\times 10^{-5}$, 2.75 $\times 10^{-5}$ and 7.33 $\times 10^{-7}$ $mg^{-1}kg^{-1}day^{-1}$ respectively for children and 5.80 $\times 10^{-5}$, 2.63 $\times 10^{-5}$, 1.18 $\times 10^{-5}$ and 3.14 $\times 10^{-7}$ $mg^{-1}kg^{-1}day^{-1}$ for adults.

Cu, Pb and Ni recorded the highest dosage for both children and adults at sampled automobile workshop at Loyola, Cr highest dosage was obtained at Idi-kanga, and Mn was at the sampled site at Conoil.

Overall, the children were more at high risk of these heavy metals due to the high intake observed from the study. Similar trend was observed in the study carried out by [12]

4.4.1.2 Hazard Quotient (HQ) Indices

The HQ for non-carcinogenic risk can be calculated by the following equation

$$HQ = \frac{EDI}{RfD} \qquad (2)$$

where, according to USEPA database the oral toxicity reference dose values (RfD) are presented in table 4.11. The exposed population is assumed to be safe when HQ<1[13].

The calculated HQ for non-carcinogenic risk in water samples from selected auto-mobile workshops in IBN and IBNE are presented in Table 4.11 and 4.12.

The HQ values obtained for Cu, Ni, Mn, Cr and Pb for both children and adults were less than 1 (HQ < 1) in all the locations studied within the two selected LGAs (IBN and IBNE), which indicate insignificant non-carcinogenic risk[14].

4.4.1.3 Cancer Risk for Water Samples from IBN and IBNE LGAs

Table 4.13 presents the results of the probability of cancer risk of four metals (Cr, Cd, Pb and Ni) in groundwater for both adult and children populations in the two local government of study (Ibadan North and Ibadan North-Est) within Ibadan. Based on the acceptable range for cancer risk of $\leq 1 \times 10^{-6}$ to 1×10^{-4} by USEPA[15]. From the result obtained for carcinogenic risk, all the values are $< 10^{-6}$, suggesting that all the water samples have negligible cancer risk due to Cr, Mn and Pb.

Table 4.11: Non-cancer Risks Index of heavy metals in groundwater at automechanic workshops in Ibadan North area of Ibadan, Oyo State.

CHILDREN	**EDI**					**HQ**				
Location	**Cr** $(\times10^{-5})$	**Ni** $(\times10^{-7})$	**Cu** $(\times10^{-6})$	**Pb** $(\times10^{-5})$	**Mn** $(\times10^{-5})$	**Cr** $(\times10^{-5})$	**Ni** $(\times10^{-5})$	**Cu** $(\times10^{-5})$	**Pb** $(\times10^{-3})$	**Mn** $(\times10^{-4})$
Secretariat	0.00	**13.40**	**8.19**	0.00	1.56	0.00	**6.72**	0.21	0.00	3.40
Bodija	0.00	**13.40**	0.00	0.00	1.56	0.00	**6.72**	0.00	0.00	3.40
TAP	0.00	11.00	0.00	0.00	**2.81**	0.00	5.50	0.00	0.00	6.11
Samonda	0.00	7.33	0.00	3.09	1.49	0.00	3.67	0.00	8.83	3.24
Orogun	1.14	9.17	4.80	1.49	2.60	0.76	4.58	0.12	4.25	5.64
NTA	2.02	7.33	1.21	2.08	1.74	1.34	3.67	**3.03**	5.93	3.78
Oke-Itunu	4.46	3.67	0.57	**3.34**	2.03	2.97	1.83	1.44	9.53	4.41
UCH1	7.39	3.67	0.00	1.77	1.41	4.93	1.83	0.00	5.06	3.07
UCH2	10.80	3.67	1.14	1.27	1.61	7.17	1.83	2.84	3.61	3.51
Dandaru	**12.00**	7.33	0.00	1.33	1.79	7.98	3.67	0.00	3.81	3.89

ADULT	**EDI**					**HQ**				
Location	**Cr** $(\times10^{-5})$	**Ni** $(\times10^{-7})$	**Cu** $(\times10^{-6})$	**Pb** $(\times10^{-5})$	**Mn** $(\times10^{-5})$	**Cr** $(\times10^{-5})$	**Ni** $(\times10^{-5})$	**Cu** $(\times10^{-5})$	**Pb** $(\times10^{-3})$	**Mn** $(\times10^{-4})$
Secretariat	0.00	**5.76**	**3.51**	0.00	0.67	0.00	**2.88**	**8.77**	0.00	1.46
Bodija	0.00	**5.76**	0.00	0.00	0.67	0.00	**2.88**	0.00	0.00	1.46
TAP	0.00	4.71	0.00	0.00	**1.21**	0.00	2.36	0.00	0.00	2.62
Samonda	0.00	3.14	0.00	1.32	0.64	0.00	1.57	0.00	3.78	1.39
Orogun	0.49	3.93	2.06	0.64	1.11	0.33	1.96	5.15	1.82	2.42
NTA	0.86	3.14	0.52	0.89	0.75	0.58	1.57	1.30	2.54	1.62
Oke-Itunu	1.91	1.57	0.25	**1.43**	0.87	1.27	0.79	0.62	4.09	1.89
UCH1	3.17	1.57	0.00	0.76	0.61	2.11	0.79	0.00	2.17	1.32
UCH2	4.61	1.57	0.49	0.54	0.69	3.07	0.79	1.22	1.55	1.50
Dandaru	**5.13**	3.14	0.00	0.57	0.77	3.42	1.57	0.00	1.63	1.67

*RfD = Oral reference dosage (mg $kg^{-1}day^{-1}$)[12]

*TAP = Trans Amusement Park

Table 4.12: Non-cancer Risks Index of heavy metals in groundwater at automechanic workshops in Ibadan North-East area of Oyo State.

CHILDREN	**Cr ($\times10^{-4}$)**	**Ni ($\times10^{-7}$)**	**Cu ($\times10^{-6}$)**	**Pb ($\times10^{-5}$)**	**Mn ($\times10^{-5}$)**	**Cr ($\times10^{-4}$)**	**Ni ($\times10^{-5}$)**	**Cu ($\times10^{-4}$)**	**Pb ($\times10^{-3}$)**	**Mn ($\times10^{-4}$)**
LOCATION			**EDI**					**HQ**		
Loyola	1.53	**7.33**	**135**	**6.13**	1.66	1.02	3.67	**33.80**	17.50	3.61
Ajumobi Mkt	2.02	1.47	9.90	0.87	1.49	1.35	**7.33**	2.48	2.49	3.24
Akinloye	2.38	1.47	14.9	1.17	2.51	1.59	0.73	3.73	3.34	5.46
Conoil	2.73	0.00	3.79	0.00	**2.75**	1.82	0.00	0.95	0.00	5.98
Agbala	2.85	3.67	0.73	0.00	1.44	1.90	1.83	0.18	0.00	3.13
Idi-Kanga	**2.98**	0.00	4.28	0.00	1.61	1.99	0.00	1.07	0.00	3.49
Ile Marun	0.22	0.00	6.72	0.00	0.18	1.47	0.00	1.68	0.00	0.39
Abayomi	0.22	0.00	10.90	0.00	0.28	1.48	0.00	2.72	0.00	0.61
Oladoke	0.66	0.00	7.58	0.00	0.12	4.40	0.00	1.89	0.00	0.26
Onipepeye	0.81	0.00	14.10	0.00	0.15	5.38	0.00	3.51	0.00	0.34
ADULT			**EDI**					**HQ**		
LOCATIONS	**Cr ($\times10^{-5}$)**	**Ni ($\times10^{-7}$)**	**Cu ($\times10^{-6}$)**	**Pb ($\times10^{-5}$)**	**Mn ($\times10^{-6}$)**	**Cr ($\times10^{-5}$)**	**Ni ($\times10^{-6}$)**	**Cu ($\times10^{-4}$)**	**Pb ($\times10^{-3}$)**	**Mn ($\times10^{-4}$)**
Loyola	6.56	**3.14**	**58.00**	**2.63**	7.12	4.38	15.70	14.50	7.51	1.55
Ajumobi Mkt	8.67	0.63	4.24	0.374	6.38	5.78	3.14	1.06	1.07	1.39
Akinloye	10.20	0.63	6.39	0.50	10.80	6.80	3.14	1.60	1.43	2.34
Conoil	11.70	0.00	1.62	0.00	**11.80**	7.81	0.00	0.41	0.00	2.56
Agbala	12.20	1.57	0.31	0.00	6.18	8.14	7.86	0.079	0.00	1.34
Idi-Kanga	**12.80**	0.00	1.83	0.00	6.88	8.52	0.00	0.46	0.00	1.50
Ile Marun	0.95	0.00	2.88	0.00	0.77	0.630	0.00	0.72	0.00	0.17
Abayomi	0.95	0.00	4.66	0.00	1.19	0.64	0.00	1.17	0.00	0.26
Oladoke	2.83	0.00	3.25	0.00	0.52	1.89	0.00	0.81	0.00	0.11
Onipepeye	3.46	0.00	6.02	0.00	0.66	2.30	0.00	1.51	0.00	0.14

Table 4.13: Cancer Risks Index of heavy metals in groundwater at automechanic workshops in Ibadan North and Ibadan North-East Local Government area, Oyo State.

		CHILDREN			ADULT		
	LOCATION	Cr ($\times10^{-6}$)	Ni ($\times10^{-6}$)	Pb ($\times10^{-7}$)	Cr ($\times10^{-7}$)	Ni ($\times10^{-7}$)	Pb ($\times10^{-8}$)
IBADAN NORTH LGA	Secretariat	0	1.22		0	5.24	0
	Bodija	0	1.22	0	0	5.24	0
	trans	0	1.00	0	0	4.29	0
	Samonda	0	0.67	2.63	0	2.86	11.30
	Orogun	0.57	0.83	1.27	2.45	3.58	5.42
	NTA	1.01	0.67	1.76	4.32	2.86	7.56
	Oke-Itunu	2.23	0.33	2.84	9.56	1.43	12.20
	UCH1	3.7	0.33	1.51	15.80	1.43	6.45
	UCH2	5.38	0.33	1.08	23.00	1.43	4.61
	Dandaru	5.98	0.67	1.13	25.60	2.86	4.86
	LOCATION	Cr ($\times10^{-6}$)	Ni ($\times10^{-7}$)	Pb ($\times10^{-7}$)	Cr ($\times10^{-6}$)	Ni ($\times10^{-7}$)	Pb ($\times10^{-8}$)
IBADAN NORTH-EAST LGA	Loyola	7.66	6.67	5.21	3.28	2.86	22.30
	Ajumobi Mkt	10.10	1.33	0.74	4.34	0.57	3.18
	Akinloye	11.90	1.33	0.99	5.10	0.57	4.26
	Conoil	13.70	0	0	5.86	0	0
	Agbala	14.30	3.34	0	6.11	1.43	0
	Idi-Kanga	14.90	0	0	6.39	0	0
	Ile Marun	1.10	0	0	0.47	0	0
	Abayomi	1.10	0	0	0.48	0	0
	Oladoke	3.30	0	0	1.41	0	0
	Onipepeye	4.03	0	0	1.73	0	0

4.5 Health Risk Assessment of Heavy Metals in Soil

The non-carcinogenic and carcinogenic effects of heavy metals in automobile workshops in IBN and IBNE LGAs were assessed using the hazard quotient (HQ), hazard index (HI) and carcinogenic risk (RI) methods.

4.5.1 Non- Carcinogenic Risk Assessment of the Intake of Water

The non-carcinogenic risk was calculated as the hazard quotient (HQ).

4.5.1.1 Estimate Daily Intake (EDI)

Estimated daily intake (EDI) (mg/kg/day) = $\frac{C \times IR \times EF \times ED}{BW \times AT} \times 10^{-6}$ (4)

C means the heavy metal concentration at the sampling points

IR = Ingestion rate (100 mg/day for adult, 200 mg/day for children)

EF = Exposure frequency (350 days/year)

ED = Exposure period (24 years for adult, 6 years for children)

BW = Body weight (55.9 kg for adults, 15 kg for children)

CF = Conversion factor (10^{-6} $kgmg^{-1}$)

AT = Average time for non-carcinogens (EF × 365 days)[1416].

HQ is the ratio of the estimated daily intake (EDI) of a heavy metal to its reference dose (RfD) (mg/kg day) for the same exposure pathway.

i.e. $HQ = \frac{EDI}{RfD}$ (5)

Non-carcinogenic effects of heavy metals in soil samples from selected automobile workshops in IBN and IBNE LGA was investigated, and the results obtained are presented in table 4.13 and

4.14. The results obtained for the daily intake of heavy metals from soil showed that the average intake of these metals is below their respective RfDs in both children and adults.

The estimated daily intake (EDI) of the studied metals obtained at IBN showed Pb as the most dose in both children and adults with EDIs of 4.35×10^{-4} $mg^{-1}kg^{-1}day^{-1}$ and 5.83×10^{-5} $mg^{-1}kg^{-1}day^{-1}$ respectively. Results obtained for other metals in children was in order Mn > Cr > Co > Ni > Cd > Cu with EDI 9.08×10^{-5}, 2.31×10^{-5}, 4.71×10^{-6}, 4.40×10^{-6}, 1.96×10^{-6} and 1.67×10^{-6} $mg^{-1}kg^{-1}day^{-1}$ respectively for children, while that of adults include: 1.56×10^{-4}, 3.30×10^{-4}, 6.30×10^{-5}, 5.90×10^{-5}, 2.60×10^{-5} and 2.10×10^{-5} $mg^{-1}kg^{-1}day^{-1}$ respectively.

The estimated daily intake (EDI) of the studied metals obtained at IBNE followed the trend Pb > Mn > Cu > Cr > Co > Ni, while Cd was below detection limit. Pb showed the most dose in both children and adults with EDI of 3.11×10^{-4} $mg^{-1}kg^{-1}day^{-1}$ and 4.18×10^{-5} $mg^{-1}kg^{-1}day^{-1}$ respectively. EDIs for Mn, Cu, Cr, Co, and Ni in children include 9.08×10^{-5}, 3.29×10^{-5}, 1.47×10^{-5}, 1.05×10^{-5} and 4.98×10^{-6} $mg^{-1}kg^{-1}day^{-1}$ respectively, and in adults: 1.22×10^{-5}, 4.40×10^{-5}, 2.00×10^{-5}, 1.41×10^{-6} and 6.70×10^{-7} $mg^{-1}kg^{-1}day^{-1}$ respectively.

4.5.1.2 Hazard Quotient (HQ) Indices

The result of non-carcinogenic for all ages across the two LGAs studied showed HQ values less than 1 (HQ<1). This suggested no significant non-carcinogenic effects.

Table 4.14: Non-cancer Risk Index of heavy metals in soil at auto-mechanic workshops in Ibadan North Local Government area, Oyo State.

IBN	Cd ($x10^{-6}$)	Cr ($x10^{-5}$)	Ni ($x10^{-6}$)	Cu ($x10^{-6}$)	Co ($x10^{-6}$)	Pb ($x10^{-5}$)	Mn ($x10^{-5}$)
CHILDREN							
Secretariat	0.00	**2.31**	1.09	1.57	0.77	1.08	0.14
Bodija	0.00	1.59	1.11	**1.67**	**4.71**	5.18	11.6
trans	0.00	0.20	1.29	0.70	0.007	3.14	4.22
Samonda	1.96	0.64	0.53	1.47	0.80	1.48	4.61
Orogun	0.00	1.40	1.20	0.46	1.45	2.00	6.99
NTA	0.00	1.73	**4.40**	0.38	1.63	31.1	5.31
Oke-Itunu	0.00	2.48	1.84	0.40	1.29	4.56	**9.08**
UCH1	0.40	0.24	1.58	0.49	3.19	6.08	7.49
UCH2	0.00	0.81	2.98	0.31	2.89	**43.50**	7.71
Dandaru	0.00	1.42	1.24	0.17	0.00	2.45	1.46
ADULT							
Secretariat	0.00	0.31	0.15	**0.21**	0.10	0.15	0.019
Bodija	0.00	0.21	0.15	0.022	**0.63**	0.70	**1.56**
Trans	0.00	0.026	0.17	0.094	8.94×10^{-3}	0.42	0.57
Samonda	0.26	0.087	0.072	0.20	0.11	0.20	0.62
Orogun	0.00	0.19	0.16	0.061	0.20	0.27	0.94
NTA	0.00	0.23	**0.59**	0.051	0.22	4.17	0.71
Oke-Itunu	0.00	**0.33**	0.25	0.054	0.17	0.61	1.22
UCH1	0.055	0.032	0.21	0.066	0.43	0.82	1.01
UCH2	0.00	0.11	0.40	0.042	0.39	**5.83**	1.03
Dandaru	0.00	0.19	0.17	0.022	0.00	0.33	0.20
RfD	**0.01**	**0.003**	**0.02**	**0.04**	**0.02**	**0.0036**	**0.14**

Table 4.15: Non-cancer Risks Index of heavy metals in soil at auto-mechanic workshops in Ibadan North-East Local Government Area, Oyo State

IBNE	Cd	Cr ($\times 10^{-5}$)	Ni ($\times 10^{-6}$)	Cu ($\times 10^{-5}$)	Co ($\times 10^{-6}$)	Pb ($\times 10^{-5}$)	Mn ($\times 10^{-5}$)
CHILDREN							
Loyola	0.00	1.13	2.24	0.063	4.05	25.5	3.25
Ajumobi Mkt	0.00	0.88	**4.98**	1.67	4.75	4.42	4.01
Akinloye	0.00	1.17	1.67	1.06	0.00	**31.1**	1.68
Conoil	0.00	**1.47**	1.49	0.076	1.11	0.76	1.98
Agbala	0.00	0.40	1.82	1.47	2.57	8.01	4.59
Idi-Kanga	0.00	0.99	1.24	0.43	**10.5**	1.73	3.49
Ile Marun	0.00	1.06	2.22	3.14	2.51	4.64	3.23
Abayomi	0.00	1.41	2.67	**3.29**	3.51	3.56	6.09
Oladoke	0.00	1.02	2.31	1.60	2.42	8.99	**9.08**
Onipepeye	0.00	1.51	1.31	0.02	0.93	2.08	6.45
ADULT							
Loyola	0.00	0.15	0.30	0.009	0.54	3.42	0.44
Ajumobi Mkt	0.00	0.12	**0.67**	0.23	0.64	0.59	0.54
Akinloye	0.00	0.16	0.22	0.14	0.00	**4.18**	0.23
Conoil	0.00	**0.20**	0.20	0.010	0.15	0.10	0.27
Agbala	0.00	0.05	0.24	0.20	0.35	1.08	0.62
Idi-Kanga	0.00	0.13	0.17	0.058	**1.41**	0.23	0.47
Ile Marun	0.00	0.14	0.30	0.42	0.34	0.62	0.43
Abayomi	0.00	0.19	0.36	**0.44**	0.47	0.48	0.82
Oladoke	0.00	0.14	0.31	0.22	0.33	1.21	**1.22**
Onipepeye	0.00	**0.20**	0.18	0.0027	0.12	0.28	0.87
RfD	**0.01**	**0.003**	**0.02**	**0.04**	**0.02**	**0.0036**	**0.14**

RfD[17,18]

Table 4.16: HQ of heavy metals in soil at auto-mechanic workshops in Ibadan North Local Government Area, Oyo State

LOCATIONS	Cd ($\times 10^{-4}$)	Cr ($\times 10^{-4}$)	Ni ($\times 10^{-5}$)	Cu ($\times 10^{-6}$)	Co ($\times 10^{-5}$)	Pb ($\times 10^{-3}$)	Mn ($\times 10^{-5}$)
				CHILDREN			
Secretariat	0.00	**76.9**	5.44	**39.2**	3.83	3.01	0.99
Bodija	0.00	53.0	5.56	4.17	**23.6**	14.4	**83.1**
trans	0.00	6.52	6.44	17.5	0.03	8.72	30.2
Samonda	0.20	21.5	2.67	36.7	4.00	4.11	32.9
Orogun	0.00	46.7	6.00	11.4	7.27	5.55	49.9
NTA	0.00	57.8	22.0	9.44	8.17	86.3	37.9
Oke-Itunu	0.00	82.7	9.22	10.0	6.47	12.7	64.9
UCH1	**4.07**	8.00	7.89	12.2	0.16	16.9	53.5
UCH2	0.00	27.0	**14.9**	7.78	14.5	**121**	55.1
Dandaru	0.00	47.5	6.22	4.17	0.00	6.80	10.4
				ADULT			
Secretariat	0.00	**103**	0.73	**5.25**	0.51	0.40	0.13
Bodija	0.00	0.71	0.75	0.56	**3.16**	1.93	0.011
trans	0.00	8.75	0.87	2.35	0.005	1.17	4.05
Samonda	**2.63**	28.8	0.36	4.92	0.54	0.55	4.42
Orogun	0.00	62.6	0.81	1.53	0.98	0.75	6.70
NTA	0.00	7.75	**2.95**	1.27	1.10	**11.6**	5.09
Oke-Itunu	0.00	11.1	1.24	1.34	0.87	1.70	**8.70**
UCH1	0.55	1.07	1.06	1.64	2.14	2.27	7.18
UCH2	0.00	3.63	2.00	1.04	1.94	0.16	7.39
Dandaru	0.00	6.37	0.84	0.56	0.00	0.91	1.40
RfD	**0.01**	**0.003**	**0.02**	**0.04**	**0.02**	**0.0036**	**0.14**

Table 4.17: HQ of heavy metals in soil at auto-mechanic workshops in Ibadan North-East Local Government Area, Oyo State

IBNE	Cd	Cr ($\times10^{-3}$)	Ni ($\times10^{-5}$)	Cu ($\times10^{-5}$)	Co ($\times10^{-5}$)	Pb ($\times10^{-3}$)	Mn ($\times10^{-5}$)
CHILDREN							
Loyola	0.00	3.77	0.11	1.58	20.3	70.8	23.2
Ajumobi Mkt	0.00	2.95	**24.9**	41.8	23.8	12.3	28.7
Akinloye	0.00	3.91	8.33	26.5	0.00	**86.5**	12.0
Conoil	0.00	4.89	7.44	1.89	5.53	2.11	14.1
Agbala	0.00	1.34	9.11	36.7	12.9	22.3	32.8
Idi-Kanga	0.00	3.30	6.22	10.8	**52.7**	4.82	24.9
Ile Marun	0.00	3.53	11.1	78.5	12.6	12.9	23.1
Abayomi	0.00	4.69	13.3	**82.3**	17.6	9.89	43.5
Oladoke	0.00	3.41	11.6	40.1	12.1	25.0	**64.9**
Onipepeye	0.00	**5.04**	6.56	0.50	4.63	5.78	46.1
ADULT							
Loyola	0.00	0.51	1.51	0.21	2.72	9.49	3.11
Ajumobi Mkt	0.00	0.40	**3.34**	5.61	3.19	1.65	3.85
Akinloye	0.00	0.53	1.12	3.56	0.00	**11.6**	1.61
Conoil	0.00	0.66	1.00	0.25	0.74	0.28	1.90
Agbala	0.00	0.18	1.22	4.92	1.73	2.99	4.40
Idi-Kanga	0.00	0.44	0.84	1.45	**7.07**	0.65	3.35
Ile Marun	0.00	0.47	1.49	10.5	1.69	1.73	3.09
Abayomi	0.00	0.63	1.79	**11.0**	2.36	1.33	5.84
Oladoke	0.00	0.46	1.55	5.38	1.62	3.35	**8.70**
Onipepeye	0.00	**0.68**	0.88	0.067	0.62	0.78	6.19
RfD	**0.01**	**0.003**	**0.02**	**0.04**	**0.02**	**0.0036**	**0.14**

4.5.1.3 Carcinogenic Risk (TCR) in soil

Estimation of the Cancer Risk (CR) for Pb, Cd Cr, and Ni in soil samples from the two LGAs is presented in Table 4.17-4.18. Based on the result of this study, the CR factor for Pb, Cd Cr, and Ni over a lifetime of exposure through contaminated soil are below the tolerable value of lifetime carcinogenic risk set by USEPA (10^{-5}), indicating that the contact with the soil might not pose a carcinogenic risk.

Table 4.17 Target Carcinogenic Risk (TCR) for heavy metals in Soil of automechanic workshop in IBN LGA

LOCATION	CHILDREN				ADULT			
	Cd ($\times10^{-5}$)	Cr ($\times10^{-6}$)	Ni ($\times10^{-6}$)	Pb ($\times10^{-7}$)	Cd ($\times10^{-6}$)	Cr ($\times10^{-6}$)	Ni ($\times10^{-7}$)	Pb ($\times10^{-8}$)
Secretariat	0.00	11.50	0.99	0.92	0.00	1.55	1.33	1.24
Bodija	0.00	7.96	1.01	4.40	0.00	1.07	1.36	5.90
trans	0.00	0.98	1.17	2.67	0.00	0.13	1.57	3.58
Samonda	2.94	3.22	0.49	1.26	3.94	0.43	0.65	1.69
Orogun	0.00	7.00	1.09	1.70	0.00	0.94	1.47	2.28
NTA	0.00	8.67	4.00	26.40	0.00	1.16	5.37	35.40
Oke-Itunu	0.00	12.40	1.68	3.88	0.00	1.67	2.25	5.20
UCH1	0.61	1.20	1.44	5.17	0.82	0.16	1.93	6.94
UCH2	0.00	4.06	2.71	37.0	0.00	0.54	3.64	49.60
Dandaru	0.00	7.12	1.13	2.08	0.00	0.96	1.52	2.79

Table 4.18: Target Carcinogenic Risk (TCR) for heavy metals in Soil of automechanic workshop in IBNE LGA.

LOCATION	CHILDREN				ADULT			
	Cd	Cr ($\times10^{-6}$)	Ni ($\times10^{-6}$)	Pb ($\times10^{-7}$)	Cd	Cr ($\times10^{-7}$)	Ni ($\times10^{-7}$)	Pb ($\times10^{-7}$)
Loyola	0.00	5.66	2.04	21.70	0.00	7.59	2.74	2.91
Ajumobi Mkt	0.00	4.42	4.53	3.76	0.00	5.93	6.08	0.51
Akinloye	0.00	5.87	1.52	26.50	0.00	7.87	2.03	3.55
Conoil	0.00	7.33	1.35	0.65	0.00	9.84	1.82	0.087
Agbala	0.00	2.01	1.66	6.81	0.00	2.70	2.22	0.91
Idi-Kanga	0.00	4.96	1.13	1.47	0.00	6.65	1.52	0.020
Ile Marun	0.00	5.29	2.02	3.94	0.00	7.10	2.71	0.53
Abayomi	0.00	7.03	2.43	3.02	0.00	9.44	3.26	0.41
Oladoke	0.00	5.12	2.10	7.64	0.00	6.87	2.82	1.02
Onipepeye	0.00	7.57	1.19	1.77	0.00	10.20	1.60	0.24

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Chapter Five

Conclusion and Recommendation

5.1 Summary of Findings

In summary, the Physico-chemical parameters of the studied hand-dug groundwater samples from the twenty (20) randomly selected automobile workshops within the two Local Government Areas (IBN and IBNE) from Ibadan ranged from 8.18 to 8.40, 73 to 394 mg L^{-1}, 148 to 790 mg L^{-1} and 295 to 300 µS cm^{-1} for pH, TDS, Conductivity and Total Hardness respectively. Elemental results showed that although the average concentrations of Ni and Cu in water samples were below the WHO permissible limits, average concentrations of Cr, Mn and Pb were above the WHO permissible limits for safe drinking water. Also, the average elemental concentrations in soil samples from the twenty randomly selected automobile workshops were below the WHO permissible limits. Data from health risk assessment suggested that there is a significant chance of non-carcinogenic effects via consumption of water from the hand-dug Wells in these randomly selected automobile workshops.

5.2 Conclusion

This study showed that several activities in automobile workshops can lead to contamination of environmental media such as soil and water. Data from this study also showed that the average concentrations of Cr, Mn and Pb were significantly elevated in more than 90% of the randomly selected hand-dug Wells found in these automobile workshops. Health risk assessment also confirmed that prolong consumption of water from these hand-dug Wells can lead to adverse health problems. Hence, the proximity of automobile workshops to human settlements can generate negative impacts on the environment and human health through groundwater contamination.

5.3 Recommendation

Based on the outcome of this study, the following are hereby made recommended:

i. Siting automobile workshops in close vicinity to human settlement should be discouraged.

ii. Indiscriminate disposal of wastes generated from automobile workshop activities should be abolished.

iii. Automobile workers should be educated on some health issues they may likely encounter.

iv. Proper Environmental Impact Assessment (EIA) should be carried out before establishing automobile workshops.

v. Government should endeavor to monitor the activities of automobile workshops, especially those close in vicinity to human settlements, and also provide potable water.

vi. Further research should be carried out on the likely hazards of automobile workshops in Nigeria.

5.4 Contribution to Knowledge

This study adds to the body of knowledge on the assessment of heavy metals in auto-mechanic shops. The findings of this research would serve as a good source of information to auto-mechanic workshop artisans and host communities on the health risks associated with the improper disposal of spent oil, metal scraps and other wastes generated from automobile workshops.

5.5 Area for Further Research

Future studies on the health dangers related to improperly disposing of spent oil and other auto-mechanic waste in Nigerian auto-mechanic workshops are anticipated to build on the findings of this study.

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APPENDIX I

Auto-mechanic workshop around Secretariat

APPENDIX II

Sampling site at Orogun

APPENDIX III

Sampling Site at UCH1m showing Artisans (Panel beaters) on duty

APPENDIX IV

Sampling site at Onipepeye (Showing artisans at work)

APPENDIX V

Sampling site at Bodija

APPENDIX VI

Collection of water sample from the Well at Samonda Mechanic village

APPENDIX VII

Sampling site at Ajumobi market

APPENDIX VIII

Wreckage of a car at Dandaru sampling site

Bio-data

A. Personal Data

Full Names	**Adeola Ebenezer Olalekan**
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Place of Birth	Ibadan
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B. Education Background with Qualifications

Lead City University, (BSc. (Hons) Chemistry)	2015-2017
FUNAAB, Abeokuta (PGD) in (Planning, Research and Statistics)	2005 - 2007
University of Ibadan (HND), Lab. Science (Chemistry/Biochemistry option)	1991-1997
Odo- Ona High School, Ring Road, Ibadan (West Africa School Certificate)	1983 -1988

C. Work Experience with Dates

State Ministry of Health, Secretariat, Ibadan.	2003 to date
World Health Organization, UCH, Ibadan.	2000 to 2002
Gamma Laboratories limited, Mokola, Ibadan.	1999 to 2000
National Youth Service Corps (Cross Rivers State)	1998 to1999

D. Membership of Academic Professional Bodies

Nigeria Institute of Science Laboratory Technology (NISLT) 2006 to date

Institute of Personality Development and Customer Relationship Management (IPD-CRM) 2017

E. Publications, Thesis and Dissertations

* Absorbent of colour from Textile effluent using modified (expoxidized) and unmodified Latex Rubber (*Haveabrasiliensis*), Final year thesis in Analytical Chemistry, Department of Chemical Science, Lead City University, Ibadan, 2017.

* Analysis of carbide lime and its Economic importance in the production of calcium compounds, a final year research Project in industrial chemistry, University of Ibadan.

* Survey/Analysis on Nutrition, Breast feeding and infant mortality an implication for Family Planning: Lagos State Metropolis a case study.

Signature	**Date**

University Compliance Certification

This is to certify that this Thesis was written by ADEOLA, EBENEZER OLALEKAN with Matric Number LCU/PG/000463 of the Department of Chemical Sciences (Chemistry Unit), Faculty of Natural Sciences, Lead City University, Ibadan is in full compliance with the approved University format and style.

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Name   **Date**