QUALITY OF SOIL AND GROUNDWATER IN AUTOMOBILE WORKSHOPS IN AKINYELE LOCAL GOVERNMENT AREA, OYO STATE, NIGERIA

BY

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A DISSERTATION SUBMITTED TO THE UNIVERSITY OF IBADAN IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF PUBLIC HEALTH (ENVIRONMENTAL HEALTH) DEGREE

DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCES
FACULTY OF PUBLIC HEALTH
COLLEGE OF MEDICINE
UNIVERSITY OF IBADAN, NIGERIA

SEPTEMBER, 2014

CERTIFICATION

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DEDICATION

This research work is dedicated to the Almighty God who alone deserves all thanks and appreciation.

ACKNOWLEDGEMENTS

I thank the Almighty God for the privilege to be a part of this programme, for strength, wisdom, favor and success throughout the duration.

I specially appreciate my supervisor Dr. Elizabeth O. Oloruntoba, who has been like a mother. I'm grateful for her words of encouragement, constructive criticism and advice. I sincerely appreciate Dr G.R.E.E Ana for his counsel and encouragement from the inception of this programme, checking on me to ensure my progress. I also thank my other lecturers Prof. Sridhar, Dr O.T. Okareh and Dr O. M. Bolaji for their inputs and advice. A big thank you to Mrs Adeola Osuntade for her assistance, advice and help rendered especially during my laboratory analysis and also Mrs Adebiyi and Mrs Kehinde for their support and words of encouragement. To the entire members of staff, Environmental Health Sciences (EHS), I say a big thank you for all the assistance given.

Sincere appreciation to my collegues, (past and present) for their advice and support, Luqman, Lawrence, Fakunle, Olapeju, Adewale Adeyemi, Ayoola Ojewusi, Zainab, Busola, Osas, Lamide, John, Jibike, Sayo, Biodun, Engr. Paul, Engr. Remi, Dr Feyi, Joy, Cynthia, Anna, Mayowa, Samuel, Akin, Ife and Dotun. Special thanks to Nafisat for your help and encouragement. God bless you.

To my parents, Revd. Dr. and Mrs P.A Ogunbunmi, thanks for everything. You were there with me from start to finish, every step of the way. I sincerely appreciate you and I trust God, you will live to reap the fruit of you labour. To my siblings, 'Bamise Olanrewaju and 'Tomipe Ogunbunmi, thanks for all you did to help me achieve this. Words cannot express my gratitude. To my in-laws, Rev. and Mrs J.S.O Ogundipe, many thanks for your support, sacrifice, time, prayers and encouragement through and through, God bless you real good.

To my children Oluwawapelumi and Erioluwa, thank you for understanding in your own little way all that we went through together to make this programme a success. I love you dearly. To my one and only husband, Adekunle Ogundipe, I sincerely love and appreciate everything you have done to help me get through this. Thank you for standing by me, helping me out, understanding and coping even when it was inconvenient. God bless you richly.

To all those whose names are not mention and have assisted me in different way, I sincerely appreciate you all.

TOLUWANIMI.O OGUNBUNMI

ABSTRACT

Heavy metal contamination from activities in automobile workshops is of public health concern. These heavy metals have capacity to remain in the environment over time. Several studies have been conducted on industrial water pollution but limited investigations have been carried out on water and soil quality around automobile workshops. This study therefore, was designed to assess the quality of soil and groundwater in automobile workshops in Akinyele Local Government Area (ALGA).

A Simple random sampling technique was employed to select three of six zones of automobile workshops in ALGA: Alphonso, Temidire and Ojoo with one residential area (Moniya - control site). Eight automobile workshops were selected from each zone based on: absence of other industries and presence of dug wells. Water samples were collected from dug well (0-50 m) around the workshops. Physico-chemical parameters (Total Dissolved Solids (TDS), Electrical conductivity, pH and Oil and grease) and heavy metals (Copper (Cu), Chromium (Cr) Cadmium (Cd) and Lead (Pb)) were determined using standard methods. Grab samples of top and sub soils were collected from the three locations and analysed. Values obtained were compared with WHO standards for potable water quality and United Kingdom Permissible Limits for soil quality. Data were analysed using descriptive statistics and ANOVA at $p<0.05$.

Mean results of water analysis revealed that TDS and Electrical conductivity for Alphonso, Temidire, Ojoo and Moniya were within WHO limits. The mean pH was 6.4±0.8, 6.8±0.7, 6.7±0.4 and 7.6±0.2 in Alphonso, Temidire, Ojoo and Moniya respectively. Median oil and grease content 1245 mg/l, 206 mg/l and 2650 mg/l in Alphonso, Temidire and Ojoo respectively, were above WHO limits. In the dug wells, mean concentrations of Cu (mg/l) was significantly higher in Alphonso (2.5±2.06) than other zones. Mean concentration of Cr (mg/l) was 0.34±0.28, 0.37±0.13 and 0.31±0.3 for Alphonso, Temidire and Ojoo respectively while it was not detected in Moniya. The median concentration for Cd (mg/l) in Alphonso, Temidire, Ojoo and Moniya were higher than the WHO limits. Lead was absent in all locations except Alphonso 8.50(0.0 -35.8) mg/l. Mean concentrations of all the metals were higher in all the zones than Moniya and WHO limits except for Cu in Temidire and Ojoo. In the soils, mean concentration of Cu (mg/kg) in Alphonso, Temidire, Ojoo and Moniya was 21.55±9.03, 50.41±2.65, 44.27±3.04 and 19.19±2.82 respectively. Mean concentrations of Cr (mg/kg) in Alphonso, Temidire, and Ojoo was 18.52±2.2, 22.52±3 and 15.4±1.73 respectively. Mean concentrations of Cd(mg/kg) in Alphonso, Temidire and Ojoo was 7.89±1.9, 5.3±3.14 and 6.07±5.6 respectively while mean concentrations of Pb (mg/kg) in Alphonso, Temidire and Ojoo was 80.19±7.43, 35.41±4 and 77.77±3.58 respectively. The mean concentrations of all the heavy metals (except Cd) were within the permissible limits for soil quality but higher than the control across the selected zones.

The concentration of heavy metals above regulatory limits in soils and dug wells indicates contamination. There is the need for strict enforcement of safe waste handling methods to reduce soil and water contamination around automobile workshops.

Keywords: Automobile workshops, Dug well, Heavy metal contamination

Word count: 483

TABLE OF CONTENTS

CHAPTER ONE

INTRODUCTION

CHAPTER TWO

LITERATURE REVIEW

CHAPTER THREE

METHODOLOGY

CHAPTER FOUR

RESULTS

CHAPTER FIVE
DISCUSSION

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

GLOSSARY OF WORDS AND ABBREVIATIONS

ALGA	Akinyele Local Government Area
ANOVA	Analysis of Variance
APHA	American Public Health Association
ATDSR	Agency for Toxic Substances and Disease Registry,
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
Cd	Cadium
Cr	Chromium
CSEM	Case Studies in Environmental Medicine
Ctc	Carbon Tetrachloride
Cu	Copper
DCM	Dichloromethane
1,2-Dca	1,2- Dichloroethane
1,1-Dce	1,1-Dichloroethene
1,2- Dcb	1,2 Dichlorobenzene
1,4-Dcb	1,4 Dichlorobenzene
ECB	European Chemicals Bureau
ECDGE	European Commission Director General Environment
EPA	Environmental Protection Agency
EU	European Union
FLAA	Flame Atomic Absorption Spectroscopy
IARC	International Agency for Research on Cancer
IAEG	International Association for Engineering, Geology and Environment
IFAS	Institute of Food and Agricultural Sciences
IOM	Institute of Medicine
IPCS	International Programme on Chemical Safety
IRIS	Integrated Risk Information System
LGAs	Local Government Areas
MCL	Maximum Contaminant Level
NEMA	Natural Environment Management Authority
ND	Not Detected

NPC	National Population Commission
NRC	National Research Council, 2000
NRCS	Natural Resources Conservation Service
NSDQW	National Standard for Drinking Water Quality
NSF	National Science Foundation
NTP	National Toxicology Program
PAH	Poly Aromatic Hydrocarbons
Pb	Lead
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated Dibenzodioxins
PCDFs	Polychlorinated Dibenzofurans
Pce	Perchloroethylene
POPs	Persistent Organic Pollutants
SPSS	Statistical Package for Social Sciences
Tcm	Trichloromethane
Tce	Trichloroethene
UK	United Kingdom
UN	United Nations
UNESCO	United Nations Organization for Education, Science and Culture
UNEP	United Nations Environment Programme
UNFAO	United Nations Food and Agriculture Organization
USDA	United States Department of Agriculture,
USEPA	United States Environmental Protection Agency
Vc	Vinyl Chloride
VOCs	Volatile Organic Compounds
WHO	World Health Organization
%	percentage
cm	Centimetre
mm	milimitre
mg/kg	milligram per kilograme
ug/l	microgramme per litre

ug/kg	microgramme per kilogramme
mg/l	miligramme per litre
E/C	Electrical Conductivity
μScm^{-1}	micro Siemens per centimetre
^{0}C	degree celcius
K_{ow}	Octanol-water partition coefficient

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND INFORMATION

Soil and water contaminants have over the years being described by researchers as substances that cause threat to the existence of man, plant and animals. They occur in various degrees, forms and quantity. Some of these contaminants include used oils which are generally seen in mechanic workshops, where automobiles and various car parts are serviced and repaired. These contaminants contain heavy metals which have adverse effect on man. These workshops are sometimes characterized by various operators functioning in areas such as spraying or painting, welding (arc/electric), battery recharging and repairs, car servicing and maintenance (Adelekan and Abegunde 2010). The workshop size varies depending on the number of function and services which they carry out on regular basis.

Over the years mechanic workshop operators have been conducting their daily operations thus dumping their used oil, grease and toxic liquids indiscriminately in the environment. These substances are usually high in hydrocarbons and heavy metals which have adverse effect on the natural wellbeing of the environment. Most operators drop these waste materials indiscriminately where they are later absorbed by the soil or washed into the nearby water bodies which in-turn contaminate the water rendering it harmful when consumed or used in its raw state.

Nwachukwu *et al.*, (2010) revealed that poor waste management of mechanic workshops around the country are causing serious ecological and public health concerns. These wastes include; engine gear waste oil, panel beating carbide, wielding and soldering wastes and accidental spills from other fluids used in the workshop. Also, according to Udeani *et al.*, (2009) complex mixture of hydrocarbons are observed in petroleum products such as engine oil, diesel, petrol and kerosene which are used on regular basis by mechanics in their workshop. They revealed that environmental pollution occurs due to spillage and improper disposal of these products either in low or large quantity. When this spillage occurs, the likelihood that hydrocarbon reaches the water table before becoming immobilized in the soil or spread horizontally on the ground water surface is relatively high. This continues to percolate into ground water, soil pore space, air and to the surface of soil particles. Examples of such hydrocarbon include Benzene, Toluene, Ethylbenzene and Xylene (BTEX) which are toxic substances, harmful to the body when inhaled or ingested.

According to Oastridge and Trent (1999), the World Health Organization (WHO) estimates that safe drinking water is unavailable to over 20% of the world population (about 1.3 billion people) and there is inadequate sanitation for over 40% of all populations. Poor water quality remains an important problem in several parts of the world. As a result, vital resources are limited and in dire circumstances, cause harm to human and other forms of life (Forum and Entwicklung, 2001). Water pollution can arise when substances dissolve in it. These could either be solid particles or insoluble liquid droplets that become suspended in it (Plant *et al.*, 2001). These substances include heavy metals and hydrocarbons which are found in water most times as a result of soil contamination from certain activities and subsequent percolation.

1.2 PROBLEM STATEMENT

Organic compounds found in petrol and petroleum products as well as heavy metals (such as those found in the mechanic workshops) have the capacity to remain in the environment over time when exposed and hence can pose serious health effects. These may range from body pains to head ache, fatigue, respiratory problems and may even cause death when inhaled or ingested in high concentrations.

Groundwater is one of the most important available sources of water in many areas in Nigeria and it is essential for survival. Many communities depend on hand-dug wells which are means of gaining access to groundwater. This is because of accessibility and affordability. Therefore, groundwater should be protected and preserved from all forms of contamination and pollution that can cause health problems.

1.3 JUSTIFICATION

The increase in the number of mechanic workshops and activities (such as auto servicing and repairs) in Nigeria due mainly to the large inflow of 'Fairly Used' vehicles into the country in the late 1990s have contributed greatly to the pollution experienced within and around these workshops. Several studies have been carried out on water pollution and contamination from industries and some manufacturing companies while very little research has been done on the soil and groundwater quality surrounding automobile workshops.

Therefore there is a need for monitoring of surface and groundwater quality as well as soil quality from time to time to detect areas that are at risk of high pollution with a view to providing remedial measures from the outcomes.

1.4 RESEARCH QUESTIONS

1. What are the physico-chemical parameters of the soil and groundwater samples around the workshops?
2. What is the concentration of organic compounds such as Benzene, Toluene, Ethylbenzene, Xylene (BTEX) in soil and groundwater samples around the workshops?
3. What is the sanitary status of groundwater sources around the mechanic workshops?
4. What is the attitude of automobile mechanics to the waste generated in the workshop?

1.5 OBJECTIVES

Broad Objective

The broad objective of this study was to assess the soil and groundwater quality in automobile workshops in Akinyele Local Government Area (ALGA) Oyo State.

Specific Objectives

The specific objectives were to:

- determine the levels of physico-chemical parameters such as pH, temperature, acidity, alkalinity, colour, turbidity, electrical conductivity, dissolved solids, oil and grease, Lead, Chromium, Cadmium and Iron in soil and groundwater samples
- determine the concentration of organic compounds such as Benzene, Toluene, Ethyl-benzene, Xylene (BTEX) in soil and groundwater samples around the workshop.
- assess the sanitary status of the groundwater sources

- assess the attitude of mechanic operators to the waste generated in the workshop.

CHAPTER TWO

LITERATURE REVIEW

2.1 SOIL

2.1.1 Definition

Soil is the thin layer covering the entire earth's surface except for open water surfaces and rocks. It can also be referred to as the material in the top layer of the surface of the earth in which plants can grow (Kang *et al.*, 1990). It is a complex environment of minerals, organic material, water, gases and living organisms. According to Turgeon 2006, the soil is a natural, unconsolidated mineral or organic material on the immediate surface of the earth that serves as a natural medium for the growth of land plants. It not only supports a huge number of organisms below its surface (bacteria, fungi, worms, insects, and small mammals) but it is essential and supports to all life on the planet. The soil is one of the important and valuable resources of the nature. Life and living on the earth would be impossible without it soil. Moreover, 95% of human food is derived from the earth (Mahdeloei *et al.*, 2012). The soil is composed of 50% of organic and inorganic matters, and 50% of air and water which fills existing vacant spaces of the soil and keeps live organisms of the soil.

2.1.2 Soil profile

Structurally, soils are composed of a series of horizons or layers. These layers differ appearance, thickness, and properties (Broderson, 2000). The horizons are normally parallel to the surface. Collectively, the horizons make up what is called the soil profile or soil "pedon". A soil profile is defined as a vertical section of the soil to expose layering. A standard soil has six layers: O, A, E, B, C and R (Figure 2.1). In soil classification, each layer has distinctive features that characterize it. Each soil layer is given a certain letter designation to indicate where it is in relation to the surface of the soil (Kang and Tripathi, 1992).

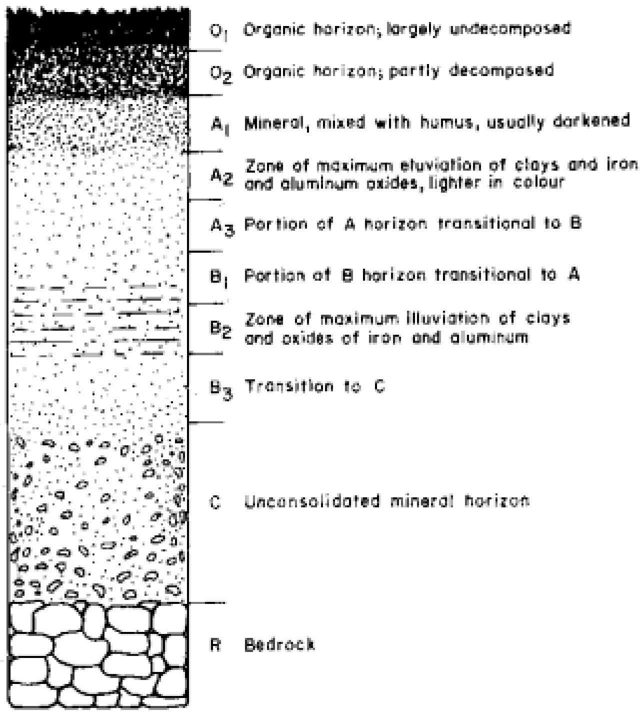


Figure 2.1 A hypothetical soil profile (Kang and Tripathi 1992)

2.1.3 Soil structure and Texture

Soil structure is the size, shape and strength of the naturally occurring soil aggregates (called peds). It creates a framework of aggregates and establishes the pore space in the soil. Many things contribute to soil structure including texture, organic and mineral composition, water content, soil organisms, biological processes such as root growth etc. Healthy soils tend to have soil particles that are bonded together into clumps or groups. The arrangement of these aggregates in the soil, along with the gaps and fissures between them, are part of what constitute soil structure. Adequate organic matter is usually required for good soil structure in surface horizons. The spaces between aggregates are important pathways for water and roots to move through the soil profile (Meyer, *et al., 2010)*. There are four main types of soil structure viz;

- Platy (plate like)
- Prismatic (columnar)
- Blocky

- Granular (crumb)

Individual soil aggregates may have differing shapes but some aggregate shapes indicate better soil structure considering plant growth. Platy structure has the potential to restrict air and water movement and hence reduce plant growth. Granular aggregates allow good plant growth because there is good water and air movement and the soil is less compact than other structure types. Blocky structure is also generally favourable to plant growth. (Cogger, 2005)

Soil Texture

Soil Texture is the relative proportion of sand, silt and clay particles found in the soil. It also refers to the size of the particles that make up the soil (IFAS, 2003). Soil texture is an important soil characteristic that influences rate of infiltration of stormwater. The textural class of a soil is determined by the percentage of sand, silt, and clay. The relative fraction of these soil particles is important since it can aid in determining the soil's water holding capacity, aeration, drainage and plant root depth (UW-CMN, 2011). Studies by Fraser, 2000 shows that the water holding capacity of the soil can determine how much each soil type can handle or retain per volume of water as observed in situations where there is heavy rainfall and loose soils drain more freely. Soils can be classified as one of three major textural classes: sands, silts, and clays. Particles that range in size from 0.05 -2.0 mm are sand. Those between 0.002-0.05 mm are referred to as silt and the smallest particles are clay with a size less than 0.002 mm (Table 2.1).

Table 2.1: Particle size ranges for sand, silt, and clay in millimetres (mm)

Type of Mineral Particle	Size Range
Very coarse sand	2.0 -1.0 mm
Coarse sand	1.0-0.5 mm
Medium sand	0.5-0.25 mm
Fine sand	0.25-0.10 mm
Very fine sand	0.10-0.05 mm
Silt	0.05 - 0.002 mm
Clay	less than 0.002 mm

Source: (IFAS, 2003)

2.1.4 Soil Quality

The concept of soil quality emerged in the literature in the early 1990s (Doran and Safely, 1997; Wienhold *et al.*, 2004), and the first official application of the term was approved by the Soil Science Society of America Ad Hoc Committee on Soil Quality (S- 581) and discussed by Karlen *et al.*, 1997. Soil quality was been defined as ‘‘the capacity of a reference soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation.’’(Doran and Parkin, 1994). Also, Parr *et al.*, 1992 defined it as he capability of soil to produce safe and nutritious crops in a sustained manner over the long-term, and to enhance human and animal health, without impairing the natural resource base or harming the environment. Sometimes soil quality is referred to as soil health. Subsequently the two terms are used interchangeably (Karlen *et al.*, 2001) although soil quality is related to soil function (Karlen *et al.*, 2003; Letey *et al*, 2003), whereas soil health presents the soil as a finite non-renewable and dynamic living resource (Doran and Zeiss, 2000).

2.1.4.1 Soil quality Indicators

Soil quality cannot be measured directly therefore, indicators are used to provide clues. Indicators are measurable properties of plants and soil. They are often grouped as follows:

- Physical indicators
- Biological indicators
- Chemical indicators

Biological Indicators

Several authors have reported identification of biological indicators of soil quality is reported as seriously crucial (Doran and Parkin, 1994; Abawi and Widmer, 2000) due to soil quality being strongly influenced by microbiological intervening processes (nutrient cycling, nutrient capacity, aggregate stability). Specific importance is to attached to identification those constituents that respond quickly to changes in soil quality (Romig *et al.*,1995). Biological indicators of soil quality that are usually measured include soil organic matter, respiration, microbial biomass (total bacteria and fungi,) and mineralizable nitrogen. The role of soil organic matter in soil function is important in the determination of soil quality, water holding capacity and susceptibility of soil to degradation (Cadisch and Giller 1997; Feller *et al.*, 2001). Also, soil organic matter may serve as a source or sink to atmospheric CO_2 (Lal and Stewart, 1995) and an increase in the soil Carbon content is indicated by a higher microbial biomass and elevated respiration (Sparling *et al.*, 2003). It is also the main reserve of nutrients such as Nitrogen (N) in the soil and some tropical soils may contain large quantities of mineral N in the top 2m depth (Havlin *et al.*, 2005).

Chemical Indicators

Smallholder farmers have to provide soil nutrients in large quantities to attain high crop yields (Sanchez and Swaminathan, 2005). Hence the possibility of altering the available nutrients by adding inorganic fertilizers, incorporating cover crops, and using other organic materials in form of manures and composts (Stocking, 2003). Soil quality indicators provide information on the capacity of soil to supply mineral nutrients, which is depends on the soil pH. Soil pH is an estimate of the activity of hydrogen ions in the soil solution. It influences plant growth by affecting plant nutrient availability, toxic metal availability and soil microorganism activity. Chemical properties include bulk density, aggregate stability and penetrate resistance.

Physical Indicators

Soil physical properties are estimated from the soil's texture, bulk density (a measure of compaction), porosity, water-holding capacity, profile depth, infiltration, penetration resistance (Karlen *et al.*, 2001). These properties are all improved through additions of organic matter to soils. Consequently, the suitability of soil for sustaining plant growth and biological activity is a function of its physical properties (porosity, water holding capacity, structure, and tilt).

2.1.5 Soil Pollution

Soil pollution is defined as the build-up in soils of persistent toxic compounds, chemicals, salts, radioactive materials, or disease causing agents, which have adverse effects on plant growth and animal health. Table 2.2 shows some sources of contaminants and their possible health. Soil is a key component of natural ecosystems because environmental sustainability depends largely on a sustainable soil ecosystem (Adriano *et al.*, 1998). When soil is polluted (contaminated), the ecosystem is altered and agricultural activities are affected. Some important soil contaminants include agricultural pesticides, fungicides or herbicides, heavy metals and persistent organic compounds. Risks from soil contamination include plants absorbing contaminants through the soil; groundwater becoming contaminated as it interacts with and flows beneath the soil; and bioaccumulation, occurring when livestock or humans ingest contaminants from vegetation growing in compromised soil (Rosen, 2002).

Table 2.2 Common Sources of contamination

General Source	Specific Contaminant
Paint (‹ 1978)	Lead
High Traffic Areas	lead, zinc, PAHs
Treated Lumber	arsenic, chromium, copper
Burning Wastes	PAHs, dioxins
Manure	coppers, zinc
Coal Ash	molybdenum, sulfur
Sewage Sludge	cadmium, copper, zinc, lead, PBTs
Petroleum Spills	PAHs, benzene, toluene, xylene
Commercial/Industrial Site Use	PAHs, petroleum products, solvents, lead, other heavy metals
Pesticides	lead, arsenic, mercury (historical use), chlordane and other chlorinated pesticides

Source: Heinegg et al., 2000

2.1.5.1 Heavy Metals

Heavy metals are one of the many classes of substances that can reach vital levels in terms of human health, food safety, soil fertility and ecological risks (Jarup 2003; Sharma and Agrawal 2005). Heavy metals are common contaminants in the soil. The retention of heavy metals in the solid phase of the soil is depends mainly on the pH, and is linked to humic substances, clay minerals, iron oxides and hydroxides, and manganese found in the soil.

2.1.5.2 Persistent Organic Pollutants (POPs)

Among the many organic compounds present in soil, the most dangerous are the persistent organic pollutants that are derived in general, from anthropical activity; they are extremely persistent in the environment and are transported for long distances (Armitage and Gobas, 2007; Christensen, 1998, Hallin-Sorensen *et al.*, 2006). Under certain environmental conditions they bioaccumulate and biomagnify, reaching significant concentrations that represent a threat for human health and ecosystems. Three out of the twelve groups of persistent organic pollutants, are acknowledged internationally viz; polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). They are present both in natural soils, due to long-distance transport, and in soils that have been contaminated by particular industrial activities (Beyer and Bizuik, 2007). Due to their high persistence in the environment, they remain in soil, which become pollutant reservoirs (Pohl *et al.*, 1995). These POPs are carcinogenic agents for humans (Dickson and Buzik, 1993).

2.1.5.3 Agricultural Applications

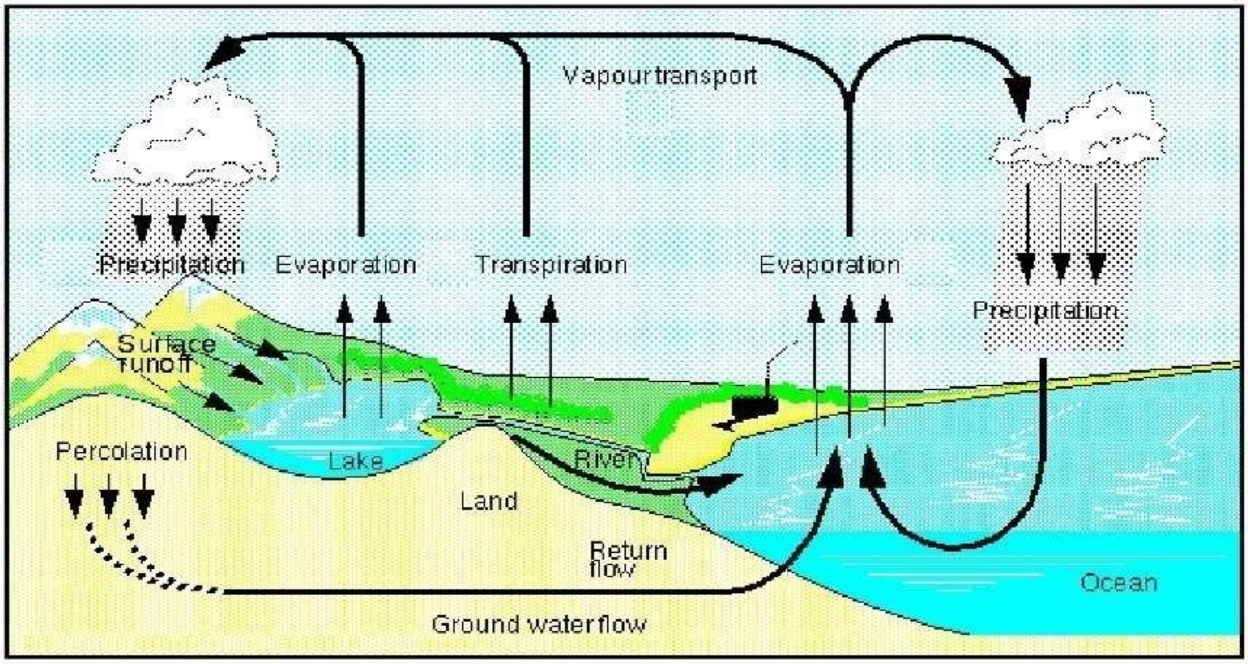
Excessive use of agricultural fertilizers (Hallberg and Kenney 1993) and pesticides, antibiotics and hormones in livestock and irrigating farms with contaminated wastewaters are agricultural factors affecting soil pollution. Pesticides enter the soil in different ways viz: direct application to soil, spraying and return of pesticides particles suspended in the air directly to the ground, toxins absorbed on surface of soil particles suspended in air and their sitting on the ground and plant residues that are added to the soil and the toxins absorbed by the soil organisms (non-lenticular). Chemical fertilizers change properties of the soil i.e. lessen soil permeability to the air and water. Generally, chemical fertilizers harden soils. Chemical pesticides create soil pollution as well (Schreier *et al., 1998*). These toxins are not decomposed easily and will remain in soil for many years

2.1.6 Human Exposure to Soil Contaminants

In general, there are three ways in which people are exposed to contaminants in soil: ingestion (eating and drinking), dermal exposure (skin contact), and inhalation (breathing) (Anigma & Sullivan, 2008; Rosen, 2002; Shaylor *et al.*, 2009b). People may accidentally ingest small amounts of soil during activities such as yard work, gardening, or playing. Ingestion also occurs when people eat farm produce grown in contaminated soil. Some contaminants, such as pesticides, can be absorbed through the skin when people come into contact with the soil. In addition, people can inhale airborne soil particles, such as dust, or contaminants that have vaporized from the soil after precipitation.

2.2 WATER

The total amount of water on the earth and in its atmosphere does not change but the earth's water is always in movement. Water undergoes different forms of movement and changes of its physical state in the nature on a given area of the Earth (a river or Lake Basin, a continent, or the entire Earth). Oceans, rivers, clouds and rain, all of which contain water, are in a frequent state of change and the motion of rain and flowing rivers transfers water in a never-ending cycle (Figure 2.2). This continuous process of circulation and conservation of earth's water as it circulates from the lithosphere to atmosphere is referred to as the 'hydrological cycle' or 'water cycle' (Kuchment, 2004). This hydrological cycle extends through the four parts of the earth system and depends largely on the local uniqueness of these systems.



Source: Max Planck Institute for Meteorology

Figure 2.2 Schematic representation of the hydrological cycle.

2.2.1 Ground Water

The largest liquid water store of the terrestrial hydrological cycle is represented by groundwater ((Kuchment, 2004). It is the most important component of the active terrestrial hydrological cycle (WHO, 2006). Groundwater is water located beneath the earth's surface or underground in cracks and soil pore spaces, in sand and in the fractures of rock formations. It is stored in-and moves slowly through-layers of soil, sand and rocks called aquifers. Groundwater can be found almost everywhere. It accounts for about two-thirds of the freshwater resources of the world and of the global quantity of available freshwater, more than 98% is groundwater stored in pores and fractures of rock strata (Scanlon *et al.*, 2005, WHO, 2006). In recent years there has been considerable attention paid to the concept of the world water balance (Table 2.3) and the most recent estimates of these data emphasize the ubiquitous nature of groundwater in hydrosphere.

2.2.2 Importance of Groundwater

Groundwater is an important resource which can act as a natural storage that can buffer against shortages of surface water, as in during times of drought. Groundwater is not only abstracted for supply or river regulated purposes, it also naturally feeds surface-waters through springs and passages into rivers and it is often important in supporting wetlands and their ecosystems. Groundwater is also an important source for industry and agriculture uses as well as sustaining rivers experiencing low flows (UNESCO, 1996). It is naturally replenished by surface water from precipitation, streams, and rivers as well as by rain and snow melt.

Table 2.3 Estimate of Water Balance of the World

Parameter	Surface area ($10^6 km^2$)	Volume ($10^6 km^2$)	Volume (%)	Resident time
Oceans and seas	361	1370	97	~ 4,000 years
Lakes and reservoirs	1.55	0.13	< 0.01	~ 10 years
Swamps	< 0.1	< 0.01	< 0.01	1-10 years
River channels	< 0.1	< 0.01	< 0.01	~ 2 weeks
Soil moisture	130	0.07	< 0.01	2 weeks- several year
Groundwater	130	8	0.5	weeks – 100,000
Icecaps and glaciers	17.8	27	2	10-100,000years
Atmospheric water	504	0.01	< 0.01	10 days
Biospheric water	< 0.1	< 0.01	< 0.01	~ 1 week

(Modified from Nace, 1971 and UNESCO, 1999)

2.2.3 Pollution of Groundwater

Water pollution is a serious problem, globally involving the discharge of dissolved or suspended substances into groundwater, streams, rivers and oceans (Alao *et al*, 2010). Over the years, industrialization and urbanization has steadily progressed with little consideration for environmental consequences which has led to groundwater pollution (Longe and Balogun, 2010). In fact, the effects of water pollution are said to be the leading cause of death for humans across the globe, moreover, water pollution affects our oceans, lakes, rivers, and drinking water, making it a widespread and global concern (Scipeeps, 2009). A groundwater pollutant is any substance that, when it reaches an aquifer, makes the water unclean or otherwise unsuitable for a particular purpose. The pollutant could be chemical, microbial or a naturally occurring pollutant (mineral and metallic deposits in rock and soil).

Groundwater pollution can also be related to waste disposal (private sewage disposal systems, land disposal of solid waste, municipal wastewater, wastewater impoundments, land spreading of sludge, brine disposal from the petroleum industry, mine wastes, deep-well disposal of liquid wastes, animal feedlot wastes, radioactive wastes) or not directly related to waste disposal (accidental spills, certain agricultural activities, mining, acid rain, improper well construction and maintenance). Polluted water consists of industrial discharged effluents, sewage water, rain water pollution (Ashraf *et al.*, 2010) and polluted by agriculture or households cause damage to human health or the environment (European Public Health Alliance, 2009) This water pollution affects the health and quality of soils and vegetation (Carter, 1985). Some water pollution effects are immediate, while others are observed in the future, months or years later (Ashraf *et al.*, 2010).

2.2.3.1 Sources of Groundwater Contamination

The sources of groundwater contamination are broadly divided into two groups.

i. point sources and;
ii. non-point sources

Point sources of contamination are identified by a well-defined or specific point of entry where pollutants reach a body of water or re discharges into surface and groundwater (WHO, 2006, ANR, 2002). Typical examples are landfills, leaking underground storage tanks, and municipal and industrial treatment facilities or effluents where treated wastewater is discharged into rivers or streams.

Nonpoint sources of contamination have no easily identified point of entry where pollutants reach a body of water. Contaminants originate from a large variety of sources over a wide area, and they penetrate surface water and groundwater at many locations, by many processes

(WHO, 2006; Mukherjee and Nelliyat, 2007). Pesticides and fertilizers applied to cropland and effluent from septic systems are commonly identified as nonpoint sources of pollution

2.2.3.2 Types Groundwater Pollution

Groundwater pollution can be from nature or as a result of anthropogenic (human) activities, although concern over groundwater pollution has mostly been centred on pollution associated with human activities.

Natural Pollution

Groundwater contains some impurities, even if it is unaffected by human activities. Hence some groundwater pollution occurs naturally. The types and concentrations of natural impurities depend on the nature of the geological material through which the groundwater moves and the quality of the recharge water. Naturally occurring processes such as decomposition of organic material in soils or leaching of mineral deposits can result in increased concentrations of several substances (WHO, 2006). Saltwater encroachment associated with over drafting of aquifers or natural leaching from natural occurring deposits are natural sources of groundwater pollution. Groundwater moving through sedimentary rocks and soils may pick up a wide range of compounds such as magnesium, calcium, and chlorides. Studies have shown some aquifers to have high natural concentration of dissolved constituents such as arsenic, radon, and selenium (Smedley and Kinniburgh, 2001; Hem, 1989; WHO, 2003b; Senior, 1998).

Anthropogenic pollution

Anthropogenic pollution occurs when manmade products such as gasoline, oil, fertilisers, pesticides and other chemicals or get into the water body and cause it to be dangerous and unfit for human use (Asonye *et al.*, 2007). Industrial activity is a major source of pollution. An increase in these activities have led to "*pollutional stress*" on surface water as well as groundwater both from industrial, agricultural and domestic sources (Ajayi and Osibanjo, 1981). Industries vary in size, nature of products, characteristics of waste discharged and the receiving environment. Industrial effluents or run offs contain toxic and hazardous materials from the wastes that settle in receiving water bodies as bottom sediments and constitute health hazards to the urban population that depend on the water as source of supply for domestic uses (Akaniwor *et al.*, 2007). Some of these industries include; metals and mining, breweries, distilleries, textile, chemical and allied and oil and gas industries.

2.2.4 Water Contaminant groups

There are four main groups of contaminants. These are microbial pathogens, organics, inorganics and radioactive contaminants.

Microbial Pathogens

Pathogens in drinking water are serious health risks. Pathogens are disease-producing micro-organisms, which include bacteria (such as giardia lamblia), viruses, and parasites. They get into drinking water when the water source is contaminated by sewage and animal waste, or when wells are improperly sealed and constructed. The zoonotic agents of greatest importance are *Giardia*, *Campylobacter*, *Cryptosporidium*, *Salmonella*, and *E. coli* in outbreaks caused by contaminated drinking water. These organisms can cause gastroenteritis, salmonella infection, dysentery, shigellosis, hepatitis, and giardiasis (a gastrointestinal infection causing diarrhea, abdominal cramps). According to Fawell and Nieuwenhuijsen, (2003) WHO, 1998 estimated that there were 2.5 million deaths and 4 billion cases due to diarrhoeal disease, including dysentery to which waterborne pathogens are a major contributor. Several studies have shown the health effects of water contamination by these organisms (Craun *et al.*, 2004; Kukkula *et al.*, 1997; Payment and Hunter, 2001). A number of pathogen contaminations have often been associated with simple deficiencies in sanitation (Howard *et al.*, 2006)

Organics

Potentially toxic chemicals and metals are capable of contaminating groundwater but only a few of the toxic organic chemicals that occur in drinking water is regulated by drinking water standards. Two organic chemical groups of key concern include:

- aromatic hydrocarbons: benzene, toluene, ethylbenzene and xylenes (BTEX);

- chlorinated hydrocarbons (aliphatic and aromatic): dichloromethane (DCM), trichloromethane (TCM, also known as chloroform), tetrachloromethane (also known as carbon tetrachloride, CTC), trichloroethene (TCE), tetrachloroethene (PCE, also known as perchloroethylene), vinyl chloride (VC), 1,2- dichloroethane (1,2-DCA), 1,1-dichloroethene (1,1-DCE), 1,2-dichloroethene (cis and trans isomers, cDCE and tDCE respectively), 1,2 dichlorobenzene (1,2- DCB) and 1,4 dichlorobenzene (1,4-DCB) (Rivet *et al*., 2006).

A third (predominantly) organic chemical group of key concern in groundwater is pesticides. Studies have shown that at high concentrations in water they are very harmful (WHO, 2004a)

Inorganics

Heavy metals are inorganic pollutants whose presence in the groundwater poses serious environmental risk to humans, animals and even the soil (Akinbile and Yusoff, 2011). Of particular concern are arsenic, mercury, cadmium and lead which are environmental pollutants threatening the health of human population and natural ecosystem (Mercier *et al*., 1998). In non-ferrous metal industries, and industries that produce batteries, pigments, stabilizers and plastics the primary heavy metals discharged are lead, zinc, and cadmium, also cement manufacture results in high emission of mercury as well as these heavy metals except zinc. Arsenic and Zinc gain access to the water environment through mining operations. Nickel and Cobalt are used in the electroplating industry. The discharges of these heavy metals into water bodies are harmful to human health either through direct ingestion or from fish and other animals or plants. Health implications arising from these include; cancer, birth defects genetic mutations or death. Hence, toxic metals are regulated in public water supplies.

2.2.5 Standards for Drinking Water Quality

As standards for several products and services are being put in place, so also has organizations such as World Health Organization (WHO) and Standard Organization of Nigeria (SON) put drinking water quality standards in place so that the health of its nation is not compromised. Table 2.4 shows some of the drinking water standards as published by

Standard Organization of Nigeria (SON) 2007 and WHO guidelines for chemicals that are of health significance in drinking water (2011).

Table 2.4 Drinking Water Standards

Parameter	Unit	SON Maximum permitted levels	WHO guidelines
Physical Parameters			
Colour	TCU	15	-
Odour	-	Unobjectionable	
Taste	-	Unobjectionable	
Temperature	0C	Ambient	
Turbidity	NTU	5	-
Chemical Parameters			
pH	-	6.5-8.5	No guideline
Total Dissolved Solids	mg/l	500	No guideline
Conductivity	µS/cm	1000	-
Sodium	Smg/l	200	200
Sulphate	mg/l	100	500
Nitrate (NO_3^{2-})	mg/l	50	50mg/l/total nitrogen
Nitrite	mg/l	0.2	50mg/l/total nitrogen
Hardness (as $CaCO_3$)	mg/l	150	No guideline
Copper	mg/l	1	2
Lead	mg/l	0.01	0.01
Mercury	mg/l	0.001	0.001
Cadmium	mg/l	0.003	0.003
Aluminium	mg/l	0.2	0.2
Chromium	mg/l	0.05	0.05
Floride	mg/l	1.5	1.5
Iron(Fe^{2+})	mg/l	0.3	-
Arsenic	mg/l	0.01	0.01
Benzene	mg/l		0.01
Ethybenzene	mg/l		0.3
Toluene	mg/l		0.7
Xylene	mg/l		0.5

2.3 ACTIVITIES OF AUTOMOBILE MECHANICS AND ITS EFFECT ON SOIL AND GROUNDWATER

There will always be a need for services of automobile mechanics as long as vehicles remain on our roads. In Nigeria, the rapid importation and influx of ‘fairly used’ vehicles, has caused a spring up of so many mechanic workshops all over the country. Currently, open vacant plots and farmlands are used as workshops by automechanics and other specialized individuals who engage in auto repair (Anoliefo and Edegbai, 2000). Diverse activities are carried out in these automobile workshops to service and maintain these automobiles and most of these are typical of auto repair (Adelekan and Abegunde 2010). Some of the various activities carried out in the workshop include:

- General servicing (engine and air condition servicing)-cleaning and washing engine parts
- Wielding
- Panel beating
- Painting and body spraying
- Electrical repair
- Vulcanizing
- Battery charging and
- Upholstery

Pollutants have continually been introduced into the environment in large quantities which is not unconnected with rapid industrialization and urbanization processes (Begum *et al.*, 2009), one of such is autorepair. Activities conducted in automechanic workshops involve working with spilling of oils, greases, petrol, diesel, battery electrolyte, paints and other materials which have capacity to contaminate the environment (Adelekan and Abegunde,2010). Studies have also shown that wastes generated as byproducts of auto repair activities can also contaminate the environment as a result of improper waste handling or disposal (Oniawa *et al.*, 2002; Ipeaiyeda and Dawodu 2008; Olusoga and Osibanjo, 2007). Some of the wastes generated include;

- wastewater
- used batteries

- used oil
- process water (eg from wet rub down of vehicles)
- waste glycol (engine coolant)
- solvent, paints and carbide
- refrigerants and aerosol cans
- plastics, used tires, wires and scrap metal

Several studies conducted on automechanic workshops have reported heavy metals (copper, lead, chromium, cadmium and zinc), hydrocarbons (oil and grease, VOCs, PAHs) and toxic chemicals (solvents, chlorinated compounds, glycols) as major pollutants of soil and groundwater around these workshops as a result of pollution from these wastes (Ipeaiyeda and Dawodu, 2008; Iwegbue, 2007; Ilemobayo and Kolade, 2008; Nwachukwu *et al.*, 2010). For instance, the spent motor oil disposed off improperly contains potentially toxic substances such as benzene (carcinogens), lead, arsenic, zinc and cadmium, which can seep into the water tables and contaminate ground water (Igwe *et al.*, 2008; Shah *et al.*, 2009). It consequently results in serious health hazard such as anemia and tremor, which can cause death.

2.4 ORGANIC POLLUTANTS OF SOIL AND WATER FROM AUTOMECHANIC ACTIVITIES

2.4.1 Volatile Organic Compounds (VOCs) –BTEX (Benzene, Toluene, Ethyl Benzene and Xylene)

Benzene, Toluene, Ethyl Benzene and Xylene (BTEX) are a group of chemical compounds made up of naturally-occurring chemicals that are found mainly in petroleum products or derivatives such as gasoline and also in other industrial products such as plastics, pesticides, explosives and paints as well as many of the common household products we use every day (López *et al.*, 2008; Fitt, 2002).

BTEX are in a class of chemicals known as volatile organic compounds (VOCs). VOC chemicals easily vaporize or change from a liquid to a vapour (gas). The VOC vapours can travel through the air and move through groundwater and soils as vapours. BTEX accounts for as much as 90% of gasoline components that are found in water–soluble fraction (Saeed and Al-Mutairi, 1999).They contaminate the soil through spills involving the release of petroleum products such as gasoline, diesel fuel, lubricating oil and heating oil from leaking oil tanks (Srijata *et al.*, 2011, Salanitro *et al.*, 1997) and at comparatively high levels, they can be associated with human health risks. When the BTEX compounds enter the water or food chain this can be fatal for human life, causing harm in the short or long term.

2.4.2 Characteristics of BTEX Components

2.4.2.1 Benzene

Benzene (C_6H_6) is a clear, colourless to light yellow liquid that is extremely volatile (Howard, 1990; Montgomery and Welcom, 1990). It has a molecular weight of 78.11 $gmol^{-1}$, a melting point of 5.5°C, and a boiling point of 80.1^0C. The specific density of benzene ranges from 0.8765 to 0.878 and the water solubility is 1791 mgL^{-1}. Its vapour pressure is 12.69 kPa at 25^0C and Henry's law constant is 5.43×10^{-3} $atmm^3mol^{-1}$. Benzene is produced through coal tar distillation, coal processing, and coal coking at petroleum refineries and solvent recovery plants (Verschueren, 1983). Natural sources of benzene are volcanoes, forest fires, volatile emissions from plants, as well as it being a constituent of crude oil (Howard, 1990).

Benzene can be found in gasoline and in products such as synthetic rubber, plastics, nylon, insecticides, paints, dyes, resins-glues, furniture wax, detergents and cosmetics. Auto exhaust and industrial emissions account for about 20% of the total nationwide exposure to benzene. Benzene can also be found in cigarette smoke. It is used in motor fuels, as a solvent for fats, inks, oils, greases, resins, and paints, and in the manufacture of plastics, synthetic rubber, detergents, explosives, textiles, packing materials, disinfectants, pesticides, pharmaceuticals, and dyestuffs (Sittig, 1985; BUA, 1992).

2.4.2.2 Toluene

Toluene (C_7H_8) is a volatile and flammable aromatic hydrocarbon which is also known as toluol, methylbenzene, and phenylmethane. It is less dense than water (0.867 gcm^3), with a water solubility of 515 mgl^{-1}, a vapour pressure of 2933 Pa, and Henry's Law constant of 648 Pa m^3mol^{-1} (Verschueren, 1983; Howard, 1990). Toluene occurs naturally as a component of many petroleum products. It occurs naturally in coal and crude oil (Nielson and Howe, 1991; Canada Environmental Protection Act, CEPA 1993). It is also a by-product of the petroleum refining process, formed by catalytic dehydrogenation of methylcyclohexane.

Toluene is present in many consumer products including gasoline, cosmetics, and cleaners (OMOEE, 1994). It is used as a solvent for paints, coatings, gums, oils and resins. Toluene is commonly used in the production of benzene and urethane. Also, it is used as lacquers, inks, adhesives, cleaning agents, pesticides, and for chemical extractions. Other uses include the synthesis of organic chemicals, dyes, and pharmaceuticals. Toluene is used as an octane enhancer in gasoline instead of lead and other compounds (CIS, 1994).

2.4.2.3 Ethylbenzene

Ethylbenzene (C_8H_{10}) is a product or by-product of petroleum and coal refining. Ethylbenzene is primarily produced by the alkylation of benzene with ethylene. It has a molecular weight of 106 $gmol^{-1}$. The specific density of ethylbenzene ranges from 0.867 and the water solubility is 152 mgL^{-1}. Ethylbenzene has a log octanol–water partition coefficient (log Kow) of 3.2, suggesting that it may be adsorbed to sediment (Chiou and Schmedding 1982). Ethylbenzene is resistant to hydrolysis, and photolysis in water is minimal (Howard, 1989).

Ethylbenzene can enter the environment during production, use, storage, transportation, and spills. It has been detected in effluents from municipalities and industries, industrialized river basins, groundwater, sediments, soil, and air (Fishbein, 1985; Howard, 1989; ATSDR 1990). There is little tendency for ethylbenzene to accumulate in the environment, and ambient levels remain low due to physical, chemical, and biological processes that remove ethylbenzene from all media (OMOEE, 1994).

2.4.2.4 Xylene

Xylenes ($C_6H_4(CH_3)_2$) are monoaromatic hydrocarbons with two methyl groups attached to the benzene ring, and are also known as alkyl benzenes. There are three forms of xylene, these are ortho-, meta-, and para- xylene (*o*-, *m*-, and *p*-xylene) depending on the position of the methyl group on the Benzene ring. Ortho-xylene is the only naturally occurring form of xylene; the other two forms are man-made. The three xylene isomers have a high vapour pressure (8.8–11.80 kPa at 25°C) and Henry's law constant (436–1115 $Pa \cdot m^{-3}/mol^{-1}$) and are subject to rapid volatilization. They also have high air saturation potential. These characteristics, combined with their low flash point, make them highly flammable. Their solubility in water is low, but is high enough to be of environmental concern. They have moderate octanol–water partition coefficients, 3.15, 3.20, and 3.18 for *o*-xylene, *m*-xylene, and *p*-xylene, respectively (MacKay, *et. al.* 1992). This indicates moderate fat solubility and consequently a moderate bioaccumulation potential (Environment Canada, 1995). Xylenes are used in gasoline and as a solvent in printing, rubber and leather industries. Table 2.5 shows a summary of the BTEX characteristics

Table 2.5 Summary of the characteristics for the six organic components in context

	Benzene	Toluene	m-Xylene	o-Xylene	p-Xylene	Ethyl benzene
Chemical Formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	C_8H_{10}
Molecular Weight [g/mole]	78	92	106	106	106	106
Water Solubility (mg/l)	1700	515	-	175	198	152
Vapor Pressure (at 20^{0}C) [mm Hg]	95.2	28.4	-	6.6	-	9.5
Specific Density (at 20^{0}C)	0.8787	0.8669	0.8642	0.8802	0.861	0.867
Octanol-water partition coeff. (at 20^{0}C) [log Kow]	2.13	2.69	3.2	2.77	3.15	3.15
Henry's law constant (at 25^{0}C) [kPa*m3/mole]	0.55	0.67	0.7	0.5	0.71	0.8
Polarity	Non-polar	Non-polar	Non-polar	Non-polar	Non-polar	Non-polar
Biodegradability	Aerobic	Anaerobic/Aerobic	Aerobic	Aerobic	Aerobic	Aerobic
Maximum Contaminant Level(MCL) [mg/l]	0.005	1	10 *	10 *	10 *	0.7

*The Environmental Protection Agency (EPA) lists an MCL of total xylenes of 10 mg/l

Source: James and Stephen 2004

2.4.3 Fate and Transport in Soil and Groundwater

The discharge of BTEX's to the environment is influenced by their fate and transport mechanisms. The BTEX emergence in soil and groundwater as well as its ability to be remediated is affected by volatilization, dissolution, sorption and degradation by microorganisms (Bedient, 1994, Schreiber and Bahr, 2002).

Volatilization affects the actual concentration of BTEX's. Of all BTEX components, benzene volatilizes easiest. According to Bedient, 1994, gasoline volatilizes due to the high solubility, the relatively low molecular weight and the high vapour pressure. Compared to the other main group of components in gasoline, such as the aliphatics, BTEX's are very soluble and the solubility's of the different BTEX components have a great effect on the concentrations that may appear in the groundwater. When gasoline is dissolved in an aqueous phase, it will be able to move with the groundwater and dissolution occurs. In soil, rather than dissolution, sorption may take place between the organics and the soil particles. The sorption is controlled by contaminant characteristics such as the solubility, polarity and the octanol-water partition coefficient (K_{ow}) (Jesper, *et. al.* 1998). In addition sorption is influenced by the characteristics of the soil matrix and the fluid media (Bedient, 1994). The BTEX's are not sorbed to the soil matrix as strong as the aliphatic components (the different alkanes), and they are more likely to contaminate larger water volumes. Sorption is a determining factor in the movement of contaminants with the groundwater flow and it favourability is due to the area of contamination which is either large or small.

The degradation of BTEX's is another aspect that affects the concentration in soil and groundwater. The natural bacterial flora in soil has an ability to aerobically degrade the BTEX's. This degradation will extensively reduce the concentration in soil and groundwater (Barker, *et. al.* 1987). The degradation techniques are sometimes recommended as a natural means of remediation (intrinsic bioremediation). Addition of nutrients and oxygen enhances the degradation process . Aerobic biodegradation can considerably reduce the concentration of BTEX (Ball and Reinhard, 1996, Lovely, *et. al.* 1994). This biodegradation has been repeatedly established when dealing with toluene, and the anaerobic biodegradation of xylenes

2.4.4 Exposure to BTEX

Most people are exposed to small amounts of BTEX compounds in the ambient (outdoor) air, at work and in the home. Virtually everyone is exposed to low levels of these chemicals in their daily activities. Larger amounts of BTEX can enter the environment from leaks from underground storage tanks, overfills of storage tanks, fuel spills and landfills. BTEX compounds easily move through soils and can make their way into the groundwater, contaminating public and private water systems and the soils in between.

2.4.5 BTEX and Human Health

2.4.5.1 Exposure Routes of BTEX

Exposure of anyone to BTEX will depend on the following:

- dose
- duration
- frequency
- General Health, Age, Lifestyle
- Vulnerability of individuals [Young children, the elderly and people with chronic (on-going) health problems].

Exposure to BTEX can occur by ingestion, inhalation or dermal contact and these exposures could be both acute (short-term) and chronic (long-term) exposures. Short or long-term exposures determine the extent of their health effect.

2.4.5.2 Effect of Human Exposure to BTEX

BTEX in water and soil above permissible limits of regulatory bodies are a threat to man (Table 2.6). All the BTEX chemicals can produce neurological impairment. In past studies of workers exposed to BTEX where these compounds were either inhaled or absorbed through the skin, major chronic health effects were noted (Jacobson, 2002). Some of these effects are discussed as follows;

Benzene

Chronic exposure to low levels of benzene can lead to aplastic anemia, blood disorders, reproductive and developmental disorders, acute myelogenous leukemia and also cause an increase in risk of getting cancer. Studies have found strong evidence between long term exposure to benzene and leukemia has been found (Cheremisinoff, 1979). Other effects of exposures to BTEX include, irritation of the skin, eyes, and upper respiratory tract, blisters on the skin (USEPA, 2011; 2012, ATSDR, 2004).

Toluene

Chronic exposure to toluene over time can lead to problems in the nervous system, kidneys and liver (US EPA, 2012). Also, irritation of the skin, eyes, and respiratory tract may occur as well as dizziness, headaches, difficulty with sleep and birth defects.

Ethylbenzene

Ethylbenzene has been found to cause liver and kidney damage as well as being ototoxic (i.e cause damage to the ear or its nerve supply due to a toxin) after chronic exposures (US EPA, 2012).Chronic exposure can cause damage to the nervous system (Jacobson, 2002). Short-term exposure may cause throat and eye irritation, chest constriction, and dizziness while long-term exposure may cause blood disorders.

Xylene

Short-term exposure to high levels of mixed xylenes may cause irritation of the nose and throat, nausea, vomiting, gastric irritation, mild transient eye irritation and neurological effects. Long-term exposure to high levels of xylene may impact the nervous system (USEPA, 2011). Inhalation of xylene in concentrations above 0.4 mg/l leads to a reduced ability of co-ordination.

Table 2.6 BTEX limits in Water

VOCs		WHO(µg/l)
Benzene	C_6H_6	10
Toluene	C_7H_8	700
Ethylbenzene	C_8H_{10}	300
Xylene	C_8H_{10}	500

Source: Modified from ATDSR, 2004

2.4.6 BTEX compounds as Cancer Causing Agents

There is no data on the cancer-causing nature of the whole mixture (benzene, toluene, ethylbenzene and xylenes); possible health hazards from exposures to BTEX are assessed using an individual component-based approach of the individual chemicals.

- **Benzene:** According to The Department of Health and Human Services (HHS) as well as the National Toxicology Program (NTP 2001), U.S. Environmental Protection Agency (EPA) (IRIS 2001), and International Agency for Research on Cancer (IARC 1987), benzene is a human carcinogen (causes cancer). It is also considered mutagenic. Workers exposed to high levels of benzene in occupational settings were found to have an increase occurrence of leukemia. Long-term exposure to high levels of benzene in the air can lead to leukemia and cancers of the blood-forming organs. It is considered one of the priority pollutants according to the Environmental Protection Agency (EPA) National Primary Drinking Standards (IAEG, 2006).
- **Ethylbenzene:** According to the International Agency for Research on Cancer (IARC, 2000), ethylbenzene is classified as a Group 2B, possibly carcinogenic to humans, based on studies of laboratory animals.
- **Toluene, and Xylenes** have been categorized as not classifiable as to human carcinogenicity by both EPA (IRIS 2001) and IARC (1999a, 1999b), due to the lack of evidence for the carcinogenicity of these two chemicals.

2.5 INORGANIC POLLUTANTS OF SOIL AND WATER FROM AUTOMECHANIC ACTIVITIES

2.5.1 Heavy Metals

Heavy metals are elements having atomic weight between 63.545 and 200.5g (Kennish, 1992). Although there is no clear definition of what a heavy metal is, density is in most cases taken to be the defining factor. Heavy metals are thus commonly defined as those having a specific density of more than 4g/cm^3 (Connel *et al.*, 1984) or 5 g/cm^3 (Fawell and Nieuwenhuijse, 2003).

It is also referred to as any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations (Lenntech, 2011). Many different definitions have been proposed. Some are based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity (Duffus, 2002). They usually include transition metals, some metalloids, lanthanides, and actinides. There are 60 heavy metals. These also include the precious metals platinum, silver and gold. Some examples of heavy metals of importance include Copper, Lead, Mercury, Cadmium, Chromium and Arsenic.

Heavy metals occur naturally or as a result of human activities in the ecosystem with large variations in concentration (Figure 2.3). They get into the environment from different sources. These could be natural or anthropogenic sources. As trace elements, some of the heavy metals are useful for body metabolism (e.g zinc and copper) but in higher concentrations they can be as toxic (Lenntech, 2011) while others are toxic even in very low concentrations. Heavy metals are dangerous because they tend to bioaccumulate finally pose serious health hazard to human beings and the animals (Ray, 1990). Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage and even death (Abdulaziz and Mohammed, 1997).

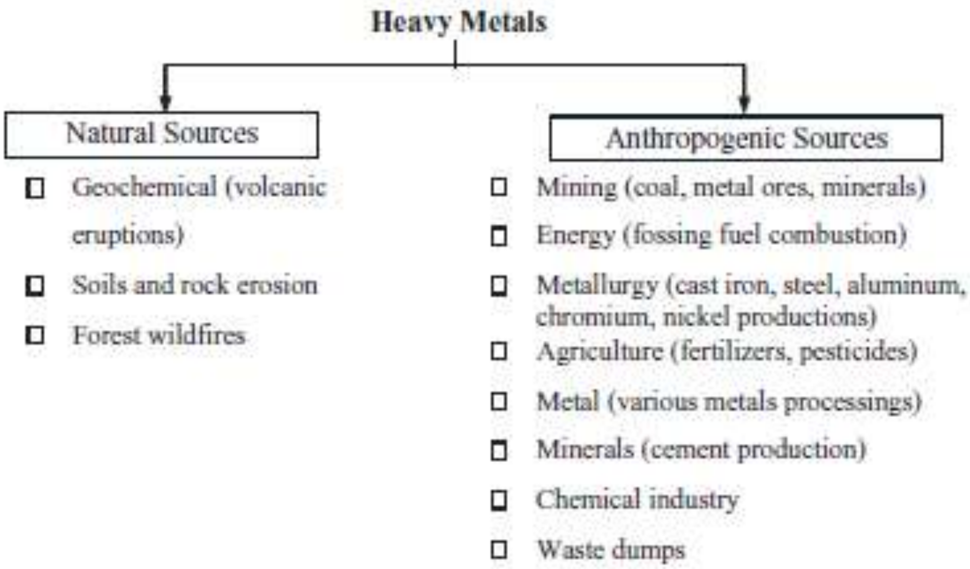


Figure 2.3 Sources of Heavy metals in the Environment (Merian, 1991)

2.5.2 Heavy Metals of Environmental Importance

2.5.2.1 Chromium

Chromium is a lustrous, brittle, hard metal. It is an odourless and tasteless metal (ATSDR, 2005). Its colour is silver-gray and it can be highly polished. Chromium is found naturally in rocks, plants, soil and volcanic dust, humans and animals. It is also found in natural deposits as ores containing other elements. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below it. (Lenntech, 2011; Kohl, 1967). Chromium found in the environment is majorly in two valence states: trivalent chromium (chromium-III), and hexavalent chromium (chromium-VI) (USEPA, 2010). Chromium (III) is an essential human dietary element and occurs naturally in many vegetables, fruits, meats, grains and yeast. Chromium (VI) occurs naturally in the environment from the erosion of natural chromium deposits but it can also be produced by industrial processes.

Applications

Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and pigments for paints, its salts colour glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in the tanning of leather; to make molds for the firing of bricks (Alloway and Ayres, 1999). Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape (Lenntech, 2011).

2.5.2.1.1 Forms of emission of Chromium in the Environment

Chromium is mined as chromite ($FeCr_2O_4$) ore. Chromium ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakihstan and the Philippines. A total of 13 million metric tonnes of chromite ore is extracted (Papp, 2003). Reserves are estimated to be of the order of 1 billion tonnes with unexploited deposits in Greenland, Canada and USA (Lenntech, 2011).

Chromium is present in air, soil and water. In nature it is mostly as chrome iron ore and naturally occurring chromium is usually present as trivalent Cr(III). It is widely found in soils and plants. It is rare in natural waters. Hexavalent chromium {Cr(VI)} in the environment is almost totally derived from human activities (Belica A *et al.*,2005). The two largest sources of chromium emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil, and coal. In water it is mainly due to leaching from topsoil and rocks, the most important natural source of chromium entry into bodies of water. Solid wastes from chromate-processing facilities, when disposed of improperly in landfills, can also be sources of contamination for groundwater. In soil large processing facilities are avenues through which chromium is emitted into the environment. Other environmental sources of chromium are cement-producing plants (cement contains chromium), the wearing down of asbestos linings that contain chromium, emissions of chromium-based automotive catalytic converters, and tobacco smoke (ATSDR-CSEM, 2008).

2.5.2.1.2 Effects of Chromium on the environment

There are different forms of chromium and they differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) form through natural processes and human activities. The main human activities that increase the concentrations of chromium (III) are steel, leather and textile manufacturing while the main human activities that increase chromium(VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium(VI) applications in the industry (USEPA, 1998). These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils. Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops.

Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur. There is a high potential for accumulation of chromium in aquatic life. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium. In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation. Repeated exposure of animals to chromium (VI) compounds causes similar effects to those observed in humans that is, irritant and inflammatory effects on the respiratory system and immunological changes (IPCS, 2006; ECB,2005)

2.5.2.1.3 Health Effects of Chromium

The toxicity of chromium depends upon its oxidation state. Chromium VI is more toxic than the Chromium III. Humans can be exposed to chromium (especially chromium VI) through inhalation, ingestion and dermal contact with chromium compounds (Dayan and Paine, 2001; ATSDR, 1998). For most people, eating food that contains chromium (III) is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, fish, yeast, grains, entrails, molluscs, lobsters, unrefined sugar and vegetable oil (Benkco, 1985). Various ways of food preparation and storage may alter the chromium contents of food (Lentech, 2011).

Chromium (III) is a nutritionally essential element in humans and is often added to vitamins as a dietary supplement. Chromium (III) has relatively low toxicity and would be a concern in drinking water only at very high levels of contamination. The recommended daily intake of chromium (III) being 50-200 ug per day for adults (ATSDR, 1998). Shortages of Chromium (III) may cause heart conditions, disruptions of metabolisms and diabetes (Mertz, 1993). But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes.

Chromium (VI) is a danger to human health. Severe and often deadly pathological changes are linked with excessive intake of Chromium VI compounds from short or long-term exposures (James and Stephen, 2004 and Lentech 2011). Acute effects such as gastrointestinal disorders, haemorrhagic diathesis, and convulsions could occur from ingestion of 1–5 g of "chromate" (not further specified). Death may occur following cardiovascular shock (Janus and Krajnc, 1990). According to Bielicka *et al.*, 2005 inhalation and retention of materials containing Chromium (VI) can cause perforation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Skin contact of Chromium (VI) compounds can induce skin allergies, dermatitis, dermal necrosis and dermal corrosion (Cieslak, 1994). Hexavalent chromium compounds are irritating and corrosive when allowed to come in contact with skin, the digestive system or lungs. Chromium trioxide (CrO3) is a common toxic hexavalent chromium compound. Chromium (VI) connected with long-term occupational exposure (such as workers in the chromate industry) is a chemical carcinogen that can cause carcinomas of the bronchial systems. Other health effects include;

- Damage to liver, kidney circulatory organs and nerve tissues;
- Coughing, wheezing and shortness of breath
- Weakened immune system and;
- Alteration of genetic material

2.5.2.1.4 Carcinogenicity

The IARC states that “there is sufficient evidence in humans for the carcinogenicity of Chromium (VI) compounds as encountered in the chromate production, chromate pigment production and chromium plating industries”. Chromium (VI) is described by the USEPA “as a known human carcinogen by the inhalation route of exposure”. Both organizations rate Chromium (VI) in their highest cancer category, Group 1 and Group A respectively (IARC, 1990; USEPA, 2001b). There is also agreement on, Chromium (III) not classified as to its human carcinogenicity, Group 3 in the IARC scheme and Group D under the USEPA guidelines (IARC, 1990; USEPA, 2001a). ATSDR 2008a also supports the fact that the hexavalent compound of Chromium is known to be a human carcinogen.

2.5.2.2 Cadmium

Cadmium is a lustrous, silver-white, ductile, very malleable metal in its elemental form. Its surface has a bluish tinge and can be easily cut by a knife at room temperature but it tarnishes in air (MERCK, 2006; ATSDR, 2008). Metallic cadmium is basically insoluble in water; however, several cadmium compounds are freely soluble (such as cadmium chloride ($CdCl_2$), cadmium nitrate [$Cd(NO_3)_2$], and cadmium sulphate ($CdSO_4$)) (Budavari et al. 1989). Cadmium has a relatively low crustal abundance, although it does occur ubiquitously in rocks and soils (Alloway, 1995; ECB, 2007). It is found rarely in its elemental form, with greenockite (CdS), octavite (CdSe), and monteponite (CdO) being its principal minerals (Kabata-Pendias and Mukherjee, 2007). It is found in natural deposits such as ores containing other elements. Cadmium is often found in association with zinc-bearing ores, which are the main source of cadmium production (Greenwood and Earnshaw, 1997; ECB, 2007; ATSDR, 2008). In several ways its chemistry is similar to zinc but it forms more complex compounds with a strong affinity for sulphur (Alloway, 1995; Greenwood and Earnshaw, 1997; Kabata-Pendias and Mukherjee, 2007).

Applications

Cadmium metal, its alloys and compounds have been used in a variety of different industrial and consumer products, although most uses are now declining due to concerns about its toxicity (ATSDR, 2008). At the beginning of the 20th century, production of commercial cadmium was initiated. Its main use was in electroplating (especially steel, where a film of cadmium only 0.05 mm thick will provide complete protection against the sea), but since 1960, cadmium has been used for manufacturing nickel–cadmium batteries. Cadmium is also used in paint pigments for plastics, glass and ceramics and in making polyvinyl chloride plastics (WHO, 2010). Cadmium has also been used as a fungicide, in corrosion-resistant coatings on steel and other non-ferrous metals. Other minor applications are; photography, photocopying, dyeing, calico printing, vacuum tube manufacture, galvanoplasty, lubricants, ice-nucleation agents, and in the manufacture of special mirrors (Alloway, 1995; ECB, 2007; Kabata-Pendias and Mukherjee, 2007; ATSDR, 2008). Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission. The percentage of cadmium consumed for use is 83% (batteries), 8% (pigments), 7% (coatings and platings), 1.2% (stabilizers for plastics) and 0.8% (nonferrous alloys, photovoltaic devices, and others (USGS, 2008).

2.5.2.2.1 Form of Emission of Cadmium in the environment

Cadmium is released to the atmosphere from both natural and anthropogenic sources. It is generally present in the environment at low levels; however, human activity has greatly increased those levels (IPCS, 1992). It is widely distributed in the earth's crust with concentrations reported between 0.1 and 0.5 ppm and higher levels in sedimentary rocks

(Morrow, 2001). One of the most important natural sources of cadmium is volcanic eruptions (on land and sea) (Nordic Council of Ministers 1992) asides this, cadmium may be released to the air from entrainment of dust particles, forest fires, or other natural phenomena (USEPA 1985; Morrow 2001). Cadmium exists in ocean waters at average levels ranging from <5 to 110 ng/L and may transport to the atmosphere through natural processes like generation of sea-salt aerosols (Morrow 2001). However, industrial activities are the main sources of cadmium release to air (WHO, 2007), and emissions from anthropogenic sources have been found to exceed those of natural origin by an order of magnitude (IARC 1993).

Major industrial sources of cadmium emissions include zinc, lead, copper, and cadmium smelting operations; coal and oil-fired boiler; other urban and industrial emissions; tobacco smoking; recycling of cadmium-plated steel scrap and electric and electronic waste phosphate fertilizer manufacture; road dust; and municipal and sewage sludge incinerators (Morrow 2001; WHO, 2000; UNEP, 2008). Application of municipal sewage sludge to agricultural soil can also be a significant source of cadmium (IPCS, 1992). Cadmium releases can be carried to and deposited on areas remote from the sources of emission by means of long-range atmospheric transport (WHO, 2000)

2.5.2.2.2 Effects of Cadmium on the environment

Cadmium is one of the elements which occur at very low concentrations in the lithosphere and in topsoils. The average total contents of Cd in soils lie between 0.07 and 1.1 mg/kg (Kabata-Pendias and Pendias 1984). Cadmium ends up in soil and water after a number of natural or industrial activities increasing its concentration in the environment. Sufficient studies have been done to indicate that cadmium is concentrated in plants, aquatic organisms, and animals (Alloway *et al.*, 1990; Beyer 1986; Handy 1992a, 1992b; Kuroshima 1992; Naqvi and Howell 1993; Roseman *et al.*, 1994; Suresh *et al.*, 1993). Atmospheric deposition of cadmium on arable soils exceeds its elimination in many countries, resulting in a gradual increase in cadmium levels in soils and crops. Uptake of plant from these contaminated soils and aquatic organisms from the polluted water leads to accumulation in the food chain (WHO, 2007). Lower cadmium concentrations are found in vegetables, cereals and starchy roots. Plants have no metabolic requirement for cadmium and the symptoms of its toxicity include stunted growth and chlorosis (Kabata-Pendias and Mukherjee, 2007).

Cadmium's phytotoxicity is as a result of its interference with the normal metabolism of some micronutrients, its inhibitory effect on photosynthesis, its ability to disturb the transpiration and fixation of carbon dioxide as well as its effect on the permeability of cell membranes (Kabata-Pendias and Pendias, 2001). Some crops, such as rice, can accumulate high concentrations of cadmium if grown on cadmium-polluted soil. The tobacco plant also, naturally accumulates relatively high concentrations of cadmium in its leaves. Thus, smoking tobacco is an important source of exposure, and the daily intake may exceed that from food in the case of heavy smokers (WHO, 2007). Cadmium is bio-persistent and, once absorbed by an organism, remains resident for years although it is eventually excreted. High cadmium levels are found in the kidney and liver of mammals fed with cadmium-rich diets and in certain species of oysters, scallops, mussels and crustaceans. Human exposure occurs mainly from consumption of contaminated food, active and passive inhalation of tobacco smoke and inhalation by workers in the non-ferrous metal industry (WHO, 2010).

2.5.2.2.3 Health Effects of Cadmium

Cadmium is hazardous and can cause acute and chronic intoxications (Bernard 2008). Cadmium is an accumulative poison and its intake has been reported to cause renal, prostate and ovarian cancers (Monterio *et al.*, 2003). Studies have demonstrated that Cd absorbed by inhalation or ingestion can cause irreversible damage to several vital organs, among which the most sensitive are the kidney, the bone and the respiratory tract (Bernard and Lauwerys 1986). The kidney is the critical target organ. Cadmium accumulates primarily in the kidneys, and its biological half-life in humans is 10–35 years (WHO, 2008). This accumulation may lead to renal tubular dysfunction, which results in increased excretion of low molecular weight proteins in the urine. This is generally irreversible. High intake of cadmium can lead to disturbances in calcium metabolism and the formation of kidney stones.

Softening of the bones and osteoporosis may occur in those exposed through living or working in cadmium contaminated areas Although first reported in French workers by Nicaud *et al.*, 1942, toxic effects of Cadmium on the bones really became evident with the outbreak of the Itai-Itai disease in the Cadmium polluted area of Toyama, Japan, where soil has been contaminated with cadmium from zinc/lead mines after World War II. Itai-Itai disease patients presented severe osteomalacia osteoporosis, painful bone fractures and kidney dysfunction and is still seen in women over 50 years of age (Hagino and Yoshioka, 1961; WHO, 2010). Recent studies in China have confirmed the bone toxicity of Cadmum. Nordberg *et al* (2007) have found decreased bone mineral density in Chinese farmers exposed to Cadmium from contaminated rice for more than 20 years. Cadmium can disrupt a number of biological systems, usually at doses that are much lower than most toxic metals (Nordberg *et al.*, 2007; Bernard 2004). High inhalation exposure to cadmium oxide fume results in acute pneumonitis with pulmonary oedema, which may be lethal. Long-term, high-level occupational exposure is associated with lung changes, primarily characterized by chronic obstructive airway disease (WHO, 2010). Other health effects of cadmium poisoning include;

- Reproductive failure and possibly even infertility
- Damage to the central nervous system
- Damage to the immune system
- Psychological disorders
- Possibly DNA damage or cancer development
- Death

2.5.2.2.4 Carcinogenicity

There is sufficient evidence that long-term occupational exposure to cadmium (e.g. through cadmium fume) contributes to the development of lung cancer. There is limited evidence that cadmium may also cause cancers of the kidney and prostate. The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as *carcinogenic to humans* (Group 1), meaning that there is sufficient evidence for their carcinogenicity in humans (IARC, 1993).

2.5.2.3 Copper

Copper is a reddish metal with a face-centered cubic crystalline structure which is found in a variety of rocks and minerals (Somika-Sarl, 2014). Copper is a reddish brown nonferrous mineral which has been used for thousands of years by many cultures (Jones and Dorgan, 2007). The name for the metal comes from *Kyprios*; the Ancient Greek name for Cyprus, an island which had highly productive copper mines in the Ancient world (Ashish *et al.*, 2013).

It reflects red and orange light and absorbs other frequencies in the visible spectrum, due to its band structure, so it has a nice reddish color (Lenntech 2011). It is malleable, ductile, and an extremely good conductor of both heat and electricity. It is superficially oxidized in air to form a greenish surface film called patina which protects the metal from further attack. In water it exists as a divalent ion, Cu^{+2}. It is classified as a heavy metal with a density greater than $5gcm^{-3}$(Fostner and Wittmann, 1979).

Applications

Most copper is used for electrical equipment (60%); construction, such as roofing and plumbing (20%); industrial machinery, such as heat exchangers (15%) and alloys (5%). The main long established copper alloys are bronze, brass (a copper-zinc alloy), copper-tin-zinc, which was strong enough to make guns and cannons, and was known as gun metal, copper and nickel, known as cupronickel, which was the preferred metal for low-denomination coins(Lenntech, 2011). Copper is ideal for electrical wiring because it is easily worked, can be drawn into fine wire and has a high electrical conductivity. It is also used to make cooking pots. In addition to being useful in manufacturing, copper is also a vital dietary nutrient, although only small amounts of the metal are needed for well-being (Ashish *et al.*, 2013). Copper is also applied in the industries and in agriculture. Its compounds can be added to fertilizers and animal feeds as a nutrient to support plant and animal growth (Landner & Lindestrom, 1999; ATSDR, 2002). Also, it can be used as food additives (e.g., nutrient and/or colouring agent) (US FDA, 1994). Copper sulfate pentahydrate is sometimes added to surface water for the control of algae (NSF, 2000).

2.5.2.3.1 Form of emission of Copper into the Environment

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. It is essential to animals and plants. The production of copper has lifted over the last decades. Due to this, copper quantities in the environment have increased (Lenntech, 2011). World production of copper amounts to 12 million tons a year and exploitable reserves are around 300 million tons, which are expected to last for only another 25 years. Several million tons a year are reclaimed by recycling (Innovations, 1998). Today copper is mined as major deposits in Chile, Indonesia, USA, Australia and Canada, which together account for around 80% of the world's copper. The main ore is a yellow copper-iron sulfide called chalcopyrite ($CuFeS_2$).

Copper can be released into the environment by both natural sources and human activities. Since copper is a component of the earth's crust, the earth’s crust is the primary natural source of copper. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and volcanoes. Anthropogenic emission sources include nonferrous metal production, wood production, iron and steel production, waste incineration, industrial applications, coal combustion, nonferrous metal mining, oil and gasoline combustion, and phosphate fertilizer manufacture. Since copper is released both naturally and through human activity it is very widespread in the environment. The main anthropogenic source is emissions from the primary non-ferrous metal industry (Pacyna *et al*., 1995).

Copper is present in the atmosphere from wind dispersion of particulate geological materials and particulate matter from smokestack emissions. Collectively, these sources account for only 0.4% of the copper released into the environment (Barceloux, 1999). Windblown dust has an estimated mean worldwide emission of 0.9–15x10^6 kg/year of copper into the atmosphere (WHO 1998). It enters the air, mainly through release during the combustion of fossil fuels and enters into soil usually after rains in a saturated environment. As a result, soils may also contain large quantities of copper after copper from the air has settled. Most copper compounds will settle and be bound to either water sediment or soil particles. Usually water-soluble copper compounds occur in the environment after release through application in agriculture. Copper is found in surface water, groundwater, seawater and drinking-water, but it is primarily present in complexes or as particulate matter (ATSDR, 2002). Global atmospheric anthropogenic and natural emissions of copper have been estimated to be 35x10^6 and 28x10^6 kg/year, respectively (Giusti, *et al.*, 1993). Soluble copper compounds form the largest threat to human health.

2.5.2.3.2 Effects of Copper on the environment

Studies have shown that copper toxicity can affect aquatic organisms. In fish, it has been observed to affect their blood characteristics and cause respiratory failure (Khangarot and Tripathi, 1991). Exposures of some fish species such as the ‘rainbow trout’ has resulted in respiratory toxicity; increase heart rate, arterial blood pressure and lactate concentration and decrease in oxygen tension (Wilson and Taylor, 1993). It has also been seen to reduce fish feeding and swimming performance (Beaumont *et al.,* 1995). Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. When copper ends up in soil it strongly attaches to organic matter and minerals. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils only a limited number of plants have a chance of survival. Effects on plants have caused reduced plant growth, photosynthesis, respiration and nitrogen fixation which results in deflagellation and physiological damage.

According to S-Rozsa and Salanki, 1990, copper has modified the effect of neutron transmitton and ionic current in the simple nerve system of some invertebrates. Activities of many molluscs have been affected and oxygen consumption greatly reduced (Mule and Lomte, 1994). Copper can interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms. The decomposition of organic matter may seriously slow down because of this. When the soils of farmland are polluted with copper, animals will absorb concentrations that are damaging to their health. Many sheep suffer a great deal from copper poisoning, because the effects of copper are manifesting at fairly low concentrations.

2.5.2.3.3 Health Effects of Copper

Copper is an essential substance to human health. The body cannot synthesize copper so the human diet is required to provide regular amounts for absorption. Food is a principal source of copper exposure for humans. Liver and other organ meats, seafood, nuts and seeds (including whole grains) are good sources of dietary copper (IOM, 2001). Results from a US Department of Agriculture survey of food consumption (1989 – 1991), about 40% of dietary copper comes from yeast breads, white potatoes, tomatoes, cereals, beef and dried beans and lentils (Subar *et al.*, 1998). Clinical dietary copper deficiencies are rare, especially in developed countries (Olivares *et al.*, 1999)

Copper concentrations in air are usually quite low, so that exposure to copper through breathing is negligible although people that live near smelters that process copper ore into metal are at risk. People that live in houses that still have copper plumbing are exposed to higher levels of copper than most people, because copper is released into their drinking water through corrosion of pipes. Copper consumption at high levels is harmful to human health and has the potential to cause the different health problems. Acorrding to Agarwal et al., 1993, toxic exposure to copper causes haematuria, intravascular haemolysis, methaemoglobinaemia, hepatocellular toxicity, acute renal failure and oliguria. Studies have also shown that at lower doses, copper ions can cause symptoms typical of food poisoning (Knobeloch *et al.,* 1994; Low *et al.,* 1996; Stenhammar, 1999).

An epidemiological investigation reported by Buchanan et al. (1999) in USA showed as association between ingestion of drinking-water containing copper and rapid-onset gastrointestinal illness. Another health effect of copper is the Wilson Disease which is an autosomal recessive disorder that leads to copper toxicity. This is because copper is not incorporated into ceruloplasmin, its normal systemic distribution is impaired, and copper accumulates in the liver, brain and eyes (Harris & Gitlin, 1996). Wilson disease generally appears in late childhood and is accompanied by hepatic cirrhosis, neurological degeneration and copper deposits in the cornea of the eye (Kayser-Fleischer rings). Other effects include anemia and irritation of the nose, mouth and eyes.

2.5.2.3.4 Carcinogenicity

The carcinogenic property of copper is yet to be determined. The US EPA (1991) classifies copper as Group D, not classifiable as to human carcinogenicity.

2.5.2.4 Lead

Lead is a bluish grey soft dense metal which tarnishes in moist air. It is malleable, ductile a poor conductor of electricity but extremely resistant to corrosion. Lead is normally found in dyes and paints used in some industries (EPA 2006). Its physical and chemical properties are applied in the manufacturing, construction and chemical industries. It is not required for human health, and even small amounts of lead and lead compounds can be toxic when ingested or inhaled.

Applications

There are eight broad categories of use: batteries, petrol additives (no longer allowed in the EU), rolled and extruded products, alloys, pigments and compounds, cable sheathing, shot and ammunition. The largest application of lead is the use of lead in lead-acid batteries, at 73 % of global consumption. The second largest application is the use of lead as a pigment and in other compounds (e.g. as a stabiliser in plastics and rubber), 11% of global consumption. The third largest application is the use of rolled and extruded lead, 6% of global consumption (ILZSG, 1999). About 80% of this rolled and extruded lead is used as building materials. Lead oxide is also used in the manufacture of fine crystal glass. Historically, lead was used for plumbing. Tetra ethyl lead was used as anti-knock in petrol and an additive in paints but due to the environmental concerns, the use in this regard has been greatly reduced. Lead is among the most recycled non-ferrous metals and its secondary production has therefore grown steadily in spite of declining lead prices.

2.5.2.4.1 Form of emission of Lead into the Environment

Lead occurs naturally in nature and it can be found in ores mainly with copper, zinc and silver. The primary lead mineral is lead sulphide (Glena). Lead is refined from glena by heating and a large amount of lead is also recovered via recycling.

Lead in the environment arises from both natural and anthropogenic sources (Figure 2.4). Exposure can occur through drinking water, food, air, soil and dust from old paint containing lead. Lead gets into the environment via various sources some of which include water in areas with lead piping and plumb solvent water, air near point of source emissions in industries such as battery factories, soil, dust, paint flakes in old houses or contaminated land (TCEQ 2012; USEPA 2014). Lead in the air contributes to lead levels in food through deposition of dust and rain containing the metal, on crops and the soil. In addition most people receive the bulk of their lead intake from food, in specific populations but this is being controlled by regulations for tolerable weekly intake recommended by the UN Food and Agriculture Organisation (UNFAO) and the World Health Organisation (WHO). Lead is persistent in the environment and accumulates in soils and sediments through deposition from air sources, direct discharge of waste streams into water bodies, mining and erosion (EPA 2006). The presence of lead in the environment affects these ecosystems present and hence loss of biodiversity, decrease in growth and development in animals and plants as well as neurological effects in vertebrates (Greene, 1993). In the general non-smoking, adult population the major exposure pathway is from food and water (Figure 2.5). Food, air, water and dust/soil are the major potential exposure pathways for infants and young children. For infants up to 4 or 5 months of age, air, milk formulae and water are the significant sources.

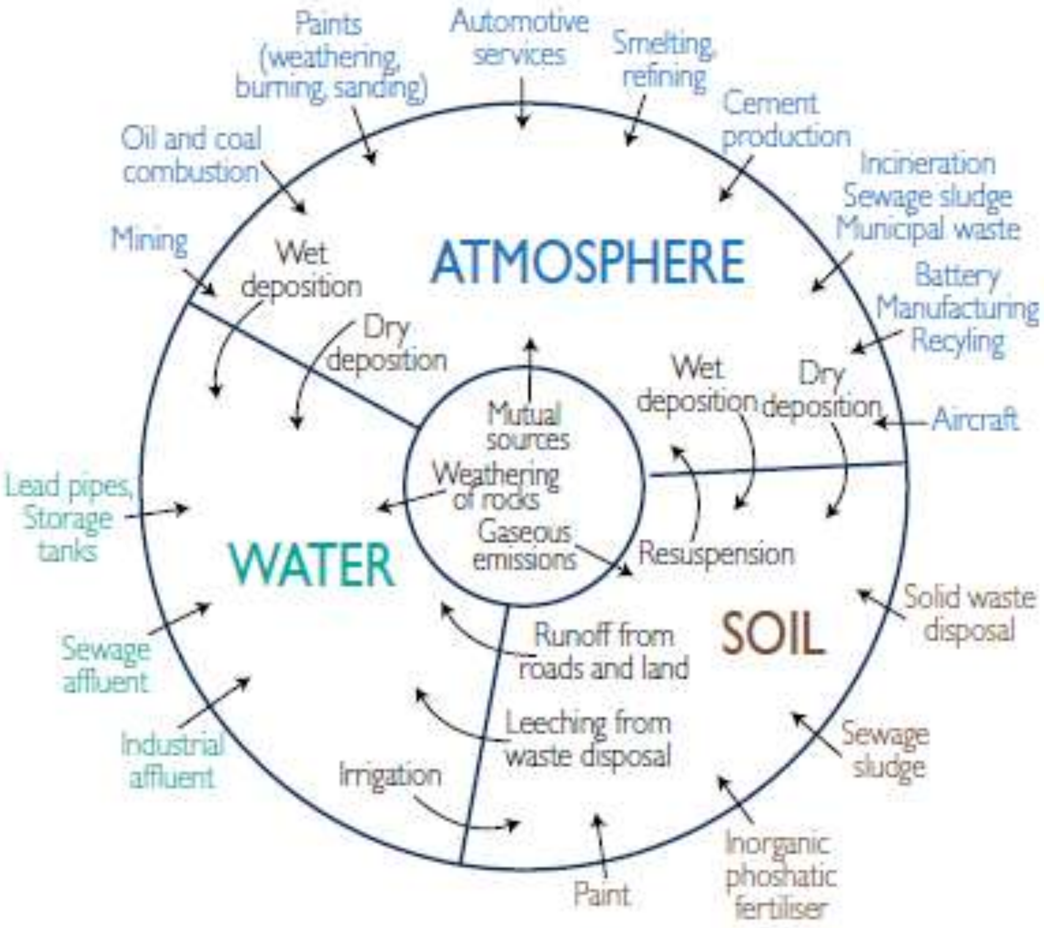


Figure 2.4: Transport pathways for lead in the environment (EPA, 2006 modified from Zabel, 1993).

2.5.2.4.2 Effects of Lead on the environment

Although lead occurs naturally in the environment, it plays no known beneficial role in biological processes (Gulson 1996). Lead is classified as a ‘toxicant’ that can affect a broad spectrum of species and remain in the environment for a long time. High levels of lead can cause death in many birds and mammals. They can also affect the population dynamics, dietary patterns, morbidity and sex distribution of animal species. Lead contamination also affects biological systems by affecting ecosystem productivity (inhibiting plant growth) and nutrient cycling (Gulson 1996). High levels of lead in soil are known to affect both soil organisms and plant productivity. Collective damage to these groups of organisms disrupts the cycling of nutrients through an ecosystem, often resulting in the displacement of lead-intolerant species with lead-tolerant species.

2.5.2.4.3 Effects of Lead on health

Humans are exposed to lead mainly by inhalation and ingestion in soil, water, dust or food (Figure 2.5). In humans exposure to lead can result in a wide range of health effects depending on the concentration and duration of exposure. Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult even at very low levels. Lead, a prime environmental pollutant is a multi-organ poison which in addition to well known toxic effects, depresses immune status (Anetor and Adedeji, 1998), causes kidney damage, central nervous system, and reproductive system (Ademoroti, 1992; Mercier et al., 1998). Ingestion leads to a disease known as plumbism. It is also known to produce developmental neurotoxicity in particular infants and children are differentially sensitive to environmental lead exposure (Johnson, 1997).

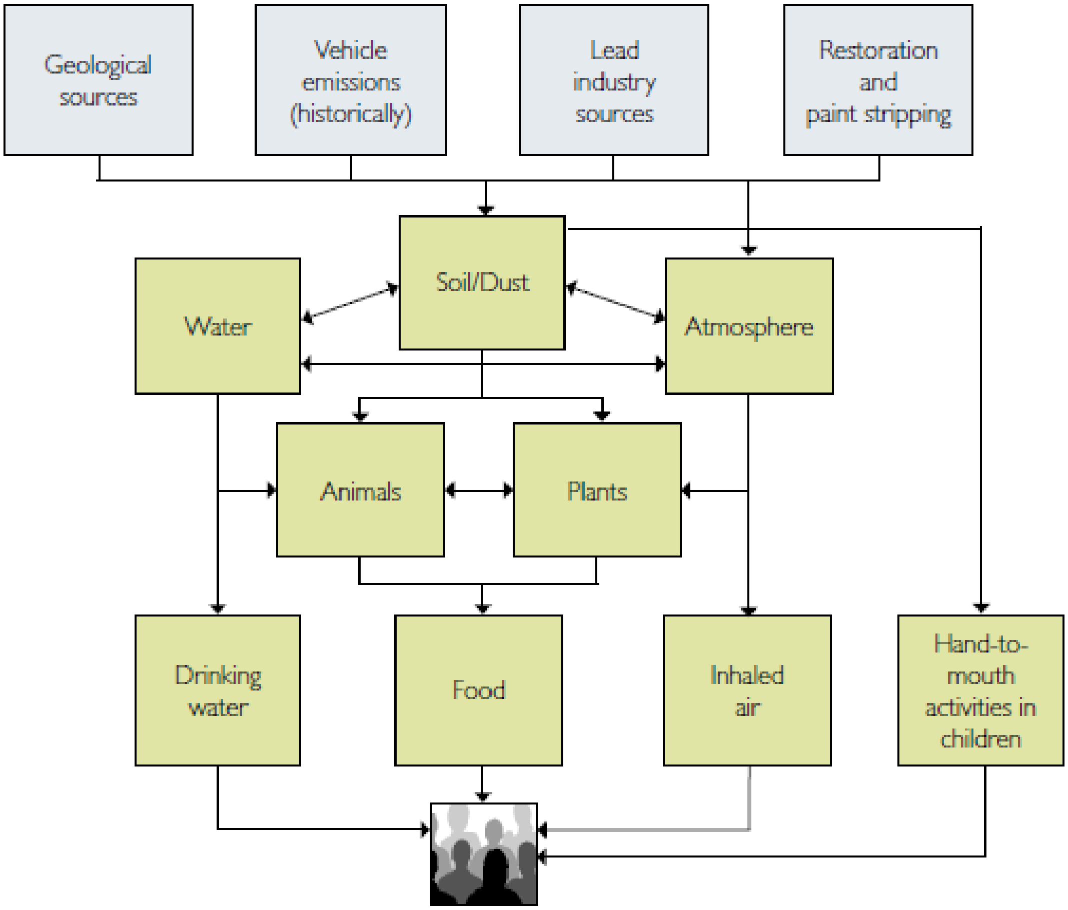


Figure 2.5 Principal pathways of lead from the environment to humans (EPA, 2006).

Lead interferes with functions performed by essential mineral elements such as calcium, iron, copper and zinc. Similarly, lead can displace calcium in bone to form softer denser spots and cause osteoporosis (brittle bone disease). It also inactivates cysteine containing enzymes, allowing more internal toxicity from free radicals, chemicals and other heavy metals (Underwood, 2002). Nervous system is susceptible to concentrations of lead and copper and the effects vary from brain damage (encephalopathy) to damage to the peripheral nerves, causing uncoordinated muscular control and poor eyesight (Monperrus *et al.*, 2005). Hyper reactivity and learning disorders have been correlated with lead intoxication in children. A relationship between lead levels and learning defects (like day dreaming as well as being easily frustrated or distracted) was found to exist. Also a decrease in the ability to follow instructions and poor learning focus in children has been observed (Underwood, 2002).

In addition, toxic concentration of lead (≥ 0.01mg/L) in human beings has been implicated for causing cerebral oedema and anaemia, (Townsend, 1991; Egborge, 1991) both by impairment of haembiosynthesis and acceleration of red blood cell destruction and depression of sperm count (Grytsyuk *et al.*, 2006). It also inhibits red blood cell – enzyme systems (Vasudevan and Streekumari, 2000). A recent review of observational studies by Navas-Acien *et al.*, 2008 concluded that while the apparent effect of lead on blood pressure was minor, the association could be causal, but there was not sufficient evidence to infer a causal relationship of lead exposure with clinical cardiovascular outcomes.

2.5.2.4.4 Carcinogenicity

The World Health Organization (WHO) International Agency for Research on Cancer (IARC) recently concluded that there is limited evidence in humans for the carcinogenicity of inorganic lead compounds, and inadequate evidence in humans for the carcinogenicity of organic lead compounds (such as once used in leaded petrol). The ATSDR considers the evidence to be inconclusive (IARC, 2006; ATSDR, 2007).

CHAPTER THREE

METHODOLOGY

3.1 Description of Study Area

Oyo state has 33 Local Government Areas (LGAs) out of which Ibadan comprises eleven (11) LGAs. Five of these LGAs are in Ibadan metropolis while the remaining six are at the outskirts of the capital city. The study area for this research was Akinyele Local Government Area in Oyo State with its headquarters at Moniya (Figure 3.1).

Akinyele local government area was created in 1976 and it shares boundaries with Afijio Local Government to the north, Lagelu Local Government Area to the east, Ido Local Government Area to the west and Ibadan North Local Government Area to the south. It lies between latitude 7^o 29’ to 7^o 40’ while its longitude ranges from 3^o 45’ to 4^o 04’. It occupies a land area of 464.892 square kilometers with a population density of 516 persons per square kilometer. The local government is divided into 12 electoral (political) wards, namely Ikereku (Ward 1), Labode/Oboda/Olanla (Ward 2), Arulogun (Ward 3), Onidundu/ Amosun (Ward 4), Moniya (Ward 5), Akinyele (Ward 6), Iwokoto/Amosun(Ward 7). Others are Ojoo/Ajibode/Orogun/Owe/Kankon (Ward 8), Ijaye (Ward 9), Alabata (Ward 10), Okegbemi/Mele (Ward 11) and Iroko (Ward 12). According to the last population census Akinyele LGA has a total population of 211,359, the male and female population being 105,633 and 105,726 respectively (NPC, 2006). The predominant population is Yoruba ethnic group, which is over 95 % of the total population of the area and major occupation of the people is agriculture.

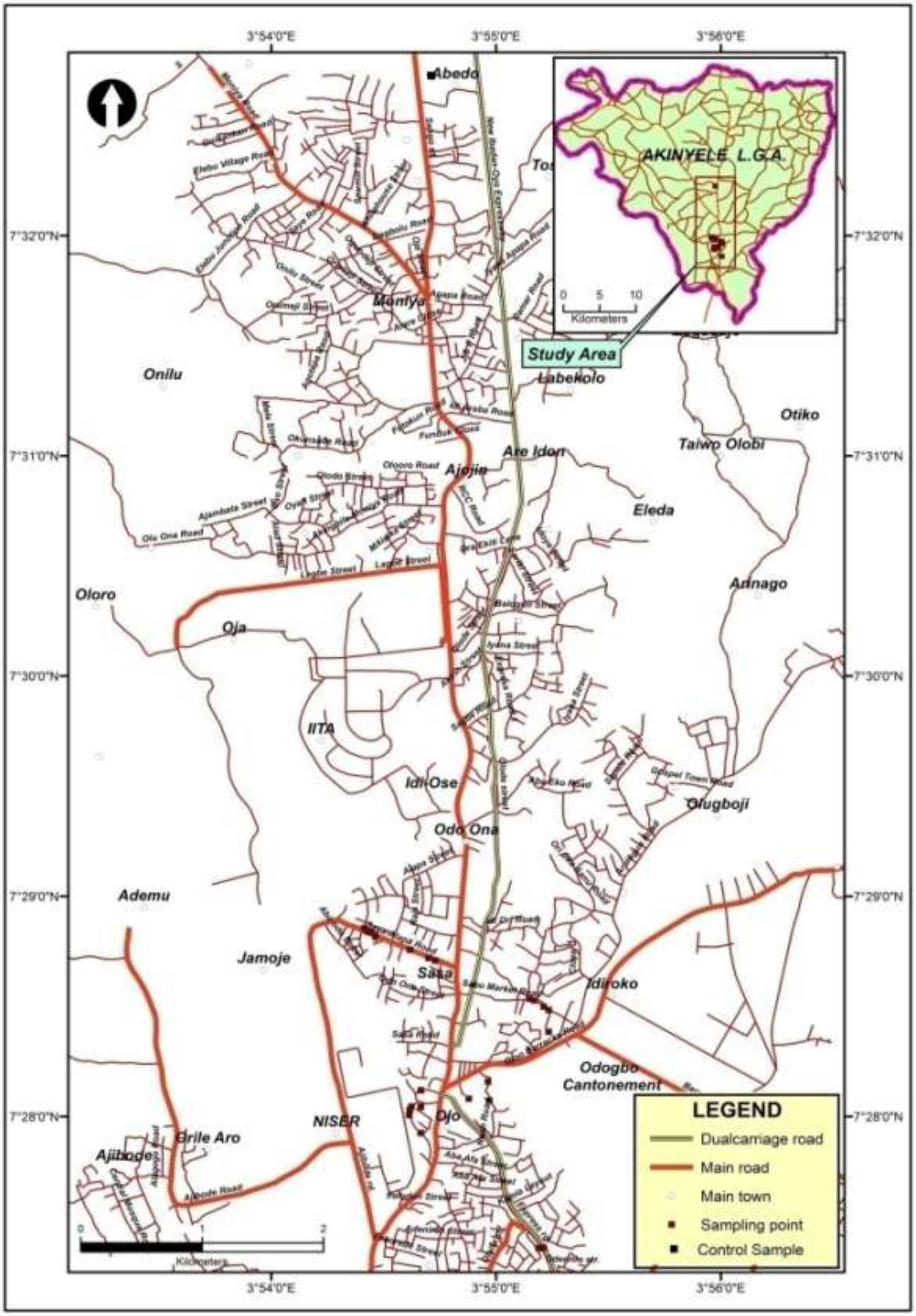


Figure 3.1: Map of Study Area showing Sampling Point

3.2 Study Design

A Simple Random Sampling method was adopted for the study which comprised two components viz: Survey and Laboratory.

3.3 Study Population

The study population is defined as mechanic operators and this included auto mechanics, panel beaters, wielders, painters, rewires, battery chargers and vulcanizes.

3.4. Sample Size

Total sampling was done considering the low population of mechanic operators in individual workshops selected.

3.5 Sampling Technique

3.5.1 Preliminary Survey

A preliminary survey of the study area was carried out prior to the actual survey. It was carried out at Akobo, Lagelu Local Government of Oyo State. This was done to assess the study area and determine the zones and workshops that fit into the study using the selection criteria for mechanic workshops. The zones were then selected based on these initial findings.

3.5.2 Sampling Method and Criteria for Mechanic Workshops

Three out of six mechanic zones were randomly selected in Akinyele Local Government Area (ALGA). The three mechanic zones selected in ALGA were: Alphonso, Temidire and Ojoo. Eight mechanic workshops were selected from each zone using the following criteria:

- number of years of operation (5years),
- absence of other industries within the area,
- presence of groundwater and
- type of activities carried out within the workshop.

A residential area (Moniya) where industries and mechanic activities were absent served as control.

3.5.3 Sampling for Respondents

A pre-visit to some workshops in ALGA revealed that individual mechanic operators in the workshops were few compared to mechanic villages. Hence a total sampling of all the mechanic operators present in the selected workshops were done for questionnaire administration.

3.6 Validity of the instrument

Various measures were taken to ascertain the validity of the instrument. Instruments were reviewed by experts (environmental health specialists, medical statisticians, epidemiologists and health education specialists) for content validity. The instrument which was drawn in English was translated to Yoruba. This was done in order not to lose the meaning of the items in the questionnaire during the process of translation. The investigator who is also fluent in Yoruba and English also reviewed the Yoruba and English versions for accuracy.

3.7 Reliability of the Instruments

The instrument i.e. the English and Yoruba version were pre-tested among automechanics in Lagelu Local Government Area. To confirm the reliability of the instrument, analysis of pre-test data was done using Cronbach's Alpha correlation coefficient of the Statistical Package for Social Sciences (SPSS). Alpha (Cronbach's) is a model of internal consistency, based on the average inter-item correlation (http://www.spss.com). This was done to ascertain the psychometric properties of the instrument. The Cronbach coefficient was 0.65

3.8 Water and Soil Sample Collection and Handling

Soil and water samples were collected in all the workshops across the three zones in Akinyele LGA.

Water Samples

Water samples were collected from dug wells around the workshops within a distance of 0 to 50 metres. For BTEX analysis water samples were collected in 750 ml glass bottles. The bottles were closed tightly and sealed to ensure that no air inflow. Distilled water was used as the sample blank to check contamination. Transportation to the laboratory was done with ice packed coolers to preserve their state. Water samples for physicochemical analysis were collected in 1litre plastic bottles from the various locations and preserved at a temperature below 4 ^{0}C until transported to the laboratory for further analysis.

Soil Samples

In each mechanic workshop, grab samples of top (0-15 cm) and sub (15-30 cm) soils were collected from three different locations respectively, using a soil auger. These samples were representative of top and sub soils respectively within each workshop. Soil samples collected for BTEX analysis was put in aluminum foil and sealed while soil samples for other chemical analysis were collected in a black cellophane bag and transported to the laboratory for further analysis.

3.9 Data Collection

A semi-structured questionnaire was self-administered to the 120 respondents and 112 questionnaires were retrieved after the survey. The information obtained was in three sections, A - demographic characteristics; B - waste generation and handling methods and C - attitude towards ensuring environmental protection and sustainability which was scored on a 12 point scale. Respondents that scored above the mean were categorized as having positive attitude while those below the mean were categorized as having negative attitude. There was a need for the instrument to be translated to the local language for easy communication due to the literacy level among the respondents. (Appendix I (English) and Appendix II (Yoruba version).

3.9.1 Sanitary Inspection of groundwater

A sanitary inspection was carried out at the location of each groundwater (dug well). This was done using a sanitary inspection form and the risk of contamination of each well was scored. The risk score was based on a 13 point scale. This was ranked as;

- 0 to 4 - Low Risk
- 5 to 7 - Medium Risk
- 8 to 10 - high risk and;
- 11 to 13 - very high risk

The ranking method adopted for the inspection was the Water Quality Surveillance guide (Howard, 2002).The sanitary inspection form used is attached as Appendix III

3.9.2 Observation

An onsite observation was carried out across all the workshops in the study area. This was done with the aid of a checklist. The observation was based on the presence and absence of information in checklist provided. The observation was rated;

- Highly present
- Moderately present
- Present
- Absent

The checklist is attached as Appendix IV.

3.10 Determination of Physico-chemical Parameters

pH

A Technel and Technel USHA table pH meter, model PHS- 25 was used to take the pH reading of the sample. The pH meter was calibrated using buffer 4 and 6.7. After this the electrode was put into 50 ml of the sample measured in a beaker and the corresponding reading recorded.

Temperature

The temperature of the water sample was taken using the thermometer in degree centigrade.

Electrical Conductivity

The electrical conductivity and total dissolved solid was measured by dipping the electrode of the portable meter which was a combination of electrical conductivity and total dissolved solid. The corresponding readings were taken after stabilization. The instrument used was a Jenwey portable Condimeter, model 470.

Total Alkalinity

Fifty millilitres of the sample was titrated with 0.02 N H_2SO_4 using 5 drops of phenolphthalein indicator. The titration proceeded while swirling the flask until the solution colour changed from pink to colourless. At this end point, bromcresol green-methyl red indicator was added to the titrated sample and swirled to mix. The titration was continued until a light pink end point was reached. The volume of H_2SO_4 used was then recorded and the alkalinity calculated (APHA, 1998).

Calculations

$$\text{Total Alkalinity, mg/L } CaCO_3 = \frac{[(\text{ml } H_2SO_4)*(\text{Normality of } H_2SO_4)*(50{,}000)]}{[\text{ml of sample used}]}$$

Oil and Grease (Partition-Gravimetric Method)

1. 500 ml of the water sample was acidified with 12.5 ml of HCl, and transferred to a separatory funnel.
2. 30 ml of n-hexane solvent was added to the funnel and the mixture shaken-vigorously for 2 minutes.

3. The upper solvent layer was transferred into a clean conical flask. The lower aqueous layer and any remaining emulsion were extracted with two portions of 30 ml n-hexane where the solvent layer was transferred to the same conical flask after each washing.
4. 10 g Anhydrous sodium sulphate was added to the extract in the conical flask to absorb traces of water.
5. The dried extract was filtered into a tarred distilling flask and then distilled at 63-69 ^{0}C.
6. The remaining oil and grease in the distilling flask was cooled in a desiccator for at least 30 minutes and weighed.
7. The procedure was repeated with deionized water as blank (APHA 1998).

Calculation

$$\text{oil and grease mg/l} = \frac{(\mathrm{A} - \mathrm{B})\mathrm{X}\ 1000}{\text{mL sample}}$$

Where:

A= Weight (mg) of distilling flask + oil and grease

B= Weight (mg) of empty distilling flask)

Moisture Content of Soil Sample

Five grammes of the air dried soil sample was weighed and transferred to a petri-dish and dried in an oven for 101- 110 ^{0}C until a constant weight was achieved. The sample was then transferred to a dessicator where it was cooled to room temperature for 30 minutes. The sample was weighed on an analytically sensitive balance to a sensitivity of 0.01gram.

Percentage moisture was then calculated thus:

$$\%\ \text{Moisture Content} = \frac{W_1-(W_3-W_2)}{W_1}\ \mathrm{X}\ 100$$

Where, W_1= Weight of sample

W_2= Constant weight of petri -dish and,

W_3= Weight of sample + petri -dish after heating and cooling

Digestion of Soil Sample for Heavy Metal Determination

The US EPA Method 3005A acid digestion procedure was used to prepare the soil samples for analysis by flame atomic absorption spectroscopy (FAAS). Five grammes of the air dried and sieved sample (using a 2 mm sieve) was measured into a beaker and 5 ml of concentrated HNO_3 and 10 ml concentrated HCl was added to it. The sample was covered with a watch glass and placed in a water bath at a temperature of 90-95 ^{0}C until the volume has reduced to about 5 ml. The beaker was removed and allowed to cool, after which the walls of the beaker were washed down with distilled water into the digested sample and filtered. The filtrate was made up to 50 ml with distilled water. The blank sample was also prepared the same way.

BTEX Analysis

This method was used to measure individual concentrations of BTEX in water and soil.

Procedure for Aqueous Sample Extraction

A 100 ml of water sample was measured in a graduated cylinder and sample was poured into a separatory funnel and the solvent was rinsed with acetone and methylene chloride.

- 100 ml of methylene chloride was added to the column and the sample poured into the LLE. Ratio 1:1.
- One ml of a surrogate was then added to spike the sample.
- The separatory funnel was sealed and shaken vigorously for 1 to 2 minutes with periodic venting to release excess pressure.
- The organic layer was allowed to separate from the water phase for a minimum of 5 minutes.
- The solvent extract was collected in a round-button flask and concentrated into about 2 ml.
- The methylene chloride was exchanged with hexane by adding 10ml of hexane to the round-button flask and re-concentrating to 2 ml final volume.
- A sample blank was extracted with each batch of samples not exceeding 20 field samples and this was done under the same conditions as that used for samples, with the use of distilled water.

Soil Sample Extraction

- A 50:50 solvent mix of acetone and methylene chloride was prepared.
- 10 gram aliquot of well-mixed soil sample was measured into a beaker.
- 50 ml of the solvent mix was added to the samples and spiked with 1ml of the surrogate mix.
- The sample was sonicated for about 10 – 15 minutes at about 700 ^{0}C.
- 10 g of anhydrous sodium Sulphate was added to the sample until a clear extract developed.
- The extract solvent was poured into a round bottom flask.
- This procedure was repeated once with an additional 50 ml of solvent mix, sonicated and allowed the beaker to settle after which it was decanted into the same round bottom flask.
- The solvent was concentrated; hexane was exchanged with it and re-concentrated to 1 to 3 ml.
- The sample was then ready to be fractionated into the aliphatic and aromatic fractions using silica gel cartridges or columns. The columns were packed with 10 g of 100-200-mesh silica gel pre-conditioned (baked) at 105 ^{0}C overnight. The silica was then mixed with hexane to form slurry.

- *Calculation for Sample Analysis.*

The concentration of each analyte and hydrocarbon range in a sample was determined by calculating the amount of analyte or hydrocarbon range injected, from the peak response, based upon the analyte /internal standard response ratio.

The contribution from the solvent front and the surrogate compound were excluded from the total area of the sample.

Water Samples

$$Cf = \frac{Area\ (p) \times Rf \times Vf \times DF \times 1000}{Vi}$$

Where:

Cf = Final Sample concentration (µg/l)

Area (p) = Measured area of peak (peaks)

Vi = initial volume of extracted (ml)

Vf = Final extract volume.

Df = Dilution factor of sample or extract.

Rf= Response factor from the calibration standard calculation.

Soil Samples

$$\mathbf{Cf = \frac{Area\ (p) \times Rf \times Vf \times DF \times 1000}{Wi}}$$

Where:

Cf = Final Sample concentration (µg/l)

Area (p) = Measured area of peak (peaks)

Wi = initial weight extracted (g dry weight)

Vf = Final extract volume (mL).

Df = Dilution factor of sample or extract.

Rf = Response factor from the calibration standard calculation

3.11 Data Management

Each filled questionnaire was inspected at the end of each day to ensure it was properly filled. After sorting, the 112 questionnaires were serially numbered. All the instruments were packed according to serial number and kept in safe place to maintain confidentiality, as there may be the need to refer to them again in the course of the research process. Data editing was done concurrently with data entry to clarify unclear values. Data cleaning was done by running frequencies of all relevant variables to identify inaccurate entries and missing values.

Quantitative data was analyzed using Statistical Package for Social Science (SPSS). Descriptive statistics, ANOVA, Chi-square test and correlation were used to analyze data. Significance was set at $p < 0.05$ and $p < 0.01$.

3.12 Ethical considerations

An approval letter was collected from the UI/UCH Ethical Review Committee, University of Ibadan, Ibadan (Appendix V). The purpose of this was to ensure that this proposal conformed to the generally accepted scientific principles and international ethical guidelines related to human subjects' researches.

CHAPTER FOUR

RESULTS

This chapter presents the results of the physico-chemical analysis of groundwater and soil, onsite observation of the activities within the workshop, the sanitary conditions around the water sources and the questionnaire survey of the auto mechanic operators.

4.1 Physico-chemical Parameters of Water

The physical and chemical parameters of the water samples in the locations were measured and the result presented in Table 4.1 – 4.3 and Figures 4.1 - 4.5

The appearance of the water samples varied from colourless to slightly brown. Alphonso was generally colourless while Temidire and Ojoo had some samples that were slightly brown and visibly contaminated with dirt. The hydrogen ion concentration (pH) of water in the study area was within the same range throughout the sampling locations. It ranged from slightly acidic to normal at varying degrees. The pH values ranged between 5.1 and 7.4 across the three zones. The range in Alphonso varied between 5.1 and 7.4, with a mean value of 6.4±0.8, Temidire varied between 5.7 and 7.4, with a mean value of 6.8±0.7, Ojoo varied between 6.1 and 7.2 with mean value of 6.7±0.4 while Moniya (the control site) had a mean concentration of 7.6±0.2. Locations in Alphonso and Temidire had pH values which were slightly acidic (Table 4.1).The result shows that some of the pH values in Alphonso and Temidire zones were lower than the WHO guideline limit for domestic use and drinking water (6.5-8.5).

The alkalinity ranged from 36 mg/l to 116 mg/l in Alphonso with an average value of 58.3±28.6 mg/l, 19 mg/l to 112 mg/l in Temidire with an average value of 59.4±46.3 mg/l and 18 mg/l to 260.8 mg/l in Ojoo with an average value of 99.5±82.5 mg/l. The control site had a mean concentration of 54.3±2.1. All the zones had the same trend in alkalinity. Electrical Conductivity (E/C) for Alphonso ranged from 64.8 μScm^{-1} to 152.48 μScm^{-1} with a mean value of 94.6±28.5 μScm^{-1}, Temidire ranged from 120.8 μScm^{-1} to 363.58 μScm^{-1}

with a mean value of 195.1±97.2 µScm^{-1} while Ojoo ranged from 60.38 µScm^{-1} to 501.58 µScm^{-1} with a mean value of 269.2±164.6 µScm^{-1}. The control site had a mean concentration of 60.5± 0.3 µScm^{-1}. The ionic concentrations in all the zones were higher than the control. In comparison with regulatory standards, Alphonso was lower than the WHO limit (300µScm^{-1}) while values in Temidire and Ojoo were higher the guideline limit.

Total dissolved solids (TDS) ranged between 38.8 mg/l to 91.4 mg/l with a mean value of 57.8±16.4 mg/l for Alphonso, 90.2 mg/l to 218 mg/l with a mean value of 117.1±58.3 mg/l in Temidire and 51.7 to 236.5 mg/l with a mean value of 152.7±85.3 mg/l in Ojoo. The control site had a mean concentration of 36.2±0.2 mg/l. The TDS results across the zones were all higher than the control but below the WHO guideline limit of 500 mg/l for groundwater quality.

The temperature of the water samples were within acceptable limits of groundwater quality. It ranged from 23.1 ^{0}C to 27.3 ^{0}C. The mean temperatures across the locations were 26.9±0.3 ^{0}C, 24.3±0.5 ^{0}C, 24.2±0.8 ^{0}C and 27.1±1^{0}C for Alphonso, Temidire, Ojoo and Moniya respectively.

The concentration for oil and grease was very high across the locations. The result shows the concentration ranges from a value of 58 mg/l to 3024 mg/l. The mean values for the three zones were of 1282.9±163.8 mg/l, 1065.6±1383.8 mg/l and 2258±955.5 mg/l for Alphonso, Temidire and Ojoo respectively. The mean concentration of the control was 58.3±0.6 mg/l. All these values were much higher than the control, indicating possible contamination from auto-mechanic activities.

Heavy Metals in Groundwater

The heavy metals were present in the groundwater samples, in varying concentrations (Figure 4.5). The mean concentrations of Cu were 2.5±2.06 mg/l, 0.03±0.01 mg/l and 0.03±0.01 mg/l for Alphonso, Temidire and Ojoo respectively. The concentration at Moniya (control site was) 1.46±0.01 mg/l. The mean concentration for Cd (mg/l) was 0.01±0.02, 0.37±0.51 and 0.64±0.79 in Alphonso, Temidire and Ojoo. Cadmium was not detected at the control site. The mean concentrations of Cr were 0.34±0.28 mg/l, 0.37±0.13 mg/l and

0.31±0.3 mg/l for Alphonso, Temidire and Ojoo respectively. The chromium was not detected at Moniya (control site). Lead was detected only in water samples from Alphonso with a mean value of 10.5±11.37 mg/l. It was found absent in water samples from Temidire, Ojoo and the control site The mean concentrations of all the heavy metals across the three zones (with the exception of copper concentrations in Temidire and Ojoo) were significantly higher than the World Health Organization (WHO) guideline limit for Heavy metals in drinking water (Cu-1 mg/l; Cd-0.003 mg/l; Cr-0.05 mg/l and Pb-0.01 mg/l).

Table 4.1 **Mean values of the Physico-chemical parameters of water across the locations and regulatory limits**

PARAMETERS	ALPHONSO			TEMIDIRE			OJOO			NSDQW STD (2007)	WHO GUIDELINE LIMITS (1993)
	Min.	Max.	Mean±STD	Min.	Max.	Mean±STD	Min.	Max.	Mean±STD		
pH	5.1	7.4	6.4±0.8	5.7	7.4	6.8±0.7	6.1	7.2	6.7±0.4	6.5-8.5	6.5 - 8.5
Alkalinity (mg/l)	36	116	58.3±28.6	19	112	59.4±46.3	18	260.8	99.5±82.5		
E/condt (µScm-1)	64.8	152	94.6±28.5	120.8	363.5	195.1±97.2	82.5	501.5	269.2±164.6	1000	300
TDS (mg/l)	38.8	91.4	57.8±16.4	72.6	218	117.1±58.3	51.7	277	152.7±85.3	500	500
Temperature(^{0}C)	26.5	27.3	26.9±0.3	23.8	25	24.3±0.5	23.1	25.3	24.2±0.8	Ambient	Ambient
Oil & Grease (mg/l)	1068	1560	1282.9±163.8	34	3174	1065.6±1383.8	218	3024	2258±955.5	-	10-30
Cu(mg/l)	0.38	6.12	2.5±2.06	0.02	0.04	0.03±0.01	0.01	0.05	0.03±0.01	1	1
Cr(mg/l)	0.00	0.66	0.34±0.28	0.2	0.57	0.37±0.13	0.00	0.79	0.31±0.3	0.05	0.05
Cd(mgl)	0.00	0.047	0.01±0.02	0.1	1.29	0.37±0.51	0.04	2.19	0.64±0.79	0.003	0.003
Pb(mg/l)	0.00	35.8	10.5±11.37	ND	ND	ND	ND	ND	ND	0.01	0.01

ND = Not Detected

NSDQW = National Standard for Drinking Water Quality

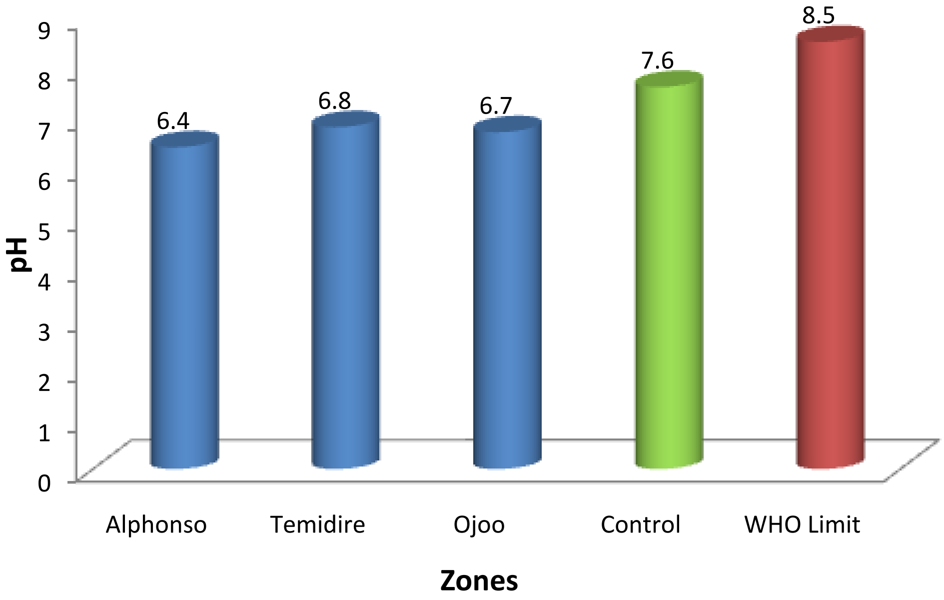


Figure 4.1 Mean pH of groundwater across the zones in comparison with the control and WHO guideline limits

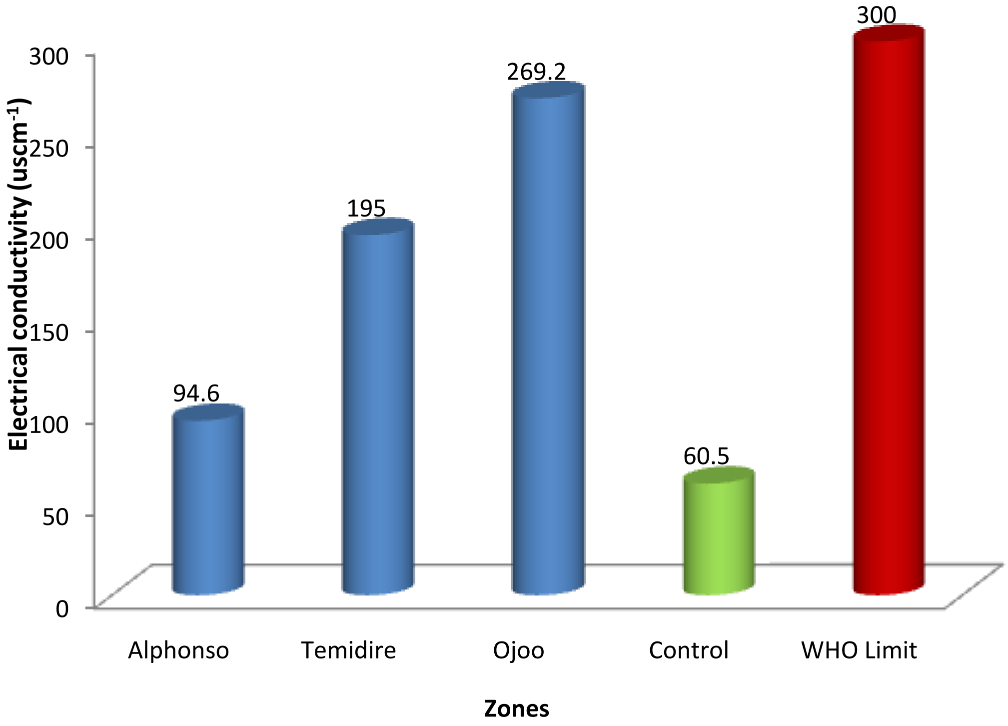


Figure 4.2 Mean Electrical Conductivity (µScm^{-1}) of groundwater across the zones in comparison with the control and WHO guideline limit

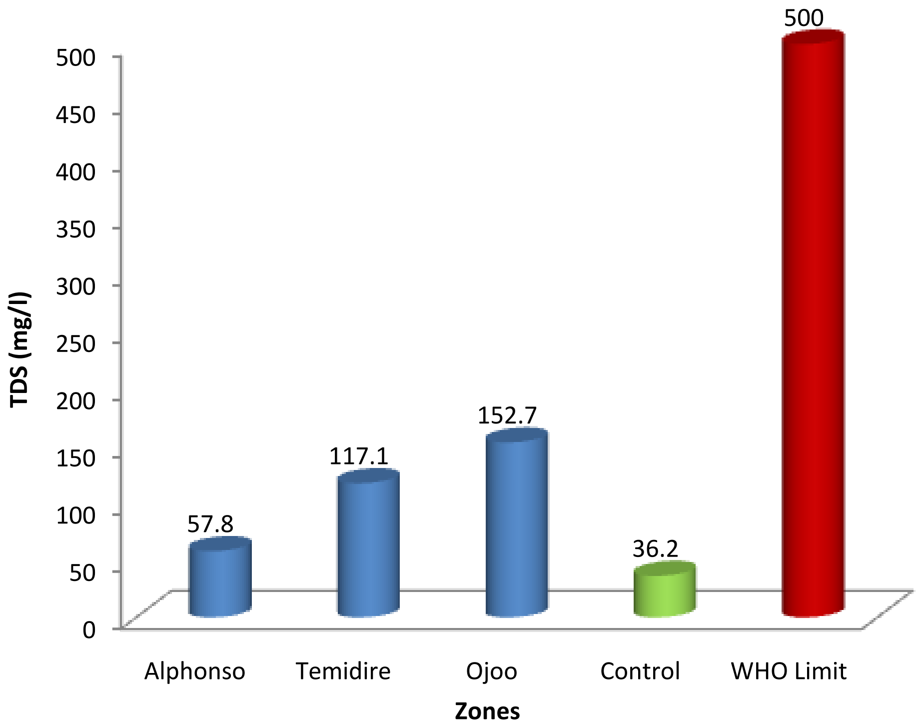


Figure 4.3 Mean TDS (mg/l) of groundwater across the zones in comparison with the control and WHO guideline limit

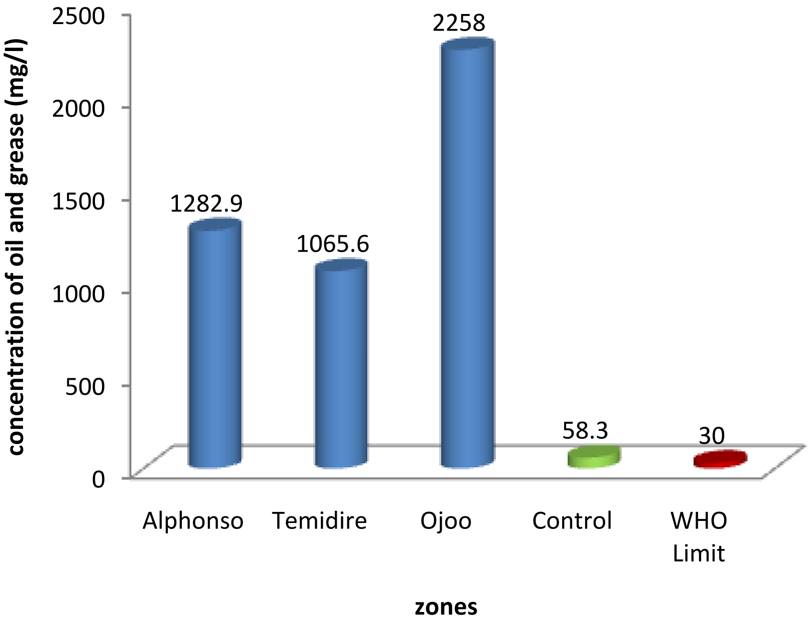
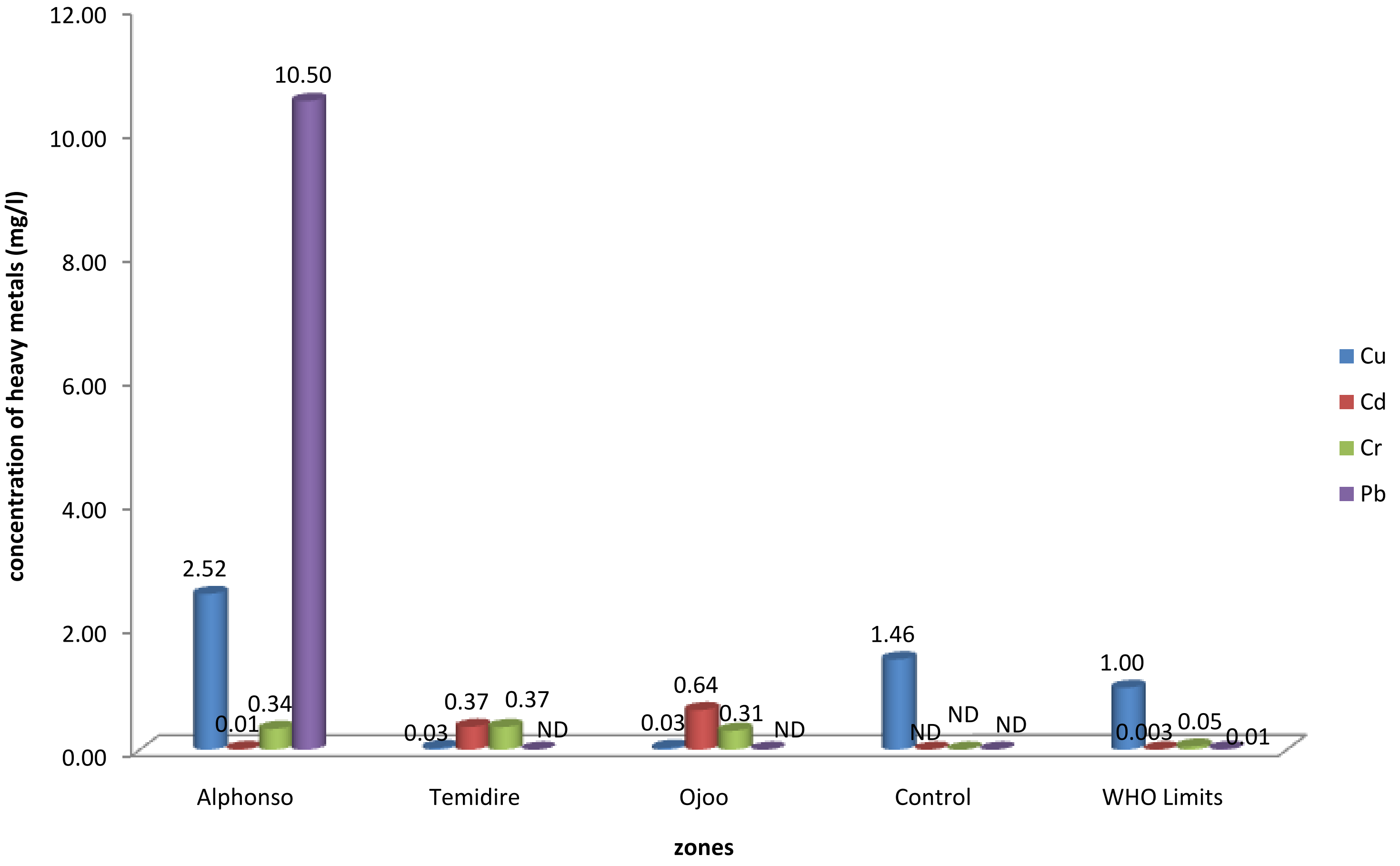


Figure 4.4 Mean Oil and Grease (mg/l) of groundwater across the zones in comparison with the control and WHO guideline limit



ND = Not Detected

Figure 4.5 Concentrations of heavy metals in groundwater across the three zones

4.1.1 Relationship between the Physico-chemical Parameters of Water across the Zones (Alphonso, Temidire and Ojoo)

A correlation analysis carried out to determine the relationship between the physico-chemical parameters of water across the zones. The result revealed that a positive relationship exists between the electrical conductivity, TDS, and Cd while a negative relationship exists between temperature, Cu and Pb across the zones respectively (Table 4.2). A positive correlation exists between TDS and electrical conductivity at $p<0.01$, $r = 0.986$. Temperature correlated negatively with alkalinity ($r = -0.475$, $p<0.05$), electrical conductivity ($r = -0.582$, $p<0.01$) and TDS ($r = -0.601$, $p<0.01$). Also, Cu correlated negatively with TDS ($r = -0.456$, $p<0.05$) and positively with temperature ($r = 0.696$, $p<0.01$). A positive correlation exists between Pb and temperature ($r = 0.625$, $p<0.01$) and also Pb and Cu ($r = -0.545$, $p<0.05$)

The relationship between the means of the physico-chemical parameters of water across all the zones was determined using ANOVA. The result revealed that there was a significant difference in the means of Electrical Conductivity, Total Dissolved Solids, Temperature, Cu and Pb ($f = 4.75, 4.95, 56.8, 8.5$ and 4.97) at $p< 0.05$ respectively across the three zones (Table 4.3).

Table 4.2 Correlation Matrix between the physicochemical parameters of water across the zones

	Zones	pH	Alkalinity	E-Cond	TDS	Temp	oil & grease	Cu	Cr	Cd	Pb
Zones	1										
pH	0.22	1									
Alkalinity	0.31	0.04	1								
E-Cond	.597**	0.03	0.16	1							
TDS	.602**	0.05	0.19	.986**	1						
Temp	-.845**	-0.20	-.475*	-.582**	-.601**	1					
Oil & Grease	0.43	0.25	-0.03	0.22	0.21	-0.10	1				
Cu	-.635**	-0.22	-0.22	-0.44	-.456*	.696**	-0.19	1			
Cr	-0.06	-0.08	0.15	0.08	0.10	-0.08	0.16	-0.36	1		
Cd	.490*	0.12	0.05	0.07	0.07	-0.37	0.42	-0.33	0.20	1	
Pb	-.545*	0.06	-0.26	-0.35	0.00	.623**	-0.16	.545*	0.35	-0.27	1

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

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

Table 4.3 ANOVA of Physicochemical Parameters of water across the zones

	df	F	Sig.
pH	2	0.658	0.53
Alkalinity		1.169	0.33
E-Cond		4.753	*0.02
TDS		4.95	*0.02
Temp		56.807	*0.00
Oil & Grease		3.346	0.06
Cu		8.503	*0.00
Cr		0.089	0.92
Cd		2.705	0.10
Pb		4.969	*0.02

***** Significant at $p<0.05$

4.2 Physico-chemical Parameters of Soil

pH

The pH of the soil varied across the locations sampled. It ranged from 5.1 to 10.2. In Alphonso, the pH value ranged from 6.4 to 8.5 with a mean concentration of 7±0.75 and from 5.1 to 10.2 with a mean concentration of 7±1.6 for top soil and sub soils respectively. In Temidire it ranged from 7.5 to 8.2 with mean a concentration of 7.75±0.27 and 7.6 to 8.6 with a mean concentration of 7.9±0.37 for top and sub soils respectively while in Ojoo, the values ranged from 7.8 to 8.6 with a mean concentration of 8.13±0.3 and 7.4 to 10 with mean concentration of 8.13±0.82 for top and sub soils respectively. The mean concentration at the control site was 8.26 ±0.25 and 7.6±0.4 for top and sub soils respectively (Figure 4.6). Across the three zones the pH values where highest in Ojoo and lowest in Alphonso.

Moisture Content

The moisture content varied at different locations ranging from 0.2% to 98.68%. In Alphonso, the range was from 1.15% to 17.1% with a mean concentration of 7.2±5.2%, and from 0.96% to 98.7% with a mean concentration of 17.9±32.8%, for top soil and sub soils respectively. In Temidire it ranged from 0.4% to 6.7% with mean a concentration of 2.8±2.1% and 0.8% to15.4% with a mean concentration of 5.8±4.6% for top and sub soils respectively while in Ojoo, the values ranged from 0.2% to 9.9% with a mean concentration of 2±3.2% and 0.7% to 11.9% with mean concentration of 8.4±5.4% for top and sub soils respectively. The mean concentration at the control site was 0.14 ±0.01% and 0.96±0.04% for top and sub soils respectively (Table 4.4).

The moisture content of top soils in Alphonso was lowest at location A6 and highest at location A7 while for bottom soil was lowest in location A6 but highest in location A2. In Temidire, moisture content for top soils was least in location B2 and highest in location B1 while for bottom soil it was least in location B2 and highest in location B8. For Ojoo, the top soil moisture was lowest in location C6 and highest in Location C5 while for bottom soil it was the same trend as the top soil. Across the three zones, there was low moisture in the soils with a higher content in sub soils than the top soils.

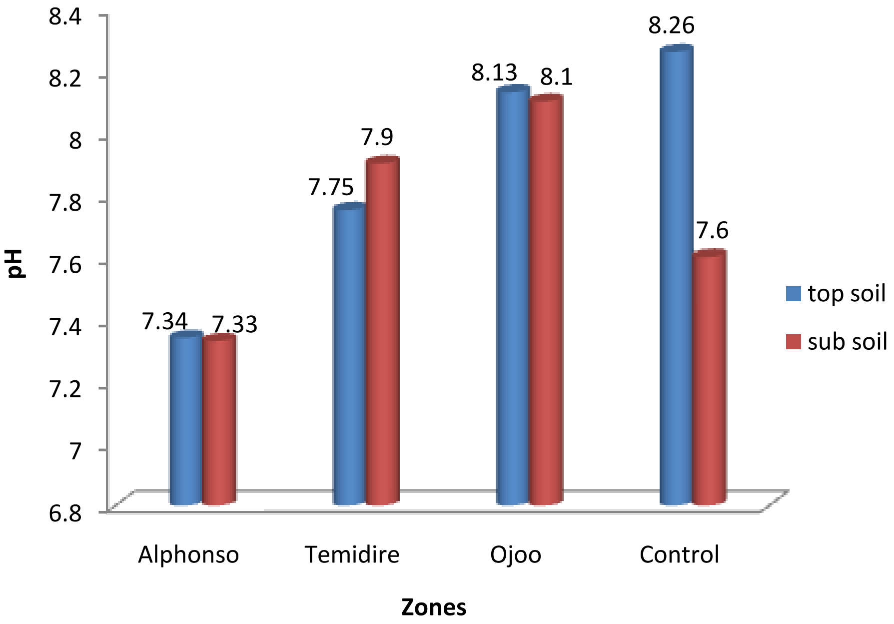


Figure 4.6 Mean concentrations of the pH of Top and Sub soils across the three zones in comparison with the control

Table 4.4 Mean concentration of moisture content in Top and Sub Soil across the Zones

Zone		Minimum (%)	Maximum (%)	Mean± Std Dev.
Alphonso	Top soil	1.15	17.12	7.2±5.2
	Subsoil	1.23	98.68	17.9±32.8
Temidire	Top soil	0.4	6.7	2.8±2.1
	Subsoil	0.8	15.4	5.8±4.6
Ojoo	Top soil	0.2	9.9	2±3.2
	Subsoil	0.7	18.4	8.4±5.4

4.2.1 Relationship between pH and Moisture Content of soil

A correlation analysis was carried out to determine the relationship between the pH and moisture content across the zones (Table 4.5). The result showed that there was a relationship between top soil ($r = 0.688$, $p<0.01$), sub soil ($r=0.408$, $p<0.05$) and the moisture content of the top soils ($r = -0.51$, $p<0.05$) across the zones. These was also a correlation between the top and sub soils across the zones ($r = 0.702$, $p<0.01$)

ANOVA was carried out across the zones (Table 4.6) and the result shows that these is a significant difference in the pH of top soils across the zones ($f = 10.1$, $p<0.05$). Also there is a significant difference in the moisture content of top soils across the zones ($f = 4.54$, $p<0.05$).

Table 4.5 Correlation Analysis of pH and Moisture content of soil

	Zones	pH top soil	pH sub soil	MC top soil	MC sub soil
Zones	1				
pH top soil	.688**	1			
pH sub soil	.408*	.702**	1		
MC top soil	-.510*	-0.311	-0.322	1	
MC sub soil	-0.204	-0.116	-0.12	0.244	1

**. Correlation is significant at the 0.01 level (2-tailed) MC = Moisture Content

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

Table 4.6 ANOVA of pH and Moisture content across the zones

	df	F	Sig.
pH of top soil	2	10.105	*0.001
pH of sub soil		2.335	0.121
Moisture content top soil		4.538	*0.023
Moisture content sub soil		0.863	0.437

*significant at $p<0.05$

4.2.2 Heavy Metals Present In Selected Soil Samples (Lead, Chromium Cadmium and Copper)

The result from the analysis of soil samples revealed the presence of heavy metals (Cu, Cr, Cd and Pb) in varying quantities, from negligible concentrations to higher concentrations. These results were compared with United Kingdom (UK) standards for soil quality (Figure 4.7 to 4.10).

Soil samples were taken from the study area to determine the presence of heavy metals the Pb, Cu, Cd and Cr in the soils as a result of spills from the activities carried out in each of the selected workshops especially car servicing which involve the use of petrol, engine and gear oil. The result of the soil analysis revealed the presence and concentrations of the heavy metals in the order Pb>Cu>Cr>Cd.

The mean concentrations of Pb were 106.1±9.28 mg/kg, 23.5±2.93 mg/kg and 92.83±2.04 mg/kg in top soils and 60.6±6.45 mg/kg, 53.3±5 mg/kg and 65.15±5.5 mg/kg in sub soils for Alphonso, Temidire and Ojoo respectively. The mean concentrations of Cu were 20.37±11.13 mg/kg, 49.12±2.5 mg/kg and 47.5±2.4 mg/kg in top soils and 22.8±8.47 mg/kg, 51.7±3 mg/kg and 41.23±4 mg/kg in sub soils for Alphonso, Temidire and Ojoo respectively while the control site (Moniya) had a concentration of 21.54±3.78 mg/kg and 17.1±2.5 mg/kg for top and sub soils respectively. The mean concentrations of Cr was 23.4±2.4 mg/kg, 22.51±4.8 mg/kg and 18.13±1.6 mg/kg in top soils and 14.7±1.9 mg/kg, 22.53±1.5 mg/kg and 13.06±1.8 mg/kg in sub soils for Alphonso, Temidire and Ojoo respectively. The mean concentrations of Cd was 7.95±1.9 mg/kg, 7.04±2.7 mg/kg and 6.62±9.66 mg/kg in top soils and 7.82±2 mg/kg, 4±3.6 mg/kg and 5.6±3.1 mg/kg in sub soils for Alphonso, Temidire and Ojoo respectively. Lead, Chromium and cadmium were not detected in the top and sub soils from the control site. Figure 4.7-4.10 shows the mean concentration of heavy metals across the three zones for top and sub soils respectively.

The result presented revealed concentrations were observed to be higher than the control sites, indicating possible contamination from activities of auto mechanics in the workshops. The mean result was also compared with the UK permissible limits of these heavy metals in soils 135 mg/kg, 400 mg/kg, 3 mg/kg and 300 mg/kg for Cu, Cr, Cd and Pb respectively. The outcome showed that copper, chromium and lead were all significantly below the limits while cadmium was above the permissible limits.

4.2.3 Relationship between Heavy Metal concentrations in Soil Samples across the zones

Statistical analysis (ANOVA) was carried out to determine if there was any significant difference in the concentration of heavy metals in soil samples across the three zones.

The result revealed that there was a significant difference in the mean concentration of Pb in top soils (0-15 cm) across the zones ($p<0.05$) while for the other metals there was no significant difference in their mean concentration of top soils across the three zones ($p>0.05$). The result also revealed no significant difference in the mean concentration of all the heavy metals in the sub soils (15-30 cm) across the three zones ($p>0.05$).

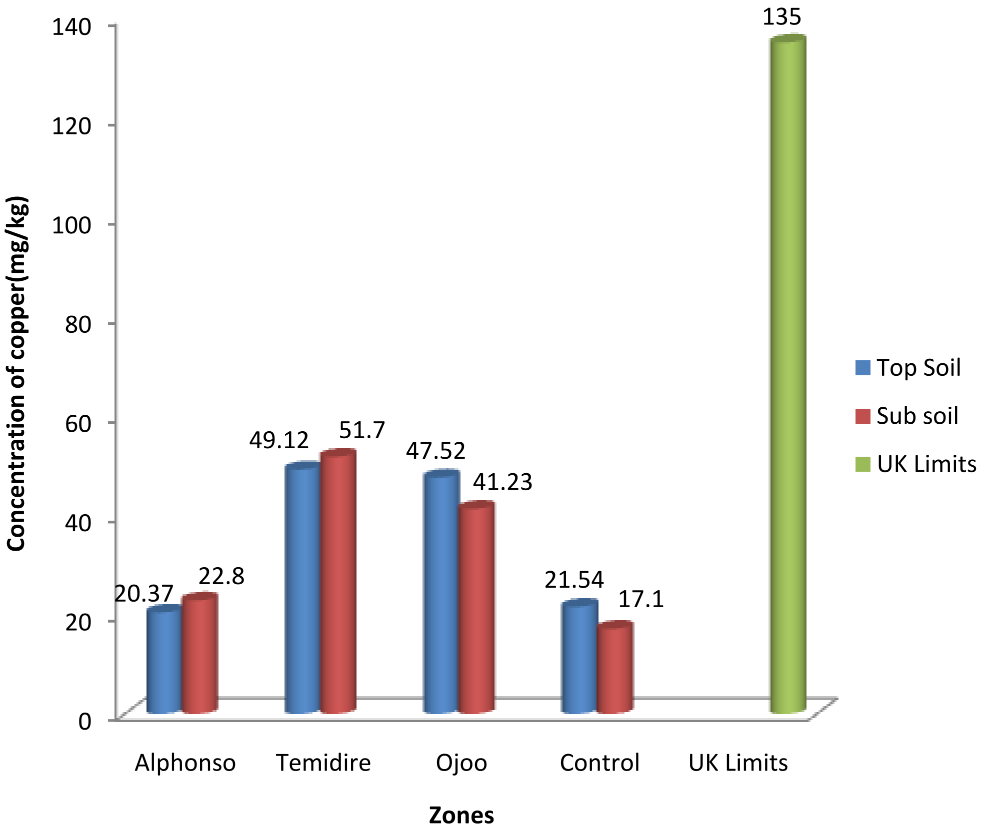


Figure 4.7 Mean Concentration of the Copper (mg/kg) in Top and Sub soils across the zones in comparison with Control and UK Limits

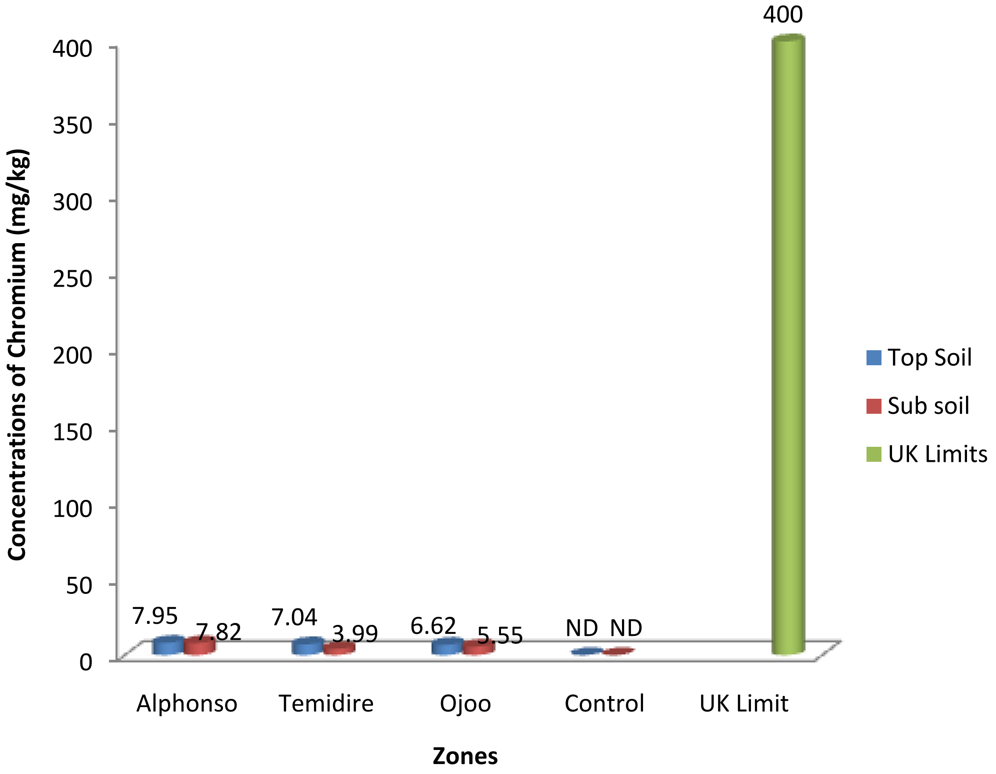


Figure 4.8 Mean Concentration of the Chromium (mg/kg) in Top and Sub soils across the zones in comparison with Control and UK Limits

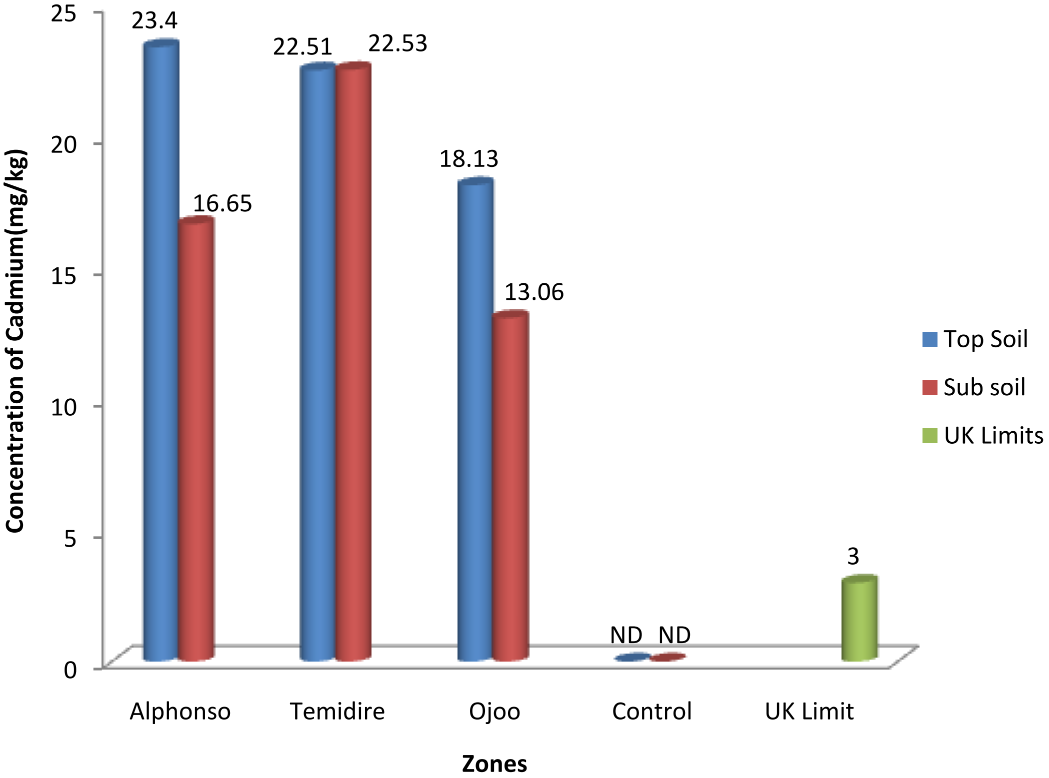


Figure 4.9 Mean Concentration of the Cadmium (mg/kg) in Top and Sub soils across the zones in comparison with Control and UK Limits

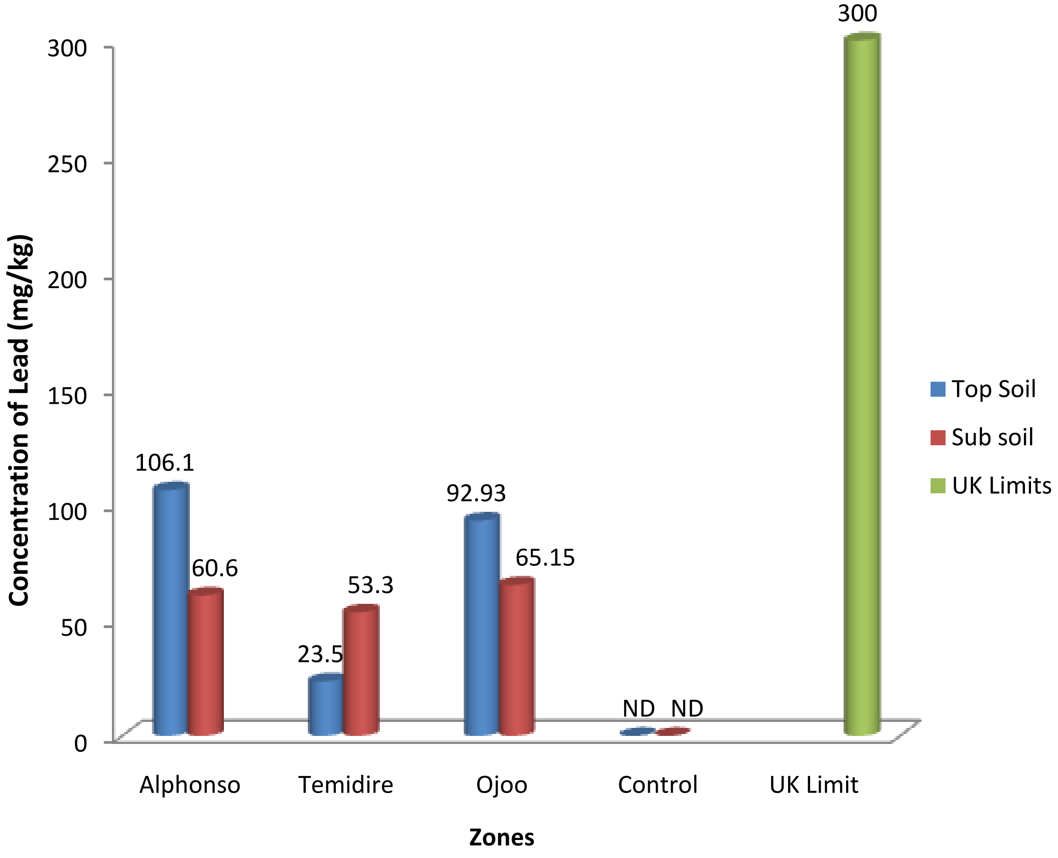


Figure 4.10 Mean Concentration of the Lead (mg/kg) in Top and Sub soils across the zones in comparison with Control and UK Limits

4.3 Concentration of Benzene, Toluene, Ethyl-benzene, Xylene (BTEX) in groundwater and soil samples around the workshops in Alphonso zone

The result of the Benzene, Toluene, Ethylbenzene and Xylene (BTEX) analysis showed varying concentrations across the mechanic workshops in Alphonso (A) for soil samples and water samples (Tables 4.7 – 4.11).

The result presented revealed aggregates of individual concentrations of the BTEX components made up the concentrations of total BTEX in the entire sample locations. The total Benzene, Toluene, Ethylbenzene and Xylene (BTEX) concentrations from the water samples ranged from values below detection limits to 9.112 µg/l. BTEX was detected in two locations only (A5 and A6). The individual component detected in location A5 was Toluene which had a value of 1.150 µg/l. On the other hand, in location A6 is as a result of the aggregate of the individual components present which were benzene, toluene, ethylbenzene, and p, o-xylene with each having concentrations of 2.031 µg/l, 2.017 µg/l, 1.026 µg/l, 2.021 µg/l and 2.016 µg/l respectively (Table 4.7). The mean concentrations of total BTEX revealed that concentrations in location A1 to A8 were<0.001 µg/l except locations A5 and A6 which had 1.15±0.0141 µg/l and 9.112±0.001 µg/l respectively (Table 4.8).

The result of BTEX concentrations in top soil showed a range from 0.007 µg/kg to 4.359 µg/kg. Some of the individual concentrations of the BTEX components were below detection limit although all the samples except the control site had total BTEX concentrations. Location A1 had the components Benzene (0.078 µg/kg) and Toluene (0.062 µg/kg) with an aggregate of 0.140 µg/kg as total BTEX concentration. Location A2 and A6 had only a single component, Toluene with a value of 0.032 µg/kg and 0.211 respectively. Location A3, A4 and A5 each comprised only p-Xylene at a concentration of 0.007 µg/kg, 0.192 µg/kg and 0.231 µg/kg respectively. Both locations A7 and A8 comprised ethylbenzene, m-xylene and o-xylene with each having values of 2.012 µg/kg, 2.020 µg/kg, 0.099 µg/kg, 1.054 µg/kg, 3.125 µg/kg and 0.180 µg/kg respectively. The total BTEX concentrations were 4.131 µg/kg and 4.359 µg/kg for Locations A7 and A8 respectively (Table 4.9).

The mean concentrations of total BTEX in top soil revealed that concentrations in location A1 to A8 were 0.14±0.014 µg/kg, 0.031±0.001 µg/kg, 0.007±0.001 µg/kg, 0.192±0.001 µg/kg, 0.231±0.001 µg/kg, 0.211±0.001 µg/kg, 4.131±0.001 µg/kg and 4.359±0.001 µg/kg respectively. Location A4 had the lowest concentration while location A8 had the highest concentration (Table 4.11).

The outcome from the analysis of sub soil samples revealed that the concentration of all individual BTEX concentrations were below detection limits for most of the locations except locations A4, A5, A6 and A7 which all had single components. Location A4 and A7 had Benzene at a value of 2.118 µg/kg and 0.542 µg/kg respectively while location A5 and A6 comprised Ethylbenzene with each being 0.931 µg/kg and 0.933 µg/kg respectively (Table 4.10). The mean concentrations of BTEX for sub soil showed that locations A1, A2, A3 and A8 had values <0.001 µg/kg while locations A4, A5, A6 and A7 had 2.118±0.001 µg/kg, 0.931±0.001 µg/kg, 0.933±0.001µg/kg and 0.543±0.001 µg/kg respectively (Table 4.11).

A comparison of the mean BTEX concentrations in the water and soil for each location revealed that results were lower than the WHO guideline limit of BTEX [Benzene (10 µg/l), Toluene (700 µg/l), Xylene (500 µg/l) and Ethylbenzene (300 µg/l)] in water and Canadian Environmental Quality Guidelines [Top Soil- Benzene (25 mg/kg), Toluene (75 mg/kg), Xylene (95 mg/kg) and Ethylbenzene (55 mg/kg) and Sub Soil- Benzene (62 mg/kg), Toluene (150 mg/kg), Xylene (190 mg/kg) and Ethylbenzene (110 mg/kg)] for coarse agricultural soils.

Table 4.7 Concentration of BTEX Components in Ground water in Alphonso zone

	BTEX COMPONENTS (µg/l)						
LOCATION	**BENZENE**	**TOLUENE**	**ETHYL BENZENE**	**P-XYLENE**	**M-XYLENE**	**O-XYLENE**	**TOTAL BTEX (µg/l)**
A1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A5	<0.001	1.15	<0.001	<0.001	<0.001	<0.001	1.15
A6	2.31	2.017	1.026	2.021	<0.001	2.016	9.112
A7	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
CONTROL	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
WHO GUIDELINE LIMITS	10	700	500		300		

Table 4.8 Mean concentration of Total BTEX in groundwater in Alphonso zone

LOCATION	WATER (µg/l)
A1	<0.001
A2	<0.001
A3	<0.001
A4	<0.001
A5	1.15±0.0141
A6	9.112±0.001
A7	<0.001
A8	<0.001
Control	<0.001

Where: A1 – A8 represents the eight mechanic workshops selected in Alphonso zone

<0.001 means below detection limit of the instrument

Table 4.9 Concentration of BTEX Components in Top Soil in Alphonso zone

	BTEX COMPONENTS (µg/kg)						
LOCATIONS	BENZENE	TOLUENE	ETHYL BENZENE	P-XYLENE	M-XYLENE	O-XYLENE	**TOTAL BTEX (µg/kg)**
A1	0.078	0.062	<0.000	<0.000	<0.000	<0.000	0.14
A2	<0.000	0.032	<0.000	<0.000	<0.000	<0.000	0.032
A3	<0.000	<0.000	<0.000	0.007	<0.000	<0.000	0.007
A4	<0.000	<0.000	<0.000	0.192	<0.000	<0.000	0.192
A5	<0.000	<0.000	<0.000	0.231	<0.000	<0.000	0.231
A6	<0.000	0.211	<0.000	<0.000	<0.000	<0.000	0.211
A7	<0.000	<0.000	2.012	<0.000	2.02	0.099	4.131
A8	<0.000	<0.000	1.054	<0.000	3.125	0.18	4.359
CONTROL	<0.000	<0.000	<0.000	<0.000	<0.000	<0.000	0
CSQG	25	75	55		95		

Where: A1 – A8 represents the eight mechanic workshops selected in Alphonso zone

<0.001 means below detection limit of the instrument

CSQG: Canadian Soil Quality Guidelines

Table 4.10 Concentration of BTEX Components in Sub Soil in Alphonso zone

	BTEX COMPONENTS						
LOCATION	BENZENE	TOLUENE	ETHYL BENZENE	P-XYLENE	M-XYLENE	O-XYLENE	**TOTAL BTEX (μg/kg)**
A1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
A4	2.118	<0.001	<0.001	<0.001	<0.001	<0.001	2.118
A5	<0.001	<0.001	0.931	<0.001	<0.001	<0.001	0.931
A6	<0.001	<0.001	0.933	<0.001	<0.001	<0.001	0.933
A7	0.543	<0.001	<0.001	<0.001	<0.001	<0.001	0.543
A8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
CONTROL	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
CSQG	62	150	110		190		

Where: A1 – A8 represents the eight mechanic workshops selected in Alphonso zone

<0.001 means below detection limit of the instrument

CSQG: Canadian Soil Quality Guidelines

Table 4.11 Mean concentration of Total BTEX in soils in Alphonso zone

LOCATION	TOP SOIL (0-15cm) µg/kg	SUB SOIL (15-30cm) µg/kg
A1	0.14±0.014	<0.001
A2	0.031±0.001	<0.001
A3	0.007±0.001	<0.001
A4	0.192±0.001	2.118±0.001
A5	0.231±0.001	0.931±0.001
A6	0.211±0.001	0.933±0.001
A7	4.131±0.001	0.543±0.001
A8	4.359±0.001	<0.001
Control	<0.001	<0.001

Where: A1 – A8 represents the eight mechanic workshops selected in Alphonso zone

<0.001 means below detection limit of the instrument

4.4 Onsite Observation

The physical state of the workshops were observed and documented at the time of visitation. Some of the things observed were the presence of oil spills at their work sites, metal scraps from containers or car parts, litters on the floor and water puddles. The result of the observed activities within the workshops are documented and presented in the Table 4.12 below while Plate 4.1 shows the view of mechanic workshop at time of visitation. The observation showed a higher presence of oil spills on the floor in Alphonso compared to the other zones (Temidire and Ojoo). Metal scraps and paints were seen to be more in Alphonso, than Temidire and Ojoo. The same trend was observed for litters on the floor of the workshop. Dirty drains and water puddles were present in Alphonso but absent in Temidire and Ojoo. A higher population of mechanic operators at the time of visitation was seen in Alphonso zone as well. Car density at time of observation was higher in Temidire and Ojoo zones compared with Alphonso.

Table 4.12 Onsite Observations of Mechanic Workshop at time of Visitation

Observations	Alphonso	Temidire	Ojoo
Presence of oil spills on the floor	+++	++	++
Presence of metal scraps, paints	+++	++	+
Litters on the floor	++	+	+
Dirty drains and water puddles on the premises	+	-	-
Presence of mechanic operators	+++	+++	++
Car density in the workshop	++	+++	+++

+++ Highly present ++ Moderately present + Present - Absent

Plate 4.1 A mechanic workshop at Alphonso during visitation

4.5 Sanitary status of the groundwater sources

An assessment of the hazards and contaminant pathways into the source that may cause contamination to the groundwater was done. The sanitary inspections focused on the source and the immediate surroundings.

4.5.1 Sanitary Inspection Score and Risk Assessment

The sanitary inspection was based on observation of the environment of the dugwells as well as activities or facilities to determine the presence of risk factors that could pose serious threats to the water sources. Plate 4.2 shows a dug well at a sampling site.

Twenty dug wells were inspected and scored on a 13 point scale using some given criteria. The risk of contamination from the sanitary inspection ranged from low to high. The inspection revealed that wells at location 1, 7, 11, 12 and 19 had risk scores between 8 and 9 indicating that they were at high risk of contamination, locations 4, 5, 8, 9, 10, 13, 14, 15 and 17 had risk scores between 5 and 7 indicating medium risk of contamination while locations 2, 3, 6, 16, 18 and 20 had risk scores between 1 and 4 (Table 4.13). The percentage risk score of the water sources are presented in Figure 4.11. In general, locations 1, 7 and 19 had the highest risk of contamination while location 3 had the lowest risk of contamination.

Overall, 25% of the water sources inspected were at high risk of contamination, 45% had medium risk while the remaining 30% had low risk of contamination.

Plate 4.2 A sampled well from a residential location 50m from the mechanic workshop

Table 4.13 Level of Risk of Groundwater Sources around the Mechanic Workshops

Locations	Risk Score…/13	Level of risk
W1	9	High
W2	2	Low
W3	1	Low
W4	6	Medium
W5	6	Medium
W6	3	Low
W7	9	High
W8	5	Medium
W9	7	Medium
W10	5	Medium
W11	8	High
W12	8	High
W13	6	Medium
W14	5	Medium
W15	5	Medium
W16	2	Low
W17	5	Medium
W18	3	Low
W19	9	High
W20	2	Low

Risk Score: 11-13= Very High; 8-10=High; 4-7= Medium; 0-4=Low; W= dug well

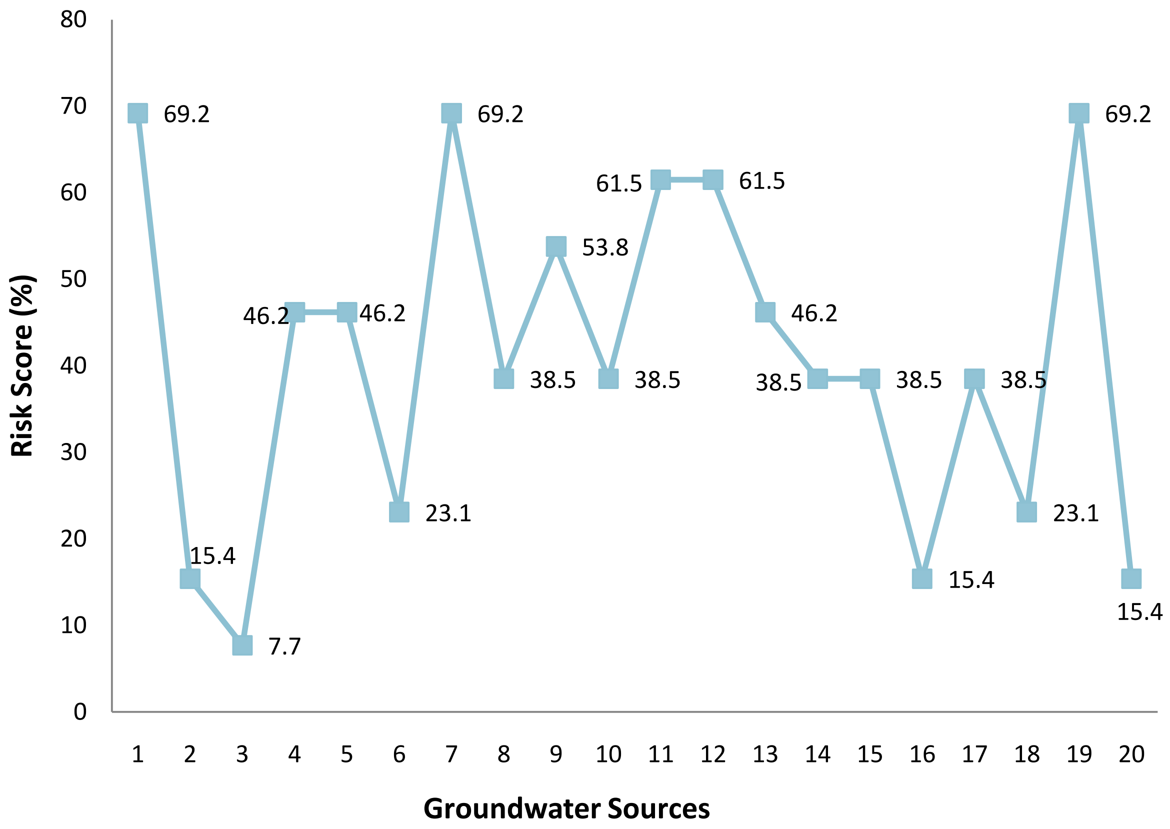


Figure 4.11 Risk Score (%) of the water sources in the study area

4.6 Description of Auto Mechanic Operators and their Activities

Auto mechanic operators across the three zones viz; Alphonso, Temidire and Ojoo participated in this study. Their socio- demographic characteristics, activities, practices and attitudes were assessed. A total number of 112 respondents were involved in the exercise.

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4.6.1 Socio -Demographic Characteristics of Mechanic Operators in the Study Area

The study revealed that the age range of the auto mechanic operators ranged from 18 to 61years of age (Figure 4.12). Less than 21yrs (2.7%), 21-30yrs(19.6%), 31-40 years(41.1%), 41-50yrs (28.6%), 51-60yrs (7.1%), and 61yrs above (0.9%). All the operators were male with 82.1 % of them being married and 17.9% single. The level of literacy of these operators showed that 86.6% of them had secondary school education, 10.7% of them had primary education while only 2.7% did not have any formal education (Table 4.14). None of them had any form of tertiary education. Most of the operators were Yoruba men (89.3%), 8.9% of them Igbo and only 1.8% were Hausa men.

The job designation varied across the respondents with a large portion of them being auto mechanics (63.4%), 12.5% panel beaters and 7.1% being wielders. Others were rewires (6.2%), painters (5.4%) and battery chargers (5.4%).The study revealed that 20.5% of the respondents were apprentices, 25.9% supervisor and 53.6% of them are foremen. The years of work experience of the operators ranges from 1 to 35years.Less than 10 years work experience (49.1%), 10-20years experience (40.2%), 21-30years work experience (3.6%) and above 31years work experience (7.1%) (Table 4.14).

Table 4.14 Demographic Characteristics of the Respondents (N=112)

Demographic Variables	**Frequency**	**Percentage**
Marital Status		
Single	20	17.9
Married	92	82.1
Total	112	100
Educational Status		
primary education	12	10.7
secondary education	97	86.6
no formal education	3	2.7
Total	112	100
Job Description		
Auto mechanic	71	63.4
Rewire	7	6.2
battery charger	6	5.4
panel beater	14	12.5
Painter	6	5.4
Welder	8	7.1
Total	112	100
Job Position		
Boss	60	53.6
Supervisor	29	25.9
Apprentice	23	20.5
Total	112	100
Years of Working Experience		
less than 10 years	55	49.1
between 10 - 20 years	45	40.2
between 21 - 30 years	4	3.6
31 years above	8	7.1
Total	112	100

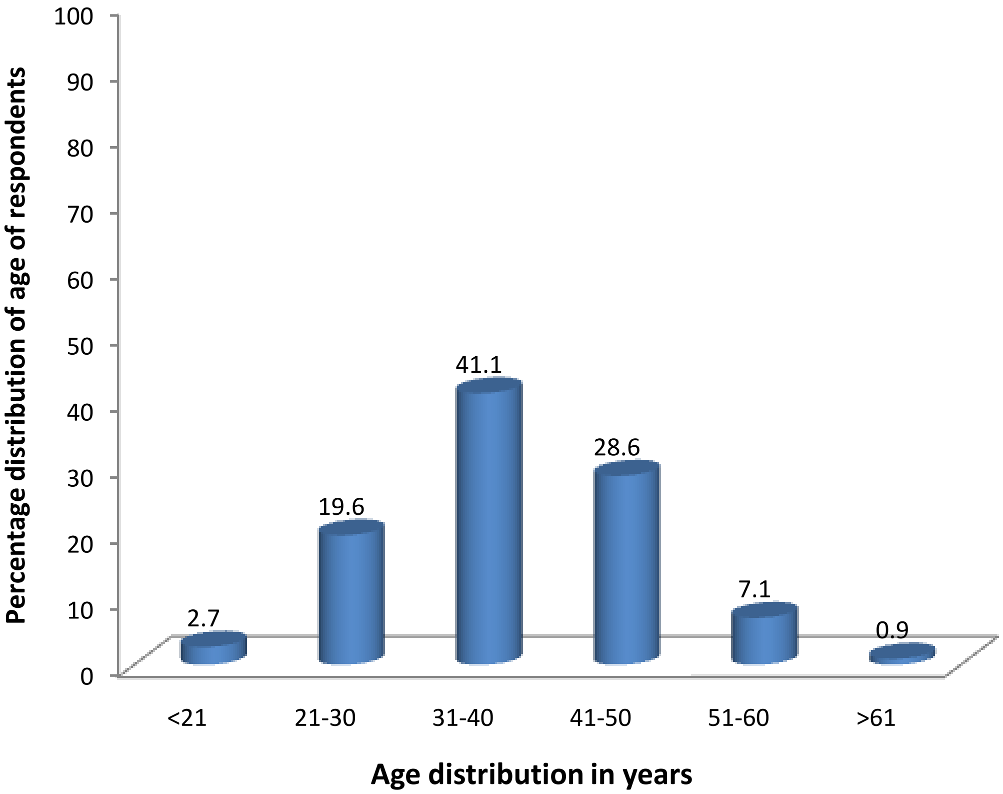

Figure 4.12 Age Distribution of the Participants in the study area

4.6.2 Activities, Practices and Types of Waste Generated in the Study Area

The workshops in the study area span between 5-18 years of existence and they had a range of activities which include auto servicing and maintenance, battery charging and repair, panel beating, welding (arc/electric), spraying, electrical repair and painting. Of all these activities, the most common that was practiced daily were the auto servicing and maintenance (88.4%), battery repair (25.9%), panel beating (50%), welding (33.9%), electrical repair (41.1%) and painting (41.1%) as seen in Figure 4.13. These activities were based on the various skilled operators functioning in different units within the workshop (Plate 4.3 – 4.4). Due to the type of activities carried out, different types of wastes were generated within the workshops. Some of these include engine oil waste, gear box oil waste, petrol, carbide, acid, metal scrap, nylons, wires, paints containers and thinners, car plugs and batteries (Plate 4.5 - 4.6). The auto servicing operators had the highest activity and in turn generated the largest amount of waste (60.1%) this included, gear oil, engine oil, and petrol spills in addition to all sorts of car parts that were not useful any more. The next to this was the carbide generated from panel beating which was 49%. Electrical repairs were also done and the waste generated from these was minimal (33%), the components included nylons, tapes wires and smelted soldering lead. The least waste generated was the acid waste from the batteries (27.7%). Figure 4.14 shows the quantity of waste generated per activity type across the workshops.

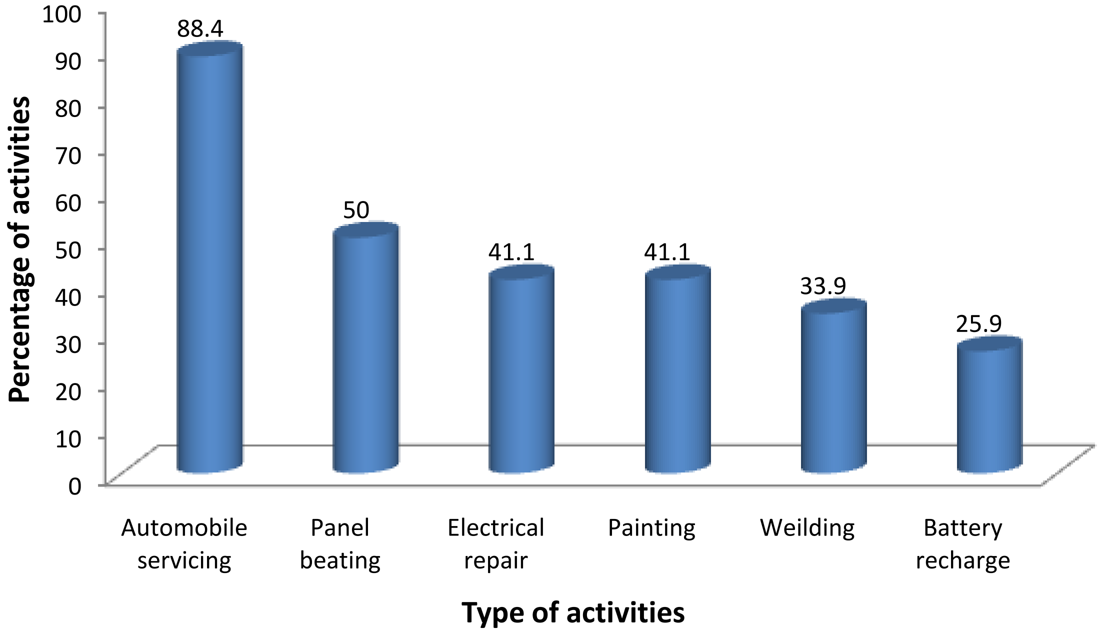

Figure 4.13 Common Activities in Mechanic Workshops in the study area

Plate 4.3 Vehicle servicing in a workshop

Plate 4.4 Panel beating activity in a workshop

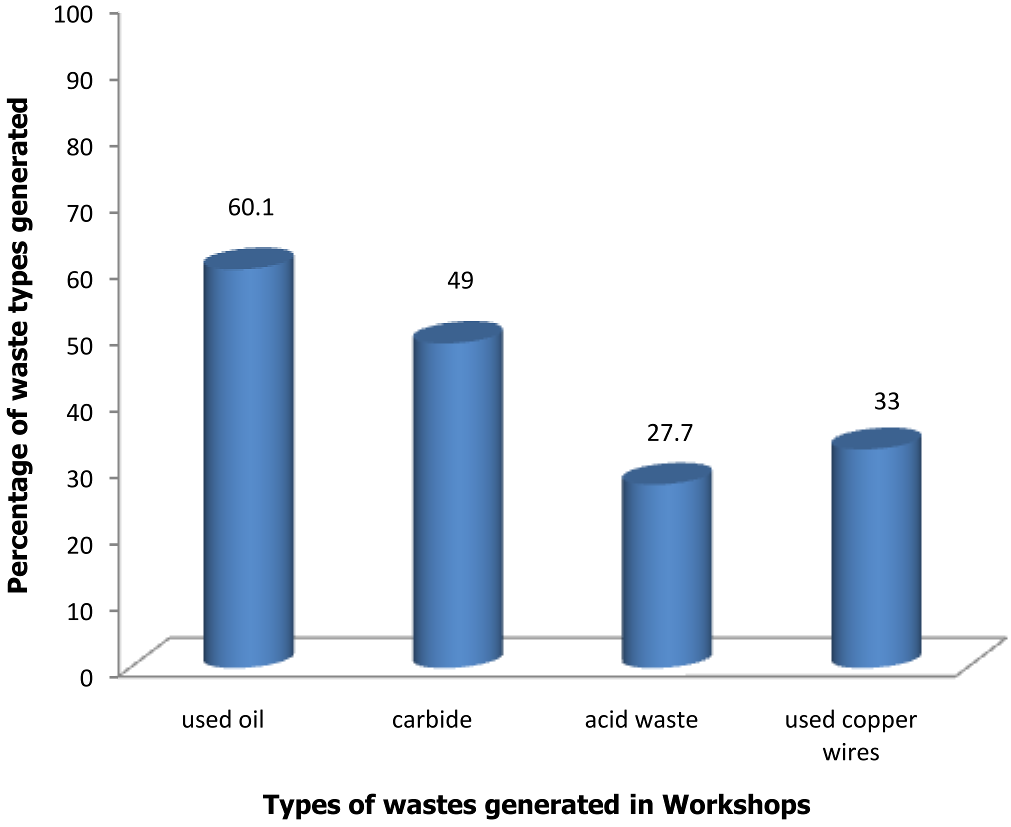

Figure 4.14 Percentage of waste generated per activity type across the workshops in the study area

Plate 4.5 Carbide waste generated from panel beating activities in a workshop

Plate 4.6 Metal scraps, nylon and oil waste from a workshop

4.6.3 Attitude of Respondents towards Ensuring Environmental Protection

The attitude of respondents towards ensuring environmental protection while carrying on their daily activities was evaluated using a 12-point scale. The result revealed that a higher population of the operators 92(82.1%) had a positive attitude while the minority 20(17.9%) had a negative attitude towards environmental protection.

This result was cross tabulated with the three zones and the result showed that in Alphonso 4(3.6%) operators had negative attitude towards environmental protection while 30(26.7%) had positive attitude. In Temidire 12(10.7%) operators had negative attitude while 47(42%) had positive attitude while in Ojoo 4(3.6%) of the operators had negative attitude and 15(13.4%) had positive attitude (Table 4.15). The result also revealed that there was no significant difference between the location of the operators and their attitude towards environmental protection ($p>0.05$) within the study area.

As part of the study the operators were asked to indicate if they would favour regular training on environmental matters and their health safety and 100% approval was given with 85% advocating for regular training while the remaining 15% advocated for training at intervals.

Table 4.15 Attitudinal Score of Mechanic Operators in the Study Area

Zones	Negative attitude	Positive attitude	Total	df	X^2	P value
A	4(3.6%)	30(26.7%)	34(30.3%)	2	1.24	0.538
B	12(10.7%)	47(42%)	59(52.7%)			
C	4(3.6%)	15(13.4%)	19(17%)			
Total	**20(17.9%)**	**92(82.1%)**	**112(100%)**			

CHAPTER FIVE

DISCUSSION

5.1 Physico-Chemical Quality of Groundwater

The findings of the study revealed that the water samples in the study area had pH values ranging between 5.1 and 7.8 which showed a range from slightly acidic to neutral. Slightly acidic waters would not be permissible for domestic use and as well as drinking because of the unpleasant effects that could arise from its use. These acidic waters were not within the permissible limits of regulatory bodies such as World Health Organization (WHO) 1993 and Nigerian Standard for Drinking Water Quality (NSDQW) 2007 with permissible limits of 6.5 - 8.5. The presence of acid in the water is an indication of possible contamination from improper disposal of battery water as well as cleaning solvents from the workshops poured on the ground directly. These hazardous constituents percolate through the soil and contaminate the surrounding groundwater easily since all mechanic workshops visited do not have cemented floors. The range of the pH is also falls into the category of slightly polluted water according to the grouping of water by Prati *et al.*, 1971. Based on the WHO guidelines (2003), the pH of the entire sampling location would not adversely affect its use for domestic purposes. The effects of acidic waters on human health and the environment have been widely reported. Rogers (2013) revealed that acidic waters have been known to cause irritation due to corrosion effects and at extreme levels worsen existing skin conditions. Also, it can cause laundry staining or blue-green stains in sinks and drains.

The study also revealed that the electrical conductivity of the water was quite high in a number of locations and above the permissible limits of 300 µS/cm (WHO, 2003), making the water source questionable and unfit for domestic use, drinking and agricultural purposes High conductivity will in most cases affect the taste of water (Langenegger, 1990). The similar observations have been reported in studies carried out by Ololade *et al.*, 2009 which revealed high electrical conductivity in both dug wells and ground water.

The very high concentration of oil and grease in ground water with values as high as 3024mg/l within the study area cannot be overlooked. It is far above the WHO limits for water (10 – 30 mg/l). This high result may not be unconnected with volume of engine and gear oil spilled during car servicing as well as the petrol spills that occur when washing some engine parts. The gradual occurrence over a period of time based on the years of existence of the workshop will have a likely impact on the groundwater quality within that environment. This calls for serious concern as consumption and domestic use of such water is dangerous. Results of total dissolved solids (38.8 – 277 mg/l) shows it was within the WHO permissible limits and Nigerian standards of water for domestic use (500 mg/l). This indicates that the dissolved solids present in the groundwater of the study area are reduced to the barest minimum as observed in similar studies by Alao *et al.*, 2010. Also the temperatures of the water samples 23.1 – 27.3 ^{0}C were within the acceptable limits of ambient temperature.

The findings of this study also revealed that the concentrations of heavy metals in the groundwater samples in the study area varied per zone although results showed that mean concentration were above the maximum permitted levels by WHO and Nigerian Drinking water standards (Cu- 1 mg/l; Cr- 0.05 mg/l; Cd - 0.003 mg/l and Pb - 0.01 mg/l). The result revealed the presence of copper(Cu), lead(Pb), chromium(Cr) and cadmium (Cd) in Alphonso, Temidire and Ojoo zones with the exception of lead in Temidire and Ojoo zones respectively. The results showed highest concentrations of these metals in Alphonso zone, the mean values being Cu-2.5 mg/l, Cr-0.34 mg/l, Cd-0.01 mg/l and Pb-10.5 mg/l. Lead had the highest concentration among the heavy metals.

Concentrations of Cu and Pb were higher than that those observed in the study carried out by Bala et al., 2008. Studies have shown, where a concentration of 0.1 mg/l had resulted in the development of neurological problem in fetuses and children (Fatoki *et al.*, 2002; EPHA, 2009) and also potential effects of Pb levels above the maximum guidelines causing kidney problems and high blood pressure in adults (Zietz *et al.*, 2007; EPHA, 2009). Also the high concentration of Cu in this study also poses potential health threats, such as liver and kidney damage if the exposure is long term (Lentech, 2011), gastrointestinal disease if short term exposure (WQA, 2005) and Wilson’s disease. There is also a link between long term exposure to copper and decline of intelligence in young adolescents (Lenntech, 2009).

The concentration of cadmium and chromium were above the maximum permitted levels and this is a source of concern considering the carcinogenic properties of cadmium (Lauwerys, 1979) as well as a long biological half-life (Orisakwe *et al*., 2006) leading to chronic effects as a result of accumulation in the liver and renal cortex (Hammer and Hammer Jr., 2004). It can also cause kidney damage as well as produce acute health effects arising from exposures to high concentrations and long term exposures (Orisakwe *et al*., 2006). Although chromium in its trivalent form is an essential nutrient, exposure to its hexavalent form is hazardous to health in excess of permitted levels is also carcinogenic. It could cause damage to liver, kidney circulatory organs and nerve tissues; as well as cancer of the lungs (OSHA, 2009).

5.2 Physico -Chemical Quality of Soil

The soil pH also revealed that the varying pH levels from strongly acidic to very strongly alkaline (5.1-10.2) and this could be as a result of the various activities carried out in the workshops which involves, wielding, battery charging, panel beating painting, auto engine servicing and repair. All these activities involve the use of certain chemicals that are either acidic or basic in nature. When used, they have the ability to affect the pH composition of soil (Adelekan and Abegunde,2010) which in turn, will affect the pH of groundwater over a period of time. This could render the water acidic and unsafe for domestic purposes. Also crop growth on soils with pH level above that which could the plant can tolerate would affect their development and the final consumer.

The moisture content of the soil was very low. This revealed that the water retention level of the soil as well as the water holding capacity was low. This could be as a result of the season in which the study was carried out (dry season) as well as the type of soils in the workshops. The low retention level of water also reveals the porosity of the soil. (Nwanchukwu *et al*., 2010). The findings further reveals that the moisture content in the bottom soils are twice the concentrations in the top, indicating the level of porosity of the top soils. Soil moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water depends on the soil moisture content (GRWTAC, 1997).

This study revealed varying concentrations of heavy metals in top and subsoil in the study area. Across the locations studied, the heavy metals copper, chromium and lead were below the permissible limits of these heavy metals in the United Kingdom (UK) which was used as reference (Cu-135 mg/kg; Cr-400 mg/kg; Cd-3 mg/kg and Pb-300 mg/kg) while cadmium exceeded this limits. The locations revealed higher concentrations of heavy metals above the control site, indicating contamination of the soils in the workshops. The concentration of heavy metals in this study was higher that studies carried out by Okoro et al 2013 on soils in mechanic villages in Owerri municipal, Imo state. Copper concentrations recorded in soil samples from workshops could have been as a result of the use of copper wires, materials as well as soldering activities in these workshops. This result corroborates findings of Adelekan and Abegunde, 2010 who recorded copper levels in a study of soil in some mechanic villages in Ibadan. According to Alloway (1990) when copper ends up in soils, it strongly attaches to organic matter and minerals. As a result, it does not travel very far after release. Due to the limited mobility, applied copper has a disposition to accumulate in soil (Slooff *et al.*, 1989). Hence higher values of copper recorded in the top soil.

Cadmium was observed in all the locations studied. It was detected in both top and sub soils at concentrations above the UK permissible limit. This could be as a result of the nature of cadmium, considering the ease of mobility compared to other metals (Alloway, 1995). When cadmium concentrations in soils are high they can influence soil processes of microorganisms and threaten the whole soil ecosystem. This supports a study by Kabala and Singh (2006), on the distribution and mobility of cadmium. Results of cadmium in this study did not correspond with findings of Ilemobayo and Kolade (2008) which did not detect cadmium in automechanic soils in Akure and the same trend was observed as regards of Adelekan and Abegunde, 2010 which also discovered that cadmium was not detected in about 50 % of the samples studied.

Chromium was present in all the samples studied and below the UK permissible limits. This also corroborates similar study carried out by Adelekan and Abegunde, 2010. Although chromium concentrations was found to be lower than the findings reported from the study of Akporido and Asagba (2013) which revealed concentrations of chromium in soil around lubricating industry was above regulatory guideline limits. Despite the low concentration of chromium in the soils studied, it is worthy of note that, gradual deposition and buildup of this heavy metal in the environment could lead to large amounts of this pollutant in biogeochemical circulation (Wyszkowska, 2002).

Concentration of Pb in this study was similar to those reported in the study carried out by Ipeaiyeda and Dawodu (2008). The observation of higher retention of Pb in the top layers of the soil at Alphonso and Ojoo corroborates the finding of Edori and Edori (2012) and Davies (1995) which stated that lead is especially prone to accumulation in surface horizons of soil because its low water solubility results in very low mobility. Also some exceptionally high values of lead have also been reported in the literature and most were in one way or the other connected to manufacturing sites of vehicle batteries. The concentration of lead in this study was found to be lower than that in a study carried out by Adie and Osibanjo (2009) which found a range of 243 to 126,000 mg/kg in soils from the environment of a battery manufacturing plant. The same was also observed in a study by Nwoko and Egunjobi (2002) who discovered Pb in high concentrations in soil and vegetation of an abandoned battery factory site. The concentrations of lead recorded above the control are not unconnected to the auto mechanic activities and the length of years of existence of these workshops (Osu and Okereke 2010).

In comparing the results from this study with standards from European communities commission (ECC), 1986 and Sweden permissible limits (ECDGE, 2010). Asides chromium, the results are higher than regulatory limits in all locations. The effect of washing down of the contaminants in soil into surface water and percolation to groundwater was observed in the heavy metal concentrations in the water sampled in the study area. The contamination of the water and soil in this study exposes man and animals to serious health dangers because heavy metals interfere with normal body biochemistry and normal metabolic processes (Okunola *et al*., 2011).

5.3 BTEX concentrations in Groundwater and Soil and its Health Effect

The study revealed that the BTEX concentrations for the groundwater within the study area were far below detection limits. It was not detected for almost all the locations except A5 and A6, where it was present in minute concentrations. This detection in locations A5 and A6 can be attributed to the mechanic activities, the length of years of existence and the practices within the workshop. In spite of this, the concentrations are minimal and hence can be implied that there will be no health effect whatsoever on the domestic users and consumers of this water. This is an indication that they are free from such health risks associated with consumption of BTEX co-ntaminated water (ATSDR, 2004). The same trend was observed in the soil where though BTEX was detected, the concentrations were minimal with higher concentrations in the top soil than the bottom soil. This result is similar to past studies carried out in Port Harcourt by Osu *et al.*, 2009 where the BTEX concentrations were discovered to be very low. The higher concentrations seen in the soil compared to water cannot be unconnected with the fact that the petrol and oils spilled to the ground are petroleum products from which these organic pollutants are released directly into the soil. Also sorption is influenced by the characteristics of soil matrix and the fluid media (Bedient, 1994)

Despite the fact that the wastes generated at the automobile workshops are mainly oil and petrol spills (a means through which this organic compound is released), a minimal effect on the contamination of soil and groundwater within the study area has been observed. This could be due to the fact that during the survey, it was discovered that the rate at which used motor oil is being drained directly to the ground has reduced over a period of time in the study area. Also, the degradation of BTEX affects its concentration in soil and groundwater since it can undergo aerobic and anerobic biodegradation (Barker *et al.*, 1987; Ball and Reinhard 1996; Lovely *et al.*, 1994) as well as natural attenuation (McDonald, 2000). The characteristics of BTEX which includes rate of volatilization, dissolution, sorption and microbial degradation to a very large extent are important in determining their concentration in soil and subsequent contamination of groundwater (Bedient, 1994; Salanitro *et al.*, 1997).

5.4 Sanitary Inspections

Sanitary inspections were carried out as a form of risk assessment to determine possible means of contamination and the potential risks. Various risks that could lead to the contamination of the wells inspected were identified. The overall sanitary inspection revealed that about 25 % of the wells visited had high risk of contamination, 45 % medium risk of contamination while 30 % had a low risk of contamination considering the criteria on which the inspection was based. The immediate surroundings of these water sources were put into consideration. The 25 % with high risk of contamination did not meet satisfactory conditions as regards sanitary inspection of dug wells. The poor sanitary conditions of these wells observed at the time of inspection were not satisfactory and this could lead to health risks if these conditions remain the same over a period of time. Hence a need for interventions and regular assessment of the water sources to prevent and ameliorate water related diseases that could arise.

5.5 Socio-demographic Characteristics and Activities of Auto mechanic Operators

The study revealed that higher populations of the auto mechanic operators were men within the age bracket 31-40 years who had been at this occupation for at least 10 years. This reveals that quite a number of these mechanic operators are adults. This is in accordance with the United Nation age classification (2005a). This can be related to the study carried out in mechanic villages in Imo, where individuals who had over 40years experience in this occupation were rare to come across (Nwanchukwu *et al.*, 2010). Also all the individuals in this occupation were male, indicating that occupation is mainly a male dominant profession especially in this part of the country/world. The highest level of education among the population studied was the junior secondary education. This implies that most auto mechanics belong to the lower economic class that cannot afford further formal education.

Highest job designation among the study participants were the automechanics who were found at least in each workshop. This can be related to the rapid increase and spread of mechanic workshops across the town as a result of the high increase in importation of ‘Fairly used’ vehicles. This is corroborated by Ajayi and Dosunmu (2002) that estimated an increase in the importation of used motor vehicles from less than 500 in 1988 to about 30,000 in 2000. Also the cost of servicing of vehicles by major car servicing centers has led to the springing up of these auto mechanics that are available and cheaper to approach. The length of years of existence of these workshops which from the study had ranged from 5-18 years had led to a level of confidence and trust in some of this operators hence, more inflow of cars for serving and repair which in turn leads to more spills of oil to the ground during the process of engine oil and change and car engine servicing (Adelekan and Abegunde, 2010). Despite the low level of education the perception of their attitude towards waste generation was positive. This indicated that, the level of literacy may not necessarily have an impact on the attitude of individuals towards their environment. The desire for the operators to have frequent health and environmental talks is one to be applauded, this shows their willingness to learn and improve themselves. It is also an opportunity to educate them on the use of PPE’s as education on the use of PPE’s would enhance their working ability and elongate their lives in the process.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

118

6.1 Conclusion

Soil and groundwater are important environmental components whose quality we cannot afford to compromise and treat with levity. This study assessed the quality of soil and groundwater in automobile workshops and results reveal that BTEX concentrations in the soil and water are far below WHO permissible limits and at such concentrations cannot cause any harm. The physico-chemical parameters assessed show that the presence of heavy metals is of most concern, especially in water. Heavy metal concentration in the soil are within the permissible limits except for Cadmium while for water, concentrations of Copper, Chromium, Cadmium and Lead are higher than WHO permissible limits across the three zones studied (Alphonso, Temidire and Ojoo). Concentration of both soil and groundwater above that of the control and regulatory guidelines indicates contamination in these areas. Sanitary conditions around the groundwater also shows that these water sources are at a risk of contamination with 25% at high risk, 45% medium risk while the remaining 30% at low risk of contamination. Despite the indications of water contamination in the study area, a higher percentage of the automechanics (92%) have a positive attitude towards ensuring environmental protection and sustainability. From the outcome of this research, the conclusion can be drawn that the quality of the groundwater and soil in these automobile workshops has been polluted and exposure to such waters particularly through ingestion poses serious health effects.

6.2 Recommendations

1. Health and environmental talks should be given occasionally to automobile operators to enhance their performance to be more safety conscious and embrace environmentally friendly practices.

2. Orientation on safe waste handling and disposal methods should be given from time to time.
3. Automobile workshops should be assessed regularly to ensure compliance to environmental regulations relevant to this industry
4. Individuals living around automobile mechanic workshops are encouraged to take their samples of their water to chemical laboratory for analyses regularly to detect any anomaly.
5. Relocation of workshops to particular sites rather than the scattering of these shops along the road within residential area. In addition to this, there should be the formation of major mechanic villages that could accommodate large number of workshops.
6. Routine groundwater monitoring in areas where automobile workshops are located.

6.3 Future Outlook

- Similar studies of this sort should be extended to areas highly proliferated with mechanic villages and workshops amidst residential areas as well as petrol stations situated in residential areas.

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APPENDIX I

ACTIVITIES OF AUTOMOBILE MECHANICS WORKSHOPS AND EFFECTS ON SOIL AND GROUND WATER QUALITY IN AKINYELE LOCAL GOVERNMENT AREA OF OYO STATE

QUESTIONNAIRE

Dear Respondent,

I am Ogunbunmi T.O., a post graduate student of Faculty of Public Health, University of Ibadan. I am carrying out a study on "Effect of Activities of Mechanic Workshops on Surrounding Soil and Ground Water Quality in Akinyele Local Government area of Oyo State". This research is purely for academic purpose, the findings will be of immense benefit in the area of water quality management. Kindly feel free to express your opinion and I assure you that your responses will be kept strictly confidential. Your honest response to the following questions will be highly appreciated.

Thank You.

Ogunbunmi T.O.

(Please tick √ where applicable, you can tick more than one option where applicable.)

SECTION A **Demographic Information**

Zone : ____

1. Location(address of workshop)_____________________________
2. Age (As at last birthday) _____ years.
3. Sex a. Male [ ] b. Female [ ]
4. Marital status a. Single [ ] b. Married [ ] c. Separated [ ] d. Divorced [ ]

   e Widowed [ ]

5. Highest Educational Qualification: a. No formal Education [ ] b. Arabic [ ] c. Primary [ ] d. Secondary [ ] e. Tertiary [ ] f. others [ ] (please write the highest degree/certificate) ______________________________________

6. Ethnic group: a. Yoruba [ ] b. Hausa [ ] c. Igbo [ ] d. Others Specify ______________

7. Job Description a. Automobile mechanic [ ] b. Electrical operator - Re-wire [ ] c. Battery Charger [ ] d. Panel Beater [ ] e. Painter [ ] f. Vulcanizer [ ] g. Others specify ______________

8. Present job position a. Owner [ ] b. Supervisor [ ] c. Apprentice [ ] d. Others specify ______________

9. Number of years of workshop existence_______

10. How long have you been on this job _______ year?

11. Activities common to the workshop a. Automobile services/repairs [ ] b. Electrical repairs

12. [ ] c. Battery repairs/recharge [ ] d. Panel Beating [ ] e. Painting [ ] f. Vulcanizing [ ] g. Others specify ______________

SECTION B Waste Generation and Handling Methods

13. What type of waste do you generate? a. engine oil [ ], b. gear oil [ ], c. petrol spills [ ], d. carbide waste [ ], e. acid waste [ ], Others specify ______________

14. What do you do with the generated waste a. thrown away [ ] b. reused [ ] c. Sold off [ ] d. Others specify ______________

15. Can the waste affect your health? a. Yes [ ] b. No [ ] c. Don't know [ ]

    If yes, specify______________

16. Can the waste affect the health of surrounding community? a. Yes [ ] b. No [ ] c. Don't know [ ]

    If yes, specify______________

17. What is the method of waste disposal in your workshop a. refuse dump [ ] b. disposal carts [ ] c. nearby drainage [ ] d. nearby bush [ ], e. dug pit [ ] f. Others specify ______________

18. For how long have you being disposing your waste_______ years?

19. Have you received any form of complain from the surrounding community? a. Yes [ ] b. No [ ] c. Don't know [ ]

If yes, specify_______________

20. Do you think mechanic workshop wastes should be separated at the point of generation? a. Yes [ ] b. No [ ] c. Don't know [ ]

21. Which of the activities below will result in water or soil pollution?

Pollution	**Yes**	**No**
a. Engine oil spills		
b. Gear oil spills		
c. Petrol spills		
d. Carbide waste		
e. Acid waste		
f. Others specify ………..		

22. Major practices employed in the actualization of daily activities

Practices	**Please tick (√)**
Welding	
Soldering	
Oiling/greasing of moving parts	
Washing of automobile unit with petrol (engine, bolt/nut, e.t.c.)	
Draining and changing of used engine oil	

1. Volume of waste oil generated per day…………………………………..litres
2. Quantity of solid waste generated………………………………………..
3. Types of vehicle serviced………………………………….
4. Number of vehicle serviced per day…………………………

SECTION C Attitude towards ensuring environmental protection and sustainability

	Strongly agree	Agree	Disagree	Strongly Disagree	Undecided
1. Receiving educational training on safe methods of handling workshop waste are good for auto mechanics					
2. All car repair materials that can be reused should not be discarded					
3.Waste should be separated according to the repair work before disposing					
4. The waste oil should be collected and sold off or discarded appropriately					
5. Each unit must be responsible for the types of waste generated for proper disposal					
6. Waste should be allowed to washed away into nearby drainage or with rain					

APPENDIX II

IPALARA TI ILE-ISE ATOKOSE MUBA ILE ATI OMI TO DA GAARA NI IJOBA IBILE AKINYELE, IPINLE OYO

IBEERE ATONA

OLUDAHUN OWON,

Emi ni Ogunbunmi T.O, Akeko ti e ka ilera gbogbogbo ile-iwe giga (fasiti) ti Ibadan. Mo n se iwadi nipa, 'Ipalara ti ile-ise Atokose n mu ba ile ati omi to da gaara ni Ijoba Ibile Akinyele, Ipinle Oyo'. Iwadi yi wulo fun Pataki eko to ye kooro ati anfani alailegbe ni Abala omi to mo gaara. O ni ominira lati so ero ngba re, pelu idaniloju pe ohunkohun ti o ba so mo wa ni ipamo. Jije olooto si awon ibeere won yi, mo fun wa ni iwuri.

Ese o

Ogunbunmi T.O.

(Jowo fala si to ye, o le fala ju ibi kan lo ti o ba nilo)

IPELE A

Agbegbe ____

1. Ipo (Apejuwe ile-ise)______________________________________
2. Ojo ori (Lati igba ibi)_______________________________(odun)
3. Eya (a) Ako[ ] b. Abo [ ]
4. Ipo igbeyawo a. Apon [ ] b. Enito ni iyawo [ ] c. Ituka [ ] d. Ikosile [ ] e.Opo [ ]
5. Ipele eto eko giga a. Eniti ko keko [ ] b. Larubawa [ ] c. Eko ibere pepe [ ] d. Eko onipelekeji[ ] e. Ile-eko giga [ ] f. Omiran [ ].
6. Eleyameya a. Yoruba [ ] b. Hausa [ ] c. Igbo [ ] d. Eya miran [ ].
7. Apejuwe ise a. Ise atun-okose [ ] b. Asatun se waya ara oko[ ] c. Atun ohun amoko sise se [ ] d. Atun eya ara oko to ni jamba se[ ] e. Akun oko[ ] f. Atun irinse oko se [ ]
8. Pore lenu ise a. Oludase sile [ ] b. Alabojuto [ ] c. Omo eko se [ ] d. Omiran [ ]
9. Odun iriri re lenu ise____

10. O to igbawo lo ti wa lenu ise yi? ____________________________________

11. Isewo lesaba mo n se ju a. Atunse/ayewo oko [ ] b. Atunse waya oko [ ] c. Atunse eroja amukorin [ ] d. Alatunse ijamba oko[ ] e. Akun oko[ ] f.Atunse amukorin [ ] g. Omiran [ ].

IPELE B **Oye nipa Ayika ati ona Isakoso Egbin**

12. Iru egbin wo ni o n da sile? A. Epo oko[ ] b. Epo ero[ ] c. Betirolu tita sile[ ] d. Aloku kabadi [ ] e.orun asidi[ ] f.omiran [ ].
13. Kini ohun se nipa egbin ti o nda sile. a. Da sonu[ ] b. Atunlo [ ] c. Taa danu [ ] d. Omiran [ ]
14. Nje egbin yi ni ipalara lori eto ilera re? a. Beni [ ] b. Beko [ ] c. Mi ko mo [ ]
    To ba je beeni salaye___________________________
15. Nje egbin ni ipalara fun agbegbe re? a. Beni [ ] b. Beko [ ] c. Mi ko mo [ ]
    To ba je beeni salaye ______________________________
16. Ona wo ni engba da egbin nu ni ile ise yin. a.Ile-ile [ ] b. Keke idalesi [ ] c. Abajade iho onimoto wa ni itosi [ ] d. Igbo to wa ni tosi [ ] e. Omiran [ ]
17. O to odun melo ti o ti n da egbin re nu? _____________
18. Nje o ti gbo aroje kankan lati odo awon aladugbo re? a. Beni [ ] b. Beeko [ ] c. Mi ko mo[ ]
    To ba je beeni salaye_______________________________
19. N je o lero pe egbin ile-ise atokose ni lati maa ya soto lati gba ti o ba ti bere? a. Beeni [ ] b. Beeko[ ] c. Mi ko mo [ ]

20. Ewo ninu ise ti o wa ni isale yi lole ko idibaje ba omi tabi erupe?

Idibaje	Beeni	Beeko
a. Itasile epo oko		
b. Itasile epo aparo irinna oko		
c. Itasile epo amokorin		
d. Ifisofo kambadi		
e. Ifisofo aside		
f. Omiran		

21. Ona pataki ti a gba se ise ojo wa

	Ise	**Jowo fa ila si [/]**
a.	Irin jijo moran	
b.	Fifi oje jo irin	
c.	Fifi epo ra eka lilo bibo ara oko	
d.	Fifi epo amokorin fo eya ara oko	
e.	Jijo ati piparo epo amoko sise to pe ye	

ISE

22. Iye jala epo oko to nbaje lojumo.________________________

23. Iye eya ara oko to n baje.______________________________

24. Iru oko to n gba tuse.__________________________________

25. Iye oko to n gba tuse lojumo.___________________________

IPELE C Ise ati iwa lati ni Idaniloju topeye lori abo Ayika

	Mi o gba	**Lai pinnu**	**Mo gba**
Gbigba eko lori ona ti a legba moju to egbin ile ise je eyi to dara			
Egbin ni ipalara fun ayika.			
egbin ni lati yasoto ki a to danu.			
Gbigba epo oko to baje jo kia to ta tabi danu.			
Eka kokan ni lati duro fun iru egbin to mu jade fun ikawo to peye.			
Fifu egbin laye lati sanlo ni to si wa.			

APPENDIX III

SANITARY INSPECTION FORM FOR DUG WELLS

		YES	**NO**
1	Is the well covered?		
2	Is it raised above the ground?		
3	Is the well deep or shallow?		
4	Is the floor around the well cemented?		
5	If the floor is cemented are there cracks in the cement floor?		
6	Are there water drains close to the well?		
7	Is the well ringed?		
8	Is there a latrine within 10m of the well?		
9	Is there any soak-away pit within 30m of the well?		
10	Is the well water a major source of drinking?		
11	Is the environment around the well dirty?		
12	Is there any other source of pollution within 10m of well?		
13	Does spilt water collect in the apron area?		

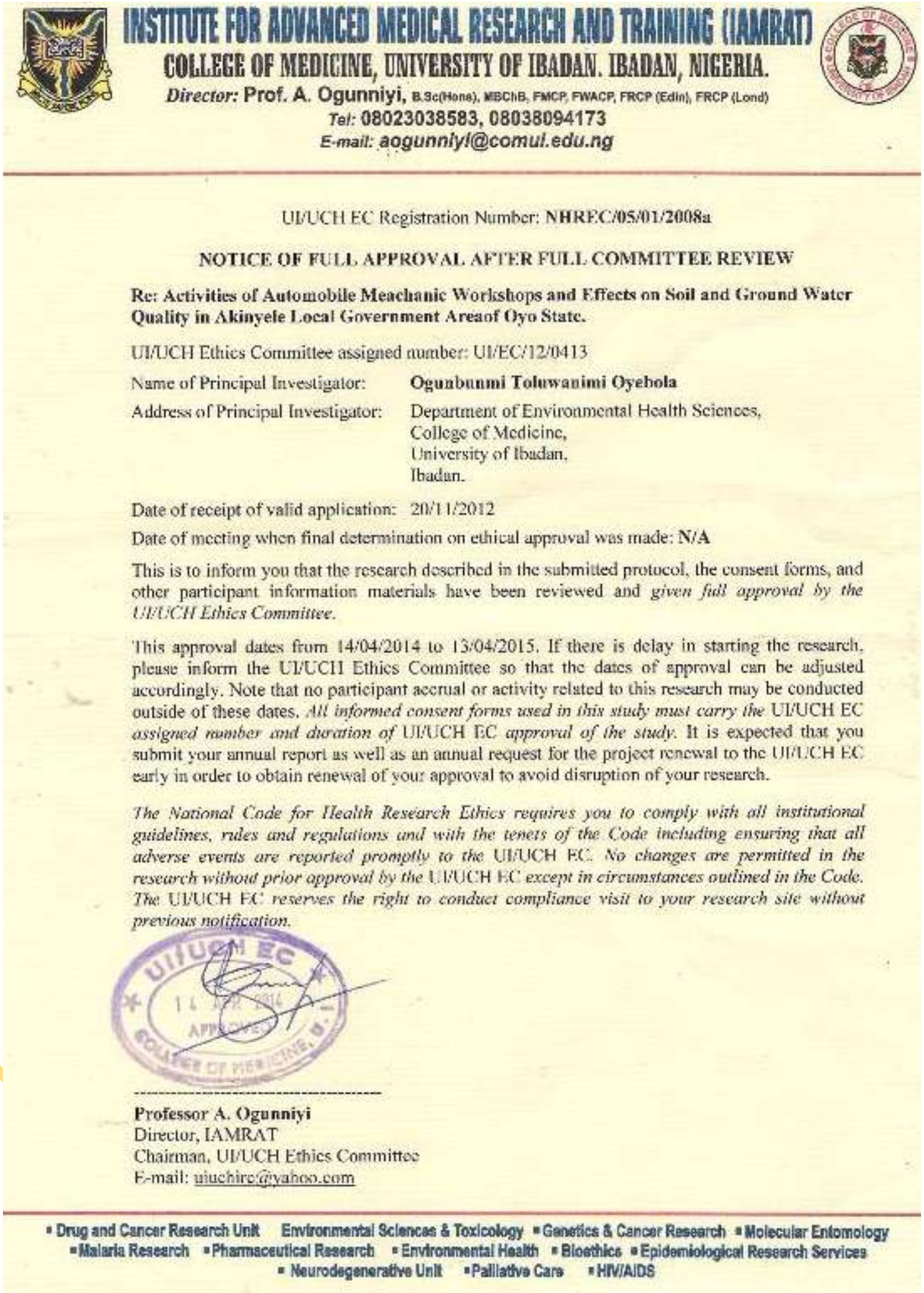
Total Score of Risks …. /13
Risk score: 11-13 = Very high; 8-10 = High; 4-7 = Medium; 0-4 = Low

APPENDIX IV

OBSERVATION CHECKLIST

Observation	Highly present	Moderately present	Present	Absent
Presence of oil spills on the floor				
Presence of metal scraps, paints				
Litters on the floor and waste generation				
Drains and water puddles on the premises				
Presence of mechanic operators				
Car density in the workshop				

APPENDIX V



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UI/UCH EC Registration Number: **NHREC/05/01/2008a**

NOTICE OF FULL APPROVAL AFTER FULL COMMITTEE REVIEW

Re: Activities of Automobile Meachanic Workshops and Effects on Soil and Ground Water Quality in Akinyele Local Government Areaof Oyo State.

UI/UCH Ethics Committee assigned number: UI/EC/12/0413

Name of Principal Investigator:	**Ogunbunmi Toluwanimi Oyebola**
Address of Principal Investigator:	Department of Environmental Health Sciences, College of Medicine, University of Ibadan, Ibadan.

Date of receipt of valid application: 20/11/2012

Date of meeting when final determination on ethical approval was made: N/A

This is to inform you that the research described in the submitted protocol, the consent forms, and other participant information materials have been reviewed and *given full approval by the UI/UCH Ethics Committee.*

This approval dates from 14/04/2014 to 13/04/2015. If there is delay in starting the research, please inform the UI/UCH Ethics Committee so that the dates of approval can be adjusted accordingly. Note that no participant accrual or activity related to this research may be conducted outside of these dates. *All informed consent forms used in this study must carry the* UI/UCH EC *assigned number and duration of* UI/UCH EC *approval of the study.* It is expected that you submit your annual report as well as an annual request for the project renewal to the UI/UCH EC early in order to obtain renewal of your approval to avoid disruption of your research.

The National Code for Health Research Ethics requires you to comply with all institutional guidelines, rules and regulations and with the tenets of the Code including ensuring that all adverse events are reported promptly to the UI/UCH EC. *No changes are permitted in the research without prior approval by the* UI/UCH EC *except in circumstances outlined in the Code. The* UI/UCH EC *reserves the right to conduct compliance visit to your research site without previous notification.*

14 APR 2014
APPROVED

Professor A. Ogunniyi
Director, IAMRAT
Chairman, UI/UCH Ethics Committee
E-mail: uiuchirc@yahoo.com

▪ Drug and Cancer Research Unit Environmental Sciences & Toxicology ▪ Genetics & Cancer Research ▪ Molecular Entomology
▪ Malaria Research ▪ Pharmaceutical Research ▪ Environmental Health ▪ Bioethics ▪ Epidemiological Research Services
▪ Neurodegenerative Unit ▪ Palliative Care ▪ HIV/AIDS

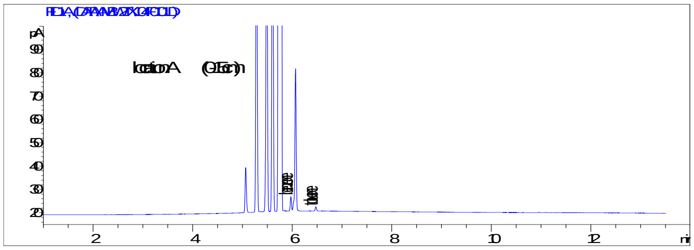
APPENDIX VI

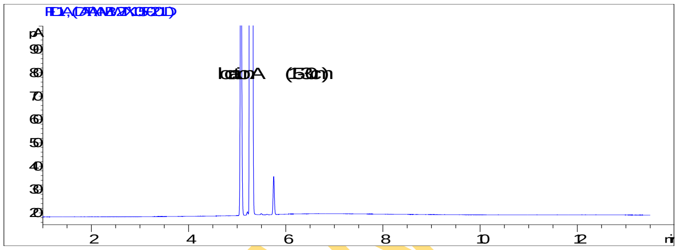
Sampling Coordinates of the Study Area

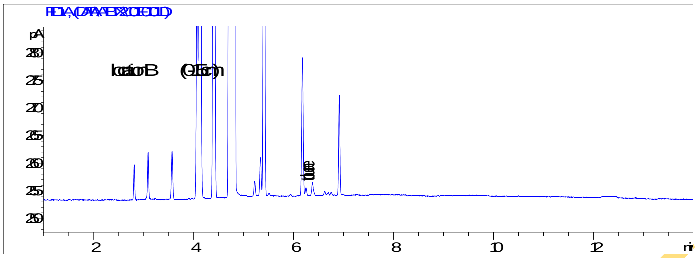
No	North	East
1	7.48091	3.90688
2	7.48067	3.90716
3	7.48062	3.9074
4	7.48039	3.90771
5	7.48027	3.9077
6	7.47929	3.91029
7	7.47867	3.91166
8	7.47846	3.91215
9	7.47558	3.91913
10	7.47545	3.91948
11	7.47498	3.9202
12	7.47473	3.92058
13	7.47308	3.92056
14	7.46931	3.91607
15	7.46787	3.91617
16	7.46801	3.91464
17	7.46844	3.91219
18	7.46865	3.91109
19	7.46741	3.91038
20	7.46716	3.91027
21	7.46677	3.91022
22	7.46541	3.91107
23	7.45669	3.91982
24	7.45673	3.92019
Control	7.54539	3.91192

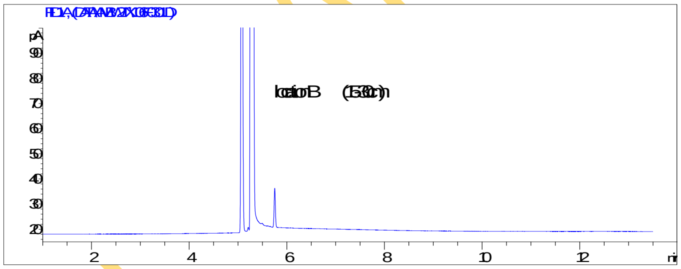
APPENDIX VII

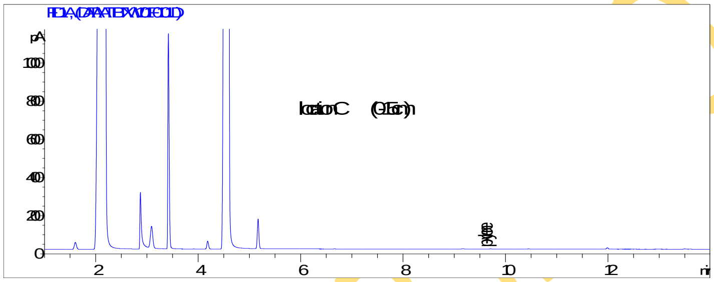
CHROMATOGRAPHS OF BTEX ANALYSIS FOR SOIL AND WATER

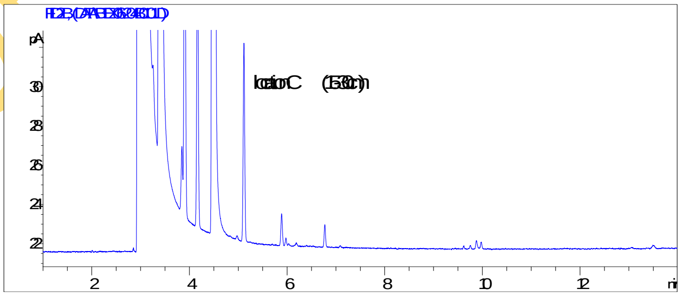


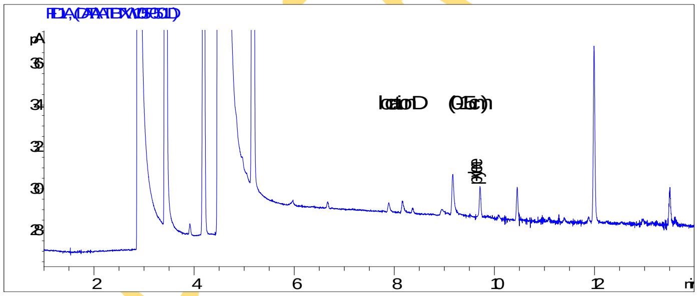


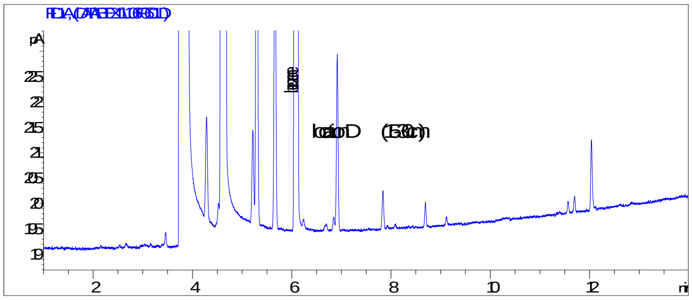


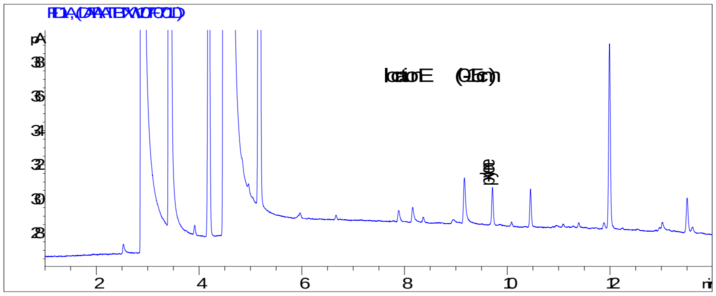


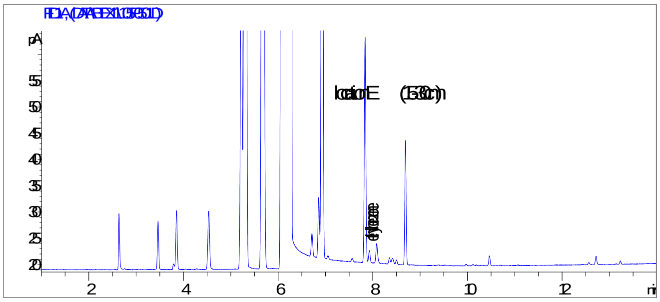


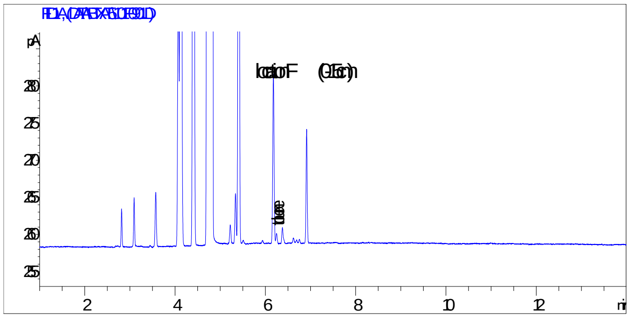








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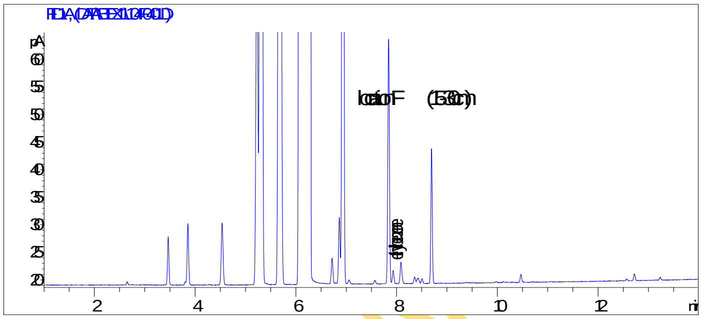
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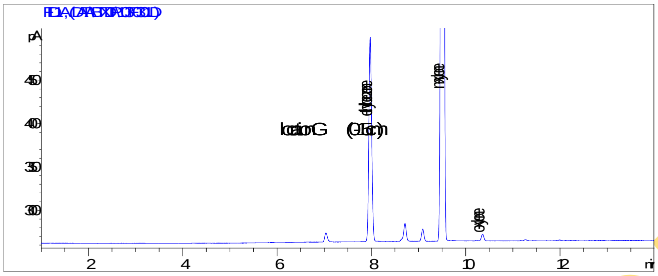
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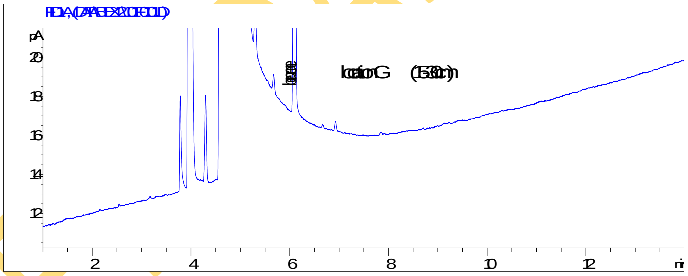
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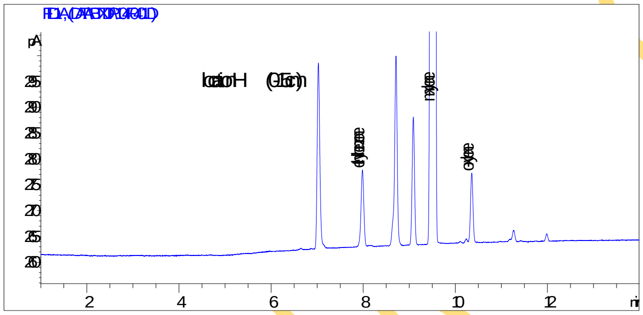
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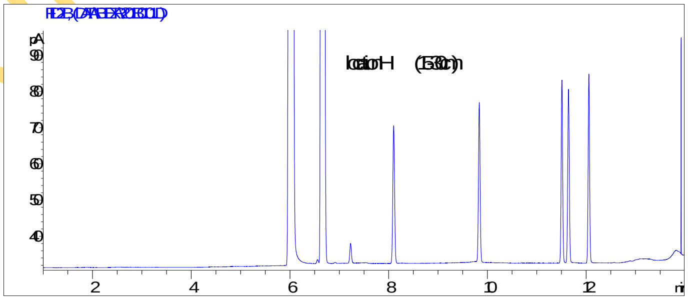
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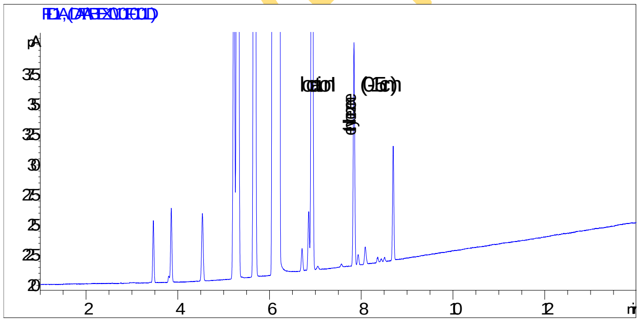
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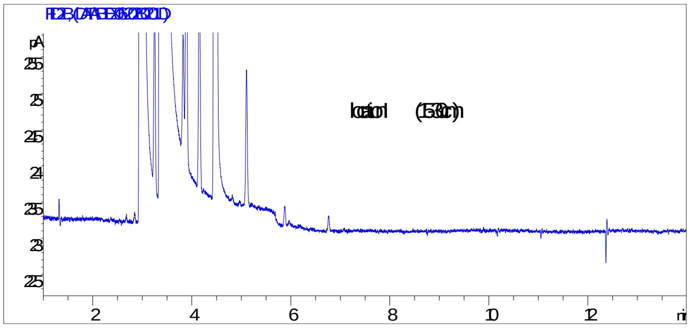
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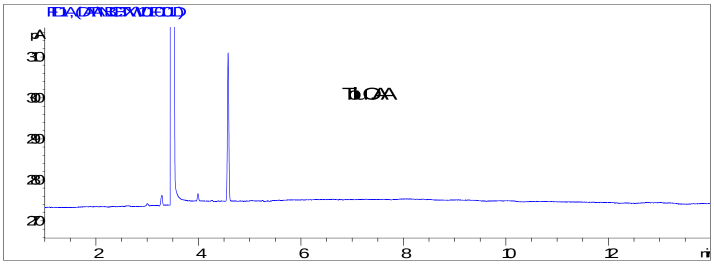
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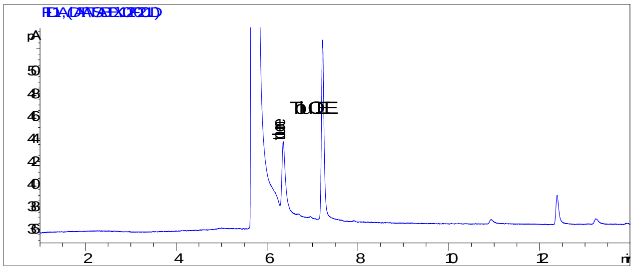
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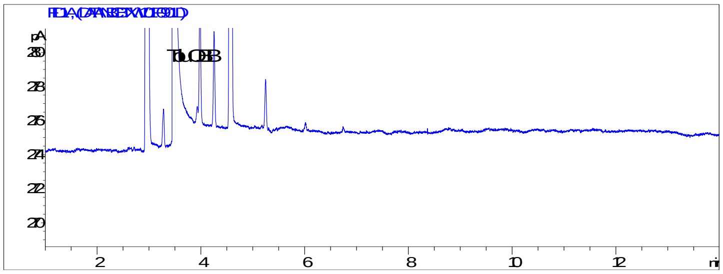
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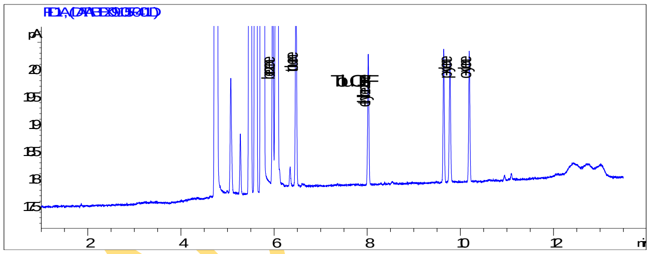
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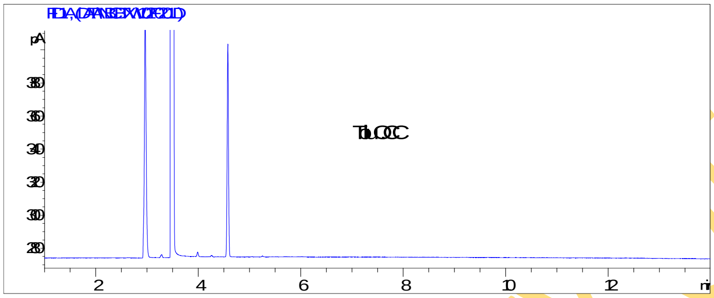
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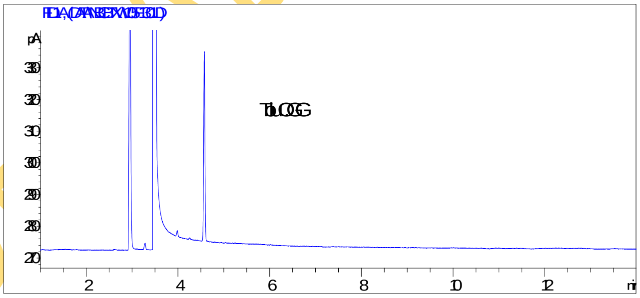
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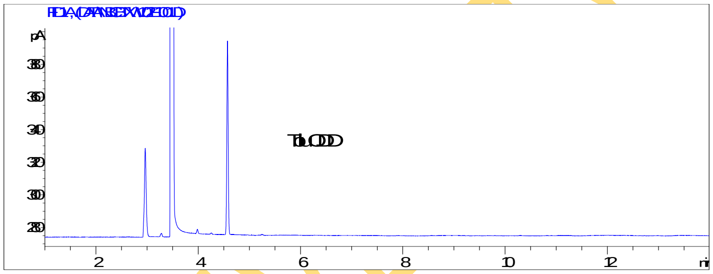
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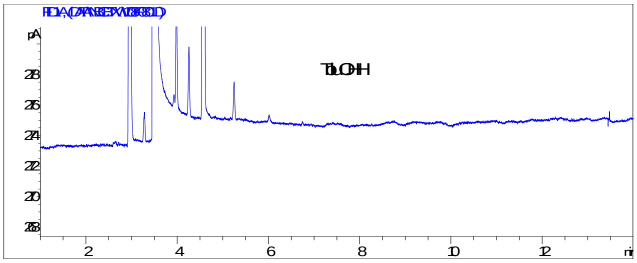
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