Assessment of Heavy Metal Contamination Levels in Topsoil at Selected Auto-workshops in Accra, Ghana

A Thesis Submitted to

THE DEPARTMENT OF NUCLEAR SCIENCES AND APPLICATIONS, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DEGREE OF MASTER OF PHYLOSOPHY (MPHIL) IN APPLIED NUCLEAR PHYSICS

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JULY, 2015

DECLARATION

I certify that this thesis work was undertaken by Mohammed Yidana, Ziblim in the Department of Nuclear Sciences and Applications, Graduate School of Nuclear and Allied Sciences, College of Basic and Applied Sciences, University of Ghana, under the supervision of **Dr. Francis Gorman Ofosu** and **Rev. (Dr.) Samuel Akoto – Bamford**

It is my conviction that, no part of this work has been presented in whole or part to any other University or Institution. Duly, other researches by other researchers cited have been acknowledged under the references.

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DEDICATION

This piece of work is dedicated especially to my wife Mrs. Lelatu Adam, and children, Yazeed Ziblim, Mohammed and Abdl-Adl Bawumia, Mohammed for their time and support given me all this while.

Also to my mother Madam Awabu Nantomah for her advices and support since childhood till now and to my late father, Mr Mahama Ziblim, my siblings, especially Mr. Adam Abraham, Ziblim, relatives and friends.

ACKNOWLEDGEMENT

"Allahu Akbar, wisdom and knowledge is His". My very special thanks goes to God for His enormous protection I have enjoyed all this while and more expecting.

Beyond all sense of appreciation, my special thanks go to **Dr. Francis Gorman Ofosu** and **Rev. (Dr.) Samuel Akoto - Bamford**, for their immense patience, thorough scientific and invaluable assistance before and during the course of this work. I do also register my profound gratitude to **Dr. Joseph B. Tandoh**, Coordinator, Applied Nuclear Physics Program, and to the staff of Department of Nuclear Sciences and Applications, University of Ghana.

To my family; Mr. Adam Abraham Ziblim, Mr. Roger Nantomah, Mr. Albert Kotia Bugri and all my other siblings: Mr. Issah Ziblim, Mr. Hamza Sulemana, Aunties: Azara Ziblim, Lamisi Judith Nantomah, Mr. Mutari Manla-amba, Mr. Nurudeen Assani.

Finally, I expressed my profound gratitude also to all my friends at the Graduate School of Nuclear and Allied Sciences most especially, Mr. Maaruf Abubakar, Mr. Saddique Gawusu, Mr. George Edusei. Also, Mr. Mike Bila Zuri, Mr. Michael Sirikyi, Mr. Abdul-Karim Adam Badimsurugu, Mr. Mohammed Salifu (Asuwey), Mr. Baba Issahaku, Mr. Muslim Abdulai, Mr. Abdul-Kadr Abdul-Karim, Madam Safiatu Kunuriwor, Ibrahim.

To everyone, I say may Allah shower His blessings.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

A	Absorbance
ABS	Skin Absorption Factor
As	Arsenic
AT	Average Time
BW	Body Weight
Cd	Cadmium
Cf	Contamination factor
Co	Cobalt
Cr	Chromium
Cu	Copper
DI	Dose Intake
ED	Exposure Duration
EF	Exposure Frequency
EPA	Environmental Protection Agency
FAAS	Flame Atomic Absorption Spectrometry
Fe	Iron
GAEC	Ghana Atomic Energy Commission
Hg	Mercury

HHRA	Human Health Risk Assessment
HI	Health Index
HQ	Health Quotient
IAEA	International Atomic Energy Agency
Igeo	Index of Geo-accumulation
IngR	Ingestion Rate
InhR	Inhalation Rate
Mn	Manganese
Ni	Nickel
Pb	Lead
PEF	Particulate Emission Factor
PLI	Pollution Load Index
QA/QC	Quality Assurance/Quality Control
RfD	Reference Dose
SA	Exposure Surface Area
SL	Skin Adherence Factor
SRM	Standard Reference Material
USEPA	United State Environmental Protection Agency
Zn	Zinc

ABSTRACT

The research was conducted to assess the levels of contamination of heavy metal in topsoil at auto-workshops in Accra, to determine the anthropogenic and crustal contributions and the human health risk associated with them. Soil samples collected from four selected auto-workshops were analysed using Atomic Absorption Spectrometer. Eleven (11) elements: Co, Fe, Cu, Mn, Cr, As, Hg, Zn, Pb, Ni and Cd were identified in each sample collected from the auto-workshops. Pollution indices; contamination factor (Cf), index of geoaccumulation (Igeo) and pollution load index (PLI), were used to assess the contamination levels. It revealed the extent of contamination at the auto-workshops for most of the elements which ranged from low to considerate contamination. Lead (Pb) recorded the greatest contamination levels at the auto-electrical location. The results from the index of geoaccumulation showed no pollution to highly pollution indicating high variations of pollution levels at different locations. The results of the PLI in almost all locations ranged from moderately to extremely polluted. Noncancer effect of children and adults due to exposure to the topsoil were also estimated with some selected metal elements. The hazard quotient (HQ) evaluation, showed ingestion to be the route of exposure to soil dust that results in a higher risk for heavy metals, followed by dermal contact. The effect due to inhalation of resuspended dust particles through the mouth and nose is relatively low. It was observed that, the auto-workshops are generally polluted with heavy metals and therefore posing ill-health effect to the humans and the environment.

CHAPTER ONE

INTRODUCTION

1.1. BACKGROUND OF RESEARCH

Pollution is the introduction of contaminants into the natural environment that causes adverse, change, instability, disorder, harm, or discomfort to the ecosystem. The sources of pollution can be naturally or anthropogenic occurring. Pollutants when occur naturally, are considered contaminants when they exceed their natural levels (Almanac, 2010, Hill, 2010).

Pollution is a serious problem the world over in which millions of world inhabitants suffer health related problems from waste generated from anthropogenic activities. In recent years pollution has increased considerably as a result of an increasing human activity such as burning of fossil fuels, industrial and automobile exhaust emissions (Kanchev et al., 2005, Amusan et al., 2003). These activities are identified to be introducing a number of toxic metals into the environment (Amusan et al., 2003). Some of these harmful or toxic chemical compounds that are released into the atmosphere or environment are carbon monoxide, sulphur dioxide, carbon dioxide, and particulate matter, which include lead from gasoline additives, zinc, copper and cadmium from tyre abrasion, lubricants, and other industrial emissions (Kanchev et al., 2005). Heavy metals contribute a greater part of these harmful or toxic chemicals released into the environment.

Heavy metals are chemical elements mostly with density greater than 4g/cm^3 found in all kinds of soils, rocks and water in terrestrial and freshwater ecosystems (Lacatusu, 1998, Duffus, 1980, Martin et al., 1982). They occur in typical background concentrations in the ecosystem. They come from different sources in urbanized areas; including vehicle emissions, industrial discharges and manufacturing, and other activities (Harrison et.al., 1981, Alloway, 1990, Thorton, 1990, Adentuji and Odetokun, 2011, Asamoah-Boateng, 2009). Heavy metals are simply metals or metalloids with a potential negative health effect or of environmental concern. These elements include vanadium, iron, manganese, cobalt, copper, zinc, selenium, strontium, lead, molybdenum, etc.

The release of heavy metals into air, water and soil is one of the most significant environmental problems caused by anthropogenic activities such as urban road construction, quarrying, agriculture, waste incinerations, sewage disposal, auto-mechanic workshops, bush burning, etc. (Alloway, 1995, Akoto et al., 2008). Some of the well-known or most occurring toxic metallic elements with regards to potential hazards in contaminated soils are; arsenic (As), cadmium (Cd), iron (Fe), mercury (Hg) and lead (Pb) (Alloway, 1995). Their presence has been considered as useful indicators for contamination in surface soil, sediments and dust environments (Harrikumar et al., 2010).

Heavy metals are used in so many industrial applications as in the manufacturing of batteries, alloys, electroplated metal parts, etc., with the products find in our homes and actually add to our quality of life when properly used. Nutritionally, trace quantities of

some of these heavy metals such as; iron, copper, manganese, and zinc are essential for a healthy life (infinitehealthresources.com).

Heavy metal pollutants are non-degradable and severely inhibit the biodegradation of organic contaminants in the environment, and will becomes threaten to humans and other biological life at any high levels upon acute and chronic exposure (Tam and Wong, 2000, Yuan et al., 2004, Mohiuddin et al., 2010, Brinkmann, 1994, Sheppard, 1998). Their accumulations not only contaminates the surface environment but also contributes to air pollution, as they may become airborne and eventually enter the drainage system to affect aquatic ecosystems. In general, the presence of heavy metals in high concentrations in the environment results in health hazards such as adverse effects of the nervous system, blood formation, renal and reproductive systems. Others include; reduced intelligence, attention deficit and behavioral abnormality, as well as its contribution to cardiovascular diseases in adults and children (Adelekan and Abegunde, 2011). For children, ingestion of contaminated soil is found to be the most significant pathway into the body (Chaney et al., 1989, EPA, 1997).

According to Adewole and Uchegbu, (2010), auto-mechanic activities are one of the major sources of heavy metal contamination of the ecosystem in Nigeria. This could also be true for Ghana as a developing country since the mode of activities in both countries is quite similar. Auto-mechanic workshops are establishments offering miscellaneous repair services (Udebuani et al., 2010) ranging from simple and fast oil change to complex engine rebuilding. They also provide body repair and painting services. The operational

processes by auto-mechanic workshops often involve the use of highly toxic and hazardous materials such as solvents, paints, and primers. It also involves battery charging, welding and soldering, automobile body works, painting/spraying and etc. Wastes from such activities include spent lubricants, worn-out parts, metal scraps, stripped oily sludge and packaging materials (Loranger et al., 1994, EEA, 2007). The car refinishing process results in the improved look of the vehicle but generates hazardous wastes that require appropriate disposal (Kostyantyn, 1997). Petrol, diesel, solvents, grease, and lubricants can either be accidentally or deliberately released into the environment.

As a result of frictional wear, the hydraulic fluids collect heavy metal debris containing Pb, Cd, Zn, Fe, Cu, etc. Usually an automobile waste will consist of auto body scraps (Al and Zn), pieces of mild steel (Fe), electrical components and wires (Cu and Pb). Many of these petroleum products are organic chemicals that can be highly toxic and hazardous to soil, flora and fauna. The use of automobiles and its repairs has generally led to heavy metals contamination in soil, which have grave consequences for soil dwelling organisms (Adewoyin et al., 2013).

1.2 PROBLEM STATEMENT

Although, much research has been carried out on heavy metal concentration in various environmental matrices, many of these researches have been done on heavy metals in developed countries. There has been limited or inadequate information generated on heavy metal pollution in developing countries (Atiemo et al., 2010, Thuy et al., 2000). In Ghana, there is little information as applied to heavy metal pollution from auto-mechanic workshops. The activities within the auto-mechanic workshops, create the potential for the accumulation of heavy metals in the working environment, near and far. These Auto-mechanic workshops are mostly located by the road side, in the open and on bare soil. The activities therein are done mostly in non-scientific ways. Consequently, contaminants from fuel, lubricants, used batteries, etc. are easily released into the environment.

These contaminants have adverse effects on soil, water and air quality in the general environment and even distant from the vicinity (Lacatusu, 1998, Ayodele and Abubakari, 2001) of the auto-mechanic workshops and poses health risk. It is therefore necessary to determine pollution levels of heavy metals at auto-mechanic workshop sites. One needs to also know the contributions from specific activities such as auto-welding, auto-spraying, auto-electrical and auto-mechanical locations within the auto-workshops. Assessment of health hazards will help established the significance of environmental and health impact of heavy metals from auto-mechanic workshops.

1.3 OBJECTIVES

The release of contaminants (heavy metals) is of great concern and has great implications to the environment and life.

1.3.1. Main Objective:

To assess heavy metal contamination levels in topsoils and the human health risk effects at the selected auto-mechanic workshops.

1.3.2. Specific Objectives:

1. To monitor heavy metal concentrations in topsoils at the selected auto-mechanic workshops using Atomic Absorption Spectrometry.
2. To assess the anthropogenic and crustal contributions of the heavy metals in the auto-mechanic workshops.
3. To evaluate health risk parameters associated with the heavy metal levels.
4. To contribute to the generation of data for the purposes of regulations.

1.4. RELEVANCE AND JUSTIFICATION

Heavy metals are natural constituents of geological matter and are usually found in low concentrations (El-Hasan et al., 2006). They occur in typical background concentrations in the ecosystems; however, anthropogenic releases can result in higher concentrations relative to their normal background concentrations. At these values, they become serious pollutants because of their toxicity, persistence and non-degradable conditions in the environment, and become threat to human health and other forms of biological life (Tam and Wong, 2000, Yuan et al., 2004, Mohiuddin et al., 2010, Brinkmann, 1994, Sheppard, 1998). Unfortunately, there is inadequate information on heavy metals and their impact on the environment and human life at auto-mechanic workshops in Ghana.

Not only workers at these auto workshops are exposed to these heavy metals which may be pollutants, but also automobile owners who go to refinishing their automobiles and the environment as a whole. This can likely pose health hazards to them which unfortunately most time is overlooked.

Since heavy metal pollutants are released from the activities in these auto-mechanic workshops (Loranger et al., 1994, EEA, 2007) and have various adverse effects on human health as well the environment (Tam and Wong, 2000, Yuan et al., 2004, Mohiuddin et al., 2010), it is important that heavy metal levels in the top soils be assessed and their health implications evaluated.

1.5 SCOPE AND DELIMITATION OF THE RESEARCH

Out of the many auto-mechanic workshops within Accra, sampling was done in four (4) auto-mechanic workshops. This was due to the fact that, auto-mechanic workshop owners were not ready to give permission to the researcher. The research seeks to determine the heavy metal levels at the auto-mechanic workshops and the health risk assessment associated with the heavy metals. The period for sampling collection was from 8th November to 20th December, 20014.

Fractionated size of 100 µm of the soil from the selected auto-mechanic workshops were analyzed using atomic absorption spectrometry (ASS) technique.

1.6 STRUCTURE OF THE RESEARCH

The research is been put into five chapters. Chapter one (1) is a brief introduction and background of the work, including problem statement, objectives, relevance and justification and the scope and delimitation. Chapter two (2) is the literature review and Details of the experimental methodology is in chapter three (3). Chapter four (4) and five (5) covers the results and analysis, and finally the conclusion and recommendations.

CHAPTER TWO

LITERATURE REVIEW

2.1. ENVIRONMENTAL POLLUTION

There has been growing concerns about environmental quality in recent years, both on the global and the local stage. The consequences of environmental pollution becomes more difficult to prevent or often too late to prevent, when it become visible.

The atmosphere or environment in today's Industrial Revolution is different from the natural environment that existed before, in relation to the chemical makeup or composition (Daly and Zannetti, 2007). There would not be clean air in our today's atmosphere, if the natural atmosphere is considered to be "clean" (Daly and Zannetti, 2007) and the soil would not be different. Soils are critical environments interfaced with air and water and anything that affects one probably affects the other. A soil pollutant is any substance in the soil that is harmful to the environment, human and other biologically life. A pollutant can also be any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Such a substance has to be present in the environment beyond a set or tolerance limit, which could be either a desirable or acceptable limit. Hence, environmental pollution is the presence of a pollutant in the environment; air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment (Duruibe et al., 2007). The pollutants may be in

the form of liquid droplets, gases or solid particles. Sources of soil pollutant can be natural or anthropogenic (Almanac, 2010, Hooda and Naidu, 2004).

Pollutants are also classified into primary or secondary (Daly and Zannetti, 2007). Primary pollutants are substances emitted directly from an identified source into the environment. These pollutants exist as such after being added or released to the environment. According to USEPA (1993), some of the undesirable elements that commonly pollute the environment include natural organics (phenols, formaldehyde); heavy metals (lead, nickel, zinc, cadmium, copper, chromium); inorganic (ammonia, cyanides, fluorides, nitrites, and sulphites); synthetic organics (pesticides, herbicides, detergents); acid and alkaline substances; mineral oils, fats and floatable substances; suspended solids and colloids; nutrient substances like nitrogen, phosphorus, sulphates as well as radioactive materials Some of these are Sulphur compounds (SO_2, H_2S), Nitrogen compounds (NO, N_2O, NH_3) and Carbon compounds (CO, CO_2, CH_4) and other volatile organic compounds (VOCs) and volcanic eruptions, etc.

Secondary pollutants on the otherhand are substances derived from primary pollutants by chemical reaction. They are not emitted directly from the sources, but from the primary pollutants (called “precursors”). The best known of the secondary pollutants are: NO_2 and HNO_3 formed from nitrous oxide (nitric acid droplets formed from nitrogen dioxide (NO_2). Also, are: Organic aerosols formed from VOCs in gas-to-particle reactions, sulphates and nitrates aerosols (e.g., ammonium (II) sulphate), formed from the reactions of sulphuric acid droplets and nitric acids droplets NO), Ozone (O_3) formed from

photochemical reactions of nitrogen oxides and VOCs, Sulphuric acid droplets formed from sulphuric dioxide (SO_2), and with NH_3, respectively (Hooda and Naidu, 2004).

Scientists estimate that the amount of low-level ozone currently in the earth's atmosphere is 100 - 200 times higher than it was only 100 years ago (Hooda and Naidu, 2004).

However, some of these pollutants may be both primary and secondary; that is, they are emitted directly and formed from other primary pollutants (NO_2). These pollutants do not just affect their immediate environment, but can also travel and affect areas afar from their points of origin.

Pollution of the natural environment (air, water and soil) by heavy metal is a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms, when they exceed a certain concentration (Ghrefa and Yusuf, 2006). The toxicity of the agents/pollutants of pollution has an inhibitory effect on plants growth, enzymatic activity, stoma functions, photosynthesis activity and accumulation of other nutrient elements, and also damage the root system (Güne et al., 2004). On the otherhand, soil is not only a medium for plant growth or pool to dispose of undesirable materials, but also a transmitter of many pollutants to surface water, groundwater, and food (Chen et al., 1997). Therefore, soil pollution may threaten human health not only through its effects on the hygienic quality of food and drinking water, but also through its effect on air quality especially in enriching trace metal content in airborne particles originating from soil (Addo et al., 2012). The determination of the metals in soils, dusts, plants and sediments are very important in monitoring environmental pollution. The

contribution of metals to environmental pollution from industrial, agricultural and mining processes besides automobile emission, have been the main subject of many studies and research in recent years. Botanical materials such as fungi, lichens, tree barks, tree rings, leaves of higher plants and soil samples have been used to detect the deposition, accumulation and distribution of metal pollution (Ndiokwere, 1984). Onder et al. (2007), has observed that the most economical and reasonable method for monitoring heavy metals in the atmosphere is using vegetation and soil samples. Hence, vegetation and soil have been widely used as cumulative matrices of long and short term exposure respectively to environmental pollution. This called for an effective means of managing and mitigating soil pollution in Ghana.

Pollution in the Ghanaian society is one which is not restricted by law (though, there are existing by-laws) that frowns against it (Selby, 2010), pertaining to workdone at auto-mechanic workshops not much is done. The Metropolitan and Districts Assemblies, which are responsible for good keeping of the environment, rather results into clearing of rubbish and the decongestion of slum areas and ignoring the act of pollution by citizens, and many people tend to pollute environment in various ways, irrespective of where they are coming from (Selby, 2010).

2.2. NATURAL SOURCES OF SOIL POLLUTION

There are many natural sources of air pollution (Hill, 2010), similarly to that of soil pollution (Radha et al., 1997, Environment Canada, 1996) since soils are critical environments interfaced with air and water (Radha et al., 1997), such natural bush/forest fires, eruption of volcanoes, weathering of mineral deposits, windblown dusts, sea salt and other biological decays (Daly and Zannetti, 2007, Environment Canada, 1996, Laude, 1995, Olade, 1987). These sources can be classified as biogenic and geogenic sources (Daly and Zannetti, 2007, Environment Canada, 1996, Laude, 1995). Biogenic sources are those emissions that come from the living, such as continental particulates, volatile organic compounds (VOCs) form forests, methane emissions from swamps (Laude, 1995, Olade, 1987, Wiedinmyer et al., 2006).

Geogenic emissions for instance, dust emissions from the earth's surface can be altered by human activity (Daly and Zannetti, 2007). Both geogenic and biogenic sources can be influence by human activities. Also, the application of nitrogen fertilizers in agriculture by human can result in an increased of biogenic emissions of nitrogen compounds from the soil (Daly and Zannetti, 2007).

2.3. ANTHROPOGENIC SOURCES OF SOIL POLLUTION

Generally, anthropogenic sources of soil pollution can be distinguished as: diffuse pollution or non-point source, and point sources (O'Shea, 2002, Nilgun, 2004). The example of the non-point source is atmospheric deposition as a result of urban, transport

and construction activities, as well as mineral fertilizer or sewage sludge application in agriculture. Diffuse sources of pollution are not easy to control, and the best methods for soil pollution control often depend on the legal regulations and management strategies.

It becomes easier to control point sources of pollution, because it usually refers to the single source that is easy to identify (local pollution caused by chance, accidentally or undertaking prohibited activities) (O'Shea, 2002), including others like; industrial factories, power plants, furnaces pollutants that are released from activities of auto-works.

Both sources are as a result of man's willingness of making life comfortable and thus a sudden increase and drive in industrial and developmental activities in various forms.

Industrialization has been one of the major causes of soil pollution. It sets a series of events into motion which destroyed and continued to destroy both natural habitats causing diseases in both humans and other species of animals. Foundry activities and manufacturing processes that involve furnaces or other processes resulting in possible dispersion of contaminants in environment, mining, emissions from automobile exhaust, waste incineration, land disposal of wastes, use of agricultural inputs, pesticides, batteries, emissions from industrial processes and forth, and wet and/or dry atmospheric deposits and constructions activities are all possible anthropogenic sources of soil or land pollution (Nilgun, 2004, Onianwa et al., 2001, Zhenli et al., 2005) and others. These activities emit different pollutants. An example is the metal industry which partly is responsible for the emissions of sulphur dioxide and large amounts of toxic dust,

according to (Comfort, 2011) and they are harmful and endanger to our health and the natural ecosystem. The chemical industry also releases emissions that probably may contain sulphur and nitrogen compounds and the refineries discharges sulphur dioxide and hydrocarbons (MNRE, 2010). These are as a result of human activities.

The intense upsurge of achieving developmental stability has brought about some of these pollutant emissions including emissions from: everyday routine, power generation, and automobiles.

2.3.1. Power Generation

Energy all over the world is produced in conventional power plants burning fossil fuels such as natural gas, coal or oil (crude) (MNRE, 2010, Ahmed and Ishiga, 2006), with a few countries using nuclear means of production. Coal and oil combustion facilities produced fine particles that are enriched with heavy metals, and that heavy oil combustion resulted in relatively pronounced ultra-fine particles smaller than 1.0 μm (Wang et al., 2010, Jang et al., 2007), that pollute the environment and possess grave health hazards (Wang et al., 2010).

2.3.2. Everyday Routine

The advent of manufacturing leads to the production of many household items and involves furnaces or other processes resulting in possible dispersion of contaminants in environment. Chemicals used in houses and gardens or agricultural activities involving

the spread of herbicides/pesticides/insecticides and fertilizers are also sources of pollution as well as toxic waste. Fumes from the burning of biomass for cooking are sources of environmental pollution, especially a major cause of indoor air pollution. According to Blacksmith Institute, in 2000 alone, between 1.5 and 2.5 million deaths were caused by indoor air pollution worldwide representing about 4 to 5 percent mortality globally for that year. Among these, children under five years, young girls and women are severely affected because they spend most of the time at home near the source.

The daily average concentration of smaller particulate matter (PM10, < 10 µm in diameter) according to the US Environmental Protection Agency, recommended not more than 150µg/m^3. In comparison, homes where solid fuel is used for cooking can reach concentration levels as high as 5,000µg/m^3 and a child directly sitting next to a stove may breathe air containing up to 50,000µg/m^3 of noxious matter, according to Blacksmith Institute.

2.3.3 Automobiles

The pollution of soils from automobile sources is a serious of environmental issues (Dolan et al., 2006) worldwide. Automobiles pollute the environment in various ways, thus: either vehicular emissions or auto-mechanic discharges.

2.3.3.1. Vehicular Emissions

This is one of the major causes of air pollution, particularly in the cities (Aslan et al., 2011), not only the air but the entire surrounding environment. Encountering some of the

effects of these emissions, researchers are trying to discover new means of energy and power. There are even now vehicles that run on natural gas as opposed to gasoline, to reduce the fog and excessive breathing of the gases. In typical urban centers, vehicular emission constitute over 60% of total pollutant emission compared to power plants, space heating, etc. (Enemari, 2001).

Vehicles and power plants drive their energies from the combustion of fossil fuel in their internal combustion chambers. In the process, a number of changes occur with some of the fuel passed out unburned. The partly burnt fuel changes form into a number of gases and impurities which combine in the process principally with air to form other compounds depending on the prevailing conditions in the combustion chamber. The products mainly gases are then emitted into the environment as exhaust gases (Enemari, 2001).

The large majority of today's cars and trucks travel by using internal combustion engines that burn gasoline or other fossil fuels (Alloway, 1995). Emissions that are released directly into the atmosphere from the tailpipes of the cars and trucks are the primary sources of vehicular pollution. But motor vehicles also pollute the air during the processes of manufacturing, refuelling, and from the emissions associated with oil refining and distribution of the fuel they burn.

Some of the major pollutants associated with motor vehicles are:

- Particulate Matter (PM). These particles of soot and metals give smog its murky colour. Among vehicular pollution, fine particles (those less than one-tenth the diameter of a human hair) pose the serious threat to human health by penetrating deep into lungs. In addition to direct emissions of fine particles, automobiles release nitrogen oxides, hydrocarbons, and sulphur dioxide, which generate additional fine particles as secondary pollution (Friedman, 2011).
- Hazardous Air Pollutants (toxics). These chemical compounds, which are emitted by cars, trucks, refineries and related sources, have been linked to birth defects, cancer and other serious illnesses. The USEPA estimates that the air toxics emitted from cars and trucks accounts for half of all cancers caused by air pollution (Friedman, 2011) and with all pollutions.
- Other pollutants are; nitrogen oxides (NO_X), carbon monoxide (CO), sulphur dioxides (SO_2) and their associated health issues (Friedman, 2011).

2.3.3.2. Auto-workshops Discharges

Vehicular emissions have however attracted the most attention as the major non-point source of lead in roadside dust. Less attention has been given to other automobile related activities. Automobile repair workshops in Ghana are not guided by site regulations and as such are found randomly situated around street corners and at times they are located close to natural water sources whose associated flood plains are used for dry season cultivation of agricultural produce such as sheldwater, maize, fruit and vegetables. Each

automobile repair workshop hosts a variety of artisans; mechanics, auto-electricians, battery service men, electroplating, vulcanizers and panel beaters; the activities of which generate sundry waste. These mechanic workshops are mostly divided into; a) auto-welding location, b) auto-spraying location, c) auto-mechanic location and d) auto-electrical location. Figure 2.1 – 2.3 shows the activities at these locations.

Table 2.1: Activities carried out on vehicles at auto-mechanic workshops and their contributions to soil pollution.

S/N	Activity	Contribution to soil pollution
1	Servicing of vehicle engines	Discharging dirty engine oil on the ground
2	Washing of vehicles and parts.	Contaminated wash water containing hydrocarbons, acids, soaps and other chemicals pour on the soil.
3	Repair of transmission systems and fuel tanks	Spilling of transmission oil, petrol and diesel bare on the ground.
4	Spray painting of vehicle bodies, rims and other vehicle parts.	Accidental spills of paints on the ground. Waste products of spraying amass on dumpsite.
5	Greasing and oiling of parts.	Greases and oils spill on the ground.
6	Welding and soldering of vehicle parts.	Discarding of waste solder and electrodes on soil dumps.
7	Grinding, threading, wiring and other working of metal parts during repair.	Metal bits are filed onto bare ground, waste wires and solders are dropped.
8	Panel beating of vehicle bodies and scraping of old vehicle body coats.	Metal bits, metallic colour coats and dusts are scraped to bare ground.
9	Overhauling of vehicle engines	Discharge of engine oil, sludge and interior scrapings on the ground.
10	Repair of clutch systems and braking systems	Spilling of clutch and brake fluid on bare ground.
11	Repair or charging batteries	Pouring of electrolyte on the ground. Discarding lead plates on waste dumps on site.
12	Improper human wastes discharge.	Human wastes deposited to the ground.
13	Rainfall.	Washing dirt from roofs and bogged vehicles onto the ground

Waste products from the repair workshops such as; used engine oil, transmission oil, brake fluid, damaged tyres, battery electrolyte, spillages, wire carbide, used parts, asbestos from brake pads, spent batteries and cells and waste solvents used for cleaning parts are often not properly disposed of and so litter the surrounding areas and much ends up in natural drainage channels. The most dangerous waste commonly created in auto-repairs shops is from the solvents used to clean parts. Many of the chemicals that make up the solvents are extremely dangerous to human and the environment (Imevbore and Adeyemi, 1981). These if not handled properly these chemicals can find their way into the air we breathed, the water we drink, our soil, lakes and streams (Adeniyi and Afolabi, 2002).

Used oil may contain components such as lead, cadmium, barium, hydrocarbons and other potentially toxic metals like chromium and cadmium electroplating (Edebiri and Nwanokwale, 1981, USEPA, 2001, Vazquez-Duhalt and Bartha, 1989). These are often used as minor additives to gasoline and various auto-lubricants, and are released during combustion and spillage (Loranger et al., 1994). Some of these metals are components of automobile parts such as tyres and engines, fluid leakages from which they are released during abrasion and wears (Dolan et al., 2006). There has been little attention given to vicinities of automobile-workshops, which are also liable to pollution arising from gasoline combustion exhausts, lubricating oil spills, and other chemical inputs to automobile operations.

Pollution problems associated with incidents of oils spills and other pollutants around automobile-repair workshops, resulting in metal contamination of topsoil needs to be looked at. The pollution of soils by these pollutants from automobile sources has a serious health and environmental issues (Dolan et al., 2006, Imevbore and Adeyemi, 1981).

Figure 2.1: Photograph at Auto-Welding Location at the Auto-Workshop (BB) [Photo: Mohammed Yidana, Ziblim]

Figure 2.2: Photograph at Auto-Spraying Location at the Auto-Workshop (TP)
[Photo: Mohammed Yidana, Ziblim]

Figure 2.3: Photograph of Auto-Mechanical Location at the Auto-Workshop (MI)
[Photo: Mohammed Yidana, Ziblim]

2.4. HEAVY METALS IN AUTO-MECHANIC WORKSHOP DISCHARGES AND THEIR IMPACTS

Heavy metal refers to any metallic chemical element that has a relatively high density and is poisonous or toxic at low concentrations. Heavy metals are also referred to as chemical elements with a specific gravity that is at least five (5) times the specific gravity of that of water or mostly with density greater than $4g/cm^3$ found in all kinds of soils, rocks and water in terrestrial and freshwater ecosystems (Lacatusu, 1998, Duffus, 1980, Martin et al., 1982). Heavy metals, unlike organic pollutants, occur naturally in the Earth crust and found in soils and rocks with a subsequent rage of natural concentration in soils, water, sediments and organisms (Hutton and Symons, 1986). The anthropogenic releases of these metals have given rise to higher concentrations relative to the normal background levels. Examples of these metals include: arsenic (As), thallium (Tl), cadmium (Cd), zinc (Zn), iron (Fe), chromium (Cr), lead (Pb) and mercury (Hg), copper (Cu), nickel (Ni), and etc. (Dolan et al., 2006, Alloway, 1995). Some interests also exist in aluminum (Al), cobalt (Co), strontium and other rare or trace metals. Some of them have been classified as priority pollutants by United State Environmental Protection Agency. Most frequently heavy metals and potential soil and water pollutants are: cadmium (Cd), zinc (Zn), iron (Fe), chromium (Cr), lead (Pb) and copper (Cu), nickel (Ni) (Alloway, 1995, Adelekan and Abegunde, 2011, Pam et al., 2013).

Regarding most heavy metals particularly Pb, Cu and Zn, anthropogenic origins put in more to pollution than natural sources (Bilos et al., 2001). These heavy metals in the terrestrial environment visibly constitute a significant risk to the quality of soils (Adriano,

2001), plants (Hooda and Naidu, 2004), natural waters (USEPA, 2003) and human health (WHO, 2004). Waste water and sludge from industrial processes may contain an important load of zinc, copper, chromium and nickel (Sollitto et al., 2010, Loranger et al., 1994).

Some of these heavy metals are needed in our bodies with a require trace amounts, including copper, zinc, iron and others, but can be dangerous at high level (Abulude etal., 2007). Others such as; lead, cadmium, arsenic, and mercury have no known benefits/uses to our bodies, and over time their accumulation can cause serious health problems and even premature death and acts as carcinogens, heavy metals are cytotoxic, metagenic and carcinogenic in nature and thereby pose serious threats to urban populations, soil, air and land (Freig, 1994, Trichopoulos et al., 1997).

Today, heavy metals are abundant everywhere in our soil, air and water. This is as a result of the industrialization of our world. They are present virtually in all aspect of modern life from medicines, fuel, processed foods, appliances, even personal care products (Comfort, 2011). It is therefore difficult for anyone to avoid exposure and one can only take steps to minimize this threat through acts of prevention and treatment to lessen their negative impact on health. The accumulation of heavy metals within the body can lead to a decline in the mental, cognitive, and physical health of the individual. Heavy metal pollution of the environment, even at low levels, and their resulting long-term cumulative health effects are among the leading health concerns all over the world (Oluyemi et al., 2008, Sheppard, 1998).

Though, many metals are biologically essential but all have the potential to be toxic to biota above a certain threshold concentrations (David and Johanna, 2000), especially when not metabolized by the body become toxic and accumulate in the tissues (Comfort, 2011). They may enter the human body through contaminated food, water, air or absorption through the skin when they come into contact with human, ingestion or inhalation (McLaughlin et al., 2000, Ling et al., 2007). For children, ingestion contaminated soil is the most significant in pathway for land (Chany et al., 1989, EPA, 1997). Children develop toxic levels from hand-to-mouth activity pathways, when they come in contact with contaminated soil or eating objects that are not food (dirt or paint chips) (Chany et al., 1989, EPA, 1997). In dusty environments, adults may ingest up to 100 mg dust/day, according to Leung et al., 2008. Children are usually exposed to greater amounts of dust than adults due to play behaviors. Exposures during radiological procedure, from inappropriate dosing during intravenous nutrition, from a broken thermometer or from a suicide or homicide attempt are the less routes of exposure (USEPA, 2013).

Health risk is especially high for children, pregnant women and the aged because of their low tolerance to toxins as well as the inadvertent ingestion of significant quantities of dust (or soil) through the hand-to-mouth pathways (Acosta et al., 2009, Tong and Lam, 2000). Children also have a much higher absorption rate of heavy metals from digestion system and higher haemoglobin sensitivity to heavy metals than adults (Hammond, 1982). The health effects and symptoms of these elements depend on the nature and quantity of the metal ingested. Heavy metal contaminants in the environment are

eventually deposited in soils in some form of a low solubility compound, such as pyrite (Huerta-Diaz and Morse, 1992) or absorbed on surface-reactive phases, such as Fe and Mn oxides (Cooper et al., 2005; Hamilton Taylor et al., 2005). Lead (Pb) is the most common environmental contaminant found in soils. Unlike other metals, Pb has no biological role, and is potentially toxic to microorganisms (Sobolev and Begonia, 2008). Its excessive accumulation in living organisms is always detrimental. Furthermore, lead (Pb) exposure can cause seizures, mental retardation, and behavioral disorders in human beings. Heavy metal exposure to human beings occurs through three primary routes namely inhalation, ingestion and skin absorption. All these occur in myriads of places including auto-mechanic workshops. Generally, toxic metals cause enzyme inactivation, damage cells by acting as anti-metabolites or form precipitates or chelates with essential metabolites. According to USDA (2000), acute (immediate) poisoning from heavy metals is rare through ingestion or dermal contact, but it is possible.

Chronic problems associated with long-term heavy metal exposures are mental lapse (lead); toxicological effects on kidney, liver and gastrointestinal tract (cadmium); skin poisoning and harmful effects on kidneys and the central nervous system (arsenic). There is a link between long term exposure to copper and decline of intelligence in young adolescents (Lenntech, 2009). Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems (Goyer and Clarkson, 2001). Human diseases have resulted from consumption of cadmium contaminated foods (Kobayashi, 1978; Nogawa et al., 1987). The threat that heavy metals pose to human and animal health is aggravated by their low environmental mobility, even under high precipitations, and their

long term persistence in the environment (Mench et al., 1994; Chirenje et al., 2004). For instance, Pb, one of the more persistent metals, was estimated to have a soil retention time of 150 to 5000 years (Sobolev and Begonia, 2008). Also, the average biological half-life of Cd, another accumulation poison similar to lead, has been estimated to be about 18 years (Forstner, 1995).

Heavy metals can accumulate in automobile workshop topsoil from the various activities within the shops which may affect population/human health if they reach a level of being considered as toxic pollutants. For easy accessibility, these auto-mechanic workshops are built or sited within residential areas, where potential contaminants from their activities are released into the environment (air and soil) that ends up affecting human and other biological life.

Soil pollutants have a wide range of impacts, with health problems being the most enduring concern. In classical polluted areas with lead (Pb) and mercury (Hg) are associated with the development of abnormalities in children and a long term intake of cadmium causes renal, prostate and ovarian cancers (Gibb and Chen, 1989). According to Somer (1994), presence of high lead level can result into brain damage, brain disorder and can cause stunted growth in plants. Excessive level of iron can seriously affect flora and fauna in water bodies.

The impacts of pollutants from automobiles and their associated activities on the environment can be into three categories which are;

- **Direct Impacts.** These are the immediate consequence of the pollutants/activities on the environment where the cause and effect relationship is generally clear and well understood (Rodrigue and Comtois, 2014).
- **Indirect Impacts.** The secondary effects of pollutants/activities on the environmental systems. They are often of higher con sequence than the direct impacts, and involved relationships that are often misunderstood and difficult to establish (Rodrigue and Comtois, 2014).
- **Cumulative Impacts.** The additive, multiplicative, or synergetic consequences of pollutants/activities. They take into account of the varied effects of direct and indirect impacts on an ecosystem, which are often unpredicted (Rodrigue and Comtois, 2014).

Pollutant metals are usually non-degradable and there are no known homeostasis mechanism for them and hence make them a critical environmental issue (Cui et al., 2005). Thus, any high level of heavy metals will threaten biological life (Nriagu, 1988, Mohiuddin et al., 2000). Their accumulation in soils to toxic concentrations affects plant and animals life. They may accumulate in the fatty tissues of our body and affects our central nervous system, or they may be deposited in our circulatory system and disrupt the normal functioning of our internal organs, or they act as cofactors in other diseases (Nriagu, 1988, Zheng et al., 2010). Contaminants may even affect far distant places, and can travel from their origin to become pollution problems in other places by running water.

Many studies have been undertaken to examine the link between environmental pollutants and health (Armah et al., 2010). A number of them demonstrated strong associations even though there are many uncertainties as to some of the precise mechanisms involved in connecting human health impacts and pollutants (Armah et al., 2010), with much work done on air pollution and little or seemingly none on soil pollution at Auto-workshops, in Ghana.

2.4.1 Review of Heavy Metals in the Environment

There have been several research works done in the field of heavy metals and their associated problems to the environment and biological life around the world, especially in the developed world with guidelines for mitigation and little in the developing world especially Africa. Unlike other pollutants like hydrocarbons and litter which may be visibly build up in the environment, trace metals may accumulate unnoticed, to toxic levels. Problems associated with heavy metal contamination were first highlighted in the industrially world due to their larger industrial discharges (Goldberg, 1976). The relatively low level of industrial activities in Africa has not been able to create the needed rational management of heavy metal discharges into our environment. Even more important of the expected increases in industrial and urban activities in all parts of the continent (Biney et al., 1994).

According to Ayodele et al., (2007), the average heavy metal concentrations assessed at auto-repairs workshop in Iwo, Nigeria were found as: Zn – 0.90 mg/kg, Ni – 11.50 mg/kg, Cr – 5.3 mg/kg, Hg – 9.40 mg/kg and Pb – 133 mg/kg, with Pb and Hg exceeding international thresholds for agricultural used. There has also been a report on the

contamination of heavy metals in the topsoil in some mechanic villages in Abeokuta Metropolis with copper ranging from 0.02 mg/kg in Idi-Aba to 126.89 mg/kg in Kotopo which was higher than the allowable limits for some European countries and zinc were: (2.89, 0.91 and 86.23) mg/kg in (Fajol, Idi-Aba and Kotopo) respectively according to Olayinka and Adedeji, (2014). Pam et al., (2013), evaluated the concentration of heavy metals in soils around auto-mechanic workshops clusters in Gboko and Makurdi, Central Nigeria and revealed that majority of heavy metal concentrations of the samples were above background levels and the threshold limits recommended for soils in some countries. The results indicated the following levels: Cu (24.60 mg/kg), Pb (123.00mg/kg), Zn (42.70 mg/kg), Mn (92.00 mg/kg), Ni (8.44 mg/kg) and Cd (0.60 mg/kg) with a distribution pattern in the other: Pb > Mn > Zn > Cu > Ni > Cd. It shows that, the environment is highly polluted with Pb and Cu, and to a lesser degree with Ni. Mn and Cu showed moderate pollution status while the soil remains unpolluted with Zn.

One of the earliest researches on heavy metals contamination, in Ghana (Amasa, 1975) examined various matrices from the Obuasi gold mining area and realized that the concentration level of arsenic exceeded the normal value. Pelig Ba et al., (1991) assessed the level of contamination of drinkable groundwater from the Upper East Regions and the Accra plains of Ghana and found out that in some areas Fe, Pb and Cr concentrations exceeded the WHO guideline limits for drinking water. A study by Akoto-Bamford (1990) for some selected heavy metals from mining activities was assessed by analyzing gold ore, sediments, water, and tailings revealed the presence of all the elements in

sediments were within the concentration range of 0.08 – 49000 µg/g, whereas only iron (Fe) and zinc (Zn) were detected in water at levels of 0.08 – 2.40 µg/ml.

Among other studies: Akoto et al., (2008) reported on the contamination of heavy metals, the results of which showed the mean concentration as: 7.21 mg/kg, 0.33 mg/kg, 0.87 mg/kg, 48.52 mg/kg, 7.33 mg/kg and 26.66 mg/kg for Cu, Ni, Cd, Fe, Zn and Pb respectively. They indicated that the enrichment factors of the measured heavy metals were: 2.26, <0.10, 0.39 and 3.47 for Cu, Ni, Zn and Pb respectively and the geoaccumulation index indicating uncontaminated to slightly contaminated for Ni and Fe, but highly contaminated for Cu and Lead (Pb). Atiemo et al., (2010) carried out work to investigate heavy metals and the human health risk associated with them of road dust. Two grain sizes, one of which is between 100 µm – 250 µm and the other less than 100 µm of the samples were analyesd and twenty (20) elements were identified. The results showed high enrichment of V, Zn, Cu, Zr, Br and Pb from the sample sites. There was no indication of significant anthropogenic contribution of manganese (Mn) which gave average enrichment factor values of 0.60 and 0.78 in the road dust at the Tema motorway and Tetteh Quarshie Interchange respectively. Risk assessment of selected heavy metal contaminants from both sites indicate that Pb gave Health Index (HI) values of 0.56 and 0.62 which falls below the safe level of one (1) and observed that ingestion which gave HI values of 2.1 and 2.3 as the highest risk of exposure pathway, with Tetteh Quarshie Interchange given the highest cumulative risk of exposure.

An investigation conducted to assess the level of contamination of surface dust from roads in the Bolgatanga Municipality, according to Victoria et al., (2014) gave values of index of geoaccumulation in the range of unpolluted indicating insignificant accumulation of heavy metals from anthropogenic sources. The analysis of variance shows that chromium (Cr), mercury (Hg), cobalt (Co), cadmium (Cd) and zinc (Zn) concentration levels were highly significant in road dust collected from zone A, B, C and D. Some elemental pairs showed a strong correlation at 5% significant level such as Fe/Cr (0.72), Ni/Co (0.64), Cd/Mn (0.81), Fe/Mn (0.70), Fe/Co (0.71) and Ni/Cd (0.81). It is also reported that the source of Cd/Ni, Cd/Mn, Cd/Cr and Cd/Co in the road dust might be accumulated from wear-and-tear of tyres, combustion of fuel and oil/lubricants, which are known to contain trace levels of cadmium.

This work considered four (4) selected auto-workshops with emphasis on the locations: electrical, mechanical/body, welding and spraying/painting in the workshops and the human health risk associated with the activities in these locations.

2.5. ANALYTICAL METHODS

Many of these research works have served to quantify levels in different situations and have produced an understanding of background and anthropogenic sources for metals in soil (McGrath et al., 2004). These are conducted on the elemental contamination of soils at Auto-workshops in developed countries; some studies have also been conducted in Africa, a lot more needs to be done especially in Ghana. The analytical tools seek to

determine the qualitative and quantitative characteristics of the various elements in the soil samples. There are a number of these tools/techniques, such as: ICP-AES, INAA, ICP-MS, XRF, ASS and TXRF that are used for elemental determination of soil. The choice of a particular technique depends on factors such as the speed of analysis, technical expertise of the analysis, the cost of analysis, availability of the instrument, and others.

These instruments measures elements in environmental samples to parts per billion (ppb) concentration of $\mu g L^{-1}$ and $\mu g K g^{-1}$ in liquids and solids samples respectively (Melamed, 2005).

2.5.1. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

This is an analytical technique used for the detection of trace metals in environmental samples. The goal of ICP is to get the elements emit characteristic wavelength of specific light which then can be measured. Samples are decomposed to neutral elements in high temperature argon plasma and analyzed based on their mass to charge ratios. Aqueous samples are introduced by a way of a nebulizer which aspirates the sample with high velocity argon, forming a fine mist. The aerosol then passes into a spray chamber where larger droplets are removed via a drain. Solid samples are introduced into the ICP by a laser ablation system (Bradford and Cook, 1997).

2.5.2. Instrumental Neutron Activation Analysis (INAA)

INAA is also an analytical tool based on the measurement of characteristic radiations emitted from radionuclides formed directly or indirectly by neutron irradiation/bombardment of the material of interest (IAEA, 2001). It is capable for simultaneous multi-elemental analysis with no or minimal chemical treatment of samples. It is a non-destructive method with adjustable parameters that can be exploited for maximum sensitivity for the desired element. With these strengths, a major setback for its use in this study is its inability to detect lead (Pb), a key element known to be prevalent in most of the waste in auto-mechanic workshops. In addition, it is time consuming due to the different irradiation, decay and counting times for the elements depending on their half-lives.

2.5.3. X-Ray Fluorescence Spectroscopy (XRF)

XRF is a non-destructive, multi-elemental, analytical technique used to identify and determine the concentrations of elements present in powdered, liquid and solid samples (www.rigakuedxrf.com). It provides a wide range and a fairly uniform detection limit across the periodic table from low-Z; beryllium (Be) to high-Z; uranium (U) and is applicable to a wide range of concentrations from a 100% to a few part per million (ppm) (www.rigakuedxrf.com).

Its advantages as a technique is that, it is a multi-elemental tool for soil/dust analysis and has not been extensively exploited in most reviewed studies and can be used to determine a very wide range of elements. The measurement is fast; less time spent within a few

seconds per element, and to hours depending on the composition complexity, requested accuracy, levels of concentration. Results are accurate, where error can be as low as 0.1% relative if adequate calibration standards are available (www.rigakuedxrf.com).

X-ray fluorescence analysis can be applied to a wide range of uses including quality control. There has been an improvement for high-sensitivity of the technique by application of filtering and lamination to eliminate the interference of background and thus making measurement of trace amounts possible and is now widespread particularly in measurements of hazardous metals in materials and soil. It is also used in the fields of metals, cement, forensics, mining and mineralogy, oil, polymers, geology. It is able to analyze heavy metals in air and water, in a case of environmental analysis.

This technique which is suitable for the research work could not be used due to its unavailability in the laboratories around, resulting into using AAS analytical tool.

2.5.4. Atomic Absorption Spectrometry (AAS)

This is another analytical technique used for elemental analysis in environmental samples. It can be used to analyze over sixty-two (62) different metals in a solution. In the assessment of heavy metal pollution in soils along major roadside in Botswana (Mmolawa et al., 2011), pollutants such as Al, Co, Cu, Fe, Pb, Ni, Zn and Mn, were determined using flame absorption atomic spectrometry (FAAS).

Atomic Absorption Spectroscopy as an elemental analytical technique that has the significant advantage in many cases of being independent of the chemical form of the

element in the sample. It has greater sensitivity and detection limit, low spectral interference and it requires a very small sample size. As a technique also, a given element can be determined in the presence of other elements without interference. Notwithstanding these, no information is obtained on the chemical form of the analyte, and often one element can be or is determined at a time which makes it time consuming. The sample preparation techniques could also be time consuming for large sample sizes and availability of appropriate gas combinations for the determination of some elements.

2.5.4.1. Basic Principle of Atomic Absorption Spectrometry (AAS)

It is an analytical procedure that employs the absorption of optical radiation (light) by ground state, free atoms in the gaseous state (free atoms are formed from the samples by an "atomizer" at high temperatures) in a flame or furnace for both quantitative and qualitative determination of chemical elements.

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample (Alloway and Ayres, 1998, Harrison and Laitinen, 1975).

The identification of elements by this method is possible due to the characteristic radiation (wavelength) absorbed by the electrons of the atoms under certain conditions. The electrons upon absorbing a characteristic wavelength become excited for a short period of time; that is "ground state" to "excited state" as shown in figure 2.4.

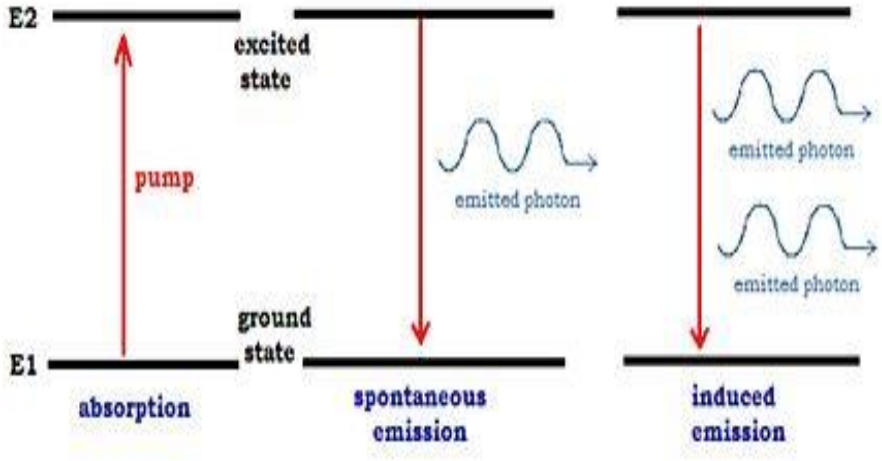

Figure 2.4: Excitation of an atom from "ground state" to "excited state"

The atom at the "excited state" is unstable and within this short period of time releases radiation energy and back to "ground state" during which time the intensity of the radiation passing through the sample is measured. The intensity - $\mathbf{I_0}$ (radiation of a given characteristic wavelength) of the light that causes the excitation is defined and is specific to a particular electron transition in a particular element and is called the incident radiation. Generally, each element corresponds to a specific wavelength and as the number of atoms in the light path increases, the amount light absorbed increases. As the intensity of the light passes through the material (solution of the analyte), it is measured as – **I.** If **I** is less than $\mathbf{I_0}$, it is obvious the sample/material absorbed some of the light at a particular rate called absorbance (**A**) as the ratio of the incident intensity of radiation to the intensity of the transmitted radiation.

Measuring these intensities allows us to determine the elemental concentrations of the individual elements. This is by applying Beer – Lambert law. The law is a combination of two and states as:

Beer's Law: states that the light absorption is proportional to the number of absorbing species in the sample.

Lambert's Law: states that the portion of light absorbed by a transparent medium is independent of the intensity of the incident light, and each successive unit thickness of the medium absorbs an equal fraction of the light passing through it.

The Beer – Lambert Law is expressed as;

$$I = I_0 \exp(-\mu l) \qquad \textbf{2.1}$$

where;

I is the transmitted intensity of the light

I_0 is the incident intensity of the light

μ is the attenuation coefficient

l is the path length of the light

The relationship between the Beer – Lambert law and the absorbance, **A** is expressed as;

$$A = log_{10}\left(I_0/I\right) \qquad \textbf{2.2}$$

A ranges from 0 – 1, an absorbance of zero (0) at some wavelength means that no light of that particular wavelength has been absorbed, and it implies that the intensities of the transmitted and incident are both the same, so the ratio $\boldsymbol{I_0/I}$ is 1 and $log_{10}1 = 0$.

An absorbance of 1 happens when 90% of the light at that wavelength has been absorbed, which means that the intensity is 10% of what it would be otherwise. In that case; $\boldsymbol{I_0/I}$ is 100/10 = 10 and $log_{10}10 = 1$

The relationship between the concentration of the element, the path length of the analyte and measured intensities is express as;

$$\boldsymbol{log_{10}\left({}^{I_0}/_{I}\right) = \varepsilon l c} \qquad \textbf{2.3}$$

where;

$\boldsymbol{\varepsilon}$ is the molar absorptivity or molar absorption coefficient

$\boldsymbol{l}$ is the path length of the light

$\boldsymbol{c}$ is the concentration of the measured analyte

From equation (2.2) and (2.3), it implies that

$$\boldsymbol{C = {}^{A}/_{\varepsilon l}} \qquad \textbf{2.4}$$

2.5.4.2 Instrumentation of the Atomic Absorption Spectrometer

The atomic absorption spectrometer consist of a light source of line spectrum of an element (hollow cathode lamp), a means of isolating an absorption line (Monochromator and an adjustable slit), a device for vaporizing the element (usually flame) and a photoelectric detector (with its associated amplifying and electronic measuring equipment).

Hollow Cathode Lamp: It consist of a tungsten anode and a cylindrical cathode sealed in a glass tube that is filled with argon or neon at a pressure of 1 or 5 torr. The cathode is constructed of the metal whose spectrum is desired to support a larger of that metal. When a high enough voltage is applied between the anode and the cathode, the filter gas becomes ionized and positive ions are accelerated towards the cathode. They strike the anode with enough energy to sputter metal atoms from the cathode into gas phase (Harrison and Laitinen, 1975). Each hollow cathode lamp is specific for a particular element and individual lamps are available for the estimation of over seventy elements. These may be single-element (mono-cathode lamp) or multi-element cathode lamps.

Monochromator and Detector: A sensitive narrow band passes monochromator is essential so that the monochromator wavelength can be adjusted to pass the element resonance line only. A detector of high sensitivity is required and a photomultiplier

with a suitable amplifier which produce a cloud of atoms of elements to be determined. The cloud of atoms produced absorbs the radiation of the resonance line from the hollow cathode lamp to give characteristic resonance radiation proportional to the energy absorbed. The radiation from the resonator is picked up by the photomultiplier and amplifier system.

Burner: There are two types of burners; the laminar-flow or premix burner and the turbulent-flow or total consumption burners. In the turbulent-flow burner, the sample is drawn up the capillary and nebulized by the venturic action. A typical sample flow rate is 1 – 3 ml/min. The merit of this burner is the introduction of relatively large and representative sample in the flame. Its demerits include short path length through the flame and a problem of clogging of the tip. The premix burner, nebulize the sample by the flow of oxidant gas past a capillary tip, it provides relatively quite flame and a long path length. These properties enhance sensitivity and reproducibility. The mixing chamber of premix burners contains a potentially explosive mixture which can be ignited by flashback if the flow rates are not sufficient (Alloway and Ayres, 1998).

2.6. DATA ANALYSIS

2.6.1. Pollution Models

Assessing soil pollution with toxic elements has to be done in comparison to baseline concentrations in soil. Pollution in this case, will be measured as the amount (or ratios) of the sample metal enrichment over the concentrations present in the background values (Abrahim et al., 2008, Lu et al., 2009). The background value of an element is the maximum level of the element in an environment beyond which the environment is said to be polluted with the element (Puyate et al., 2007). In order for assessing the impact of toxic metal pollution by using various enrichment calculation methods, several works have been done (Adomako et al., 2008, Abrahim, 2005). Pollution indices are often used to evaluate the extent of heavy metal pollution in various environmental media including air, water, soil, dust and sediments. In this study, the following contamination indices have been used to express the extent of soil pollution. They include: index of geo-accumulation, contamination factor, and pollution load index.

2.6.1.1. Index of Geoaccumulation (Igeo)

The index of geoaccumulation index (Igeo) was originally used with bottom sediment by Muller (Muller, 1969). It is widely used in assessing the contamination by comparing the level of heavy metal obtained to a background level. It is computed according to the equation (2.5) below;

$$I_{geo} = log_2\left[\frac{C_n}{1.5B_n}\right] \qquad 2.5$$

where

Cn is the measured concentration of the examined metal in the sample, Bn is the geochemical background concentration/value or reference value of the metal (n). The factor or constant 1.5 allows for the analysis of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences (Oingjie et al., 2008).

Table 2.2: Categories of index of geoaccumulation

Classes	I_{geo}	Designation of quality
0	$I_{geo} \leq 0$	Unpolluted
1	$0 < I_{geo} < 1$	Unpolluted to moderately polluted
2	$1 < I_{geo} < 2$	Moderately polluted
3	$2 < I_{geo} < 3$	Moderately polluted to highly polluted
4	$3 < I_{geo} < 4$	Highly polluted
5	$4 < I_{geo} < 5$	Highly polluted to very highly polluted
6	$I_{geo} > 5$	Very highly polluted

Cited from: (Muller, 1969)

The elemental concentrations in Class six (6) may be hundredfold greater than the geochemical background value.

2.6.1.2. Contamination Factor Analysis (Cf)

The contamination factor (Cf) which gives an indication of the level of contamination, proposed by Hakanson (1980), and computed for soil samples using the measured

concentrations of the toxic elements and their corresponding values in rock samples. It is calculated according to equation (2.6) below;

$$\boldsymbol{Cf} = \frac{\boldsymbol{C_{hm}}}{\boldsymbol{C_{crustal}}} \qquad \textbf{2.6}$$

where

Cf is the contamination factor of the heavy metal

$\mathbf{C_{hm}}$ is the concentration of the heavy metal in the sample

$\mathbf{C_{crustal}}$ is the concentration of the heavy metal in the continental crustal average/ baseline concentration.

Table 2.3: Scales of contamination factors (levels)

Cf	Destination of quality
$Cf < 1$	Low contamination
$1 \geq Cf \leq 3$	Moderate contamination
$3 > Cf \leq 6$	Considerate contamination
$Cf > 6$	Very high contamination

The highest number indicates that the metal concentration is hundredfold greater than what would be expected in the crust (Bhuiyan et al., 2010).

2.6.1.3. Pollution Load Index (PLI)

The pollution load index close to one (1) indicates heavy metal loads near the background level, while values above one (1) indicate soil pollution (Cabrera et al., 1999). The

pollution load indexes (PLI) were determined for the various sampling areas as the nth root of the product of the contamination factor as shown in equation (2.7) below.

$$\boldsymbol{PLI = \sqrt[n]{(Cf_1 x Cf_2 x \dots\dots\dots x Cf_n)}} \qquad \textbf{2.7}$$

where;

n is the number of element analysed.

The PLI provides a comparative means of assessing a sample site quality. The ranks of values and its implications are as follows:

Table 2.4: Implications of the values of Pollution Load Indexes

PLI	Implications
$PLI < 1$	Unpolluted
$1 \leq PLI < 2$	Moderately Polluted
$2 \leq PLI < 3$	Strongly Polluted
$PLI \geq 3$	Extremely Polluted

Cited: (Shuanxi, 2014).

2.7. HUMAN HEALTH RISK ASSESSMENT (HHRA)

Human health risk assessment is a method of determining risk due to exposure to contaminants (www.dec.state.ak.us/spar/csp). It is one means of protecting workers and others in and around these sites and helps to focus on the risk that really matter at

workplaces–the ones with the potential to cause harm (www.hse.gov.uk/risk/five/steps.html).

The effects of pollution or heavy metals on human and the environment depend on the combination of their chemical characteristics of the heavy metals, particle sizes and time of exposure. The effect of these metals will be mild even in higher concentrations if the time of exposure is small, however, the effect can be bad if the exposure time is of an extended period (Comfort, 2011).

Exposure of heavy metals can occur via three main paths: (1) direct ingestion of substrate particles (Ding); (2) inhalation of resuspended particles through mouth and nose (Dinh); and (3) dermal absorption of trace elements in particles adhered to exposed skin (Ddermal) (USEPA, 1989). The dose received through each of the four paths was calculated using equations (2.8) – (2.10) (Acosta et al., 2009, USEPA, 1989, 1996).

Dose intake by dermal contact (D_{derm}) is given as:

$$\boldsymbol{D_{derm} = C * \frac{SL*SA*ABS*EF*ED}{BW*AT} * 10^{-6}} \qquad \textbf{2.8}$$

Dose intake by ingestion (D_{ing}) is given as:

$$\boldsymbol{D_{ing} = C * \frac{IngR*EF*ED}{BW*AT} * 10^{-6}} \qquad \textbf{2.9}$$

Dose intake by inhalation (D_{inh}) of soil particles is given as:

$$D_{inh} = C * \frac{InhR * EF * ED}{PEF * BW * AT} \quad \textbf{2.10}$$

where

C is the concentration of elements in the sample (mg/kg),

BW is the body weight (kg),

EF is the exposure frequency (days/year),

ED is the exposure duration (years),

AT is the average time (days),

IngR is the ingestion rate (mg/day),

InhR is the inhalation rate (m^3/day),

PEF is the particulate emission factor (m^3/kg),

SA is the exposed surface area (cm^2/day),

SL is the skin adherence factor (mg/ cm^2/day),

ABS is the skin absorption factor (unitless),

In risk assessment for non-carcinogenic toxicants, a tolerable daily intake or a reference dose is assumed to be tolerated by the organism with low or no risk of adverse health effects (Ferreira-Baptista and de Miguel, 2008). For the determination of non-carcinogens or non-cancer risk of exposure, the equation (2.11) (USEPA, 2000, 2013) is used:

$$HQ = \frac{DI}{RfD} \quad \textbf{2.11}$$

where

HQ is hazard quotient for a particular route of exposure,

DI is the dose intake by agiven route of exposure,

RfD is the reference dose for a particular element through a particular route of exposure. It is an estimate of a daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a life-time.

The hazard index (HI) is calculated to determine the overall risk of exposure via ingestion, inhalation, and dermal contact using equation (2.11). The hazard index is generated as the sum of the hazard quotients of each metal through the routes of exposure (Leung et al., 2008). According to USEPA (2013), the occupant is at safe level of non-cancerous effect when the hazard index is equal to one (1). When it is less than one (1), it shows a little or non-cancer effect/ no adverse health risk and greater than one (1), there may be concern for potential health effects; which have been recognized as a useful index to evaluate the health risk associated with (Rupert et al., 2004). Therefore, interventions and protective measurements should be taken.

$$HI = HQ_{ing} + HQ_{inh} + HQ_{derm} \quad \textbf{2.12}$$

where

HI is the hazard index

HQ (ing, inh, and derm) represent the hazard quotients of the routes of exposure.

Table 2.5: Parameters for the Determination of Dose Intake

Symbol	Definition	Population	
		Children	Adults
IngR	Ingestion Rate	200	100
BW	Body Weight	15	70
AT	Averaging Time	ED*365	ED*365
PEF	Particulate Emission Factor	1.32E+09	1.32E+09
InhR	Inhalation Rate	7.6	20
SA	Exposed Surface Area	2800	5700
EF	Exposure Frequency	180	180
ED	Exposure Duration	6	24
SL	Skin Adherence Factor	0.2	0.7
ABS	Skin Absorption Factor	0.001	0.001

Cited from: (Acosta, et al., 2009, USEPA, 1989, 1996, 2013

CHAPTER THREE

METHODOLOGY

3.1. SITE SELECTION AND DESCRIPTION

The study areas are located in the La-Nkwantanang Municipal Assembly in the Greater Accra Region. Four Auto-mechanic workshops were selected from the areas. The sampled workshops were coded as: BB, MI, MP and TP. Care was taken not to selected areas characterized by intense human activity to avoid other sources of pollution to the auto-mechanic workshops. The auto-mechanic workshops are operated in the open and on bare soil. Figure 3.1 show the sampling locations for this work.

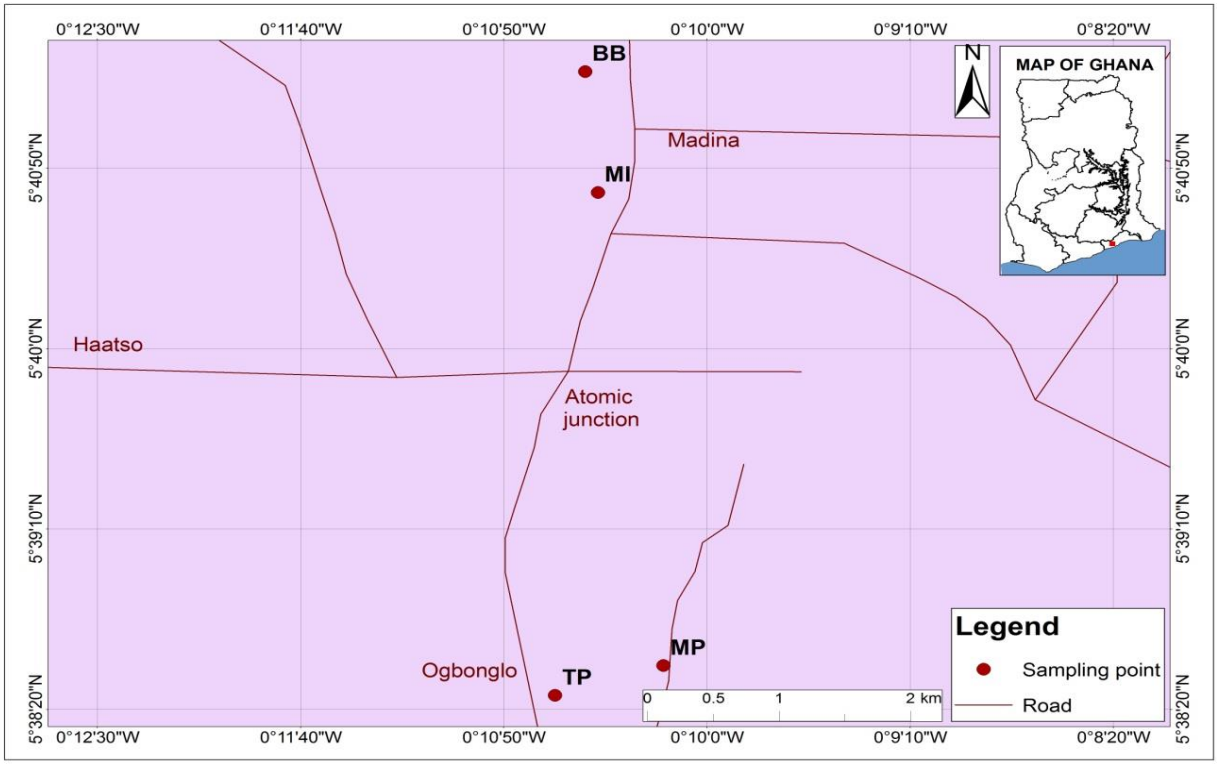

Figure 3.1: Map showing the sampling locations.

3.2. SAMPLE COLLECTION

Surface soils are the first locus of input of metals where they tend to accumulate on a relatively long term basis (Abechi et al., 2010). These pollutants normally contaminate the upper layer of the soil at a depth (0 - 40) cm (Krishna and Grovil, 2007) and more prevalent within the surface soils at mining and industrial sites (Huang, et al., 1997). This implies that, high concentration of these pollutants could be present at this depth if assessed. Topsoil samples were collected from the sampling locations indicated in Fig 3.1 A total of eighty soil samples were collected from the four locations in the selected Auto-mechanic workshops. Sampling was done once every two weeks for two months (November to December). At each sampling point, samples were collected at the following locations: Auto-Welding (W), Auto-Mechanical (M), Auto-Electrical (E) and Auto-Spraying/Painting (S). Reference soil samples were also collected from locations of about (150 -200) m from each of the sampling areas to serve as control samples. The soil samples were gathered and collected with a soft touch brush and a plastic dust pan into pre-cleaned polyethene bags and sealed, and then taken to the analytical laboratory. At each sampling point, the brush and the plastic pan were cleaned with acetone and cotton to avoid cross contamination (Ahmed and Ishiga, 2006; Bosco et al., 2005).

3.3. SAMPLE PREPARATION

3.3.1. Sieving of Samples

The soil samples were air-dried over one week at an average temperature of 81^{o}F (27^{o}C). This was done to reduce the moisture content. The samples were disaggregated. Each one of the samples was then sieved using meshes (metric test Sieve Bs 410 WS Tyler) with geometric diameters 500 µm, 200 µm, 100 µm, and 50 µm on a mechanical shaker (model: Retch AS200) at an amplitude of 15mm/g for 3 minutes to separate them into different particle size fractions. Any large stones or foreign objects above 500 µm were considered as debris. The sieves were cleaned with acetone between samples as a means to avoid cross contaminations. Those particles below 500 µm were labelled as "200 µm", between 200 µm and 100 µm were labelled as "100 µm", between 100 µm and 50 µm labelled as 50 µm, and those below 50 µm was labelled as " - 50 µm", were the particles sizes considered and placed in ziplock plastic sample bags. A total of eighty (80) samples of the 100 µm were prepared for heavy metals analysis. This is because; the anthropogenic contributions to the soil contaminants are mostly of fine sizes (Comfort et al., 2013). Figure 3.2 shows the setup of the sieving process.

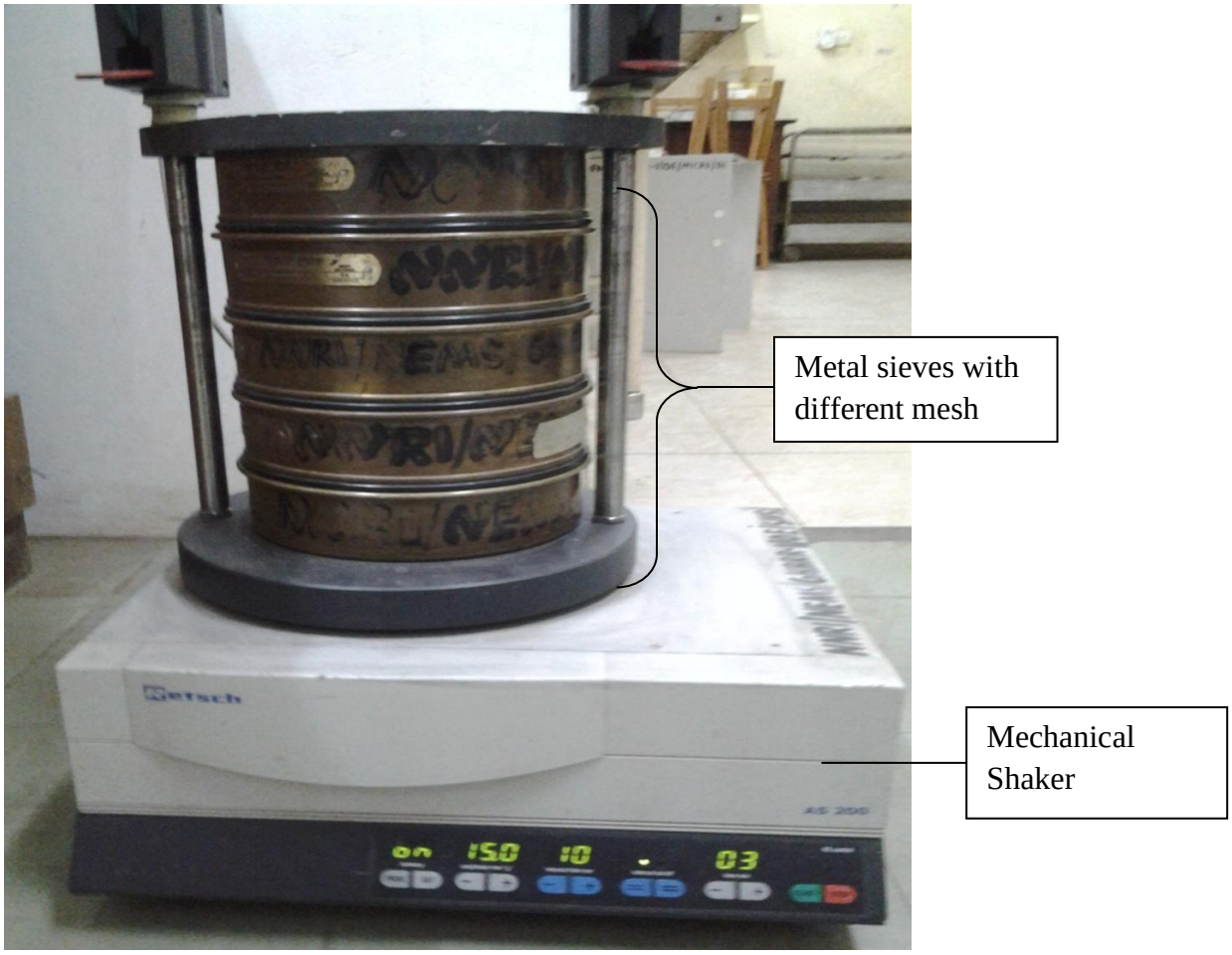

Figure 3.2: Sieving setup used in this work. [Photo by: Mohammed Yidana, Ziblim]

3.3.2. Sample Digestion

2.0 g of each of the dried sieved soil samples were weighed with a digital weighing balance model: METTLER TOLEDO XS603S into acid washed 125 ml beakers. The samples were digested with 25 ml aqua-regia (3ml 65% HNO_3: 1ml 35% HCl) for 3 hours on a hot plate (45^0 C). This was done to reduce the interference of organic matter and to convert metal associated particulate to a form solution (free metal). The digested

samples were allowed to cool at room temperature. The sides of the beakers were washed with de-ionized water and diluted to a volume of 30 ml and transferred into the appropriate test tube.

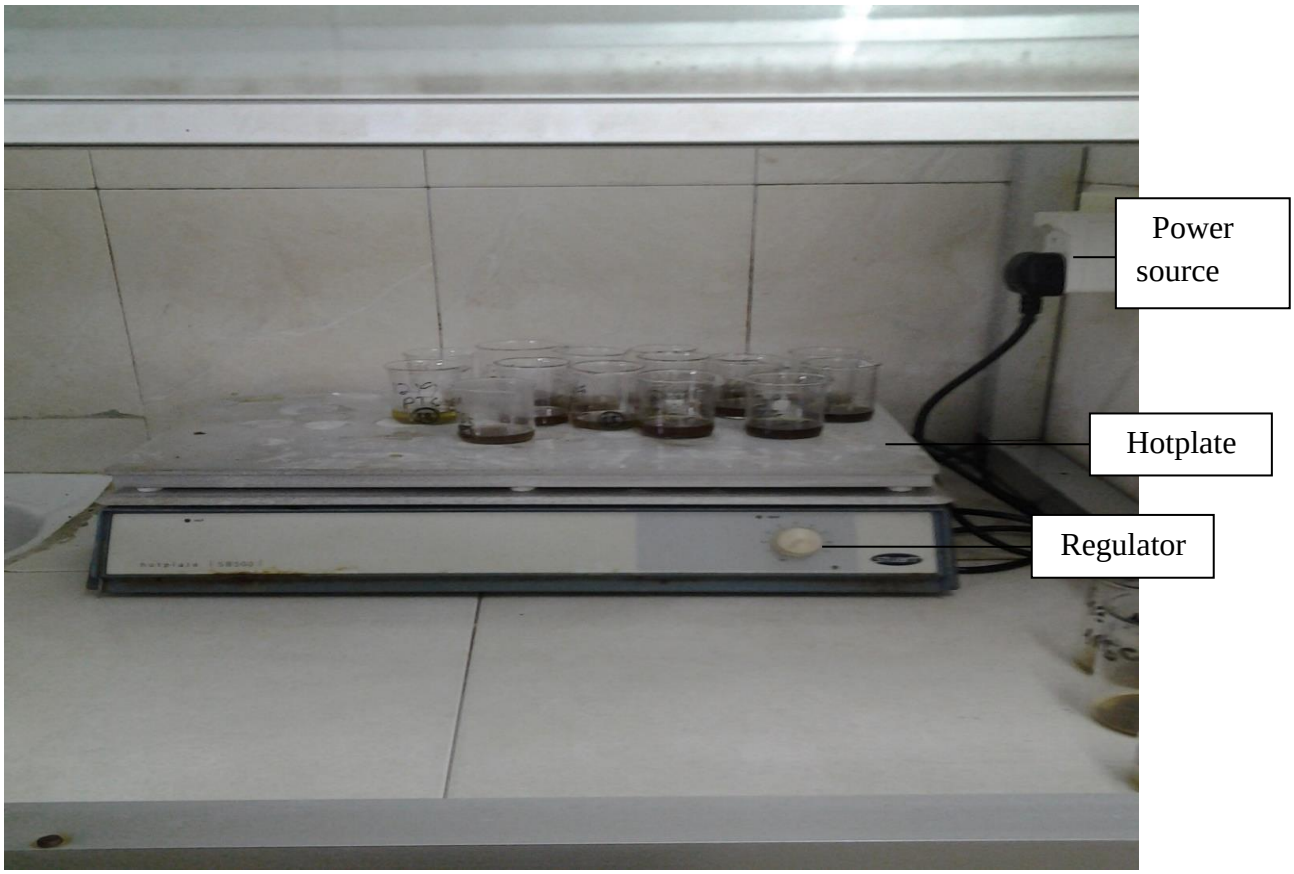

Figure 3.3: Digestion setup used in this work. [Photo by: Mohammed Yidana, Ziblim]

3.4. ELEMENTAL ANALYSIS

The digestate were assayed to measure the concentrations of the elements of interest using VARIAN AA240FS-Flame Atomic Absorption Spectrometer model, at the Nuclear

Chemistry and Environmental Research Center, Ghana Atomic Energy Commission (GAEC), Accra. The software for the analysis is the manufacturer's in-built software and the operational specifications and conditions of the spectrometer in Table 3.1 (VARIAN. Publication No 85-100009-00 Revised March 1989). Figure 3.4 and 3.5 shows the setup of the Flame Atomic Absorption Spectrometer (FAAS) and schematic diagram of atomic absorption spectrometry (AAS) respectively. Mercury and Arsenic were determined under cold vapor condition, not to allowed the elements vaporised.

Table 3.1: Operational working conditions (FAAS)

Element	Hollow Cathode Lamp		Slit Width (nm)	Fuel	Support
	Wavelength (nm)	Lamp Current (nA)			
Zn	213.90	5.00	1.00	Acetylene	Air
Ni	232.00	4.00	0.20	Acetylene	Air
Cu	324.80	4.00	0.50	Acetylene	Air
Fe	248.30	5.00	0.20	Acetylene	Air
Mn	279.50	5.00	0.20	Acetylene	Air
Cd	228.80	4.00	0.50	Acetylene	Air
Pb	217.00	5.00	1.00	Acetylene	Air
Cr	357.90	7.00	0.20	Acetylene	Air
Mo	313.30	7.00	0.50	Acetylene	Nitrous Oxide
As (By Hydride)	193.70	10.00	0.50	Acetylene	Nitrous Oxide
Hg (By Hydride)	253.70	4.00	0.50	Acetylene	Air

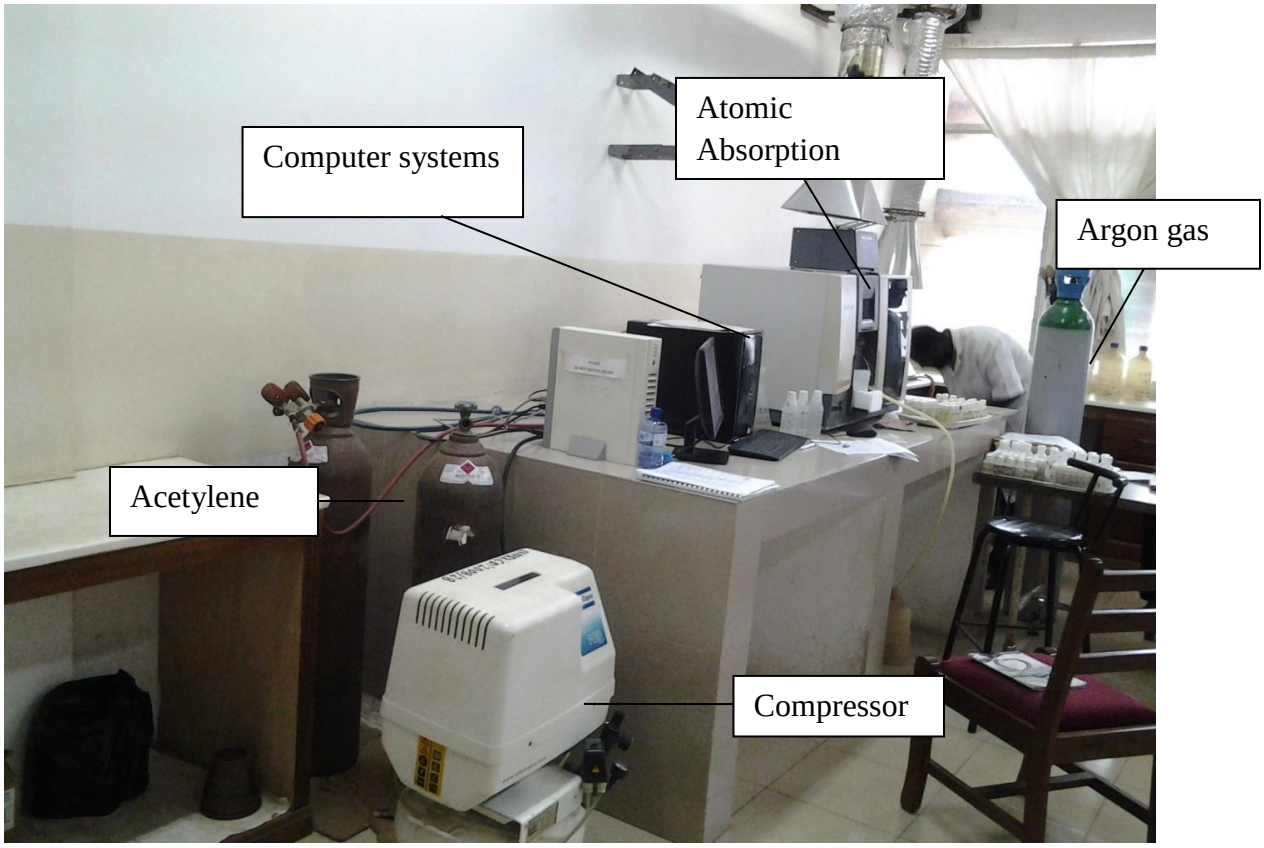

Fig. 3.4: FAAS setup used in this work. [Photo by: Mohammed Yidana, Ziblim]

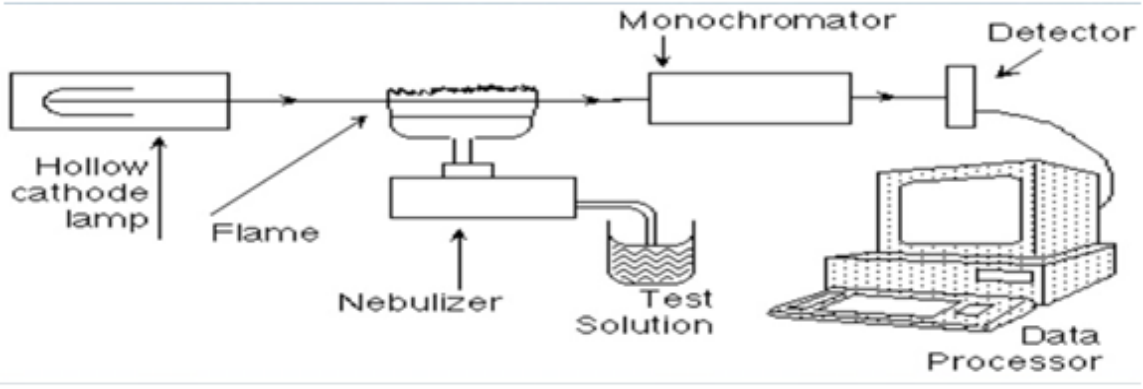

Figure 3.5: Schematic diagram of atomic absorption spectrometry (AAS)

3.5. QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Quality Assurance comprises of quality control and quality assessment. Quality Assurance is defined as the total sum of activities employed by the laboratory to ensure that the data it produces meet the quality desired for decision making (Ibe and Kullenberg, 1995).

Quality control refers to the set of procedures undertaken by the laboratory for continuous monitoring of operations and results in order to ensure the results are good enough to be released (Ibe and Kullenberg, 1995).

The following QA/QC guidelines were undertaken during sampling and analysis to produce acceptable results.

- In sampling from the sites, the samples are collected and placed in pre-cleaned polyethene bags and tightened and at each sampling point, the soft and plastic pan were cleaned with acetone and cotton to avoid cross contamination.
- The samples collected were provided with sample identification codes, to avoid mix-ups.
- All glassware and sampling containers were soaked in nitric acid for three (3) days and rinsed with de-ionised water before used. It is to ensure that the glassware were free from contamination.
- The instrument used was calibrated with standard chemical solutions and validated with Standard Reference Materials (SRM).

Standard Reference Materials are used for the elements of interest, blanks and duplicates were digested the same conditions as the samples. These served as internal positive controls. Standard Reference Material used is the IAEA-SOIL-7. Blanks were used to check contamination during sample preparation, duplicates also to check the reproducibility of the method used. These were to check the efficiency of the equipments being used. The experimental data was treated statistically using excel.

A calibration curve was drawn using diluted standard solution from stock and quantification of the elements of interest was achieved using the calibration curve for each of the element. Each standard (Reference Standard Materials) solution was prepared from FLUKA ANALYTICAL (Sigma-Aldrich Chemie GmbH, Switzerland).

The quantitative analysis involved the calculation of the final concentrations from the identified elements' initial concentrations using:

$$C_{final} = \frac{(C_{initial} \times V_{nominal})}{W_{sample}} \qquad \textbf{3.1}$$

where;

C_{final} is the final concentration of the sample element

$C_{initial}$ is the initial concentration of the element in the analyte

$V_{nominal}$ is the nominal volume of the analyte

W_{sample} is the weight of the sample in grams

CHAPTER FOUR

RESULTS AND DISCUSSION

The results obtained from the experiments are discussed in this chapter; the elements identified and their concentrations, validation of those results and the possible effects they may have on the environment, using pollution indices/models such as; contamination factor, index of geoaccumulation and pollution load index.

The human health risk aspect of the identified elements were also looked at, using dose intake, health quotient and health index for a particular route of exposure for a particular element of interest.

4.1. ELEMENTS IDENTIFIED

The following elements were identified and quantified in this work; Cr, Fe, Co, Mn, Cu, Zn, Pb, Cd, As, Hg and Ni. The mean concentration values of the elements at the various sites are shown as in appendix A1 – A5.

4.2. VALIDATION OF THE RESULTS

IAEA-SOIL-7 was used as a standard reference material (SRM) for the validation of the analytical results (Nwachukwu et al., 2010). The results of the IAEA-SOIL-7 obtained are shown in Table 4.1.

Table 4.1: Analytical results of IAEA – Soil – 7 certified values (mg/kg)

Elements	Experimental Values (mg/kg)	IAEA Certified Values (mg/kg)	Ratio: Experimental/Certified
As	13.65	13.4(12.5 – 14.2)	1.02
Cd	1.29	1.3(1.1 – 2.7)	0.99
Co	8.85	8.9(8.4 – 10.1)	0.99
Cr	73.05	60(49 – 74)	1.22
Cu	10.98	11(9 – 13)	0.99
Fe	25770.15	25700(25200 – 26300)	1.00
Hg	0.05	0.04(0.03 – 0.07)	1.18
Mn	631.03	631(604 – 650)	1.00
Ni	36.01	26(21 – 37)	1.39
Pb	64.37	60(55 – 71)	1.07
Zn	105.33	104(101 – 113)	1.01

The certified values were taken from the IAEA report on soil-7 and the experimental values were measured at the laboratory using the IAEA-SOIL-7 sample. The ratios of the experimental values to the IAEA certified values were calculated to determine the variation or correlation between the two values.

All the experimental values were within the IAEA Certified values range and the ratios between the experimental and certified values found to be approximately one (1). It shows that the experimental values agreed with the certified IAEA values. This could

also indicate the instrument calibration (AAS instrument) was calibrated well to ensure accurate results.

4.3. ANALYSES OF SOIL SAMPLES

The elemental concentrations of the heavy metals identified: Co, Cr, Fe, Mn, Cu, Zn, Pb, Cd, As, Ni, Hg as indicated earlier are shown in figure 4.1 – 4.4. These metals can be classified as;

- Potentially toxic (cadmium, mercury, lead, arsenic, aluminum, etc.)
- Probably essential (nickel, vanadium, cobalt)
- Essentially (iron, manganese, selenium, zinc, sodium, molybdenum, copper, etc.) (Uluozlu et al., 2008).

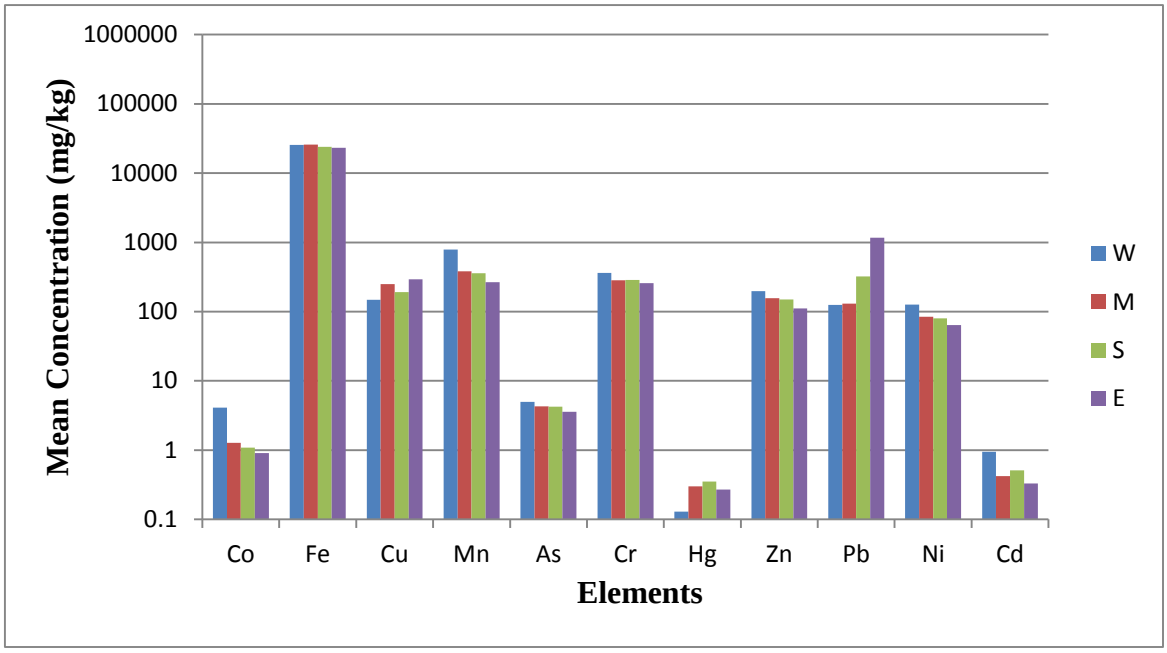

Figure 4.1: Elemental concentrations in topsoil in the various locations at auto-workshop BB

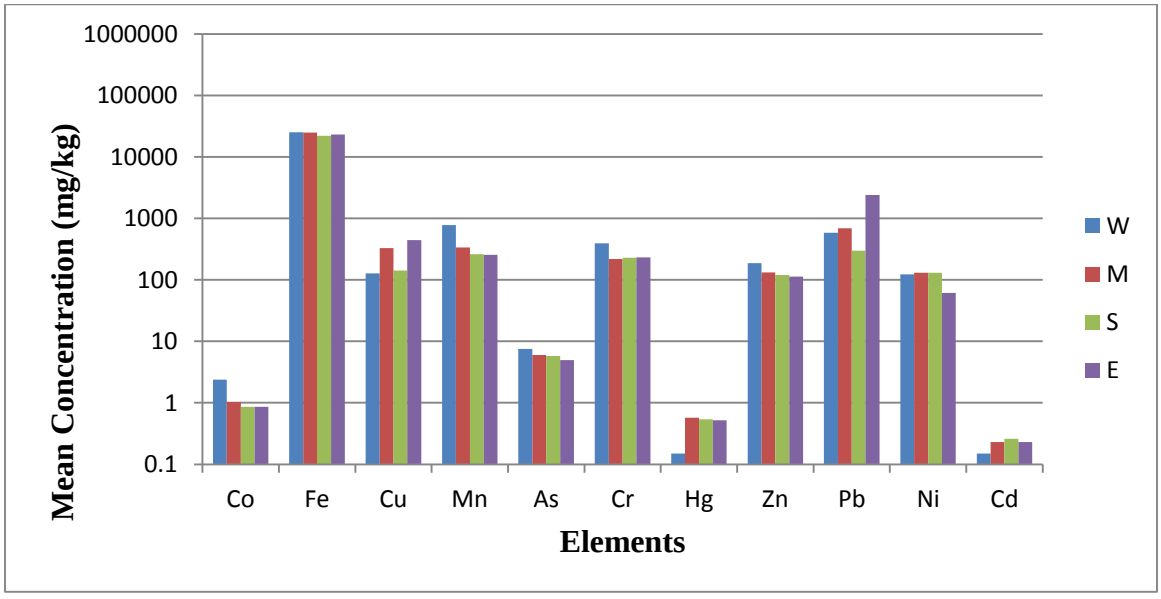

Figure 4.2: Elemental concentrations in topsoil in the various locations at auto-workshop MI

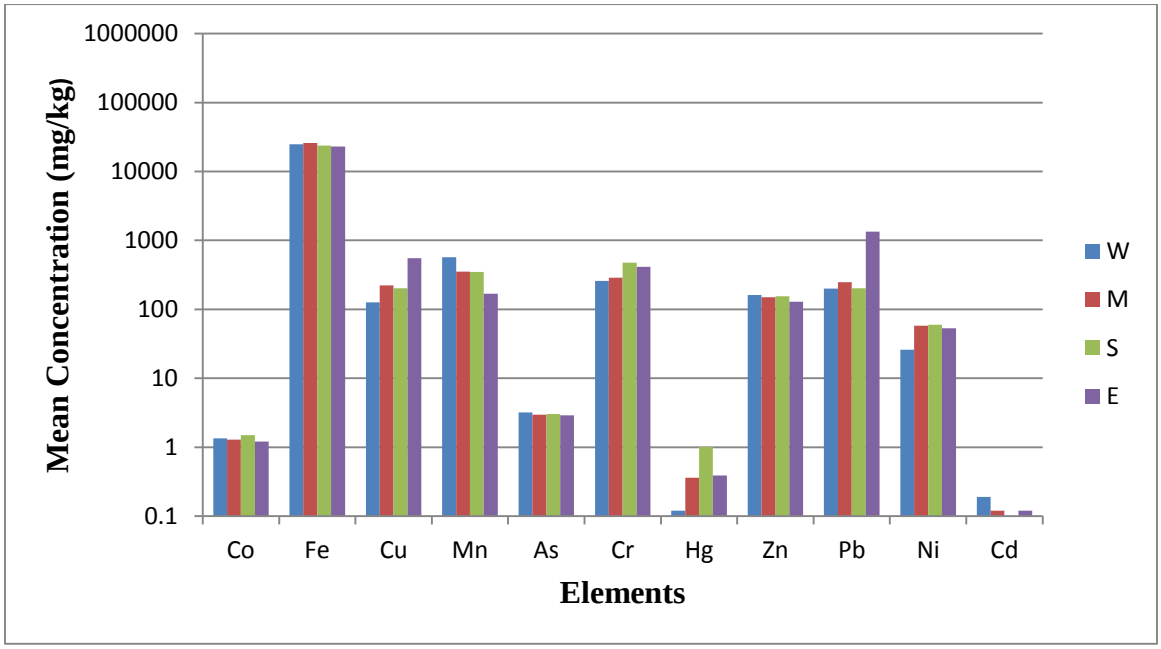

Figure 4.3: Elemental concentrations in topsoil in the various locations at auto-workshop MP

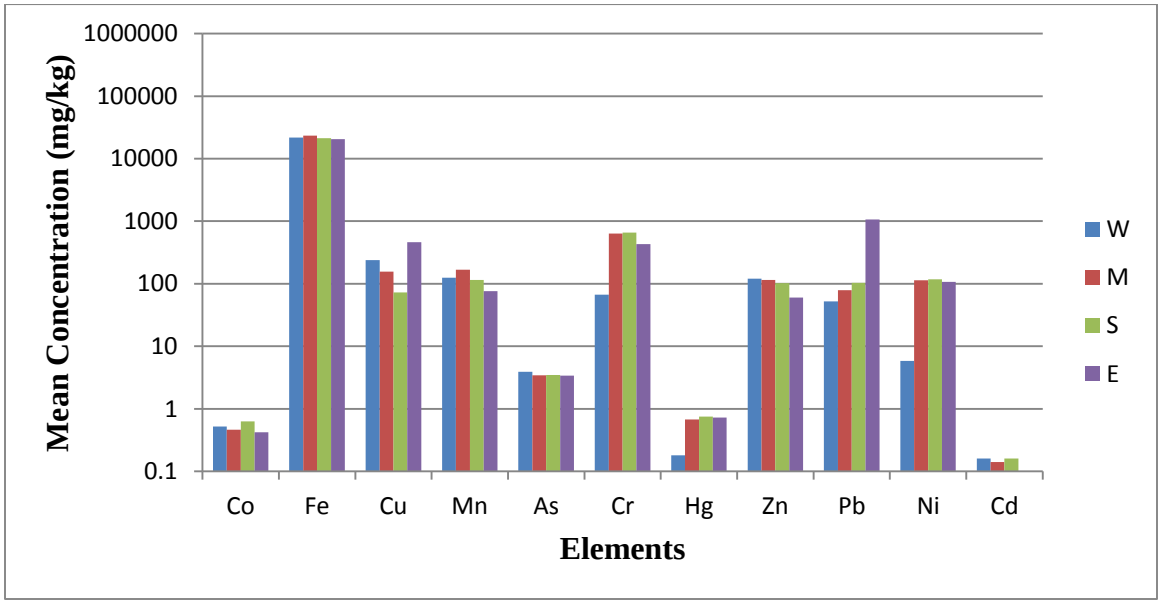

Figure 4.4: Elemental concentrations in topsoil in the various locations at auto-workshop TP

The results of the elemental concentrations obtained at the four auto workshops showed that iron (Fe), which is mostly of crustal origin is seen to be in higher concentration in all the four auto workshops as in figure (4.1 – 4.4). Fe could also be coming from mild steel from auto-body scraps (Nwachukwu et al., 2010). Mn which is an essential element is also seen to be present in moderately high concentration in all the auto workshops. Cr, Ni, Cu, Zn, Cd, Pb, Hg and As which are mostly of anthropogenic origin (Comfort et al., 2013) are also found to be in trace quantities. The elemental concentration ratios at the auto-workshops to that of the control site as shown in table (4.2 – 4.5) below, for most of the elements gave values higher than 3.0. The highest ratio of 20.61 occurred at the auto-electrical location at auto-workshop BB for lead (Pb). This is similar to reports by Ayodele et al., (2007) and Aloysius et al., (2013). It is possible that, these levels of Pb are as a result of leaded batteries at the auto electrical shops (Pam et al., 2013). The mean concentration values of Pb obtained are deemed to be higher at all the locations in the auto-workshops than the control sites. The concentrations of Pb obtained are lower than the 501.58 mg/kg reported by Udousoro et al., (2010) and 1162 mg/kg reported by Nwachukwu et al., (2010) for their works at auto workshops.

Table 4.2: Elemental concentrations at the various locations and that of control at auto-workshop BB (mg/kg)

Elements	*BBC	BBW	Ratio (BBW/BBC)	BBM	Ratio (BBM/BBC)	BBS	Ratio (BBS/BBC)	BBE	Ratio (BBE/BBC)
As	2.93	4.98	1.70	4.28	1.46	4.22	1.44	3.58	1.20
Cd	0.18	0.95	**5.28**	0.42	2.33	0.51	0.83	0.33	1.83
Co	1.02	4.13	4.05	1.28	1.25	1.09	1.07	0.91	0.89
Cr	169.10	361.10	2.14	282.40	1.67	286.88	1.70	258.40	1.53
Cu	34.60	148.60	4.29	248.80	**7.19**	190.50	5.51	294.11	**8.50**
Fe	24442.90	25545.80	1.05	25892.30	1.06	23896.88	0.98	23288.10	0.95
Hg	0.17	0.06	0.35	0.30	1.76	0.35	2.06	0.27	1.59
Mn	190.80	787.35	4.13	381.41	2.00	356.63	1.87	266.81	1.39
Ni	11.90	125.90	**10.58**	84.00	**7.06**	80.10	6.73	63.80	5.36
Pb	56.90	124.71	2.19	129.80	2.28	322.60	5.67	1172.70	**20.61**
Zn	36.70	198.31	5.40	157.10	4.28	149.70	4.08	111.10	3.02

*BCC is the control location

Table 4.3: Elemental concentrations at the various locations and that of control at auto-workshop MI (mg/kg)

Elements	*MIC	MIW	Ratio (MIW/MIC)	MIM	Ratio (MIM/MIC)	MIS	Ratio (MIS/MIC)	MIE	Ratio (MIE/MIC)
As	1.66	7.54	4.54	5.97	3.59	5.76	3.47	4.95	2.98
Cd	0.06	0.15	2.50	0.23	**3.83**	0.26	**4.33**	0.23	**3.83**
Co	1.15	2.37	2.06	1.03	0.89	0.86	0.75	0.86	0.75
Cr	340.10	393.00	1.16	218.60	0.64	228.38	0.67	223.11	0.66
Cu	47.70	127.91	2.68	329.31	**6.90**	141.30	2.96	442.40	**9.27**
Fe	25159.90	25339.90	1.01	24897.80	0.99	22144.13	0.88	23303.31	0.93
Hg	0.98	0.15	0.15	0.57	0.58	0.54	0.55	0.52	0.53
Mn	156.75	773.18	4.93	336.90	2.15	261.60	1.67	256.84	1.64
Ni	14.90	123.31	8.28	130.80	**8.78**	129.90	**8.72**	61.30	4.11
Pb	254.60	585.61	2.30	693.04	2.72	299.90	1.18	2404.50	**9.44**
Zn	51.70	188.10	**3.64**	131.71	**2.55**	119.70	2.32	113.60	2.20

*MIC is the control location

Table 4.4: Elemental concentrations at the various locations and that of control at auto-workshop MP (mg/kg)

Elements	*MPC	MPW	Ratio (MPW/MPC)	MPM	Ratio (MPM/MPC)	MPS	Ratio (MPS/MPC)	MPE	Ratio (MPE/MPC)
As	1.85	3.21	1.73	2.97	1.61	3.01	1.63	2.89	1.56
Cd	–	0.19	–	0.06	–	–	–	0.06	–
Co	0.87	1.34	1.54	1.28	1.47	1.50	1.72	1.21	1.39
Cr	124.50	258.80	2.08	287.60	2.31	475.88	**3.82**	415.10	3.33
Cu	44.50	126.45	2.84	222.00	4.98	201.10	4.52	551.90	**12.40**
Fe	24493.90	24845.30	1.01	25990.01	1.06	23820.11	0.97	22955.30	0.94
Hg	1.46	0.06	0.04	0.36	0.25	1.01	0.69	0.39	0.27
Mn	175.39	572.29	3.26	350.89	2.00	347.74	1.98	169.16	0.96
Ni	14.50	25.81	1.78	58.11	**4.01**	59.60	**4.11**	53.10	3.54
Pb	81.50	200.63	0.41	246.11	3.02	202.70	2.49	1341.80	**16.46**
Zn	37.90	162.04	**4.27**	150.40	**3.97**	154.50	4.08	129.10	3.41

*MPC is the control location

Table 4.5: Elemental concentrations at the various locations and that of control at auto-workshop TP (mg/kg)

Elements	*TPC	TPW	Ratio (TPW/TPC)	TPM	Ratio (TPM/TPC)	TPS	Ratio (TPS/TPC)	TPE	Ratio (TPE/TPC)
As	1.83	3.91	2.14	3.42	1.87	3.46	1.89	3.37	1.84
Cd	0.11	0.16	**1.45**	0.14	1.27	0.16	1.45	–	–
Co	0.18	0.52	2.89	0.46	2.56	0.63	3.50	0.42	2.33
Cr	81.00	67.10	0.83	633.80	**7.82**	660.00	8.15	432.00	5.33
Cu	16.00	237.40	**14.84**	155.90	9.75	72.20	4.51	459.20	**28.70**
Fe	22100.60	21726.40	1.02	23289.80	1.05	21264.00	0.96	20523.40	0.93
Hg	6.82	0.18	0.03	0.67	0.09	0.75	0.11	0.72	0.11
Mn	81.90	124.46	1.52	167.93	2.05	115.58	1.41	75.75	0.92
Ni	8.50	5.88	0.69	113.10	**13.31**	118.10	**13.90**	106.70	**12.55**
Pb	14.90	52.10	3.50	79.20	**5.32**	102.94	**6.91**	1064.93	**71.47**
Zn	23.40	119.80	**5.12**	114.40	**4.89**	102.30	4.37	60.40	2.58

*TPC is the control location

Manganese recorded higher ratios at auto-welding and mechanical locations at auto-workshop BB, MI and MP. The concentration of Ni in the soil investigated showed higher concentrations in the various locations in all the workshops than the control site. The results in this work are higher than the value of 0.33 mg/kg reported in Akoto et al., (2008), 11.5 mg/kg in Ipeaiyeda et al., (2007), 8.44 mg/kg in Pam et al., (2013) and 11.50 mg/kg in Ayodele et al., (2007). The anthropogenic distribution of Ni at the auto-electrical locations could be attributed to the disposal of spent automobile batteries from the auto-battery charger (Udousoro et al., 2010). Ni is also known to be present in diesel. Ni gave higher ratios at auto-mechanical location for almost all the auto-workshops. Most of the locations at the workshops have their concentrations lower than that reported by Akoto et al., (2008). Copper (Cu) was present in all the locations of the auto-workshops and had higher concentrations at the auto workshops than that at the control sites. Copper (Cu) at the auto-electrical locations are higher in concentration and mostly coming from cables and connecting wires. Cu gave higher ratios at auto-electrical locations for all the auto-workshops (Table 4.2 – 4.5). The presence of Cu could also be an indication of corrosion of metallic parts of automobiles derived from engine wear, thrust bearing, brushing and bearing metals (Divrikli et al., 2010).

Zn content in all the locations at the auto-workshops were higher than that at the control sites and suggest that, there is anthropogenic contribution. The fact that no industries exist in the vicinities of these areas, it is assumed that the primary source of Zn are probably the attrition of automobile tire rubber, lubrication oils in which Zn is found to be an additives (Zincdithiophates), and also an additives in motor oil, scraps from auto-

body parts could be contributing Zn in the topsoil (Abenchi et al., 2010). Zn is used in brass coating, to reinforce tyre structure and steel plates and wires. It recorded high ratios at the auto-welding locations. This may be due to electroplating (Dolan et al., 2006). Zn also recorded high ratios at the auto-mechanical locations at the workshops (Table 4.3 – 4.5) which could be due to waste oil, and scraps from auto-body (Abenchi 2010). The concentrations of Zn in all the auto workshops at the various locations in this investigation are more compared with results reported by Akoto et al., (2008) and Ayodele et al., (2007). The concentrations in this investigation are bigger than that of 42.70 mg/kg reported by Pam et al., (2013).

The mean concentrations of Cd are higher than 0.87 mg/kg that reported by Akoto et al., (2008) in all auto-locations in auto-workshops BB, MI and TP (Table 4.2, 4.4 and 4.5). Similarly, the concentrations of Cd at the various auto workshops are relatively generally low compare to the concentration of Cd (0.60 mg/kg) as reported by Pam et al., (2013) with the exception 0.95 mg/kg at the auto-welding location at auto workshop BB (figure 4.1). The Cd concentrations at the various auto workshops are relatively higher than at the control site which suggests that, there is anthropogenic contribution. The observed Cd concentrations and high ratios, especially at the auto-mechanical and auto-welding locations at the auto workshops could be attributed spillages of used oil, impurities from electroplating steel and wear-out tyres of automobile (Edebiri and Nwanokwale, 1981, Vazquez-Duhalt and Bartha, 1989, Dolan et al., 2006).

Chromium (Cr) levels are higher in all the locations at the various auto workshops when compared to the report by Ayodele et al., (2007) (5.3 mg/kg). Cr is used in the manufacturing of pigments for paints, metal alloys; electroplating (Vazquez-Duhalt and Bartha, 1989, Luoma, 1990) and this could be the reason for the high concentration levels. Brake dust is known to be enriched in Cr as compared to parent brakes linings (Thorpe and Harrison, 2008, Kennedy and Gadd, 2003). During deceleration, vehicle brakes linings are subjected to larger frictional heat generation and associated wear. The wear generates brake lining particles which can be released during brakes repairs at the auto workshops. These could be attributed to the high ratios at the auto-mechanical locations at the workshops.

The mean concentrations of mercury (Hg) in this investigation ranging from (0.06 – 0.18) mg/kg in auto-welding locations, (0.30 – 0.67) mg/kg in auto-mechanical locations, (0.35 – 1.01) mg/kg in auto-spraying locations and (0.27 – 0.59) mg/kg in auto-electrical locations when compared to the concentration of 9.40 mg/kg as reported by Ayodele et al., (2007) were very low.

The mean concentrations of the elements in the various locations at the auto workshops followed the same trend with relatively small differences. An exception to this trend is found in figure 4.1 and 4.4, where there is much variation between the mean concentration of chromium (Cr) in the auto-welding location and the auto (electrical, spraying and mechanical) locations respectively at auto workshop TP. This is similar to nickel (Ni) in the same auto workshop. From figure 4.1 – 4.4, it clear that Hg and Cd

extremely have low concentrations at the entire sampling points (auto workshops) across all the auto-locations. This is followed by Co, especially at auto workshop TP.

Table 4.6: Comparison of this work to the Dutch lists of metal contamination (mg/kg) in soil

Element		As	Cd	Cr	Pb	Ni	Co	Hg	Cu	Zn
Dutch List	OPtimum Level	29	0.8	100	85	35	9	0.3	36	140
	Action Level	55	12	380	530	210	240	10	190	720
This Work	BBW	4.98	0.95	361.10	124.71	125.90	4.13	0.06	148.60	198.31
	BBS	4.22	0.51	286.88	322.60	80.10	0.70	0.35	190.50	149.70
	BBE	3.58	0.33	258.40	1172.70	63.80	0.91	0.27	249.11	111.10
	BBM	4.28	0.42	282.40	129.80	84.00	1.28	0.31	248.80	157.10
	MIW	7.54	0.04	393.00	585.61	123.31	2.37	0.15	127.91	188.10
	MIS	5.76	0.26	228.38	299.90	129.90	0.86	0.54	141.30	119.70
	MIE	4.95	0.23	223.10	2404.50	61.30	0.86	0.52	442.40	113.60
	MIM	5.97	0.23	218.16	693.04	130.80	1.03	0.57	329.31	131.71
	MPW	3.20	0.19	258.81	200.63	25.81	1.34	0.06	126.45	162.04
	MPS	3.01	<IDL	475.88	202.70	59.60	1.50	1.01	201.10	154.50
	MPE	2.89	0.06	415.10	1341.80	53.10	1.21	0.44	551.90	129.10
	MPM	2.97	0.06	287.60	246.11	58.11	1.28	0.36	222.00	150.40
	TPW	3.91	0.17	67.11	52.10	5.88	0.52	0.18	237.40	119.80
	TPS	3.46	0.16	660.00	102.90	118.10	0.63	0.75	72.20	102.30
	TPE	3.37	0.08	400.10	1064.93	106.70	0.42	0.59	459.20	60.40
	TPM	3.42	0.14	633.80	79.20	113.10	0.46	0.67	155.99	114.40

Cited from: (Comfort et al., 2013, en.m.wikipedia.org/wiki/Dutch_standards)

The mean concentrations of the elements obtained from the soil samples within the workshops were compared with the New Dutch (ND) list values. The ND list is a guideline regarding the tolerable contamination of soil and is based on a publication of intervention values and target values of soil quality standards issued by the Netherlands Ministry of Housing, Spatial Planning and Environment (en.m.wikipedia.org/wiki/Dutch_standards, Comfort et al., 2013,). Table 4.6 gives the mean concentrations of the metal elements As, Cd, Cr, Pb, Ni, Co, Hg, Cu and Zn in the work compared to the New Dutch list.

It can be seen from Table 4.6 that the elements; As, Co and Cd had their concentrations below the optimum level. With the exception of Cadmium (Cd) (0.95 mg/kg) at BBW, all the other locations are below the optimum level. This could be attributed to electroplating at the auto shop. The other locations are below the optimum level. Hg, Ni and Zn at all the auto-workshops are below the action level. Cu is also seen to be above the optimum levels at all the auto workshops. Cu is extremely higher than the action levels at BBE, MIE, MPE and TPE. This could be due to Cu wires and other components made from copper. Chromium (Cr) at TPW is observed to be below the optimum level, the rest are above this level. Cr is above action levels at MPS (475.88), MPE (415.10), MIW (393.00), TPS (660.00), TPE (400.10) and TPM (633.80). This is quite expected at MPS, MIW, TPS and TPM. Lead (Pb) recorded higher concentration values at BBE (1172.72), MIE (2404.50), MPE (1341.80) and TPE (1064.93). It also recorded values below the optimum level at TPW and TPM.

Per the ND standard, precautions are needed at the various locations where the elemental concentrations are above the action levels. Notwithstanding the fact that the concentrations of some of the elements are below the optimum levels, measures are needed to ensure that those auto shops do not elevate to the action levels, since at these optimum levels, the elements are potentially toxic.

4.4. INDEX OF GEOACCUMULATION (Igeo)

It was used as a reference to estimating the extent of elemental pollution. Tables 4.7 – 4.8 shows the calculated indices of geoaccumulation for the elements at the various locations.

Table 4.7: Indices of geoaccumulation of the elements for auto-workshops BB and MI

Elements	BB				MI			
	W	M	S	E	W	M	S	E
As	0.88	0.66	0.64	0.41	1.48	1.14	1.69	0.87
Cd	1.66	0.49	0.77	0.14	-1.00	-0.38	-0.21	-0.38
Co	-3.18	-4.87	-5.10	-5.36	-3.98	-5.19	-5.45	-5.45
Cr	1.27	0.91	0.94	0.78	1.39	0.54	0.61	0.64
Cu	0.85	1.59	1.21	1.83	0.63	1.99	0.78	2.42
Fe	-1.73	-1.71	-1.82	-1.86	-1.74	-1.76	-1.93	-1.86
Hg	-1.00	1.54	1.54	1.17	0.32	2.25	2.17	2.12
Mn	-0.86	-1.90	-1.99	-2.42	-0.88	-2.08	-2.45	-2.47
Ni	0.16	-0.42	-0.51	-0.82	0.13	0.22	0.21	-0.88
Pb	2.73	2.79	4.10	5.97	4.96	5.21	4.00	7.00
Zn	0.92	0.58	0.51	0.08	0.84	0.33	0.19	0.11

The Igeo values for the elements at the BB and MI auto workshops for the various sections showed no pollution for most of the elements (Table 4.7). However, the Igeo values of Hg ranged from – 1 to 1.54 at auto-workshop BB and 0.32 to 2.25 at auto-workshop MI. This indicates no pollution to moderate pollution and no pollution to high pollution, respectively for BB and MI. Co, Fe, Mn, Zn Ni and As showed generally no pollution at auto-workshop BB. The high value of Igeo of Cr is associated with the auto-welding location and that of Pb and Cu are associated with the auto-electrical location respectively are expected. The degree of pollution or contamination of these elements follows the order of Pb > Cu > Cr > Cd. Similarly at auto workshop MI, the Igeo values of As and Cr ranged from 0.87 to 1.48 and 0.54 to 1.39, thus unpolluted to moderately polluted. Cu had Igeo values ranging from 0.63 to 2.42 indicating unpolluted to highly polluted. Pb ranged from 4.00 to 7.00 indicating a situation of very highly condition of pollution. Both Cu and Pb recorded their highest Igeo values at the auto-electrical location. It can be seen that, the degree of pollution or contamination of these elements at MI follows the order of Pb > Hg > As > Cu > Cr.

Table 4.8: Indices of geoaccumulation of the elements for auto-workshops MP and TP

Element	MP				TP			
	W	M	S	E	W	M	S	E
As	0.52	0.55	0.16	0.10	0.45	0.49	0.36	0.32
Cd	-0.19	-0.14	-	-2.32	-0.18	-0.17	-0.91	-
Co	0.22	0.23	-4.64	-4.95	0.32	0.34	-5.90	-6.48
Cr	-0.07	0.07	1.67	1.47	0.08	0.07	2.14	1.53
Cu	0.08	0.08	1.29	2.74	0.08	0.08	-0.19	2.48
Fe	0.03	0.03	-1.83	-1.88	0.03	0.03	-1.99	-2.04
Hg	0.12	-0.18	3.07	1.70	-0.15	-0.21	2.64	2.58
Mn	0.05	0.06	-2.03	-3.07	0.06	0.06	-3.62	-4.23
Ni	0.10	0.09	-0.92	-1.08	0.12	0.08	0.07	-0.08
Pb	0.09	0.09	3.43	6.16	0.11	0.11	2.46	5.83
Zn	0.08	0.08	0.56	0.30	0.08	0.08	-0.04	-0.80

The Igeo values for the elements at the MP and TP auto workshops for the various locations showed no pollution and moderately polluted for most of the elements (Table 4.8). Cu and Pb recorded high Igeo values at the auto-electrical location at both auto-workshops. However, the Igeo values of Co, Fe, As, Mn, Zn, Cd and Ni ranged from -4.95 to 0.23, -1.88 to 0.03, 0.10 to 0.55, -3.07 to 0.06, 0.08 to 0.56, -2.32 to -0.14 and -1.08 to 0.10, gives an overall indicating of no pollution at auto-workshop MP. The Igeo values of lead (Pb) ranges from 0.09 to 6.16, thus indicating no pollution to a very highly pollution condition at auto-workshop MP. For lead (Pb), pollution is very high at location MPE. Cu also recorded high pollution at the auto-electrical location. The degree of pollution or contamination of these elements follows the order of Pb > Cu > As > Zn.

Similarly at auto workshop TP, the Igeo values of As and Cr ranged from 0.32 to 0.49 and 0.07 to 2.14, thus indicating unpolluted to moderately polluted and unpolluted to highly polluted, respectively. Cd, Co, Fe, Zn, As and Ni showed no pollution through all the auto-locations. Hg and Cr associated with the auto-spraying location. Lead (Pb) and copper (Cu) had high Igeo values associated with the auto-electrical location. The degree of contamination of these elements at TP follows the order of Pb > Cr > As > Cu.

It is generally observed that lead (Pb) is highly polluted than the other elements in both auto-workshops.

4.5. CONTAMINATION FACTOR (Cf) AND POLLUTION LOAD INDEX (PLI)

The contamination factors (Cf) and pollution load indices (PLI) were calculated using equation (2.6) and (2.7) respectively and are shown in Tables 4.9 – 4.10. To determine the contamination factors, Taylor continental crustal averages (Taylor, 1964) were used as the baseline or background data and the concentrations of the elements in the work.

For proper assessment of the degree of contamination, the PLI was calculated. The PLI estimates the number of times the metal content in the soil exceeds the average natural background content and indicate the overall level of heavy metal toxicity in a particular sample. The PLI is used to estimate the metal contamination status and necessary action or measures that should be taken, according Angulo (1996). The severity along the sites

was determined with the use of PLI as the quickest way of comparatively looking at the pollution status at different places.

Table 4.9: Contamination factors (Cf) of the elements with corresponding Pollution Load Index (PLI) for auto-workshops BB and MI

Element	BB				MI			
	W	M	S	E	W	M	S	E
As	2.767	2.378	1.321	1.989	4.189	3.317	3.200	2.750
Cd	4.750	2.100	**10.500**	1.650	0.750	1.150	1.300	1.150
Co	0.165	0.051	0.002	0.036	0.095	0.041	0.034	0.034
Cr	**3.611**	2.824	0.028	2.584	**3.930**	2.186	2.284	2.331
Cu	2.702	4.524	0.082	**5.347**	2.326	5.987	2.569	**8.044**
Fe	0.454	0.460	**8.17E-06**	0.414	0.450	0.442	0.393	0.414
Hg	0.750	3.750	**46.875**	3.375	1.875	7.125	6.750	6.500
Mn	0.829	0.401	0.001	0.281	0.814	0.355	0.275	0.270
Ni	**1.679**	1.120	0.015	0.851	1.644	**1.744**	**1.732**	0.817
Pb	9.977	**10.384**	0.831	**93.816**	46.849	**55.443**	23.992	**192.360**
Zn	2.833	2.244	0.032	1.587	2.688	1.882	1.710	1.623
PLI	**2.774**	**2.749**	**5.426**	**10.175**	**5.964**	**7.243**	**3.997**	**19.663**

The results of the contamination factor show that most of the elements in the different locations at the different auto workshops recorded low contamination levels. Fe which is of crustal origin recorded extremely low contamination level in auto-spraying location at

BB (Table 4.9) which is expected. The elements Ni, Zn, As, Mn, and Co which are mostly of anthropogenic origin had levels from low contamination to considerable contamination for the greater part. Lead (Pb) level showed extremely very high contamination at BB and MI, especially, in the auto-electrical locations and that is expected. The high levels of Pb at the auto-mechanical locations could be due to waste oils that are released into the soil during automobile servicing. It is observed that mercury (Hg) at auto workshop BB (Table 4.9) had very high levels in auto-spraying location. Cr recorded high values of contamination factor at the auto-welding location for both auto-workshops. This could be due to electroplating been done at this location. The Ni values at auto-welding and auto-spraying locations at BB and MI respectively could be attributed to spent batteries and waste pigment (Udousoro et al., 2013). Ni which is also present in diesel could contribute to the high level at auto-mechanical location at BB.

The pollution load index (PLI), which gives the combined effect of all elements analysed, predicts higher PLI values (Figure 4.5 – 4.6) in the auto-electrical location at BB and MI. At auto-workshop BB (Figure 4.5), the auto-welding and auto-mechanical locations suggested strongly pollution levels.

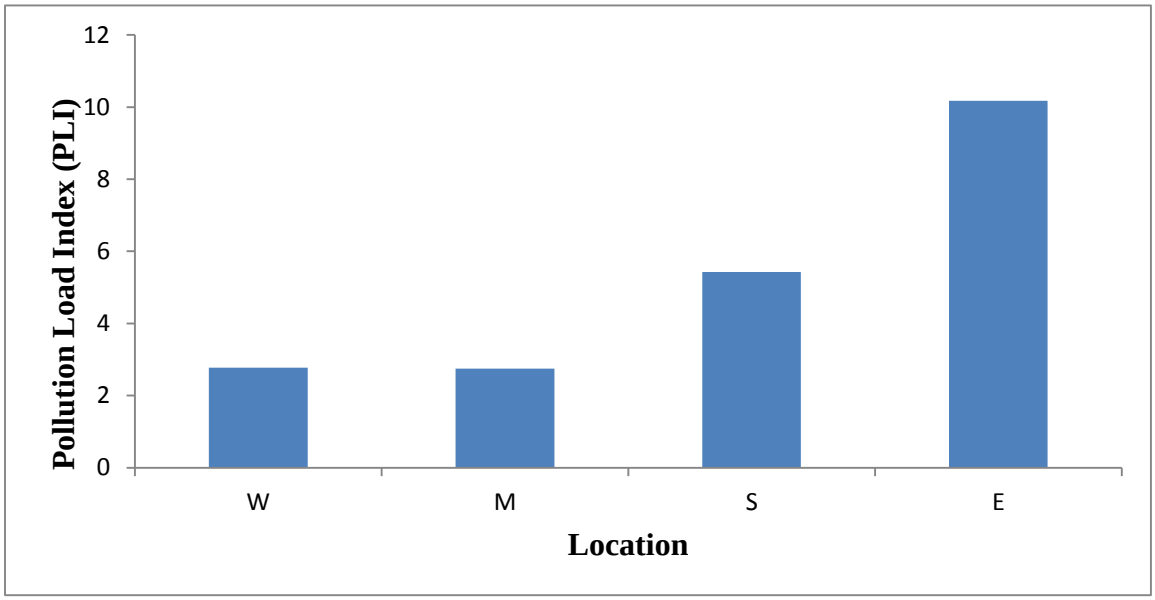

Figure 4.5: Pollution Load Index for auto-workshop BB

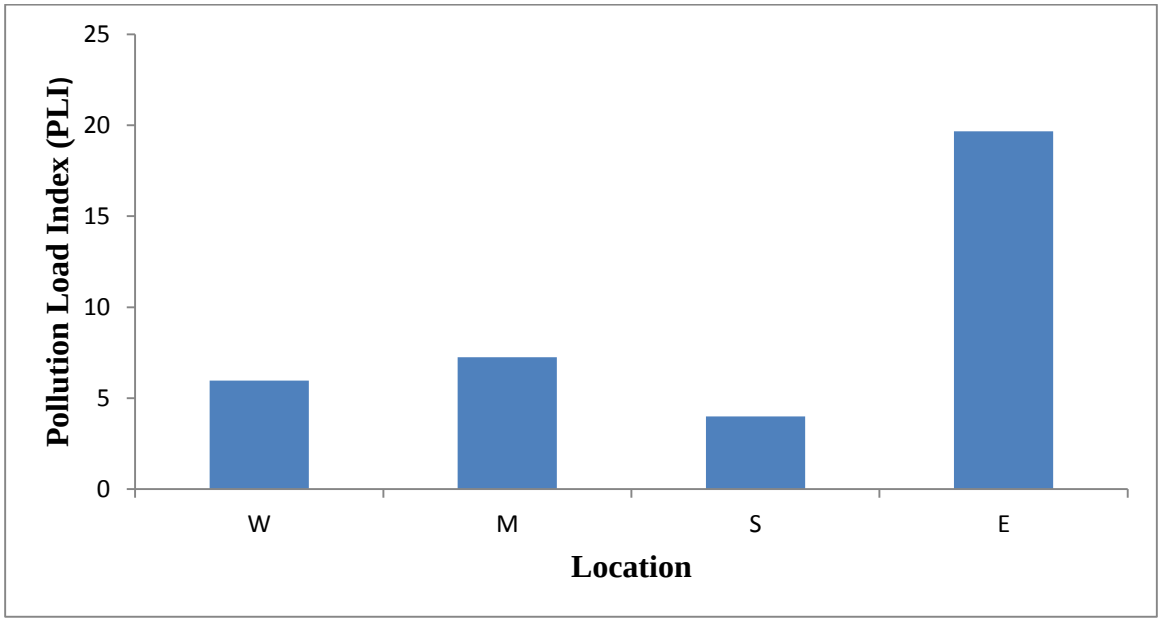

Figure 4.6: Pollution Load Index for auto-workshop MI

Table 4.10: Contamination factors (Cf) of the elements with corresponding Pollution Load Index (PLI) for auto-workshops MP and TP

Element	MP				TP			
	W	M	S	E	W	M	S	E
As	1.778	1.650	1.672	1.606	2.172	1.900	1.922	1.872
Cd	**0.950**	0.300	-	0.300	**0.800**	**0.700**	**0.800**	-
Co	0.054	0.051	0.060	0.048	0.021	0.018	0.025	0.017
Cr	2.588	2.876	4.759	4.151	0.671	**6.338**	6.600	4.320
Cu	2.299	**4.036**	3.656	**10.034**	4.316	2.836	1.312	**8.349**
Fe	0.441	0.462	0.423	0.408	0.386	0.414	0.378	0.365
Hg	0.750	4.500	12.625	4.875	2.250	8.375	9.375	9.000
Mn	0.602	0.369	0.366	0.178	0.131	0.177	0.122	0.080
Ni	0.344	0.775	**0.794**	0.708	0.078	1.508	**1.574**	1.423
Pb	16.050	19.688	16.216	**107.344**	4.168	6.336	8.232	**85.194**
Zn	**2.315**	2.149	2.207	1.844	1.711	**1.634**	1.461	0.863
PLI	**2.561**	**3.350**	**3.889**	**11.954**	**1.716**	**2.749**	**2.891**	**10.135**

The elements Cd, Fe, Mn and Co recorded contamination factors less than one. Moderate contamination was obtained for arsenic (As) at all the auto-location for both auto-workshops. Lead (Pb) obtained moderate contamination to very high levels for both workshops. Lead (Pb) at both auto-workshops MT and TP attained extreme pollution condition at the auto-locations. Pb and Cu recorded higher values at the auto-electrical locations for both auto-workshops. This could be attributed to spent batteries and wires

made from lead (Pb) and copper (Cu). Cr at auto workshop (MP) recorded moderate to considerable contaminations with values ranging from 2.588 to 4.759. Cr level at the auto- mechanical location at auto-workshop TP is expected since it forms automobile brake linings. Co recorded the least values of contamination factors across the auto workshops. Cd recorded low contamination levels at auto-workshops MP and TP. The high value of Ni at auto-spraying location at MP could be due to the disposal of various waste pigments (Udousoro et al., 2013).

The results of the pollution load index (PLI) predict moderately pollution to extremely pollution (Figure 4.7 – 4.8). The auto-electrical locations at both auto-workshops recorded high PLI values.

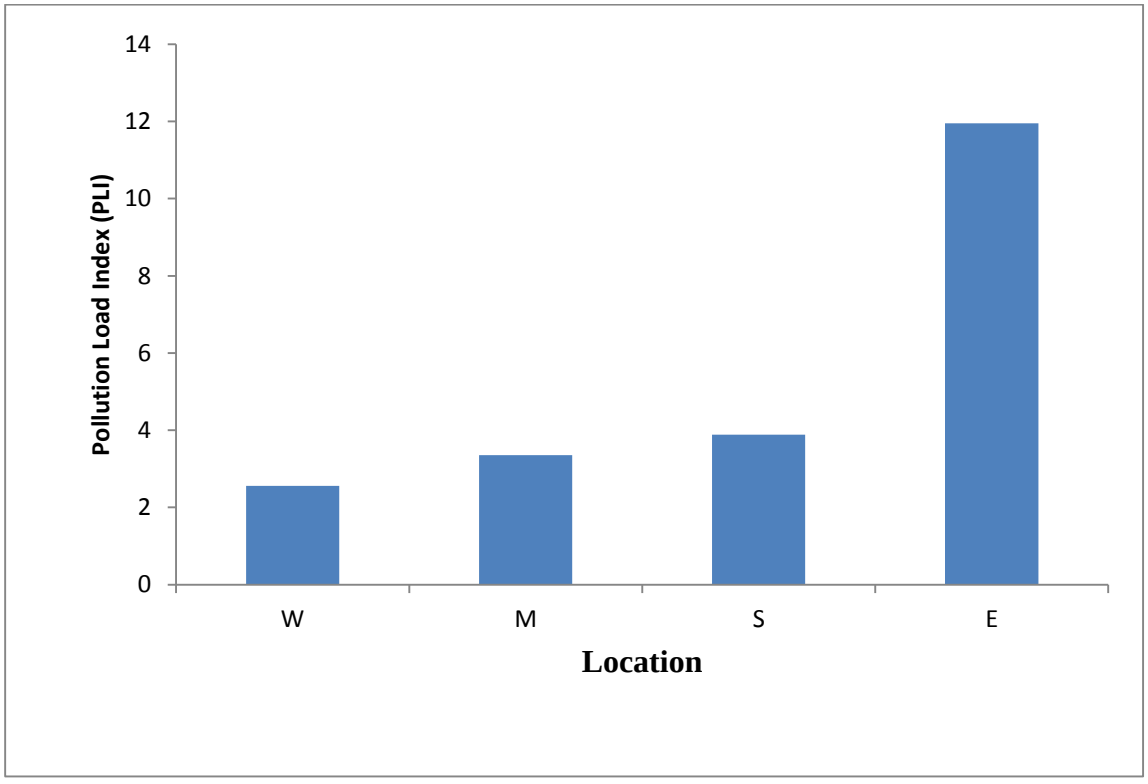

Figure 4.7: Pollution Load Index for auto-workshop MP

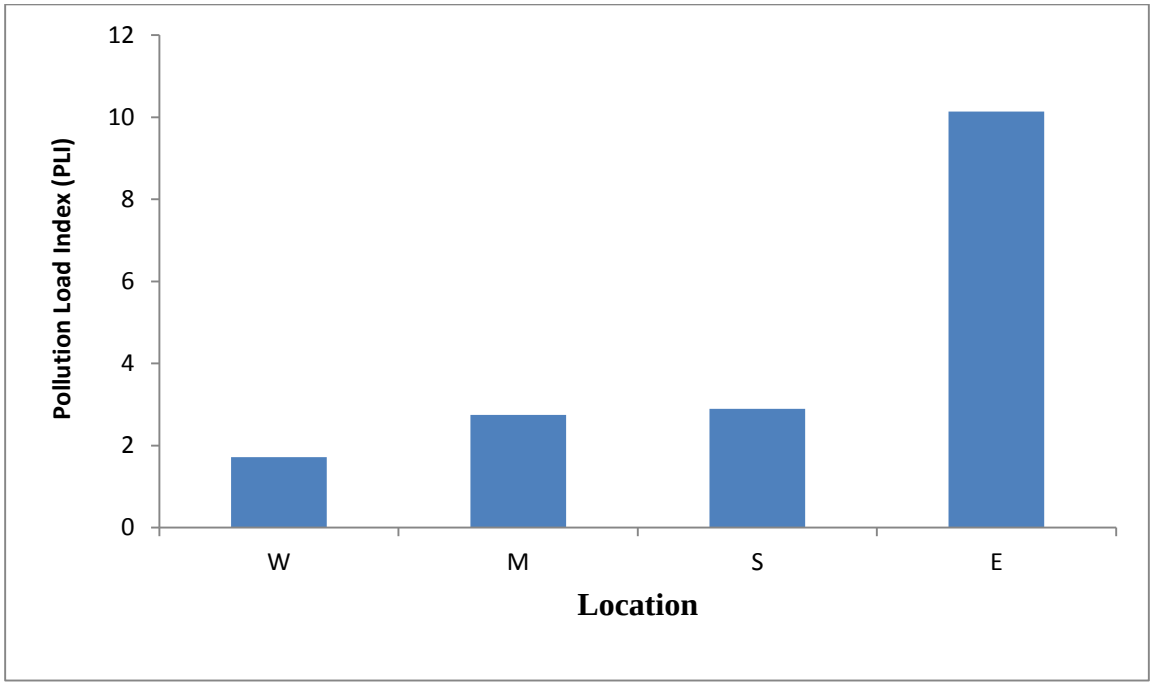

Fig. 4.8: Pollution Load Index for Auto workshop TP

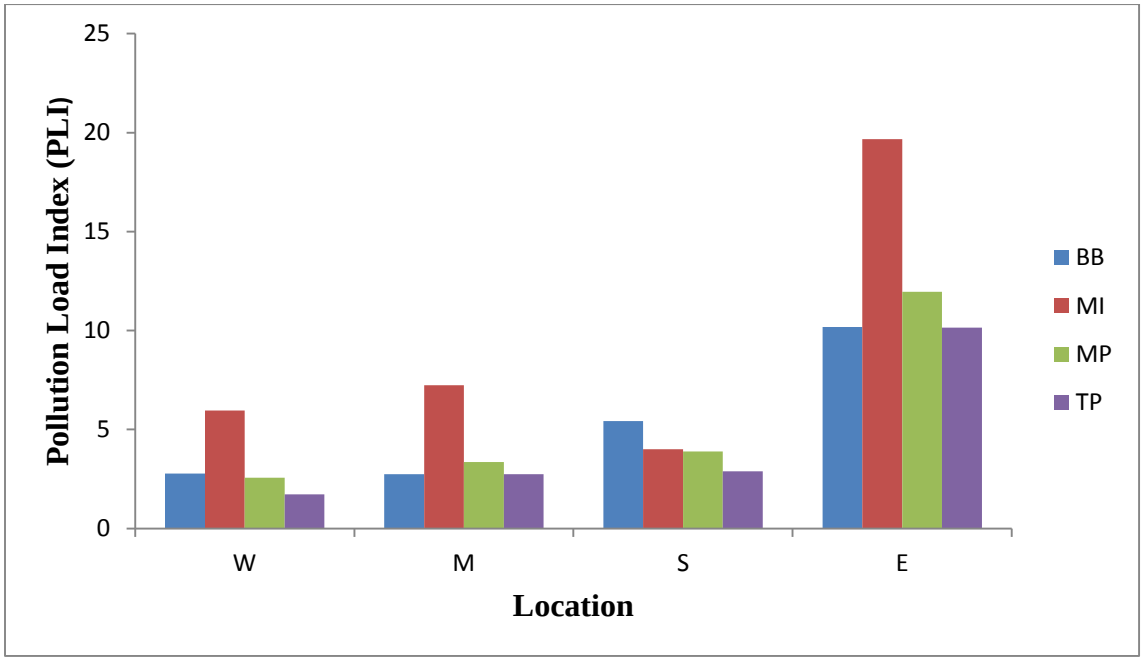

Figure 4.9: Comparison of the Pollution Load Indices at the various auto-workshops

Figure 4.9 shows the variations of the pollution load index (PLI) between the various locations at the various auto workshops. It is observed that, all the auto workshops generally have severe pollution at the auto-electrical locations. It is observed that, auto-workshop MI is generally more polluted than the other auto-workshops.

4.6. HUMAN HEALTH RISK ASSESSMENT (HHRA)

The exposure assessment calculations in Tables 4.11 – 4.15 were done based on the assumptions discussed in section 2.6 and guideline parameters in Table 2.5 to determine the human health risk with some selected elements identified in this work. These involve quantifying the estimated intake of the contaminant by humans for each exposure pathway identified. These elements become toxic if its concentration exceeds the tolerable upper intake level (UL). Some of these elements even at low concentrations can be very harmful (causing morphological abnormalities; reduce growth and increase mortality and mutagenic effects) when ingested over a long period of time (Uluozlu et al., 2008, David and Johanna, 2000, Abulude et al., 2007). The reference dose (RfD) for the selected elements for the individual exposure pathways are cited from Ferreira-Baptista and de Miguel (2005) and de Miguel et al., (2007) (Ying et al., 2014).

Table 4.11: Reference dose (RfD) for selected elements for the three exposure routes

Element/ Mg/kg-d	Pb	Zn	Ni	Mn	Cu
RfDing	3.50E-03	3.0E-01	2.0E-02	4.60E-02	4.00E-02
RfDinh	3.52E-03	3.0E-01	2.06E-02	1.84E-03	4.02E-02
RfDder	5.25E-05	6.0E-02	5.4E-03	1.43E-05	1.20E-02

Cited from: Ferreira-Baptista and de Miguel (2005) and de Miguel et al., (2007) (Ying et al., 2014).

Table 4.12: Human health risk assessment for the selected elements at auto-workshop BB

Element	Location	Age group	Dermal		Ingestion		Inhalation		HI =∑HQ
			Dder	HQder	Ding	HQing	Dinh	HQinh	
Pb	W	Child	2.3E-06	4.4E-02	8.2E-04	2.3E-01	2.4E-08	6.7E-06	2.8E-01
		Adult	3.5E-06	6.7E-02	8.8E-05	2.5E-02	1.3E-08	3.8E-06	9.2E-02
	M	Child	2.4E-06	4..6E-02	8.5E-04	2.4E-01	2.5E-08	7.0E-06	2.9E-01
		Adult	1.8E-06	3.4E-02	9.1E-05	2.6E-02	1.4E-08	3.9E-06	6.0E-02
	S	Child	5.9E-06	1.1E-01	2.1E-03	6.1E-01	6.1E-08	1.7E-05	7.2E-01
		Adult	9.1E-06	1.7E-01	2.3E-04	6.5E-02	3.4E-08	9.8E-06	2.4E-01
	E	Child	2.2E-05	4.1E-01	7.7E-03	2.2E+00	2.2E-07	6.3E-05	2.6E+00
		Adult	3.3E-05	6.3E-01	8.3E-04	2.4E-01	1.3E-07	3.6E-05	8.6E-01
Zn	W	Child	3.7E-06	6.1E-05	1.3E-03	4.3E-03	3.8E-08	1.3E-07	4.4E-03
		Adult	5.6E-06	9.3E-05	1.4E-04	4.7E-04	2.1E-08	7.1E-08	5.6E-04
	M	Child	2.9E-06	4.8E-05	1.0E-03	3.4E-03	3.0E-08	9.9E-08	3.5E-03
		Adult	4.4E-06	7.4E-05	1.1E-04	3.7E-04	1.7E-08	5.6E-08	4.4E-04
	S	Child	2.8E-06	4.6E-05	9.8E-04	3.3E-03	2.8E-08	9.5E-08	3.3E-03
		Adult	4.2E-06	7.0E-05	1.1E-04	3.5E-04	1.6E-08	5.3E-08	4.2E-04
	E	Child	2.0E-06	3.4E-05	7.3E-04	2.4E-03	2.1E-08	7.0E-08	2.5E-03
		Adult	3.1E-06	5.2E-05	7.8E-05	2.6E-04	1.2E-08	3.9E-08	3.1E-04
Ni	W	Child	2.3E-06	4.3E-02	8.3E-04	4.1E-02	2.4E-08	1.2E-06	8.4E-02
		Adult	3.5E-06	6.6E-02	8.9E-05	4.4E-03	1.3E-08	6.5E-07	7.0E-02
	M	Child	1.5E-06	2.9E-02	5.5E-04	2.8E-02	1.6E-08	7.7E-07	5.6E-02
		Adult	2.4E-06	4.4E-02	5.9E-05	2.9E-03	8.9E-09	4.4E-07	4.7E-02
	S	Child	1.5E-06	2.7E-02	2.6E-04	1.3E-02	1.5E-08	7.4E-07	4.0E-02
		Adult	2.6E-06	4.2E-02	5.6E-05	2.8E-03	8.6E-09	4.2E-07	4.5E-02
	E	Child	1.2E-06	2.2E-02	4.2E-04	2.1E-02	1.2E-08	5.9E-07	4.3E-02
		Adult	1.8E-06	3.3E-02	4.5E-05	2.2E-03	6.8E-09	3.3E-07	3.5E-02
Mn	W	Child	1.4E-05	1.0E+00	5.2E-03	1.3E-01	1.5E-07	8.1E-05	1.1E+00
		Adult	2.2E-06	1.6E-01	5.5E-04	1.2E-02	8.4E-08	4.6E-05	1.7E-01
	M	Child	7.0E-06	4.9E-01	2.5E-03	5.5E-02	7.2E-08	3.9E-05	5.5E-01
		Adult	1.1E-06	7.5E-02	2.7E-04	5.9E-03	4.1E-08	2.2E-05	8.1E-02
	S	Child	6.6E-06	4.6E-01	2.3E-03	5.1E-02	6.8E-08	3.7E-05	5.1E-01
		Adult	0.0E+00	0.0E+00	2.5E-04	5.5E-03	3.8E-08	2.1E-05	5.5E-03
	E	Child	4.9E-06	3.4E-01	1.8E-03	3.8E-02	5.1E-08	2.7E-05	3.8E-01
		Adult	7.5E-07	5.2E-02	1.9E-04	4.1E-03	2.8E-08	1.6E-05	5.7E-02
Cu	W	Child	2.7E-06	2.3E-04	9.8E-04	2.4E-02	2.8E-08	7.0E-07	2.5E-02
		Adult	4.2E-06	3.5E-04	1.0E-04	2.6E-03	1.6E-08	4.0E-07	2.9E-03
	M	Child	4.6E-06	3.8E-04	1.6E-03	4.1E-02	4.7E-08	1.2E-06	4.1E-02
		Adult	6.9E-06	5.8E-04	3.5E-04	8.8E-03	2.7E-08	6.6E-07	9.4E-03
	S	Child	3.5E-06	2.9E-04	1.3E-03	3.1E-02	3.6E-08	8.9E-07	3.2E-02
		Adult	5.4E-06	4.5E-04	1.3E-04	3.4E-03	2.0E-08	5.1E-07	3.8E-03
	E	Child	5.4E-06	4.5E-04	1.9E-03	4.8E-02	5.6E-08	1.4E-06	4.9E-02
		Adult	8.3E-06	6.9E-04	2.1E-04	5.2E-03	3.1E-08	7.8E-07	5.9E-03

Table 4.13: Human health risk assessment for the selected elements at auto- workshop MI

Element	Location	Age group	Dermal		Ingestion		Inhalation		HI =∑HQ
			Dder	HQder	Ding	HQing	Dinh	HQinh	
Pb	W	Child	1.1E-05	2.1E-01	3.9E-03	1.1E+00	1.1E-07	3.2E-05	1.3E+00
		Adult	1.6E-05	3.1E-01	4.1E-04	1.2E-01	6.3E-08	1.8E-05	4.3E-01
	M	Child	1.3E-05	2.4E-01	4.6E-03	1.3E+00	1.3E-07	3.7E-05	1.6E+00
		Adult	1.9E-05	3.7E-01	4.9E-04	1.4E-01	7.4E-08	2.1E-05	5.1E-01
	S	Child	5.5E-06	1.1E-01	2.0E-03	5.6E-01	5.7E-08	1.6E-05	6.7E-01
		Adult	8.4E-06	1.6E-01	2.1E-04	6.0E-02	3.2E-08	9.1E-06	2.2E-01
	E	Child	4.4E-05	8.4E-01	1.6E-02	4.5E+00	4.6E-07	1.3E-04	5.4E+00
		Adult	6.8E-05	1.3E+00	1.7E-03	4.8E-01	2.6E-07	7.3E-05	1.8E+00
Zn	W	Child	3.5E-06	5.8E-05	1.2E-03	4.1E-03	3.6E-08	1.2E-07	4.2E-03
		Adult	5.3E-06	8.8E-05	1.3E-04	4.4E-04	2.0E-08	6.7E-08	5.3E-04
	M	Child	2.4E-06	4.0E-05	4.3E-04	1.4E-03	2.5E-08	8.3E-08	1.5E-03
		Adult	3.7E-06	6.2E-05	9.3E-05	3.1E-04	1.4E-08	4.7E-08	3.7E-04
	S	Child	2.2E-06	3.7E-05	7.9E-04	2.6E-03	2.3E-08	7.6E-08	2.7E-03
		Adult	3.3E-06	5.6E-05	8.4E-05	2.8E-04	1.3E-08	4.3E-08	3.4E-04
	E	Child	2.1E-06	3.5E-05	7.5E-04	2.4E-03	2.2E-08	7.2E-08	2.5E-03
		Adult	3.2E-06	5.3E-05	8.0E-05	2.7E-04	1.2E-08	4.0E-08	3.2E-04
Ni	W	Child	2.3E-06	4.2E-02	8.1E-04	4.1E-02	2.3E-08	1.1E-06	8.3E-02
		Adult	3.5E-06	6.4E-02	8.7E-05	4.3E-03	1.3E-08	6.4E-07	6.9E-02
	M	Child	2.4E-06	4.5E-02	8.6E-04	4.3E-02	2.5E-08	1.2E-06	8.8E-02
		Adult	3.7E-06	6.8E-02	9.2E-04	4.6E-03	1.4E-08	6.8E-07	7.3E-02
	S	Child	2.4E-06	4.4E-02	8.5E-04	4.3E-02	2.5E-08	1.2E-06	8.7E-02
		Adult	3.7E-06	6.8E-02	9.2E-05	4.6E-03	1.4E-08	6.7E-07	7.2E-02
	E	Child	1.1E-06	2.1E-02	4.0E-04	2.0E-02	1.2E-08	5.6E-07	4.1E-02
		Adult	1.7E-06	3.2E-02	4.3E-05	2.2E-03	6.5E-09	3.2E-07	3.4E-02
Mn	W	Child	1.4E-05	9.9E-01	5.1E-03	1.1E-01	1.5E-07	8.0E-05	1.1E+00
		Adult	2.2E-06	1.5E-01	5.4E-04	1.2E-02	8.3E-08	4.5E-05	1.6E-01
	M	Child	6.2E-06	4.3E-01	2.2E-03	4.8E-02	6.4E-08	3.5E-05	4.8E-01
		Adult	9.5E-07	6.6E-02	2.4E-04	5.2E-03	3.6E-08	2.0E-05	7.1E-02
	S	Child	4.8E-06	3.4E-01	1.7E-03	3.7E-02	4.9E-08	2.7E-05	3.7E-01
		Adult	7.4E-07	5.1E-02	1.8E-04	4.0E-03	2.8E-08	1.5E-06	5.5E-02
	E	Child	4.7E-06	3.3E-01	1.7E-03	3.7E-02	4.9E-08	2.6E-05	3.7E-01
		Adult	7.2E-06	5.1E-01	1.8E-04	3.9E-03	2.7E-08	1.5E-05	3.0E-01
Cu	W	Child	2.4E-06	2.0E-04	8.4E-04	2.1E-02	2.4E-08	6.0E-07	2.1E-02
		Adult	3.6E-06	3.0E-04	9.0E-05	2.3E-03	1.4E-08	3.4E-07	2.6E-03
	M	Child	6.1E-06	5.1E-04	2.2E-03	5.4E-02	6.2E-08	1.6E-06	5.5E-02
		Adult	9.3E-06	7.7E-04	2.3E-04	5.8E-03	3.5E-08	8.7E-07	6.6E-03
	S	Child	2.6E-06	2.2E-04	9.3E-04	2.3E-02	2.8E-08	6.7E-07	2.3E-02
		Adult	3.9E-06	3.3E-04	9.9E-05	2.5E-03	1.5E-08	3.8E-07	2.8E-03
	E	Child	8.1E-06	6.8E-04	2.9E-03	7.3E-02	8.4E-08	2.1E-06	7.3E-02
		Adult	1.2E-05	1.0E-04	3.1E-04	7.8E-03	4.7E-08	1.2E-06	8.8E-03

Table 4.14: Human health risk assessment for the selected elements at auto-workshop MP

Element	Location	Age group	Dermal		Ingestion		Inhalation		HI =∑HQ
			Dder	HQder	Ding	HQing	Dinh	HQinh	
Pb	W	Child	3.7E-06	7.0E-02	1.3E-03	3.8E-01	3.8E-08	1.1E-05	4.5E-01
		Adult	5.6E-06	1.1E-01	1.4E-04	4.0E-02	2.1E-08	6.1E-06	1.5E-01
	M	Child	4.5E-06	8.6E-02	1.6E-03	4.6E-01	4.7E-08	1.3E-05	5.5E-01
		Adult	6.9E-06	1.3E-01	1.7E-04	5.0E-02	2.6E-08	7.5E-06	1.8E-01
	S	Child	3.7E-06	7.1E-02	1.3E-03	3.8E-01	3.8E-08	1.1E-05	4.5E-01
		Adult	5.7E-06	1.1E-01	1.4E-04	4.1E-02	2.2E-08	6.2E-06	1.5E-01
	E	Child	2.5E-05	4.7E-01	8.8E-03	2.5E+00	2.5E-07	7.2E-05	2.9E+00
		Adult	3.8E-05	7.2E-01	9.5E-04	2.7E-01	1.4E-07	4.1E-05	9.9E-01
Zn	W	Child	3.0E-06	4.9E-05	1.1E-03	3.6E-03	3.1E-08	1.0E-07	3.6E-03
		Adult	4.6E-06	7.6E-05	1.1E-04	3.8E-04	1.7E-08	5.8E-08	4.6E-04
	M	Child	2.8E-06	4.6E-05	9.9E-04	3.3E-03	2.8E-08	9.5E-08	3.3E-03
		Adult	4.3E-06	7.1E-05	1.1E-04	3.5E-04	1.6E-08	5.4E-08	4.2E-04
	S	Child	2.8E-06	4.7E-05	1.0E-03	3.4E-03	2.9E-08	9.8E-08	3.4E-03
		Adult	2.4E-06	7.2E-05	1.1E-04	3.6E-04	1.6E-08	5.5E-08	4.4E-04
	E	Child	2.4E-06	3.9E-05	8.5E-04	2.8E-03	2.4E-08	8.2E-08	2.9E-03
		Adult	3.6E-06	6.1E-05	9.1E-05	3.0E-04	1.4E-08	4.6E-08	3.6E-04
Ni	W	Child	4.8E-07	8.8E-05	1.7E-04	8.4E-03	4.9E-09	2.4E-07	8.6E-03
		Adult	7.3E-07	1.3E-04	1.8E-05	9.1E-04	2.8E-09	1.3E-07	1.0E-03
	M	Child	1.1E-06	1.9E-04	3.8E-04	1.9E-02	1.1E-08	5.3E-07	1.9E-02
		Adult	1.6E-06	3.0E-04	4.1E-05	2.1E-03	2.2E-07	1.1E-05	2.3E-03
	S	Child	1.1E-06	2.0E-04	3.9E-04	1.9E-02	1.1E-08	5.5E-07	2.0E-02
		Adult	1.7E-06	3.1E-04	4.2E-05	2.1E-03	6.4E-09	3.1E-07	2.1E-03
	E	Child	9.8E-07	1.8E-04	3.5E-04	1.8E-02	1.0E-07	4.9E-07	1.8E-02
		Adult	1.5E-06	2.8E-04	3.7E-05	1.9E-03	5.7E-09	2.8E-07	2.1E-03
Mn	W	Child	1.1E-05	7.4E-01	3.8E-03	8.2E-02	1.1E-07	5.9E-05	8.2E-01
		Adult	1.6E-06	1.1E-01	4.0E-04	8.8E-03	6.1E-08	3.3E-05	1.2E-01
	M	Child	6.5E-06	4.5E-01	2.3E-03	5.0E-02	6.6E-08	3.6E-05	5.0E-01
		Adult	9.9E-07	6.9E-02	2.5E-04	5.4E-03	3.7E-08	2.0E-05	7.4E-02
	S	Child	6.4E-06	4.5E-01	2.3E-03	4.9E-02	6.6E-08	3.6E-05	4.9E-01
		Adult	9.8E-07	6.8E-02	2.4E-04	5.3E-03	3.7E-08	2.0E-05	7.4E-02
	E	Child	3.1E-06	2.2E-01	1.1E-03	2.4E-02	3.2E-08	1.7E-05	2.4E-01
		Adult	4.8E-07	3.3E-02	1.2E-04	2.6E-03	1.8E-08	9.8E-06	3.6E-02
Cu	W	Child	2.3E-06	1.9E-04	8.3E-04	2.1E-02	2.4E-08	6.0E-07	2.1E-02
		Adult	3.6E-06	2.9E-04	8.9E-05	2.2E-03	1.4E-08	3.4E-07	2.5E-03
	M	Child	4.1E-06	3.4E-04	1.5E-03	3.7E-02	4.2E-08	1.1E-06	3.7E-02
		Adult	6.2E-06	5.2E-04	1.6E-04	3.9E-03	2.4E-08	5.9E-07	4.4E-03
	S	Child	3.7E-06	3.1E-04	1.3E-03	3.3E-03	3.8E-08	9.5E-07	3.3E-02
		Adult	5.7E-06	4.7E-04	1.4E-04	3.5E-03	2.1E-08	5.3E-07	4.0E-03
	E	Child	1.0E-05	8.5E-04	3.6E-03	9.1E-02	1.0E-07	2.6E-06	9.2E-02
		Adult	1.6E-05	1.3E-03	3.9E-04	9.7E-03	5.9E-08	1.5E-06	4.9E-02

Table 4.15: Human health risk assessment for the selected elements at auto-workshop TP

Element	Location	Age group	Dermal		Ingestion		Inhalation		HI =∑HQ
			Dder	HQder	Ding	HQing	Dinh	HQinh	
Pb	W	Child	9.6E-07	1.8E-02	3.4E-04	9.8E-02	9.9E-09	2.8E-06	1.2E-01
		Adult	1.5E-06	2.8E-02	3.7E-05	1.1E-02	5.6E-09	1.6E-06	3.8E-02
	M	Child	1.5E-06	2.8E-02	5.2E-04	1.5E-01	1.5E-08	4.2E-06	1.8E-01
		Adult	2.2E-06	4.2E-02	5.6E-05	1.6E-02	8.5E-09	2.4E-06	5.8E-02
	S	Child	1.9E-06	3.6E-02	6.8E-04	1.9E-01	1.9E-08	5.5E-06	2.3E-01
		Adult	2.9E-06	5.5E-02	7.3E-05	2.1E-02	1.1E-08	3.1E-06	7.6E-02
	E	Child	1.9E-05	3.7E-01	7.0E-03	2.0E+00	2.0E-07	5.7E-05	2.4E+00
		Adult	2.9E-05	5.7E-01	7.5E-04	2.1E-01	1.1E-07	3.2E-05	7.8E-01
Zn	W	Child	2.2E-06	3.7E-05	7.9E-04	2.6E-04	2.3E-08	7.6E-08	2.7E-03
		Adult	3.4E-06	5.6E-05	8.4E-05	2.8E-05	1.3E-08	4.3E-08	3.4E-04
	M	Child	2.1E-06	3.5E-05	7.5E-04	2.5E-04	2.2E-08	7.2E-08	2.5E-03
		Adult	3.2E-06	5.4E-05	8.1E-05	2.7E-05	1.2E-08	4.1E-08	3.2E-04
	S	Child	1.9E-06	3.1E-05	6.7E-04	2.2E-04	1.9E-08	6.5E-08	2.3E-03
		Adult	2.9E-06	4.8E-05	7.2E-05	2.4E-05	1.1E-08	3.6E-08	2.9E-04
	E	Child	1.3E-06	2.2E-05	4.7E-04	1.3E-04	1.3E-08	4.4E-08	1.6E-03
		Adult	1.9E-06	3.3E-05	4.9E-05	1.4E-05	7.5E-09	2.5E-08	2.0E-04
Ni	W	Child	1.1E-07	1.9E-05	3.8E-05	1.9E-03	1.1E-09	5.3E-08	1.9E-03
		Adult	1.6E-07	3.0E-05	4.1E-06	2.0E-04	6.2E-10	3.0E-08	2.3E-04
	M	Child	2.1E-06	3.9E-04	7.4E-04	3.7E-02	2.1E-08	1.0E-06	3.8E-02
		Adult	3.2E-06	5.9E-04	7.9E-05	3.9E-03	1.2E-08	5.9E-07	4.6E-03
	S	Child	2.2E-06	4.0E-04	7.8E-04	3.9E-02	2.2E-08	1.1E-06	3.9E-02
		Adult	3.3E-06	6.2E-04	8.3E-05	4.2E-03	1.3E-08	6.1E-07	4.8E-03
	E	Child	2.2E-06	3.6E-04	7.0E-04	3.5E-02	2.2E-08	9.8E-07	3.5E-02
		Adult	2.9E-06	5.6E-04	7.5E-04	3.8E-05	1.1E-08	5.5E-07	4.3E-03
Mn	W	Child	2.3E-06	1.6E-01	8.2E-04	1.8E-02	2.4E-08	1.3E-05	1.8E-01
		Adult	3.5E-07	2.5E-02	8.8E-05	1.9E-03	1.3E-08	7.2E-06	2.6E-02
	M	Child	3.1E-06	00E+00	1.1E-03	2.4E-02	3.2E-08	1.7E-05	2.4E-02
		Adult	4.7E-07	3.3E-02	1.1E-04	2.6E-03	1.8E-08	9.7E-06	2.0E-02
	S	Child	2.1E-06	1.5E-01	7.6E-04	1.7E-02	2.2E-08	1.2E-05	1.7E-01
		Adult	3.2E-07	2.3E-02	8.1E-05	1.8E-03	1.2E-08	6.7E-06	2.4E-02
	E	Child	1.4E-06	9.8E-02	5.0E-04	1.1E-02	1.4E-08	7.8E-06	1.1E-01
		Adult	2.1E-07	1.5E+02	5.3E-05	1.2E-03	8.1E-09	4.4E-06	1.6E-02
Cu	W	Child	4.4E-06	3.6E-04	1.6E-03	3.9E-02	4.5E-08	1.1E-06	3.9E-02
		Adult	6.7E-06	5.6E-04	1.7E-04	4.2E-03	2.5E-08	6.3E-07	4.7E-03
	M	Child	2.9E-06	2.4E-04	1.0E-03	2.6E-02	3.0E-08	7.3E-07	2.6E-02
		Adult	4.4E-06	3.7E-04	1.1E-04	2.8E-03	1.7E-08	4.1E-07	3.1E-03
	S	Child	1.3E-06	1.1E-04	4.7E-04	1.2E-02	1.4E-08	3.4E-07	1.2E-02
		Adult	2.0E-06	1.7E-04	5.1E-05	1.3E-03	7.7E-09	1.9E-07	1.4E-03
	E	Child	8.5E-06	7.1E-04	3.0E-03	7.6E-02	8.7E-08	2.2E-06	7.6E-02
		Adult	1.3E-06	1.1E-04	3.2E-04	8.1E-03	4.9E-08	1.2E-06	9.2E-03

Non-carcinogenic effects for the selected elements were estimated for both children and adults through the exposure routes: dermal, ingestion and inhalation. The results showed that, the Health Index (HI) values of the selected heavy metals, in all the sections of the auto-workshops were mostly less one (1). Lead (Pb) is the only element that recorded HI values greater than one (1), which occurred mostly at the auto-electrical locations and mostly for children. At the auto-electrical locations, Pb recorded 2.6E+00, 2.9E+00, 2.4E+00, 5.4E+00, 1.8E+00 at auto-workshop BB, MP, TP and MI respectively and 1.3E+00, 1.6E+00 for MI at the auto-welding location. Manganese also recorded 1.1E+00 at the auto-welding location for auto-workshop BB and MI (Table 4.14 – 4.15). These values are above the acceptable value HI=1 (safe level for non-cancerous effect). Pb is cumulative poison and neurotoxic hence prolong exposure can trigger neurological and developmental disorders in children (Atiemo et al., 2010). The high values of HI, indicates high risk of non-cancerous effect at these locations.

The other locations generally recorded the least health indexes than one (1), indicating little or no adverse health risk. However due to heavy metals accumulation in the body, long time exposure can have possibly adverse health effect. It is also observed that the exposure route with the least risk of non-cancerous was inhalation (HQinh), with ingestion (HQing) recording the highest route of exposure. It is observed that the children are exposed to higher risk than adults as their HI and HQinh values are consistently higher than that of the adult. This indicates that children are more vulnerable than adults.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSION

The work investigated the elemental contents of topsoils at some selected auto-workshops in Accra. The soil samples were collected from four auto-workshops and analysed. The elemental concentrations for eleven (11) elements: As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn of the soil samples were determined using atomic absorption spectrometry (ASS) technique. Cu, Mn, Cr, Zn, Pb, As and Ni showed substantial concentrations. The results of elemental concentrations were used to compute for pollution models: indices of geoaccumulation, contamination factors and pollution load index to determine the extent of heavy metal contamination in the surface soil samples. Human health risk assessment was done for the following elements: Pb, Zn, Ni, Mn and Cu to determine the risk effects of exposure to the soils. Generally, As, Cr, Cu, Mn, Ni, Pb and Zn elements at the various locations at the workshops recorded concentrations values greater than that of the general environment within the close vicinity, indicating anthropogenic contributions of the elements to surface soil.

The extent of contamination at the auto-workshops for the various locations for most of the elements ranges from unpolluted to considerable polluted. Lead (Pb), was the greatest contaminant and mostly found to be very high at the auto-electrical locations in all the

auto-workshops. Hg, Zn and Ni showed considerate contaminations throughout the auto-locations. Pb recorded highest value of Cf (9.382) and Cf (19.236) at BB and MI respectively. Hg and Cd as well recorded 46.875 and 10.500, with the highest PLI (3.067) at the electrical location at MI.

The exposure pathway that resulted in the highest risk is ingestion, followed by dermal contact while inhalation is the least. The health index obtained for the selected elements at the auto-workshops showed that Pb and Mn gave higher values than the safe level (1) for children at some of the locations. Generally the auto-electrical location recorded HI values higher than the safe level value (1) mostly for lead (Pb) for both child and adults. Manganese (Mn) gave high value than the safe value (1) for children at the auto-welding location for auto-workshops BB and MI. This means that both adult and children exposed to these elements could be at risk. Generally, children could be more at risk than adults hence should avoid staying at the auto-workshops for longer periods.

5.2. RECOMMENDATIONS

It is evident that, the auto-workshops are gradually becoming polluted. This is as the result of the unprofessional approach to the auto-mechanic repairs and the indiscriminate disposal of wastes at these auto-workshops. Therefore, the activities of the auto-mechanics should be checked as they can significantly contribute to pollution in the environment leading to negative effect on the environment and human health.

More research works should be carried out in other automobile workshops so as to verify any variations in comparisons with the results obtained in this work. Where necessary, the Environmental Protection Agency (EPA) of Ghana should study more on automobile workshops to estimate the contamination levels of heavy metals and remedial actions necessary taken.

Government should consider establishing mechanic villages to be able to monitor activities at the automobile workshops. This is to enable easy monitoring of the contamination levels at the automobile workshops; which is due to the unprofessional approach to auto-mechanic repairs and the indiscriminate disposal of wastes at the workshops.

In order to minimize the exposure health risk at these auto-workshops, technicians should be more professional in the way they handle water and food items since this could be one of the ways they are exposed to these chemicals.

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APPENDICE

APPENDIX A

Table A1: Elemental Concentrations (mg/kg) at Auto-workshop BB

ELEMENT	BB											
	BBW			BBM			BBS			BBE		
	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN
As	4.98	5.04	4.95	4.28	4.32	4.25	4.22	4.49	3.99	3.58	3.75	3.39
Cd	0.95	1.77	0.15	0.42	0.56	0.24	0.51	0.62	0.29	0.33	0.54	0.15
Co	4.13	5.42	2.12	1.28	1.74	0.75	1.09	1.64	0.70	0.91	1.35	0.47
Cr	361.10	399.00	325.50	282.40	303.00	237.00	286.88	316.50	259.50	258.40	303.00	232.50
Cu	148.60	180.80	95.10	248.80	302.70	176.30	190.50	242.06	133.18	294.11	343.18	218.30
Fe	25545.80	25660.50	25480.51	25892.32	25951.50	25843.50	23896.88	23988.00	23728.50	23288.10	23950.50	22081.50
Hg	0.06	0.09	0.05	0.30	0.33	0.27	0.35	0.39	0.30	0.27	0.32	0.21
Mn	787.35	833.40	757.50	381.41	484.35	314.40	356.63	396.91	289.95	266.81	378.45	154.35
Ni	125.90	148.14	78.61	84.00	172.15	32.17	80.10	148.12	27.19	63.80	115.08	22.70
Pb	124.70	147.23	106.22	129.80	130.72	129.00	322.60	373.41	204.20	1172.70	2560.09	289.80
Zn	198.31	204.09	183.10	157.10	168.08	141.10	149.70	158.01	141.30	111.10	142.80	76.62

Cd (IDL): 0.002, IDL: < Instrument Detection Limit

Table A2: Elemental Concentration (mg/kg) at Auto-workshop MI

ELEMENT	MI											
	MIW			MIM			MIS			MIE		
	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN
As	7.54	8.33	5.33	5.97	6.03	5.94	5.76	5.85	5.66	4.95	5.59	4.52
Cd	0.15	0.15	< IDL	0.23	0.35	0.14	0.26	0.30	0.17	0.23	0.35	0.09
Co	2.37	3.09	1.49	1.03	1.41	0.69	0.86	1.44	0.15	0.86	1.13	0.42
Cr	393.01	441.00	351.00	218.60	270.00	153.00	228.38	283.50	165.00	223.11	282.00	180.00
Cu	127.91	191.70	104.11	329.30	497.33	124.80	141.30	215.32	50.44	442.41	524.11	295.06
Fe	25339.91	25531.50	25209.00	24897.82	25213.51	24420.00	22144.13	22630.50	21226.50	23303.31	23424.00	23043.00
Hg	0.15	0.17	0.12	0.57	0.60	0.54	0.54	0.62	0.49	0.52	0.72	0.38
Mn	773.18	853.65	712.65	336.90	498.15	234.75	261.60	310.95	163.35	256.84	371.70	190.50
Ni	123.30	204.08	71.90	130.80	246.01	31.51	129.90	259.05	33.30	61.30	147.09	31.70
Pb	585.60	1080.08	313.11	693.04	839.90	549.15	299.90	382.11	136.15	2404.50	2577.31	2230.02
Zn	188.10	238.11	164.41	131.71	155.03	95.04	119.70	145.08	80.41	113.60	131.19	88.21

Cd (IDL): 0.002, IDL: < Instrument Detection Limit

Table A3: Elemental Concentrations (mg/kg) at Auto-workshop MP

ELEMENT	MP											
	MPW			MPM			MPS			MPE		
	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN
As	3.20	3.24	3.15	2.97	3.00	2.96	3.01	3.12	2.87	2.89	3.24	2.58
Cd	0.19	0.27	0.08	0.06	0.06	< IDL	< IDL	< IDL	< IDL	0.06	0.06	< IDL
Co	1.34	1.94	0.99	1.28	1.53	0.87	1.50	1.76	1.20	1.21	1.52	0.93
Cr	258.80	376.50	204.00	287.60	406.50	219.00	475.88	1027.50	232.50	415.10	901.50	204.00
Cu	126.45	210.06	62.71	222.00	279.50	187.51	201.10	246.10	163.19	551.90	865.71	150.05
Fe	24845.30	25087.51	24487.50	25990.10	26242.50	25645.51	23820.01	23934.00	23743.50	22955.30	23173.50	22474.52
Hg	0.06	0.08	0.05	0.36	0.42	0.32	1.01	3.03	0.27	0.39	0.44	0.35
Mn	572.29	643.80	430.65	350.89	418.65	291.60	347.74	397.20	299.71	169.16	214.80	111.90
Ni	25.81	34.50	19.81	58.10	98.17	32.60	59.60	106.51	30.00	53.10	92.10	28.10
Pb	200.63	231.00	133.21	246.11	253.51	240.00	202.70	233.11	155.61	1341.80	2183.90	949.71
Zn	162.04	176.91	147.90	150.40	155.09	143.91	154.50	161.31	144.50	129.10	153.18	103.90

Cd (IDL): 0.002, IDL: < Instrument Detection Limit

Table A4: Elemental Concentrations (mg/kg) at Auto-workshop TP

ELEMENT	TP											
	TPW			TPM			TPS			TPE		
	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN
As	3.91	3.93	3.90	3.42	3.47	3.33	3.46	3.51	3.41	3.37	3.62	3.17
Cd	0.16	0.26	< IDL	0.14	0.18	< IDL	0.16	0.24	< IDL	0.08	0.17	0.05
Co	0.52	0.66	0.38	0.46	0.65	0.27	0.63	0.96	0.33	0.42	0.72	0.21
Cr	67.10	84.00	40.50	633.80	996.00	360.00	660.00	1051.50	432.00	400.10	783.00	154.50
Cu	237.40	295.51	178.50	155.90	257.91	90.50	72.20	86.10	47.71	459.20	612.12	307.70
Fe	21726.40	22395.00	20721.00	23289.80	23455.50	23023.50	21264.00	21978.01	19966.51	20523.40	21042.00	19506.00
Hg	0.18	0.20	0.17	0.67	0.69	0.66	0.75	0.81	0.72	0.59	0.62	0.54
Mn	124.46	152.25	74.40	167.93	178.80	161.10	115.58	149.55	61.35	75.75	88.05	53.85
Ni	5.80	8.62	3.20	113.10	157.71	60.91	118.10	166.18	62.70	106.70	146.31	60.50
Pb	52.10	61.17	34.80	79.20	82.50	72.01	102.94	156.50	44.41	1064.93	1391.70	868.21
Zn	119.80	177.01	87.51	114.40	151.11	99.90	102.30	117.21	60.42	70.20	80.40	52.41

Cd (IDL): 0.002, IDL: < Instrument Detection Limit

Table A5: Elemental Concentrations (mg/kg) at the Auto-workshops for the various control/reference locations

ELEMENT	CONTROL SECTION											
	BB			MI			MP			TP		
	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN	MEAN	MAX	MIN
As	2.93	3.06	2.82	1.66	1.70	1.62	1.85	1.98	1.62	1.83	1.92	1.88
Cd	0.18	0.35	< IDL	0.06	0.06	< IDL	< IDL	< IDL	< IDL	0.11	0.14	< IDL
Co	1.02	1.10	0.86	1.15	1.43	1.01	0.87	0.96	0.72	0.18	0.32	0.08
Cr	169.10	204.00	135.00	340.10	420.00	250.50	124.50	147.00	102.00	81.00	132.00	33.00
Cu	34.60	43.23	23.61	47.70	62.40	39.19	44.50	60.20	23.61	16.00	20.70	10.10
Fe	24442.9	24640.5	24064.5	25189.9	25509.0	24336.0	24493.9	24810.0	24267.0	22100.6	24091.5	20109.0
Hg	0.17	0.20	0.15	0.98	1.02	0.95	1.46	1.49	1.44	0.82	0.80	0.78
Mn	190.80	221.40	166.20	156.75	172.50	146.40	175.39	201.60	151.65	81.90	119.25	51.90
Ni	11.90	14.41	7.81	14.90	21.80	11.01	14.50	17.40	12.91	8.50	10.51	7.42
Pb	56.90	57.52	56.61	254.60	579.01	111.00	81.50	121.50	46.71	14.90	16.11	13.12
Zn	36.70	56.71	16.40	51.70	56.14	45.21	37.90	51.20	24.21	23.40	50.03	7.22

Cd (IDL): 0.002, IDL: < Instrument Detection Limit

APPENDIX B

Appendix B1

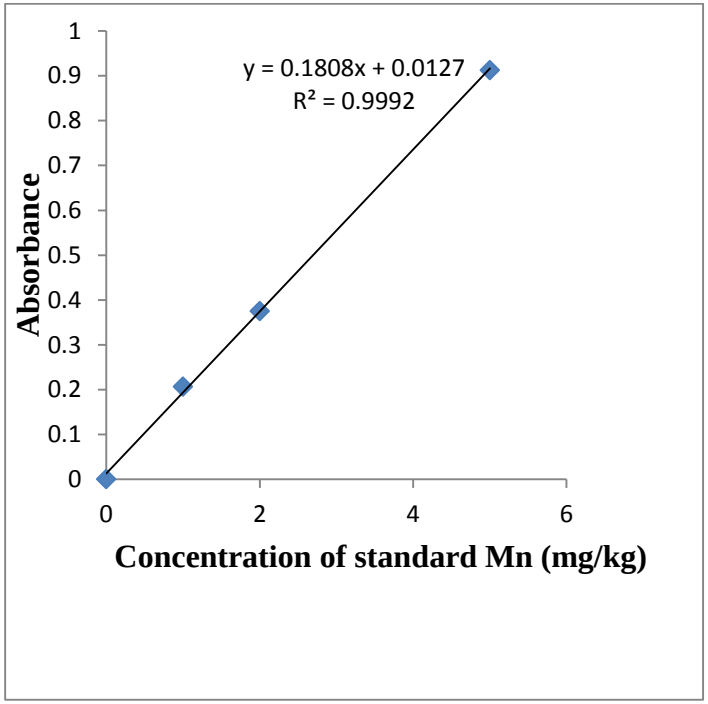

Figure A: Graph of absorbance against concentration

Appendix B2

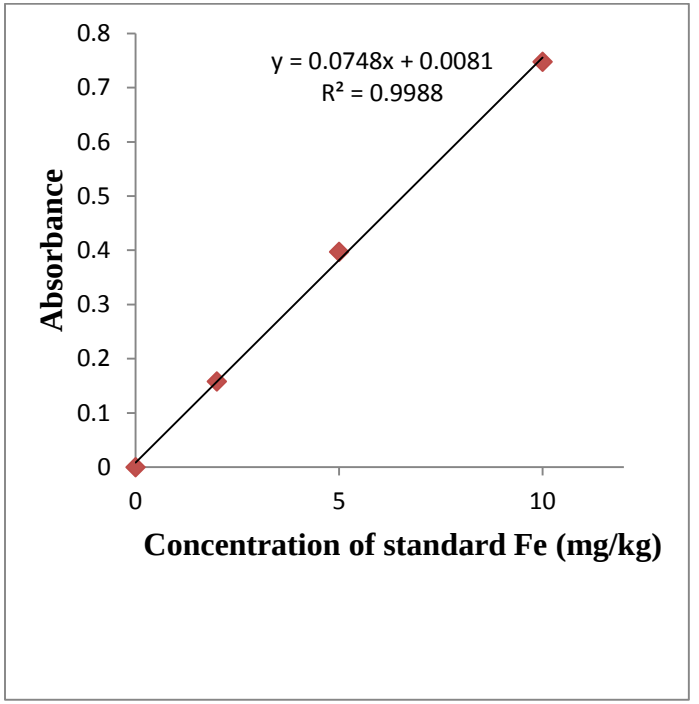

Figure B: Graph of absorbance against concentration

Appendix B3

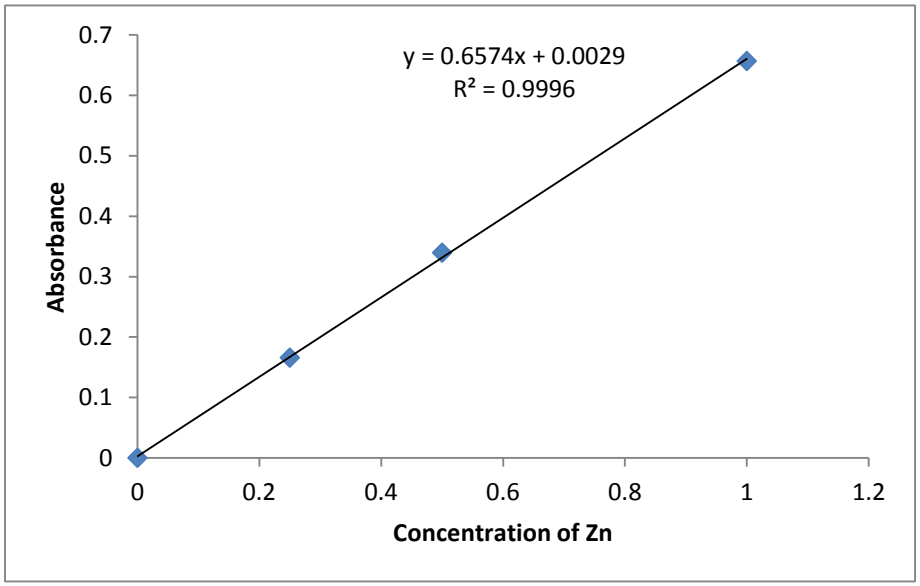

Figure C: Graph of absorbance against concentration