KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY

COLLEGE OF SCIENCE

DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY

MULTIVARIATE AND METAL POLLUTION STU1.1DIES IN SURFACE SOIL FROM ASAFO IN KUMASI, GHANA

BY

JOYCE AGYEMANG

A THESIS SUBMITTED TO THE DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN ENVIRONMENTAL SCIENCE

JULY, 2019

MULTIVARIATE AND METAL POLLUTION STUDIES IN SURFACE SOIL FROM ASAFO IN KUMASI, GHANA

BY

JOYCE AGYEMANG

A THESIS SUBMITTED TO THE DEPARTMENT OF THEORETICAL AND APPLIED BIOLOGY KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY, KUMASI IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN ENVIRONMENTAL SCIENCE

JULY, 2019

DECLARATION

I hereby declare that this submission is my own work towards the masters of science in Environmental Science and that, to the best of my knowledge; it contains no material(s) previously published by another person(s) which have been accepted for the award of any other degree of the university, except where acknowledgement has been made in the text

Joyce Agyemang (PG 7198016) …… ……

(Student Name & ID) **Signature** **Date**

Certified By:

Dr. Osei Akoto …… ……

(Supervisor) **Signature** **Date**

Certified By:

Prof. G.M. Addo …… ……

(Head of Department) **Signature** **Date**

DEDICATION

A special dedication to my Husband Lawyer Augustine Gyamfi and my lovely kids Nana Adwoa Acheampomaa Gyamfi and Obaapa Akua Owusuaa Gyamfi and all my family members without their prayers and guidance, the accomplishment of this thesis would have not been possible and also for all the artisans at Asafo and its environs in Ashanti Region.

ACKNOWLEDGEMENTS

The author is greatly indebted to many people and organization for their marveious assistance as this thesis went through the various stages of production. First of all, I am most grateful to my supervisor Dr. Osei Akoto, Department of Chemistry, KNUST, for his invaluable advice, intellectual and constructive criticism. This research would have not been successful without his dedication, unreserved guidance, inspiration and encouragement.

The author is also greatly indebted to Mr. Eric Gyimah and Collins Nimako for giving me constructive suggestions and guidance as this research went through all the various stage of production. I am also indebted to all the staff of Department of Civil Engineering KNUST and the Environmental Service Department Laboratory of AngloGold Ashanti Limited who assisted during the laboratory examination. Not everyone who has directly or indirectly contributed to the success of this special study can be listed, but my gratitude and deep affection to my family and some friends for their inspiration, constant moral support, encouragement, and love throughout my life.

Finally, I want to thank the Almighty God for his divine favour and protection.

ABSTRACT

Heavy metals pollution and the resultant accumulation to toxic levels in soil may threaten human health through possible routes of exposures. Twenty composite soil samples were taking from different locations within two different zones at the Asafo automobile shops. The soil samples were analyzed for the presence and levels of heavy metals including Fe, Cu, Cr, Zn, Pb and Cd using Atomic Absorption Spectrophotometry. Physicochemical properties such as, pH, electrical conductivity, total organic matter and carbon contents were determined using standard methods to identify the pollution status of the soil. Pearson's correlation principal component analysis and cluster analysis were used to determine the relationship between the heavy metals and their possible sources. Pollution indexes such as enrichment factor (EF), geoaccumulation index (Igeo) and pollution index (PI) estimations were used to assess the extent of heavy metal pollution of the top soil from the study area. Recorded mean values of the physicochemical parameters of soil samples from the two zones were slightly above their respective parameters of the control soil sample. The extent of heavy metal pollution of soil in Asafo was in the decreasing order of Fe > Pb > Cu > Cr > Zn > Cd for zone 1 whereas the order of metal concentrations of soil in zone 2 was Fe > Pb > Zn > Cd > Cu > Cr. The mean EF values calculated for Cd and Pb in the soil samples from Zone 1, using Fe concentrations in the background value were greater than one (1). Also, an extreme contamination ((I_{geo} <5) of Cr and Zn in most soil samples from zone 2 was observed. The present study therefore concluded that the artisanal activities at the Asafo automobile shops could contaminate the soil and eventually pose threat to humans. The study indicated that the main pollution source within the area of study could be related to the anthropogenic activities, mainly metal fabrication and auto works.

TABLE OF CONTENTS

LIFT OF TABLES

LIST OF FIGURES

CHAPTER ONE

INTRODUCTION

1.1 Background

Soil pollution by heavy metals and metalloids has become an important issue of global concern. This concern is as a result of their nonbiodegradable nature and therefore persist in the environment and their potential toxicity to living organisms (Akoto *et al*., 2016). Soil could be contaminated with heavy metals from various sources and the metals in the soil exhibit different behaviour (Soltan *et al*., 2012). The extent of heavy metal contamination of surface soil in relation to the type of element as well as its concentration is influenced by the anthropogenic activities within the vicinity.

Heavy metals naturally exist in the soil in varying concentrations due to weathering as well as other natural processes (Opaluwa *et al*., 2012). The soil serves as a sink for most contaminants and may contain an elevated amount of heavy metals depending on the human activities and the surrounding geological environment (Dube *et al*., 2001). Heavy metals contamination through the activities of auto mechanic shops have been topical in recent years owing to the fact that these artisanal activities within the cities and towns are not well monitored, hence contribute to heavy metal pollution in soil and other components of the environment (Briki *et al*., 2015).

Heavy metals are non-biodegradable hence become integral component of the soil and may bioaccumulate in the soil matrices upon release (Abdel-Baki *et al*., 2011). The physical and chemical properties (pH, electrical conductivity, cation exchange capacity, organic matter content) of the soil are important factors that influences the mobilization

of heavy metals in the soil. This effect of mobilization and other possible biogeochemical process of the metals in the soil result in their transport and subsequently threaten human health by contamination of water and food. The toxicity and the subsequent human health risks of metal contaminants depends greatly on the metal's concentration (Lin *et al*., 2016). Although Cr, Zn, Fe and other essential metals are required in a regulatory amounts for the necessary biochemical functions, excess amounts could be detrimental to human health (Akoto *et al*., 2008). Heavy metals like Cd and Pb have no known beneficial effects in human biological systems and are toxic even at low concentrations hence their accumulation over time become increasingly dangerous to human health (Nkansah and Ansah, 2014).

1.2 Problem statement

The establishment of auto mechanic villages and roadside mechanic workshops are still found scattered haphazardly in larger cities. Artisanal activities at these establishments generate large volume of untreated wastes which are discharged indiscriminately and subsequently pollute the soil with heavy metal (Abii, 2012). Asafo is one of the hubs of auto mechanic shops settings in the Kumasi Metropolis. Their activities include car engine servicing, car body spraying, engine oil replacement and car body works. These activities contribute largely to heavy metals pollution in the environment especially in top soil. Spent engine oil and scrapped car parts contain heavy metals which could accumulate in the soil at Asafo where these activities are rampant. Heavy metals are considered to be harmful owing to their persistent and toxic nature (Sadick *et al*., 2015). Despite the potential sources of heavy metals from the mechanic shops in Asafo, the heavy metal pollution profile at the mechanic shops within the Asafo community are not well studied. The present study therefore seeks to determine the extent of heavy metal

pollution in topsoil from Asafo Township. The outcome of the study could help in regular monitoring of the artisanal activities that take place at Asafo.

1.3 General objectives

To determine the extent of heavy metal pollution in surface soil around automobile workshops within the Asafo Township and predict the possible sources of these metals.

1.4 Specific objectives

- To measure the concentration of heavy metals (Fe, Cu, Cr, Zn, Pb and Cd) in surface soil around automobile workshops within the Asafo Township.
- To measure the physicochemical properties (organic matter content, pH, electrical conductivity and organic carbon) of the top soil.
- To estimate the extent of heavy metals pollution of the soil using pollution indices.
- To identify heavy metal sources of pollution in the soil using Principal Component Analysis and Cluster Analysis.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals

There have been several considerations in defining what a heavy metals is. In relation to specific gravity, a heavy metal is any element which has a high relative density, thus at least five times that of water (Nagajyoti *et al*., 2010). Also, the consideration of heavy metals in terms of toxicity is well known. A heavy metal is considered as a metallic element or metalloid that is able to induce toxicity at low level of exposure. Complete avoidance of human exposure to the heavy metals is not possible (Singh et al. 2007). This notion has resulted in heavy metal exposure of entire life history of human resulting in several possible adverse health effects.

2.2 Heavy Metals in the Environment

Heavy metals are known to be intrinsic components of the lithosphere as a result of natural processes such as weathering and volcanic eruption (Ozuni *et al*., 2010). However, human economic activities have resulted in elevated levels of these contaminants in the environment. Artisanal activities such as industrial manufacturing, smelting of metalliferous ore, electroplating, etc. produce wastes that contain heavy metals (Akoto *et al*., 2016). Also, paints, batteries and vehicular parts which are generated as waste in mechanic shops are potential sources of heavy metals in the environment (Odoi et al., 2011). Assessment of spatial variability of heavy metals in soils under the influence of industrial soap and detergent waste water discharge. IJRRAS. 9 (2): 322-329.). Heavy metals occur in distinctive background concentrations in the environment. However, anthropogenic releases can result in higher concentrations

of these metals relative to their normal background values. Heavy metal pollution refers to instances where the measures of these elements in an environmental matrices exceed the maximum allowable concentrations which could result in detrimental effects to biological life within such vicinity (Adelekan and Abegunde, 2011).

2.3 Environmental fate of Heavy Metals

Human exposure to heavy metal pollution results from anthropogenic activities such as mining, agricultural use of metals based pesticides and metal-containing compounds, domestic sewage and atmospheric deposition (Saha and Zaman, 2013). The potential health effects of heavy metals on humans have become a global concern despite the bio-importance of some heavy metals as trace elements (Nkansah and Ansah, 2014). Point sources including mining, metal-based industrial operations have been very noticeable in environmental pollution of heavy metals (Mahurpawar, 2015). The environmental damage caused upon the released of heavy metals greatly depends on the fate of known physical or chemical processes (Murtala *et al*., 2012).

The soil serves as the main reservoir for pollutants including heavy metals, hence accumulation of heavy metals increases in soil than other reservoirs of the ecosystem. However, physical processes such as leaching, erosion, runoff, atmospheric deposition and absorption of metal pollutants from point sources are important factors in fate of heavy metal pollution. Also, processes such as solubility, adsorption, and chemical form of a metal pollutant influence the biogeochemical processes of heavy metal pollution in the environment (Gołdyn *et al*., 2015).

2.4 Heavy Metals Toxicity in Humans

Heavy metals such as Hg, Pb, Cd and Zn can accumulate in biological and environmental samples to toxic levels, resulting in ecological damages and human health implications (Zheng *et al*., 2007). Heavy metals show signs of their harmful effects in humans as well as other organisms when exposed to them above the bio-recommended limits through possible routes. Ingestion of heavy metal contaminated food and water had been identified as the major pathway of human exposure to toxic metals, accounting for about 90% relative to other exposure pathways such as ocular, inhalation and dermal contact (Zheng *et al*., 2007). The toxicity of heavy metals in humans is as a result of the non-degradable biotoxic complexes formed between the stable oxidation states of the metal and the sulfhydryl group (-SH) of protein biomolecules in humans (Duruibe *et al*., 2007). The stable biotoxic complex molecule formed becomes difficult to breakdown by known detoxification processes. This could disrupt several biological enzymes resulting in several impaired physiological functions of organs such as the brain, kidney, liver, etc. (Mahurpawar, 2015).

2.5 Occurrence, Uses and Toxicity of Heavy Metals selected in this Study

2.5.1 Lead

Lead occurs in a variety of minerals naturally, but the major source of Pb is galena (PbS). Lead is a soft, malleable, and ductile and can combine with other metals to form alloys. Lead exists in both inorganic and organic forms in the environment (ATSDR, 2015) with a varying oxidation states of 0, +2, +4 (ATSDR, 2015).

The global production of Pb is about 4.5 million metric tons per year, of which about half is used in acid battery production. Other industrial applications of Lead include its use as shielding device in X-ray production, as pigment in paints, and in manufacturing

of Lead arsenate pesticides. Pb exist in trace amount in soils and could be incorporated into the soils from atmospheric wet and dry deposition. Pb is relatively immobile in soil and has a long residence time leading to its strong adsorption to soil particles and remains in the upper layer of soil, particularly soil with high organic matter content. Soil properties such as pH, cation exchange capacity and organic matter content influences the extent to which Pb binds to soil particles.

All forms of Pb, including the organic and inorganic are potentially toxic and the toxicity can be acute or chronic based on the duration of exposure. Pb has no known biochemical importance to humans and its absorption in the humans is greatly dependent on several factors such as age and physiological status (Zaza *et al*., 2015). Human exposure to Pb remains a serious health problem because Pb is a systemic toxicant that affects several organs like kidneys, liver, the central nervous system as well as the reproductive system in the body (ATSDR, 2015). Pb poisoning could also result in inhibition of haemoglobin synthesis, dysfunctions in kidneys, joints and reproductive system, cardiovascular and can also cause damage to the central nervous system and peripheral nervous system (Sharma and Singh, 2015).

2.5.2 Zinc

Naturally, Zn enters the environment through weathering, volcanic eruptions, forest fires and aerosol formation (ATSDR, 2015). However, several human activities through the production and use of zinc in brass, paints, alloys, fuel combustion and refuse incineration contribute greatly to large amounts of zinc in the environment (Sharma and Singh, 2015). The adsorption of Zn on the surface of soil particulates especially clay minerals can retard its mobility in the soil. Factors including pH, redox potential and cation exchange capacity affect Zn sorption and migration in soils.

Zinc is an essential micronutrient and is needed for several physiological functions in humans. However, excess amount of Zn can cause system dysfunctions that can lead to growth and reproduction deficiencies in humans. Abdominal cramps, diarrhoea, pleuritic chest pain, respiratory tract infection and pneumonitis are some clinical signs associated with Zn poisoning via inhalation and ingestion (Sharma and Singh, 2015).

2.5.3 Cadmium

Cadmium (Cd) exhibits chemical similarities with Zn and is obtained as a byproduct of mining and smelting of Zn, Pb and Cu ores. Volcanic activity, erosion, weathering and river transport are major processes that contribute to the release of cadmium to the Earth surface (Yang et al., 2012). Cd is considerably used in various industrial applications such as the production of batteries, alloy and pigment stabilizers for PVC (WHO, 2015). Human activities which includes refining of non-ferrous metals (zinc, lead, and copper) and the recycling of cadmium-plated steel scrap contributes hugely to elevated levels of Cd in the environment.

Similar to Pb, Cd is of no known biological essentiality in humans and has no homeostasis mechanism. Major routes of Cd exposure to humans are ingestion of contaminated food as well as drinking and inhalation or cigarette smoking (UNEP, 2013). Cadmium is a bio-persistent pollutant and once absorbed into living tissues, remains resident for many years owning to its slow excretion rate. In humans, Cd is found mainly distributed in the circulatory system but blood vessels are known to be the main stream organs of Cd toxicity (Okyere *et al*., 2015). Lethal doses of Cd affect various organs in animals which includes the liver, kidney, lungs, testes, skeletal, nervous as well as the immune system.

2.5.4 Chromium

Chromium is highly resistant to oxidation, even at high temperatures (ATSDR, 2015). Chromium occurs in varying oxidation states ranging from Cr^{3+} to Cr^{6+} with the elemental form being rare in nature (Mahurpawar, 2015). Chromium forms stable compounds in the +3 and +6 oxidation states with Cr (III) compound being the most stable (Amonette and Rai, 1990). Cr has a wide range of industrial applications. Chrome plating, leather tanning, paint pigments and corrosion inhibitors are some of the industrial uses of Cr. Cr has become a major environmental contaminant of great concern owing to its numerous applications.

The health effects of Cr are related to the oxidation state of the metal at the time of exposure. The trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) forms are thought to be the most biologically significant compounds. Cr (+3) is an essential dietary mineral in low doses. Cr (+3) is required in trace amounts to regulate glucose, fat and protein metabolism by potentiating the action of insulin (Saha and Zaman, 2013). The human toxicity of Cr is mainly attributed to the Cr (+6) form because the Cr (+3) is poorly absorbed by any route (Riser and Bailey, 1992). Cr (+6) compounds are known carcinogens and are generally considered to 1,000 times more toxic than Cr (+3) (Sharma and Singh, 2015).

2.5.5 Iron

Iron exists in two main forms; the ferrous (Fe^{2+}) and ferric (Fe^{3+}) in nature. However, the soil properties such as pH and aeration determine which form of Fe predominates. The concentration of Fe in the soil also decreases sharply as the soil pH increases. The solubility of Fe depends greatly on its oxidation state of the compounds in which it is found and the pH of the surroundings.

Iron is an essential element in human nutrition but the minimum daily requirement for iron is dependent on sex, physiological status, age and iron bioavailability. According to Lin *et al*. (2016), elevated body iron concentration has been shown to increase the risk of several cancers, including breast cancer in humans. During the past decade, considerable evidence has supported the role of oxidative stress in the development of atherosclerosis and related cardiovascular diseases (Li *et al*., 2008). Iron is known to accumulate naturally in vital organs such as heart, liver, and kidney, therefore puts the organs at risk for serious damage. In addition, once the body's storage capacity for iron is exceeded, non–transferrin-bound iron is created (Wei and Yang, 2010) which is a toxic form of iron that causes oxidative stress, attacking organ systems at the cellular level and causing tissue damage (Zheng *et al*., 2007).

2.5.6 Copper

Copper is a component in many primary minerals, the most common being sulfides such as chalcocite (Cu_2S), covellite (CuS), and villamaninite (CuS_2). The sulfide minerals are quite soluble and provide a continuous release of Cu ions to solution where they interact with soil constituents. Anthropogenic and industrial activities (incineration of municipal waste, mining, producing products from copper such as pipes, sheet metal wire, and fossil fuel combustion) release copper into the environment. Copper exist mainly as Cu^{2+} on the surfaces of clayey materials of soils and the presence of particulate organic materials influences the rate of adsorption (Van Herk, 2012). Dissolved Cu can be adsorbed onto the surfaces of soil or may be precipitated out of solution. Copper is a trace element important to plants, animals, and humans and can catalyze a variety of metabolic activities (Nazir *et al*., 2015). Ingestion of lethal dose of copper sulfate ($CuSO_4$) can cause temporary gastro-intestinal distress and liver damage. Also copper

deficiency can result in low numbers of white blood cells, anemia, defects in connective tissue leading to skeletal problem and osteoporosis in infants and children.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

Asafo is a suburb of Kumasi in the Ashanti Region of Ghana. It is located between the latitudes 6°41'2.64"N and longitudes 1°37'9.21"W. The sampling sites were selected in order to cover areas within the Asafo Township where auto mechanic activity is intense. To provide a satisfactory geographical representation of the site, the study area was divided into two (2) zones, that's; Zone A and B of which every zone was segmented into ten (10) grids. Zone 1 was to the south and Zone 2 was to the north (Fig. 3.1).

3.2 Chemicals and Reagents

3.2.1 Reagents

High purity reagents were used in all laboratory tests for the study. Reagents used were products of Sigma-Aldrich, Germany. All reagents conformed to the specifications of the committee on Analytical Reagent grade of American Chemical Society unless otherwise stated**.** Double distilled water was used for the preparation of all solutions.

3.2.2 Chemicals

- Potassium permanganate ($KMnO_4$); 95% purity
- Perchloric acid ($HClO_4$) ; 70% purity
- Sulphuric acid (H_2SO_4); 95% purity
- Nitric acid (HNO_3); 73% purity

3.3 Cleaning of Apparatus

All glassware used in the work were washed with detergent, rinsed and soaked overnight in 10% (v/v) HNO_3 solution. They were rinsed with distilled water followed by 0.5% (w/v) $KMnO_4$ solution and finally rinsed with distilled water and dried before use (USEPA, 2012).

3.4 Sampling

Owing to the siting of the automobile shops within the Asafo Township, the sampling area was categorized into two zones and were represented as Zone 1 and Zone 2. Twenty (20) composite top soil samples were collected around automobile workshops within the two zones at Asafo Township. Soil samples were taken using soil depth-calibrated auger, at the depths of 0-10 cm. Soil samples were then mixed together to obtain a composite soil sample from which a representative of the area was obtained. The composite soil samples were placed in separate polythene bags, labelled and transported to the laboratory for analysis processes. The location of each selected sampling point was noted and recorded with a hand-held global positioning system (GPS) as presented in Fig. 3.1. The procedure above was also used to obtain soil samples from KNUST botanical garden also in Kumasi. This soil sample was used as the control or background sample.

Fig 3.1: Map of the sampling zones showing the sampling points

3.5 Analysis of Physicochemical Parameters of Soil Samples

Physicochemical parameters of soil samples were measured using the facilities at the Department of Chemical Engineering at the Kwame Nkrumah University of University and Technology, Kumasi. All instruments used were calibrated prior to use with all parameter readings being recorded in triplicates.

3.5.1pH

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

3.5.2 Electrical Conductivity

The conductivity of the soil samples were determined using PHWE electrical conductivity meter. The instrument was initially calibrated by rinsing with potassium chloride (KCl) solution. The conductivity of this standard is known to be 1413 µS/cm; the electrode was rinsed with distilled water and then immersed in a soil-water suspension (1:2.5) for the actual conductivity reading.

3.5.3 Organic Matter Content

About 10.0 g of sieved sample was weighed into a crucible. The crucibles was placed in an oven set at 105 ^{o}C and the sample dried for about 4 h. The crucibles was removed from the drying oven and place in a dessicator and allowed to cool. When cooled, the weight of the dried sample and the crucible were taken. The crucible with the dried sample were placed into the muffle furnace, and the temperature was set to 400 ^{o}C and ashed in the furnace for 4 h. The crucible was removed from the muffle furnace, cooled in the dessicator and weighed.

The percentage organic matter (OM) of the soil sample is given by:

$$\%OM = \frac{(W1-W2)}{W1} X100$$

Where

W_1 is the weight of sample at 105 ^oC

W_2 is the weight of sample at 400 ^oC

3.6 Carbon Content

The percent of organic Carbon in the soil samples was calculated using the expression

Carbon content = % OM x 0.58

3.7 Digestion of soil samples

One gram (1.0 g) of the sieved soil samples were weighed into a conical flask. About 1 mL of distilled water was added followed by 1 mL of nitric acid, 1 mL of perchloric acid and 5 mL of sulphuric acid. The mixture was then heated on a hot plate for about 30 min till the solution became clear. It was allowed to cool and filtered through a Whitman No.1 filter paper into a 50 mL volumetric flask. The filtrate was then topped up to the 50 mL mark with distilled water.

3.8 Heavy Metal Analysis

Analyses of heavy metals (Fe, Cu, Cd, Cr, Zn and Pb) concentrations in soil samples were done at Anglogold Ashanti Obuasi Mine, Obuasi. The concentrations of the heavy metals were determined using the SpectrAA 220 Graphite Atomic Absorption Spectrophometer. The instrument was calibrated with series of standard solutions in accordance with the manufacture's instruction. Analyses of heavy metals were done

using hollow cathode lamp (HCl). Standard calibrations, the use of analytical blank solutions as well as triplicate analysis were used to ascertain quality assurance.

3.9 Enrichment Factor

The enrichment factor (EF) is used to determine the presence and intensity of heavy metals by anthropogenic contaminant deposition in soil compared to their abundance in the soil. The EF calculation is defined by relating the contaminated element of the soil sample to the concentration of a known element moderately immobile in the soil sample compared to the same ratio as shown in equation 3.1. Iron (Fe) was chosen as a stationary reference element because Fe is naturally abundant in soil. Also, it is part of the reference materials used in the literature widely (Liu *et al*., 2005).

$$EF = \frac{(X/Fe)soil}{(X/Fe)background} \qquad (3.1)$$

Where $(X/Fe)_{soil}$ is the ratio of heavy metal (X) to Fe in the soil from the study site

$(X/Fe)_{background}$ is the natural background value of the metal to Fe ratio.

Table 3.1: The intensity of heavy metal anthropogenic contamination in soils (Rubio *et al*., 2000)

Value	Soil quality
EF<1	Indicates no enrichment
1-3	Minor
3-5	Moderate
5-10	Moderately severe
10-25	Severe
25-50	Very severe
EF>50	Extremely severe

3.10 Geoaccumulation index (I_{geo})

The geoaccumulation index is used to determine the intensity of metal pollution in the soil. The index of metal accumulation of the soil in this study was calculated using the model proposed by Muller (1969) (Banat *et al*., 2005) as presented in equation 3.2

$$I_{geo}=\log_2 C_m/1.5B_n \qquad (3.2)$$

C_m= measured concentration of metal in soil

B_n= background values of metals

1.5 = the background matrix correction factor due to the lithogenic effects.

The I_{geo} scale consists of seven grades (0-6) ranging from uncontaminated soil to extremely contaminated soil is presented in Table 3.2.

Table 3.2: Classes of heavy metal contamination of soil (Banat *et al.*, 2005: Muller 1981)

Class	Value	Soil quality
0	Igeo ≤ 0	Uncontaminated
1	0< Igeo <1	Uncontaminated to moderately contaminated
2	1 < Igeo <2	Moderately contaminated
3	2< Igeo <3	Moderately to heavily contaminated
4	3< Igeo <4	Heavily contaminated
5	4< Igeo <5	Heavily to extremely contaminated
6	Igeo ≥ 5	Extremely contaminated

3.11 Pollution Index

Pollution index (PI) was used to evaluate the pollution status of heavy metals in soil. The PI of each metal was used to assess the soils environmental quality (Li *et al.*, 2008). The PI was calculated using equation 3.3.

Pollution index for soil quality is presented in Table 3.3

$$P_i = C_i / S_i \qquad (3.3)$$

Where P_i the pollution index of heavy metals i.

C_i (mg/kg) is the concentration of heavy metals in the soil.

S_i (mg/kg) is the concentration of standard heavy metal value for soil quality.

Table 3.3: Ranges of heavy metal pollution index for soil quality (Hakanson, 1980)

Value	Soil quality
PI<1	Low
1<PI<3	Moderate
PI>3	High

3.12 Integrated Pollution Index

To further assess the contamination levels of the metals in the soil around the automobile shops at Asafo, an integrated pollution index (IPI) of the metals was calculated in the study. The IPI is defined as the mean value of the pollution index (PI) of an element. The IPI is classified as: IPI≤1 low level of pollution; 1<IPI≤2 moderate level of pollution; 2<IPI≤5 high level of pollution; IPI>5 extreme high level of pollution (Zahida, *et al*., 2005: Wei and Yang, 2010).

3.13 Identification of sources of heavy metals

For further assessment of the extent of heavy metal contamination in the study, source identification and metal distribution were used. A loading plot was used to identify the sources of metals in the samples. Three (3) components were extracted. These three components constitute the metals and their association with samples. These 3 components play a significant role in explaining metal contamination in the study area.

3.14 Statistical Analysis

Knowledge in interpretation of data of the preset study was achieved using statistical tools and models. Statistical analysis has been very useful and widely applied in recent times to investigate heavy metal concentration, accumulation and distribution in soils. The mean of the replicates and the evaluation of significant differences between analyzed metals in samples were estimated using inferential statistics; analysis of variance (ANOVA).

Inter-element relationships between metals were examine using the Pearson's correlation. Pearson's correlation analysis measures the strength of a linear relationship between any two variables on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympathetic relation). In this study, it is employed to identify the inter-element relationships between the analysed heavy metals in soil samples. Principal Component Analysis (PCA) was used as a multivariate analytical procedure to identify the principal sources of heavy metal pollution in the top soil around automobile workshops at Asafo. This useful method allows identification of the different groups of metals that correlate and thus can be considered as having a similar behaviour and principal sources of pollution in relations to the artisanal activities in the study area. In this study PCA was applied to the large data-set of concentrations of six (6) metals analysed in soil samples from two different study zones at Asafo. The elements coming from the same source can be found all in the same component with a high weight and the component can be associated to that specific source.

CHAPTER FOUR

RESULTS

4.1 Physicochemical Parameters of Soil

A summary of results recorded for the physicochemical characteristics of soil samples from the various sampling points in the two sampling zones at Asafo as well as that of the control sample from KNUST Botanical garden are presented in Table 4.1

4.1.1 Organic Matter and Carbon content of Soil

The percentage organic matter (OM) of the soil samples from Zone 1 ranged from 9.67% - 18.38% whereas that recorded for soil sampled from Zone 2 ranged from 7.77% - 17.82% (Table 4.1). The mean OM content for the control sample in the present study was 11.34. Results in Table 4.1 revealed the mean OM content of soil samples from the two sampling zones at Asafo were relatively higher than that of the control soil sample. Percentage organic carbon (OC) content of soil greatly affected its organic matter contents. The results of the OC of soil samples from the two sampling zones at Asafo is presented in Table 4.1. Analogous to OM, the mean percentage organic carbon of the soil at Asafo recorded in the present were higher than that recorded for the control soil sample (Table 4.1). Both the organic matter and carbon content of soil were influenced by the nature of human activities carried out within the vicinity. The contents of the organic matter and the organic carbon of soil showed affinity for soil pollutants such as heavy metals and hence decreasing the mobility and the availability of heavy metals in the soil.

4.1.2 pH and Electrical Conductivity of Soil

Soil pH affects the metal chemistry of the soil in terms its mobility and adsorption. The availability and mobility of heavy metals were greatly influenced by low soil pH. The pH of soil samples for both sampling zones and the control are presented in Table 4.1. The results of the study indicated that the soil samples from Asafo were moderately alkaline with mean pH values for Zone 1 and Zone 2 being 7.87±0.22 and 7.92±0.36, respectively (Table 4.1). The mobility of heavy metals in alkaline soil is low compared to acidic soil hence heavy metals get adsorbed onto the soil and may persist in the soil environment for a longer time, which may have serious health implications on the artisans and the environment. The electrical conductivity of soil which is a measure of the metal ions was greatly affected by soil pH. The electrical conductivity (EC) of soil samples from the two sampling zones at Asafo in this present study is presented in Table 4.1. The EC of Zone 1 ranged from 651.00 - 6840.00 µS/cm with a mean value of 2320.10±2004.03 µS/cm whereas the EC of Zone 2 ranged from 341.00 – 1143.00 µS/cm with a mean value of 630.10±246.52 µS/cm (Table 4.1). However, the mean EC for both sampling zones were higher than that of the control soil sample.

4.2 Heavy Metal Analysis of Soil Samples

The results for heavy metal concentrations of soil samples collected from the various sampling points within the two sampling zones at Asafo and that of the control samples are presented in Table 4.2.

4.2.1 Lead

The concentrations of Pb in soil samples from Zone 1 and Zone 2 at Asafo are presented in Table 4.2. The results of the study revealed that the levels of Pb in soil from Zone 1 ranged from 1.55-5.50 mg/kg with a mean value of 3.67±1.44 mg/kg). Soil samples from Zone 2 recorded a range of Pb level, 1.50-5.05 mg/kg with a mean value of 3.64±1.46 mg/kg. The results of the study showed that the mean values of Pb of soil from the two zones were significantly higher than the recorded value of 0.25 mg/kg for the control soil sample.

4.2.2 Iron

The level of Fe in soil samples from Zone 1 ranged from 34.95-101.40 mg/kg with a mean value of 68.95±21.86 mg/kg. However, a range of 0.50-148.35 mg/kg and mean of 99.68±31.08 mg/kg were observed for Fe in soil samples from Zone 2 of the study area. The concentration of Fe recorded in the control soil sample was 5.15 mg/kg (Table 4.2). The result shown in this study is an indication of a relatively higher level of Fe from the study area.

4.2.3 Copper

Level of Cu in soil samples in Zone 1 ranged from 1.25-3.85 mg/kg with a mean value of mg/kg. However, a range of 0.50-1.75 mg/kg and mean of 1.14±0.44 mg/kg were observed for Cu in soil samples from Zone 2 of the study area. The concentration of Cu recorded in the control soil sample was 0.85 mg/kg (Table 4.2). The result shown in this study is an indication of a relatively higher level of Cu at the study area.

Table 4.1: Mean physicochemical properties of Soil from the study area and that of the control samples

	Physicochemical properties			
ZONE 1	**%OM**	**%OC**	**pH**	**E.C (µS/cm)**
Z1 A	17.00	9.86	7.46	651.00
Z1 B	14.05	8.15	7.87	926.00
Z1 C	18.38	10.66	7.56	721.00
Z1 D	10.95	6.35	8.05	486.00
Z1 E	12.11	7.02	7.89	6840.00
Z1 F	9.67	5.61	8.00	2163.00
Z1 G	13.51	7.84	8.07	3220.00
Z1 H	11.29	6.55	7.83	3160.00
Z1 I	11.02	6.39	8.14	1204.00
Z1 J	15.29	8.87	7.80	3830.00
Mean ±SD	**13.33±2.86**	**7.73±1.66**	**7.87±0.22**	**2320.10±2004.03**
ZONE 2				
Z2 A	11.56	6.71	7.97	398.00
Z2 B	8.20	4.75	7.70	345.00
Z2 C	10.20	5.92	7.22	341.00
Z2 D	15.29	8.87	8.49	655.00
Z2 E	6.31	3.66	8.37	658.00
Z2 F	17.82	10.34	7.90	1143.00
Z2 G	15.09	8.75	8.10	651.00
Z2 H	13.57	7.87	7.88	720.00
Z2 I	7.77	4.51	7.70	542.00
Z2 J	12.58	7.29	7.85	848.00
Mean ±SD	**11.84±3.73**	**6.87±2.16**	**7.92±0.36**	**630.10±246.52**
CONTROL	11.34	6.58	7.90	342.00

Table 4.2: Heavy Metal Concentration (mg/kg) of Soil from the study area as well as the control

Zones/Metal	Pb	Fe	Cu	Cd	Cr	Zn
ZONE 1						
Z1 A	5.40	75.25	1.95	0.85	3.50	4.50
Z1 B	4.60	101.40	1.65	0.20	2.75	0.25
Z1 C	2.20	96.80	2.40	0.25	3.15	1.95
Z1 D	2.50	80.20	3.85	0.40	2.25	0.95
Z1 E	1.55	39.10	3.85	0.55	2.50	1.55
Z1 F	5.50	77.55	2.40	5.00	2.50	1.15
Z1 G	2.40	34.95	1.85	5.30	2.05	2.55
Z1 H	3.85	61.15	1.25	0.45	2.05	4.00
Z1 I	4.00	58.95	4.50	0.30	1.60	1.55
Z1 J	4.65	64.15	1.55	0.30	1.25	4.10
Mean ±SD	3.67±1.44	68.95±21.86	2.53±1.13	0.41±0.19	2.36±0.68	2.26±1.48
ZONE 2						
Z2 A	2.85	87.30	0.65	0.60	0.35	1.10
Z2 B	5.05	73.75	1.45	1.40	1.95	1.40
Z2 C	5.25	67.85	0.85	1.40	1.50	1.30
Z2 D	1.90	112.85	1.45	0.30	0.55	3.05
Z2 E	4.95	115.20	1.00	0.30	0.65	1.10
Z2 F	2.05	61.75	0.70	1.95	1.15	1.50
Z2 G	4.80	145.95	1.50	0.90	1.60	4.45
Z2 H	4.55	78.30	1.50	1.55	0.45	1.60
Z2 I	3.45	105.50	0.50	1.85	1.65	3.20
Z2 J	1.50	148.35	1.75	4.80	1.20	3.30
Mean ±SD	3.64±1.46	99.68±31.08	1.14±0.44	1.51±1.30	1.11±0.57	2.20±1.19
CONTROL	0.25	5.15	0.85	0.75	2.40	1.20

4.2.4 Cadmium

Levels of Cd in soil samples in Zone 1 ranged from 0.20-5.30 mg/kg with a mean value of 0.41±0.19 mg/kg (Table 4.2). The levels of Cd in soil samples in Zone 2 ranged from 0.30- 4.80 mg/kg with a mean value of 1.51±1.30 mg/kg. However, the concentration of Cd recorded in the control soil sample was 0.75 mg/kg.

4.2.5 Chromium

Level of Cr in soil samples in Zone 1 ranged from 1.25-3.50 mg/kg with a mean value of 2.36±0.68 mg/kg. Levels of Cr recorded in soil samples in zone 2 ranged from 0.35-1.95 mg/kg with a mean value of 1.11±0.57 mg/kg. The concentration of Cr recorded in the control soil sample was 2.40 mg/kg (Table 4.2).

4.2.6 Zinc

Level of Zn in soil samples in Zone 1 ranged from 0.25-4.5 mg/kg with a mean value of 2.26 ±1.48 mg/kg. Levels of Cr recorded in soil samples in zone 2 ranged from 1.10-4.45 mg/kg with a mean value of 2.20±1.19 mg/kg. The concentration of Cr recorded in the control soil sample was 1.20 mg/kg (Table 4.2).

4.3 Enrichment Factor

The enrichment factor of each heavy metal in relation to the contamination of soil in the soil sampled from Zone 1 and Zone 2 were calculated and presented in Tables 4.3 and 4.4 respectively. Table 4.3 and 4.4 presents the mean EF calculation values of the studied metals in the selected Zones. The recorded EF values for most zones were less than 1 which indicates no enrichment or minor enrichment of metals in the surface soil at Asafo.

EF values calculated for Cd and Pb in the soil samples from Zone 1, using Fe concentrations in the background value were greater than one (1), indicating that there is a minor pollution of Cd and Pb in the surface soil of Asafo, also the main sources of contamination of such metals within these areas were mainly from lithogenic processes.

Table 4.3: Enrichment Factors for Soil Quality Estimations in Zone 1

Metal/Zone	Z1A	Z1B	Z1C	Z1D	Z1E	Z1F	Z1G	Z1H	Z1I	Z1J
Pb	**1.48**	0.93	0.47	0.64	0.82	**1.46**	**1.41**	**1.30**	**1.40**	**1.49**
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cu	0.16	0.10	0.15	0.29	0.60	0.19	0.32	0.12	0.46	0.15
Cd	0.08	0.01	0.02	0.03	0.10	0.44	**1.04**	0.05	0.03	0.03
Cr	0.10	0.06	0.07	0.06	0.14	0.07	0.13	0.07	0.06	0.04
Zn	0.26	0.01	0.09	0.05	0.17	0.06	0.31	0.28	0.11	0.27

Table 4.4: Enrichment Factors for Soil Quality Estimations in Zone 2

Metal/Zone	Z2A	Z2B	Z2C	Z2D	Z2E	Z2F	Z2G	Z2H	Z2I	Z2J
Pb	0.67	1.41	1.59	0.35	0.89	0.68	0.68	**1.20**	0.67	0.21
Fe	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cu	0.05	0.12	0.08	0.08	0.05	0.07	0.06	0.12	0.03	0.07
Cd	0.05	0.13	0.14	0.02	0.02	0.22	0.04	0.14	0.12	0.22
Cr	0.01	0.06	0.05	0.01	0.01	0.04	0.02	0.01	0.03	0.02
Zn	0.05	0.08	0.08	0.12	0.04	0.10	0.13	0.09	0.13	0.10

4.4 Geo-accumulation Index

Table 4.5: Geo-accumulation Index for Zone 1

Metal/Zone	Z1A	Z1B	Z1C	Z1D	Z1E	Z1F	Z1G	Z1H	Z1I	Z1J
Pb	**6.46**	5.87	3.03	3.53	1.69	**6.56**	3.37	5.19	5.33	5.91
Fe	0.81	0.83	0.85	0.82	0.68	0.81	0.66	0.77	0.76	0.78
Cu	0.76	0.57	0.99	1.53	1.53	0.99	0.70	0.25	1.70	0.50
Cd	-0.21	-2.06	-1.78	-1.18	-0.77	2.06	2.14	-1.02	-1.54	-1.54
Cr	0.50	0.41	0.46	0.32	0.37	0.37	0.29	0.29	0.19	0.09
Zn	2.07	-0.13	2.02	-12.84	2.45	5.70	1.89	2.00	2.45	2.01

Table 4.6: Geo-accumulation index for Zone 2

	Pb	Fe	Cu	Cd	Cr	Zn
Z2 A	4.03	0.83	4.83	0.17	**27.92**	**27.92**
Z2 B	**6.23**	0.80	**7.76**	0.10	**74.91**	**74.91**
Z2 C	**6.38**	0.79	**8.10**	0.10	**83.30**	**83.30**
Z2 D	2.47	0.88	2.80	0.32	**8.87**	**8.87**
Z2 E	**6.15**	0.89	**6.94**	0.13	**54.35**	**54.35**
Z2 F	2.76	0.77	3.59	0.21	**16.70**	**16.70**
Z2 G	**6.03**	0.93	**6.48**	0.14	**45.18**	**45.18**
Z2 H	5.83	0.81	**7.16**	0.11	**62.91**	**62.91**
Z2 I	4.76	0.87	5.48	0.16	**34.46**	**34.46**
Z2 J	1.56	0.93	1.67	0.56	2.99	2.99

Table 4.7: Heavy metal Pollution Index (PI) of Soil at Asafo

	Zone 1									
Metal/sampling points	A	B	C	D	E	F	G	H	I	J
Pb	21.60	18.40	8.80	10.00	6.20	22.00	9.60	15.40	16.00	18.60
Fe	14.61	19.68	18.79	15.57	7.59	15.05	6.78	11.87	11.44	12.45
Cu	2.29	1.94	2.82	4.52	4.52	2.82	2.17	1.47	6.11	6.64
Cd	4.66	3.66	4.20	3.00	3.33	3.33	2.73	2.73	2.13	1.66
Cr	1.45	1.14	1.31	0.93	1.04	1.04	0.85	0.85	0.66	0.52
Zn	3.75	0.20	1.62	0.79	1.29	0.95	2.13	3.33	1.29	3.42
	Zone 2									
Pb	11.40	20.20	21.00	7.60	19.80	8.20	19.20	18.20	13.80	6.00
Fe	16.96	14.32	13.17	21.91	22.36	11.99	28.33	15.20	20.48	28.80
Cu	0.76	1.70	1.00	1.70	1.17	0.82	1.76	1.76	0.59	2.05
Cd	0.80	1.87	1.87	0.40	0.40	2.60	1.20	2.07	2.47	6.40
Cr	0.15	0.81	0.63	0.23	0.27	0.48	0.67	0.19	0.69	0.50
Zn	0.92	1.17	1.08	2.54	0.92	1.25	3.70	1.33	2.67	2.75

The results of the PI of soil at Asafo is presented in Table 4.7. Results of the study indicates that Fe and Pb recorded PI values > 3 in all soil samples from the two sampling zones (Zone 1 and 2). This indicates the severity of pollution of Pb and Fe in the soil of the study areas. The PI value recorded for Cd for all the sampling points from the two zones were below 3 except for that recorded in sampling point J of zone 2.

4.5 Sources of Heavy Metals

The score plot Fig.4.3b represent sampling sites with similar metals distributions, thus sites Z1J, Z2D, Z2H and Z2E for example have similar metal distribution, whiles sites Z1A, Z2J, Z1H, ZiF and Z1C also have similar metal characteristics. Fig. 4.3c, is a superimposition of Fig. 4.3a and Fig. 4.3b and therefore shows the association of the sampling sites with the heavy metals. Here it can be observed that sites Z1J, Z2D, Z2H and Z2E were associated with Cu. Again, sites Z1A, Z2J, Z1H, ZiF and Z1C were associated with Pb, Fe and Zn.

There was no association observed between metals and the control samples as the concentration of all metals within the control zones were low. Similarly, low metal concentrations were detected in samples from sites Z1E, Z1G, Z2F and Z1D in the back box as they had no associations with the metals (Fig. 4.3b and 4.3c) which suggests these areas had low metal concentrations or the presence of the metal in the samples were from natural sources.

4.6 Correlation Analysis

Correlation determines the interrelationship of the determined physico-chemicals parameters and heavy metals present relating them to the correspondence of their points of pollution. The results of the study indicate a strong positive correlation ($r = 1.00$) between Cd and Cr at p-value <0.05 in zone 1.This indicates that these two metals might be influenced by the same anthropogenic activity or geochemical process. There was a poor correlation between pH and heavy metal parameters. A strong negative correlation ($r = -0.82$) was observed between pH /OM and pH/OC. This indicates a reciprocal effect of pH on organic matter content and carbon content of soil at zone 1. A strong positive correlation of pH/OM ($r = 1.000$, $p < 0.05$) was observed in zone 2. Deduction from the

observed correlative is that an increase in organic matter of the soil could directly affect the soil pH. Also, EC showed a moderate positive correlation with OM and EC of soil in zone 2 at $P < 0.05$.

4.8 Correlation Analysis for Zone 1

Table 4.8: Correlation Analysis for Zone 1

Variables	Pb	Fe	Cu	Cd	Cr	Zn	%OM	%OC	pH	EC
Pb	1									
Fe	0.3592	1								
Cu	0.2213	-0.1863	1							
Cd	0.0303	0.4767	-0.7244	1						
Cr	0.0303	0.4767	-0.7244	**1.0000**	1					
Zn	0.2656	-0.3031	0.1738	-0.0798	-0.0798	1				
%OM	-0.0322	0.3362	-0.0530	0.4706	0.4706	0.3955	1			
%OC	-0.0322	0.3362	-0.0530	0.4706	0.4706	0.3955	1.0000	1		
pH	-0.1828	-0.4060	0.2687	**-0.6641**	**-0.6641**	**-0.5314**	**-0.8232**	**-0.8232**	1	
EC	-0.3706	-0.7367	0.0526	-0.3491	-0.3491	0.1585	-0.2294	-0.2294	0.1666	1

Values in bold are different from 0 with a significance level alpha=0.05

4.9 Correlation Analysis for Zone 2

Table 4.9: Correlation Analysis for Zone 2

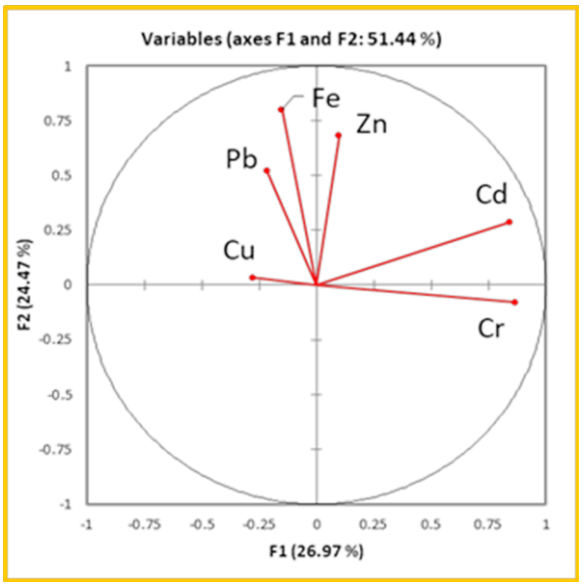
Variables	Pb	Fe	Cu	Cd	Cr	Zn	%OM	%OC	pH	EC
Pb	1									
Fe	-0.2232	1								
Cu	-0.0179	0.4900	1							
Cd	-0.4411	0.2722	0.3130	1						
Cr	0.3181	0.0218	0.0179	0.2928	1					
Zn	-0.2553	0.7820	0.4010	0.2686	0.3195	1				
%OM	-0.5251	0.0084	0.2382	0.1168	-0.2254	0.3148	1			
%OC	-0.5251	0.0084	0.2382	0.1168	-0.2254	0.3148	**1.0000**	1		
pH	-0.3143	0.4700	0.2665	-0.3815	-0.5608	0.2312	0.2210	0.2210	1	
EC	-0.5699	0.1438	0.1184	0.3852	-0.2045	0.1971	**0.6435**	**0.6435**	0.3449	1

Values in bold are different from 0 with a significance level alpha=0.05

The results showed a significantly lower ($p < 0.05$) concentrations of Cu, Cd, Cr in Zone 2 compared to Zone 1. However, although the levels of Pb and Zn were comparable between the zones, Fe was significantly higher in Zone 2.

4.10 Principal Component Analysis (PCA) and Cluster Analysis

The varimax rotation for data reduction produced the PCA which could be used to infer natural or anthropogenic sources of heavy metals pollution. The results for the loading plot and score plot are shown in the Figures 4.3a and 4.3b, respectively



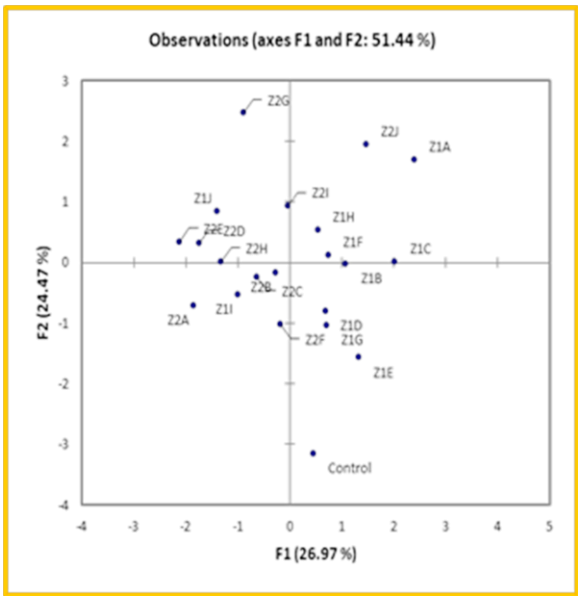


Figure 4.3a: Loading plot of PCA **Figure 4.3b: Score plot of PCA**

Superimposition of Figure 4.3a and Figure 4.3b results in a biplot (Figure 4.3c) which shows the association of the samples (soil) with the variables (heavy metals). The PCA biplot is shown below

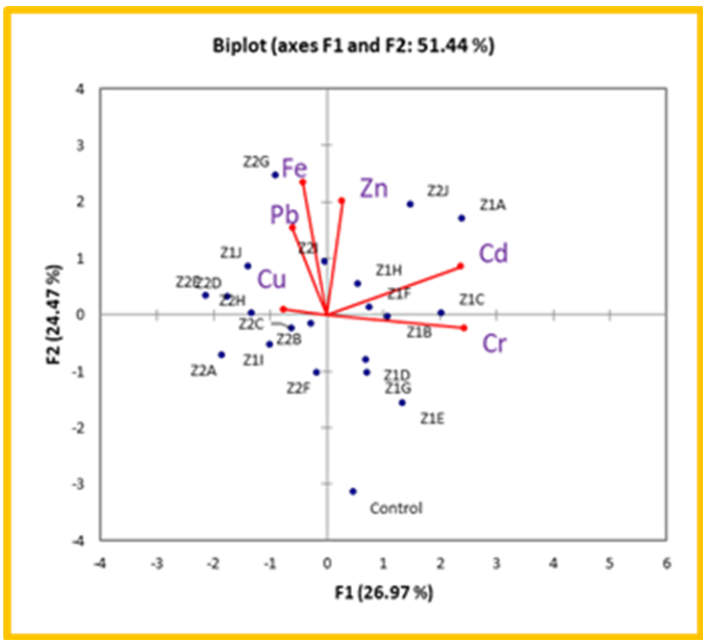


Figure 4.3c: PCA biplot

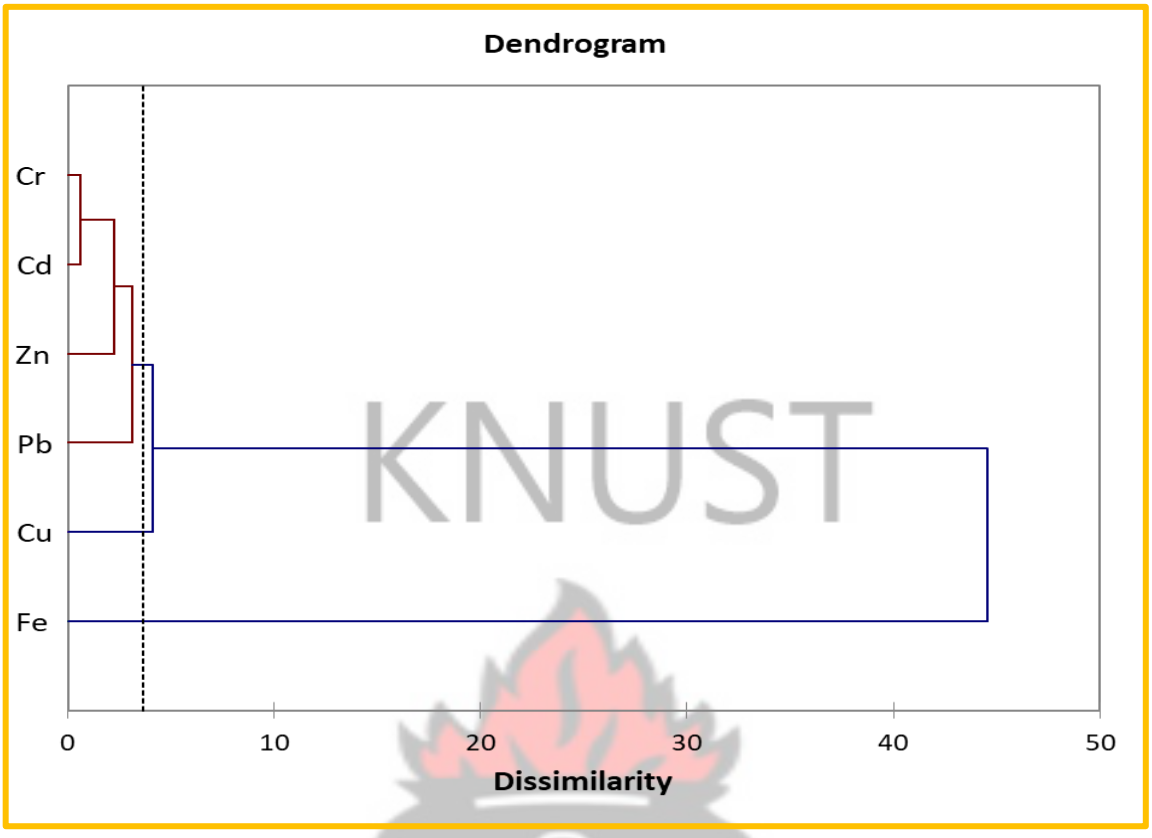


Figure 4.4: Dendrogram of clustering of heavy metals in Soil.

Cluster analysis organizes variables into homogeneous groups where variables within the same cluster exhibit associations with each other and dissimilar to variables in other clusters (Muhammad *et al*., 2011). Clusters are formed based on existing similarities which become useful for data interpretation and pattern recognition. In this study, heavy metals detected in soil samples were grouped into clusters based on Euclidean distance using Ward's clustering method. The result for the cluster analysis is presented in a dendrogram as shown in Figure 4.4.

CHAPTER FIVE

DISCUSSIONS

5.1 Physicochemical properties of Soil at Asafo

Table 4.1 present the results of the physicochemical properties of soil samples of the sampling points within the two sampling zones at Asafo. The mean and the standard deviation of each parameter is compared to the control soil sample in predicting the effect of the various human activities on the soil at the study area. The results of the study indicate varying measured values for all selected parameters of soil for the two zones. The recorded mean values of the physicochemical parameters of soil samples from the two zones were slightly above their respective parameters of the control soil sample.

The recorded mean values between parameter, except for EC, showed no statistical difference at $p < 0.05$. Soil samples at Asafo where slightly alkaline in nature. However, pH is considered as the major chemical parameter that controls the bio-availability of heavy metals in soil and it can change the performance of metals easily (Lasat, 2002). For most heavy metals, the acidity of the soil results in a higher solubility than in adsorption. Thus, mobility of metals is promoted by an acidic pH (Kabata-Pendias, 2004). Therefore the pH of the soil at the study site may not influence significantly the mobility and availability of the heavy metals.

The electrical conductivity (EC) of soil is a direct measure of ions in the soil. The mean EC of soil samples recorded in both zones were higher relative to that of the control soil sample. Zone 1 recorded a mean value of 2320.10±2004.03 µS/cm, which is almost 6

times higher than that recorded in zone 2. Apparently, the activities of mechanics in both zones include fitting, alignment, spraying, engine repairs and other body works. Due to the higher activities in zone 1 as a result of the area being the first to site compared to zone 2, electrical conductivity (EC) is higher in zone1. This could possibly account for the high metal ions in the soil and the relatively high EC values. EC is likely to increase as clay contents in soil increase (Stadler *et al*., 2015), because clayey soils have high water holding capacity, so more ions/salts would go into solution and increase their contents in the soil (Chandrasekaran and Ravisankar, 2015).

5.2 Heavy Metal Concentration of Soil Samples

Soil serves as a compartment for waste disposal thereby, receiving significant amounts of pollutants (Addo *et al*., 2012). The results of the study revealed that the order of heavy metal pollution of soil in zone 1 was in the order Fe > Pb > Cu > Cr > Zn > Cd whereas the order of metal concentrations of soil in zone 2 was Fe > Pb > Zn > Cd > Cu > Cr (Table 4.2). The mean concentration of Pb recorded in study for soil at Asafo were 3.67 ± 1.44 and 3.64 ± 1.46 for zone 1 and 2, respectively. There was no statistical significant difference between the recorded mean values for Pb. However, the recorded mean values of Pb concentrations in surface soil at Asafo were significantly higher than that for the control soil sample. These significant variations could be attributed to the human activity taking place at the study site. The use of Pb compound as an anti-knocking agent in fuel, a combined element in paint for spraying cars, could be a factor of Pb pollution on the surface soil at Asafo mechanic shops. Exposure to Pb laden soil from the study area could be detrimental to human. Acute Pb exposure could lead to respiratory disorders whereas chronic exposure could cause degeneration of the central nervous system, anaemia and renal failure.

Cadmium, a toxic metal is one of the major components of paint pigment hence monitoring the level of Cd at automobile/mechanic shops is an issues of concern. Human exposure to Cd could result in several detrimental effects to health. Such adverse effects include Osteoporosis, renal tubular dysfunction as well as disturbance of calcium metabolism. In the present study, the mean concentrations of Cd recorded in surface soil from zone 2 at Asafo was higher than that recorded for the control sample (Table 4.2). Excessive use of automobile paints for spraying car bodies could be contribute to the relatively high levels of Cd in Asafo automobile shops. The high levels of Cd at the study sites is an indication of inputs from the use of paints.

The results of the present study report a high level of Fe in soil samples from automobile shops in Asafo as compared to that of the control soil sample (Table 4.2). Although Fe is well known as the most abundant element in the earth crust, the relatively high concentration of Fe recorded could be attributed to the excessive use of Fe alloys. Steel (an alloy of Fe and Cu) as used in most car bodies could be the primary source of Fe contamination in the surface soil at Asafo. Analogous to Fe, the high level of Cu in surface soil at Asafo could be as a result of the excessive use of steel in the various activities on site. There is also a significant positive correlation between Fe and Cu at $P < 0.05$ (Table 4.9).

The levels of essential metals, Zn and Cr recorded in soil samples at Asafo were slightly above that of the control soil sample. However, the differences between levels of Zn and Cr were not statistically significant between the two zones. The levels of Zn and Cr could be attributed to alloying as well as the excessive of Cr paint in spraying of car bodies.

5.3 Assessment of Soil Contamination Intensity in Surface Soil at study site

Enrichment factor (EF) estimations have been widely used for geochemical studies in differentiating heavy metal contamination of surface soil that originate from human activities and lithogenic processes (Praveena *et al*., 2008).

EF values calculated for Cd and Pb in the soil samples from Zone 1, using Fe concentrations in the background value were greater than one (1), indicating that there is a minor pollution of Cd and Pb in the surface soil of Asafo, also the main sources of contamination of such metals within these areas were mainly from lithogenic processes. These metals are highly toxic with no known biological importance and also have the potential to enter the food chain and cause adverse health impacts to humans and animals (Mandal and Suzuki, 2002). It is therefore necessary to monitor their pollution in surface soils.

5.3 Geo-accumulation Index (I_{geo})

Geo-accumulation (I_{geo}) was used to determine and describe contamination in the soils by comparing recent concentrations with background levels. The seven classes of I_{geo} include (0-6) varying from uncontaminated to extremely contaminated. Calculated means I_{geo} for heavy metal concentrations in zone 1 ranged from uncontaminated to moderately contaminated ($0< I_{geo} <1$) (Table 4.4), which suggests contamination of some metals in some sampling points. However, the mean I_{geo} for Pb in zone 1 ranged from heavily to extremely contamination ($I_{geo} <5$) which falls in the sixth class of classifying heavy metal contamination under I_{geo} criteria. Mean I_{geo} of soil samples in zone 2 showed that the soil is uncontaminated with Fe and Cd. However, there is an extreme contamination of Cr, Zn in almost all soil samples from the zone 2, which indicate the

possibility of the excessive use of Cr, and Zn paints on the soil. Lead and Cu exhibited extreme contamination in soil from some sampling points within zone 2.

5.5 Principal Component Analysis

To be able to identify the possible sources and better understand the relationship and behaviour among the heavy metals in the soil, PCA was applied to the experimental data as indicated by Chandrasekaran *et al*. (2015). The results, presented in Fig. 4.3a show that only three eigenvalues were >1.00 and explained 87.6% of the total variance of the system.

The first component accounted for 52.5% of the total variation and was dominated by Pb, Zn and Fe (Fig. 4.3a). This association could be tentatively traced to metal fabrication, since the common source of occurrence of these metals is vehicular activities, For example, Fe may be due to metal parts used in fabrication of the body of the vehicles, Pb might come from lead accumulated batteries and paints whiles Zn might be part of additives that are added to lubricants and also form ware of metals.

The second component also accounted for 20.4% of the total variance and was highly dominated by Cr and Cd. The mean concentration of these metals in the top soil from the study area were not significant from that of the control site. Again results from EF, Igeo, as well as PI for these metals showed that Cr and Cd are not significantly affected by the active anthropogenic activities taking place in the study area. It can, therefore, be stated that levels of Cd and Cr in the soil from the study area are controlled mainly by natural factors of the lithogenic process during weathering process of parent rocks. Component 3 accounted for 14. 7% of the total variance and was dominated by Cu.

5.6 Cluster analysis (CA)

CA organizes variables onto homogenous groups where variables within the same cluster exhibit associations with each other and dissimilar to variables in other clusters. Clusters are formed based on existing similarities which become useful for data interpretation and pattern recognition. In this study, the variables (heavy metals) were grouped into clusters based on Euclidean distance using Ward's method. The results of the CA are presented in a dendrogram as shown in Fig.4.4. In this dendrogram, all metals were grouped into three (3) statistically significant clusters.

Cluster 1 is composed of Cr, Cd and Zn indicating similarities of these heavy metals content in topsoil samples from the study sites. Thus, the content of these heavy metal in the top soil from these sites were not affected by the human activities and could be attributed to lithogenic sources. Cluster 2 is represented by Pb and Cu, whiles the third cluster was dominated by Fe. This result was consistent with that of the loading plot, Fig.4.3a.

Correlation analysis, PCA and CA highlight the sources of heavy metals in the topsoil of the study site. The combination of these three (3) statistical analyses showed a strong correlation between Pb and Fe indicating significant associations. Furthermore, these metals had high positive loads which explains that the level of pollution of these metals was not affected by their natural characteristics in the soil, but precisely by anthropogenic activities within the study area.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

The study assessed the impact of human activities at Asafo auto mechanic shops on the surface soil in relation to the heavy metal (Pb, Fe, Cu, Cd, Cr and Zn) pollution levels.

1. Top soils around Asafo mechanic shops have relatively high enrichment factor (EF) values for Pb, Zn and Cd indicating the extent of pollution. This was supported by geoaccumulation index (I_{geo}) ranging from uncontaminated to moderate contamination ($0 < I_{geo} < 1$) to extremely contaminated ($I_{geo} \geq 5$).
2. A strong positive correlation between Cd and Cr in zone 1 indicates the similar human activities that could be contribute to the high levels of Cd and Cr at Asafo. The present study showed a preliminary yet relevant information in relation to the metal pollution status of the automobile activities on soils at Asafo.

The study therefore recommend the follow:

- Heavy metals levels in human samples such as the hair, blood and nails of worker the artisans at Asafo automobile shops should be conducted.
- Levels of heavy metals in air and other environmental components within the Asafo township could be conducted and the risk they posed to humans be estimated.

REFERENCES

Abii, T. A. (2012). Levels of heavy metals (Cr, Pb, Cd) available for plants within abandoned mechanic workshop in Umuahia Metropolis. Research Journal of Chemical Sciences. 2, (2):79-82.

Abdel-Baki, A. S., Dkhil, M. A., & Al-Quraishy, S. (2011). Bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of Wadi Hanifah, Saudi Arabia. *African Journal of Biotechnology*, *10*(13), 2541–2547. https://doi.org/10.5897/AJB10.1772.

Addo, M.A., Darko, E.O., Gordon, C., Nyarko, B.J.B., Gbadago, J.K., Nyarko, E., Affum, H.A., Botwe, B.O. (2012). Evaluation of heavy metals contamination of soil and vegetation in the vicinity of a cement factory in the Volta Region, Ghana. International Journal of Science and Technology, 2, 40–50

Adelekan, B. A., & Abegunde, K. D. (2011). Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nigeria. *International Journal of the Physical Sciences*, *6*(5), 1045–1058. https://doi.org/10.5897/IJPS10.495

Akoto, O. Bruce, N. T. and Darko, G. (2008). Heavy metals pollution profiles in streams serving the Owabi reservoir; Afr. J. Environ. Sci. and Tech., 2 (11), 354- 359

Akoto O,. Nimako C., Asante, J. and Bailey, D. (2016). Heavy Metals Enrichment in Surface Soil from Abandoned Waste Disposal Sites in a Hot and Wet Tropical Area. Environ. Process.

DOI 10.1007/s40710-016-0183-x

Amonette, J.E. and D. Rai, 1990. Identification ofnoncrystalline (Fe, Cr)(OH)3 by Infrared Spectroscopy. Claysand Clay Minerals, 38(2), 129-136.

ATSDR. (2015). Agency for Toxic Substances and Disease Registry Case Studies in Environmental Medicine (CSEM) Lead Toxicity. *Environmental Health and Medicine Education*.

ATSDR, (2017). Lead Toxicity; What Are Routes of Exposure to Lead? https://www.atsdr.cdc.gov/csem/csem.asp?csem=34&po=6 Assessed 115th January 2019.Replace Okyere

Banat, K .M., Howari, F. M, and Al-Hamad, A. A. (2005). Heavy metals in urban soils of central Jordan: should we worry about their environmental risks? Environ Res. 2005 Mar;97(3), 258-273.

Briki Meryem, Hongbing Ji, Li Cai, Gao Yang (2015). Characterization, distribution and risk assessment of heavy metals in agricultural soil and products around mining and smelting areas of Hezhang, China. Environmental Monitoring and Assessment 187(12). DOI: 10.1007/s10661-015-4951-2

Chandrasekaran, A., & Ravisankar, R. (2015): Molecular and Biomolecular Spectroscopy Spatial distribution of physico-chemical properties and function of heavy metals in soils of Yelagiri hills , Tamilnadu by energy dispersive X-ray florescence spectroscopy (EDXRF) *Spectrochimica acta part a:*, *150*, 586–601. https://doi.org/10.1016/j.saa.2015.05.083

Dube, A. Zbytniewski, R. Kowalski, T., Cukrowska, E. and Buszeski, B. (2001). Adsorption and migration of heavy metals in soil.Environmental Studies,10,pp.1-10.

Duruibe, J. O., Ogwuegbu, M. O. C., & Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences*, *2*(5), 112–118. https://doi.org/10.1016/j.proenv.2011.09.146

Emsley J (2011). *Nature's Building Blocks: An A-Z Guide to the Elements*, Oxford University Press, New York, 2nd Edition

Gabby PN, (2006). Lead: in Mineral Commodity Summaries, Reston, VA: U.S, Geological Survey.

Gasana J, Hlaing WM, Siegel KA, Chamorro A, and Niyonsenga T.(2006). Blood lead levels in children and environmental lead contamination in Miami inner city, Florida. Int J Environ Res Public Health. 3,(3): 228-34.

Gołdyn, B., Chudzińska, M., Barałkiewicz, D., & Celewicz-Gołdyn, S. (2015). Heavy metal contents in the sediments of astatic ponds: Influence of geomorphology, hydroperiod, water chemistry and vegetation. *Ecotoxicology and Environmental Safety*, *118*(10902414), 103–111. https://doi.org/10.1016/j.ecoenv.2015.04.016

Hossini H and Makhdoumi M (2016). Toxicological, Environmental, Health effects and Treatment methods of Hexa-/Tri-valent chromium in water/wastewater: a review. Acta Medica Mediterranean. 32, 1443

Kabata-Pendias, A. (2004). Soil-plant transfer of trace elements- An Environmental Issue. *Geoderma*, *122*, 143–149.

Lasat, M. M. (2002). Phytoextraction of toxic metals: a review of biological mechanisms. *Journal of Environmental Quality*, *31*(1), 109–120.

Leu et al, Emerit et aland Chau et al

Lin, Q., Liu, E., Zhang, E., Li, K., & Shen, J. (2016). Spatial distribution, contamination and ecological risk assessment of heavy metals in surface sediments of Erhai Lake, a large eutrophic plateau lake in southwest China. *Catena*, *145*, 193–203. https://doi.org/10.1016/j.catena.2016.06.003

Li, W.X., Zhang X.X., Wu B., Sun S.L., Chen Y.S., Pan W.Y., Zhao D.Y., Cheng S.P. (2008). A Comparative Analysis Of Environmental Quality Assessment Methods for Heavy Metal-Contaminated Soils Pedosphere (18), Pp. 344-352

Mahurpawar, M. (2015). Effects of heavy metals on human health. *International Journal of Research-Granthaalayah*, *2350*(0530), 2394–3629.

Mandal BK, Suzuki KT (2002) Arsenic round the world: a review, Talanta, 58:2 01–235

Muhammad, S., Shah, M. T., & Khan, S. (2011). Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. *Microchemical Journal*, *98*(2), 334–343. https://doi.org/10.1016/j.microc.2011.03.003

Murtala, B., O. Abdul, W., & A. Akinyemi, A. (2012). Bioaccumulation of Heavy

Metals in Fish (Hydrocynus forskahlii, Hyperopisus bebe occidentalis and Clarias gariepinus) Organs in Downstream Ogun Coastal Water, Nigeria. *Journal of Agricultural Science*, *4*(11), 119–133. https://doi.org/10.5539/jas.v4n11p51

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: A review. *Environmental Chemistry Letters*, *8*(3), 199–216. https://doi.org/10.1007/s10311-010-0297-8

Nazir, R., Khan, M., Masab, M., Rehman, H. U., Rauf, N. U., Shahab, S., … Shaheen, Z. (2015). Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat. *Journal of Pharmaceutical Sciences and Research*, *7*(3), 89–97.

Nkansah, M. A., & Ansah, J. K. (2014). Determination of Cd , Hg , As , Cr and Pb levels in meat from the Kumasi Central Abattoir, *4*(8), 1–4.

Odoi, J. O.; Armah, F. A. and Luginaah, I. (2011). Assessment of spatial variability of heavy metals in soils under the influence of industrial soap and detergent waste water discharge. IJRRAS. 9 (2): 322-329.

Okyere, H., Voegborlo, R. & Agorku, S. 2015. Human exposure to mercury, lead and cadmium through consumption of canned mackerel, tuna, pilchard and sardine. Food Chem 179, 331-335.

Opaluwo, O. D., Aremun, M. O. Ogbo, I. O. Abiola, K. A., Odiba, I. E., Abubakar, M. M. and Nmeze, N. O.. (2012). Heavy metals concentrations in soils, plant leaves and crops grown around dumpsites in Lafia metropolis, Nasarawa State, Nigeria Advance in Applied Science Research, (2), 780 – 784.

Ozuni, E., Dhaskali, L., Abeshi, J., Zogaj, M., Haz Iri, I., Beqiraj, D., & Latifi, F. (2010). Heavy Metals in Fish for Public Consumption and Consumer Protection. *Natura Montenegrina*, *9*(Cd), 843–851. Retrieved from http://www.pmcg.co.me/NM9/Ozuni *et al* ISEM4.pdf

Patlolla and Dayan 2000

Praveena, S. M., Ahmed, A., Radojevic, M., Abdullah, M. H., & Aris, A. Z. (2008). Heavy metals in mangrove surfacesediment of Mengkabong Lagoon, Sabah: multivariateand geo-accumulation index approaches, International Journal of Environmental Research, 2(2), 139–148.

Replace Wilson with

Replaced USEPA 2012

Riser, J.A. and G.W. Bailey, 1992. Spectroscopic Study ofSurface Redox Reactions with Manganese Oxides. SoilScience Society of America Journal, 56: 82-88.

Sadick A, Amfo-Otu R, Acquah SJ, Nketia KA, Asamoah E, Adjei EO. Assessment of heavy metal contamination in soils around auto mechanic workshop clusters in central agricultural station, Kumasi, Ghana. Appl Res J [Internet]. 2015 [cited 2016 Apr 12];1(2):12-9. Available from: http://www.arj.presbyuniversity.edu.gh/index.php/ARJ/article/view/17/7

Sadick A, Amfo-Otu R, Acquah SJ, Nketia KA, Asamoah E, Adjei EO. Assessment of heavy metal contamination in soils around auto mechanic workshop clusters in central agricultural station, Kumasi, Ghana. Appl Res J [Internet]. 2015 [cited 2016 Apr 12];1(2):12-9. Available from: http://www. arj.presbyuniversity.edu.gh/index.php/ARJ/article/ view/17/7

Sadick A., Amfo-Out R, Acqual S.J., Nketia K.A., Asamoah E., Adjei E.O. (2015). Assesment of heavy metal contamination in soils around auto mechanic workshop clusters in central agricultural station, Kumasi, Ghana. Appl Res J [Internet]. cited 2016 April Apr 12;1(2),12-9. Available from http://www.arj.presbyuniversity.edu.gh/index.php/ARJ/article/view/17/7

Saha, N., & Zaman, M. R. (2013). Evaluation of possible health risks of heavy metals by consumption of foodstuffs available in the central market of Rajshahi City, Bangladesh. *Environmental Monitoring and Assessment*, *185*(5), 3867–3878. https://doi.org/10.1007/s10661-012-2835-2

Sharma, V., & Singh, P. (2015). International Journal of heavy metals pollution and it's

effect on environment and human. *International Jour Journal of Recent Scientit Scientific Re of Rec Recent Scienti Research*, *6*(12), 7752–7755.

Singh N, Kumar D, Sahu A. Arsenic in the environment: effects on human health and possible prevention. J Environ Biol. 2007;28(2 Suppl),359–365.

Stadler, A., Rudolph, S., Kupisch, M., Langensiepen, M., van der Kruk, J., & Ewert, F. (2015). Quantifying the effects of soil variability on crop growth using apparent soil electrical conductivity measurements. *European Journal of Agronomy*, *64*, 8–20. https://doi.org/10.1016/j.eja.2014.12.004

Soltan, M.E., Fawzy, E.M., AND Rashed, M.N (2012). Assesment on the Degree of Immobilization of Heavy Metals in Contaminated Urban Soils by Selected Phosphate Rocks of Different Particle sizes.

UNEP, 2013.Environmental Risks and Challenges of Anthropogenic Metals Flows and Cy-cles. A Report of the Working Group on the Global Metal Flows to the InternationalResource Panel (van der Voet, E., Salminen, R., Eckelman, M., Mudd, G., Norgate, T.,Hischier, R.), p. 231.6

Van Herk, A. (2012). Physicochemical Parameters in Soil and Vegetable Samples from Gongulon Agricultural Site, Maiduguri, Borno State, Nigeria. *International Journal of Chemistry*, 21–36.

Wei, B., & Yang, L. (2010). A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchemical Journal*, *94*(2), 99–107. https://doi.org/10.1016/j.microc.2009.09.014

WHO. 2015. Global Health Observatory data repository. Burden of disease. Lead attribut-able DALYs.http://apps.who.int/gho/data/node.home(last accessed: December2015).

Wu,Y, Tang L, and Chen B. (2014). Oxidative Stress: Implications for the Development of Diabetic Retinopathy and Antioxidant Therapeutic Perspectives. Oxidative Medicine and Cellular Longevity. http://dx.doi.org/10.1155/2014/752387. Assessed 15th January 2019

Yang, L. S., Zhang X W, Li Y H, Li H R, Wang Y, Wang W Y (2012). Bioaccessibility and Risk Assessment of Cadmium from Uncooked rice using an in vitro digestion model. Biological Trace Element and Resources, 145 (1), 81-86.

Zahida, K., Qureshi, B. A. Mumtaz, M. (2015). Geochemical baseline determination and pollution assessment of heavy metals in urban soils of Karachi, Pakistan. *Ecological Indicators* 48:358–364 DOI:10.1016/j.ecolind.2014.08.032

Zheng, N., Wang, Q., Zhang, X., Zheng, D., Zhang, Z., & Zhang, S. (2007). Population health risk due to dietary intake of heavy metals in the industrial area of Huludao city, China. *Science of the Total Environment*, *387*(1–3), 96–104. https://doi.org/10.1016/j.scitotenv.2007.07.044.