KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

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CONTAMINATION AND HUMAN HEALTH RISK DUE TO TOXIC METALS IN DUST FROM TRANSPORT STATIONS AND MARKETS IN THE KUMASI METROPOLIS, GHANA

A Thesis Submitted to the Department of Chemistry, Kwame Nkrumah University of Science and Technology in Partial Fulfillment of the Requirements for the Degree of

MASTER OF PHILOSOPHY IN CHEMISTRY

BY

ALMACHIUSI RWEGASIRA RWEYEMAMU

(BSc. Education)

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DECLARATION

I hereby declare that this submission is my own work toward the degree of M.Phil 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.

Almachiusi Rwegasira Rweyemamu …… ……
(Student ID: PG-20445098) Signature Date

Certified By:

Dr. Marian A. Nkansah …… ……
(Supervisor) Signature Date

Dr. Godfred Darko …… ……
(Supervisor) Signature Date

Dr. Nathaniel O. Boadi …… ……
(Head of Department) Signature Date

DEDICATION

This work is dedicated to the Almighty God for his vast blessings, love, wisdom, favor, courage, strength, knowledge and gift of life he has provided me till today and also to

my dear wife, Macklina A. Rugemalila and children, Alice and Jacinta for their enormous love, care, support, encouragement and patience during the whole period of my absence.

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ABSTRACT

Heavy metals are very harmful to human health and their increasing contamination of dust in the urban areas calls for serious attention to them. The aim of this study was to determine the concentrations and assess the potential human health risk associated with exposure to selected heavy metals in dust from transport stations and markets within the Kumasi metropolis, Ghana. A total of 50 dust samples from transport stations and markets were collected by sweeping ground surface dust and analyzed for Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Nickel (Ni), Lead (Pb), Zinc (Zn), Iron (Fe), Mercury (Hg) and Antimony (Sb). The concentrations of Hg were determined by Atomic Absorption Spectrophotomery using a Lumex RA-915M Zeeman Automatic Mercury Analyzer while the levels of other metals were determined by using X-ray Fluorescence analyzer (Niton XL3t GOLDD+). The concentrations of As, Cd, Cr, Hg, Cu, Ni, Pb, Zn, Fe and Sb in transport stations ranged from below detection to 9.66, below detection to 37.13, below detection to 260.11, 0.01 to 0.62, below detection to 143.77, below detection to 47.62, below detection to 61.73, 48.89 to 218.61, 3768.97 to 40936.07 and below detection to26.01 mg/kg respectively.The concentrations of As, Cd, Cr, Hg, Cu, Ni, Pb, Zn, Fe and Sb in markets ranged from below detection to 6.20, below detection to 14.61, below detection to 232.90, 0.01 to 1.38, below detection to 181.85, below detection to 44.79, below detection to 72.10, 59.29 to 293.68, 8283.66 to 34953.63 and below detection to 21.72 mg/kg respectively. The study revealed no significant difference between the mean concentrations of heavy metals in dust from transport stations and markets at 95% confidence limit of T-test analysis ($p>0.05$). The mean geo-accumulation, contamination factor and modified degree of contaminations indicated that dust from both transport stations and markets were moderately to extremely polluted by metals compared to their abundance in the dust of the control site (KNUST Botanic Gardens). Mean enrichment factors indicated that metals were highly

enriched in the dust and originated from anthropogenic sources. Pollution load index which ranged from 1.39 to 12.55 for transport stations and from 1.48 to 15.62 for markets revealed high pollution load. The hazard index (HI) and carcinogenic risk index (CRI) were used to assess human health risk. Hazard indices for all the metals were less than the safe limit of 1, signifying no potential non-carcinogenic risk for both children and adults. Exposure to multiple metals was observed as a major concern of non-carcinogenic risk to children. Among the metals assessed for carcinogenic risk, the CRI of Cd in both transport stations and markets exceeded the safe limit of $1x10^{-4}$ for children. Health risk assessment indicated children to be highly exposed to heavy metals in dust via ingestion compared to adults. This study observed high pollution load of heavy metals in the studied areas and therefore appropriate measures need to be taken in order to manage the pollution.

Key words: Soil dust pollution, Human Health risk, Toxicity, Exposure

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LIST OF ABBREVIATIONS/ACRONYMS

ADD	Average Daily Dose
ATP	Adenosine Triphosphate
ATSDR	Agency for Toxic Substances and Disease Registry
CCME	Canadian Council of Ministers of the Environment
Dc	Degree of Contamination
CF	Contamination Factor
CRI	Carcinogenic Risk Index
EF	Enrichment Factor
GPS	Global Position System
HI	Hazard Index
HQ	Hazard Quotient
IARC	International Agency for Research on Cancer KNUST

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mCd	Modified Degree of Contamination
NIST	National Institute of Standards and Technology
NIOSH	National Institute of Occupational Safety and Health
OSHA	Occupational Health and Safety Administration
PLI	Pollution Load Index
RfD	Reference Dose
SD	Standard Deviation
USEPA	United States Environmental Protection Agency
XRF	X-Ray Fluorescence

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

The term "heavy metals" has no agreed general definition and has been used variably by different authors depending on the context. Basing on various criteria such as density, atomic weight, chemical properties, toxicity, periodic position, and atomic numbers, different meanings have been given to heavy metals. Heavy metals were defined by Duffus, (2002) as metals and metalloids with potential ecotoxicity or toxicity properties. Considering density criterion, heavy metals were defined as those metals and metalloids with a specific gravity greater than 4 g/cm^3 (Adelekan and Abegunde, 2011).

Heavy metals pollution is listed as one of the environmental problems faced by the world today due to their potential toxicity and health effects on humans. Naturally, heavy metals are found as constituents of the earth crust and are released by weathering of rocks (Duruibe *et al*, 2007). Demands for use of some of the heavy metals and human activities have significantly contributed to the availability of these metals on the earth's surface to the extent that it is dangerous to human health (Sayadi *et al.*, 2015). The amount of heavy metals accumulated from human activities to the environment is significantly higher compared to that generated from natural processes such as volcanic eruptions (Lu *et al.*, 2010).

Heavy metals such as zinc (Zn), lead (Pb), cadmium (Cd), mercury (Sb), nickel (Ni), chromium (Cr), arsenic (As), copper (Cu), iron (Fe) and antimony (Sb) are released in the environment at variable concentrations from different sources. These metals are non-biodegradable and when they accumulate in the environment, they have no precise physical mechanism for their removal and therefore remain as part of a lifetime human

exposure (Popoola *et al.*, 2012). For the fact that heavy metals are known to be stable and persistent, they are almost found everywhere in the environment such as in soils, water, sediments, dust, plants and the atmosphere (Wei et *al*., 2010). Apart from human activities, the dispersion of these metals to different parts of the environment appears to be influenced by other factors such as weather conditions (wind and rainfall) and metal characteristics especially the form in which the metals exist.

Heavy metal contamination in dust of urban areas is a current prevailing health concern to urban dwellers globally (Hu *et al.*, 2011). Dust which settles on the ground surface act as the receptor of metal contaminants emitted from different anthropogenic activities and atmospheric deposition of airborne particles. Humans are exposed to these metals through inhalation, dermal contact and ingestion of contaminated dust (Olowoyo *et al*., 2016). Wang *et al.*, (2013) has shown that ingestion of dust particles is a major pathway for exposure to heavy metals in dust followed by dermal contact.

Considering the human population groups that are exposed to metals; children, women and the aged are considered to be significantly affected from exposure to heavy metals in urban dust (Li, *et al*., 2014). Studies have shown that young children aged 1-6 years are more exposed to heavy metals in dust due to their behaviors such as playing with ground surface soil, mouthing fingers and hands, and eating non-food objects and unwashed fruits (Latif *et al.*, 2014; Nkansah *et al.*, 2015; Praveena., *et al* 2015). In this perspective, children are considered to be at risk of suffering from health effects associated with heavy metals compared to adults (Praveena et al., 2015). The exposure to metals from dust in all sensitive groups of the human population seems to occur unintentionally.

Due to the increasing rate of accumulation of heavy metals in the environment, humans are persistently exposed to them on a daily basis. Exposure to the amount of metals greater than the acceptable limit can seriously result in clinical health effects of which some can be irreversible (Sharma and Agrawal, 2005).This is because when these metals enter the human body, they cannot be metabolized and therefore they accumulate in the fatty tissues, muscles, bones or may be deposited in the circulatory system. The human body can only tolerate metals below the threshold values but when accumulation exceeds these values, the biological performance of the body systems, organs and macromolecules such as proteins and enzymes become affected (Duruibe *et al.*, 2007).

Although some metals are required by the body for biochemical and metabolic activities, toxic metals such as mercury, lead, arsenic, and cadmium are non-essential metals and therefore are not required for biological activities of the body. In the past decade, attention had been given to these metals because they adversely affect human health at lower concentrations (Adaramodu *et al*., 2012). Even though other metals such as copper, zinc, nickel, manganese and chromium are nutritionally essential for healthier life, nevertheless they demonstrate serious health effects when their concentrations exceed the tolerable limits (Otitoju et al., 2014). On the other hand, deficiency of essential metals may cause different biological abnormalities and diseases. For example, deficiency of iron may result in anemia, a disease which indicates the deficiency of oxygen supply to body cells.

The potential health impacts associated with human exposure to toxic metals are metal-dependent and solely depend on the length of exposure, dose taken and bioavailability of metals. Chronic exposure to metals such as lead may cause memory loss and decreased intellectual ability. Lead is also associated with damage of kidney, liver and central nervous system while chronic exposure to cadmium can cause kidney disease, bone

defects, lung dysfunction, and cancer. Inorganic arsenic (As) is a human carcinogen and may conceal proteins, form complexes with enzymes and hinders the production of the energy store compound (ATP) during respiration (Philip *et al.*, 2017). Similarly, chronic exposure to other metals such as Zn, Cu, Cr, Ni, and Co, may adversely affect human health depending on the level of toxicity and exposure. The health effects associated with exposure to metal pollutants, concentration of metals in the contaminated dust and potential sources of these metals are important concerns to many researchers and are frequently investigated.

Studies related to heavy metal contamination in dust have been largely conducted in developed nations with background of industrialization (Madrid and Madrid, 2002; Shi *et al.*, 2008; Kidak, 2017). Industries are noted to have a significant contribution to the contamination of environmental media such as soil, water and dust with heavy metals. Research has shown that dust from urban areas with many industrial activities is highly contaminated with heavy metals than that from areas with less industrial activities (Dehghani *et al.*, 2017). Polluted industrial dust can be transported by air movement to contaminate different urban areas such as markets, streets and schools. In developing countries including Ghana, dust has been ignored as an important environmental medium for heavy metals pollution and studies related to that is limited. Due to urbanization and industrialization of many cities, heavy metal contamination in dust has been reported from streets, highways, urban parks, roadsides, residential buildings, industrial areas and elementary schools (Meza-figueroa *et al.*, 2007; Kong *et al.*, 2011; Olowoyo *et al.*,2016; Ajayi *et al.*, 2017; Shao *et al.*, 2018). The pollution of these areas with metal contaminants has been shown to be associated with the increasing anthropogenic activities such as combustion of fossil fuels, coal combustion, metal smelting, industrial activities, vehicular movement, construction, renovation and demolishing activities (Al-

khashman, 2013; Atiemo *et al.*, 2012; Latif *et al.*, 2014). Other studies have shown that unmonitored waste incineration, auto mechanical workshops, weathering of buildings, deterioration of galvanized metal components and metal fabrications may intensify the level of contamination of urban dust with metal pollutants (Lu *et al.*, 2014; Hu *et al.*, 2011).

For most growing cities like Kumasi with increasing number of urban traffics, industries and other human activities, it is expected that the contamination of surface soils and dust with metal pollutants will be on the increase. This is because vehicular traffics and industries are the most contributing activities to heavy metal pollution in air and land surfaces (Feng e*t al*., 2012). Many other studies have confirmed the significant contribution of high traffic volume to metal pollution of the urban dust (Apeagyei *et al*., 2011; Khairy *et al.*, 2011; Atasoy *et al*., 2015). The common heavy metals released from vehicles include Pb from the combustion of leaded gasoline and storage batteries, Zn, Cd and Cu from car components, lubricant oils, brake lining wear, tyre wear and engine exhausts. Chromium and nickel are considered to be from deterioration of car parts and plating of some parts of the motor vehicle with chromium-containing materials (Shi and Wang, 2013; Elnazer *et al.*, 2015). These metals may be released in significant amounts into urban dust and may affect the health of urban dwellers since high concentration of toxic metals is totally unsafe for human life. Therefore, understanding the level of contamination of urban dust by these metals and their associated risk will help to develop appropriate measures and strategies required for the protection of the exposed human population.

1.2 Problem Statement

The Kumasi metropolis is one of the fastest growing cities in Ghana in terms of human population and economic activities (Ghana Statistical Service, 2014). As the city

continues to grow, human activities related to heavy traffics, industries, welding, constructions and metal fabrications are also on the increase. These activities have been noted to be the major potential sources of heavy metal contamination in urban areas (Kong *et al.*, 2011). Transport stations and markets are among the places to be likely polluted with heavy metals due to the high traffic volume and other anthropogenic activities in these areas. Dust from these places may contain significant amounts of heavy metals and human exposure to these metal contaminants can adversely affect their health and make them potential victims of heavy metal poisoning (Atiemo *et al.*, 2015). Even though studies have been conducted to address the levels and risks of heavy metal pollution in dust from different areas such as fuel filling stations and schools within the Kumasi metropolis (Nkansah *et al.*, 2015, 2017), no published work conducted on dust from transport stations and markets is available. There is, therefore, the need to determine the contamination levels of heavy metals in dust and perform human risk assessment to establish the potential health risks associated with exposure from markets and transport stations.

1.3 General Objective

The aim of this study is to assess the contamination levels and human helth risk of selected heavy metals in dust from markets and transport stations in the Kumasi metropolis.

1.4 Specific Objectives

This research is intended to:

(i) Determine the concentrations of Pb, Hg, As, Cd, Ni, Cr, Cu, Sb, Fe and Zn in dust from selected transport stations.

(ii) Determine the concentrations of Pb, Hg, As, Cd, Ni, Cr, Cu, Sb, Fe and

Zn in dust from selected markets.

(iii) Assess the potential health risks associated with human exposure to heavy metals in dust from transport stations and markets.

1.5 Justification of the Study

Heavy metals are very dangerous to human health and their increasing contamination of dust in the urban areas calls for serious attention. Numerous studies have reported the toxicological effects of heavy metals such as Cu, As, Hg, Pb, Cd, Cr, Ni and Zn on human health (Jiménez-capdeville and Giordano, 2003; Henson and Chedrese, 2004; ATSDR, 2007, 2015; Wuana and Okieimen, 2011). Heavy metals such as nickel, chromium, cadmium, lead, and arsenic are human carcinogens and are known to cause different types of cancers to the body organs such as lung, liver, kidney and nasal sinus (IARC, 1990). Apart from cancer, nickel is also known to cause various allergic reactions in humans via skin contact and when excessively ingested can induce mutagenesis (Das *et al*., 2008; ATSDR, 2015).

Oral intake of arsenic causes a decrease in red and white blood cell count, damage in blood vessels, damage to both central and peripheral nervous system (ATSDR, 2007). On the other hand, prolonged human exposure to metallic mercury will cause neurological disorder and brain damage leading to mental confusions such as shyness, tremor, insomnia, restiveness, poor vision, nervousness, irritability and instabilities (Griswold, 2009). People who are exposed to high doses of copper fumes or dust for a long period of time may experience coughing, headache, eye and nose irritations, nausea, dizziness, pulmonary fibrosis and sometimes diarrhea (ATSDR, 2004). Exposure to large amounts of other metals such as zinc can cause thickening and scarring of connective

tissues in the lungs, respiratory distress syndrome (RDS) and collapse of lungs (ATSDR., 2005).

However, in order to minimize the health risks posed by these metal contaminants through dust to human population, a better understanding of their contamination levels and their potential health risks need to be investigated. The outcomes of this study will serve as the reference to Ghana policy makers and environmental regulatory bodies in setting strategies that will serve in the protection of residents against potential health effects of toxic metal pollutants in dust from urban areas. In addition to that, this study will also provide baseline data for future investigations of heavy metals in the dust from other univestigated areas in the Kumasi metropolis and Ghana at large.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Description of Dust, its Sources and Composition

Different meanings have been given to the term "dust" by different writers according to their perceptions. Philip *et al.*, (2017) defined dust as a dry powder that consists of fine particles of solid matter that may be re-suspended or settled on the ground while Yap *et al.*, (2011) considered dust as tiny particles of an average aerodynamic diameter less than 5µm. Basing on the origin of dust components, Wahab *et al.*, (2012) has described dust as a solid matter which constitutes soil anthropogenic metallic components and naturally originated biogenic materials. Therefore, dust can be viewed as a heterogeneous mixture of many substances which are in the form of fine dry powder.

Studies have shown that dust particulates are virtually found everywhere in the environment except in water bodies simply because they are fine particles that can be easily dispersed by wind from their origin to a wide range of the environment (Kong *et al.*, 2011). For this reason, dust particles can be obtained particularly from the ground surface as deposits, in the atmosphere as displaced or suspended aerosol particles blown by physical or natural forces, inside the buildings (deposited on the surfaces of appliances and objects, window seals, floors, ceiling fans, top of doors, tables and roofs), and even on plant barks or leaves (Ferreira-Baptista and De Miguel, 2005). Dust present inside buildings is called indoor dust and about 70% of it come from outdoor which is always described as street dust (Shraim *et al.*, 2016).

In urban areas, dust particles originate from several sources which consist of natural and anthropogenic origins (Khairy *et al.*, 2011). Anthropogenic dust originates from industrial activities, vehicular traffics, demolishing and construction activities, land ploughing, weathering of buildings, urban waste incineration, power production,

combustion of coal, domestic emission, metal smelting and welding (Bilos *et al.*, 2001). A significant amount of dust in the urban environment is influenced by the displacement of surface soil via human activities.

Dust particles originating from both human activities and natural sources contain several contaminants which may be harmful to human health (Du *et al.*, 2013). The contamination levels of toxic components in both outdoor and indoor dust and their potential impacts on human health are what is regularly studied by most researchers. Urban dust may serve as a sink of contaminants such as pet dander, pollen from plants, dust mites which are microscopic pests and insect droppings. All these are considered to be allergic triggers and may not be considered to pose a serious permanent health risk to humans (Tischer *et al.*, 2016).

Dust may contain a variety of chemical components ranging from elemental species to organic and inorganic compounds (Norouzi and Khademi, 2015). Some of the organic compounds (OCs) include polycyclic aromatic hydrocarbons (PAHs), polychlorinated byphenyls (PBs) and dichlorane plus (DPs) (He *et al.*, 2017). The inorganic components of dust may include heavy metals such as Pd, Cr,Ni, Cr, As Hg, Cd, Zn, Fe, Sb and Cu. These elements pose a major health concern to humans upon excessive exposure (Kong *et al.*, 2011).

2.2 Heavy Metals

2.2.1 Sources of Heavy Metals in dust

Heavy metals naturally exist in the environment and can originate from both anthropogenic and geochemical sources (Akoto *et al.*, 2008). Their emission to the environment and distribution is through human activities and natural processes (Shi *et al.*, 2008). There are different routes or pathways in which metals can be released to the

environment. Some involve direct emission to the air followed by atmospheric deposition on the ground surface while other metals can be deposited directly on the ground surface from the point or diffuse sources (Man et al.,2009). Emission of heavy metals to the air and the deposition on the ground surfaces are a major concern of metal contamination in dust. On the average, a higher amount of heavy metal contamination in dust is significantly contributed by anthropogenic activities compared to natural processes (Bilos *et al.*, 2001; Akoto *et al.*, 2017).

In urban areas, industrial activities such as metal cutting and crushing, chemicals production, metal smelting, welding, metallurgy, electroplating, and accumulator manufacturing are involved in the emission of several kinds of toxic metals into the environment (Bortey-sam *et al.*, 2018). Many other industries engaged in fertilizer, pigments, dyes and textiles production, and electronic waste (e-waste) recycling and processing also contribute to the emission of toxic metals of different kinds, forms and concentration into the urban environment (Al-Khashman, 2004). Toxic metals contamination in dust such as Cu, Pb, Cd, and Cr and Zn have been frequently reported from the catchment areas of e-waste processing industries (Atiemo *et al*., 2012).

Emissions from motor vehicles were revealed in many studies as the major sources of heavy metal contamination in urban road dust (Al-khashman, 2004; Latif *et al.*, 2014). Fossil fuel combustion (engine exhausts), lubricating oil, brake lining wear, tire wear and corrosion of some parts of the motor vehicle are major sources of metals emission from automobiles (Acosta *et al.*, 2015). Brake lining is made up of a high amount of iron and copper, and hence frictions and heat which occur when brakes are applied can result in the release of iron and copper into the environment (Adachi and Tainosho, 2004). Zinc oxide is usually incorporated as an activator during vulcanization of tires, and therefore

wear and tear of tires result into the emission of a large amount of zinc into the environment (Adachi and Tainosho, 2004; Elnazer *et al.*, 2015). Metals such as Ba, Ni and Cd are the major components of oil additives while Cr is released from the deterioration of car components because most of the car parts are plated with chrome materials (Charlesworth *et al.*, 2003). Lead is released into the environment as a result of combustion of leaded gasoline (Khoder *et al.*, 2012). A study conducted by Yang *et al.*, (2016) reported high levels of chromium, cadmium, zinc, copper and nickel in the road dust which is due to traffic emission. Dust contaminations by molybdenum, chromium, lead, copper, zinc, tin and manganese from automobiles were also reported in Duzce, Turkey (Atasoy *et al*., 2015). Similarly, in Nigeria, automobile emissions contribute to about 80% of air pollution by heavy metals (Anapuwa and Precious, 2015).

Other human activities considered to concentrate heavy metals in urban dust include municipal metal waste disposal (Acosta *et al.*, 2015), waste incineration, energy production, domestic heating, coal burning (Atiemo *et al.*, 2015), demolishing and construction of building, use of volatile pesticides containing toxic metals such as arsenic and copper for wood preservation, agricultural use of inorganic fertilizer, welding, auto mechanical workshops, and extensive road construction and painting (Faiz *et al.*, 2009; Du *et al.*, 2013; Xia *et al.*, 2014). Iron is largely used in road construction as well as one of the main components of bridge construction hence deterioration and welding of the iron parts contribute to the emission of iron metal in the environment. Heavy metals can also be released into the environment through igneous rocks such as olivine and augine that add excessive amounts of Cu, Ni, Co, Mn, Co, and Zn to the soil layers and can be released into dust by human activities such as agriculture (Garrett, 2010).

2.2.2 Human Biological Benefits of Metals

The effects of metals can either be beneficial or harmful to the biological systems depending on the amount the body is exposed to, type of metal and the rate of exposure. Essential metals are necessary for appropriate functioning of the human body systems, organs, and macromolecules such as enzymes. Many critical life processes in the body such as development, respiration, metabolism, muscle contraction, nerve transmission, and signal transduction require essential metals in order to function properly (Andreini *et al.*, 2008).

The roles of metals range from subcellular to cellular levels and systems. Metals such as copper, zinc, cobalt, iron, chromium, manganese, molybdenum are known to be crucial elements for human living. These metals are largely beneficial at lower concentrations and can be obtained naturally from fruits, foods and are commercially accessible from multivitamin products. Other metals such as lead, cadmium, mercury and arsenic are toxic metals at lower concentration because they have no known biological roles in the human body (Caussy *et al.*, 2003).

Some metals such as copper and zinc perform major functions in the active centers of metalloenzymes (Reeder and Schoonen, 2006). For example, copper acts as an active centre in tyrosinase, cytochrome oxidase and superoxide dismutase while zinc acts as an active centre of carboxypeptidase-A, carboxypeptidase, hydrase, and alcohol dehydrogenase enzymes. Tyrosinase enzyme which catalyzes the synthesis of skin melanin was the first enzyme in the human body to which copper was shown to be necessary for metabolic function (Festa and Thiele, 2011). Zinc has the structural role of binding proteins (zinc fingers) during DNA-RNA transcription (Rawlings and Barrett, 2006). Symptoms associated with zinc deficiency include growth retardation and poor sexual development in young men. Iron in the body forms part of major proteins which

participate in oxygen transportation, storage (haemoglobin and myoglobin) and electron transfer (cytochromes) during respiration process. Iron is the most abundant trace element in the human body and its deficiency may result in anemia. Other metals such as vanadium and chromium (III) are required by the body only in very trace amounts. Their general biological roles are not clear but they are only known to be important for sugar metabolism. Chromium imbalance affects glucose metabolism, the reproductive system and can lead to obesity and cardiovascular diseases. Cobalt is known for its biological function in vitamin B_{12}, coenzyme B_{12} and related enzymes such as isomerases (Williams, 2003). Metals are known to function as activators of body enzymes which regulate and control several metabolic activities. Therefore, metals have important chemistry of the living systems and most of the body biomolecules and physiological processes always depend on essential metals (Sevanian and Hochstein, 1985).

2.2.3 Economic Benefits of Metals

Besides the biological benefits, metals have unique applications in different fields such as industry, agriculture, medicine, construction and building (Zheng *et al.*, 2007). In agriculture, metals have been used for some decades now for manufacturing agricultural chemicals. Metals such as tin, arsenic, mercury, and copper are included in the manufacture of pesticides and herbicides (ATSDR, 2004). Pesticides containing metals are used to control both agricultural and woods attacking pests. Some metals such as manganese and magnesium are common ingredients in the production of chemical fertilizers for good agricultural yield. In industries, metals have a wide range of applications, for examples metals are used in the production of catalysts, laboratory chemicals, pigments, paints and manufacture of aerosols. In the building industry, metals are processed into casting, tubes, and sheets and they are modulated to build marine vessels, automobiles and aircraft. Copper is well known for industrial production pipes

and tubes (ATSDR, 2004). Electronic equipment, electric cables and wires are all products of metals. Precious metals such as gold and silver currently are used in the production of decorative items such as jewelry. Globally, mercury is known for its role as an amalgamator in gold extraction and it is a component of batteries and electrical switches. Even though the use of mercury is illegal in some countries such as Denmark, Sweden and Norway, it is still used in many countries as amalgams in the dental filling (U.S. EPA, 2008).

In the medical field, metals are used as diagnostic agents, anticancer, antimicrobial and antiparasitic agents. The cisplatin is one of the best anticancer drugs and it contains platinum metal in the complex (Guo and Sadler, 1999). Arsenic, bismuth and gold are used as substrates of production of antimicrobial and antiparasitic agents for many diseases. Today, metal supplements such as vitamins are produced largely from metals in order to supplement the deficiency of essential minerals in humans and animals (Guo and Sadler, 1999). Metals such as technitium and gallium are widely used in medical diagnosis. Mercury has been widely used in therapeutic applications such as purgative, cathartic, vermifuge, and ant-inflammatory agent (Peraza *et al.*, 1998). The numerous applications and uses associated with metals, make it economically noteworthy and can contribute abundantly to the growth of the economy if they are used effectively with all required environmental protective measures.

2.2.4 Exposure Pathways of Heavy Metals

The exposure pathways to which humans are exposed to toxic metals are fully portrayed in many studies because of their associated toxicological health effects. Exposure to each metal contaminant takes place through various pathways which depend on the specific contaminated media such as dust, food, soil, air or water (Caussy *et al.*, 2003). Ingestion,

inhalation and dermal contact are common exposure pathways to heavy metals in dust (Reeder and Schoonen,2006). Ingestion occurs through the gastrointestinal tract, inhalation is via the respiratory tract and dermal involves skin absorption. The physical state or chemical form in which metals exist such as liquid, gas or solid suggests the level of exposure via a particular pathway (Reeder and Schoonen, 2006). Inhalation is a primary route of exposure to airborne toxic metals and contaminated dust particles which are suspended in the atmosphere. The potential impacts associated with inhalation of toxic metals are influenced by several factors such as the volume, intensity of inspiration, type of organ involved (oral or nasal), age, and sex of the exposed individual. Toxic metals such as cadmium, lead, nickel and arsenic are ordinary airborne metals and can enter the body via inhalation (Vincent, 2005). The amount of metals that are absorbed through the skin depends on the dermal absorption factor of each metal and the exposed surface area. Therefore, all exposure pathways allow a significant amount of heavy metals to enter the body of the exposed individual although the amount may differ from one pathway to another (Oves *et al.*, 2016).

2.2.5 Health Effects due to Exposure to Heavy Metals

Detrimental health effects and toxicity associated with heavy metal contaminants is of greater concern to regulatory agencies and researchers globally. Elevated levels of toxic metals in the human body seriously affect the performance of the physiological processes such as metabolism, nerve transmission and can cause damage to body organs, systems, cancer and even death. Heavy metals such as zinc, copper, cadmium, chromium, nickel, mercury and lead are known to be stable; therefore, they cannot be digested or metabolized by the body. These metals tend to accumulate in the body tissues, organs, and bones, and after a large amount of accumulation, their harmful effects begin to

appear. The human body can only tolerate heavy metals within the recommended value. Both acute and chronic symptoms are sometimes observed after exposure to a higher concentration of toxic metals. Chronic toxicity which is associated with a long period of exposure to heavy metals is usually the type most pertinent to environmental toxicants (Reeder and Schoonen, 2006). Most of the researchers are interested in this type simply because heavy metals are released in the environment at low concentrations and their effects take a long time to appear in the exposed population.

Investigations indicate that toxicities of heavy metals to the living systems depend on the forms in which the heavy metals exist in the environment. Metals can exist in organic, inorganic and metallic forms. For example, organic forms of mercury, arsenic and lead are known to be more toxic than their inorganic forms. Most of the metals such as lead, chromium, nickel, mercury, copper, and arsenic exist in variable oxidation states, therefore, their toxicities depend on the oxidation numbers (Reeder and Schoonen, 2006). Other factors such as sex, exposure dosage, genetic background, exposure pathway, nutritional status, and age will also determine the toxicological effects of heavy metals to the exposed individual.

2.2.5.1 Health Effects of Arsenic

Arsenic is one of the toxic metals that adversely affect human health. Ingestion of contaminated food, water and dust and inhalation of airborne arsenic are common exposure pathways of arsenic (ATSDR, 2007). Inorganic arsenic is listed as a group 1 human carcinogen and exposure to it increases the risk of developing lung, kidney and bladder cancers (IARC, 1990). Ingestion of inorganic arsenic may cause a reduction of the production of white and red blood cells which can cause abnormal rhythmic

movements of the heart and damage to the blood vessels (Jiménez-capdeville and Giordano, 2003).

When arsenic is ingested in excess amounts, the person may experience noticeable symptoms such as vomiting, nausea, stomach pain, diarrhea, stomach and intestinal irritations, and sometimes may cause nerve damage which is accompanied with burning sensation in hands and feet (ATSDR, 2007). Skin contact with arsenic may cause skin irritation, lesions, swelling and sometimes skin redness. The available data indicate that children who are exposed to inorganic arsenic for a long time may have reduced cognitive abilities (low IQ) and motor functions due to neurological impairment

(Naujokas *et al.*, 2013).

Both acute and chronic exposure to all forms of arsenic has been reported to cause human death especially in occupational workers who are exposed to high levels of arsenic (ATSDR, 2007; Naujokas *et al.*, 2013). The organic form of arsenic is very toxic and is identified to cause serious health effects on the central nervous system, cardiovascular system and vascular system of humans (ATSDR, 2007). The incidence of massive arsenic poisoning and death in life history was reported from Bangladesh in 1970, where adults and children were intoxicated with arsenic from drinking tube well water (ATSDR, 2007).

2.2.5.2 Health Effects of Lead

High level of exposure to lead affects body organs such as lungs, kidney, heart, brain and reproductive organs (European Commission, 2013). Lead poisoning may lead to acute abdominal pain, irritability, bluish discoloration of gum (cyanosis), headache, saturnine gout (severe pain, redness and tenderness in joints), and cardiac toxicity (Gottesfeld and Pokhrel, 2011).

Chronic exposure to lead can cause neurological disorders such as muscle weakness, paralysis, convulsions, lethargy and hematological disturbance (Reeder and Schoonen, 2006). Epidemiological studies had indicated that chidren exposed to lead during the early stage of development have reduced intelligent Quotient (IQ). Other studies suggested that for every rise of 10µg/dL in blood lead, intelligent Quotient is decreased by 1-5 points for children who are chronically exposed to lead (Mielkel and Reagan, 1998; Cory-slechta *et al.*, 2003; European Commission, 2013). Exposure to lead is also related to the development of schizophrenia, a condition in which individuals develop chronic and severe mental disorders.

According to Reeder and Schoonen (2006), elevated concentration of lead in the blood can cause interference in signal transduction mediated by calcium and individuals may experience reduced nerve transmission and loss of skin sensitivity. Lead intoxications in pregnant women may cause premature birth and spontaneous abortion while the decrease in sperm quality and low sperm count are some of the effects of lead exposure in men (Peraza *et al.*, 1998). US EPA and IARC have classified lead and its compounds as human carcinogens, therefore there is the chance for individuals who have been chronically exposed to them to develop cancer in their lifetime (IARC, 1990).

2.2.5.3 Health Effects of Cadmium

Cadmium is ranked 7th among the top twenty list of toxic metals according to ATSDR classification and has no known biological functions in the human body. The preliminary results about adverse health effects of human exposure to cadmium were first reported in 1948 at the 9th International Congress on Industrial Medicine in London after a case study conducted among workers of cadmium battery factory (Friberg, 1984). A study

conducted by Henson and Chedrese, (2004) is one of the later studies that confirmed negative health effects associated with both occupational and non-occupational exposure to cadmium.

Nephropathy is the most prevalent health effect of cadmium intoxication in human which typically happens in the form of tubular or renal dysfunction (Griswold, 2009). The interruption of phosphate and calcium metabolism due to chronic cadmium nephropathy leads to the formation of kidney stones, demineralization of bones and bone fractures (Bernard, 2008). The Itai-Itai disease which was reported from Japan in the1950s was as a result of bone damage in individuals due to long term exposure to cadmium (Henson and Chedrese, 2004). Cadmium has been classified as a human and animal carcinogen by IARC and is well known for causing prostate cancer in men (IARC, 1990). Long term exposure to airborne cadmium may affect lung function, cause lung cancer and pulmonary diseases such as emphysema and bronchiectasis (Bernard, 2008).

The epidemiological study shows that men who are exposed to cadmium for a long time may suffer from reduced sperm count, loss in the germ cell, hemorrhage, testicular edema and sterility (Peraza *et al.*, 1998). In addition to that, cadmium exposure in pregnant women may cause premature birth, reduced birth weight and may cause decreases in 50% of progesterone in pregnant women (Henson and Chedrese, 2004).

2.2.5.4 Health Effects of Mercury

Human exposure to high level of mercury can cause irreversible brain damage (Peraza *et al.*, 1998). Long term exposure to elemental mercury causes neurological disorder and mental confusions such as shyness, insomnia, restiveness, poor vision, nervousness, irritability and instabilities (Griswold, 2009). Other conditions such as atopic dermatitis

(eczema), loss of memory, gingivitis, inflammation of the lips and mouth (stomatitis), visual fields constriction and pain in the hands and limbs may occurs in individuals who are exposed to high level elemental mercury (Rice *et al.*, 2000; Park and Zheng, 2012).

Chronic exposure to metallic mercury can cause damage to the central nervous system and kidney. Occupational workers who have been exposed to a greater amount of elemental mercury vapour have been reported to have reduced peripheral and sensory nerve conduction (Clarkson, 1997). Neurological cancer and a decrease in mental development in young children have been associated with exposure to mercury (Park and Zheng, 2012).

Acute symptoms associated with methylmercury poisoning are related to brain and central nervous system damages (European Commission, 2013). The Minamata disease outbreak of 1956 in Japan, which caused the death of more than 52 people, was a result of ingesting methylmercury contaminated fish. Other Minamata disease survivals suffered from cerebral palsy, focal cramps, low IQ, ataxia and several developmental deformities in children (Harada, 1995).

Short term exposure to a high dose of inorganic mercury may cause damage in the digestive tract, burning pain in the chest, nails discoloration and corrosive burns in mucous membrane (Sweet and Zelikoff, 2010). Infants and fetuses can be exposed to mercury from their mothers. Research reported that the offspring of pregnant women who survived in both the Iraqi and Japanese organic mercury poisoning outbreaks suffered from psychomotor impairments (Karagas *et al.*, 2012).

2.2.5.5 Health effects of Nickel

Harmful health effects of nickel and its compounds have been well studied in both occupational and non-occupational workers. A study conducted by Chashschin *et al*., (1994) indicated that occupational workers are more affected from inhalation and dermal contacts with nickel fumes and dust. Nickel is known to cause allergic skin reaction and the effects are more prevalent among those who are more sensitive to nickel (Das *et al*., 2008). Nickel and its compounds are classified as human carcinogens and were reported to cause different kinds of cancer in occupationally exposed workers
(European Commission, 2009). Sino-nasal sarcoma, pharyngeal and lung cancers are various types of cancers which have been reported from occupational workers exposed to above 10 mg nickel/m^3 (ATSDR, 2015).

Nickel is also associated with damage of chromosomes, mitochondria dysfunction, induced mutagenesis and inhibition of repairing damaged DNA (Beveridge, 2008). Body weakness, headache, vomiting, nausea, irritability, sleep depression, cyanosis (bluish discoloration in hands or feet), persistent cough, skin and eye irritation, visual problems, shortness breath (dyspnoea), and vertigo are among the symptoms associated with acute exposure to high amount of nickel and its compounds (Das *et al*., 2008).

Long term exposure effects of nickel poisoning such as asthma, inflammation of lungs, septum perforation, renal injury, loss of sense of smell, inflammation of nasal sinus (sinusitis) have been reported from occupational workers who are exposed to high concentration of nickel (Chashschin *et al*., 1994; Beveridge, 2008; Xu *et al.*, 2012). Nickel has been linked with the dysfunction of hormonal systems and is known to cause oxidative stress by inducing lipid peroxidation (Watanabe *et al.*, 2018). Occupational pregnant workers in nickel factories and smelting industries were reported to undergo

spontaneous abortion and malformation of body organs is one of the defects observed in newborns (Chashschin *et al*., 1994).

2.2.5.6 Health Effects of Copper

Metallic copper is an essential element for good health due to its significance in human biological systems. However, this element is reported to have harmful effects on human health when its physiological concentration exceeds the recommended concentration limit (Katz and Salem, 2005). People who are exposed to high dose of copper fumes or dust for a long period of time may experience coughing, headache, eye and nose irritations, nausea, dizziness, pulmonary fibrosis and sometimes diarrhea. Occupational workers may suffer from hematological effects such as reduced haemoglobin concentration and low red blood cell count if they are exposed to 0.64 – 1.05 mg/m^3 of airborne copper (ATSDR, 2004). Workers engaged in grinding and sieving of coppercontaining dust have been reported to have abnormalities in endocrine and gastrointestinal systems (ATSDR, 2004). Sexual impotence, anorexia, arterial hypertension, hypophyseal adenoma, and red faces are also linked to chronic copper poisoning. Studies have shown that exposure to copper fumes or dust at concentrations 0.075-0.012 mg/m^3 lead to metal fume fever (Katz and Salem, 2005). Other harmful health effects associated with long term exposure to copper include black tarry stool (melena), Wilison's disease and coma. Liver damage, pancreas damage, and anemia are linked to exposure to copper sulfate (ATSDR, 2004; Shi *et al.*, 2013).

2.2.5.7 Health Effects of Chromium

The toxicity of chromium (Cr) metal depends on the oxidation number and form in the environment. Cr(III) is an essential element and relatively less toxic compared to

chromium(VI) which is more toxic. Cr(VI) is on the list of special health toxic substances listed by health authorities. The Occupational Health and Safety

Administration (OSHA) has restricted occupational worker's exposure to an average of 1.0 mg/m^3 Cr(0), 0.005 mg/m^3 Cr(VI) and 0.5 mg/m^3Cr (III) in air for an 8-hour workday. Similarly, National Institute of Occupational Safety and Health (NIOSH) recommends an exposure limit of 0.5 mg/m^3chromium as Cr (0) and Cr(III) compounds in air averaged over 8-hour workday while the legalized limit of exposure to Cr(VI) compounds in air is 0.001 mg/m^3 for over 10-hour work day (ATSDR., 2012).

Exposure to a high dose of chromium than the above set limits may cause health effects of chromium poisoning. Short term exposure to chromium can cause skin burn, eye and skin irritation and in some severe cases may cause damage to the eye. Exposure to chromium via inhalation of chromium dust or fumes can cause metal fume fever and irritation of the throat and nose. Acute symptoms associated with metal fume fever include headache, coughing, fever, and chills. Long term exposure to hexavalent chromium compounds for workers can cause chronic respiratory effects such as pneumonia, bronchitis, nasal septum ulceration, and reduced pulmonary functioning (Katz and Salem, 2005; ATSDR., 2012).

Short term human exposure to the high amounts of Cr(VI) via ingestion may result in adverse gastrointestinal problems such as vomiting, bloody diarrhoea, abdominal pain, stomach and intestinal ulceration and ulcers in the mouth (U.S.EPA, 1998). Hypersensitive workers from chromium industries have been reported to have developed erythema and skin rashes from skin contact with chromium-containing products (ATSDR., 2012). Long–term exposed workers have been diagnosed of lung cancer and several incidences of the death of workers due to lung cancer have been reported (U.S.EPA, 1998; Katz and Salem, 2005).

2.2.5.8 Health Effects of Zinc

Although zinc metal is an essential element for humans, sometimes when taken in excess amount, it can cause health problems. Short-term occupational exposure to the excess amount of zinc metal and zinc compounds such as zinc oxide via inhalation can cause metal fume fever. The symptoms such as headache, dry cough, chills, shortness of breath, fever, general body discomfort, persistent pain in the chest and joint pain are indicative of metal fume fever (ATSDR., 2005). These symptoms are always reversible and may disappear within four days after acute exposure or when exposure ceases (Plum *et al*., 2010). Prolonged exposure to zinc metal and zinc chloride in zinc dust or fumes can cause respiratory problems such lung inflammation and damage, reduced vital capacity of lungs, sleepiness, irritation in the respiratory tract and burning throat (Walsh *et al.*, 1994; ATSDR., 2005). Persistent exposure to a large amount of zinc salt mainly zinc chloride up to a severe dose was reported to cause thickening and scarring of connective tissues in the lungs, respiratory distress syndrome and collapse of lungs (ATSDR., 2005). It has been observed that workers who are exposed to large amounts of zinc and zinc sulfate via oral intake and breathing in zinc fumes or dust may experience intermediate symptoms of zinc poisoning such as vomiting, pain in the abdomen, nausea, anemia, vertigo, epigastric pain and sometimes diarrhoea (Plum *et al*., 2010; Shi *et al.*, 2013).

2.2.5.9 Health Effects of Antimony

Adverse health effects of antimony (Sb) and its compounds have been well studied in both occupational and non-occupational workers. The toxicity of antimony depends on the nature of antimony compounds and the oxidation state in which antimony exist. Sb (V) is less toxic than Sb (III). Occupational workers have been reported to have

developed acute clinical symptoms associated with Sb (III) poisoning such as vomiting, ulcers, abdominal pain, nausea and muscle and joint pain (ATSDR, 2017). These symptoms normally occur when the level of ingested Sb exceeds 0.529 mg/kg (Sundar and Chakravarty, 2010). Elemental Sb is not listed as a human carcinogen except antimony trioxide which is classified as a group 2B human carcinogen by IARC and has been reported to cause lung cancer in antimony occupational workers (ATSDR, 2017). Chronic exposure to amounts higher than 0.003 mg/m^3 via inhalation of airborne antimony has been reported to cause pulmonary dysfunction in humans (Sundar and Chakravarty, 2010). Exposure to high level of antimony can also cause oxidative damage to DNA and this was reported from occupational workers who have been exposed to Sb for a long time. Other human health incidences associated with exposure to Sb compounds include dermatitis, cardiovascular effects, respiratory tract irritation and pneumoconiosis (ATSDR, 2017).

2.3 Methods of Heavy Metal Determination

Several analytical methods can be employed to determine the concentrations of heavy metals in environmental samples such as soil, sediments, dust, water and biological samples. The most frequently used analytical techniques include Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma-Atomic Emission Optical Spectrometry (ICP-OES), Atomic Fluorescent Spectrometry (AFS), X-Ray Fluorescence Spectroscopy (XRF), Thermal Decomposition Atomic Absorption Spectrometry (TD-AAS), Neutron Activation Analysis (NAA), Anodic Stripping Voltammetry (ASV) and Flame

photometry (FP), In most cases, the selection of the analytical method is largely based on the availability of the instrument, cost of analysis, detection limits and sensitivity, and nature of the sample to be analyzed (Helaluddin *et al.*, 2016).

In this study, X-ray fluorescence spectrometer (XRF) and Portable Zeeman Automatic Mercury Analyzer (RA-915M) were used to determine the concentrations of heavy metals in the dust samples. XRF technique has been successfully used by many researchers for field and laboratory determination of elemental compositions in dust and soil samples (Yeung *et al*, 2003; Atiemo *et al.*, 2012; Kodom *et al.*, 2012). The detection limits of XRF analyzer are always below the regulatory levels for many elemental metals and its results have been compared with other laboratory methods such as ICP-MS. A strong positive correlation (r^2 greater than 0.9) between XRF results with other laboratory methods such as ICP – MS analysis has been reported (Furl *et al*.,
2012).

2.4 Principle of X-Ray Fluorescence (XRF) Spectroscopy

The XRF spectroscopy is a non-destructive analytical method that measures the intensity of secondary X-rays or characteristic fluorescent emitted by atoms of each element present in a sample after a sample containing elements is irradiated with higher energy X-ray beams. When the high energetic X-ray from the X-ray source is stricken with a sample, it causes the removal of the tightly held electrons from the inner shell of atoms of the elements present in the sample. This process creates empty vacancies in the inner shell of the atoms that is required to be refilled in order for an element to attain its original stability or structural configuration. This results in a prompt shift of the outer shell electrons to the inner shell of the elements. In order to fill the empty vacancies, the process is accompanied by the release of energy in the form of secondary X-ray

fluorescence. The intensity of secondary X-rays or fluorescence is what is measured as a characteristic of elemental concentrations in the sample and the intensity of the energy of secondary X-ray emission is proportional to the concentration of each element in the sample. The identification of the element is mainly based on the electronic energy level and its characteristic energy value (keV). Since each element has its own unique ionization potential, emission of fluorescent occurs independently and it gives XRF the ability to measure concentrations of multiple elements in a single scan (Helaluddin *et al.*, 2016; Ribeiro *et al.*, 2017).

CHAPTER THREE

3.0 METHODOLOGY

3.1 Description of the Study Area

Kumasi metropolis is one of the thirty (30) administrative districts and the capital city of the Ashanti Region. It is the second largest populated city next to the National capital city (Accra) in Ghana and it covers about 254 Km^2 of land area which is about 0.9% of the region's surface area. The population of Kumasi is over 2.5 million (Akoto *et al.*, 2017) with a growth rate of more than 5.4% annually. The metropolis lies between Latitude 6.35^{o}N – 6.4^{o}S and Longitude 1.30^{o}W-1.35^{o}E with an elevation which ranges between 250 to 300 meters above sea level (Ghana Statistical Service, 2014). According to the Ghana Statistical Service (2014), the metropolis's climate lies within the subequatorial type and is characterized by average minimum and maximum temperatures of 21.5^{o}C to 30.7^{o}C respectively. The average humidity is approximately 84.16% at sunrise and 60% at sunset, and the annual rainfall is averagely 625 mm. Both temperature and humidity have a direct effect on the environment and growth of the population. The metropolis experiences two maxima rainfall regimes with peaks of 214.3 mm in June and

16.2 mm in September. The longer rainy season which is major happens between March to July and September to October as a shorter rainy season (Ghana Statistical Service, 2014). In addition to that, Kumasi experiences dry season called Harmattan lasting from November to early February and is a major cause of dry up of small streams.

There are many streams and rivers within the Kumasi metropolis such as Owabi River, Offin River, Sisai River, Daban River, Subin River, Aboabo River, Wiwi River, and Oda River. These water bodies serve as the important sources of drinking water and other socio-economic activities to inhabitants, not only in the metropolis but the Ashanti region as a whole. The metropolis also provides a range of human services at different levels in the field of transport, education, electricity, financial services, health care, retail and wholesale trade to the residents and non-residents (Ghana Statistical Service, 2014).

In the Ashanti region, Kumasi metropolis is known as the converging point of commercial activities. The major commercial and economic centers in the metropolis include the Kumasi Central Market, Adum Shopping Centre, Asokwa (industrial area), Asafo market, Bantama market, Atonsu market, Ayigya market, Suame magazine (vehicle repair centre), Tafo market, Asawase market and many others that run economic activities. Many activities ranging from large to small scale industries are on the increase in the metropolis. Activities involving road traffic, furniture works, metal fabrications, leather works crafts, gas and fuel filling, electronic repair shops, auto mechanical activities, metal construction works, welding, and industries are all occurring in the Kumasi metropolis (Akoto *et al.*, 2017).

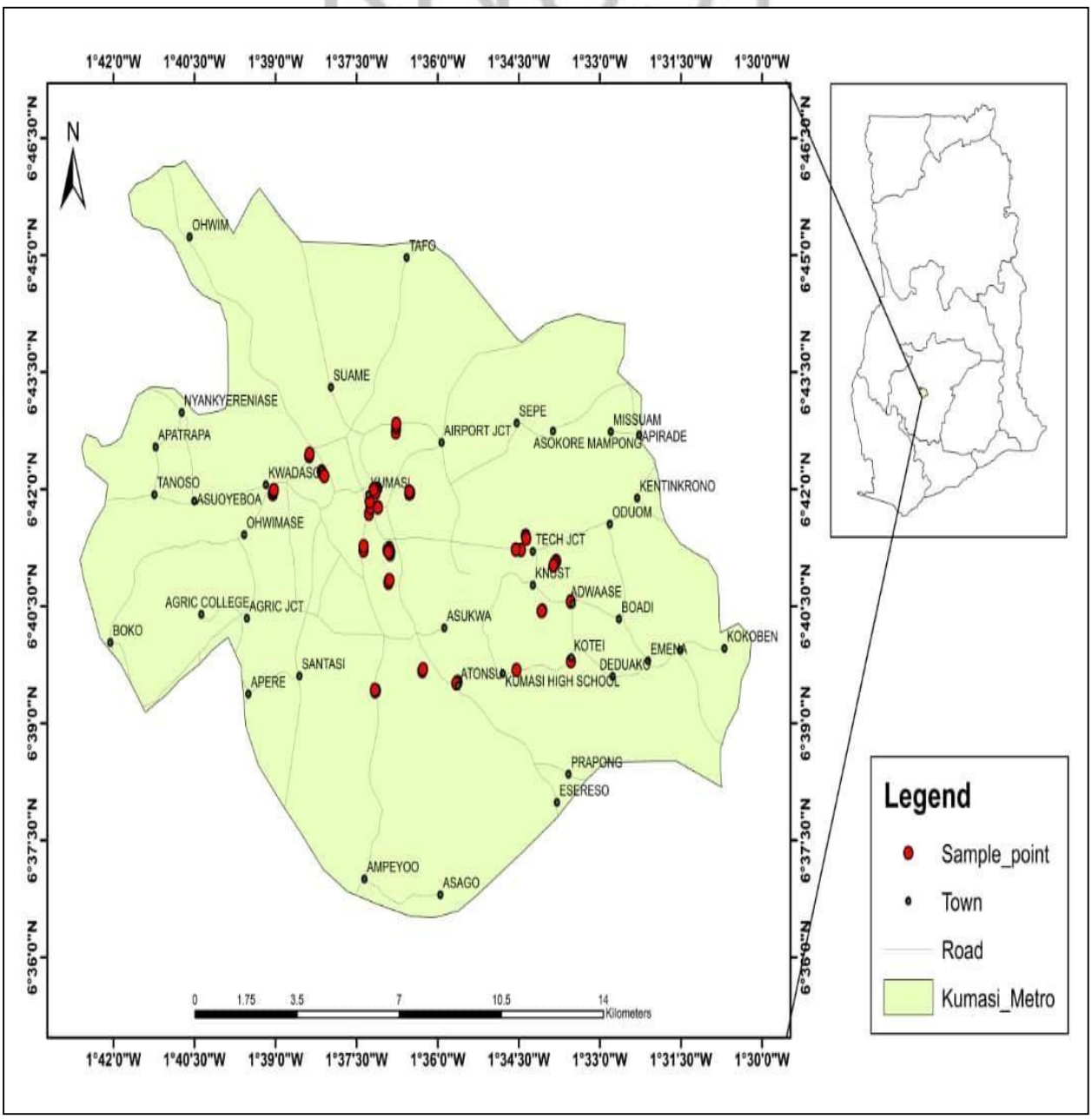

Figure 3.1: Map of Kumasi metropolis showing sampling points

3.2 Pre-Sampling Feasibility Study and Health and Safety Precautions

Prior information of the nature and location of the sampling sites were obtained before conducting actual field sampling to assist the identification of the easily available routes and potential hazards that may affect the sampling process. Measures were taken into account in order to control and alleviate hazards found to have effect on health and safety such as wearing protective gloves during the collection of samples.

3.3 Dust sampling and Handling

A total of 50 dust samples were collected in October, 2018 from 13 markets and 18 transport stations in the Kumasi metropolis. A total of thirty two (32) samples were obtained from transport stations and eighteen (18) samples from markets. Most of the transport stations sampled were located in the vicinity of the markets namely; Kotei, Central market, Adum, Dr Mensah, Tech Junction, Bantama, Mayanka, Ahodwo, Atonsu, Roman Hill, Krofrom, Ayigya, Asafo, Sofoline and Abinkyi with the exception of a few transport stations such as Metro Mass Transport and High School Junction which were a bit far from the markets. Three pristine dust samples were also collected from the KNUST Botanic Gardens at different points to serve as control samples since the dust from this area is considered to be free of any contamination from anthropogenic activities such as vehicular activities. Every sampling site was given a specific sampling code derived from the name of the site. The location of each site was recorded by using a hand-held global positioning system (GPS) as presented in Figure 3.1.

At each selected sampling site, five (5) dust sub-samples were collected at different randomly selected points within an area of about 9 m^2 and mixed to form a composite sample (Popoola *et al.*, 2012; Durowoju *et al.*, 2018). All samples were collected by sweeping the deposited dust on the ground surface using small paint brush and plastic

dust pan. Non dust objects such as large stones were removed immediately from the collected samples on sites and the samples were packed into sealed and labeled polyethylene zip-lock bags. After the collection of samples from each site, the dust pan and paint brush were wiped with tissue paper several times to avoid cross- contamination of the samples. All the samples were taken to the Analytical Chemistry Laboratory at KNUST for storage and further treatment prior to analysis.

3. 4 Sample Preparation

Dust samples were dried at ambient temperature in the laboratory for 24 hours to ensure that they were free of moisture. Non-dust objects such as grits were removed from dried dust samples before grinding with porcelain mortar and pestle for homogenization. The dried samples were sieved through a <250 µm mesh size using U.S.A Standard Testing Sieve ASTM E1. Sieving was necessary in order to remove coarse dust components and obtain fine dust particles of the same average particle size. After each sieving, the test sieve was wiped several times with clean tissue paper in order to avoid cross-contamination of samples. The sieved dust samples were packed into sealed and coded polyethylene zip lock bags and stored for analysis.

3.5 Sample Analysis

3.5.1 Determination of As, Pb, Fe, Cd, Ni, Cr, Cu, Zn and Sb

The concentrations of As, Pb, Fe, Cd, Ni, Cr, Cu, Zn, and Sb were determined with Thermo Scientific Niton X-ray Fluorescence (XRF) analyzer (Niton XL3t GOLDD+). The XRF analysis method was adopted from previous studies (Yeung *et al*., 2003; Kodom *et al*., 2012; Nkansah *et al*., 2017). The XRF instrument was calibrated with

certified standard reference material (NIST 2709a PP) before it was used for the heavy metal concentration analysis. During analysis, a polyethylene container (approximately 3cm) with openings on both ends was used to hold the sample after a Mylar film (polypropylene XRF thin film) was placed on one of the ends and secured with an open cup. The capped container was filled with the sieved dust sample to about threequarters full. The filled container was then placed in the XRF shroud and the sample scan was conducted for 180 seconds. The same procedure was followed for all samples.

3.5.2 Determination of Mercury (Hg) concentration

The total mercury concentration in the dust samples was determined by a unique technique called "Thermal Decomposition Atomic Absorption Spectrometry (TDAAS)". Portable Zeeman Automatic Mercury Analyzer (RA -915M) manufactured by Lumex Instruments (Canada) was used for mercury analysis in the dust samples. A known mass of dry dust sample was weighed on the electronic analytical balance and placed in the sample cell of the Pyro-915+. The cell was then inserted in the sample compartment and the window was closed tightly. The analytical peak was developed after 45 seconds of the instrument run. The concentration of mercury (in mg/kg) in the sample was found by integrating the obtained peak height and area with reference to the calibration curve. The same procedure was repeated for the all other samples.

3.6 Quality Assurance and Quality Control

In order to ensure the validity, reliability, and accuracy of the results, various quality assurance and control measures were employed in this study. Dust samples were handled with great care on sites and in the laboratory to avoid contamination. Polyethylene zip lock bags containing the samples were carefully sealed and coded with a permanent

marker to avoid samples contamination and confusion. All equipment used for sampling and sieving such as test sieve, dust pan and brush were cleaned in order to reduce the possibility of cross contamination. During XRF analysis, after each sample scan, the polyethylene container and cap were washed with tap water and rinsed with distilled water and then dried at room temperature before reuse. To assess the reproducibility of the obtained results, a duplicate analysis was conducted after every 8^{th} sample. A certified standard reference material (NIST 2709a PP) was used to validate XRF results and was analyzed under similar conditions as the samples.

3.7 Statistical Analysis

Statistical analysis is the procedure of performing various statistical operations which involves the use of statistical tools. It is very useful as it provides the basis of interpreting data and making decisions on them. In this study, descriptive statistics such as mean, standard deviation, skewness, kurtosis, minimum and maximum concentrations and median were determined using IBM Statistical Product and Service Solution (SPSS) version 20. Microsoft Excel (version 2013) was also employed to compute pollution indices and risk assessment. Pearson's correlation analysis was also conducted using IBM-SPSS Statistics to determine the relationship between heavy metal concentrations in dust samples. The comparison between the average concentrations of heavy metals in dust from transport stations and markets was conducted by using Independent Samples t-test at 95% confidence limit. The concentrations of heavy metals were first checked for normality distributions using one sample Shapiro-Wilk normal test ($p > 0.05$) before statistical analysis (Qing, Yutong and Shenggao, 2015). Results that were reported to be less than the method detection limit (<LOD) were rejected from the data set for statistical analysis.

3.8 Estimation of Heavy Metals Contamination through Pollution indices

Assessment of the degree of pollution by a given heavy metal requires a comparison of the heavy metal contaminant with a reference value which is used as a reference point for data presentation. The reference values which show the extent of pollution are well presented in various pollution indices. Pollution indices have been frequently used to estimate the degree of heavy metal pollution in various environmental media such as soil, dust and sediments (Likuku, Mmolawa and Gaboutloeloe, 2013). The extent of heavy metals contamination in the dust samples from transport stations and markets were estimated using pollution indices: goeaccumulation index (Igeo), pollution load index (PLI), contamination factor (CF), metal enrichment factor (EF) and modified degree of contamination (mCd) (Atiemo, Ofosu and Aboh, 2012; Atiemo *et al.*, 2015; Elnazer *et al.*, 2015; Ajayi *et al.*, 2017).

3.8.1 Geo-accumulation index (Igeo)

The index of geoaccumulation is used to evaluate the pollution level of metal contaminants in soil and sediments and has also been used to assess the intensity of pollution caused by heavy metals in dust (Lu *et al.*, 2009). The value of Igeo is calculated by comparing the level of the heavy metal contaminants in the dust sample with the concentration of the heavy metal in the background or reference sample. Geoaccumulation index was calculated using equation (1) below as proposed by Muller (1979).

$$\text{Geoaccumulation index} = \log_2\left[\frac{Cn}{1.5 \times Bn}\right] \quad (1)$$

Where "C_n" is the measured concentration of metal in the dust samples (mg/kg) and "Bn" is the metal concentration in the reference sample (mg/kg). In the present study, the

background or reference concentrations of the metals used for calculation of Igeo values were adopted from the study conducted by Akoto *et al.*, (2017). A constant factor of 1.5 was introduced to correct or reduce the effect of likely variations in the background values due to lithogenic effects (Lu *et al.*, 2009). Geoaccumulation index (Igeo) was classified by Muller (1979) into seven classes which are: a. (Igeo < 0, unpolluted), b. (0≤Igeo<1, unpolluted to moderately polluted), c. (1≤Igeo<2, moderately polluted), d. (2≤Igeo<3, moderately to strongly polluted), e. (3≤Igeo<4, strongly polluted), f. (4 ≤Igeo<5, strongly to very strongly polluted and g. (Igeo ≥ 5 (very strongly polluted). This classification was used to evaluate the pollution status of each metal in the dust samples (Atiemo, Ofosu and Aboh, 2012; Barbieri, 2016).

3.8.2 Enrichment factor

Enrichment factor (EF) is a common approach of evaluating the degree of anthropogenic influence on heavy metal contamination in dust (Meza-figueroa *et al.*, 2007). The extent to which a metal is enriched in the dust sample with respect to a specific source is obtained by calculating EF. Enrichment factor was therefore used to distinguish between the heavy metal contaminants originating from natural sources and those from human activities (Meza-figueroa *et al.*, 2007). The background sample was used as the benchmark for measuring and comparing the metal concentrations in the contaminated dust sample. Iron (Fe) which is frequently used for normalization was employed as a reference element in this study. This is because iron has relatively high natural concentration in the soil dust and it is therefore less expected to be enriched from human activities (Meza-fiueroa *et al.*, 2007).

Enrichchment factor (EF) was calculated using equation 2 below.

$$EF = \frac{Ms \times Fer}{Mr \times Fes} \quad (2)$$

Where; Ms and Fes represent concentration of the metal and Fe in the analyzed dust sample respectively while Mr and Fer are concentrations of measured metal and Fe in the background sample. EF > 1 indicates that the metal is enriched in the dust sample in relation to the background values and may originate from anthropogenic activities. EF < 1 shows that the metal is not enriched in the dust and the source may be the natural crust. EF =1 means that the level of metal concentration in the sample and its background value are similar. Basing on the values of EF, further five contamination classes were given, EF <2 indicates minimum enrichment, EF=2–5 moderate enrichment, 5< EF ≤20 significant enrichment, 20 < EF ≤40 very high enrichment and EF>40 extremely high enrichment (Lu *et al.*, 2009).

3.8.3 Contamination factor

Contamination factor (CF) is used to evaluate the level of heavy metal contamination in the dust sample and is given as the fraction of the concentration of the metal in the dust sample to the background concentration of the corresponding metal (Hakanson, 1980; Hahladakis and Smaragdaki, 2013). The background concentrations of metals employed here were similar to that adopted for Igeo calculation. The CF for the individual metal was calculated using equation (3).

$$\text{Contamination factor (CF)} = \frac{C_{sample}}{C_{reference}} \quad (3)$$

Where "C_{sample}" is the concentration of the scrutinized metal in the dust sample (mg/kg) and "$C_{reference}$" represents the concentration of the metal in the reference sample (mg/kg) (Hakanson, 1980). The decision on the level of contamination was based on four (4) classification classes of CF: low contamination (CF<1), moderate contamination (1≤ CF < 3), considerable contamination (3≤CF≤ 6) and very high contamination (CF > 6).

3.8.4 Pollution load index

The pollution load index (PLI) of metal pollutants is used to assess the overall degree of pollution for a dust sample (Qing, Yutong and Shenggao, 2015). PLI provides an understanding of the dust sample quality and indicates the trends of deterioration of the study area with the metal contaminants over time. The PLI was calculated using equation (4) developed by Tomlinson *et al.*, (1980).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n} \quad (4)$$

Where "n" represents the number of metals studied and "CF" is the contamination factor of a metal. Tomlinson *et al.*, (1980) classified the degree of PLI values into three classes as PLI<1 (denotes perfection, means no pollution load), PLI = 1(only baseline level of pollutants are present) and PLI > 1 (progressive deterioration of site quality).

The interpretation of results was conducted based on the degree of this classification.

3.8.5 Modified degree of contamination

The modified degree of contamination is used to describe the overall contamination status of the dust sample site. The calculation of the modified degree of contamination (mC_d) is based on the determination of the degree of contamination (Dc) (Likuku *et al.*, 2013). The formulae for calculation of the degree of contamination was proposed by Hakanson, (1980) as the sum of all CFs of metals analyzed in the sample and is given in equation (5) below.

$$Dc = \sum_{i=1}^{n} CF \quad (5)$$

Where: *'n'* is the number of analyzed elements and *'i'* is i^{th} element and CF is the contamination factor.

The modified degree of contamination was evaluated using equation (6) as recommended by Abrahim and Parker, (2008).

$$mCd = \frac{Dc}{n} \quad (6)$$

Where "n" is the number of analyzed chemical elements in dust sample and Dc represents degree of contamination. The modified degree of contamination (mCd) was classified as indicated in Table 3.1 (Abrahim and Parker, 2008).

Table 3.1: Modified degree of contamination and its interpretation

mCd values	**Contamination description**
mCd<1.5	Zero to very low degree of contamination
1.5≤mCd<2	Low degree of contamination
2≤mCd<4	Moderate degree of contamination
4≤mCd<8	High degree of contamination
8≤mCd<16	Very high degree of contamination
16≤mCd<32	Extremely high degree of contamination
mCd≥32	Ultra-high degree of contamination

3.9 Human Health Risk Assessment

The risk assessment on human health for both carcinogenic and non-carcinogenic health effects was conducted based on the model developed by U.S.EPA (U.S. EPA, 1989, 2007, 2011, 2017).

3.9.1 Non-Carcinogenic Health Risk

The non-carcinogenic health risk was assessed by means of Hazard Quotients and Hazard Indices. The estimation Hazard Quotient demands the determination of average daily doses (ADDs) (mg/kg/day) of metal contaminants via ingestion (ADDing), dermal

contact (ADDderm) and inhalation (ADDinh) of dust particles for both children and adults. The ADD indicates the daily exposure levels of specified parameters for humans, without any substantial risk of their harmful effects during a lifetime. The ADDs were calculated for both children and adults separately using equation (7), (8) and (9) (U.S. EPA, 2001; Du *et al.*, 2013; Atiemo *et al.*, 2015)

$$\text{ADDing} = \text{Cdust} \times \frac{\text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6} \quad (7)$$

$$\text{ADDinh} = \text{Cdust} \times \frac{\text{InhR} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{BW} \times \text{AT}} \quad (8)$$

$$\text{ADDderm} = \text{Cdust} \times \frac{\text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times 10^{-6} \quad (9)$$

Where; "ADDing", "ADDinh" and "ADDderm" represent average daily doses of heavy metals in mg/kg/day via ingestion, inhalation and dermal contact respectively. Exposure parameters and their values used in the model employed to estimate ADD and human risk are shown in Table 3.2.

The values of average daily doses (ADDs) (in mg/kg-day) computed for each metal and exposure pathway were divided by the corresponding chronic reference dose (RfD) in mg/kg-day to obtain the non-cancer HQ as shown in equation (10).

$$\text{HQ} = \frac{\text{ADD}}{\text{RfD}} \quad (10)$$

Table 3.2: Parameters used in the Exposure Model for Health Risk Assessment

Factor	Description	Unit	Values		Reference
			Children	Adults	

C	Metal concentration in dust	mg/kg	-------	-------	This study
IngR	Ingestion rate of dust	mg/kg	200	100	(U.S. EPA, 2014)
EF	Exposure frequency	Days/year	350	350	(U.S. EPA, 2014)
ED	Exposure duration	Years	6	30	(U.S. EPA, 2014)
Bw	Body weight of exposed individual	Kg	15	70	(US. EPA, 2014)
AT	Average time (for non - carcinogens) Average time (for carcinogens)	Days Days	365ED 365 x70	365ED 365 x70	(U.S. EPA, 1989)
InhR	Inhalation rate of dust	m^3/day	7.6	20	(U.S. EPA, 1989)
PEF	Particle emission factor	m^3/kg	1.32 $x10^9$	1.32 $X10^9$	(U.S.EPA, 1996)
SA	Exposed skin surface area	cm^2	2800	5700	(U.S. EPA, 2014)
AF	Skin adherent factor	mg/cm^2/day	0.2	0.07	(U.S. EPA, 2014)
ABS	Dermal absorption factor	Unitless	0.001for all metals except As is 0.03	0.001 for all metals except As is 0.03	(Du *et al.*, 2013; Swarnalatha *et al.*, 2015)

The reference dose (RfD) is the maximum daily dose of a metal from a particular exposure pathway for both children and adults. The RfD of a metal is assumed not to cause any substantial risk of harmful effects to sensitive individuals throughout a life time. The values of RfD for different elements are summarized in Table 3.3. HQ ≤ 1, shows that there will be no adverse non-carcinogenic health effects to human, and HQ > 1, indicates the likelihood of a metal to negatively affect human health by noncarcinogenic effects (U.S. EPA, 1989).

The overall potential non-carcinogenic risk posed by a metal through a combination of exposure pathways is expressed as a hazard index (HI). Hazard index (HI) for a given metal was calculated as the summation of Hazard Quotients (HQs) from all the three exposure pathways (ingestion, inhalation and dermal contact) as shown in equation (11) (Atiemo *et al.*, 2015).

$$\text{Hazard Index (HI)} = \text{HQ (ingestion)} + \text{HQ (dermal)} + \text{HQ (inhalation)} \quad (11)$$

HI value <1, indicates no significant risk of non-cancer health effects, and HI > 1 indicates that there is a likelihood of non-carcinogenic health effects to occur (U.S. EPA, 2001).

3.9.2 Carcinogenic Health Risk

Carcinogenic health risk is considered as the incremental probability of a person to develop any kind of cancer at some point in a life time following the exposure to carcinogenic hazards (U.S. EPA, 1989; Atiemo *et al.*, 2015).

Equation (12) was used to calculate carcinogenic health risk:

$$\text{Carcinogenic Risk Index (CRI)} = \sum \text{ADDc} \times \text{SF} \quad (12)$$

Where "ADDc" is the estimated average daily dose for carcinogenic metals in mg/kg/day and "SF" represents slope factor in $(mg/kg/day)^{-1}$. The value of slope factor represents the chance of developing cancer per unit exposure level in $(mg/kg/day)^{-1}$. The values of SF for carcinogenic metals (Cd, Ni, As, Pb) are presented in Table 3.3 and carcinogenic health risk was estimated only for these metals with known slope factors.

The acceptable range for CRI is set between 1×10^{-6} and 1×10^{-4} according to the guideline of the Environmental Protection Agency of the United States (U.S. EPA, 1989).

The CRI which fall below 1 x 10^{-6} indicates a negligible carcinogenic risk to human health, and CRI >1 × 10^{-4} is likely to cause cancer to humans (U.S. EPA, 1989).

Table 3.3: Slope factors (SF) in $(mg/kg/day)^{-1}$ and reference dose (RfD) in mg/kg/day for different heavy metals used in the study

Metal	Cr	Ni	Cu	Zn	Pb	As	Cd	Hg
R_fDing	3.0E-3	0.02	0.040	0.3	1.4E-3	3.00E-4	5.0E-4	3.0E-4
R_fDderm	1.5 E-5	5.40E-3	0.012	0.06	4.2E-4	1.23E-4	5.0E-5	2.10E-5
RfDihn	3.0E-5	2.06E-5	4.02E-2	0.30	3.52E-3	3.00E-4	5.7E-5	8.6E-5
SFing	-	0.91	-	-	0.042	1.50	15.0	-
SFderm	-	0.91	-	-	0.042	3.66	15.0	-
SFinh	-	0.84	-	-	4.2E-2	15	6.3	-

(ATSDR, 2005; Ferreira-Baptista and De Miguel, 2005; Swarnalatha *et al.*, 2015; Kamunda et al., 2016; Liang *et al.*, 2017).

Where R_fDing –chronic reference dose for ingestion, RfDinh – reference dose for inhalation, R_fDderm- Chronic reference dose for dermal contact, SFing- slope factor for ingestion, SFderm- slope factor for dermal contact and SFinh-slope factor for inhalation.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The findings of the present study from both transport stations and markets are presented in the following tables and the concentrations of metals based on dry weight are expressed in mg/kg.

4.1 HEAVY METALS CONCENTRATION IN DUST FROM TRANSPORT STATIONS

The concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, Fe and Sb were analyzed in the dust samples from the selected transport stations in the Kumasi metropolis and the results are presented in Table 4.1. Descriptive statistics of the heavy metals concentration measured in the dust samples are presented in Table 4.2.

Amongst the heavy metals studied, Fe showed the highest value of 40936.07 mg/kg, with an average value of 16517.60 mg/kg while mercury showed the lowest maximum concentration of 0.62 mg/kg and a mean value of 0.07 mg/kg. The mean concentrations of heavy metals followed the decreasing order; Fe > Cr > Zn > Cu > Ni > Pb > Cd > Sb > As > Hg. The values of skewness of Hg, Pb, Cu and Fe indicated in Table 4.2 were greater than one, indicating that these metals were positively skewed in the direction of low concentration. The negative kurtosis values of As, Sb, Cd, Ni, Zn and Cr showed that their distribution in dust from transport stations were less steep than normal. The kurtosis values of Hg, Pb and Fe were larger than zero signifying that their distribution in dust was steeper than normal (Qing et al., 2015).

Table 4.1: Concentrations of heavy metals in dust from transport stations (mg/kg)

Sample Site	N	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb
Tech Junction	2	Bd	29.23	172.07	18.94	0.02	25.03	9.68	126.97	12742.85	22.57
High School Junction	1	Bd	37.13	174.41	12.47	0.01	17.90	10.38	50.01	11057.10	26.01
Abinkyi	2	5.66	31.98	200.85	25.25	0.02	37.20	Bd	130.11	28733.38	18.23
Dr Mensah	2	Bd	12.07	119.74	74.20	0.62	17.55	21.46	135.34	14684.65	14.32
Mayanka	1	6.46	Bd	149.43	25.27	0.02	31.66	18.86	218.61	27323.48	Bd
Metro Mass Transport	2	9.55	8.75	260.11	29.19	0.04	46.84	4.48	79.01	40936.07	17.26
Atonsu	1	Bd	10.95	96.21	Bd	0.02	25.16	Bd	48.89	10955.78	17.49
Ahodwo	2	Bd	32.43	191.19	143.77	0.01	23.71	Bd	54.81	13510.21	22.82
Sofoline	2	3.96	9.15	142.81	141.11	0.01	33.66	12.46	68.49	16885.71	12.89
Asafo	4	Bd	Bd	28.43	77.51	0.26	28.33	61.73	130.13	12850.85	8.30
Asawase	1	Bd	Bd	14.56	68.90	0.02	19.57	22.90	142.94	8813.76	Bd
Krofrom	2	9.66	8.21	101.99	94.82	0.03	47.62	18.02	204.47	27330.64	10.58
Bantama	2	5.04	Bd	47.12	15.22	0.03	33.24	44.31	183.53	15929.44	8.93
Ayigya	2	Bd	Bd	Bd	Bd	0.01	23.48	Bd	93.1	8973.56	6.58
Adum	3	4.77	Bd	125.93	45.04	0.01	37.58	17.16	137.77	3768.97	10.00
Central Market	1	Bd	Bd	Bd	15.70	0.02	Bd	Bd	107.76	9369.46	Bd
Kotei	1	Bd	Bd	Bd	Bd	0.01	Bd	Bd	56.32	11768.56	8.17
Roman Hill	1	3.71	Bd	131.08	27.72	0.02	31.09	20.55	192.52	21682.38	Bd
Control sample	**3**	**Bd**	**Bd**	**Bd**	**Bd**	**0.01**	**Bd**	**Bd**	**19.79**	**8215.54**	**6.20**

***Bd- indicates below detection**

Table 4.2: Descriptive statistics of heavy metals concentration in dust samples from transport stations (mg/kg)

Heavy metals	Minimum	Maximum	Mean	Median	Standard deviation	Skewness	Kurtosis
Hg	0.01	0.62	0.07	0.02	0.15	3. 48	12.3
As	Bd	9.66	6.10	5.35	2.33	0.89	-0.73
Sb	Bd	26.01	14.58	13.61	6.25	0.47	-1.02
Cd	Bd	37.13	19.99	12.07	12.27	0.34	-2.23
Pb	Bd	61.73	21.83	18. 44	15.99	1.74	3.02
Ni	Bd	47.62	29.98	29.71	9.22	0.55	-0.32
Cu	Bd	143.77	54.34	29.19	44.29	1.08	0.10
Zn	48.89	218.61	120.04	128.54	54.75	0.30	-0.96
Cr	Bd	260.11	130.39	131.08	66.83	-0.09	-0.10
Fe	3768.97	40936.07	16517.60	13180.53	9266.06	1.26	1. 44

***Bd- indicates below detection**

Table 4.3: Elemental Detection Limits

Element	Limits of Detection (mg/kg)
As	3.00
Cu	12.00
Ni	17.00
Cr	12.00
Hg	0.00005
Zn	6.00
Fe	35.00
Cd	7.00
Pb	4.00
Sb	6.00

Table 4.4: Value of Maximum Allowable limits for heavy metals in soil (mg/kg) from different countries (CCME, 2006; Mtunzi *et al*., 2015)

Chemical element	Australia	Canada-CCME (Commercial)	Poland	Japan	Great Britain	Germany
Cd	5.00	22.00	3.00	-	3.00	2.00
Cr	100.00	87.00	100.00	-	50.00	250.00
Cu	100.00	91.00	100.00	125.00	100.00	50.00
Ni	100.00	89.00	100.00	100.00	50.00	100.00
Pb	100.00	260.00	100.00	400.00	100.00	500.00
Zn	300.00	410.00	300.00	250.00	300.00	300.00
As	-	12.00	-	-	-	-
Hg	-	24.00	-	-	-	-
Sb	-	40.00	-	-	-	-

Various studies of heavy metal contaminations in dust have been compared the concentrations of metals in dust with soil guidelines due to lack of sufficient guidelines of maximum allowable limits of heavy metals in dusts (Hassan 2012; Khoder *et al*., 2012; Lu *et al.*, 2014). In this study the levels of heavy metals in dust were compared with soil guidelines from different countries as indicated in Table 4.4.

4.1.1a Arsenic concentration in transport station dust

The concentration of arsenic (As) was recorded in eight (8) sample sites out of 18 (Table 4.1). Arsenic concentration ranged from below the detection limit to 9.66 mg/kg, with a mean value of 6.10 mg/kg (Table 4.2). This mean value is in line with the value reported in a privious study (6.2 mg/kg) conducted from fuel filling stations in the Kumasi metropolis (Nkansah *et al.*, 2017). The dust sample from Krofrom gave the highest As concentration of 9.66 mg/kg dry weight followed by Metro Mass transport which gave the concentration of 9.55 mg/kg dry weight. Even though the levels of As obtained from

this study were below the maximum acceptable limit in commercial soil (12 mg/kg) of Canada (Table 4.4), the values were higher than that of the control dust sample which recorded below 3 mg/kg (detection limit) (Table 4.1). This suggests that the pollution of arsenic in these car stations may be as a result of anthropogenic activities such as combustion of fossil fuels from motor vehicles and atmospheric deposition of arsenic from industrial areas in the metropolis (Soukup *et al.*, 2012). Arsenic is a non essential element, therefore human exposure to large amount may cause health disorders such as damage to the central nervous system, kidneys and cardiovasiculars system (ATSDR, 2007).

4.1.1b Cadmium concentration in transport station dust

Cadmium (Cd) concentration was recorded in nine (9) sample sites out of 18 (Table 4.1). The concentration of Cd in all samples ranged from below 7.00 mg/kg (detection limit) to 37.13 mg/kg, with a mean value of 19.99 mg/kg of the measured values (Table 4.2). The mean concentration of Cd recorded in this study was higher than the value (8.13 mg/kg) repoted in a similar study conducted by Tokalioglu *et al*., (2003) in Kayseri, Turkey. Table 4.1 indicates that four transport stations recorded the highest level of Cd; High school Junction (37.13 mg/kg), Ahodwo (32. 43 mg/kg), Abinkyi (31.98 mg/kg) and Tech Junction (29.23 mg/kg) compared to other transport stations which recorded below 13 mg/kg of Cd. However, all the recorded cadmium concentrations in 9 sample sites were above the maximum allowable concentration in soils of different countries such as Australia (5 mg/kg), Polland (3 mg/kg), Great Britain (3 mg/kg) and Germany (2 mg/kg) except for Canadian commercial soil (22 mg/kg). Cadmium is used as an additive in the automibile lubricating oils and vulcanization of tyres, therefore the high levels of cadmium recorded in these transport stations may have been released from lubricating

oil, car components, break lining wear, tyre wear and engine exhausts of the motor vehicles (Elnazer *et al.*, 2015).

4.1.1c Chromium concentration in transport station dust

Chromium (Cr) in the dust samples gave the concentrations which ranged from below detection limit to 260.11 mg/kg which is the second highest concencetration of heavy metals recorded in this study (Table 4.2). Only three sample sites recorded Cr concentration below detection limit (Table 4.2). The maximum concentration of chromium was recorded from Metro Mass transport sample (260.11 mg/kg) which is almost twice the mean concentration of Cr (130.39 mg/kg) recorded in this study. The mean concentration of Cr obtained in this study is lower than the average concentration (210 mg/kg) reported by Atiemo *et al.*, (2012) from road dust in major highways of Accra, Ghana and 6 times higher than the average concentration of 21.5 mg/kg recorded in a similar study conducted in Kyseri, Turkey (Tokalioglu *et al*., 2003). Table 4.1 shows that twelve (12) sample sites recorded the concentrations of Cr greater than 87 mg/kg which is the maximum acceptable value in Canadian commercial soil. The highest concentration of Cr observed in Metro Mass transport and other transport stations can be associated with corrosion of the car components since chrome materials made up of chromium and nickel are used in plating of motor vehicle components (Christoforidis and Stamatis, 2009).

4.1.1d Copper concentration in transport station dust

The concentrations of copper (Cu) recorded in this study ranged from below 12 mg/kg (detection limit) to 143.77 mg/kg (Table 4.2). Three sample sites; Kotei, Atonsu and Ayigya recorded copper concentration below detection limit (Table 4.1). The average value of Cu calculated from all samples was found to be 54.34 mg/kg which is about

2.5 times lower than the maximum Cu concentration obtained in this study (Table 4.2). The highest copper concentration was measured from Ahodwo station (143.77 mg/kg) followed by Atonsu station (141.11 mg/kg). Apart from these sites, Dr. Mensah, Asawase, Asafo, Krofrom and Adum also recorded the values of Cu higher than the maximum allowable limit in dust (32 mg/kg) (Abdulrahman *et al*., 2013). However, the mean concentration of Cu obtained in this study was lower than maximum allowable limits in soil of different countries shown in Table 4.4. The mean concentration of copper obtained in this study was 2 times lower than the mean value (27.8 mg/kg) reported in a similar study conducted by Tokalioglu *et al*., (2003) in Kayseri, Turkey and almost similar to the value (52.35 mg/kg) reported by Shinggu *et al.*, (2007). According to Christoforidis and Stamatis, (2009), copper and zinc are commonly found in urban environment and their high concentration is associated with heavy traffics. Therefore, the high level of Cu recorded in transport stations could be associated with its release from corrosion of car components, leakage of lubricating oils, break lining wear, tyre wear and engine exhausts (Khoder *et al*., 2012). Copper is an essential element but its high concentration in the body greater than acceptable limit is dangerous to human health.

4.1.1e Mercury concentration in transport station dust

Mercury (Hg) is one of the major toxic metals in the environment. The release of mercury in the environment is a result of anthropogenic activities such as gold mining, industrial production of cement and natural processess such as volcanic eruption and weathering of Hg- containing rocks (Reeder and Schoonen, 2006). The concentration of

Hg in this study was recorded in all dust samples and ranged from 0.01 mg/kg to 0.62 mg/kg (Table 4.2**).** The mean concentration of Hg was found to be 0.07 mg/kg and is the lowest mean concentration calculated from transport stations compared to the mean

values of other metals. The highest Hg concentration was recorded from Dr. Mensah (0.62 mg/kg) followed by Asafo (0.26 mg/kg). The values of Hg obtained in this study were lower than the average concentration of 13.5 mg/kg reported by Ozaki *et al.*, (2004) from road dust in Japan. The natural level of Hg in soil normally ranges from 0.001 mg/kg to 0.08 mg/kg and does not exceed 0.1 mg/kg (European Union, 1998). Therefore, the values of Hg in dust samples recorded from Dr. Mensah and Asafo were higher than expected amounts in soil and control dust sample but lower than the maximum acceptable limit (24 mg/kg) in Canadian commercial soil.

The possible source of mercury pollution in these places could be associated with gasoline combustion from motor vehicles, atmospheric deposition of mercury particulates (Ozaki *et al*., 2004; Reeder and Schoonen, 2006).

4.1.1f Nickel concentration in transport station dust

Nickel concentration in the analyzed dust samples ranged from below detection limit to 47.62 mg/kg, with a mean concentration 29.98 mg/kg (Table 4.2). The average concentration of nickel recorded from transport stations was lower than the mean value of 44.05 mg/kg in dust reported from fuel filling stations in the Kumasi Metropolis (Nkansah *et al.*, 2017) and higher than that reported from the road dust (23 mg/kg) in Islamabad Expressway, Pakistan (Faiz *et al.*, 2009).

A similar study conducted in Kayseri, Turkey by Tokalioglu *et al*., (2003) reported average Ni concentration of 38 mg/kg which is lower compared to the mean value recorded in this study. Dust samples from Kotei and Central Market stations recorded Ni concentrations below the detection limit while the highest value of 47.62 mg/kg was recorded from Krofrom. The mean concentration of Ni obtained in this study was lower than the maximum permissible limit in soil of different countries listed in Table 4.4 and

higher than the value measured from the control dust sample which recorded below detection limit. The source of nickel in study sites could be attributed to deterioration of car components plated with nickel containing material such as chrome, the use of nickel–cadmium bateries, atmospheric fallouts and deposition and natural crust due to re-suspension of surface soil by human activities (Elnazer *et al.*, 2015).

4.1.1g Lead concentration in transport station dust

Lead (Pb) concentration ranged from below 4 mg/kg (detection limit) to 61.73 mg/kg, with an average value of 21.83 mg/kg (Table 4.2). Table 4.1 indicates that six (6) sample sites recorded lead (Pb) concentration below the detection limit. The highest concentration of Pb was measured from Asafo station (61.73 mg/kg) which is over three times the maximum allowable limit of 20 mg/kg in dust (Abdulrahman *et al*., 2013). The average concentration of Pb recorded in this study was 3.66 times lower than the mean value of 80 mg/kg reported in a similar study conducted by Tokalioglu *et al*.,(2003) and about 11 times lower than the mean concentration (241.34 mg/kg) reported by Shinggu *et al.*, (2007). The concentrations of Pb recorded in this study were lower than the maximum allowable limit in soil of different countries as indicated in Table 4.4. However, since the dust samples from Dr. Mensah, Asafo, Asawase, Bantama and Roman Hill recorded Pb concencentrations above the safe limit in dust (20 mg/kg), people commercializing in these areas may be at risk of exposure to high level of Pb. The possible source of Pd can be attributed to combustion of leaded gasoline, and leaks and spills from bateries and radiators (Atiemo *et al.*, 2012).

4.1.1h Zinc concentration in transport station dust

Zinc was detected in dust samples from all sample sites and its concentration ranged from 48.89 mg/kg to 218.61 mg/kg, with a mean value of 120.04 mg/kg (Table 4.2).

The mean concentration of Zn recorded in this study is in line with the mean value of 127 mg/kg reported in a similar study conducted by Tokalioglu *et al*., (2003) in Kayseri, Turkey. Mayanka station recorded the highest zinc concentration (218.61 mg/kg) followed by Krofrom (204.04 mg/kg), Roman Hill (192.52 mg/kg) and Bantama (183.53 mg/kg) while other sample sites recorded concentrations below 148 mg/kg. All the sample sites recorded zinc concentration far higher than the value measured from the control dust sample (19.79 mg/kg) and this suggests anthropogenic contribution to zinc contamination of dust from transport stations. The concentrations of zinc recorded in this study were however lower compared to the maximum allowable level in soils of different countries as indicated in Table 4.4. The observed concentration of zinc is thought to be contributed by motor vehicles in the transport stations. The use of zinc based chemical additives such as zinc dialkyldithiophate and zinc dithiophosphate as anti-wear additives during vulcanization of tyres and corrosion prevention in car engines contributes to the release of zinc from motor vehicles during wearing of tyres and engine parts (WieszaŁa and WyciŚlik, 2008).

4.1.1i Iron concentration in transport station dust

Iron (Fe) is an essential element which is most abundant in the earth's crust and it originates from both natural and anthropogenic activities. The natural content of iron in the soil is far higher than the rest of the heavy metals (Tokalioglu *et al*., 2003). The concentration of Fe in this study ranged from 3768.97 mg/kg to 40936.07 mg/kg, with a mean value of 16517.60 mg/kg (Table 4.2). The average value of Fe calculated from transport stations was the highest compared to the mean values of other metals and lower than the mean value of 20500.75 mg/kg reported from car parks in Mubi, Adamawa State, Nigeria (Shinggu *et al.*, 2007). Table 4.1 indicates that the highest value of Fe was

recorded from the Metro Mass transport station (40936.07 mg/kg) followed by Abinkyi (28733.38 mg/kg), Krofrom (27330.64 mg/kg), Mayanka (27323.4 mg/kg) and Roman Hill (21682.38 mg/kg). However, all sample sites recorded iron concentration higher than the value recorded from the control sample (8215.54 mg/kg) except Adum which recorded the lowest value (3786.97 mg/kg) and this is considered to be from natural crust. Iron contamination was viewed to be due to corrosion of some parts of motor vehicles as indicated in the study conducted by Shinggu *et al.*, (2007). On the other hand, metal grinding, cutting and fibrication and auto mechanical workshops were dotted around some car stations such as Roman Hill, Metro Mass transport and Krofrom and these activities can also contribute to iron contamination of dust in these areas. Human exposure to excess amount of iron above 10 mg/kg causes blood coagulation in the blood vessels, rapid increase in pulse rate and hypertension (Nazir *et al.*, 2015).

4.1.1j Antimony concentration in transport station dust

Antimony (Sb) is one of the potential hazardous metals to human health and its distribution in the environment is by anthropogenic activities and natural processes. Its natural content in the earth crust is about 0.3 mg/kg (Fujiwara *et al.*, 2011). In this study, Sb concentration ranged from below detection limit (6 mg/kg) to 26.01 mg/kg and the average concentration of the measured values was found to be 16.58 mg/kg (Table 4.2). This mean value is about 22.7 times higher than the mean concentration (0.73 mg/kg) reported by Ozaki *et al*., (2004) from roadside dust in Japan. The results indicated in Table 4.2 show that four sample sites recorded Sb concentration below the detection limit of 6 mg/kg . The dust sample from High School Junction recorded the highest Sb concentration (26.01 mg/kg) which is about 4.2 times higher than the concentration recorded from the control dust sample (6.2 mg/kg). Although all the

recorded Sb concentrations in the 14 transport stations were below the maximum allowable limits in Canadian soil (40 mg/kg), the concentrations were higher than the value recorded from the control site. This indicates the anthropogenic contribution to the contamination of Sb in the sample sites. A study conducted by Ozaki *et al*, (2004) showed that automobiles contribute greatly to the release of Sb in the urban dust. Other studies revealed that the use of antimony containing compounds such as dialkyldithiol carbamate in motor oil and grease, Sb_2S_3 in brake lining to improve friction stability and minimize vibrations and antimony trioxide as flame retardant in the process of vulcanization of rubber contribute to the emission of Sb from motor vehicles

(WieszaŁa and WyciŚlik, 2008; Fujiwara *et al.*, 2011). Therefore, break lining wear, oil leaks, tires wear and combustion of fossil fuel may be considered as the major sources of high level of Sb contamination of dust from transport stations.

4.1.2 Pearson's Correlation Analysis for transport station dust

In the present study, the relationship between heavy metals concentrations in dust samples from transport stations was conducted by employing Pearson's correlation analysis at $p < 0.05$. Pearson's correlation coefficients were determined and are presented in Table 4.5 in the form of correlation matrix.

Table 4.5: Pearson's correlation matrix for heavy metals in dust from transport stations

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb
As	1									
Cd	0.197	1								
Cr	-0.034	-0.283	1							

Cu	-0.511	-0.416	0.054	1						
Hg	-0.371	-0.256	0.254	0.341	1					
Ni	-0.722*	0.199	-0.170	0.244	0.254	1				
Pb	-0.258	-0.309	-0.613*	0.043	-0.044	-0.177	1			
Zn	0.643*	-0.261	-0.295	0.277	0.111	-0.215	-0.028	1		
Fe	0.404	-0.344	0.040	-0.222	-0.042	-0.323	0.131	0.289	1	
Sb	0.186	0.732*	-0.297	0.061	0.031	-0.233	-0.015	0.182	-0.072	1

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

From correlation analysis results, As showed a strong significant negative correlation with Ni ($r = -0.722$, $p < 0.05$) and moderate positive correlation with Zn ($r = 0.643$, $p < 0.05$) signifying that As originated from the same anthropogenic source with Ni and Zn. Different studies indicated that As, Ni and Zn may be released into the environment from industrial activities, electronic wastes and automobiles via combustion of fossil fuel, tires wear and corrosion of car parts (Ozaki *et* al., 2004; WieszaŁa and WyciŚlik, 2008). Cadmium showed a significant and strong positive correlation with Sb ($r = 0.732$, $p < 0.05$), which indicates that these metals my be originating from the same source. Another moderate negative correlation existed between Cr and Pb ($r = -0.63$, $p < 0.05$) which showed that Cr and Pb could be originating from similar anthropogenic sources such as motor vehicles (Elnazer *et al.*, 2015). Other metals had no significant correlation with each other.

4.1.3 Assessment of the heavy metal contamination in dust from transport stations

The assessment of the heavy metals contamination in the dust from transport stations was based on the calculations of pollution indices.

4.1.3.1 Geo-accumulation index (Igeo) of transport station dust

The calculated values of Igeo of heavy metals in dust from transport stations are presented in Table 4.6. Igeo values with symbol “Nc” indicate that the Igeo was not calculated and the sample sites were considered to be unpolluted by the respective metal since the concentration recorded was below detection limit. The negative Igeo value shows that dust samples were unpolluted (Ige<0) by a given metal.

Table 4.6: Geo-accumulation index (Igeo) of heavy metals in dust from transport stations

Sample sites	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb
Tech Junction	Nc	10.93	4.62	0.00	1.20	1.96	-0.29	3.50	0.05	1.28
High School Junction	Nc	11.27	4.64	-0.60	0.42	1.48	-0.19	2.15	-0.16	1.48
Abinkyi	3.65	11.06	4.84	0.42	1.12	2.53	Nc	3.53	1.22	0.97
Dr Mensah	Nc	9.65	4.10	1.97	6.36	1.45	0.85	3.59	0.25	0.62
Mayanka	3.84	Nc	4.41	0.42	1.21	2.30	0.67	4.28	1.15	Nc
Metro Mass transport	4.41	9.19	5.21	0.63	2.27	2.87	-1.41	2.81	1.73	0.89
Atonsu	Nc	9.51	3.78	Nc	1.60	1.97	Nc	2.12	-0.17	0.91
Ahodwo	Nc	11.08	4.77	2.93	0.47	1.88	Nc	2.29	0.13	1.29
Sofoline	3.14	9.25	4.35	2.90	0.72	2.39	0.07	2.61	0.45	0.47
Asafo	Nc	Nc	2.02	2.04	5.09	2.14	2.38	3.53	0.06	-0.16
Asawase	Nc	Nc	1.06	1.87	1.31	1.61	0.95	3.67	-0.48	Nc
Krofrom	4.42	9.10	3.86	2.33	1.94	2.89	0.60	4.19	1.15	0.19
Bantama	3.49	Nc	2.75	-0.31	2.14	2.37	1.90	4.03	0.37	-0.06
Ayigya	Nc	Nc	Nc	Nc	0.24	1.87	Nc	3.05	-0.46	-0.50
Adum	3.41	Nc	4.17	1.25	0.57	2.55	0.53	3.62	-1.71	0.10
Central Market	Nc	Nc	Nc	-0.27	1.64	Nc	Nc	3.26	-0.40	Nc
Kotei	Nc	Nc	Nc	Nc	0.38	Nc	Nc	2.33	-0.07	-0.19
Roman Hill	3.04	Nc	4.23	0.55	1.71	2.28	0.79	4.10	0.82	Nc
Mean	3.68	10.12	3.92	1.07	1.69	2.16	0.57	3.26	0.22	0.52
Maximum	4.42	11.27	5.21	2.93	6.36	2.89	2.38	4.28	1.73	1.48
Minimum	3.04	9.10	1.06	-0.60	0.24	1.45	-1.41	2.12	-1.71	-0.50
SD	0.52	0.94	1.14	1.19	1.61	0.44	0.99	0.72	0.80	0.63

Nc – mean not calculated because the recorded concentration was below detection limit.

The mean Igeo values of the metals decreased in the following sequence; Cd > Cr > As > Zn > Ni > Hg > Cu > Pb > Sb > Fe. The mean Igeo value of Pb, Fe, and Sb fall within the class b ($0 \leq Igeo < 1$) and this indicates that dust samples from some transport stations were unpolluted to moderately polluted. The mean Igeo value of Cu and Hg indicate that dust samples were moderately polluted ($1 \leq Igeo < 2$) by these metals. However, the results show that dust samples from Dr. Mensah and Asafo were extremely polluted by Hg ($Igeo \geq 5$). The mean Igeo of Ni (2.16) showed that dust samples were moderately to strongely polluted with Ni. On the other hand, the average Igeo of As, Cr and Zn indicate that some sample sites were strongly polluted by these metals ($3 \leq Igeo < 4$). The Igeo values of Cd which ranges between 9.10 to 11.27, signify that dust samples from Tech Junction, High School Junction, Abinkyi, Dr. Mensah, Atonsu, Ahondwo, Sofoline, Krofrom and Metro Mass transport were very strongly polluted ($Igeo \geq 5$) by Cd. The average Igeo values of Zn, Cu, Cr and Ni observed in this study were higher compared to that observed in a study conducted by Atiemo *et al.*, (2015). Similarly, As and Hg showed the highest mean Igeo values compared to Igeo values reported by Wang *et al.*, (2013). The calculated Igeo values of all the metals indicate that there may be anthropogenic contribution to heavy metals pollution in dust from transport stations.

4.1.3.2 Enrichment factor (EF) of transport station dust

The values of EF for different metals in each transport station are presented in Table 4.7.

Table 4.7: Enrichment factors (EF) of heavy metals in dust from transport stations

Sample sites	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb

Tech Junction	Nc	1884.51	23.76	0.97	2.23	3.77	0.79	10.93	1.00	2.35
High SJ	Nc	2758.80	27.75	0.74	1.49	3.11	0.98	4.96	1.00	3.12
Abinkyi	5.39	914.38	12.30	0.57	0.93	2.49	Nc	4.97	1.00	0.84
Dr Mensah	Nc	675.27	14.34	3.29	68.96	2.29	1.52	10.11	1.00	1.29
Mayanka	6.47	Nc	9.62	0.60	1.05	2.22	0.72	8.78	1.00	Nc
Metro Mass transport	6.39	175.61	11.18	0.46	1.45	2.20	0.11	2.12	1.00	0.56
Atonsu	Nc	821.12	15.45	Nc	3.41	4.41	Nc	4.89	1.00	2.12
Ahodwo	Nc	1972.06	24.90	6.94	1.26	3.37	Nc	4.45	1.00	2.24
Sofoline	6.42	445.18	14.88	5.45	1.21	3.83	0.77	4.45	1.00	1.01
Asafo	Nc	Nc	3.89	3.93	32.77	4.23	4.99	11.11	1.00	0.86
Asawase	Nc	Nc	2.91	5.10	3.46	4.26	2.70	17.79	1.00	Nc
Krofrom	9.68	246.79	6.56	2.26	1.73	3.34	0.68	8.21	1.00	0.51
Bantama	8.66	Nc	5.20	0.62	3.41	4.01	2.89	12.64	1.00	0.74
Ayigya	Nc	Nc	Nc	Nc	1.62	5.02	Nc	11.38	1.00	0.97
Adum	34.66	Nc	58.78	7.79	4.85	19.14	4.73	40.09	1.00	3.52
Central Market	Nc	Nc	Nc	1.09	4.09	Nc	Nc	12.62	1.00	Nc
Kotei	Nc	Nc	Nc	Nc	1.36	Nc	Nc	5.25	1.00	0.92
Roman Hill	4.69	Nc	10.64	0.83	1.86	2.75	0.98	9.74	1.00	Nc
Maximum	34.66	2758.80	58.78	7.79	68.96	19.14	4.99	40.09	1.00	3.52
Minimum	4.69	175.61	2.91	0.46	0.93	2.20	0.11	2.12	1.00	0.51
Mean	10.30	1099.30	16.14	2.71	7.62	4.40	1.82	10.25	1.00	1.50
SD	9.98	896.62	13.99	2.54	16.95	4.02	1.64	8.44	0.00	0.98

From Table 4.7, the mean values of EF of all the metals exceeded 1 except for Fe, which indicated that metals were highly enriched in dust from transport stations and originated from anthropogenic activities. The EF of Cd which ranged from 2758.80 to 175.61, with a mean value of 1099.30 indicates that Cd was extremely enriched (EF > 40) in dust and originated from anthropogenic sources such as motor vehicles. The mean EF

of Pb (1.82), Sb (1.50) and Fe (1.00) were less than 2 and this indicates a minimum enrichment. However, Pb and Sb were moderately enriched in the dust sample from Adum as their EF values fall between 2 and 5. The average EF of Cu (2.71) and Ni (4.4) show that these metals were moderately enriched in the dust samples. Cu was significantly enriched in dust from Ahodwo, Sofoline, Asawase and Adum. The mean EF values of other metals such as As (10.30), Cr (16.14) and Zn (10.25) signify very high enrichment of these metals in dust and this can be attributed to anthropogenic activities such as vehicular activities in the study sites. The dust sample from Dr. Mensah was extremely enriched with Hg (EF = 68.96) and that from

Asafo equally showed very high enrichment of Hg (EF =32.77). The enrichment of As, Cd, Cr, Cu, Hg, Ni, Pb, Zn and Sb in the dust samples is an indication of anthropogenic contribution to their pollution. This was also revealed by Atiemo *et al.*, (2012) who indicated that the enrichment of Cu, Zn and Pb in road dust is as a result of anthropogenic activities such as vehicular exhaust and non-exhaust emissions.

4.1.3.3 Contamination factor (CF) of transport station dust

Contamination factor was also employed as one of the assessment tools of the level of heavy metals contamination in the dust samples. The calculated values of CF are presented in Table 4.8. The symbol "Nc" indicates that the CF was not calculated since the metal concentration was recorded below detection and the sample sites are considered to be uncontaminated by the respective metals.

Table 4.8: Contamination factors (CF) of heavy metals in dust from transport stations

Sample Site	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb

Tech Junction	Nc	2923.00	36.85	1.50	3.45	5.85	1.22	16.95	1.55	3.64
High School Junction	Nc	3713.00	37.35	0.99	2.00	4.18	1.31	6.68	1.35	4.20
Abinkyi	18.87	3198.00	43.01	2.00	3.26	8.69	Nc	17.37	3.50	2.94
Dr Mensah	Nc	1207.00	25.64	5.89	123.26	4.10	2.71	18.07	1.79	2.31
Mayanka	21.53	Nc	32.00	2.01	3.48	7.40	2.38	29.19	3.33	Nc
Metro Mass transport	31.83	875.00	55.70	2.32	7.23	10.94	0.57	10.55	4.98	2.78
Atonsu	Nc	1095.00	20.60	Nc	4.55	5.88	Nc	6.53	1.33	2.82
Ahodwo	Nc	3243.00	40.94	11.41	2.08	5.54	Nc	7.32	1.64	3.68
Sofoline	13.20	915.00	30.58	11.20	2.48	7.86	1.58	9.14	2.06	2.08
Asafo	Nc	Nc	6.09	6.15	51.25	6.62	7.80	17.37	1.56	1.34
Asawase	Nc	Nc	3.12	5.47	3.71	4.57	2.90	19.08	1.07	Nc
Krofrom	32.20	821.00	21.84	7.53	5.77	11.13	2.28	27.30	3.33	1.71
Bantama	16.80	Nc	10.09	1.21	6.61	7.77	5.60	24.50	1.94	1.44
Ayigya	Nc	Nc	Nc	Nc	1.77	5.49	Nc	12.43	1.09	1.06
Adum	15.90	Nc	26.97	3.57	2.23	8.78	2.17	18.39	0.46	1.61
Central Market	Nc	Nc	Nc	1.25	4.66	Nc	Nc	14.39	1.14	Nc
Kotei	Nc	Nc	Nc	Nc	1.95	Nc	Nc	7.52	1.43	1.32
Roman Hill	12.37	Nc	28.07	2.20	4.92	7.26	2.60	25.70	2.64	Nc
Maximum	32.20	3713.00	55.70	11.41	123.26	11.13	7.80	29.19	4.98	4.20
Minimum	12.37	821.00	3.12	0.99	1.77	4.10	0.57	6.53	0.46	1.06
Mean	20.34	1998.89	27.92	4.31	13.04	7.00	2.76	16.03	2.01	2.35
SD	7.77	1227.16	14.31	3.51	29.7	2.15	2.02	7.31	1.13	1.01

Nc- means not detected because the recorded concentration was below detection limit

The CF values of Cu and Pb which ranged from 0.99 to 11.41 and 0.57 to 7.80 respectively indicate low contamination to very high contamination of sample sites. The

CF values of Hg which range from 1.77 to 123.26 indicate that some sample sites were moderately contaminated ($1 \leq CF < 3$), considerable contaminated ($3 \leq CF \leq 6$) while others were very highly contaminated particularly Dr. Mensah and Asafo stations (CF > 6). The values of CF for Fe and Sb indicate moderate contamination to considerable contamination of the sample sites. The mean CF values of the metals follow the decreasing order, Cd > Cr > As > Zn > Hg > Ni> Cu > Pb > Sb > Fe. The CFs of As, Ni, Cu, Hg and Cr calculated in this study were significantly higher than CF values reported by Wang *et al.*, (2013). According to Ozaki et al., (2004), the contamination of these metals in dust can be attributed to automobiles.

4.1.3.4 Pollution load index (PLI) and modified degree of contamination (mCd) of transport station dust

The calculated values of PLI and mCd of heavy metals in various transport stations are shown in Table 4.9.

Table 4.9: Pollution load index (PLI) and modified degree of contamination (mCd) of heavy metals in dust from transport stations

Sample Sites	PLI	MCd
Tech junction	7.22	299.40
High school junction	5.96	377.10
Abinkyi	11.02	329.76
Dr. Mensah	10.64	139.08
Mayanka	4.92	10.13
Metro Mass transport	10.90	100.19
Atonsu	5.21	113.67
Ahodwo	7.74	331.56
Sofoline	9.32	99.52
Asafo	4.53	9.82

Asawase	2.65	3.99
Krofrom	12.57	93.41
Bantama	4.58	7.60
Ayigya	1.64	2.18
Adum	3.93	8.01
Central Market	1.58	2.14
Kotei	1.39	1.22
Roman Hill	4.66	8.58
Maximum	12.57	377.10
Minimum	1.39	1.22
Mean	6.14	107.63
SD	3.53	133.58

All the sample sites (18) recorded PLI > 1, indicating the progressive deterioration of site quality by heavy metals**.** The PLI values indicate that Abinkyi, Dr. Mensah, Krofrom and Metro Mass transport had high pollution load compared to other sample sites while Kotei station had the least pollution load. The mCd ranged from 1.22 to 377, with a mean value of 107.63 which indicates ultra-high degree of contamination (mCd≥32). However, the highest values of mCd seen Table 4.9 (ranging from 93.1 to

377.10) were attributed to high level of Cd in the sample sites as it revealed by CFs of Cd shown in Table 4.8. The mCd values for dust samples from Ayigya, Asawase and Central Market stations indicate that these sites were moderately contaminated (2≤mCd<4). Other sample sites with mCd ranging between 8 and 16 were considered to have very high degree of contamination and this can be attributed to anthropogenic activities. The mCd for Kotei station indicates that this site has zero to very low degree of contamination. Most of the transport stations within the Kumasi metropolis appeared

to have high metal pollution load compared to fuel filling stations which were reported to be moderately polluted (Nkansah *et al.*, (2017).

4.1.4 Human health risk assessment of heavy metals in transport station dust

The human health risk assessment was conducted on both noncarcinogenic and carcinogenic risks of heavy metals.

4.1.4.1 Non-carcinogenic health risk of heavy metals in transport station dust Non-carcinogenic risks for both children and adults were assessed by using Hazard index (HI) which was obtained by summing up the Hazard quotients (HQs) across the three exposure pathways (ingestion (ing), inhalation (inh) and dermal (derm) contact) for each metal. The results of non-carcinogenic risks are presented in Table 4.10. The HI of the individual exposure route was obtained from the sum of the HQs of all the metals in the same exposure pathway.

Table 4.10: Hazard quotients (HQ) and hazard index (HI) for non-carcinogenic risks of heavy metals in dust from transport stations

Metals	Children				Adults			
	HQing	HQinh	HQderm	HI	HQing	HQinh	HQderm	HI
As	2.28E-01	6.56E-06	4.67E-02	0.27	7.64E-04	1.16E-06	7.44E-03	0.01
Cd	3.09E-01	7.79E-05	8.64E-03	0.32	1.03E-03	1.38E-05	1.38E-03	0.00
Cr	5.59E-01	1.61E-03	3.13E-01	0.87	1.87E-03	2.84E-04	4.98E-02	0.05
Cu	9.33E-03	2.67E-07	8.71E-05	0.01	3.13E-05	4.72E-08	1.39E-05	0.00
Hg	8.52E-04	8.56E-08	3.41E-05	0.00	2.86E-06	1.51E-08	5.43E-06	0.00
Ni	1.90E-02	5.31E-04	1.97E-04	0.02	6.37E-05	9.37E-05	3.14E-05	0.00
Pb	1.68E-01	1.93E-06	1.57E-03	0.17	5.64E-04	3.40E-07	2.50E-04	0.00
Zn	5.48E-03	1.58E-07	7.67E-05	0.01	1.84E-05	2.78E-08	1.22E-05	0.00

Fe	2.41E-01	6.93E-06	6.74E-04	0.24	8.07E-04	1.22E-06	1.07E-04	0.00
Sb	Nc	Nc	Nc	Nc	Nc	Nc	Nc	Nc
HI	1.54E+00	2.23E-03	3.71E-01	1.91	5.16E-03	3.94E-04	5.90E-02	0.06

"Nc" means not calculated since the reference daily doses of Sb could not be assessed

The results of non-carcinogenic risks showed that HI of each metal across the three exposure routes was less than acceptable safe limit of 1. This indicates that noncarcinogenic health risk for both children and adults is not likely to occur from exposure to heavy metals in dust from transport stations. However, since the HI for Cr (0.87) across the three exposure pathways was close to a safe limit of 1 for children, the long term accumulation of chromium may potentially trigger non-carcinogenic health effects associated with chromium exposure. This was equally reported by Du *et al.*, (2013) who observed HI of 0.805 for Cr in children due to exposure in road dust. On the other hand, the total hazard index of all the heavy metals in children (HI =1.91) via the three exposure pathways exceeded the safe limit of 1. This indicates that cumulative effect of all these metals in the body is likely to cause non-cancer health effects in children compared to adults (HI =0.06).

The Hazard indices of the metals for children decreased in the following order: Cr > Cd > As > Fe > Pb >Ni > Cu, Zn > Hg. Ingestion was observed as the main exposure pathway to heavy metals in dust followed by dermal contact and inhalation in children while in adults the average exposure pathways of heavy metals followed the decreasing order: dermal contact > ingestion > inhalation. This is consistent with a study conducted by Zheng *et al.,* (2010) who observed dermal contact (for adults) and ingestion (for children) to be the highest exposure pathways of heavy metals in street dust. The results also showed that HI value of metals via each exposure route is less than 1, except HI

(1.54) for ingestion route which exceeded hazard level of 1 in children, signifying no likelihood of non-cancer risk. The cumulative effect of all the metals via ingestion proves to be a major concern of non-carcinogenic health risk in children compared to other exposure pathways. Compared to adults, non-carcinogenic health risk for children due to exposure to heavy metals in transport station dust was observed to be high. This was also observed by Zheng *et al.*, (2010) from street dust in China.

4.1.4.2 Carcinogenic health risk of heavy metals in transport station dust The carcinogenic health risk (CRI) was assessed for As, Ni, Cd and Pb in which their cancer slope factors were assessed from the literature and the results are presented in Table 4.11.

Table 4.11: Average daily dose (ADDc) and carcinogenic risks (CRI) of heavy metals in dust from transport stations

Metals	CHILDREN				ADULTS			
	ADDc			CRI	ADDc			CRI
	Ingestion	Inhalation	Dermal		Ingestion	Inhalation	Dermal	
As	5.86E-06	1.69E-10	1.64E-06	1.48E-05	2.09E-06	3.17E-10	2.51E-07	4.06E-06
Cd	1.32E-05	3.81E-10	1.23E-07	2.00E-04	4.72E-06	7.16E-10	1.88E-08	7.11E-05
Ni	3.26E-05	9.37E-10	3.04E-07	2.99E-05	1.16E-05	1.76E-09	4.64E-08	1.06E-05
Pb	2.02E-05	5.82E-10	1.89E-07	8.16E-07	7.22E-06	1.09E-09	2.88E-08	3.04E-07

With respect to the results of this study, the CRI ranged from 3.04E-07 to 1.06E-05 for adults and 8.16E-07 to 2.00E-04 for children. The acceptable range for carcinogenic risk is set between 1×10^{-6} and 1×10^{-4} according to the guidelines of the Environmental

Protection Agency of the United States (U.S. EPA, 1989). The CRI values of As, Cd, and Ni for adults were within the acceptable limits. Similarly, the CRI values of As, Ni and Pb for children were within the tolerable range except Cd with CRI (2.00E-04) which was above the maximum acceptable carcinogenic risk (1E4). This indicates that children are at high risk of getting cancer associated with exposure to Cd-contaminated dust from transport stations in the Kumasi metropolis. Chronic exposure to low level of cadmium may cause lung cancer (IARC, 1990). The results of carcinogenic health risk assessment indicated ingestion as the dominant exposure pathway to metal carcinogens followed by dermal contact and inhalation for both children and adults. This is consistent with the study conducted by Nkansah *et al.*,
(2017).

4.2 HEAVY METALS CONCENTRATION IN DUST FROM MARKETS

The concentration of As, Cd, Cu, Hg, Ni, Cr, Pb, Zn, Fe and Sb in dust samples were determined and the results are presented in Table 4.13. The descriptive statistics of heavy metals concentration (mg/kg) are presented in Table 4.12. The overall heavy metal concentrations showed that Fe recorded the highest value of 34953.63 mg/kg with an average value of 19634.10 mg/kg while mercury recorded the lowest maximum concentration of 1.38 mg/kg and a mean value of 0.15 mg/kg. The mean concentrations of heavy metals decreased according to the order;

Fe > Zn > Cr > Cu > Ni > Pb > Sb > Cd > As > Hg.

Table 4.12: Concentrations of heavy metals in dust from markets (mg/kg)

Sample Sites	**N**	**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**Fe**	**Sb**
Abinkyi	1	Bd	13.69	33.18	19.94	0.01	36.92	Bd	83.38	34953.63	21.72
Dr Mensah	2	4.30	14.61	173.03	68.64	1.38	32.40	7.99	133.12	19427.12	14.25
Mayanka	1	Bd	6.27	140.67	58.43	0.01	35.78	7.46	220.27	26710.00	9.90
Atonsu	1	4.01	11.45	232.90	135.10	0.01	27.46	5.82	97.46	19267.36	16.77
Ahodwo	1	3.85	9.23	179.81	153.51	0.01	28.81	Bd	59.29	16022.18	21.17
Sofoline	1	Bd	Bd	93.68	181.85	0.04	44.79	16.54	93.63	33799.05	8.36
Asafo	2	Bd	Bd	20.55	59.59	0.13	25.40	26.76	107.55	11637.69	10.66
Asawase	2	6.20	Bd	55.81	43.83	0.04	42.47	72.10	293.68	20356.67	15.59
Krofrom	2	3.45	Bd	69.33	16.09	0.03	27.07	31.42	214.21	22564.49	7.82
Bantama	1	3.37	Bd	13.47	10.85	0.03	Bd	Bd	113.19	13288.94	Bd
Ayigya	2	Bd	Bd	Bd	9.19	0.01	Bd	Bd	198.56	8283.66	Bd
Kotei	1	Bd	Bd	21.19	Bd	0.02	Bd	Bd	92.31	13274.06	Bd
Central Market	1	Bd	Bd	27.87	16.31	0.28	Bd	11.34	233.61	15658.39	Bd
Control sample	**3**	**Bd**	**Bd**	**Bd**	**Bd**	**0.01**	**Bd**	**Bd**	**19.79**	**8215.54**	**6.20**

"**Bd" means below detection**

Table 4.13: Descriptive statistics of heavy metals concentration (mg/kg) in dust from markets

Metals	Minimum	Maximum	Mean	Median	Standard Deviation	Skewness	Kurtosis
Hg	0.01	1.38	0.15	0.03	0.33	3.38	11.66
As	Bd	6.20	4.20	3.93	1.04	1.86	3..82
Cd	Bd	14.61	11.05	11.45	3.39	-0.55	-0.97
Sb	Bd	21.72	14.02	14.25	5.23	0.35	-1.32
Pb	Bd	72.10	22.43	13.94	22.14	1.94	4.05
Ni	Bd	44.79	33.45	32.40	7.00	0.53	-1.11
Cu	Bd	181.85	64.44	51.13	60.13	1.02	-0.29
Cr	Bd	232.90	88.46	62.57	75.09	0.78	-0.76
Zn	59.29	293.68	149.25	113.19	73.27	0.68	-0.81
Fe	8283.66	34953.63	19634.10	19267.36	8149.78	0.76	-0.11

"Bd" means below detection limit

The values of skewness of Hg, As, Pb and Cu were greater than one, indicating that the concentrations of these metals were positively skewed in the direction of low concentration. The negative kurtosis values of Cd, Sb, Ni, Cu, Cr, Zn and Fe showed that the distribution of these metals in dust from markets was less steep than normal. Hg, As and Pb had greater than zero kurtosis values, indicating that their distribution in dust samples from l markets was steeper than normal (Qing *et al*., 2015).

4.2.1a Arsenic in concentration in market dust

Arsenic (As) concentration ranged from below detection limit to 6.20 mg/kg, with a mean value of 4.20 mg/kg (Table 4.13). Only six sample sites had As concentration and the highest concentration was recorded from Asawase market (6.20 mg/kg) (Table 4.12). The mean concentration of As recorded from markets was lower than the mean value of 41.3 mg/kg reported from the fuel filling station dust in the Kumasi metropolis (Nkansah *et al.*, 2017). Arsenic concentrations obtained from this study were lower than the maximum allowable limit in Canadian commercial soil (12 mg/kg) but higher than the value of the control dust sample which recorded below detection limit. This indicates that As was released from human activities. Combustion of fossil fuels from motor vehicles and atmospheric deposition of arsenic from industrial areas in the metropolis can be attributed to the level of As obtained in dust samples (Soukup *et al.*, 2012).

4.2.1b Cadmium concentration in market dust

The concentration of Cd in all samples ranged from below detection (7.0 mg/kg) to 14.61 mg/kg, with a mean value of 11.05 mg/kg (Table 4.12). The highest Cd concentration

was measured from Dr. Mensah (14.61 mg/kg) out of four sample sites that recorded Cd concentration (Table 4.13). The mean value of Cd recorded from this study exceeded the mean value of 1.33 mg/kg reported in a similar study conducted by Shinggu *et al.*, (2007). The values of Cd recorded in the dust samples of the five markets as shown in Table 4.12 were above the control sample value which recorded below detection and the maximum allowable limit of 0.2 mg/kg in dust (Abdulrahman *et al*., 2013). The measured levels of Cd in these markets can be attributed to automobile activities around the markets. All these markets are located in the vicinity of high traffic density and Cd is thought to be released from different motor vehicles parts such as brake lining wear, lubricating oils and engine exhausts (Elnazer *et al.*, 2015). Other activities such as electronic waste disposal and auto mechanical workshops which were dotted around some markets (Abinkyi, Atonsu and Dr. Mensah) may contribute to Cd pollution in market dust.

4.2.1c Chromium concentration in market dust

Chromium (Cr) concentrations presented in Table 4.12 ranged from below detection (12 mg/kg) to 232.90 mg/kg, with a mean value of 88.46 mg/kg. The mean value of Cr recorded in this study is lower than the mean values of 146 mg/kg, 105 mg/kg and 140 mg/kg reported from a similar study conducted from different food markets in Jeongeup, South Korea (Kim *et al*., 2016). In the current study, it was observed that five sample sites; Dr. Mensah, Mayanka, Atonsu, Ahodwo and Sofoline recorded the highest values of Cr which exceeded the maximum allowable concentration in Canadian commercial soil (87 mg/kg). However, dust from Ayigya market recorded Cr concentration below detection limit and this site was considered to be unpolluted by Cr. The recorded values of Cr in this study were above that of the control sample which gave below detection limit signifying the anthropogenic contamination of Cr in the market dusts. High level of

Cr observed in this study can be attributed to anthropogenic activities in the metropolis such as vehicular activities (Christoforidis and Stamatis,

2009).

4.2.1d Copper concentration in market dust

The concentration of copper (Cu) in all dust samples ranged from below 12 mg/kg (detection limit) to 181.85 mg/kg (Table 4.13). The mean concentration of Cu was 64. 44 mg/kg. This value exceeded the average values of 61 mg/kg, 44 mg/kg but lower than 111 mg/kg which were reported in a similar study conducted from different tradtional markets in Jeongeup, South Korea (Kim *et al*., 2016). Cu concentration in dust sample from Kotei market was below detection limit while Sofoline, Asafo, Mayanka, Dr. Mensah, Ahodwo, Atonsu and Asawase markets gave copper

concentration above the tolerable limit in dust (32 mg/kg) (Abdulrahman *et al*., 2013). Market workers seem to be exposed to unacceptable level of Cu in these markets and this can be unsafe to their health. The Cu concentration recorded in this study may be attributed to the presence of electronic repair shops, motor mechanical activities and vehicular traffics in the vicinity of the markets.

4.2.1e Mercury concentration in market dust

The concentration of Hg in this study was recorded in all dust samples and ranged from 0.01 mg/kg to 1.38 mg/kg (Table 4.13 **).** The mean concentration of Hg was found to be 0.03 mg/kg. This value is 44 times lower than the concentration recorded from Dr. Mensah (1.38 mg/kg) which is the highest concentration of Hg recorded from transport stations. The natural level of Hg in soil normally ranges from 0.001 mg/kg to 0.08 mg/kg and does not exceed 0.1 mg/kg (European Union, 1998). The results from this study as shown in Table 4.12 indicate that, Hg concentration recorded from Asafo, Dr. Mensah

and Central Market exceded the natural level in soil and this revealed that dust samples from these markets were polluted. On the other hand, the average concentration of Hg calculated from markets did not exceed the maximum allowable limit in commercial soil of Canada (24 mg/kg). The source of mercury can be associated with combustion of fossil fuel in automobiles (Ozaki et al., 2004), atmospheric deposition and emissions from industrial zones.

4.2.1f Nickel concentration in market dust

Nickel concentration in dust samples ranged from below detection limit to 44.79 mg/kg, with a mean concetration of 33.45 mg/kg (Table 4.13) which was higher than the world average value in soil (20 mg/kg) (Alloway,1995). The average concentration of nickel recorded in this study was higher than the mean values of 24 mg/kg and 32 mg/kg, and lower than 50 mg/kg and 52 mg/kg reported in a similar study conducted from differrent tradtional markets in Jeongeup, South Korea (Kim *et al*., 2016). The results in shown Table 4.12 indicate that dust from Sofoline recorded the higest concentration of Ni while dust from Bantama, Ayigya and Kotei markets recorded the concentration below detection limit and were considered to be unpolluted with this metal. All the recorded Ni concentrations in the ten markets were below the maximum permissible limit in the Canadian commercial soil (89 mg/kg) but higher than the control sample which was below detection limit. The source of nickel in these areas could be attributed to vehicular activities, and natural crust due to displacement of surface soils (Elnazer *et al.*, 2015).

4.2.1g Lead concentration in market dust

Lead (Pb) concentration in markets ranged from below detection limit to 72.10 mg/kg, with a mean value of 22. 43 mg/kg (Table 4.13). Dust samples from five (5) markets

recorded lead concentration below detection limit as indicated in Table 4.12. The mean concencetration of Pb recorded in this study was lower than the mean values of 49 mg/kg, 63 mk/kg, 68 mg/kg and 241 mg/kg reported by Kim *et al*., (2016) from different markets in Jeongeup, Northen Korea. The concentration of Pb recorded from Krofrom (31.42 mg/kg), Asawase (72.10 mg/kg) and Asafo (26.76 mg/kg) markets exceeded the maximumu allowable limits in dust of 20 mg/kg (Abdulrahman *et al*., 2013). This indicates that market workers and food sold in open spaces of these markets are exposed to Pb- polluted dust which is dangerous to human health. High level of Pb in these markets could be linked to high traffic density, electronic repair shops and auto mechanical activities which were observed in the vicinity of the markets at the time of study.

4.2.1h Zinc concentration in market dust

Low concentration of Zn is essential to human health. In this study, the recorded concetrations of Zn were in the range of 59.29 mg/kg to 293.68 mg/kg, with a mean value of 149.25 mg/kg (Table 4.13). The mean concentration of Zn was lower than the mean values of 372 mg/kg, 697 mg/kg, 544 mg/kg reported from a similar study conducted by Kim *et al*., (2016) from different markets in Jeongeup, Northen Korea. Table 4.12 shows that all the recorded Zn concentrations were above the average value measured from the control dust sample (19.79 mg/kg) and this indicates that dust samples were polluted. Market workers who spend most of their working hours in these markets may be exposed to high levels of zinc in dust which is thought to be released from vehicular activities, waste disposal, electronic rapair shops and industrial sources

(WieszaŁa and WyciŚlik, 2008; Kim et al., 2016).

4.2.1i Iron concentration in market dust

Iron has high natural content in the soil compared to other heavy metals (Tokalioglu *et al*., 2003). The concentration of Fe in the dust samples ranged from 8283.66 mg/kg to 34953.63 mg/kg, with a mean value of 19634.10 mg/kg which is the highest mean value obtained amongst all the heavy metals studied (Table 4.13). The average level of Fe measured from this study was higher than the value of 5330.50 mg/kg reported in a similar study from Mubi, Adamawa State, Nigeria (Shinggu *et al.*, 2007). The concentrations of Fe recorded from all the markets were higher than the average value recorded from the control dust sample (8215.54 mg/kg), which indicates the anthropogenic contribution to elevated level of Fe concentration. Human activities related to metal fabrication and grinding, vehicular activities (corrosion of car parts) and construction works were linked to the release of Fe in the market dusts. Human exposure to excess amount of Fe above 10 mg/kg causes coagulation in the blood vessels, rapid increase in pulse rate and hypertension (Nazir *et al.*, 2015).

4.2.1j Antimony concentration in market dust

Antimony (Sb) is one of the potentially hazardous metals to human health and its distribution in the environment is by anthropogenic activities and natural processess such as windblown dust. The natural content of Sb in the earth crust is about 0.3 mg/kg (Fujiwara *et al.*, 2011). In this study, Sb concentration ranged from below detection limit to 21.72 mg/kg, with an average value 14.02 mg/kg (Table 4.13). This value is about 31 times higher than the mean concentration (0.73 mg/kg) reported by Ozaki *et al*., (2004) from roadside dust in Japan. The highest Sb concentration was recorded from Abinkyi (21.72 mg/kg) followed by Ahodwo market (21.17 mg/kg). However, all the recorded Sb values exceeded the average value recorded from the control dust sample (6.2 mg/kg),

which is an indication that dust in the markets were polluted. On the other hand, Sb concentrations recorded in this study were below the maximum permissible limit in soil of 40 mg/kg. The observed Sb concentrations in this study was linked with automobiles due to presence of high trafic movement around the markets. Sb compounds are used as major additives in motor oils and grease, and as flame retardants in tires during vulcanization process of rubber used in the production of tires. Therefore, Sb can be released via oil spillage and wearing of tires (Ozaki *et al*., 2004; WieszaŁa and WyciŚlik, 2008; Fujiwara *et al.*, 2011).

4.2.2 Pearson's Correlation Analysis for market dust

The relationship between heavy metals concentration in dust samples from markets was conducted by employing Pearson's correlation analysis. Siginificant correlation was considered at p <0.05. Pearson's correlation coefficients were determined and are presented in Table 4.14.

Table 4.14: Pearson's correlation matrix for heavy metals in dust from market

Metals	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb
As	1									
Cd	0.236	1								
Cr	0.483	-0.202	1							
Cu	-0.077	-0.275	0.685*	1					.	
Hg	-0.097	0.587	0.323	0.021	1					
Ni	-0.552	0.006	-0.246	0.144	-0.077	1				
Pb	-0.371	-0.187	-0.149	0.736*	-0.247	0.306	1			
Zn	-0.064	-0.503	-0.174	-0.415	-0.005	0.288	-0.388	1		
Fe	-0.252	0.119	0.185	0.313	-0.054	0.692*	0.213	-0.087	1	
Sb	0.242	0.432	0.224	0.053	-0.018	-0.055	-0.464	-0.395	-0.026	1

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

The correlation analysis indicate a significant correlation between Cu and Cr, Cu and Pb and Ni and Fe. Other metal had no significant correlation. Cu showed a moderate positive correlation with Cr (r = 0.685, p <0.05), signifying that the two metals originated from the same source. Cu and Pb showed a strong positive linear correlation (r = 0.736, p<0,05), indicating a similar anthropogenic source such vehicular activities in the metropolis. Ni showed a moderate and significant positive linear correlation with Fe (r = 0.692, p <0,05), signifying that these metals may have originated from a common anthropogenic source.

4.2.3 Assessment of the heavy metal contamination in dust from markets

4.2.3.1 Geo-accumulation index (Igeo) of market dust

The calculated values of Igeo of heavy metals in dust from markets are presented in Table 4.15. Igeo values with symbol "Nc" indicate that the Igeo was not calculated and the sample sites were considered to be unpolluted by the respective metal since the concentration was recorded below detection limit. The negative Igeo value indicates that the dust samples were unpolluted (Ige < 0) by a given metal.

Table 4.15: Geo-accumulation index (Igeo) of heavy metals in dust from markets

Sample sites	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb
Abinkyi	Nc	9.83	2.24	0.08	-0.02	2.52	Nc	2.89	1.50	1.22
Dr. Mensah	3.26	9.93	4.63	1.86	7.53	2.34	-0.57	3.57	0.66	0.62
Mayanka	Nd	8.71	4.33	1.63	0.96	2.48	-0.67	4.29	1.12	0.09
Atonsu	3.16	9.58	5.06	2.84	-0.13	2.10	-1.03	3.12	0.64	0.85
Ahodwo	3.10	9.27	4.68	3.02	0.75	2.17	Nd	2.40	0.38	1.19
Sofoline	Nc	Nc	3.74	3.27	2.37	2.80	0.48	3.06	1.46	-0.15
Asafo	Nc	Nc	1.55	1.66	4.13	1.98	1.17	3.26	-0.08	0.20
Asawase	3.78	Nc	2.99	1.21	2.27	2.73	2.60	4.71	0.72	0.75
Krofrom	2.94	Nc	3.31	-0.23	1.77	2.08	1.40	4.25	0.87	-0.25

Bantama	2.90	Nc	0.94	-0.80	1.79	Nc	Nc	3.33	0.11	Nc
Ayigya	Nc	Nc	Nc	-1.04	0.79	Nc	Nc	4.14	-0.57	Nc
Kotei	Nc	Nc	1.60	Nc	1.52	Nc	Nc	3.04	0.11	Nc
Central Market	Nc	Nc	1.99	-0.21	5.20	Nc	-0.07	4.38	0.35	Nc
Maximum	3.78	9.93	5.06	3.27	7.53	2.80	2.60	4.71	1.50	1.22
Minimum	2.90	8.71	0.94	-1.04	-0.13	1.98	-1.03	2.40	-0.57	-0.25
Mean	3.19	9.46	3.09	1.11	2.23	2.35	0.42	3.57	0.56	0.50
SD	0.32	0.49	1.41	1.52	2.20	0.30	1.24	0.71	0.60	0.55

The mean Igeo values of the heavy metals decreased in the following sequence; Cd > Zn > As > Cr > Ni > Hg > Cu > Fe > Sb > Pb. The mean Igeo value of Pb, Fe, and Sb fall within the range of $0 \leq Igeo < 1$ and this indicates that dust from most of the markets was "unpolluted" to "moderately polluted". The mean Igeo of Cu indicates that dust samples were moderately polluted ($1 \leq Igeo < 2$). However, the results showed that dust samples from Dr. Mensah and Central Market were very strongly polluted by Cu ($Igeo \geq 5$). The average Igeo values of Hg and Ni which fell within class d

($2 \leq Igeo < 3$), signify that dust samples were "moderately" to "strongly polluted" by these metals. On the other hand, the average Igeo of As, Zn and Cr showed that some sample sites were strongly polluted by the metals ($3 \leq Igeo < 4$). The Igeo values of Cr in dust samples from Dr. Mensah, Mayanka and Ahodwo indicated that these markets were very strongly polluted ($4 \leq Igeo < 5$). The Igeo values of Cd which ranged between 8.71 to 9.93, indicate that dust samples from sample sites were very strongly polluted by this metal ($Igeo \geq 5$). This study recorded the highest average Igeo values of Cr, Cu and Zn and lowest values of As, Ni and Pb compared to Igeo means reported by Wang *et al.*, (2013). However, Lu *et al.*, (2010) reported the mean Igeo values of Cu and Pb in street dust of Boaji, NW China higher than what was calculated in this study. Generally, the observed heavy metal pollution via Igeo calculation may be as a result of anthropogenic activities in the metropolis.

4.2.3.2 Enrichment factor (EF) of market dust

The calculated enrichment factors of heavy metals in dust are presented in Table 4.16. The symbol "Nc" indicates that the EF was not calculated since the concentration was below detection limit and the respective metal was considered to be enriched at very low concentration below the detection limit.

Table 4.16: Enrichment factors (EF) of heavy metals in dust from markets

Sample sites	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb
Abinkyi	Nc	321.77	1.67	0.37	0.35	2.03	Nc	2.62	1.00	0.82
Dr. Mensah	6.06	617.84	15.67	2.30	116.88	3.20	0.43	7.52	1.00	0.97
Mayanka	Nc	192.85	9.27	1.43	0.90	2.57	0.29	9.05	1.00	0.49
Atonsu	5.70	488.22	21.27	4.57	0.59	2.74	0.31	5.55	1.00	1.15
Ahodwo	6.58	473.28	19.74	6.25	1.29	3.45	Nc	4.06	1.00	1.75
Sofoline	Nc	Nc	4.88	3.51	1.88	2.54	0.51	3.04	1.00	0.33
Asafo	Nc	Nc	3.11	3.34	18.58	4.19	2.39	10.14	1.00	1.21
Asawase	8.34	Nc	4.82	1.40	2.93	4.00	3.68	15.82	1.00	1.01
Krofrom	4.19	Nc	5.41	0.46	1.86	2.30	1.45	10.41	1.00	0.46
Bantama	6.94	Nc	1.78	0.53	3.21	Nc	Nc	9.34	1.00	Nc
Ayigya	Nc	Nc	Nc	0.72	2.57	Nc	Nc	26.29	1.00	Nc
Kotei	Nc	Nc	2.81	Nc	2.67	Nc	Nc	7.63	1.00	Nc
Central Market	Nc	Nc	3.13	0.68	28.97	Nc	0.75	16.36	1.00	Nc
Maximum	8.34	617.84	21.27	6.25	116.88	4.19	3.68	26.29	1.00	1.75
Minimum	4.19	192.85	1.67	0.37	0.35	2.03	0.29	2.62	1.00	0.33
Mean	6.30	418.79	7.80	2.13	14.05	3.00	1.23	9.83	1.00	0.91
SD	1.38	164.22	7.09	1.90	32.04	0.76	1.22	6.53	0.00	0.45

The value of EF > 1 shows that the metal was enriched in the dust samples and may be originating from anthropogenic activities while EF < 1 indicates that the heavy metal in the dust sample originated from the natural source such as the earth crust and was less enriched. The results showed that the EF of Cd ranged from 617.84 to 192.85, with a mean value of 418.27 which indicates that Cd was extremely enriched (EF > 40) in dust and originated from anthropogenic sources such as motor vehicles and electronic wastes. The mean EF of Pb (1.23) and Sb (0.91) were less than 2 and this indicates minimum

enrichment of these metals except Asawase and Asafo dust samples which were moderately enriched by Pb, $2< EF \leq 5$. The mean EF of Ni was within the range of 2-5 which indicates moderate enrichment of Ni in the dust. Mercury showed very high enrichment in dust samples from Asafo and Central Market ($20 < EF \leq 40$), and extreme enrichment in dust from Dr. Mensah (EF>40). The mean EF values of other metals such as Cr (7.80), As (6.30) and Zn (9.83) signify very high enrichment of these metals in the dust samples and this may be attributed to anthropogenic activities. The general trend of the mean EF of heavy metals follows the decreasing order; Cd > Hg > Zn > Cr > As > Ni > Pb > Fe > Sb. Cd, Cr, Pb, Zn and Ni were highly enriched in market dust compared to their enrichment in urban street dust of Chengdu, China (Li *et al.*, 2017). Ni and Zn were less enriched in the market dust of this study relative to street dust of Boaji, NW China (Lu *et al.*, 2010).

4.2.3.3 Contamination factor (CF) of market dust

The calculated values of CF of heavy metals in dust from markets are presented in Table 4.17. The symbol "Nc" indicates that the CF was not calculated since the metal concentration was below detection limit and the sample sites were considered to be uncontaminated by the respective metals.

Table 4.17: Contamination factors (CF) of heavy metals in dust from markets

Sample sites	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Fe	Sb
Abinkyi	Nc	1369.00	7.10	1.58	1.48	8.63	Nc	11.13	4.25	3.50
Dr. Mensah	14.33	1461.00	37.05	5.45	276.38	7.57	1.01	17.77	2.36	2.30
Mayanka	Nc	627.00	30.12	4.64	2.92	8.36	0.94	29.41	3.25	1.60
Atonsu	13.37	1145.00	49.87	10.72	1.38	6.42	0.74	13.01	2.35	2.70
Ahodwo	12.83	923.00	38.50	12.18	2.53	6.73	Nc	7.92	1.95	3.41
Sofoline	Nc	Nc	20.06	14.43	7.73	10.46	2.09	12.50	4.11	1.35
Asafo	Nc	Nc	4.40	4.73	26.32	5.93	3.38	14.36	1.42	1.72
Asawase	20.67	Nc	11.95	3.48	7.26	9.92	9.12	39.21	2.48	2.51

Krofrom	11.50	Nc	14.85	1.28	5.12	6.32	3.97	28.60	2.75	1.26
Bantama	11.23	Nc	2.88	0.86	5.19	Nc	Nc	15.11	1.62	Nc
Ayigya	Nc	Nc	Nc	0.73	2.60	Nc	Nc	26.51	1.01	Nc
Kotei	Nc	Nc	4.54	Nc	4.31	Nc	Nc	12.32	1.62	Nc
Central Market	Nc	Nc	5.97	1.29	55.21	Nc	1.43	31.19	1.91	Nc
Maximum	20.67	1461.00	49.87	14.43	276.38	10.46	9.12	39.21	4.25	3.50
Minimum	11.23	627.00	2.88	0.73	1.38	5.93	0.74	7.92	1.01	1.26
Mean	13.99	1105.00	18.94	5.11	30.65	7.82	2.84	19.93	2.39	2.26
SD	3.47	338.98	16.08	4.77	75.35	1.63	2.80	9.78	0.99	0.84

The CF values of As, Cd, Ni, and Zn showed that dust samples from markets were very highly contaminated by these metals (CF > 6), except Asafo which showed considerable contamination by Ni ($3 \leq CF \leq 6$). The CF values of Cu which ranged from 0.73 to 14.43 indicate low to very high contamination of the sample sites.

Mercury showed very high contamination in dust samples from Dr. Mensah, Sofoline, Asafo, Asawase and Central Market while other sample sites showed moderate to considerable contamination by this metal. The average CF values of Pb (2.80), Fe (2.39) and Sb (2.26) signify that most of the sample sites were moderately contantaminated by these metals ($2 \leq CF < 3$) except Asawase which had very high contamination. The average CFs of Pb, Zn, Cu, Cr, Fe and Ni calculated in this study were higher than the CF values reported by Afrifa *et al.,* (2013) from fuel filling station dust in Accra, Ghana. The overall metal contamination in dust samples from markets ranged from low to very high contamination.

4.2.3.4 Pollution load index (PLI) and modified degree of contamination (mCd) of market dust

The results of pollution load index and modified degree of contamination of heavy metals in various markets are shown in Table 4.18.

Table 4.18: Pollution load index (PLI) and modified degree of contamination (mCd) of heavy metals in dust from markets

Study site	PLI	mCd
Abinkyi	5.64	140.67
Dr. Mensah	15.62	182.52
Mayanka	7.06	70.82
Atonsu	9.21	124.55
Ahodwo	9.33	100.91
Sofoline	4.50	7.27
Asafo	3.62	6.23
Asawase	6.52	10.66
Krofrom	4.41	7.56
Bantama	2.26	3.69
Ayigya	1.48	3.08
Kotei	1.82	2.28
Central Market	2.86	9.70
Maximum	15.62	182.52
Minimum	1.48	2.28
Mean	5.72	51.53
SD	3.94	64.34

All the thirteen (13) tradtional markets recorded PLI > 1, indicating the progressive deterioration of site quality by heavy metals**.** The PLI values indicate that Abinkyi, Dr. Mensah, Mayanka, Atonsu, and Ahodwo had high polution load of heavy metals compared to other sample sites while Ayigya market had the least pollution load. The mCd which ranged from 2.28 to 182.52 with a mean value of 51.53, indicates ultrahigh degree of contamination (mCd≥32) of sample sites by heavy metals. This most observed contaminated sites were Dr. Mensah, Abinkyi, Mayanka, Atonsu and Ahodwo markets. The mCd values of heavy metals for Bantama, Ayigya and Kotei markets indicate that these markets were moderately contaminated. On the other hand, sample sites with mCd ranging between 8 and 16 were considered to have very high degree of contamination. This study observed high pollution load of heavy metals in market dust compared to the

PLI reported by Afrifa *et al.*, (2013). The overall results indicate that the studied markets were highly polluted when compared to the control site (KNUST Botanic Gardens).

4.2.4 Human health risk assessment of heavy metals in market dust

The human health risk assessment from exposure to heavy metals in dust from markets was conducted using both noncarcinogenic risk and carcinogenic risk indices.

4.2.4.1 Non-carcinogenic health risk of heavy metals in market dust

Non-carcinogenic risks for both children and adults were assessed using Hazard index which was obtained by summing the Hazard quotients of the three exposure routes for each metal. The results are presented in Table 4.19.

Table 4.19: Hazard quotients (HQ) and hazard index (HI) for non-carcinogenic risk of heavy metals in dust from markets

Metal	Children				Adults			
	HQing	**HQinh**	**HQderm**	**HI**	**HQing**	**HQinh**	**HQderm**	**HI**
As	0.1675	4.82E-06	3.43E-02	0.20	1.87E-02	2.84E-06	5.46E-03	0.02
Cd	0.2915	7.36E-05	8.16E-03	0.30	3.26E-02	4.33E-05	1.30E-03	0.03
Cr	0.2667	7.68E-04	1.49E-01	0.42	2.98E-02	4.51E-04	2.38E-02	0.05
Cu	0.0163	4.68E-07	1.53E-04	0.02	1.83E-03	2.75E-07	2.43E-05	0.00
Hg	0.0013	1.28E-07	5.11E-05	0.00	1.43E-04	7.55E-08	8.14E-06	0.00
Ni	0.0207	5.79E-04	2.15E-04	0.02	2.31E-03	3.40E-04	3.42E-05	0.00
Pb	0.1273	1.46E-06	1.41E-04	0.13	1.42E-02	8.57E-07	2.26E-05	0.01
Zn	0.0048	1.39E-07	6.75E-05	0.00	5.39E-04	8.17E-08	2.15E-06	0.00
Fe	0.3519	1.01E-05	9.85E-04	0.35	3.93E-02	5.96E-06	1.57E-04	0.04
Sb	Nc	Nc	Nc	Nc	Nc	Nc	Nc	Nc
HI	1.88	0.003	0. 423	1.44	0.211	0.0016	0.067	0.14

The results of non-carcinogenic risk showed that HI for each metal via the three exposure routes was less than 1 (safe limit), indicating that there is no potential noncarcinogenic health risk for both children and adults associated with exposure of heavy metals in dust from markets in the Kumasi metropolis. However, the overall HI (1.44) of all the metals via the three exposure pathways for children indicated the likelihood of non-carcinogenic health risk which may occur if all the metals accumulate in their body. The Hazard index of heavy metals in children decreased in the order: Cr > Fe > Cd > As > Pb > Cu, Ni > Hg, Zn. From the results, ingestion was observed for both children and adults as the most important exposure pathway of the heavy metals in dust followed by dermal contact and inhalation. Also, this study indicated that the cumulative effect of all the heavy metals via oral intake of dust particles is a major concern of non-carcinogenic risks (HI=1.88, 81.51%) for children compared to adults (HI = 0.211, 75.46%). This can be linked to the behavior of children like playing with ground surface soil dust and hand to mouth activities such as finger sucking and eating non-food objects which may result into ingestion of significant amount of contaminated dust particles (Latif *et al.*, 2014; Praveena., *et al* 2015). Inhalation of dust particles was considered as insignificant route of exposure to heavy metals in dust for both children and adults which was also revealed by Zheng *et al.*, (2010).

4.2.4.2 Carcinogenic health risk of heavy metals in market dust

The results of carcinogenic health risk (CRI) of heavy metals (As, Cd, Ni and Pb) are presented in Table 4.20.

Table 4.20: Average daily dose for carcinogenic risk (ADDc) and carcinogenic risks (CRI) of heavy metals in dust from markets

Metals	CHILDREN		ADULTS	
	ADDc		ADDc	

	Ingestion	Inhalation	Dermal	CRI	Ingestion	Inhalation	Dermal	CRI
As	4.31E-06	1.29E-10	3.62E-07	7.79E-06	1.60E-06	2.33E-10	1.92E-07	3.11E-06
Cd	1.25E-05	3.77E-10	3.51E-08	1.89E-04	4.67E-06	6.79E-10	1.86E-08	7.04E-05
Ni	3.66E-05	1.10E-09	1.02E-07	3.34E-05	1.36E-05	1.98E-09	5.44E-08	1.25E-05
Pb	1.53E-05	4.59E-10	4.28E-08	6.43E-07	5.69E-06	8.27E-10	2.27E-08	2.40E-07

According to the results of this study, the carcinogenic risk ranged from 6.43E-07 to 1.89E-04 for children and 2.4E-07 to 7.04E-05 for adults. The acceptable range for carcinogenic risk is set between 1×10^{-6} and 1×10^{-4} according to the guidelines of Environmental Protection Agency of United States (U.S. EPA, 1989). The CRI values of As, Cd, and Ni for adults were within the acceptable level of carcinogenic risks except Pb which was below the threshold level (1×10^{-6}) for both adults and children, indicating no carcinogenic risk. On the other hand, CRI values of As and Ni for children were within the acceptable range of carcinogenic risk which indicates no carcinogenic risk that can be attributed to these metals. The CRI of Cd (1.89E-04) for children was above the maximum acceptable carcinogenic risk (1×10^{-4}). This showed that children are at risk of getting cancer associated with exposure to Cd-contaminated dust from markets in the Kumasi metropolis. Chronic exposure to low level of cadmium can cause lung cancer (IARC, 1990). The results of carcinogenic health risk assessment indicated ingestion as the main exposure pathway to metal carcinogens followed by dermal absorption and inhalation for both children and adults. This agrees with the study conducted by Nkansah *et al.*, (2017).

4.3 Comparison of the heavy metals concentration in dust samples from transport stations and markets in the Kumasi metropolis

The comparison of concentrations of heavy metals in the dust samples from transport stations and markets was conducted using Independent Samples t-test at 95% Confidence Interval using IBM –SPSS statistics. The results are indicated in Table 4.21.

Table 4.21: Statistical comparison of mean concentrations of heavy metals in dust from transport stations and markets in the Kumasi metropolis

Element	Mean Concentration ± SD (mg/kg) in Transport Stations	Mean concentration± SD (mg/kg) in Markets	P-value (2-tailed) at α =0.05
As	6.10 ± 2.33	4.20 ± 1.04	0.133
Cd	19.99 ± 12.27	11.05 ± 3.39	0.142
Cr	130.39 ± 54.75	88. 46 ± 75.09	0.138
Cu	54.34 ± 44.29	64.44 ± 60.13	0.619
Hg	0.07 ± 0.15	0.15 ± 0.33	0.372
Ni	29.98 ± 9.22	33. 45 ± 7.00	0.230
Pb	21.8 ± 15.99	22.43 ± 22.14	0.945
Zn	120.04 ± 66.83	149.25 ± 73.27	0.213
Fe	16517.60 ± 9266.06	19634.10 ± 8149.78	0.340
Sb	14.50 ± 6.25	14.02 ± 5.23	0.827

The Independent Samples t-test analysis results showed no statistical significant difference between the mean concentrations of heavy metals in the dust samples from transport stations and markets in the Kumasi metropolis ($p > 0.05$). This indicates that dust from the markets and transport stations had almost similar contamination or pollution status. Probably human activities such as traffic volume, metal works and construction works may be the contributing factors of heavy metal pollution. However,

automobile activities seem to be the dominant factor of heavy metal pollution in transport stations and markets with respect to a study conducted by Shinggu *et al.*, (2007).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study has offered the baseline data on the concentrations, pollution status and human health risks associated with heavy metals (As, Cd, Cr, Hg, Cu, Ni, Pb, Zn, Fe and Sb) in dust from transport stations and markets in the Kumasi metropolis, Ghana. According to the results of this study, Fe, Hg and Zn were detected in all dust samples from transport stations and markets compared to other metals. Fe recorded the highest mean values while Hg recorded the lowest mean values among the heavy metals studied. The average concentrations of heavy metals in dust from transport stations followed the decreasing order: Fe > Cr > Zn > Cu > Ni > Pb > Cd > Cd > Sb > As > Hg and in markets the sequence was as follows: Fe > Zn > Cr > Cu > Ni > Pb > Sb > Cd > As > Hg. All the recorded concentrations of heavy metals were above the level recorded from the control dust sample, signifying anthropogenic contamination of sample sites by heavy metals. However, all the heavy metals recorded the mean concentrations below the maximum allowable limits in Canadian commercial soil according to CCME guidelines except Cr which recorded the highest values than the allowable limit for both transport stations and markets.

Independent Samples T-test analysis at 95% Confidence limit indicated no significant difference between the mean concentrations of the heavy metals in dust from transport stations and markets ($P > 0.05$). This signifies that these two study areas had almost similar contamination levels which could be attributed to anthropogenic activities such as motor vehicles and metal works. Strong and moderate significant correlations which were observed between some of the heavy metals in both transport stations and markets indicate the common anthropogenic sources of these metals. The pollution levels of heavy metals

in dust samples from both transport stations and markets were determined by pollution indices such as geo-accumulation, contamination factor, enrichment factor, modified degree of contamination and pollution load index. The average Igeo values indicated that dust samples from transport stations and markets were in the range of unpolluted to very strongly pollute by heavy metals. Both study areas were strongly polluted by Cd, Zn, As and Cr, and unpolluted to moderately polluted by Fe, Sb and Pb, which was also revealed by contamination factors. The mean values of EFs of metals in transport stations and markets were > 1, except Sb in markets which had EF <1. The findings of PLI revealed the deterioration of site quality by heavy metals since in both transport stations and markets PLI values were greater than a unit. The calculation of mCd indicated moderate to ultra-high degree of contamination of dust samples from transport stations and markets.

Human health risk associated with exposure to heavy metals concentration in dust from both transport stations and markets was assessed via three exposure routes (ingestion, dermal contact and inhalation. The results of HI values for metals across the three exposure pathways were < 1, signifying no non-carcinogenic risk for both children and adults. However the cumulative effect of multiple metals (total HI >1) via the three exposure routes for children was a major concern of non carcinogenic risk in both transport stations and tradtional markets. Ingestion route for children had HI >1 for both transport stations and markets which indicates that there is a likelihood for children to develop non-carcinogenic effects associated multiple metals.

Results of carcinogenic risks from both transport stations and markets indicated that, the CRI values of Ni and As were within the acceptable range, and Pb was below the threshold limit of 1×10^{-6} for both adults and children, indicating no likelihood of carcinogenic risk. Cadmium had the CRI values within the acceptable range for adults while for children its CRI values were above the maximum acceptable level of 1×10^{-4},

indicating children to be at risk of getting cancer associated with exposure to Cdcontaminated dust in both transport stations and markets in the Kumasi metropolis. For this reason, the pollution of Cd should not be overlooked. The exposure routes to carcinogenic metals for both children and adults followed the order; ingestion > dermal contact > inhalation. Generally, the results from this study revealed that dust in both the markets and transport stations were polluted by heavy metals and regular monitoring is required.

5.2 RECOMMENDATION

- This study observed that most of the sample sites were polluted by heavy metals and therefore appropriate strategies need to be taken by environmental regulatory bodies in the Kumasi metropolis to manage heavy metal pollution in transport stations and markets.
- There is the need for further studies to be conducted to determine the bioaccessibility of heavy metals in transport stations and market dust.
- Further research needs to be conducted on the speciation of heavy metals in dust and their potential heath risks.
- Seasonal monitoring of heavy metals in dust before the rainy season, after the rainy season and during the dry season needs to be studied in the future in order to have a clear picture of the effect of seasonal variation on heavy metal pollution in the metropolis.

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APPENDIX

A-1: Table showing Average daily doses (ADD-mg/kg-day) of heavy metals for Children and Adults in transport stations

Metals	CHILDREN			ADULTS		
	ADDing	ADDinh	ADDderm	ADDing	ADDinh	ADDderm
As	6.840E-05	1.969E-09	5.746E-06	2.293E-07	3.474E-10	9.149E-07
Cd	1.543E-04	4.443E-09	4.321E-07	5.173E-07	7.838E-10	6.880E-08
Cr	1.676E-03	4.825E-08	4.693E-06	5.618E-06	8.512E-09	7.472E-07
Cu	3.732E-04	1.074E-08	1.045E-06	1.251E-06	1.895E-09	1.664E-07
Hg	2.557E-07	7.361E-12	7.160E-10	8.571E-10	1.299E-12	1.140E-10
Ni	3.799E-04	1.094E-08	1.064E-06	1.273E-06	1.929E-09	1.693E-07
Pb	2.358E-04	6.787E-09	6.601E-07	7.903E-07	1.197E-09	1.051E-07
Zn	1.643E-03	4.731E-08	4.602E-06	5.509E-06	8.347E-09	7.327E-07
Fe	1.685E-01	4.851E-06	4.719E-04	5.649E-04	8.559E-07	7.513E-05
Sb	1.739E-04	5.008E-09	4.870E-07	5.831E-07	8.834E-10	7.755E-08

A-2: Table showing Average daily doses (ADD-mg/kg-day) of heavy metals for Children and Adults in markets

	CHILDREN			ADULTS		
Metals	**ADDing**	**ADDinh**	**ADDderm**	**ADDing**	**ADDinh**	**ADDderm**
As	5.025E-05	1.446E-09	4.221E-06	5.614E-06	8.506E-10	6.720E-07
Cd	1.458E-04	4.196E-09	4.081E-07	1.629E-05	2.468E-09	6.498E-08
Cr	8.000E-04	2.303E-08	2.240E-06	8.939E-05	1.354E-08	3.566E-07
Cu	6.537E-04	1.882E-08	1.830E-06	7.304E-05	1.107E-08	2.914E-07
Hg	3.836E-07	1.104E-11	1.074E-09	4.286E-08	6.494E-12	1.710E-10
Ni	4.142E-04	1.193E-08	1.160E-06	4.629E-05	7.013E-09	1.847E-07
Pb	1.782E-04	5.131E-09	4.990E-07	1.991E-05	3.017E-09	7.946E-08
Zn	1.447E-03	4.166E-08	4.052E-06	1.617E-04	2.450E-08	6.452E-07
Fe	2.463E-01	7.092E-06	6.898E-04	2.752E-02	4.170E-06	1.098E-04
Sb	1.822E-04	5.245E-09	5.101E-07	2.036E-05	3.084E-09	8.123E-08

A-3: Table showing GPS Reading for Dust Sampling (Coordinates)

Sample location	CODE	Latitude	Longitude
Tech Junction 1	TC 1	6.687010	-1.574345
Tech Junction 2	TC 2	6.687103	-1.575917
Ayigya 1	AGY 1	6.690005	-1.578552
Ayigya 2	AGY 2	6.690012	-1.572892
Ayigya 3	AGY 3	6.689940	-1.572875
Ayigya 4	AGY 4	6.689415	-1.572658
Asawase 1	AWS1	6.699242	-1.608435
Asawase 2	AWS 2	6.699028	-1.608773
Asawase 3	AWS 3	6.699492	-1.608767
Dr. Mensah 1	DM 1	6.700148	-1.618645
Dr. Mensah 2	DM 2	6.699803	-1.619280
Dr. Mensah 3	DM 3	6.699266	-1.619118
Dr. Mensah 4	DM 4	6.699945	-1.619760
Krofrom 1	KFM 1	6.712523	-1.612848
Krofrom 2	KFM 2	6.712140	-1.612913
Krofrom 3	KFM 3	6.713405	-1.612822
Krofrom 4	KFM 4	6.713967	-1.612758
Bantama 1	BM 1	6.703782	-1.635765
Bantama 2	BM 2	6.703287	-1.635425
Bantama 3	BM 3	6.702808	-1.634947
Metro Mass transport 1	MMT 1	6.707047	-1.639643
Metro Mass transport 2	MMT 1	6.707543	-1.639503
Sofoline 1	SL 1	6.698900	-1.650867
Sofoline 2	SL 2	6.699490	-1.650680

Sofoline 3	SL 3	6.699789	-1.650473
Adum 1	ADM 1	6.686855	-1.622865
Adum 1	ADM 2	6.687822	-1.622848
Adum 3	ADM 3	6.694728	-1.621192
Abinchi 1	AB 1	6.680485	-1.615047
Abinchi 2	AB 2	6.679980	-1.615175
Abinchi 3	AB 3	6.680515	-1.614835
Asafo 1	AF 1	6.686100	-1.614710
Asafo 2	AF 2	6.686540	-1.614570
Asafo 3	AF 3	6.686847	-1.614730
Asafo 4	AF 4	6.687366	-1.614945
Asafo 5	AF 5	6.686947	-1.615490
Asafo 6	AF 6	6.686582	-1.615175
Ahodwo 1	AD 1	6.656971	-1.619000
Ahodwo 2	AD 2	6.656813	-1.619320
Ahodwo 3	AD 3	6.657135	-1.604718
Mayanka 1	MK 1	6.661127	-1.604718
Mayanka 2	MK 2	6.661540	-1.604535
Atonsu 1	AS 1	6.658822	-1.593872
Atonsu 2	AS 2	6.658522	-1.594255
High School J	HSJ	6.661366	-1.575705
Kotei Station	KS	6.675983	-1.558977
Kotei Market	KM	6.663215	-1.558930
Central Market S	CMS	6.696070	-1.620722
Central Market I	CM1	6.697351	-1.620995
Roman Hill	RH	6.696075	-1.618385
Botanic Garden 1	BG 1	6.684625	-1.563443
Botanic Garden 2	BG2	6.684191	-1.565957
Botanic Garden 3	BG 3	6.683670	-1.564313