

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY**

**COLLEGE OF SCIENCE**

**DEPARTMENT OF CHEMISTRY**



**CONTRIBUTION OF ARTISANAL ACTIVITIES TO HEAVY METAL  
CONTAMINATION OF SOIL AND WATER RESOURCES AT SUAME  
MAGAZINE**

**By**

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**(BSc. Chemistry)**

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the degree of**

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## DECLARATION

I hereby declare that this submission is my own work towards the award of the MPhil and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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## DEDICATION

This work is dedicated to the Almighty God for His unfailing love, grace, guidance and protection throughout the entire duration of the research; also to my lovely parents, Mr. William Yeboah Korankye and Mrs. Hilda Serwaa Appiah Korankye for their prayers, financial assistance and encouragement.



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## ABSTRACT

The Suame Magazine industrial area is a well-known automotive repair village in Ghana and West Africa. Artisanal activities at Suame Magazine industrial area generate waste containing hazardous contaminants such as heavy metals which are disposed of indiscriminately onto the soil. A total of forty-five (45) soil samples and nineteen (19) water samples determined for six heavy metals (Cd, Zn, Cu, As, Pb, Fe). The heavy metal concentration for the six metals determined in soil and water samples was in the order; Fe > Zn > Cd > As > Pb > Cu and the levels of these metals decreased with depth of the soil profile. Assessment of heavy metal contamination at Suame Magazine industrial area using indices of pollution indicated that the study area is highly polluted with these metals in the order; Fe > Zn > Cd > As > Pb > Cu. Also statistical analysis was used to determine the correlativity of the metals and their possible source of origin (natural or anthropogenic). Health risk indices such as hazard coefficient and the cancer risk were calculated and the results showed that artisans are likely to suffer from cancer through ingestion of soil and water as a result of the exposure.

**Key words:** Artisanal activities, heavy metals, indices of pollution, health risk assessment, toxicity.

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## ABBREVIATION



Agency for Toxic Substances and Disease Registry.....	ATSDR
Atomic Absorption Spectrometer.....	AAS
Cation Exchange Capacity.....	CEC
Chronic Daily Intake.....	CDI
Contamination Factor.....	CF
Electrical Conductivity.....	EC
European Food Safety Authority.....	EFSA
Hazard Index.....	HI
Hazard Quotient.....	HQ
International Agency for Research on Cancer.....	IARC
Pollution Load Index.....	PLI
Quantification of Concentration of anthropogenic metal.....	QoC
Reference Dose.....	RfD
United States Environmental Protection Agency.....	USEPA
World Health Organisation.....	WHO

# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND

The Suame Magazine industrial area located, in the Suame sub-metro in the northeastern part of the Kumasi Metropolis, is the nerve-centre of the artisanal engineering industry in Ghana and West Africa. It is the single largest industrial cluster of artisans in sub-saharan Africa and has a working population of over 20,000 engaged mainly in vehicle repair and maintenance, welding and metal fabrication, spraying (Adeya, 2006). These artisanal activities contribute to waste generation in the environment which includes metal scraps, used batteries, packaging materials, spent lubricants and worn-out parts, which contain contaminants such as heavy metals (Pam *et al.*, 2013a; Pam *et al.*, 2013b ). Artisanal activities in most mechanical villages are not properly monitored and regulated; these activities give rise to elevated levels of metals in the environment. Soils may contain large amounts of heavy metals with varying concentration ranges depending on anthropogenic and natural activities occurring or once occurred and the surrounding geological environment. Heavy metals contaminate the soil from different sources and show different behavior in soil (Soltan *et al.*, 2012). According to Dube *et al.*, 2001, the ability of soil to immobilise introduced chemicals like heavy metals depends on sorption properties of the soil (soil texture, pH, moisture content and cation exchange capacity). Metals on the surface of the soil may be carried by run off water and transported to the groundwater (Wuana and Okieimen, 2011).

## 1.2 PROBLEM STATEMENT

Artisanal activities at Suame Magazine generate large amount of gaseous, solid and liquid wastes which are disposed of indiscriminately. The primary recipient of these metal contaminants is the soil (Abii, 2012) which may be washed away into the surrounding water bodies. Suame Magazine is located at the head of the Owabi watershed that drains into the Owabi reservoir which provides about one- third of the pipe-borne water for the Kumasi metropolis and its surroundings. The potential of this waste, such as used oil, which contains heavy metals ending up in the reservoir, is high as it is disposed of poorly and indiscriminately. Heavy metals are considered harmful pollutants due to its non-biodegradable nature, long biological half-lives, persistence and toxicity (Sadick *et al.*, 2015). The wide mobility of these metals in the soil can have adverse effects on plants, humans, and the environment (Adelekan and Abegunde, 2011). Therefore, the need for long term monitoring and assessing the levels of heavy metals pollution of water resources and soil as a result of artisanal activities in Suame Magazine industrial area is imperative.

### **1.3 GENERAL OBJECTIVE**

To assess the extent of heavy metal contamination in soil and water resources due to artisanal activities taking place at the Suame Magazine industrial area.

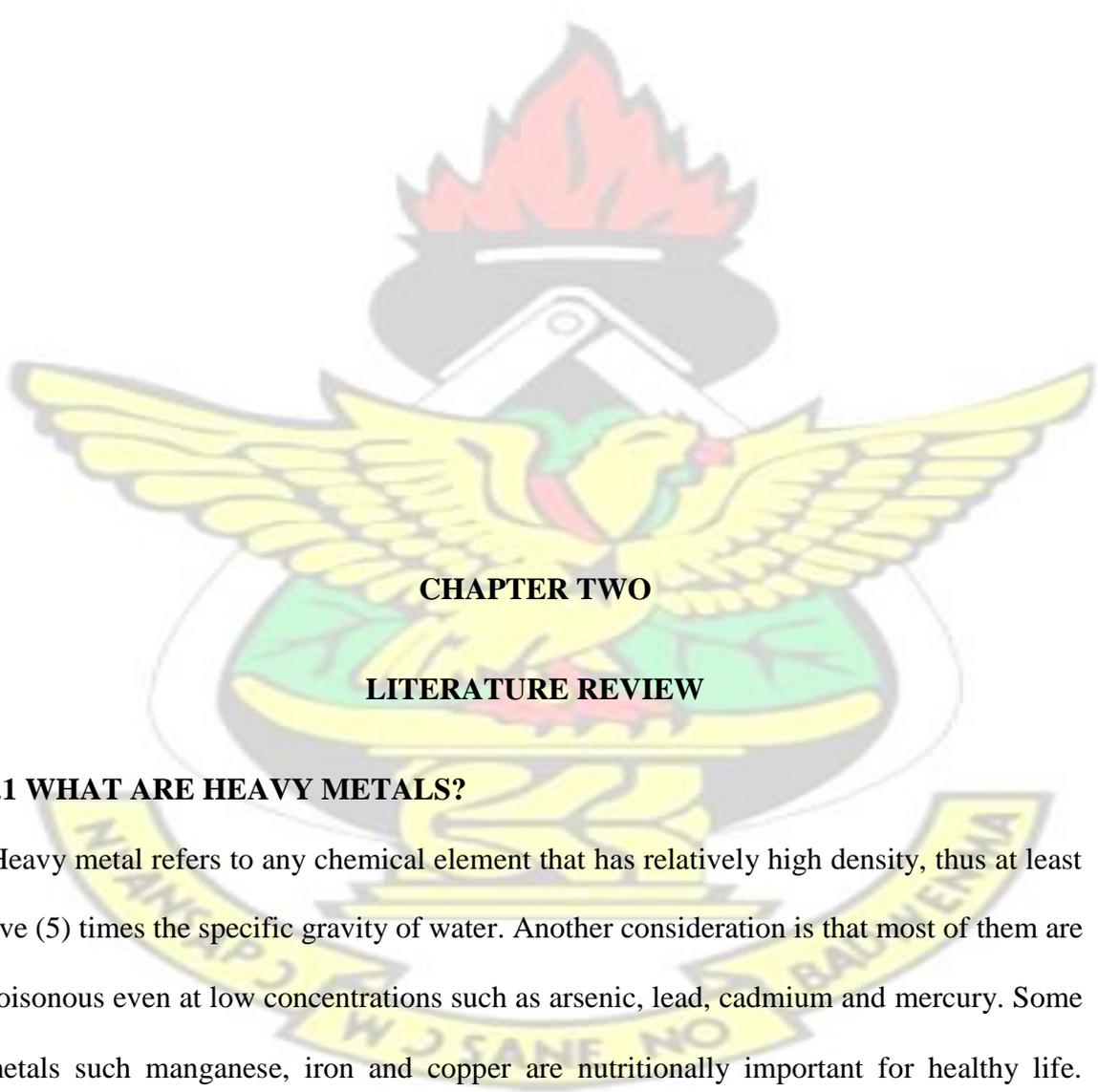
**Specific objectives** are as follows:

- To determine physico-chemical properties of soil (moisture, organic matter content, pH, electrical conductivity, particle size and cation exchange capacity) and water samples (total dissolved solids, pH, electrical conductivity and total hardness).
- To study the distribution of the metals at different depth of the soil profile and assess the extent of contamination of the soil using indices of pollution.
- To evaluate the correlativity between metals in the soil and to apportion natural or anthropogenic sources using statistical approach.
- To assess the potential risks of heavy metals on health of artisans through two exposure routes (ingestion and dermal) from soil and water resources at Suame Magazine industrial area.

### **1.4 SCOPE OF STUDY**

This thesis will first review the available information on heavy metals specifically copper, cadmium, zinc, arsenic, lead and iron. Also, the information regarding the physical and chemical properties, exposure routes, fate in the environment, toxicity and potential health effects on humans are addressed in Chapter 2. A brief description of the study area, sampling (for both soil and water), determination of physico-chemical parameters, analysis of samples for heavy metals using Atomic Absorption Spectrometry (AAS) and statistical analysis are reported in Chapter 3. Information obtained from the heavy metal analysis,

the effect of physiochemical parameters on metal distribution on soil, the possible sources (anthropogenic or natural) of these metals and their correlativity in the environment have been explained in Chapter 4. Also assessment of extent of heavy metal pollution and the impact on health of artisans at Suame Magazine industrial area are reported in Chapter 4. Finally, recommendations and conclusions are presented in Chapter 5.

The logo of Kenyatta University of Science and Technology (KNUST) is centered in the background. It features a yellow bird with its wings spread, perched on a green base. Above the bird is a black mortar and pestle with a red flame rising from it. The entire emblem is set against a white background with the letters 'KNUST' in a large, light grey font above it.

## **CHAPTER TWO**

### **LITERATURE REVIEW**

#### **2.1 WHAT ARE HEAVY METALS?**

Heavy metal refers to any chemical element that has relatively high density, thus at least five (5) times the specific gravity of water. Another consideration is that most of them are poisonous even at low concentrations such as arsenic, lead, cadmium and mercury. Some metals such manganese, iron and copper are nutritionally important for healthy life. Humans are exposed to heavy metals through two main absorption pathways; inhalation and ingestion (Islam *et al.*, 2007). Complete avoidance of exposure to the toxic metals

completely is not possible (Singh, 2011) and metal toxicity risk can be reduced through lifestyle choices that limit the potential of heavy metal uptake (Peraza *et al.*, 1998).

The following sections will address the properties of Cu, Cd, Zn, As, Pb and Fe exposure routes in the environment, fate in the environment, toxicity and the health effects on humans.

KNUST

## **2.1 COPPER**

### **2.1.1: Physical and chemical properties of copper**

Copper (Cu) is a metallic element with atomic number 29 and atomic 63.546 g. It has a density of  $8.96 \text{ gcm}^{-3}$ , melting point of  $1084^{\circ}\text{C}$  and boiling point of  $2562^{\circ}\text{C}$ . Copper exist naturally as the free metal, or associated with other elements in compounds and forms divalent (cupric) cation the monovalent (cuprous). Cu also exists in trivalent copper (III), but this is rarely the case and found only in the solid form. Almost all copper found in nature exists as one of two stable isotopes, Cu-63 (occurring 69.09%) and Cu-65 (30.91%). Metallic copper is soft, ductile, malleable and a good conductor of heat and electricity. According to Hardy *et al.*, 2008, copper is also used as a component in metal alloys, leather and fabrics and electrical wiring.

### **2.1.2: Exposure routes of copper into the environment**

#### **Natural sources**

Copper is a component in many primary minerals, the most common being sulfides such as chalcocite ( $\text{Cu}_2\text{S}$ ), covellite ( $\text{CuS}$ ), and villamaninite ( $\text{CuS}_2$ ). The sulfide minerals are quite soluble and provide a continuous release of Cu ions to solution where they can then interact with soil constituents.

#### **Anthropogenic sources**

Human and industrial activities (incineration of municipal waste, mining, producing products from copper such as pipes, sheet metal wire, and fossil fuel combustion) release copper into the environment.

### **2.1.3: Fate of copper in the environment**

#### **Copper in soil**

Copper exist mainly as  $\text{Cu}^{2+}$  on the surfaces of clayey materials of soils and the presence of particulate organic materials influences the rate of adsorption (Landner & Lindstrom, 1999). Dissolved Cu can be adsorbed onto the surfaces of the soil or may be precipitated out of solution.

#### **Copper in water**

The behavior and chemistry of elemental copper in water are controlled by dissolved oxygen, presence of oxidizing agents and chelating compounds or ions and pH, (USEPA, 1995). In an aquatic ecosystem, Cu undergo can several processes such as chelation, coprecipitation and sorption.

#### **Copper in air**

Copper particulates are emitted into the atmosphere by natural and anthropogenic processes. In the atmosphere, Cu particles can be resuspended into the atmosphere in the form of dust, but can settle out or be removed by precipitation. Atmospheric copper is removed by rain, dry disposition, snow and gravitational settling.

### **2.1.4: Toxicity of copper**

Toxicity of copper can result from both deficiencies and over exposures. The recommended daily intake for adults is 2 mg/day. Metallic copper has little toxicity, but copper soluble salts such as copper sulfate ( $\text{CuSO}_4$ ) are very poisonous.

### **2.1.5: Health effects of copper**

Copper is a trace element important to plants, animals, and humans and can catalyze a variety of metabolic activities (Devez *et al.*, 2005; Yan *et al.*, 2006). Ingestion of lethal dose of copper sulfate ( $\text{CuSO}_4$ ) can cause temporary gastro-intestinal distress and liver damage. Also copper deficiency can result in include low numbers of white blood cells, anemia, defects in connective tissue leading to skeletal problem and osteoporosis in infants and children.

## **2.2 CADMIUM**

### **2.2.1 Chemical and physical properties of cadmium**

Cadmium, Cd, atomic number 48 and atomic weight 112.41 g is a soft, lustrous, bluishwhite metallic element. It has a melting point of  $320.9^\circ\text{C}$  and boiling point  $765^\circ\text{C}$  under atmospheric pressure. Cadmium metal is very ductile and malleable; resistant to corrosion but it tarnishes in air. The oxidation state of almost all cadmium compounds is +2 (e.g cadmium sulfide ( $\text{CdS}$ ), cadmium oxide ( $\text{CdO}$ ) or cadmium sulfate ( $\text{CdSO}_4$ ), although a few compounds have been reported in +1 state. Some cadmium salts are water soluble such as  $\text{CdSO}_4$ ,  $\text{Cd}(\text{NO}_3)_2$  and  $\text{CdCl}_2$ . Other insoluble salts can become more soluble by interaction with acids, light or oxygen.

### **2.2.2 Exposure route of cadmium in the environment**

#### **Natural sources of cadmium**

The elemental form of cadmium in nature is not known; it appears mainly in association with ores containing lead, zinc, and copper in the Earth crust. The most common natural compounds of cadmium are cadmium carbonate ( $\text{CdCO}_3$ ) and cadmium sulfide ( $\text{CdS}$ ).

Volcanic activity, erosion, weathering and river transport are major processes that contribute to the release of cadmium to the Earth surface (WHO, 2000).

### **Anthropogenic sources of cadmium**

Anthropogenic activities contribute 3-10 times more cadmium to the environment than natural activities. Cadmium may be derived from human activities which includes refining of non-ferrous metals (zinc, lead, and copper and recycling of cadmium-plated steel scrap) contributes to high levels of cadmium in the environment.

### **2.2.3 Fate of cadmium in the environment**

#### **Cadmium in air**

Cadmium is released into the atmosphere in particulate form by variety of process such as sea spray, forest fires and volcanoes. Cadmium in the form of  $\text{CdCl}_2$ ,  $\text{CdSO}_4$  and  $\text{CdO}$  are usually bound to fine particulate matter with particle size  $< 1.0 \mu\text{m}$  and can travel a considerable distance before settling to the Earth surface as dust, rain or snow. The deposition and range of cadmium emissions depend on the forms of cadmium in the atmosphere, meteorology and particle size. (Nriagu and Pacyna, 1988).

#### **Cadmium in soil**

The chemistry of cadmium in soil is influenced by pH and mobility increases with a decreasing pH of the soil. The rate of cadmium transfer in the soil depends humus, the presence of other elements, availability of organic matter, on the type of soil,

#### **Cadmium in water**

In an aquatic environment, concentrations of cadmium are relatively low and may be present as inorganic complexes (hydroxides, chlorides, carbonates, or sulfates) or as organic complexes with humic acids.

#### **2.2.4 Toxicity of cadmium**

Cadmium can enter the human body through smoking cigarettes, contaminated water due to landfills, certain foods such as shellfish, and mostly through handling the metal itself.

Cadmium is a very toxic metal and needs to be handled with great caution.

#### **2.2.5 Health effects**

Lethal doses of cadmium affect various organs in animals which includes the liver, kidney, lungs, testes, skeletal, nervous and immune system and can also results in osteomalacia and osteoporosis. Cadmium is a category 1 carcinogen.

### **2.3 ZINC**

#### **2.3.1 Chemical and physical properties of zinc**

Zinc is a soft, lustrous, blue-white metal with an atomic number of 30 and atomic weight of 65.39 g. It has a melting point of 419.5°C and boiling point of 908°C. Zn is brittle at low temperatures but becomes malleable between 100-150°C and is a fair electrical conductor. Zinc metal is highly reactive; it is not found as the free element in nature, rather occurs in the +2 oxidation state in most of its minerals e.g. zincite (zinc oxide) and phalerite (zinc sulfide) (Lindsay, 1979).

#### **2.3.2 Exposure route of zinc in the environment**

##### **Natural sources**

Natural sources of zinc to the environment include weathering volcanic eruptions, forest fires and aerosol formation (ATSDR, 2005). Most rocks and many minerals such as zincite, smithsonite and phalerite contain zinc in varying amounts.

##### **Anthropogenic sources of zinc**

Industrial and human activities (production and use of zinc in brass, paints, alloys, fuel combustion and refuse incineration) contribute greatly to large amounts of zinc in the environment.

### **2.3.3 Fate of zinc in the environment**

#### **Zinc in air**

Zinc exists as oxide particles in the atmosphere and the chemical interaction may affect the anionic speciation of the compound. The deposition velocities of zinc particles depend on the particle size; small particles may be transported from their emission source to distant regions.

#### **Zinc in soil**

Adsorption of zinc on the surface of soil particulates especially clay minerals can retard its mobility in the soil. pH, redox potential and cation exchange capacity are the main factors affecting zinc sorption and migration in soils. Within a given soil, equilibrium exists between the different forms of zinc (exchangeable, adsorbed, insoluble complexes, secondary minerals) in the liquid and solid phases of the soil.

#### **Zinc in water**

Zinc exists in the +2 oxidation state in an aquatic environment and are adsorbed by suspended matter in water. In natural waters, the stability of the complexes and complexing agents such as humic acids depend on the pH of the water and the nature of the complex.

The mobility of Zn in aquatic system depends on the salinity, pH and solubility.

### **2.3.4 Toxicity of zinc**

Zinc is an essential micronutrient important for survival, with the LD<sub>50</sub> value estimated to be 27 g zinc/day for humans based on comparison with equivalent studies in rats and mice. Zinc is considered to be relatively non-toxic, particularly if taken orally (Fosmire, 1990).

### **2.3.5 Health effects of zinc**

Absorption pathways such as inhalation, dermal contact and ingestion are the means for entry of zinc into the body (Plum *et al.*, 2010). Abdominal cramps, diarrhoea, pleuritic chest pain, respiratory tract infection and pneumonitis are associated with inhalation and ingestion of lethal doses of zinc.

## **2.4 ARSENIC**

### **2.4.1 Chemical and physical properties of arsenic**

Arsenic (As) is a metalloid and can exist in four oxidation states: -3, 0, +3, and +5 (Baig *et al.*, 2014) and commonly found in association with chlorides, oxides, or sulfate and sulfides. When heated in air, arsenic combines with oxygen to form a white cloud arsenic oxide (As<sub>2</sub>O<sub>3</sub>). Arsenic does not dissolve in water and most cold acids. It does react with some hot acids such as nitric acid, cold hydrochloric acid, and sulfuric acid to form arsenous acid (H<sub>3</sub>AsO<sub>3</sub>) or arsenic acid (H<sub>3</sub>AsO<sub>4</sub>).

### **2.4.2 Exposure route for arsenic to the environment**

#### **Natural sources of Arsenic**

Arsenic occurs naturally in the earth's crust primarily in its sulfide form. The chemistry of arsenic resembles that of sulfur very closely, and hence the greatest concentration of

arsenic tends to occur in sulfide-bearing minerals. Arsenic is present mineral species such as arsenopyrite, cobaltite ( $\text{CoAsS}$ ), arsenolite ( $\text{As}_2\text{O}_3$ ) and olivenite ( $\text{Cu}_2\text{OHAsO}_4$ ) (Mandal and Suzuki, 2002, Bhattacharya *et al.*, 2007). According to Alshaebi *et al.*, 2010, natural processes such as geothermal activities, volcanoes and weathering of rocks distribute As into the environment

### **Anthropogenic sources of Arsenic**

Major industrial processes such as metal smelting, burning of fossil fuels and mining contribute to arsenic contamination of air, water and soil in the environment.

### **2.4.3: Fate of arsenic in the environment**

#### **Arsenic in air**

In the atmosphere, arsenic exists as particulate matter, mostly less than  $2\ \mu\text{m}$  in diameter; can stay in the air for many days and can travel long distances. Arsenic can exist in both organic and inorganic forms, in vapor and particulate states and the predominant form in the atmospheric air is inorganic arsenic.

#### **Arsenic in soil**

Arsenic has a great tendency to adsorb to soils and sediments and exist as both organic and inorganic arsenic species. In soils, arsenic forms solids with iron, aluminum, calcium, magnesium and nickel (Nriagu, 1996) and speciation of arsenic is relatively complex. The speciation of arsenic in water is controlled by redox potential (Eh) and pH. Soil with high organic matter can compete with arsenate and arsenite for soil retention positions (Bernal *et al.*, 2009).

#### **Arsenic in water**

Arsenic usually exist as oxy-anions, arsenite ( $\text{As}^{3+}$ ) and arsenate ( $\text{As}^{5+}$ ) in ground water and are capable of adsorbing to various subsurface materials such as ferric oxides and clay particles. In water, an increase in the pH to an alkaline condition will cause both arsenite and arsenate to desorb; hence, both are expected to be very mobile in an alkaline environment. The arsenic oxy-anions are also sensitive to redox conditions, and the speciation differential between them will change with changing redox potential (Rajaković *et al.*, 2013).

#### **2.4.4: Toxicity of arsenic**

Arsenic is highly toxic and carcinogenic; the degree of toxicity depends on its chemical form and oxidation state; for example trivalent ( $\text{As}^{3+}$ ) compounds are generally more toxic than pentavalent ( $\text{As}^{5+}$ ) compounds. It has been established that inorganic arsenic is more toxic than the organic form (Rajaković *et al.*, 2013).

#### **2.4.5 Health effects of Arsenic**

Exposure to arsenic has been linked to various vascular diseases affecting both the large and small blood vessels. The chronic exposure of arsenic during pregnancy makes the foetus period more dangerous which creates impact on optimal brain development. It also leads to impairment of behaviors and skills, including cognitive abilities and social competence that are further developed and fine-tuned during childhood and adolescence. Several epidemiology studies indicate that inorganic arsenic is potentially neurotoxic.

## **2.5 LEAD**

### **2.5.1 Chemical and physical properties**

The heavy metal lead, Pb with atomic number of 82 and atomic weight 207.2 g is a bluish metal, and occurs in nature in the form of ores. Lead has a high density of  $11.3\text{g cm}^{-3}$ , melting point (mp) of  $327.5^{\circ}\text{C}$  and boiling point (bp) of  $1749^{\circ}\text{C}$ . Lead can exist in three oxidation states: 0, +2, +4 (ATSDR, 2007). Lead in ambient air exists primarily as lead vapours, very fine lead particles, and organic halogens such as lead bromide ( $\text{PbBr}_2$ ) and lead chloride ( $\text{PbCl}_2$ ). Lead is soft, malleable, and ductile and can combine with other metals to form alloys. Lead does not readily react with oxygen in air. However, it reacts quickly with hot acids but slowly with cold acids.

### **2.5.2: Exposure routes for lead to the environment**

#### **Natural sources of Lead**

Lead occurs naturally in the earth crust and release into the environment through processes such as windblown dusts, sea sprays, forest fires and volcanic activity (Nriagu, 1978a).

#### **Anthropogenic sources of Lead**

Human and industrial activities such as production of lead-acid batteries and paints; jewellery making, use of leaded petrol (gasoline); coal burning, ceramics and soldering contribute largely to the elevated levels of lead in the environment (Verkleji, 1993).

### **2.5.3 Fate of lead in the environment**

#### **Lead in air**

Lead exists primarily in the form of lead sulfate and lead carbonate in the atmosphere (ATSDR, 1992) and emitted from automobiles as lead halides (e.g.,  $\text{PbBrCl}$ ) and as the double salts with ammonium halides (e.g.,  $2\text{PbBrCl}$ ,  $\text{NH}_4\text{Cl}$ ). Estimates of the dispersion

of lead emissions into the environment indicate that the atmosphere is the major initial recipient.

### **Lead in soil**

Lead is a minor component of many soils and can be incorporated into the soils from atmospheric wet and dry deposition; relatively immobile and has a long residence time. Lead adsorbs strongly to soil particles and remains in the upper layer of soil, particularly soil with high organic matter content. The ability of soils to bind lead is dependent on soil pH and the cation exchange capacity of the soil components (e.g., hydrous iron oxides on clay and organic matter).

### **Lead in water**

Lead is usually a minor constituent of surface and ground waters; and can be deposited from the atmosphere and enter aquatic systems through direct fallout or through erosion of soil particles and runoff (from automotive sources such as used oil and building materials). The amount of lead dissolved in surface waters is dependent on the pH and the dissolved salt content of the water. Carbonate, hydroxide, sulfide, and, more rarely, sulfate may act as solubility controls in precipitating lead from water. Also soluble lead is little affected by redox potential (Gambrell *et al.*, 1991).

#### **2.5.4 Toxicity of lead**

Epidemiological and toxicological studies have shown that low levels of exposure to lead can over time damage several organs in the human body such as the heart, brain, and kidney. All forms of lead, including the organic and inorganic forms, are potentially toxic and the toxicity can be acute or chronic. The clinical manifestations of lead poisoning are variable depending upon the age of the patient as well as the severity and chronicity of the exposure.

### **2.5.5 Health effects of lead**

In humans, lead has been shown to have effects on many biochemical processes depending upon the level and duration of exposure. Data from European Food Safety Authority (EFSA) have related exposure to Pb to effects like neurotoxicity, nephrotoxicity, carcinogenicity and endocrine and reproductive failures in adults (Herrerros *et al.*, 2008). Moderate exposure to Pb can also significantly reduce human semen quality and is related to damage to DNA in children and impairment of the reproductive function in adults (Telisman *et al.*, 2000). The International Agency for Research on Cancer (IARC) has classified inorganic lead compounds as possibly carcinogenic to humans (Group 2A) based on limited evidence of carcinogenicity in humans and sufficient evidence in animals (IARC, 2006).

## **2.6 IRON**

### **2.6.1: Physical and chemical properties of iron**

Iron with an atomic number of 26 and atomic mass of 56 is the most abundant metal in the Earth crust. Iron belongs to group 8 of the Periodic Table, along with Ru and Os. Iron has two oxidation states (+2 and +3) and four naturally occurring isotopes (Fe-54, Fe-56, Fe-57 and Fe-58); Fe-56 is the major isotope at 92% of the total mass. Iron is silver-gray in colour and a good conductor of heat and electricity. It also has high tensile strength. Iron has a melting point of 1535°C and a specific gravity of 7.86 at 25°C. It forms positive ions in its chemical reactions and dissolves readily in dilute acids.

### **2.6.2: Exposure route for iron to the environment**

#### **Natural sources**

Iron is present in several minerals, including magnetite  $\text{Fe}_3\text{O}_4$ , pyrite  $\text{FeS}_2$ , siderite  $\text{FeCO}_3$  and haematite  $\text{Fe}_2\text{O}_3$ . Many rock-forming minerals, including garnet, pyroxene, amphibole, mica and olivine contain varying amounts of iron.

### **Anthropogenic sources**

Anthropogenic sources of iron include sewage and dust from iron mining, iron and steel industry. Iron sulfate is also used as herbicide and fertilizer. (Reimann *et al.*, 2003).

### **2.6.3: Fate of iron in the environment**

#### **Iron in soil**

Iron in the soil exists in the ferrous ( $\text{Fe}^{2+}$ ) and ferric ( $\text{Fe}^{3+}$ ) forms; soil pH and aeration determine which form predominates. The concentration of iron in the soil also decreases sharply as the soil pH increases. The solubility of Fe depends greatly on the oxidation state of the Fe compounds involved and the pH; with ferric iron compounds having low solubility in the soil solution.

#### **Iron in water**

Iron exists in different forms in water such as the soluble ferrous ion ( $\text{Fe}^{2+}$ ) and the insoluble ferric ion ( $\text{Fe}^{3+}$ ). In solution, iron (Fe) has the ability to undergo hydrolysis and complexation and the retention of iron in solution is consequently affected by the pH of the solution.

The solubility of ferrous ion ( $\text{Fe}^{2+}$ ) increases 100-fold for every unit increase in pH and it is usually controlled by redox conditions above pH of 4. In contrast to  $\text{Fe}^{2+}$ , solubility of ferric ion ( $\text{Fe}^{3+}$ ) decreases 1000-fold for every unit increase in pH and is usually

unavailable at  $\text{pH} > 4$ . At  $\text{pH} < 1$ , the hexa aqua ion  $[(\text{Fe}(\text{H}_2\text{O})_6)]^{3+}$  is the predominant species.

### **Iron in air**

In the atmosphere, Fe and its compounds exist as contaminants and can cause harmful effects on humans and animals. Analyses of urban air samples show that the iron content averages  $1.6 \text{ mg/m}^3$ , with the iron and steel industry being the probable source of emission (Gurzau *et al.*, 2003).

#### **2.6.4: Toxicity**

Excess iron accumulates in the heart, liver, and other vital organs and cannot be removed naturally by the body; therefore puts the organs at risk for serious damage. In addition, once the body's storage capacity for iron is exceeded, non-transferrin-bound iron is created (Porter, 2001; Cabantchik *et al.*, 2005) which is a toxic form of iron that causes oxidative stress, attacking organ systems at the cellular level and causing tissue damage (Vichinsky, 2001).

#### **2.5.5: Health effects**

Iron is an essential element in human nutrition with estimates of the minimum daily requirement for iron dependant on sex, physiological status, age and iron bioavailability and ranges from about 10 to 50 mg/day. According to Liehr and Jones (2001), elevated body iron storage has been shown to increase the risk of several cancers, including breast cancer in humans. During the past decade, considerable evidence has supported the role of oxidative stress in the development of atherosclerosis and related cardiovascular diseases (Lieu *et al.*, 2001; Emerit *et al.*, 2001; Chau, 2000).

## **2.7: BEHAVIOR OF HEAVY METALS IN WATER**

In an aquatic environment heavy metals may be found dissolved in the water or adsorbed to the suspended matter. The adsorption to the suspended matter which acts as carriers leads to the sedimentation of the heavy metals (transportation of heavy metals out of the water column into the sediment). Heavy metals may be resuspended or undergo diffusive transfer into the water column due to the concentration difference.

## **CHAPTER THREE**

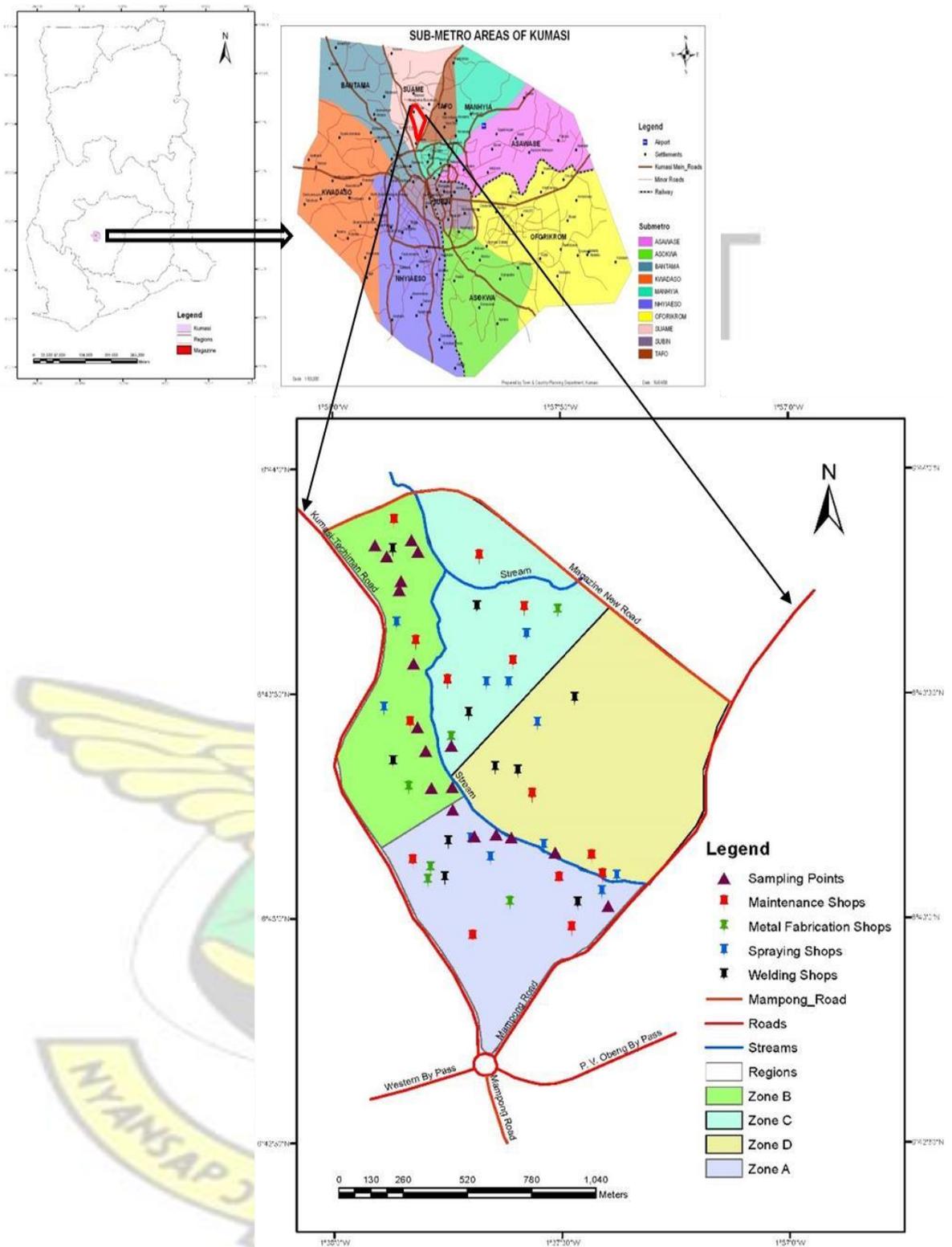
### **MATERIALS AND METHODS**

#### **3.1. STUDY AREA**

The study area is located at Suame Magazine. “Suame magazine” is an industrial cluster located in Suame, a suburb of Kumasi in the Ashanti Region of Ghana. It occupies an area of approximately 1.8 km long and 0.3 km wide (Adeya, 2006) with a general elevation of 200 m above sea level. Geographically, it lies on latitude 6°43'00'' North and longitude 1°38' 00'' West. The basement rocks at Suame form part of the Cape Coast Granites which generally weather into medium to coarse textured soils with fairly high moisture holding capacity, therefore good for farming purposes. Suame Magazine land area spreads from high elevation towards the bank of the rivers or streams giving room for increased contaminant transport. The study area was divided into four zones using the natural drainage (Nkradan stream) as a landmark

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**Figure 3.1: A map of Suame Magazine showing the sampling points**

## 3.2 Materials and Methods

### 3.2.1. Reagent

- Sodium hexametaphosphate [Na (PO<sub>3</sub>)<sub>6</sub>] Sigma-Aldrich, Germany
- Sodium chloride Sigma-Aldrich, Germany
- Nitric Acid (HNO<sub>3</sub>) Sigma-Aldrich, Germany
- Hydrochloric Acid (HCl) Sigma-Aldrich, Germany
- Ethylenediaaminetetraacetic acid (EDTA) Sigma-Aldrich, Germany
- Ammonium acetate (NaOAC) Sigma-Aldrich, Germany

### 3.2.2. Equipment

- PHWE Electrical Conductivity meter Germany.
- Perkin Elmer pinnacle 900T AAS, United States of America (USA)
- Mechanical shaker Panasonic MIR-S100, UK.
- Magellan Hand held GPS Triton 2000, USA.
- Hanna 909 pH meter Germany
- Furnace, ST-1700MX Henam China.

## 3.3. SAMPLING (for both soil and water)

### 3.3.1 Soil sampling

A total of forty-five (45) composite soil samples were collected from fifteen (15) selected automobile workshops within Suame magazine using soil depth-calibrated auger, at the depths of 0-10 cm, 10-20 cm and 20-30 cm representing the top, sub and bottom soils, respectively. Initially, soil samples were collected at random from four different locations of each automobile shop which were then mixed up to obtain a composite soil sample at each soil depth separately. The soil samples were placed in polythene bags and transported to the laboratory. The location and elevation of each selected site was recorded with a

global positioning system (GPS). The control samples were collected from the St Louis Training College located at Mbrom, 200 m away from the point of impact where there are neither car repairs nor commercial activities, with no drainage influence and no likelihood of contamination from used motor oil.

### **3.3.1.1: Soil sample treatment and analysis**

Soil samples were air-dried at room temperature for 48 hours to avoid microbial degradation. The samples were homogenized and gently crushed repeatedly using a mortar and pestle, and passed through a 2-mm plastic sieve prior to analysis. The bioavailable heavy metals in the soil sample were extracted by acid digestion using aqua regia i.e. (hydrochloric acid (HCl): nitric acid (HNO<sub>3</sub>) in a ratio of 3:1. The digested sample solution were analysed using the atomic absorption spectrometer (Perkin Elmer pinnacle 900T AAS). Standard solutions of the various heavy metals were analysed. All soil samples were analysed in triplicate to minimize error.

### **3.3.1.2 Water sampling**

A total of nineteen water samples were collected from seventeen water sources (3 pipebornes, 2 boreholes, 4 hand-pump wells, 7 hand dug wells and a stream) located within the Suame Magazine industrial area. Water samples from the “Nkradan” stream were taken from upstream, midstream and downstream. The Barekese dam was used as a control site. A blank test sample was also analysed for correction of background and other sources of error.

### **3.3.1.3: Water sample treatment and analysis**

All water samples were collected using 500 ml plastic bottles, placed in an ice chest and transported to the laboratory. Five (5 ml) of concentrated nitric acid was added to minimize

adsorption of metals on the container and for preservation of the water samples. Addition of 5 ml of concentrated  $\text{HNO}_3$  to 50 ml of the water sample was followed by heating the mixture slowly to evaporate to a volume of about 15 – 20 ml on a hot plate. Continuous heating and adding of concentrated  $\text{HNO}_3$  as necessary was employed until digestion is complete as shown by a light-colored, clear solution. The wall of the beaker was washed down with double distilled water and then filtered with a 0.45  $\mu\text{m}$  pore filter paper. The filtrate was transferred to a 50 ml volumetric flask and topped to the mark. The digested samples were analysed using the atomic absorption spectrometer (Perkin Elmer pinnacle 900T).

### **3.4 Analysis of samples**

#### **3.4.1 Determination of physico-chemical parameters**

##### **3.4.1.1: pH**

A soil-water suspension was prepared using a soil to water ratio of 1:2.5. The contents were allowed to equilibrate for 30 minutes and the pH was recorded with the aid of a calibrated Hanna 909 pH meter. The pH meter was initially calibrated by placing the pH electrode into a buffer solution of known pH (pH 4.2) and (pH 7). The instrument was adjusted until the meter read the known pH value of the buffer solution. With the pH meter calibrated, the electrode was then rinsed three times with distilled water. The electrode was placed in the soil water suspension, allowed to stabilize and the pH value was read from the instrument. Triplicate pH values were taken.

##### **3.4.1.2: Electrical Conductivity**

The conductivity of the soil samples were determined using PHWE electrical conductivity meter. The instrument was initially calibrated by rinsing with potassium chloride (KCl) solution. The conductivity of this standard is known to be 1413  $\mu\text{S}/\text{cm}$ ; the electrode was

rinsed with distilled water and then immersed in a soil: water suspension (1:2.5) for the actual reading. Triplicate values were taken.

#### **3.4.1.3: Moisture and organic matter content**

The crucible was cleaned and placed in an oven at 105°C to dry to a constant weight and recorded as  $W_0$ . Air-dried soil sample of weight 5g ( $W_1$ ) was also placed in the crucible and dried at 105°C to constant weight and recorded as  $W_2$ . The difference in the weight of the soil gives the estimate of the moisture content.

Weight of crucible =  $W_0$

Weight of crucible + air-dried soil sample before heating =  $W_1$

Weight of crucible + air dried sample after heating =  $W_2$

Moisture content =  $W_1 - W_2$

In order to determine the organic matter content, the oven dried soil sample was placed in the oven at a temperature of 360°C and allowed to ash for 5 hours. The crucible was removed with the help of a pair of tongs, placed in a desiccator and allowed to cool. The crucible and its contents were weighed and the weight recorded as  $W_3$ . The organic matter was calculated according to equation 1.

Organic matter content =  $W_2 - W_3$

#### **3.4.1.4: Cation Exchange Capacity**

The total number of exchangeable cations that the soils can hold (cation exchange capacity) was determined by flame photometry. Five grams (5 g) of each of the soil samples was transferred into a 50 ml centrifuge tube and 25 ml of 1.0 M of sodium acetate (NaOAc) solution was added. The soil samples were placed in a mechanical shaker and shake for 5 minutes. The suspension was centrifuged at 2000 rpm for 5 minutes until the supernatant liquid became clear. The supernatant liquid was decanted completely and the extraction of

the soil samples with the sodium acetate was repeated five times. The decant was discarded and the cations present in the soil were generated using ammonium acetate. Standard solutions of 0, 2, 4, 6, 8 and 10 ppm of sodium chloride solution (NaCl) were run on the flame photometer and the readings were used to construct a calibration curve. Thus flame photometry was used for the determination of exchangeable sodium ions (Na<sup>+</sup>). Calcium ions (Ca<sup>2+</sup>), magnesium ions (Mg<sup>2+</sup>), aluminum ions (Al<sup>3+</sup>) and hydrogen ions (H<sup>+</sup>) were determined by titration. Summation of these ions gives the cation exchange capacity of the soil.

#### 3.4.1.5: Particle size analysis – Hydrometer method

Soil sample of mass 50 g was weighed into a 250 ml volumetric flask; 50 ml of calgon (a solution of sodium hexametaphosphate, Na<sub>6</sub>(PO<sub>3</sub>)<sub>6</sub> and sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>) and 100 ml of deionised water were added. The suspension was stirred vigorously for 1 minute using a glass rod. The suspension was transferred into a mixer with baffled cups and mixed for 15 minutes at a medium speed. The suspension were transferred into a 1L volumetric flask and made up to the mark with deionised water. The hydrometer was placed into the suspension until it floated and the initial hydrometer reading (H<sub>1</sub>) was taken after 40 seconds. The hydrometer was removed and the initial temperature (T<sub>1</sub> in °F) of the suspension was measured with a thermometer. The final hydrometer (H<sub>2</sub>) and temperature (T<sub>2</sub> in °F) readings were measured after the suspension was left to stand for 3 hours. The respective percentages were calculated according to equations 2-4.

$$\% \text{ Sand} = 100 - [H_1 + 0.2 (T_1 - 20) - 2.0] * 2 \dots \dots \dots \text{Equation 2}$$

$$\% \text{ Clay} = [H_2 + 0.2 (T_2 - 20) - 2.0] * 2 \dots \dots \dots \text{Equation 3}$$

$$\% \text{ Silt} = 100 - (\% \text{ Sand} + \% \text{ Clay}) \dots \dots \dots \text{Equation 4}$$

Where H<sub>1</sub> = hydrometer reading after 40 seconds

$T_1$  = temperature after 40 seconds

$H_2$  = hydrometer reading at 3 hours

$T_2$  = temperature reading at 3 hours

$0.2(T-20)$  = temperature correction to be added to the hydrometer reading -

2.0 = salt correction to be added to hydrometer reading

### 3.4.2 Water samples

#### 3.4.2.1: Measurement of pH, electrical conductivity and total dissolved solids

The pH meter was calibrated with two buffer solutions of pH 4.2 and 7.00. The water sample was placed in a beaker and the electrode was rinsed with distilled water. The electrode was also rinsed with some of the water sample to be measured. The electrode was placed in the beaker and readings were taken after it was stable. The conductivity and the total dissolved solids were determined using PHWE electrical conductivity meter. The instrument was initially calibrated by rinsing the electrode with potassium chloride (KCl). The conductivity of this standard is known to be 1413  $\mu\text{S}/\text{cm}$ . The electrode was rinsed with distilled water and immersed in the water sample for the actual reading. Duplicate values were taken. The total dissolved solids (TDS) of the water samples were determined by selecting the TDS key on the instrument. The TDS value in mg/l displayed on the screen was recorded.

#### 3.4.2.2: Total hardness

A volume of 50 ml of each water sample was pipetted into a 250 ml conical flask and a buffer solution of pH 10 was added. Erichrome Black T (EBT) indicator was added and a violet colour was observed. The sample solution was titrated with 0.1 M EDTA solution to a distinct blue end point.

### 3.4.3 Statistical analysis

Statistical analysis is very useful in providing knowledge and assisting in the interpretation of data. It is widely applied in recent times to investigate the heavy metal concentration, accumulation and the distribution in soils (Qishlaqi and Moore, 2007). Statistical analyses of heavy metal contents in soil samples from Suame magazine were performed using Pearson's correlation analysis, Principal Component Analysis (PCA) by the software package SPSS version 16.0.

#### **A: Pearson correlation analysis**

Inter-element relationships can provide interesting information on element sources and pathways. Pearson's correlation analysis measures the strength of a linear relationship between any two variables on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympathetic relation). In this study, it is employed to identify the relationship between the various heavy metals in soil samples analysed from Suame Magazine industrial area.

#### **B: Principal Component Analysis (PCA)**

PCA is a statistical method aiming at the identification of the principal sources of pollution (Gupta *et al.*, 2014). This powerful method allows identification of the different groups of metals that correlate and thus can be considered as having a similar behaviour and principal sources of pollution. In this study, Principal Component Analysis (PCA) was applied to the large data-set of concentrations of six (6) metals in soil samples from four different zones at Suame Magazine industrial area. The elements coming from the same source can be found all in the same component with a high weight and the component can be associated to that specific source.

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## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 DATA ON SOIL ANALYSIS

##### 4.1.1 Effect of pH and electrical conductivity of soil on metal distribution

Soil pH is a major factor influencing metal chemistry (Gambrell, 1994) and it has great effects on solute concentration and absorption in soil. The availability and mobility of heavy metals are greatly favoured by low soil pH. The results obtained indicate that soil samples in Zones A, C and D are slightly acidic to moderately alkaline. Soil samples from Zone B (i.e. at the sub and bottom of the soil profile) are however moderately acidic to slightly acidic as indicated in Table 4.1. The pH for the control samples were also slightly acidic (6.51, 6.38, 6.02) representing the top, sub and bottom soils respectively. The mobility of the heavy metals in moderately alkaline soils in all the zones will be low, more of the heavy metals will be adsorbed onto the soil and may persist in the environment for a longer time, which may have serious health implications on the artisans and the environment. According to Rhoades, (1982), soils with conductivities values  $> 150 \mu\text{S}/\text{cm}$  are highly saline. The soil samples in all the zones recorded conductivities values in the range 151-1250  $\mu\text{S}/\text{cm}$  as indicated in Table 4.1.

**Table 4.1: pH and conductivity for soil samples expressed as range values**

Soil properties	Soil depth (cm)	Zone A	Zone B	Zone C	Zone D
<b>pH</b>	top (0-10cm)	7.25-7.62	6.45-7.76	6.98-8.37	7.56-7.76
	sub (10-20cm)	6.78-7.48	5.41-7.60	6.85-8.25	7.55-7.95
	bottom (20-30cm)	6.45-7.21	3.68-7.55	6.78-7.80	7.38-8.02
<b>Control samples</b>	0-10-cm	6.51			
	10-20 cm	6.38			
	20-30 cm	6.02			
<b>Conductivity</b>	0-10cm	252-692	154-782	328-1250	369-537
	10-20cm	175-644	162-564	297-556	358-502
	20-30cm	151- 823	164-338	225-441	351-687
<b>Control samples</b>	0-10-cm	110			
	10-20 cm	103			
	20-30 cm	89			

Analysis of the soil samples from the different zones revealed that conductivities of soil samples are higher as compared to 110, 103, 89  $\mu\text{s}/\text{cm}$  for the control samples representing the top, sub and bottom soils respectfully. This finding is in-line with the study done by Akpoveta *et al.*, (2010) for automobile dumpsites at Agbor and Abraka in Nigeria.

The high conductivity may be attributed to the availability of a high amount of metal substances in the wastes at the auto-mobile shops whose content are eventually leached into the underlying soils. The pH and the conductivity values of the soils in almost all the soil samples from the various zones decreased with depth. In general, sorption increases with increasing pH, the lower the pH value, the more the metal can be found in solution. The pH and the conductivity of the soil samples from maintenance shops and spraying shops in Zone D, metal fabrication shops in Zone C, spraying shops in Zone B and D increased with depth. This can be attributed to the oxidation states of certain heavy metals. The conductivity of a heavy metal which is proportional to the mobility and metal concentration is highly dependent on the redox state. For example arsenic (As) generally occurs in soils in two oxidation states:  $\text{As}^{3+}$  in arsenite primarily as  $\text{As}(\text{OH})_3$ ,

As<sup>5+</sup> in arsenate (such as H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>). The As<sup>3+</sup> forms are significantly more mobile and toxic in the environment than the As<sup>5+</sup> species (Rajaković *et al.*, 2013).

#### 4.1.2: Effect of moisture content of soil on metal distribution

In soils, oxidizing conditions favour the retention of metals while reducing conditions accelerate the migration of metals. The soil samples from maintenance shops across all the zones were very low as indicated in Figure 4.1; and can be attributed to the low permeability and low infiltration of water in the spent lubricating oil polluted soil in the various maintenance shops. This can be attributed to the low permeability and low infiltration of water in the spent lubricating oil polluted soil in the various maintenance shops. The moisture content decreased gradually with depth in all the four different zones.

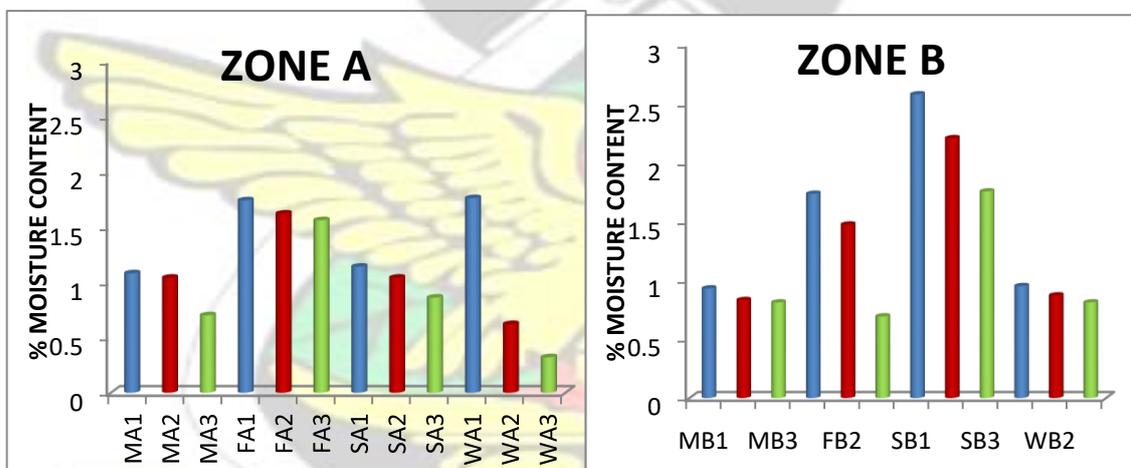
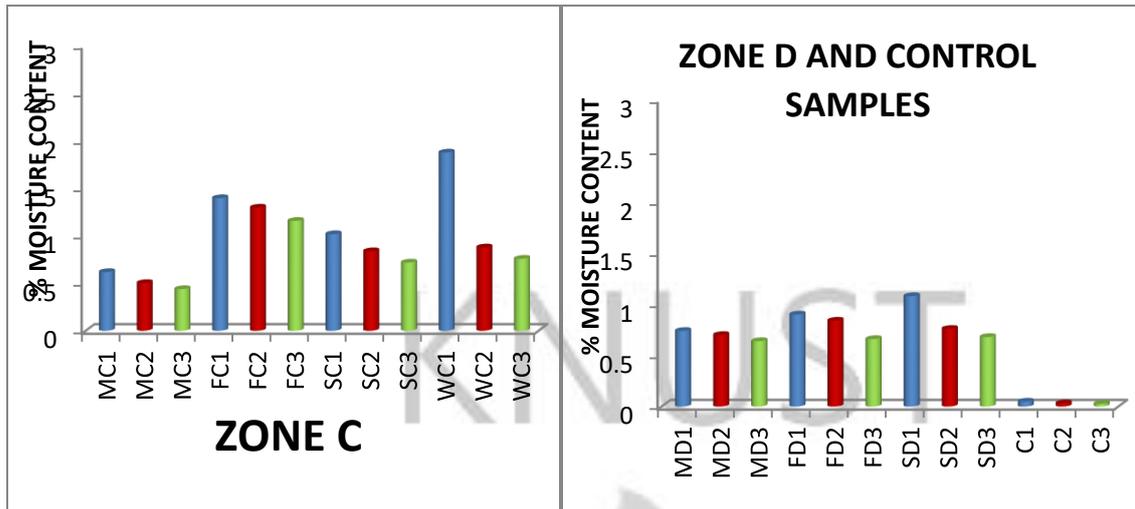


Figure 4.1a: Percent moisture content of soil samples from different zones

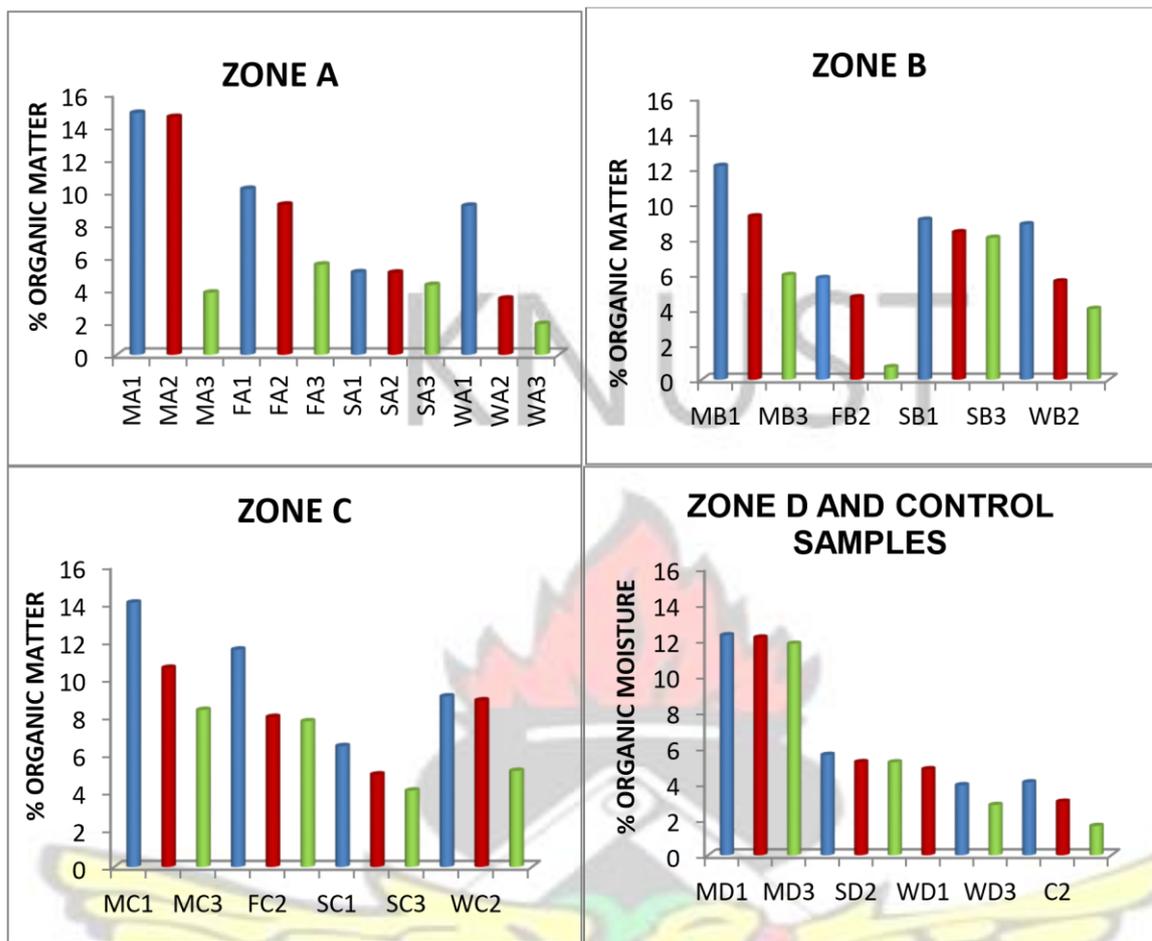


**Figure 4.1b: Percent moisture content of soil samples from different zones**

M=Maintenance      A= zone A      1 = 0-10 cm      C1=Control sample at 0-10cm  
 F=Metal fabrication      B= Zone B      2 = 10-20 cm      C2=Control sample at 10-20 cm  
 S=Spraying      C= Zone C      3 = 20-30 cm      C3=Control sample at 20-30cm  
 W=Welding      D= Zone D

#### 4.1.3: Effect of organic matter content of soil on metal distribution

The organic matter content of the soil samples are shown in Figure 4.2. The percent organic matter contents for the studied samples were high compared to those of the control samples (4.06%, 2.98% and 1.63%) representing the top, sub and bottom samples respectively. Percent organic matters for maintenance shops are highest for all the zones. The high percent organic matter content may be attributed to the indiscriminate disposal of spent lubricants on the soil at maintenance shops which may have contributed to increased organic carbon in addition to the carbon already present in the soil.

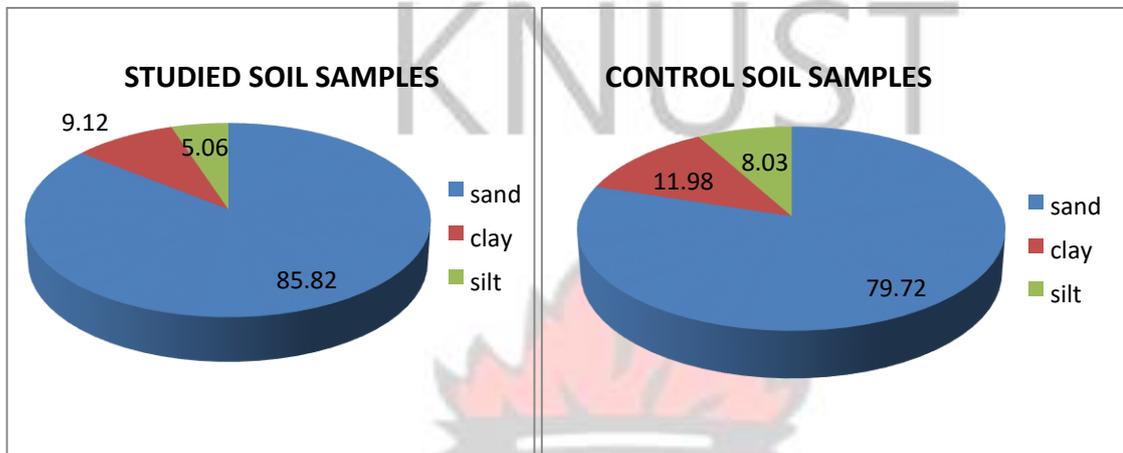


**Figure 4.2: Percent organic matter content (OM) of soil samples from different zones**

All soil samples from the four different zones coming from the bottom of the soil (20-30 cm) depth have the lowest organic matter content; thus the percent organic matter content decreased with soil depth. This is to be expected since the natural organic components of the soil contain organic functional groups such as carboxyl or phenolic based groups which have high affinity for heavy metals decreasing the mobility and availability of heavy metals down the soil profile. The percent organic matter decreases with depth of the soil profile.

#### 4.1.4: Effect of soil texture and particle size on metal distribution

The particle size distribution for soil samples at the different depth in all the four zones and the control samples contains a high percentage of sand followed by clay and silt as shown in Figure 4.3a and 4.3b.



**Figure 4.3a: Average particle size distribution (% sand, % clay, % silt) in studied and control soil samples**

The amount of heavy metals retained in the soil depends not only on the metal concentration and redox state of the metal but also the soil type and texture. Soil texture plays an important role in the mobility of heavy metals in the soil. Soils with high clays/ fine content can retain significant amount of the metal contaminant while sandy soils will enhance the transport of the contaminants. From the results, it can be inferred that adsorption of heavy metals on the soils due artisanal activities at Suame Magazine industrial area may be low and the transport of these metals are likely to occur.

#### 4.1.5: Effect of cation exchange capacity of the soil on metal distribution

The cation exchange capacity of all the soil samples in the different zones as well as the control samples were  $< 25$  meq/ 100g. Soil samples from maintenance shops across all zones contain the highest cation exchange capacity as presented in Table 4.2

**Table 4.2: Cation Exchange Capacity in meq/100 g for soil samples**

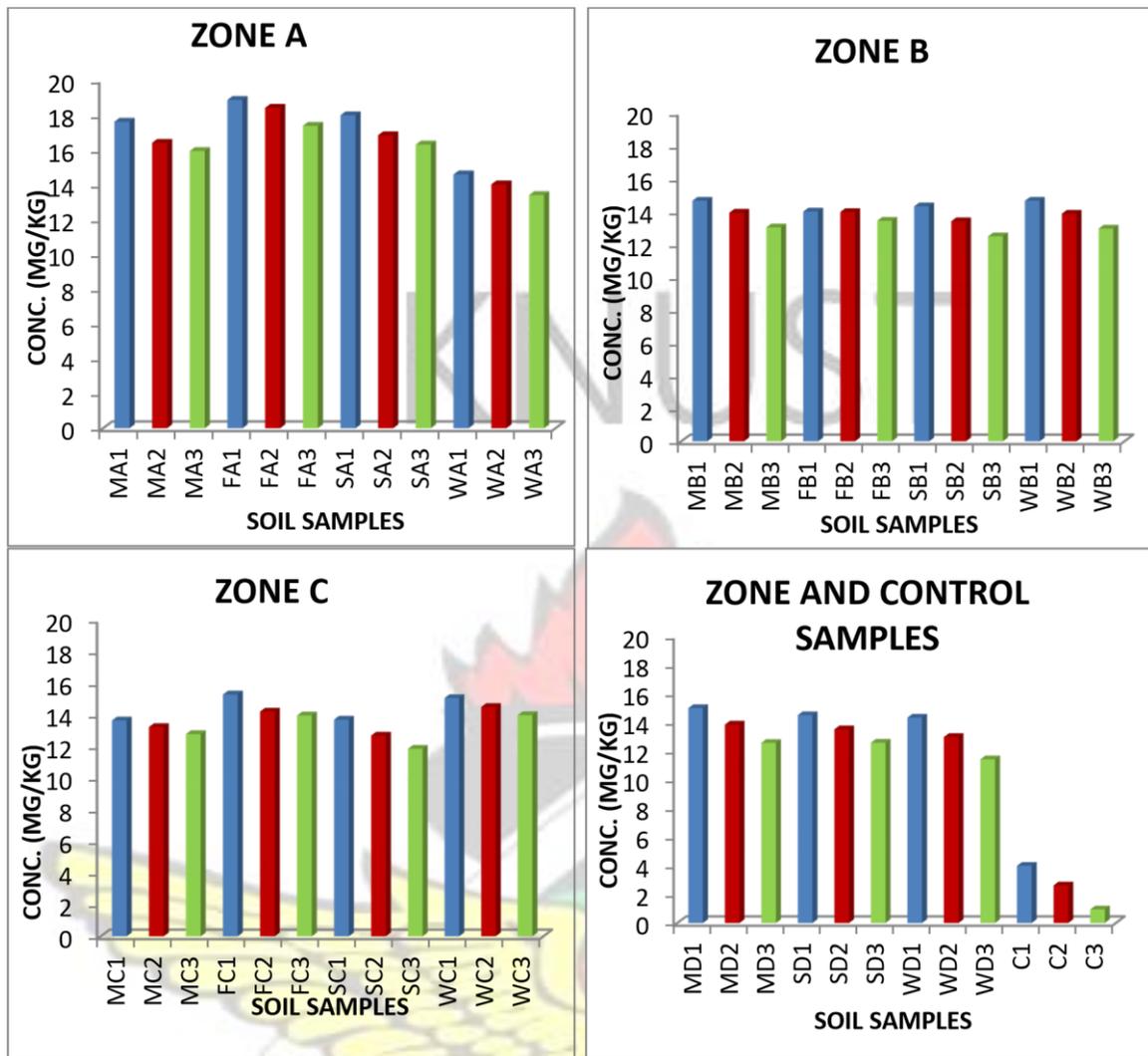
Soil properties	Soil depth (cm)	Zone A	Zone B	Zone C	Zone D
<b>Maintenance shop</b>	0-10cm	17.23	15.86	15.54	14.96
	10-20cm	16.98	13.42	13.67	14.54
	<u>20cm-30cm</u>	15.74	12.08	12.28	13.62
	<b>Average</b>	<b>16.65</b>	<b>13.78</b>	<b>13.81</b>	<b>14.37</b>
<b>Metal fabrication shop</b>	0-10cm	12.08	10.29	11.15	10.71
	10-20cm	11.72	10.13	10.78	9.92
	20cm-30cm	11.06	8.64	10.62	9.03
	<b>Average</b>	<b>11.62</b>	<b>9.68</b>	<b>10.85</b>	<b>9.88</b>
<b>Spraying shop</b>	0-10cm	8.65	9.78	6.72	9.65
	10-20cm	7.54	7.92	5.23	6.80
	<u>20cm-30cm</u>	6.93	6.15	3.38	6.27
	<b>Average</b>	<b>7.71</b>	<b>7.95</b>	<b>5.11</b>	<b>7.57</b>
<b>Welding shop</b>	0-10cm	7.18	6.74	8.95	7.75
	10-20cm	6.89	5.92	8.31	5.86
	<u>20cm-30cm</u>	6.36	4.03	6.62	5.31
	<b>Average</b>	<b>6.81</b>	<b>5.56</b>	<b>7.96</b>	<b>6.29</b>
<b>Control samples</b>	0-10cm	6.49			
	10-20cm	5.88			
	<u>20cm-30cm</u>	5.16			
	<b>Average</b>	<b>5.84</b>			

The organic matter content and the amount of clayey soil are the two main factors for determining the cation exchange capacity of the soil. Therefore, high CEC in maintenance shops can be related to its high organic matter content (organic carbon from the spent lubricants). Based on the total soils examined; it can be seen that the clay mineral and organic components of the studied samples have low negative charged sites (such as NO<sub>3</sub>, SO<sub>4</sub>, Cl<sup>-</sup>) on their surfaces, thus the potential to absorb and hold positively charged ions (cations) through electrostatic attraction will be low indicating that transport of metals will be high.

## 4.2 HEAVY METAL CONCENTRATIONS

### 4.2.1 Trend of copper distribution in the soil samples

Copper (Cu) was present in all the soil samples from the different depth of the soil profile in the four zones (A, B, C and D) that were investigated. The concentration of copper in the soil samples decreased with depth in the different artisanal shops (maintenance, metal fabrication, spraying and welding in all the four zones. The highest concentration of copper in Zone A and C was recorded in soil samples from metal fabrication shops ( $18.88 \pm 0.23$ ,  $18.43 \pm 0.16$ ,  $17.39 \pm 0.21$ ) mg/kg and ( $15.30 \pm 0.25$ ,  $14.21 \pm 0.86$ ,  $13.97 \pm 0.57$ ) mg/kg representing the top (0-10 cm), sub (10-20 15.301) and bottom (20-30 respectively. In Zone B and D, the highest concentration of copper was present in soil samples from maintenance shops ( $14.66 \pm 0.31$ ,  $13.94 \pm 0.53$ ,  $13.04 \pm 0.28$ ) mg/kg and ( $15.01 \pm 0.28$ ,  $13.86 \pm 0.94$ ,  $12.58 \pm 0.67$ ) mg/kg representing top, sub and bottom of the soil profile. In Ghana no standard limit has been set for copper, therefore maximum allowable limits set by countries like Australia, Canada and others were used in the discussion. Although these values were below the maximum allowable limit (100 mg/kg) in Australia, Canada, Poland, Britain, Japan (125 mg/kg), and Germany (50 mg/kg) (Lacatusu, 2000) and also the toxic limit of 250 mg/kg set by USEPA (1986) for agricultural soils, these values are higher than those at the various control sites (4.00, 2.63, 0.95) mg/kg representing the top, sub and bottom soils respectively.

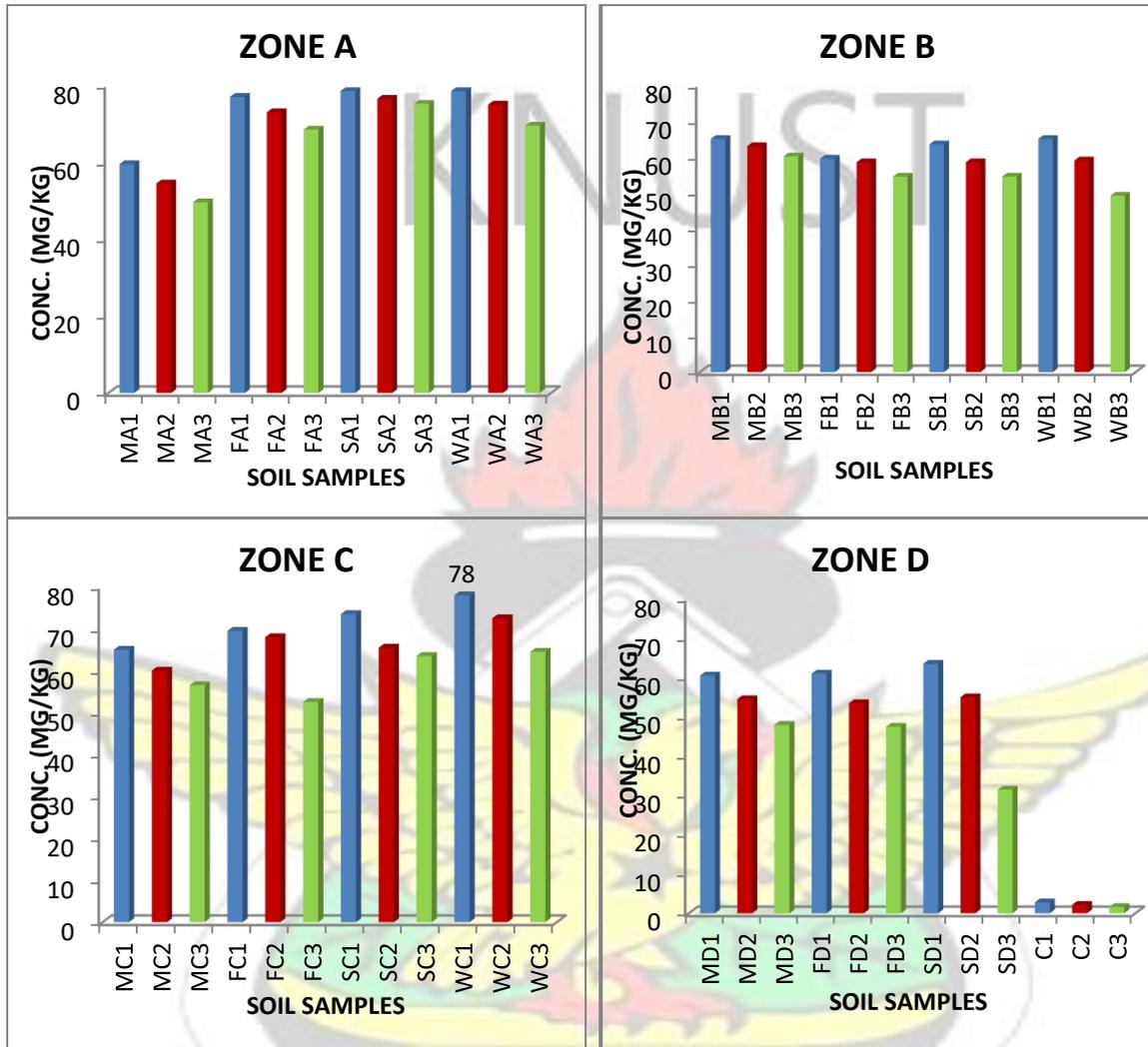


**Figure 4.4: Trend of copper levels in soil samples at different depth of the soil profile from the different zones (A, B, C, and D)**

The soils in this study exhibited elevated levels of contamination than 7.21 mg/kg reported by Akoto *et al.*, (2008) as shown in Figure 4.4. The high levels of copper on the top soil in the different auto-mechanic shops may be attributed to the high use of copper conductors and wires, tubes, solders and alloys from corroding vehicle scraps which have littered the vicinity of these clusters for a long time, with metals released from the corrosion gradually leaching into the soil (Nwachukwu *et al.*, 2011). Copper concentration decreases with depth of the soil profile.

#### 4.2.2 Trend of cadmium distribution in the soil samples

Soil samples at different depth of the soil profile show elevated levels of cadmium in all the four zones with the concentration of cadmium in the soil sample decreasing with depth as shown in Figure 4.5.



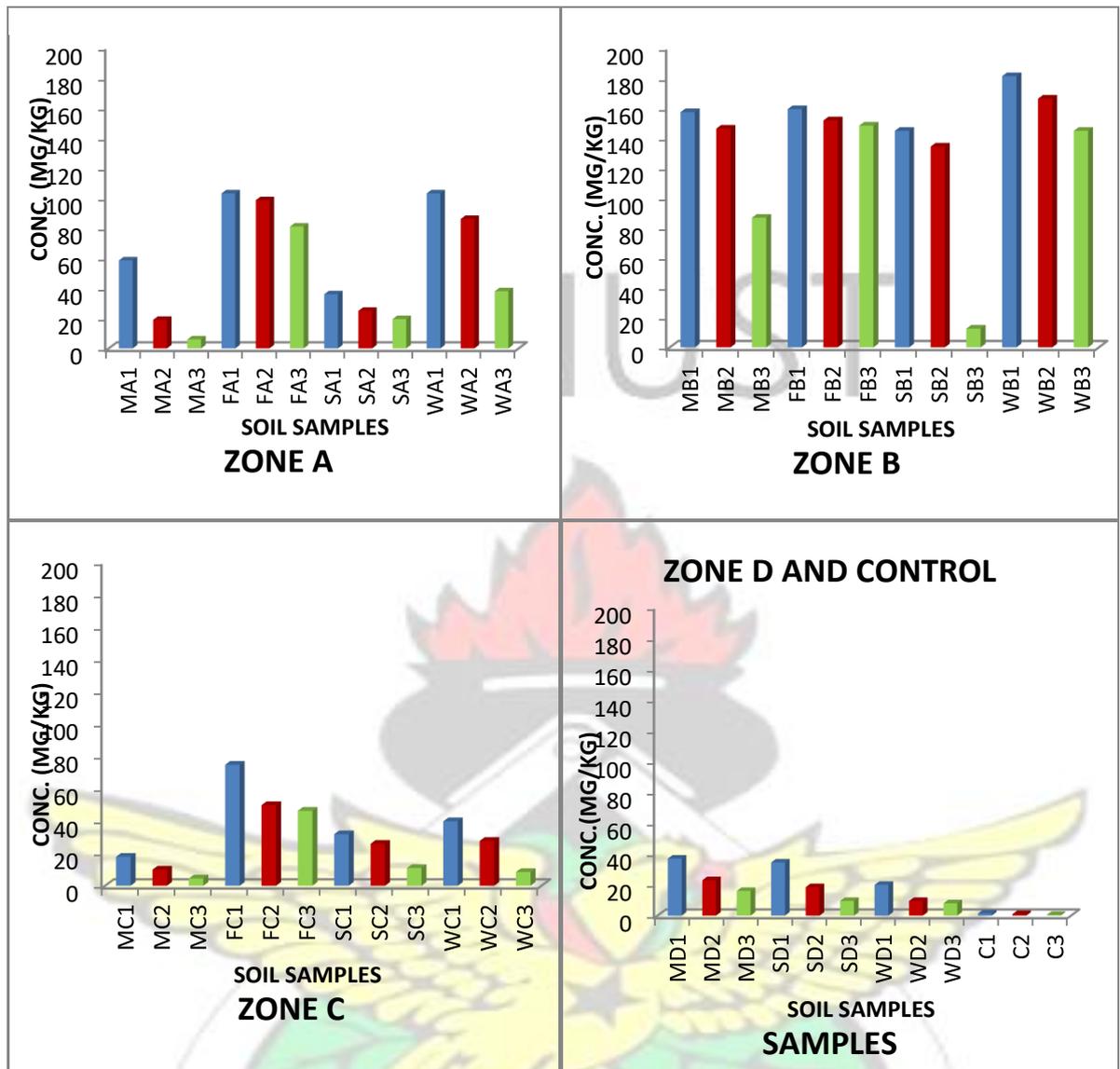
**Figure 4.5: Trend of cadmium (Cd) levels in soil samples at different depth of the soil profile from the different zones (A, B, and C, D)**

Soil samples from spraying shops in Zone A and C had the highest concentration of cadmium ( $78.5 \pm 0.01$ ,  $76.5 \pm 0.25$ ,  $75.2 \pm 0.09$ ) mg/kg and ( $78 \pm 0.79$ ,  $72.5 \pm 0.56$ ,  $64.5 \pm 0.28$ ) mg/kg. In Zone B, the highest concentration of cadmium was recorded in maintenance shops ( $65.00 \pm 0.34$ ,  $63.00 \pm 0.16$ , and  $60.13 \pm 0.37$ ) mg/kg representing the top, sub and bottom respectively. The highest concentration of cadmium in soil samples in Zone D was recorded in welding shops ( $63.5 \pm 0.62$ ,  $55 \pm 0.29$ ,  $31.5 \pm 0.41$ ) mg/kg as indicated in Figure

4.5. The values are higher than the control site (2.80 mg/kg, 2.15 mg/kg, and 1.60 mg/kg) and can be attributed to the artisanal activities at Suame magazine. Also the values were higher than the acceptable limits of 50 mg/kg in Germany (Lacatusu, 2000). The result of Cd concentration recorded in this study agrees with what was obtained in a similar study by Uba *et al.*, 2008 who reported a higher concentration of Cd in refuse dumpsites soils. Nevertheless, the Cd concentration was inconsistent with that of Luter *et al.*, 2011 who investigated heavy metals in soils of auto-mechanic shops and refuse dump sites in other parts of Makurdi, Central Nigeria and reported a range of 0.6 - 3.5 mg/kg. The accumulation of Cd in the areas studied is likely to come from lubricating oils, vehicle wheels and metal alloys used for hardening of engine parts (Dabkowska and Naskret, 2004) and nickel-cadmium batteries, and disposal sludge on the dumpsites (Jarup, 2003, Ebong *et al.*, 2008).

#### **4.2.3 Trend of zinc distribution in the soil samples**

Soil samples in welding shops in Zone B recorded the highest concentration of zinc ( $181.00 \pm 0.18$ ,  $166.00 \pm 0.09$ ,  $144.50 \pm 0.47$ ) mg/kg representing the top, sub and bottom respectively as shown in Figure 4.6, and the zinc concentration decreased down the profile at each sampling point. The highest concentration of zinc in soil samples from Zone A was found in welding shops and in Zone D, maintenance shops had the highest concentration. These values are far higher than those at the control site (1.40 mg/kg, 0.96 mg/kg, and 0.51 mg/kg) and suggest that, there is anthropogenic contribution to the levels.

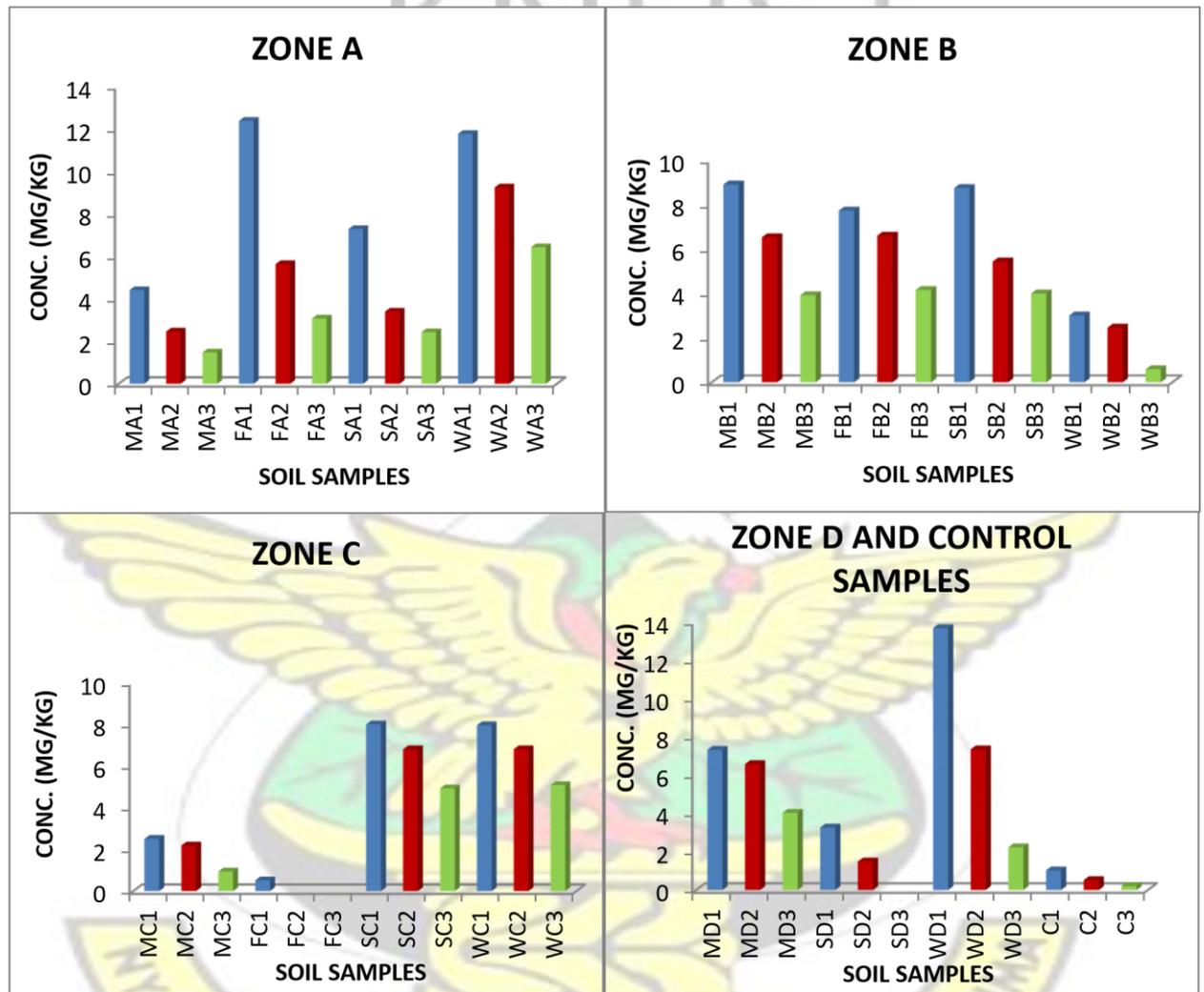


**Figure 4.6: Trend of Zinc (Zn) in soil samples at different depth of the soil profile from the different zones (A, B, C, D)**

The elevation of zinc levels may be attributed to the use of zinc based additives such as zinc dithiophosphate (ZnDTP) and zinc dialkyldithiophate (ZDDP) to prevent corrosion, anti-wear additive and to keep engines running longer. However, the concentration of Zn in this investigation is lower compared with many other studies (Nwachukwu *et al.*, 2010; Nwachukwu *et al.*, 2011 and Shinggu *et al.*, 2007) which recorded very high concentrations of zinc.

#### 4.2.4 Trend of arsenic distribution in the soil samples

Soil samples from metal fabrication shops in Zone A and maintenance shops in Zone B recorded the highest concentration of arsenic as  $(12.405 \pm 0.67, 5.655 \pm 0.78, 3.085 \pm 0.51)$  mg/kg and  $(8.915 \pm 0.52, 6.540 \pm 0.59, 3.935 \pm 0.36)$  mg/kg respectively.



**Figure 4.7: Trend of arsenic (As) in soil samples at different depth of the soil profile from the different zones (A, B, C, D)**

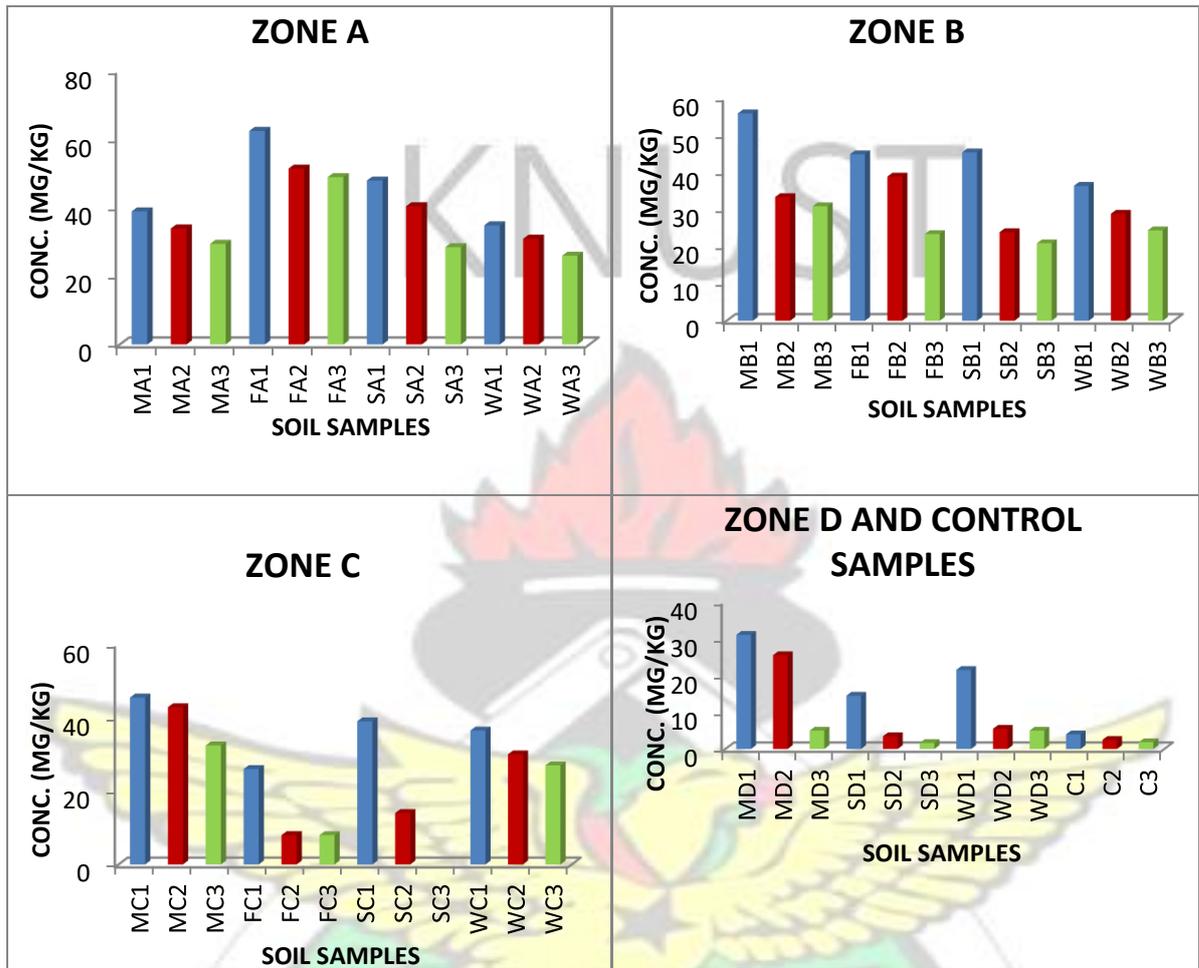
Although these values were below the maximum allowable limit (100 mg/kg) in Australia, Canada, Poland, Britain, Japan (125 mg/kg), and Germany (50 mg/kg) (Lacatusu, 2000) and also the toxic limit of 250 mg/kg set by USEPA (1986) for agricultural soils, these values are higher than those at the control site (1.03 mg/kg, 0.52

mg/kg and 0.21 mg/kg) and suggest that, there is anthropogenic contribution to the levels obtained except in Zone C where arsenic concentration was below detection at 10-20 cm and 20-30 cm. The values of As obtained in this study were higher than 0.13- 0.71 mg/kg reported by Emmanuel *et al.*, 2014 in soils around oil filling and service stations in the Tamale metropolis. The concentration of As fall within the values reported by Chaoyang *et al.*, 2009 (2.466-422) mg/kg in soil from mining-smelting activities in Shuikoushan, Hunan Province, China. High arsenic levels may result in lung, kidney, bladder and skin disorders.

#### **4.2.5 Trend of lead distribution in the soil samples**

The highest concentrations of lead (Pb) obtained at the different depth of the soil profile in zone A was recorded in soil samples from metal fabrication shops (62.50±0.56, 51.50±0.38, 49.00±0.62) mg/kg. Soils samples from the three other Zones (B, C, D) recorded highest concentration in maintenance shops (56.00±0.28, 33.50±0.46, 31.00±0.21) mg/kg, (45.50±0.36, 42.85±0.68, 32.45±0.42) mg/kg and (31.05± 0.59, 25.50±0.27, 5±0.09) mg/kg respectively representing the top (0-10 cm), sub (10-20 cm) and bottom (20-30 cm) of the soil profile as shown in Figure 4.8. The values of Pb obtained in this study were lower than the 1162 mg/kg reported by Nwachukwu *et al.*, 2011 for auto mechanic workshop in the Owerri area, South-East Nigeria, 501.58 mg/kg reported by Udousoro *et al.*, 2010 in South-South Nigerian; and those in industrial areas in North West Nigeria (151.50 – 540.00) mg/kg. The values obtained in this study were higher than those at the control sites (4.00, 2.50, and 1.85) mg/kg. The USEPA, (2008) considered Pb to be hazardous when it exceeds 400 mg/kg on bare soils, thus implying that the content of Pb at the different Zones (A, B, C and D) were far below the maximum limit of Pb content on

bare soil. Although the concentration is very low, long term exposure can have serious implications on the health of artisans at Suame Magazine industrial area.



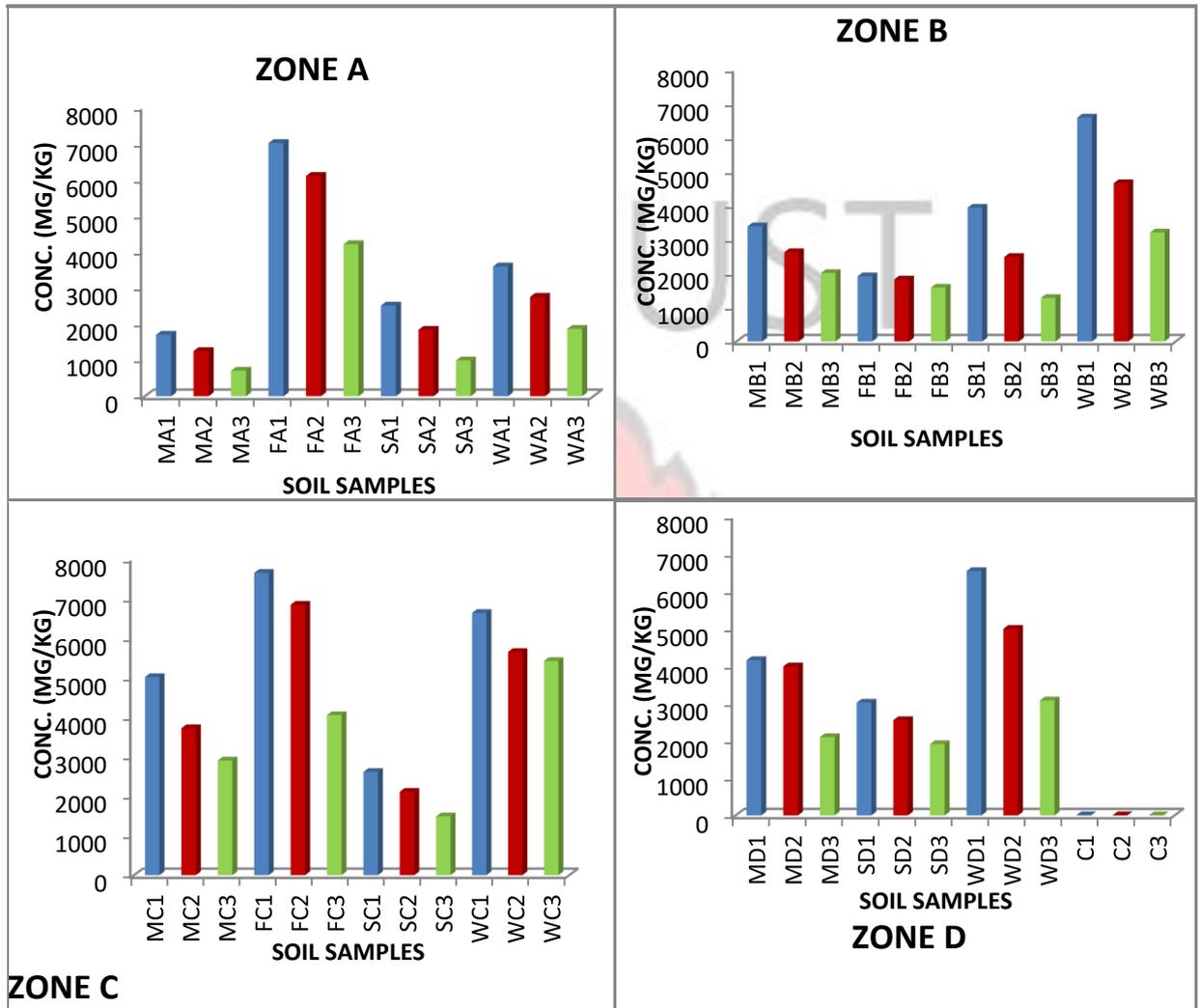
**Figure 4.8: Trend of lead (Pb) levels in soil samples at different depth of the soil profile from the different zones (A, B, C and D)**

The increase in the value of Pb could have resulted from Pb containing compounds such as batteries, vanishes, and paints used at the workshop (Abidemi, 2011; Adelekan and Abegunde, 2011). In addition, the amount of waste oil, presence of automobile emissions, and expired motor batteries indiscriminately dumped by battery chargers and auto mechanics in the surrounding areas can contribute to high levels of lead.

#### 4.2. 6 Trend of iron distribution in the soil samples

Iron was present in all the soil samples that were analysed and recorded the highest concentration among the other heavy metals (copper, cadmium, zinc and lead). The highest

concentration of iron was present in soil samples from metal fabrication shops in Zone (A and C) and welding shops in Zone (B and D).

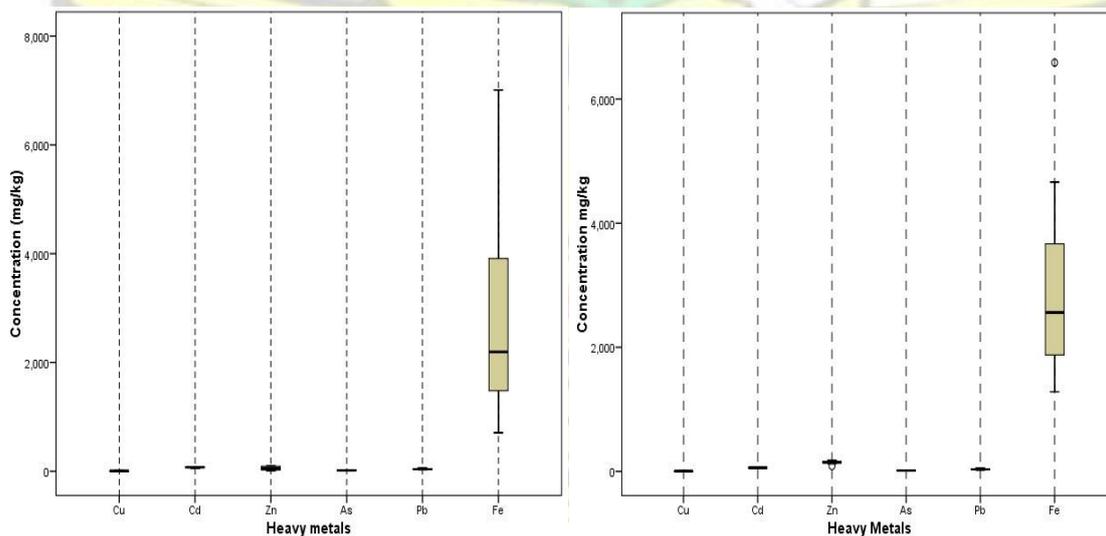


**Figure 4.9: Trend of iron (Fe) levels in soil samples at different depth of the soil profile from the different zones (A, B, and C, D)**

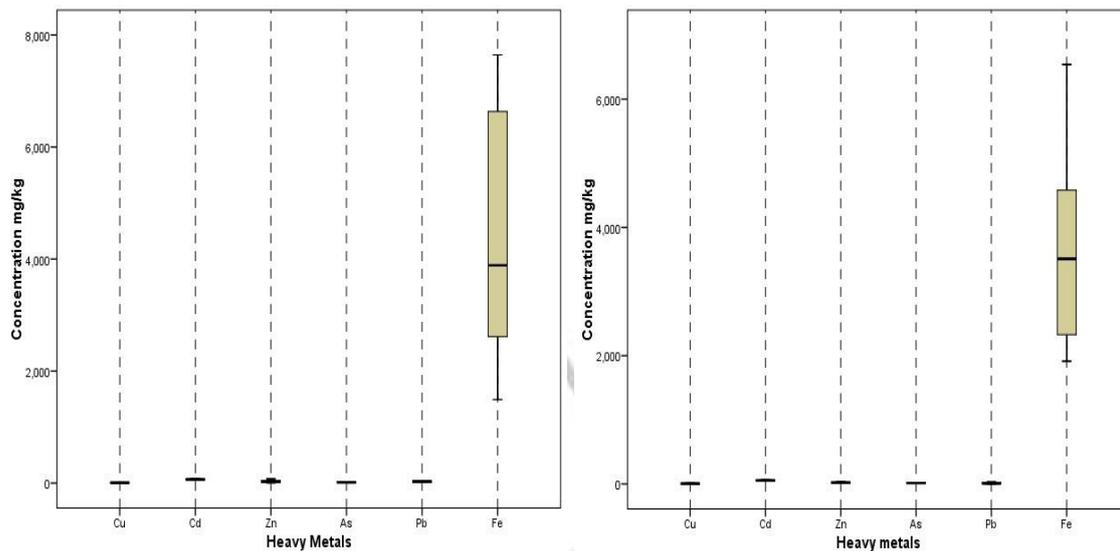
The results from the studies show higher values than those from the control site (7.40 mg/kg, 5.85 mg/kg, and 4.05 mg/kg) as shown in Figure 4.9. This result was however higher than the result obtained by Adewole and Uchegbu (2010) (1564-1238 mg/kg). Dumping of iron scraps, hydraulic fluid, unused body parts of vehicles, spent lubricants, tin can and solvents can contribute to elevated levels of iron on the soil at these workshops (Ayeni, 2010; Abidemi, 2011).

#### 4.2.7 Levels of heavy metals in each zone

The multiple box and whisker plots show the statistical distribution of heavy metal concentrations in the Suame magazine industrial area. Boxplots summarize information about the shape, dispersion, and center of the data and can also help spot outliers. The rectangular part of the plot extends from the 1st quartile to the 3rd quartile, which cover the central half of the concentrations of each element, representing 50% of the values. The central line within each box shows the location of the median concentration of each element. The whiskers extend on either side of the box up to 1.5 times the interquartile range; outliers are plotted as individual points (+). From the results no outliers were obtained. All studied elements have high concentrations, and the greatest in all the zones is shown by Fe in Figure 4.10a and 4.10b. The heavy metal concentration for the six metals is in the order  $Fe > Zn > Cd > As > Pb > Cu$ .



**Figure 4.10a: Boxplots showing heavy metal concentration (mg/kg) in Zone A and Zone B**

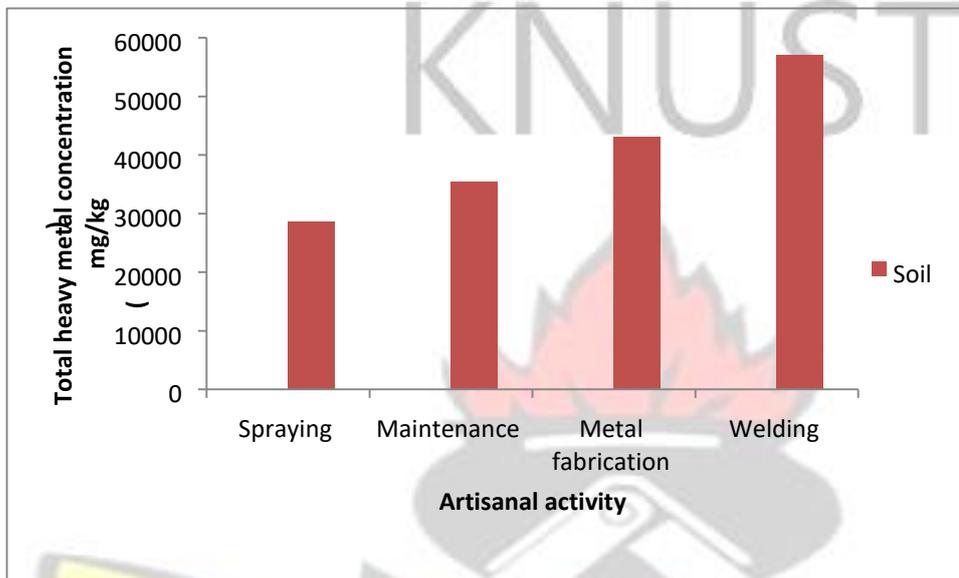


**Figure 4.10b: Boxplots showing heavy metal concentration (mg/kg) in Zone C and Zone D**

#### **4.2.8: Total levels of heavy metal concentration in soil samples from the four artisans shops**

In Ghana and most developing nations, increased automobile repairs/workshops activities (spraying, welding, metal fabrication etc) are due to ever-increasing demand for personal and commercial vehicles. These activities contribute to the generation of hazardous waste such as spent lubricants, hydraulic fluids, worn-out parts, packaging materials, metal scraps, used batteries, discarded cans and stripped oily sludge (Chaney *et al.*, 1999) which may contain heavy metals and hydrocarbons. The high level of heavy metal concentration was recorded in welding shops and metal fabrication shops (57086.32 mg/kg and 43197.63 mg/kg) respectively as shown in Figure 4.11; and this can be attributed to worn-out parts, soldering, machinery wear and metal scraps. Maintenance shops also showed significant total heavy metal concentration of 35522.99 mg/kg and can be related to the indiscriminate disposal of spent lubricants, spent hydraulic fluids, engine and gear box recycling and used batteries on the soil; for example lubricating oils contain anti-wear and antioxidant additives such as zinc dialkyl dithiophosphate (ZnDDP) which undergoes chemical

degradation releasing zinc (Zn), sulphur (S) and phosphorous (P). Also wear and tear of the metal parts of the engine can release heavy metals into the spent oil. Paints used for spraying vehicles at automobile shops contain trace amount of heavy metals and may account for the low concentration of heavy metals in the spraying shops.



**Figure 4.11: Average total heavy metal concentration (mg/kg) in combined soil samples from different depth from four artisanal activities at Suame Magazine industrial area**

### 4.3. INDICES OF POLLUTION

#### 4.3.1 Parameters for assessing pollution

Assesment of heavy metal contamination at at Suame Magazine industrial area offers some insight into the levels of contamination of the soils in automobile shops within the vicinity.

Data obtained were compared with those from the control sample points, taken as control or reference values. Various quantitative indices such as contamination factor, (CF), pollution load index (PLI), geoaccumulation index (Igeo) and quantification of concentration of anthropogenic metal (QoC) have been employed to assess the impact of human activities on heavy metal contamination in soils located within the Suame magazine industrial area.

**A: Contamination factor (CF)**

The first approach is using the Contamination factor to assess the degree of anthropogenic influence (Fagbote and Olanipekun, 2010). (CF) which is calculated according to the equation 5

$$\text{Contamination factor} = \frac{\text{Concentration of sample from the study area}}{\text{Concentration of control or reference sample}} \dots\dots\dots \text{Equation 5}$$

**Table 4.3: Categories of contamination factors**

Contamination factor	Category
CF <1	Low contamination factor
1 <CF <3	Moderate contamination factor
3 < CF < 6	Considerable contamination factor
CF >6	Very high contamination factor

(Hakanson, 1980; Dasaram *et al.* (2010))

**Table 4.4a: Average Contamination factors (CF) of heavy metals in soils in Zone A from automobile shops at Suame magazine industrial area (n=12)**

SAMPLE ID	Cu	Cd	Zn	As	Pb	Fe
MA1	2.87	31.00	61.39	32.16	16.76	230.74
MA2	2.27	25.34	20.30	16.73	13.60	214.70
MA3	1.56	21.25	11.76	13.77	9.75	175.10
FA1	8.06	42.83	158.82	35.07	20.60	1043.00
FA2	5.19	33.95	105.2	18.78	15.61	1041.00
FA3	3.59	27.50	73.10	14.75	12.70	947.29
SA1	9.76	47.00	38.23	32.91	16.20	340.00
SA2	3.13	35.58	26.71	17.17	12.00	315.00
SA3	2.21	27.67	25.90	14.06	11.35	245.00
WA1	8.51	43.43	91.88	27.07	97.00	486.89
WA2	7.66	34.00	74.50	14.30	12.40	471.96
WA3	6.79	28.00	73.10	11.42	8.73	461.48

**Table 4.4b: Average Contamination factors (CF) of heavy metals in soils in Zone B from automobile shops at Suame magazine industrial area (n=12)**

SAMPLE ID	Cu	Cd	Zn	As	Pb	Fe
MB1	9.34	37.57	169.65	26.29	16.76	497.77
MB2	6.07	29.30	155.98	14.12	14.00	458.14

<b>MB3</b>	5.79	23.21	111.43	11.45	13.40	449.74
<b>FB1</b>	6.06	34.06	290.19	27.09	15.60	391.85
<b>FB2</b>	5.03	27.21	161.86	14.23	12.70	312.82
<b>FB3</b>	4.39	21.25	112.85	10.94	11.25	259.59
<b>SB1</b>	5.68	33.44	244.12	25.19	11.35	519.32
<b>SB2</b>	5.00	27.20	143.16	13.66	11.29	425.98
<b>SB3</b>	4.23	20.89	102.5	11.19	9.60	316.79
<b>WB1</b>	2.27	36.87	283.00	26.14	13.24	890.00
<b>WB2</b>	1.96	27.44	177.35	14.12	11.60	797.09
<b>WB3</b>	0.61	21.07	128.46	11.45	9.13	793.08

**Table 4.4c: Average Contamination factors (CF) of heavy metals in soils in Zone C from automobile shops at Suame magazine industrial area (n=12)**

<b>SAMPLE ID</b>	<b>Cu</b>	<b>Cd</b>	<b>Zn</b>	<b>As</b>	<b>Pb</b>	<b>Fe</b>
<b>MC1</b>	2.02	37.58	12.78	25.81	17.89	986.66
<b>MC2</b>	1.60	29.30	10.68	13.49	17.14	677.73
<b>MC3</b>	0.99	23.44	8.82	10.67	11.38	536.50
<b>FC1</b>	0.34	34.06	59.18	28.18	6.50	1169.23
<b>FC2</b>	nd	27.20	53.42	14.47	4.96	1033.12
<b>FC3</b>	nd	21.25	51.23	11.95	4.02	1000.00
<b>SC1</b>	6.26	33.44	27.78	23.93	9.75	630.00
<b>SC2</b>	5.26	27.20	22.71	12.93	5.60	361.00
<b>SC3</b>	5.02	20.89	21.56	10.71	0.24	305.00
<b>WC1</b>	6.26	36.87	29.38	28.22	14.59	1235.42
<b>WC2</b>	5.37	27.44	28.39	14.78	12.00	965.81
<b>WC3</b>	5.18	21.07	16.67	11.77	9.13	896.62

**Table 4.4d: Average Contamination factors (CF) of heavy metals in soils in Zone D from automobile shops at Suame magazine industrial area (n=12)**

<b>SAMPLE ID</b>	<b>Cu</b>	<b>Cd</b>	<b>Zn</b>	<b>As</b>	<b>Pb</b>	<b>Fe</b>
<b>MD1</b>	6.06	30.00	31.37	14.12	10.20	683.07
<b>MD2</b>	4.78	25.34	26.26	11.73	7.76	562.57
<b>MD3</b>	4.26	21.61	24.57	6.80	2.70	518.52
<b>FD1</b>	*	*	*	*	*	*
<b>FD2</b>	*	*	*	*	*	*
<b>FD3</b>	*	*	*	*	*	*
<b>SD1</b>	6.77	29.69	24.13	13.77	14.40	472.22
<b>SD2</b>	2.13	24.88	19.76	11.33	8.92	436.75
<b>SD3</b>	nd	21.78	18.63	6.80	3.63	408.78
<b>WD1</b>	8.89	25.59	14.19	14.77	5.37	883.78
<b>WD2</b>	6.78	22.65	10.15	11.76	2.70	854.71
<b>WD3</b>	2.36	19.68	7.45	7.54	2.20	741.23

“nd” means not detected”.\* means no sample from metal fabrication shops

Contamination factors for Cu, As and Fe decreased with the depth of the soil profile;thus

these heavy metals maybe adsorbed to the soil surface limiting its mobility down the soil

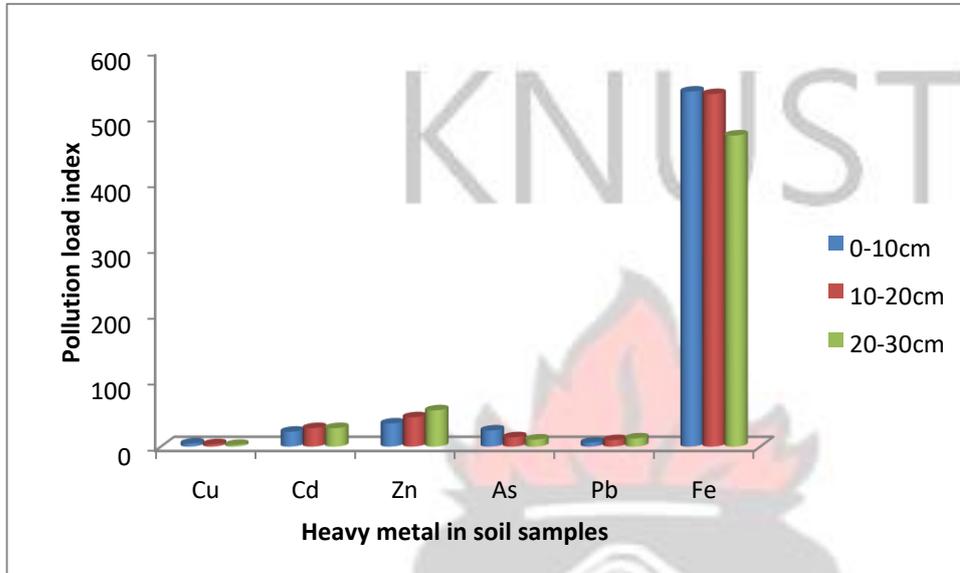
profile. Therefore, the topsoil may contain high levels of Cu, As and Fe. Contamination factors for Cd, Zn and Pb increased with the depth of the soil profile. Soils in all the zones (A, B, C and D) show high contamination factors for all the heavy metals (Cu, Cd, Pb, Zn, As, and Fe) ranging from moderate contamination ( $1 < CF < 3$ ) to very high contamination ( $6 < CF$ ). The high values of contamination factors (CF) in Table 4.4a, 4.4b, 4.4c, 4.4d for Cu, Cd, Zn, As, Pb and Fe, is a clear indication that the contamination of the soils in the vicinity of the Suame Magazine industrial area originates from human activities such as (spraying, welding and fabricating of metallic substances) most probably in the auto mechanic workshops. The order of anthropogenic inputs in the investigated soil samples from automobile shops in all the zones is  $Fe > Zn > Cd > As > Pb > Cu$ .

#### **B: Pollution load index**

The extent of heavy metal contamination for Suame Magazine industrial area was evaluated by employing the method based on the pollution load index (PLI) developed by Thomilson *et al.*, (1980), according to equation 6.

$PLI = (CF_1 * CF_2 * CF_3 * CF_4 * \dots * CF_n)^{1/n}$  ..... Equation 6 Where n is the number of metals studied and CF is the contamination factor. In this study the contamination factor for each metal in the soil samples from the four (4) different zones at Suame magazine industrial area were calculated. The pollution load index was calculated based on the contamination factor for each metal in the four (4) zones. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI  $< 1$  denote perfection; PLI = 1 present that only baseline levels of pollutants are present and PLI  $> 1$  would indicate deterioration of site quality (Thomilson *et al.*, 1980).

All the soil samples (n=45) recorded PLI values greater than 1 indicating deterioration of site quality. The order of deterioration of soil quality at Suame magazine industrial area with heavy metals is Fe > Zn > Cd > As > Pb > Cu as indicated in the Figure 4.12.



**Figure 4.12: Pollution load index for heavy metals in soil samples at Suame Magazine industrial area**

### C: Geoaccumulation index

The extent of heavy metal contamination was assessed using geoaccumulation index (Igeo) and the Igeo values were calculated using equation 7 according to (Muller, 1969; Ji *et al.*, 2008; Fagbote and Olanipekun, 2010; Adepoju and Adekoya, 2012).

$$\text{Geoaccumulation index} = \left( \log_2 \frac{C_{\text{metal}}}{1.5 C_{\text{ref}}} \right)$$

Where  $C_{\text{metal}}$  is the measured concentration of the heavy metal in the soil sample and  $C_{\text{ref}}$  is the concentration of the metal in the reference or control sample. The factor 1.5 is introduced to minimize the possible variations in the background or control values which may be attributed to lithogenic variations in the soil. The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as indicated in the Table 4.5.

**Table 4.5: Categories for Geo-accumulation index (Igeo) (Muller, 1969)**

Igeo value	IgeoClass	Value of Soil Quality
Igeo <0	0	unpolluted
0<=Igeo<1	1	unpolluted to moderately polluted
1<=Igeo<2	2	moderately polluted
2<=Igeo<3	3	moderately to strongly polluted
3<=Igeo<4	4	strongly polluted
4<=Igeo<5	5	strongly to very strongly polluted
Igeo>=5	6	very strongly polluted

**Table 4.5a: Average Geoaccumulation index (Igeo) of heavy metals in soils in Zone A from automobile shops at Suame magazine industrial area (n=12)**

SAMPLE ID	Cu	Cd	Zn	As	Pb	Fe
MA1	0.93	4.36	5.35	4.42	3.48	7.26
MA2	0.59	4.07	3.76	3.47	3.18	7.16
MA3	0.05	3.82	2.97	3.20	2.70	6.87
FA1	2.42	4.83	6.73	4.55	3.77	9.44
FA2	1.79	4.50	6.13	3.64	3.38	9.41
FA3	1.26	4.20	5.60	3.30	3.08	9.30
SA1	2.70	4.96	4.67	4.45	3.43	7.85
SA2	1.05	4.57	4.15	3.52	3.00	7.72
SA3	0.55	4.20	4.11	3.22	2.92	7.35
WA1	2.50	4.86	5.94	4.17	3.11	8.34
WA2	2.35	4.53	5.63	3.25	3.05	8.29
WA3	2.17	4.22	5.61	2.92	2.54	8.26

**Table 4.5b: Average Geoaccumulation index (Igeo) of heavy metals in soils in Zone B from automobile shops at Suame magazine industrial area (n=12)**

SAMPLE ID	Cu	Cd	Zn	As	Pb	Fe
MB1	2.65	4.65	6.81	4.13	3.48	8.37
MB2	2.00	4.29	6.70	3.24	3.22	8.26
MB3	1.95	3.95	6.21	2.93	3.15	8.23
FB1	2.02	4.51	6.87	4.18	3.38	8.03
FB2	1.74	4.18	6.75	3.24	3.08	7.70
FB3	1.55	3.82	6.23	2.86	2.90	7.44
SB1	1.92	4.49	6.94	4.07	2.93	8.44
SB2	1.74	4.18	6.57	3.18	2.90	8.15
SB3	1.50	3.80	6.09	2.89	2.68	7.72
WB1	0.59	4.62	6.99	4.12	3.14	9.21
WB2	0.38	4.19	6.88	3.23	2.95	9.05
WB3	-1.28	3.81	6.42	2.93	2.60	9.03

**Table 4.5c: Average Geoaccumulation index (Igeo) of heavy metals in soils in Zone C from automobile shops at Suame magazine industrial area (n=12)**

SAMPLE ID	Cu	Cd	Zn	As	Pb		Fe
MC1	0.43	4.56	3.09	4.10	3.55	3.55	9.36

<b>MC2</b>	0.12	4.22	2.83	3.17	3.51	3.51	8.84
<b>MC3</b>	-0.60	3.95	2.56	2.83	2.92	2.92	8.72
<b>FC1</b>	-2.15	4.45	5.93	4.23	2.12	2.12	9.60
<b>FC2</b>	nd	4.39	5.16	3.27	1.52	1.52	9.42
<b>FC3</b>	nd	4.05	5.14	3.00	1.41	1.41	9.38
<b>SC1</b>	2.06	4.73	4.21	4.23	2.70	1.09	8.72
<b>SC2</b>	1.79	4.34	3.92	3.27	1.90	0.64	7.91
<b>SC3</b>	1.74	4.13	3.85	2.99	1.03	nd	7.88
<b>WC1</b>	2.08	4.75	4.29	3.99	3.28	3.28	9.68
<b>WC2</b>	1.84	4.49	4.24	3.11	3.00	3.00	9.33
<b>WC3</b>	1.80	4.22	3.47	2.84	2.60	2.60	9.25

**Table 4.5d: Average Geoaccumulation index (Igeo) of heavy metals in soils in Zone D from automobile shops at Suame magazine industrial area (n= 9)**

<b>SAMPLE ID</b>	<b>Cu</b>	<b>Cd</b>	<b>Zn</b>	<b>As</b>	<b>Pb</b>	<b>Fe</b>
<b>MD1</b>	2.01	4.32	4.39	4.08	2.76	8.83
<b>MD2</b>	1.67	4.07	4.13	3.23	2.37	8.55
<b>MD3</b>	1.51	3.85	4.03	2.97	0.85	8.43
<b>FD1</b>	*	*	*	*	*	*
<b>FD2</b>	*	*	*	*	*	*
<b>FD3</b>	*	*	*	*	*	*
<b>SD1</b>	0.51	4.31	4.00	4.08	2.58	8.30
<b>SD2</b>	-0.13	4.05	3.72	3.19	1.27	8.18
<b>SD3</b>	nd	3.86	3.63	2.92	0.83	8.09
<b>WD1</b>	2.56	4.02	3.24	4.23	1.84	9.20
<b>WD2</b>	2.17	3.93	2.97	3.30	0.85	9.15
<b>WD3</b>	0.65	3.71	2.75	2.97	0.55	8.95

“nd” means not detected”. \* means no sample from metal fabrication shops

The descending orders of the calculated Igeo for heavy metals in the four sampling zones were as follows Zone A: **Fe > Zn > Cd > As > Pb > Cu**; Zone B: **Fe > Zn > Cd > As > Pb > Cu**; Zone C: **Fe > Zn > Cd > As > Pb > Cu**; Zone D: **Fe > Zn > Cd > As > Pb > Cu**.

The pollution status of the metals in all the four zones (A, B, C and D) expressed in terms of this index showed that the soils are very strongly polluted with Fe ( $I_{geo} \geq 5$ ) and to a lesser degree with Cu; Cd, Zn, As and Pb show moderate ( $1 \leq I_{geo} < 2$ ) to strongly pollution status ( $3 \leq I_{geo} < 4$ ) as shown in Table 4.5a, 4.5b, 4.5c, 4.5d. It may be inferred that the soil samples (WB3, MC3, FC1, SD2, SD3) are not polluted with Cu ( $I_{geo} < 0$ ).

Generally, the geoaccumulation index (Igeo) of each metal in this study showed very high values, indicating that the studied soils were moderately polluted ( $1 \leq I_{geo} < 0$ ) or very

strongly polluted ( $I_{geo} \geq 5$ ), which was consistent with the previous results calculated for contamination factor.

#### D. Quantification of Concentration of anthropogenic metal.

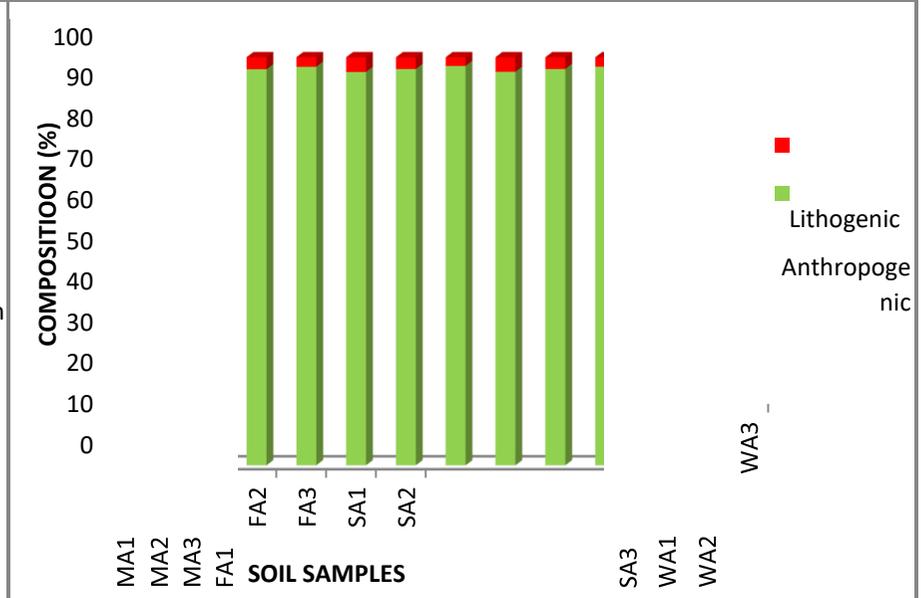
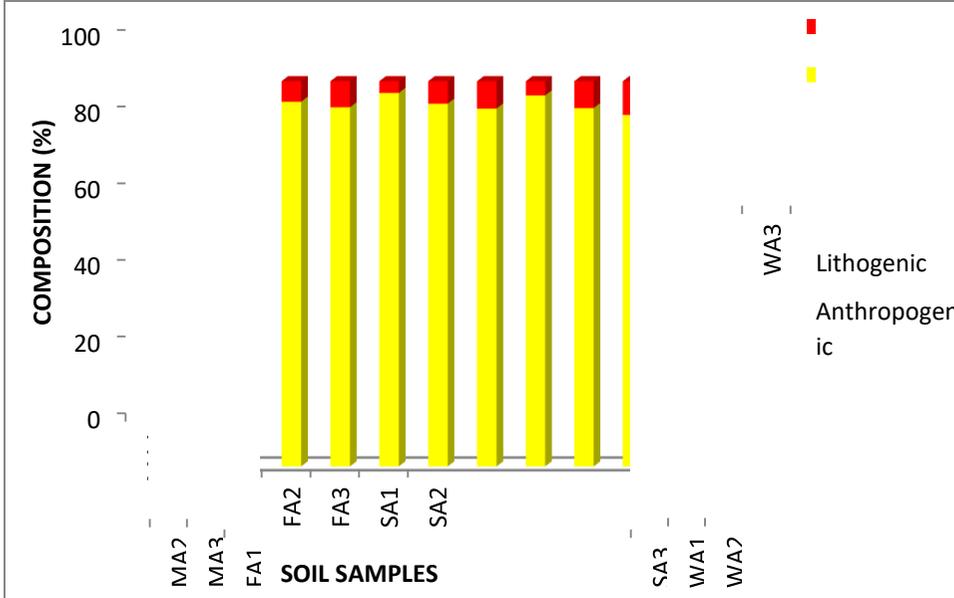
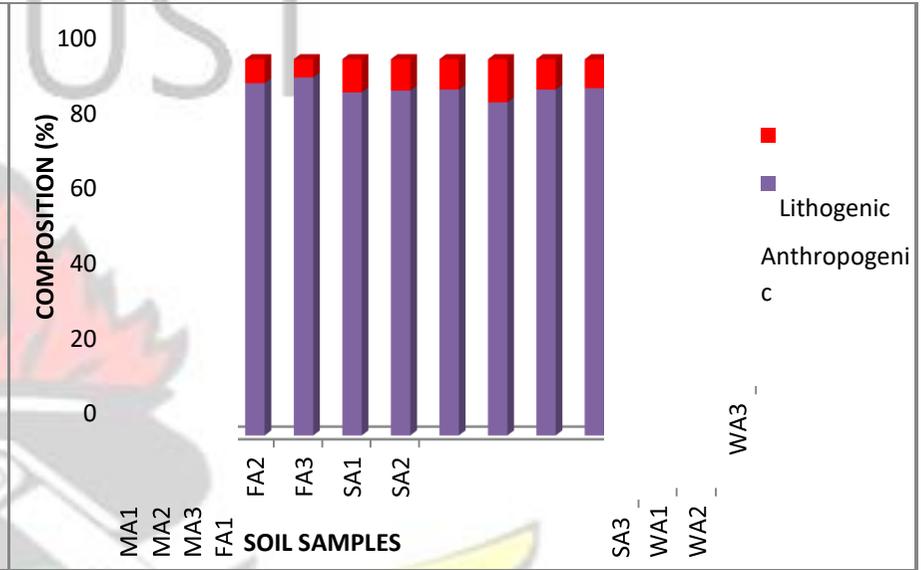
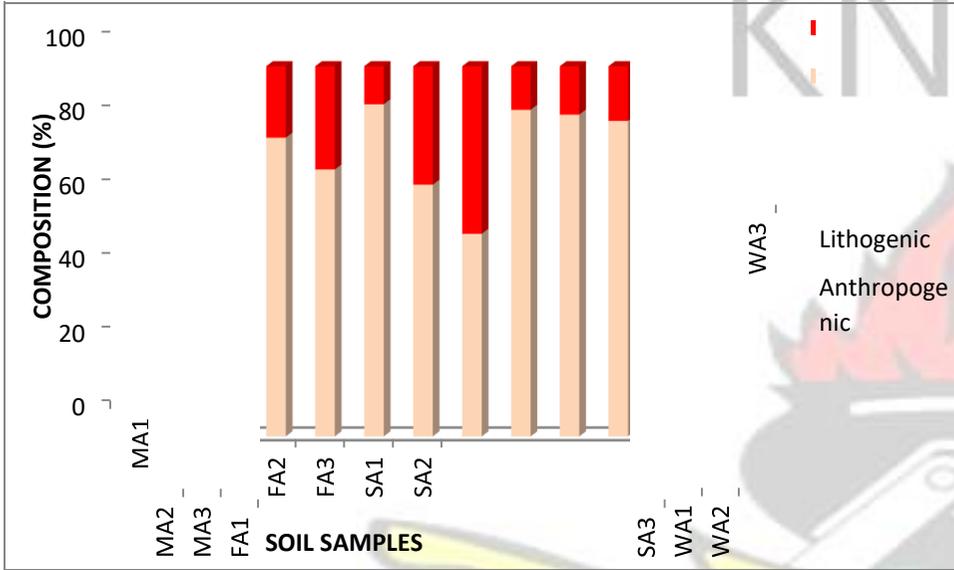
The third approach is the quantification of anthropogenic concentration of metal in the soil sample and it employs the concentration in the control samples to represent the lithogenic metal. This is calculated in accordance with equation :

$$\text{Quantification of anthropogenic concentration of metal} = \frac{x - x_c}{x} \times 100$$

Where  $x$  = average concentration of the metal in the soil under investigation

$x_c$  = average concentration of the metal in the control samples (Victor *et al.*, 2006).

On the basis of quantification of anthropogenic input of the heavy metals in the soils, contamination with individual metals could be presented in an order as follows: Zone A: (Fe > Zn > Cd > As > Pb > Cu), Zone B: (Fe > Zn > Cd > As > Pb > Cu), Zone C: (Fe > Zn > Cd > As > Pb > Cu), Zone D: (Fe > Zn > Cd > As > Pb > Cu). For example in Zone A, the decreasing order of anthropogenic metal input is Fe (99.56 - 99.90%) > Zn (94.55- 99.37%) > Cd (94.35-97.05%) > As (91.24-97.12 %) > Pb (88.53-95.12%) > Cu (54.77-89.75 %) as indicated in Figure 4.13. This could simply be an indication that the anthropogenic sources of the metals in the soils are as a result of artisanal activities at Suame Magazine industrial area which contributes greatly to heavy metal contamination in soils.



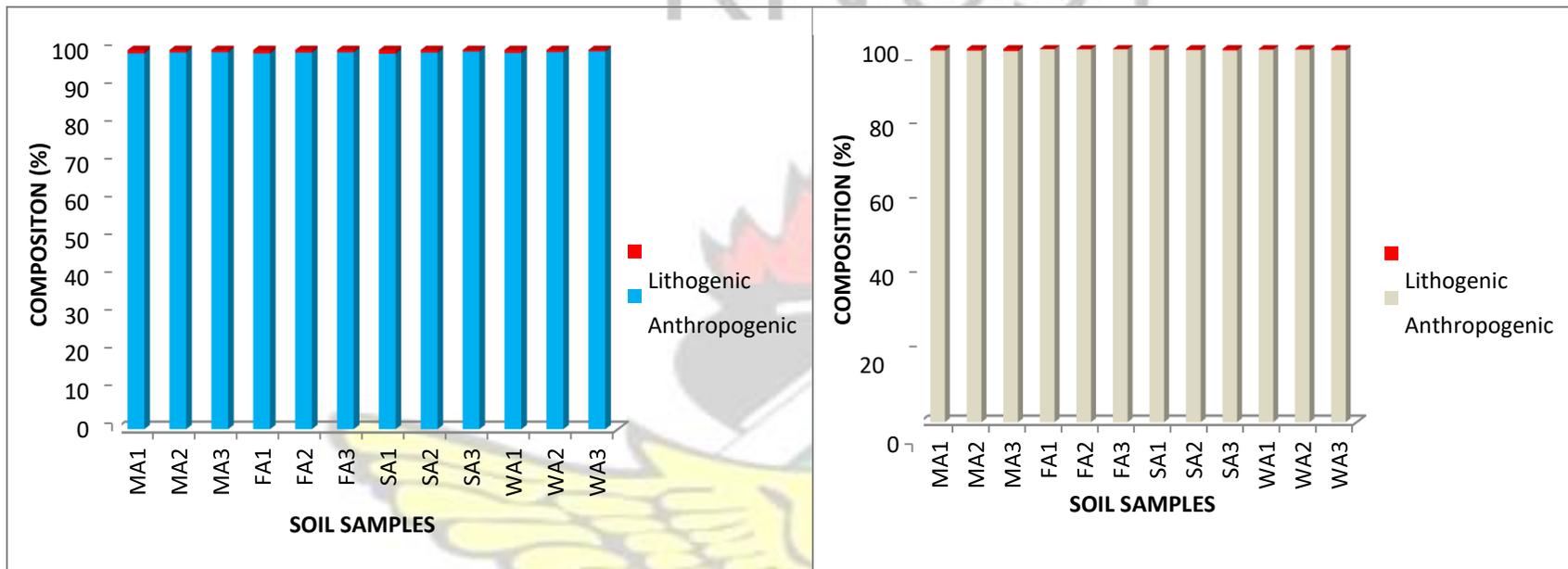


Figure 4.13: Stacked bar charts showing percentage composition of lithogenic and anthropogenic of Cu, Pb, As, Zn, Cd and Fe in the soil samples for zone A



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### A: Pearson correlation analysis

In this study, Pearson correlation was employed to identify the relationship between the various heavy metals in soil samples analysed from Suame Magazine industrial area. The data for soil samples from Suame magazine industrial area show a positive correlation at the 0.01 significance level between all the metals in the four zones (A, B, C, and D); with the exception of  $As^{ZA}$  and  $Cu^{ZD}$  which showed no correlation with the other metals in the different zones as indicated in Table 4.6. Major correlation exists between  $As^{ZD}$ -  $As^{ZB}$  ( $r = 0.965$ ),  $As^{ZD}$ -  $Cd^{ZD}$  ( $r = 0.927$ ),  $As^{ZD}$ -  $Pb^{ZB}$  ( $r = 0.918$ ),  $Fe^{ZC}$ -  $As^{ZC}$  ( $r = 0.910$ ),  $As^{ZD}$ -  $Cu^{ZB}$  ( $r = 0.938$ ) and  $Zn^{ZC}$ - $Fe^{ZA}$  ( $r = 0.957$ ) as indicated in Table 4.6a.

**Table 4.6a: Pearson correlation coefficient between (r) pairs of heavy metals in soil at 0.01**

Correlation coefficient between metals	Correlation coefficient (r)	Correlation between metals	Correlation (r)
$Zn^{ZA}/Cu^{ZA}$	+0.761**	$Pb^{ZA}/As^{ZA}$	+0.836**
$Fe^{ZA}/Zn^{ZA}$	+0.854**	$Fe^{ZA}/Pb^{ZA}$	+0.837**
$Cu^{ZB}/As^{ZA}$	+0.871**	$Zn^{ZB}/Cu^{ZA}$	+0.735**
$Zn^{ZB}/Zn^{ZA}$	+0.779**	$As^{ZB}/Cd^{ZB}$	+0.805**
$Pb^{ZB}/Cu^{ZB}$	+0.769**	$Pb^{ZB}/As^{ZB}$	+0.805**
$Cd^{ZC}/Cu^{ZA}$	+0.793**	$Cd^{ZC}/Fe^{ZB}$	+0.735**
$Zn^{ZC}/Zn^{ZA}$	+0.824**	$Zn^{ZC}/Pb^{ZA}$	+0.892**
$Zn^{ZC}/Fe^{ZA}$	+0.957**	$As^{ZC}/Cu^{ZA}$	+0.872**
$As^{ZC}/Zn^{ZA}$	+0.870**	$As^{ZC}/Fe^{ZA}$	+0.750**
$As^{ZC}/Zn^{ZB}$	+0.751**	$As^{ZC}/Zn^{ZC}$	+0.716**
$Fe^{ZC}/Cu^{ZA}$	+0.749**	$Fe^{ZC}/Zn^{ZA}$	+0.854**
$Fe^{ZC}/Fe^{ZA}$	+0.756**	$Fe^{ZC}/As^{ZC}$	+0.910**
$Cd^{ZD}/Cu^{ZB}$	+0.838**	$Cd^{ZD}/As^{ZB}$	+0.900**
$Zn^{ZD}/Cu^{ZB}$	+0.8028**	$Zn^{ZD}/Pb^{ZB}$	+0.910**
$As^{ZD}/Cu^{ZB}$	+0.938**	$As^{ZD}/As^{ZB}$	+0.965**
$As^{ZD}/Cd^{ZB}$	+0.825**	$As^{ZD}/Zn^{ZD}$	+0.882**
$Pb^{ZD}/Cd^{ZB}$	+0.880**	$Fe^{ZD}/Cd^{ZB}$	+0.847**
		$As^{ZD}/Cd^{ZD}$	+0.927**

\*\*Correlation is significant at the 0.01 level (2-tailed). ZA- Zone A, ZB- Zone B, ZC- Zone C, ZD-

### Zone D

At 0.05 significance level, strong correlations in the soil exist between all the metals with significant correlation existing between Pb<sup>ZD</sup>- As<sup>ZD</sup> (r = 0.784), Pb<sup>ZD</sup>- Cu<sup>ZB</sup> (r = 0.797), Pb<sup>ZD</sup>- Fe<sup>ZB</sup> (r = 0.777) and Pb<sup>ZD</sup>- Pb<sup>ZC</sup> (r= 0.783). Zn<sup>ZD</sup> had negative correlation with Cd<sup>ZC</sup> (r = -0.698) as indicated in Table 4.6b. The correlation coefficients between the concentrations of the different metals indicate strong association between them, which probably reflects their related or common origin. Therefore it can be concluded that about 75% of the wastes which are indiscriminately disposed within the various workshops are possible sources of these metals.

**Table 4.6b: Pearson correlation coefficient between (r) pairs of heavy metals in soil at 0.05**

Correlation between metals	Correlation coefficient (r)	Correlation between metals	Correlation coefficient (r)
Cd <sub>ZA</sub> /Cu <sub>ZA</sub>	+ 0.633*	Cu <sup>ZB</sup> /Pb <sup>ZA</sup>	+0.654*
Fe <sub>ZA</sub> /Cu <sub>ZA</sub>	+ 0.635*	As <sub>ZB</sub> /Zn <sub>ZB</sub>	+0.693*
Cd <sub>ZB</sub> /Cu <sub>ZB</sub>	+0.627*	Fe <sub>ZB</sub> /As <sub>ZB</sub>	+0.620*
Fe <sub>ZB</sub> /Cu <sub>ZA</sub>	+0.604*	Cd <sub>ZC</sub> /Zn <sub>ZB</sub>	+0.631*
Fe <sub>ZB</sub> /Zn <sub>ZB</sub>	+0.607*	Zn <sub>ZC</sub> /Cu <sub>ZA</sub>	+0.664*
Cd <sub>ZC</sub> /Cd <sub>ZA</sub>	+0.676*	Pb <sub>ZB</sub> /Cd <sub>ZB</sub>	+0.714*
As <sub>ZC</sub> /As <sub>ZB</sub>	+0.636*	Fe <sub>ZC</sub> /Zn <sub>ZC</sub>	+0.635*
Fe <sub>ZC</sub> /Zn <sub>ZB</sub>	+0.668*	Cd <sub>ZD</sub> /Pb <sub>ZB</sub>	+0.769*
Cd <sub>ZD</sub> /Cd <sub>ZB</sub>	+0.756*	Cd <sub>ZD</sub> /Fe <sub>ZB</sub>	+0.748*
Cd <sub>ZD</sub> /As <sub>ZC</sub>	+0.676*	Zn <sub>ZD</sub> /Cd <sub>ZB</sub>	+0.723*
Zn <sub>ZD</sub> /As <sub>ZB</sub>	+0.777*	Zn <sub>ZD</sub> /Fe <sub>ZC</sub>	+0.670*
Zn <sub>ZD</sub> /Cd <sub>ZD</sub>	+0.685*	As <sub>ZD</sub> /Fe <sub>ZB</sub>	+0.725*
As <sub>ZD</sub> /As <sub>ZC</sub>	+0.683*	Pb <sub>ZD</sub> /Cu <sub>ZB</sub>	+0.797*
Pb <sub>ZD</sub> /Pb <sub>ZB</sub>	+0.753*	Pb <sub>ZD</sub> /As <sub>ZB</sub>	+0.743*
Pb <sup>ZD</sup> /Fe <sup>ZB</sup>	+0.777*	Pb <sub>ZD</sub> /Pb <sub>ZC</sub>	+0.783*
Pb <sup>ZD</sup> /Zn <sup>ZD</sup>	+0.763*	Pb <sub>ZD</sub> /As <sub>ZD</sub>	+0.784*
Fe <sup>ZD</sup> /Cd <sup>ZC</sup>	+0.669*	Zn <sup>ZD</sup> /Cu <sup>ZC</sup>	-0.698*

\*\*Correlation is significant at the 0.05 level (2-tailed). ZA- Zone A, ZB- Zone B, ZC-Zone C, ZDZone D

## **B: Principal Component Analysis (PCA)**

In this study, special attention is given to the metals with PV coefficients (or loadings) higher than 0.5. The PCA yielded 3 components which indicates 87.84 % total variance in the data, the first component accounts for 38.11% of the total variance and contains the following;  $\text{Cu}^{\text{ZB}}$ ,  $\text{Cd}^{\text{ZB}}$ ,  $\text{As}^{\text{ZB}}$ ,  $\text{Pb}^{\text{ZB}}$ ,  $\text{Cd}^{\text{ZC}}$ ,  $\text{Pb}^{\text{ZC}}$ ,  $\text{Cd}^{\text{ZD}}$ ,  $\text{Zn}^{\text{ZD}}$ ,  $\text{As}^{\text{ZD}}$ ,  $\text{Pb}^{\text{ZD}}$  and  $\text{Fe}^{\text{ZD}}$ , displaying high loadings (0.941, 0.855, 0.894, 0.836, 0.882, 0.669, 0.762, 0.900, 0.710, 0.920, 0.917, 0.742) respectively as indicated in Table 4.7. The second component accounts for 37.53% of the total variance and heavily loaded with  $\text{Cu}^{\text{ZA}}$ ,  $\text{Cd}^{\text{ZA}}$ ,  $\text{Zn}^{\text{ZA}}$ ,  $\text{As}^{\text{ZA}}$ ,  $\text{Pb}^{\text{ZA}}$ ,  $\text{Fe}^{\text{ZA}}$ ,  $\text{Zn}^{\text{ZB}}$ ,  $\text{Zn}^{\text{ZC}}$ ,  $\text{As}^{\text{ZC}}$  and  $\text{Fe}^{\text{ZC}}$  with loadings (0.816, 0.612, 0.969, 0.915, 0.949, 0.979, 0.680, 0.961, 0.955 and 0.872) respectively. The third component accounts for of the 12.19% of the total variance and contains  $\text{Cd}^{\text{ZA}}$ ,  $\text{Cu}^{\text{ZC}}$ ,  $\text{Fe}^{\text{ZD}}$  displaying with holdings (0.732, 0.835, and 0.561) as presented in Table 4.7. These elements had mean concentrations that were higher than the control or background values and with higher contamination factor lower and geoaccumulation index. Thus, the high concentration is traceable to high use of copper conductors and wires, spent lubricants, batteries, paints, automobile emissions, iron scraps, unused body parts of vehicles, hydraulic fluid, used at the workshop have been dumped and discharged heavily in Suame Magazine industrial area. This suggest that the presence of the elements Cu, Cd, Zn, As, Pb and Fe in the top soil, sub soils and bottom soils of the soil profile is mainly as a result of anthropogenic or industrial activities, in addition to the original content from the weathered soil.

**Table 4.7: The rotated component matrix of heavy metals in soil samples from**

**Zones (A,B,C, D) at Suame Magazine industrial area**

<b>Rotated Component Matrix</b>			
	Component		
	PC1	PC2	PC3
CuA	.357	<b>.816</b>	.021
CdA	.126	<b>.612</b>	<b>.732</b>
ZnA	-.060	<b>.969</b>	.000
AsA	.316	<b>.915</b>	.186
PbA	.054	<b>.949</b>	.235
FeA	-.162	<b>.974</b>	.054
CuB	<b>.941</b>	.315	.044
CdB	<b>.885</b>	-.339	-.259
ZnB	.469	<b>.680</b>	.231
AsB	<b>.894</b>	.329	.004
PbB	<b>.836</b>	.305	-.313
FeB	<b>.882</b>	-.356	.254
CuC	-.309	.084	<b>.835</b>
CdC	<b>.669</b>	.358	.338
ZnC	-.103	<b>.961</b>	.165
AsC	.146	<b>.955</b>	-.171
PbC	<b>.762</b>	-.425	-.444
FeC	.047	<b>.872</b>	-.409
CuD	-.013	-.061	.055
CdD	<b>.900</b>	.286	.162
ZnD	<b>.710</b>	.362	-.579
AsD	<b>.920</b>	.336	-.177
PbD	<b>.917</b>	-.149	-.266
FeD	<b>.742</b>	-.270	<b>.561</b>
Total	9.147	9.008	2.926
% of Variance	38.113	37.535	12.192
Cumulative %	38.113	75.648	87.84

#### 4.4. HEALTH RISK ASSESSMENT (SOIL SAMPLES)

Plain data on the metal content of soil samples obtained from the analysis is inadequate to describe the full risk that may arise from the exposure of artisans at Suame Magazine industrial area to the different heavy metals from the soil. Therefore health risk assessment is necessary to estimate the potential of occurrence of any adverse health effects over a specified time period and is a function of the hazard and exposure (Naveedullah *et al.*, 2014). Risk assessment involves exposure assessment, toxicity assessment and risk characterization

**A: Exposure assessment** involves estimation of the magnitude of actual and /or potential human exposure and may occur through different absorption pathways. In this study, health risk assessment was examined via ingestion and dermal route.

##### **B. Toxicity assessment**

Toxicity assessment involves the determination of adverse health effects associated with exposure to different chemicals.

##### **C: Risk characterization**

Risk characterization summarizes and combines the outputs of the calculations of exposure and toxicity assessments and for the present investigation comprises of calculations of carcinogenic and non-carcinogenic risk for ingestion and dermal contact of soil.

In the light of the two pathways discussed above, the chronic daily intake (CDI) and Hazard quotient (HQ) were calculated for the different heavy metals that were analysed in soil samples at Suame Magazine industrial area using the equations in Table 4.8.

**Table 4.8: Defining equations of daily intake via various exposure pathways**

Medium	Exposure pathway	Calculation formulae
Soil	Ingestion	$CD_{ingest - soil} = \frac{C_{Soil} * IRS * EF * ED * CF}{BW * AT}$
	Dermal contact	$CD_{dermal - soil} = \frac{C_{Soil} * SA * AF * ABS * EF * ED * CF}{BW * AT}$
Water	Oral intake	$CD_{oral - water} = \frac{C_{water} * IR_{oral}}{BW * AT}$
	Dermal intake	$CDI_{dermal-water} = \frac{C_{water} * EF * ED}{BW * AT}$

(USEPA, 2002, 2011; Wang *et al.*, 2005; Liu *et al.*, 2013,

\*ED= equivalent to average life time (65 years for Ghanaian population); \*AT=EF\*ED

The detailed explanations for all the parameters are listed in Table 4.9.

**Table 4.9: Parameters for exposure of metals in soil and water samples used in the study**

Exposure factors	Unit	Value
Concentration in soil sample (C soil)	mg/kg	-
Concentration in water sample (C water)	mg/kg	
Exposure frequency (EF)	days/year	365
Exposure duration (ED) for soil	Year	65
*Average time for non-carcinogens (AT) in soil	Days	23725
Exposure duration (ED) for water	Year	30
*Averaging time for non-carcinogens (AT) in water	Days	10,950
Body weight (BW)	Kg	70
Exposed skin area: (SA)	cm <sup>2</sup>	5700
Adherence factor (AF)	mgcm <sup>-2</sup>	0.07
Dermal absorption fraction(ABS)		0.03 (As) , 0.001 (other metals)
Units conversion factor (CF)	kgmg <sup>-1</sup>	10 <sup>-6</sup>

Ingestion rate(IRS)	mgd <sup>-1</sup>	100
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An estimate of risk to human health (HQ) for the artisans at Suame Magazine industrial area through the ingestion and dermal contact with soils was calculated for each metal. Thus non-carcinogenic risk from individual heavy metals can be expressed as the hazard quotient and was calculated using equation 8.

$$HQ = \frac{CDI}{RFD} \dots\dots\dots \text{Equation 8}$$

Where the non-cancer hazard quotient (HQ) is the ratio of exposure to hazardous substances, and RFD is the chronic reference dose of the toxicant (mg kg<sup>-1</sup> d<sup>-1</sup>). A HQ less than 1 (HQ<1) means the exposed population is unlikely to experience obvious adverse effects; whereas a HQ above 1 (HQ>1) means there is a chance of noncarcinogenic effect, with an increasing probability as the value increases (Liu *et al.*, 2013).

**Table 4.10: Reference doses (RFD) mg kg<sup>-1</sup> day<sup>-1</sup> for heavy metals used in the study**

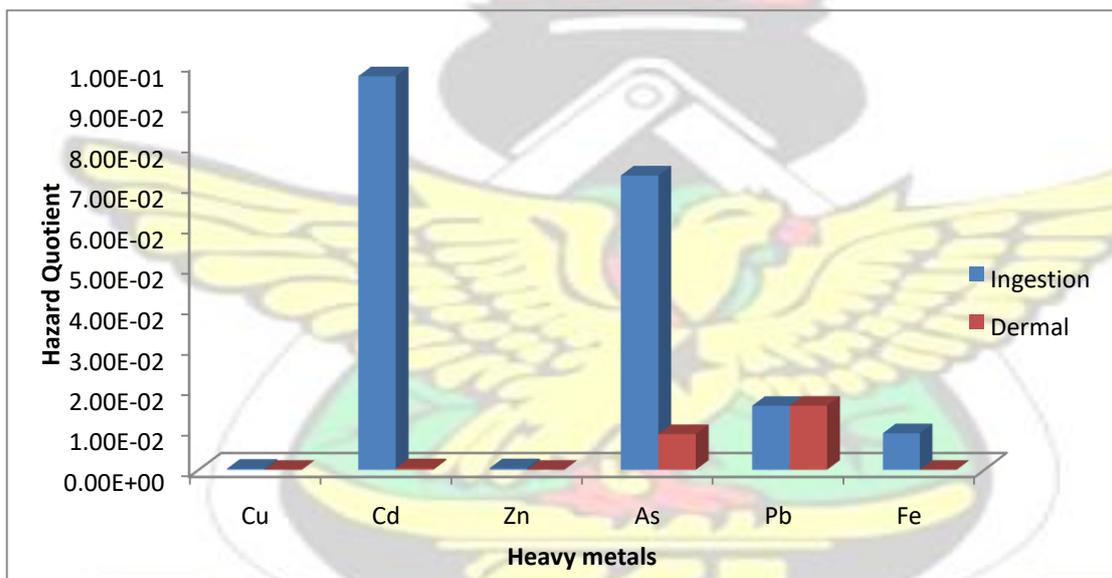
Heavy metals	Reference Doses (RFD)
Cu	4.0E-2
Cd	1.0E-3
Zn	3.0E-1
As	3.0E-4
Pb	3.5E-3
Fe	7.0E-1

(Chauhan and Chuahan, 2014; FAO/WHO (Codex Alimentarius Commission, 2013)

**Table 4.11: Chronic daily intake (CDI) and non-carcinogenic risks (HQ) through**

**two (2) exposure pathways in soil samples**

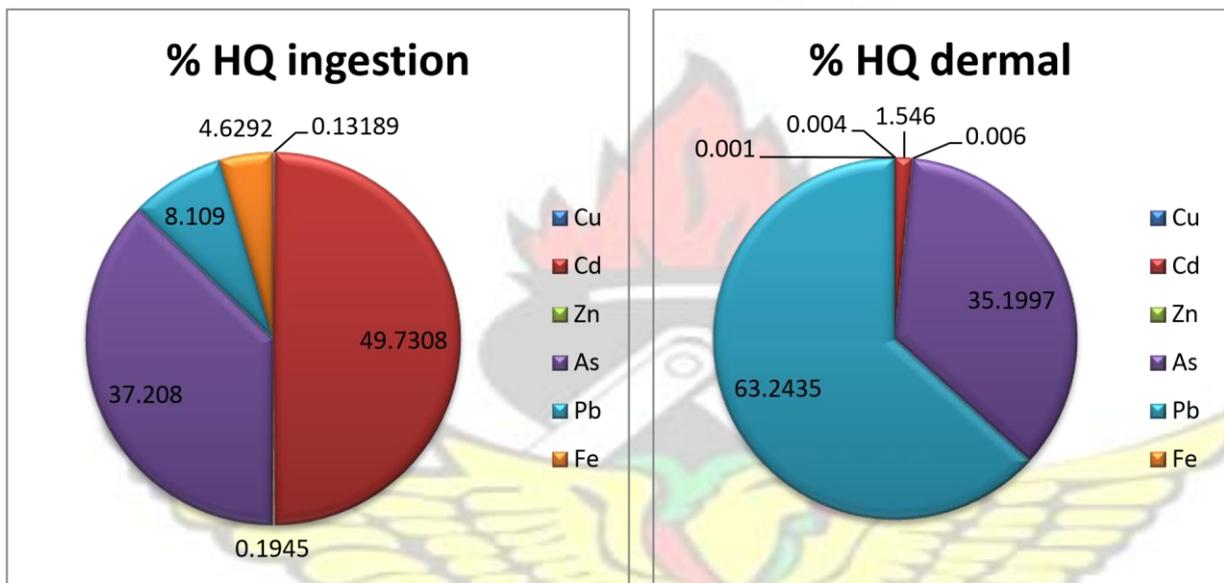
Metals	Exposure pathway: ingestion and dermal routes.			
	CDI ingest-soil	CDI dermal-soil	HQ ingestion	HQ dermal absorption
Cu	1.029E-5	4.09E-8	2.565E-4	1.023E-6
Cd	9.690E-5	3.866E-7	9.690E-2	3.866E-4
Zn	1.142E-4	4.556E-7	3.794E-4	1.517E-6
As	2.176E-5	2.604E-6	7.251E-2	8.805E-3
Pb	5.537E-5	2.209E-7	1.581E-2	1.582E-2
Fe	6.316E-3	2.529E-5	9.023E-3	3.156E-7



**Figure 4.14: Hazard quotient for heavy metals in soils through two exposure pathways**

From the results, the CDI ingest-soil, CDI dermal-soil, HQ ingest-soil and HQ dermalsoil presented in Table 4.11 for the individual metals were found to be less than unity ( $CDI < 1$ ) indicating that artisans at Suame Magazine industrial area would not experience any significant health risk. Among the heavy metals examined in this study, for exposure route through ingestion, Cd ( $HQ = 9.690E-2$ ) and As ( $HQ = 7.251E-2$ ) presented relatively higher potential health risks accounting for 49.731% and 37.208% respectively whiles for

exposure route through dermal contact, Pb (HQ=1.582E-2) and As (HQ= 8.805E-3) accounting for 63.243% and 35.199% would have a relatively higher potential health risk as indicated in Figure 4.15 although the HQ value was very low (HQ < 1). The HQ ingest-soil of the metals decreased in the following order: Cd > As > Pb > Fe > Zn > Cu and the trend for HQ dermal-soil of the metals is Pb > As > Cd > Zn > Cu > Fe as shown in Figure 4.15



**Figure 4.15: % Hazard quotient for the individual metals in soils through two exposure routes**

### Hazard index (HI)

Exposure to two or more pollutants may result in additive and /or interactive effects (Akoto *et al.*, 2014; Zheng *et al.*, 2007). Therefore the hazard index of heavy metals in the soil samples from Suame Magazine industrial area was treated as the arithmetical sum of the hazard quotient of the individual metals.

$$\text{Hazard index (HI ingestion)} = \text{HQCu} + \text{HQCd} + \text{HQZn} + \text{HQAs} + \text{HQPb} + \text{HQFe}$$

$$\text{Hazard index (HI dermal)} = \text{HQCu} + \text{HQCd} + \text{HQZn} + \text{HQAs} + \text{HQPb} + \text{HQFe}$$

The hazard index of heavy metals through ingestion and dermal contact as a means of exposure was 0.1949 and 0.0250 respectively means the exposed artisans are unlikely to

experience obvious adverse effects. Although the hazard index (HI) is less than unity (1), their cumulative effect is of concern. It can be estimated that the overall noncarcinogenic health risk assessment at Suame Magazine industrial area indicated more risk via the ingestion route (HI=0.1949).

### Carcinogenic Risk

Cancer risk represents the probability of an individual lifetime health risks from carcinogens.

Of the six metals investigated, only As and Cd, induce both non-carcinogenic and carcinogenic risk, while Cu, Zn, Pb and Fe induce only non-carcinogenic risk. It is necessary to calculate the cancer risk value to estimate whether the artisans at Suame Magazine industrial area are likely to suffer from cancer and this can be evaluated from equation 9.

$$\text{Cancer risk} = CDI * SF \dots\dots\dots \text{Equation 9}$$

Where CDI is the chronic daily intake of carcinogens ( $\text{mg kg}^{-1} \text{d}^{-1}$ ); SF is the slope factor of hazardous substances ( $\text{mg kg}^{-1} \text{d}^{-1}$ ).

**Table 4.12: Cancer risk for two exposure pathways for soil**

Metal	CDI ingestion	CDI dermal	(SF)	Ingestion-soil	Dermal absorption – soil
As	2.176E-5	2.604E-6	1.499	3.263E-5	3.906E-6
Cd	9.690E-5	3.866E-7	*	*	*

**\*Means the value of cancer slope for Cd could not be assessed in IRIS, provided by USEPA database (USEPA , 2005).**

The results show cancer risk of 3.263E-5 and 3.906E-6 for arsenic which is higher than the acceptable or tolerable risk (1E-06 to 1E-04) (USEPA, 2001, Liu *et al.*, 2013).

Therefore, As appears to be the main pollutant source to produce cancer among these

heavy metals and the dominating exposure route for As to artisans at Suame Magazine industrial area is through ingestion (oral).

#### **4.5 DATA ON WATER ANALYSIS**

##### **4.5.1 Physicochemical parameters of water samples**

Artisanal activities at Suame Magazine industrial area generate hazardous waste which can affect the quality of water resources within the vicinity. These activities can have effect on the physical and chemical properties such as pH, electrical conductivity, total dissolved solids and total hardness of the water. Upon analyses of water samples within Suame Magazine industrial area, pH values in the range of 6.52- 10.26 were obtained. The pH of the water samples (boreholes, hand dug wells, hand pump wells and pipe borne) were within the range of 6.5- 8.5 stipulated for drinking and domestic purpose (WHO, 2003; WHO, 2013) except the water sample from Nkradan stream which gave high pH range of 9.85- 9.88, 10.24- 10.26 and 9.92- 9.95 representing the upstream, midstream and the downstream respectively as indicated in the Table 4.13. Electrical Conductivities (EC) for all the water samples range from 170.30-326.00  $\mu\text{S}/\text{cm}$  and were within the WHO standard for quality drinking water (700  $\mu\text{S}/\text{cm}$ ). Again the water samples from the Nkradan stream gave a high EC value of 812.31, 956.90 and 1025.20  $\mu\text{S}/\text{cm}$  representing the upstream, midstream and downstream respectively as indicated in Table 4.13. The indiscriminate disposal of waste by artisans at Suame Magazine industrial area onto the soil and eventually into the Nkradan stream may have contributed to the high pH and conductivities values of the Nkradan stream. It can also be deduced that these activities may also have contributed to high values of total hardness for the Nkradan stream. The total dissolve solids (TDS) for all the water samples were within the WHO standard for quality drinking water (1000 mg/l).

**Table 4.13: pH range, Electrical conductivity, total dissolved solids and total hardness values for water samples**

SAMPLE ID	pH Range	EC (uS/cm)	TDS (mg/l)	TOTAL HARDNESS
B1	8.02- 8.04	300.20	186.12	0.083
B2	7.30-7.33	239.80	146.56	0.012
HDW 1	7.15-7.20	228.15	142.89	0.010
HDW 2	6.52-6.55	170.30	93.42	8.1*10 <sup>-4</sup>
HDW 3	7.39-7.41	242.60	147.68	0.016
HDW 4	7.08-7.12	219.29	136.64	6.08*10 <sup>-3</sup>
HDW 5	7.45-7.48	242.06	148.53	0.0213
HDW 6	8.16-8.20	314.32	192.59	1*10 <sup>-3</sup>
HDW7	7.53-7.55	252.10	151.36	0.0220
HPW 1	7.64-7.67	259.40	155.64	0.0281
HPW 2	7.48-7.52	246.80	149.54	0.0219
HPW 3	8.22-8.25	326.20	198.72	0.0855
HPW4	7.31-7.35	237.51	141.06	0.012
UPS	9.85-9.88	812.31	487.96	0.0415
MID	10.24-10.26	1025.20	620.52	00.529
DOWNS	9.92-9.95	956.90	574.24	0.0485
P1	6.95-6.99	184.55	104.21	1.08*10 <sup>-3</sup>
P2	6.88-6.90	174.81	95.43	9.89*10 <sup>-4</sup>
P3	6.90-6.94	180.56	98.75	1.0214*10 <sup>-3</sup>
Raw water	7.12-7.16	194.31	113.40	1.175*10 <sup>-3</sup>
Fine water	7.05-7.08	186.02	94.58	9.802*10 <sup>-4</sup>

**B- Borehole, HDW-Hand Dug Well, HPW- Hand Pump well, UPS- Upstream, MID- Midstream, DOWNS- Downstream, P- Pipe-borne water**

#### **4.6: HEAVY METAL CONCENTRATION**

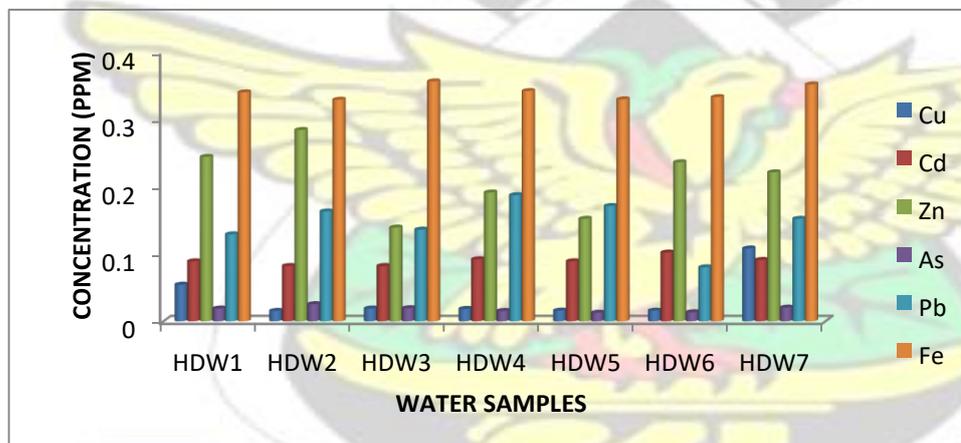
Heavy metals have the potential of leaching into the underground water or may be carried away by erosion which may eventually enter the water resources especially surface water such as the Nkradan stream. Therefore the heavy metal concentrations in water samples within the vicinity were determined and the results are shown in Figure 4.16a, 4.16b, 4.16c

and 4.16d. The heavy metal concentrations of the water samples were compared with the WHO standard for quality drinking water in Table 4.14.

**Table 4.14: Drinking water quality standard /guidelines in ppm (WHO, 2013)**

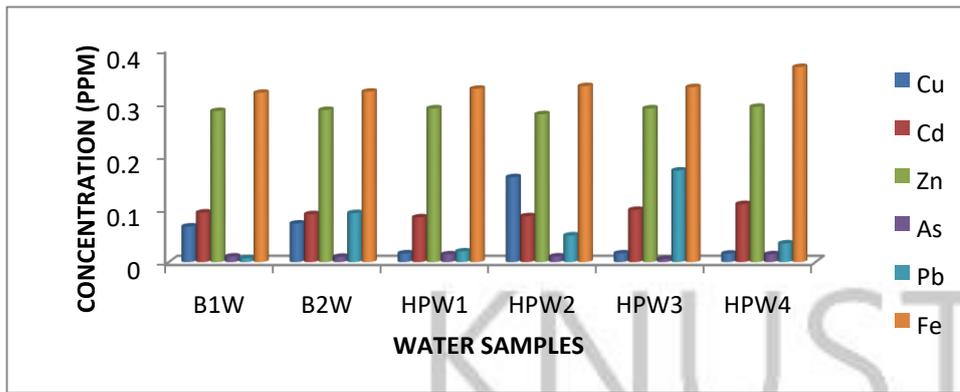
Metal	WHO
Cu	2.00
Cd	0.003
Zn	3.00
As	0.01
Pb	0.01
Fe	0.30

For hand dug wells, the concentration of copper (Cu) and zinc (Zn) were within the WHO permissible value whiles other metals like Pb and As were slightly higher than the WHO guidelines.



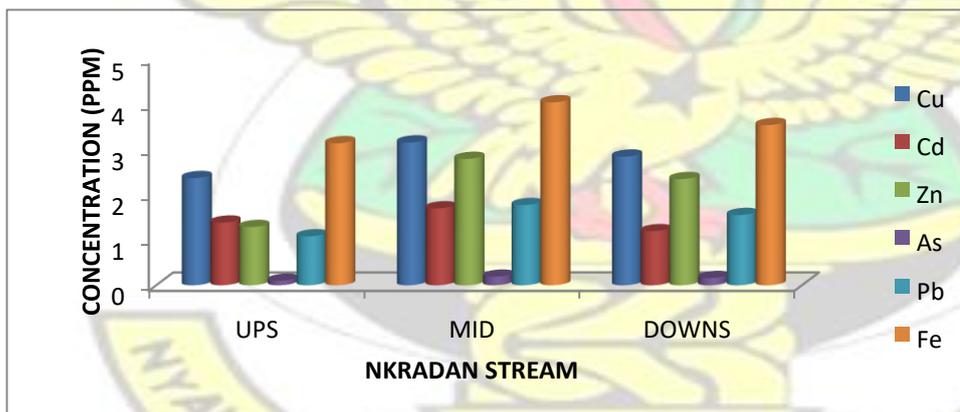
**Figure 4.16a: Heavy metal concentrations (ppm) in water samples from hand dug wells**

The concentration of heavy metals in the borehole water (B1 and B2) and hand pump wells (HPW1, HPW2, HPW3, HPW4) were within the World Health Organization (WHO) maximum permissible value except cadmium (Cd) which gave high concentration values in the range (0.089-0.093) ppm and (0.084-0.109) ppm for bore hole and hand pump well water samples respectively.



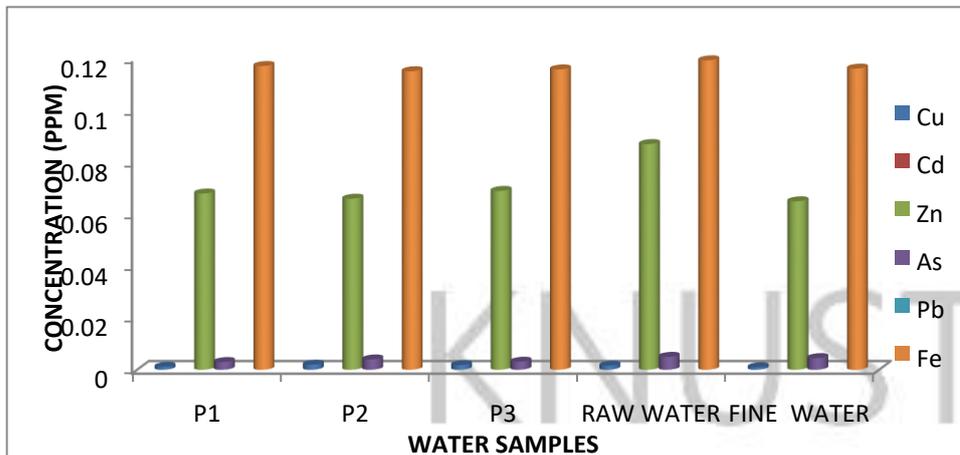
**Figure 4.16b: Heavy metal concentrations (ppm) in water samples from borehole and hand pump well**

Water samples from the Nkradan stream show relatively higher concentrations above the WHO maximum permissible value for all the heavy metals. It can be suggested that the artisanal activities at Suame Magazine industrial area greatly affect the Nkradan stream in terms of pollution with contaminants like heavy metals. Thus the indiscriminate disposal of waste onto the soil can result in the transportation of these wastes by runoff water into the stream due to the topography of the land.



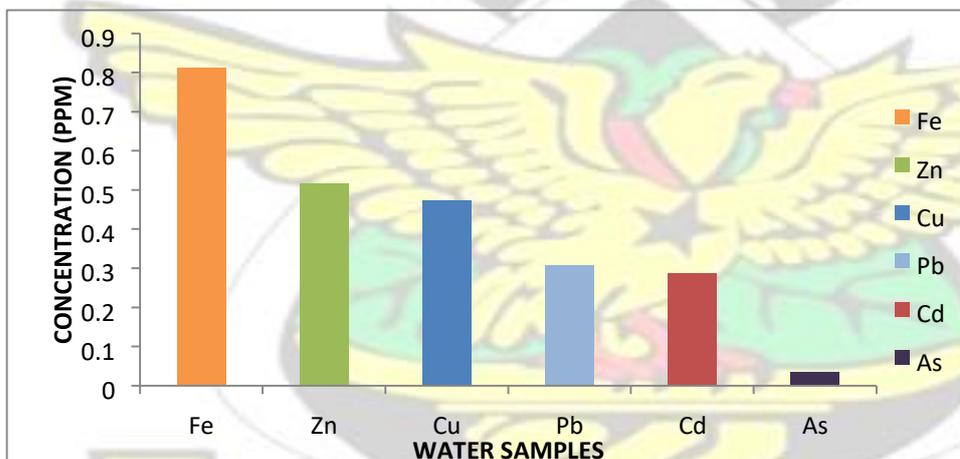
**Figure 4.16c: Heavy metal concentrations (ppm) in water samples from the Nkradan stream**

Meanwhile, the concentration of heavy metals in pipe borne water and the reference water samples were within the acceptable limits of the WHO guidelines for quality drinking water as indicated in the Table 4.1.4.



**Figure 4.16d: Heavy metal concentrations (ppm) in water samples from pipe-borne and reference water samples**

The mean concentration of the six metals in the water samples from Suame Magazine industrial area show a decreasing order of  $Fe > Zn > Cu > Pb > Cd > As$  as indicated in Figure 4.17.



**Figure 4.17: Trend of heavy metal concentration (ppm) in water samples at Suame Magazine industrial area**

#### 4.7: Principal Component Analysis (PCA) for water samples.

In this study, the physicochemical parameters (pH, conductivity, total hardness and total dissolved solids) and heavy metal concentrations of the water samples were analysed using PCA to determine the correlativity between them.

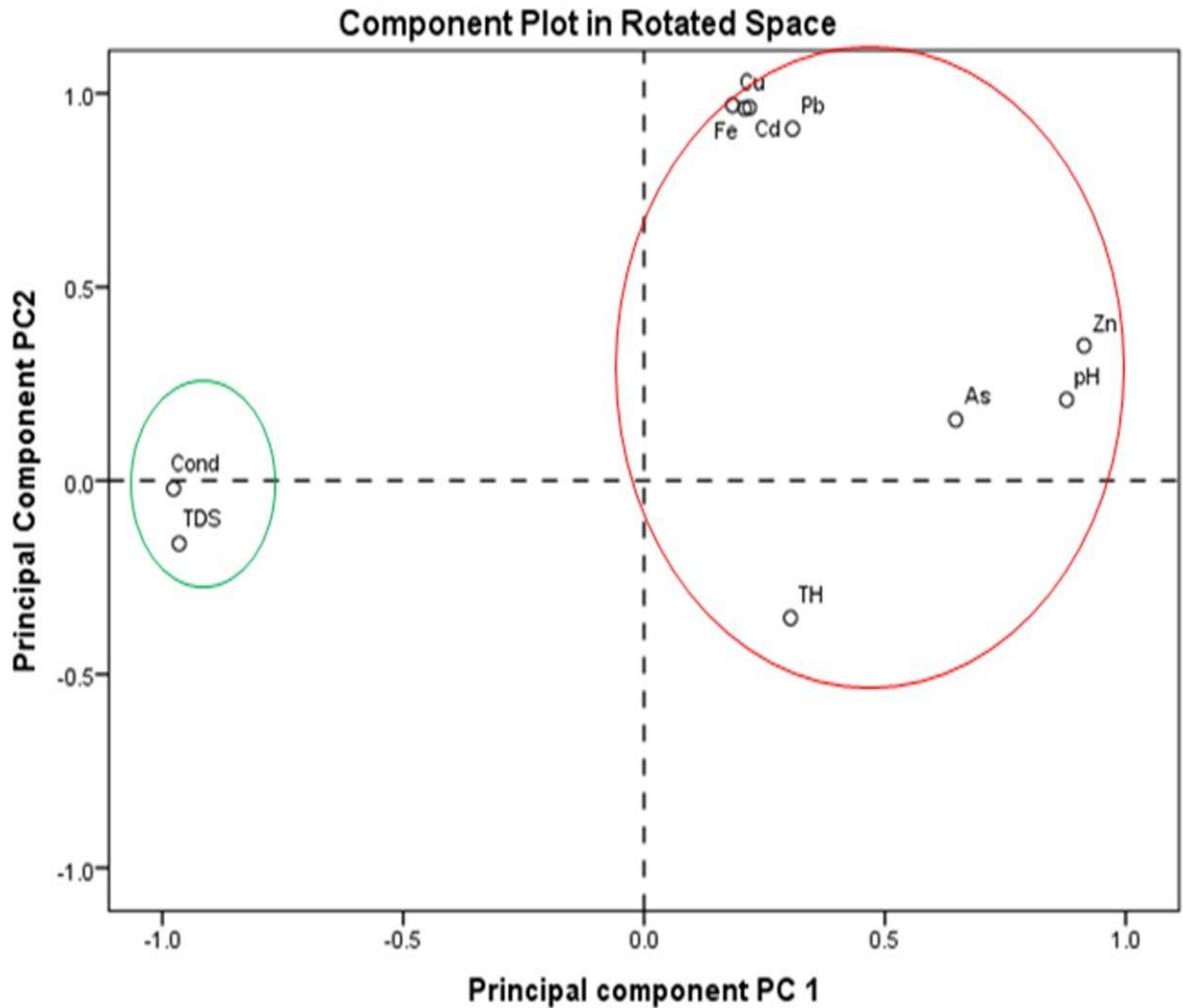
From the PCA, the two components extracted explained 81.81% of the cumulative variances in the dataset. Principal component 1 (PC1) explained 42.21 % of total variance

and had strong positive loadings for the pH, total hardness and heavy metals (Cu, Cd, Zn, As, Pb and Fe) as indicated in Table 4.15. Also PC2 with a variance loading of 39.60% is dominated by the conductivity (EC) and total dissolved solids (TDS).

**Table 4.15: The rotated component matrix for heavy metals and the physicochemical parameters in water samples from Suame Magazine industrial area**

	Component	
	PC1	PC2
Zn	0.914	0.349
Fe	0.209	0.961
Cu	0.184	0.969
Cd	0.219	0.963
As	0.647	0.157
Pb	0.308	0.909
pH	0.877	0.209
Cond	-0.977	-0.020
TH	0.304	-0.355
TDS	-0.965	-0.163
Total	4.221	3.96
% of Variance	42.212	39.601

Groups 1 and 2 as illustrated in Figure 4.18 suggest that groundwater chemistry at Suame Magazine industrial area is controlled by the dissolution of these metals, its ability to exchange ions and also the movement of these ions in solution. Since the conductivities and the total dissolved solids for the water resources were very high especially the Nkradan stream, it can be deduced that the activities at Suame Magazine are the main contributors and that the high concentrations of the metals in the water resources is mainly anthropogenic.



**Figure 4.18: plot of rotated principal component loadings for heavy metals and physicochemical parameters of water samples.**

#### **4.8 HEALTH RISK ASSESSMENT (WATER SAMPLES)**

##### **4.8.1 Chronic and hazard quotient**

The water resources (boreholes, hand dug well, hand pump well, pipe-borne water, Nkradan stream) at Suame Magazine are used by the artisans for domestic purposes such as washing, cleaning of machinery parts and others. Therefore assessing the health risks on artisans is important since they are exposed to heavy metals in water through two main routes (ingestion and dermal). The chronic daily intake through ingestion and dermal contact of the water samples were calculated using equations in Table 4.8. The health risk associated with drinking water depends on the volume of water consumed and the weight

of the individual. In this regard, health risk assessment (chronic daily intake and the hazard quotient) was determined using the maximum and the minimum heavy metal concentration in the water samples and the results are presented in Table 4.18 and 4.19

**Table 4.16: Chronic daily intake (CDI) through two (2) exposure pathways in heavy metals**

Metals	CDI ingest-water		CDI dermal-water	
	minimum	maximum	minimum	maximum
<b>Cu</b>	3.393E-3	9.919E-2	8.860E-11	1.774E-9
<b>Cd</b>	2.641E-3	5.349E-2	4.609E-10	9.569E-9
<b>Zn</b>	4.368E-3	8.784E-2	7.814E-10	1.571E-8
<b>As</b>	4.215E-4	5.962E-2	8.433E-10	3.199E-8
<b>Pb</b>	2.208E-4	5.578E-2	3.926E-11	9.978E-9
<b>Fe</b>	1.00E-2	1.269E-1	1.845E-9	2.271E-8

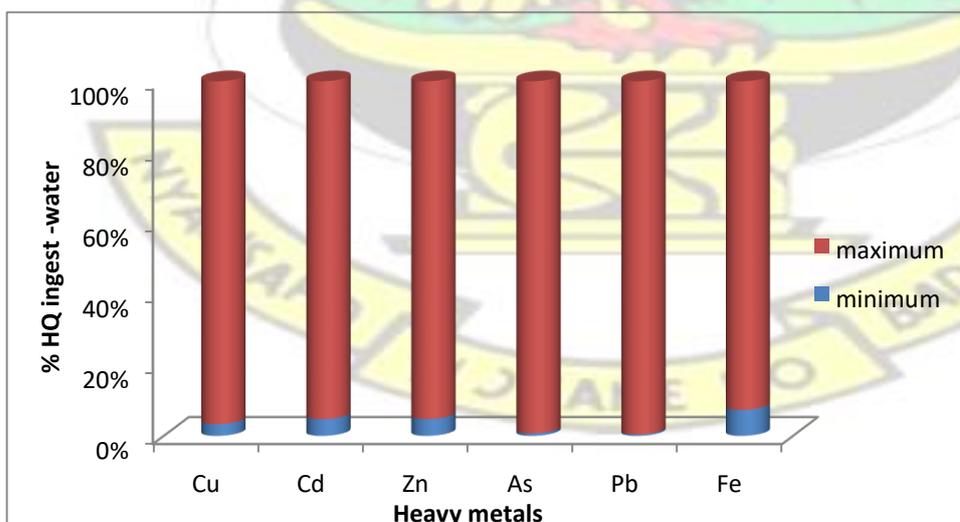
From the results the CDI ingest-water and CDI dermal-water (taking into consideration the minimum and maximum concentration) for the individual metals were found to be less than unity ( $CDI < 1$ ) indicating that artisans at Suame Magazine industrial area would not experience any significant health risks. The exposure route through ingestion (CDI ingest-water) presented relatively higher potential of health risk than through dermal contact.

**Table 4.17: Non-carcinogenic risks (HQ) through two (2) exposure pathways in heavy metals**

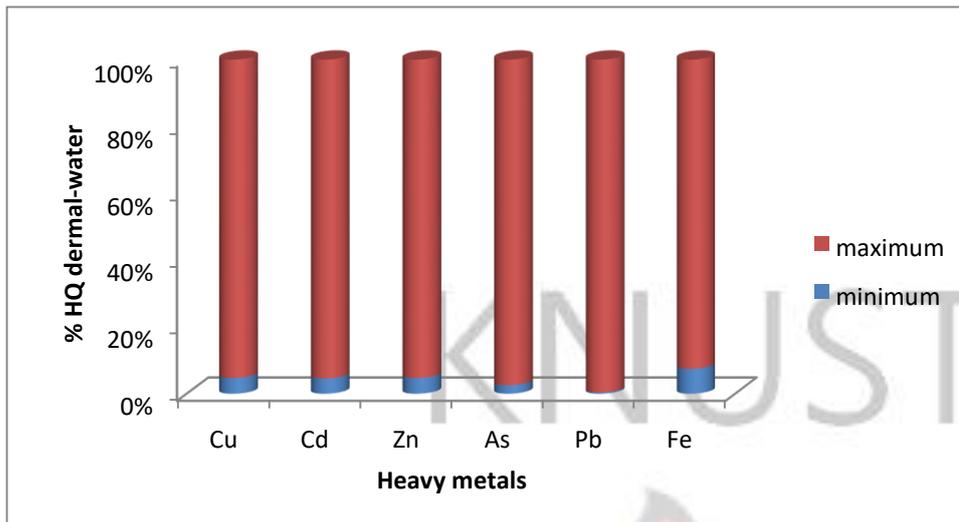
Metals	HQ ingest-water		HQ dermal-water	
	minimum	maximum	minimum	maximum
<b>Cu</b>	8.440E-2	2.479E+00	2.215E-9	4.435E-8
<b>Cd</b>	2.641E+00	5.349E+01	4.609E-7	9.569E-6
<b>Zn</b>	1.456E-2	2.928E-1	2.604E-9	5.236E-8
<b>As</b>	1.405E+00	1.987E+02	2.811E-6	1.066E-4
<b>Pb</b>	6.308E-2	1.593E+01	1.122E-8	2.851E-6

<b>Fe</b>	1.429E-2	1.812E-1	2.636E-9	3.242E-8
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The HQ ingest-water of the metals were greater than unity (HQ>1) for the maximum concentration of the individual metals (2.479E+00, 5.349E+01, 1.987E+02, 1.593E+01) representing Cu, Cd, As and Pb respectively as indicated in Table 4.19. The maximum concentration used in this calculations were from the Nkradan stream implying that artisans who use water from the Nkradan stream are likely to suffer from adverse health effects such as hypertension, diabetes, has a negative impact on reproductive processes (infant mortality and weight of newborn babies), cancer and other health related problems. Artisans who use the Nkradan stream have the probability of experiencing 99.99% of Pb and As health related problems compared to those who use the other water resources (borehole, hand pump well and hand dug well) as shown in Figure 4.19a. Although the exposure through dermal contact presents a lower health risk, artisans who use the Nkradan stream are likely to experience 99.99% Pb related problems as indicated in Figure 4.19b. The trend of HQ ingest-water and HQ derma-soil of the metals is As > Cd > Pb > Cu > Zn > Fe respectively.



**Figure 4.19a: % HQ ingest- water for the minimum and maximum concentration of the individual metals in water through ingestion pathway**



**Figure 4.19b: % HQ dermal- water for the minimum and maximum concentration of the individual metals in water through dermal absorption pathway**

#### 4.8.2: Hazard index

The hazard indices of heavy metals in the water samples from Suame Magazine industrial area was treated as the arithmetic sum of the hazard quotient of the individual metals

$$\text{Hazard index (HI ingestion)} = \text{HQCu} + \text{HQCd} + \text{HQZn} + \text{HQAs} + \text{HQPb} + \text{HQFe}$$

$$\text{Hazard index (HI dermal)} = \text{HQCu} + \text{HQCd} + \text{HQZn} + \text{HQAs} + \text{HQPb} + \text{HQFe}$$

The hazard indices of heavy metals through ingestion and dermal contact as a means of exposure were in the range (4.22E+00- 2.71E+02) and (3.290E-6- 1.191E-4) respectively with the HI > 1. Thus Artisans at Suame Magazine industrial area are likely to experience serious health implications. Although the HI of exposure through dermal contact is less than 1 (HI < 1), their cumulative effect is of concern. It can be inferred that the overall non-carcinogenic health risk assessment at Suame Magazine industrial area indicated significant risk via the ingestion route (HI = 4.22E+00 - 2.71E+02).

### 4.8.3: Carcinogenic risk

The carcinogenic risk through ingestion and dermal contact as means of exposure in heavy metals is presented in the Table 4.18.

**Table 4.18: Cancer risks for two exposure pathways in heavy metals**

Metal	Ingestion –water		Dermal absorption –water	
	minimum	maximum	minimum	maximum
As	2.810E-4	3.974E-2	5.622E-10	2.133E-8
Cd	*	*	*	*

\*means the value of cancer slope for Cd could not be assessed in IRIS, provided by USEPA database, 2005).

The results showed higher cancer risk values for arsenic in the range (2.810E-4 -3.974E2) and (5.622E-10 -2.133E-8) for ingestion and dermal contact of water as indicated in Table 4.20.

The cancer risk (CR) value for ingestion of water samples was higher than the acceptable or tolerable risk limit (1E-06 to 1E-04) by USEPA (2001) but the cancer risk value for dermal contact was below the USEPA acceptable value. Therefore, As appears to be the main pollutant source to produce cancer among these heavy metals and the dominating exposure route for As to artisans at Suame Magazine industrial area is through ingestion (oral).

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSION

The pH and the conductivity values of the soils in almost all the soil samples from the various zones decreased with depth. Soil samples in zone A, C and D are moderately alkaline (within the range 7.1- 8.5) with the exception of zone B which is slightly acidic.

The soil samples in all the zones are highly saline (have conductivity values  $> 150$  us/cm).

The percent moisture content in all soil samples from the four zones were high with the exception of soil samples from maintenance shops in Zone A, Zone B, Zone C and Zone D which were very low and this can be attributed to the low permeability and low infiltration of water in the spent lubricating oil polluted soil in the various maintenance shops. Soil samples from maintenance shops from Zone A, Zone B, Zone C, and Zone D respectively have the highest organic matter content which can be attributed to the increase in organic carbon in addition to the carbon already present in the soil. The particle size distribution for soils at the different depth in all the four zones contains a higher percentage of sand followed by clay and silt resulting in low cation exchange capacity ( $< 25$  meq/100g).

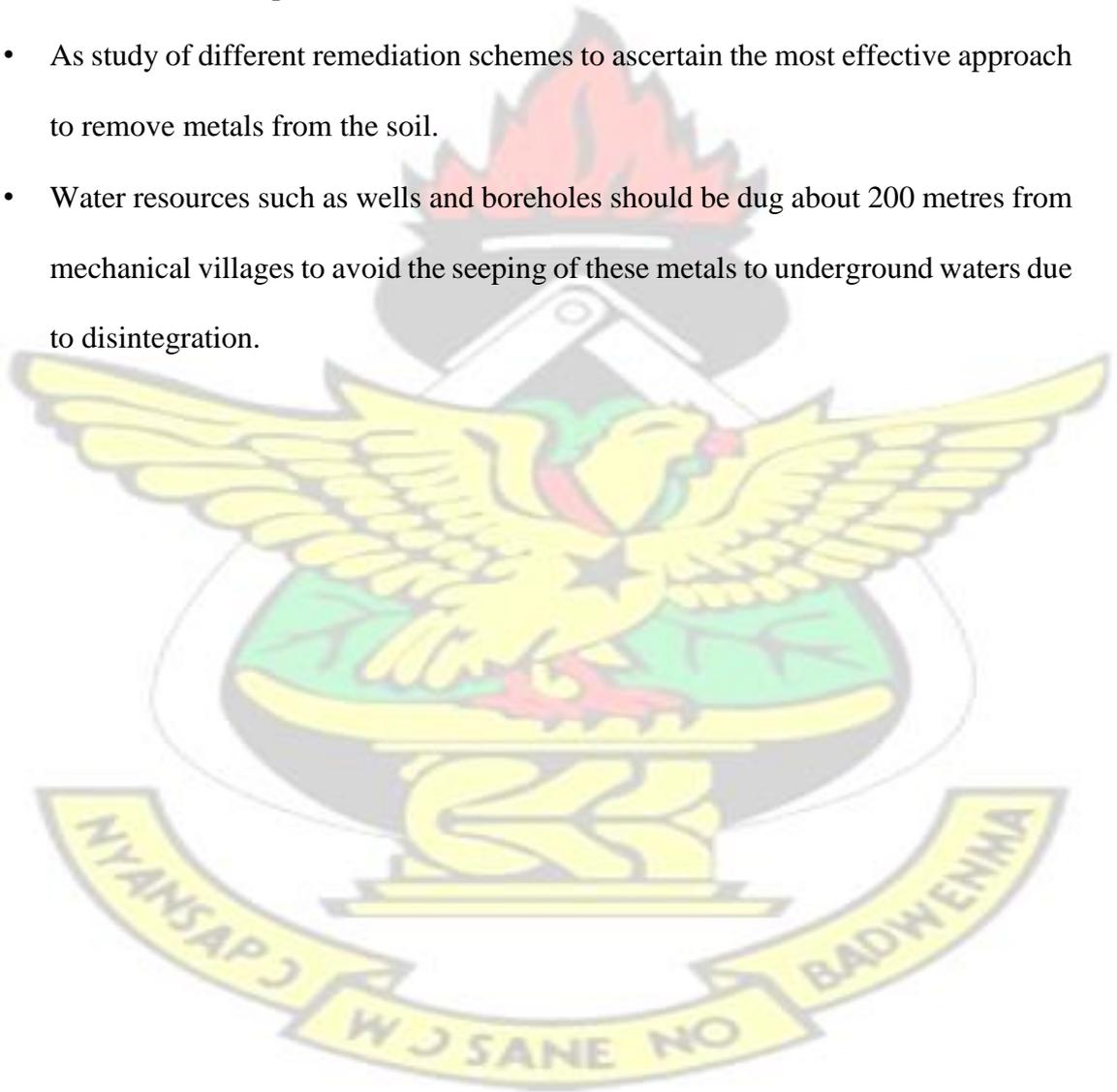
The heavy metal concentration for the six metals determined is in the order;  $Fe > Zn > Cd > As > Pb > Cu$  and the levels of these metals decreased with depth of the soil profile. Artisanal activities such as welding and metal fabrication contributed to high levels of the metals. Assessment of heavy metal at Suame Magazine industrial area using indices of pollution (contamination factor, geo-accumulation index pollution load index and quantification of anthropogenic metal ) revealed that the study area is highly polluted with these metals in the order  $Fe > Zn > Cd > As > Pb > Cu$ .

Also multivariate statistical analysis such as PCA analysis, coupled with correlation analysis, were used to gain additional insight into the correlativity of these metals and their origins. The high correlation coefficients between the different metals indicate strong association between them, which probably reflects their related or common origin. The PCA yielded 3 components which explained 87.84 % of the total variance in the data, and this suggests that the three components containing Cu, Cd, Zn, As, Pb is mainly the result of anthropogenic or industrial activities, in addition to the original content from the weathered soil because these metals had mean concentrations that were higher than the control or background values.

The impact of high concentration of these metals on the health of artisans due to their activities was also assessed through two exposure routes (ingestion and dermal contact). This study revealed that water resources at Suame Magazine is influenced by artisanal activities due to the high concentration of the metals above the permitted levels by WHO standard for quality drinking water. Also the water resources are influenced by physicochemical parameters such as pH, conductivity, total dissolved solids and total hardness. Multivariate statistical analysis indicated that the two- component extracted from the dataset explained 81.81% of the cumulative variance was sufficient to give an idea about the data structure. The hazard coefficient and the cancer risk were calculated and the results show that artisans are likely to suffer from cancer through ingestion of soil and water as a means of exposure. From the study, it can be concluded that soils at Suame Magazine industry area are highly polluted and the main water which was highly polluted was the surface water (Nkradan Stream)

## 5.2 RECOMMENDATION

- Further works on speciation of the metals should be carried out in order to ascertain the form in which the various metals exist since it may have effect on its mobility in the soil.
- Modern waste disposal facilities should be acquired by relevant authorities and appropriate waste disposal sites be chosen to avoid the injurious effects of indiscriminate disposal of wastes.
- As study of different remediation schemes to ascertain the most effective approach to remove metals from the soil.
- Water resources such as wells and boreholes should be dug about 200 metres from mechanical villages to avoid the seeping of these metals to underground waters due to disintegration.



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