**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,**

**KUMASI**

# DISTRIBUTION AND RISK ASSESSMENT OF HEAVY METALS IN PERI-URBAN

# AREAS OF KUMASI

**BY:**

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**A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY.**

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## DECLARATION

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



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## ABSTRACT

The occurrence of heavy metals in urban soil is of great environmental concern due to the effects associated with excessive exposure. The main purpose of the work was to measure the levels and determine possible health risks due to excessive exposure to some selected metals. A total of 73 soil samples were collected from the top soil of Peri- Urban areas of Kumasi at a depth of 0-10 cm and subjected to the X - ray fluorescence spectroscopy analysis. Soil pH, conductivity and total organic content were also determined. pH and electrical conductivity were in a range of 6.5 - 8.5 and 153 μS/cm - 8990 μS/cm respectively for all samples. The mean concentrations of metals analyzed were Pb (18.60 ± 0.53 mg/kg), Cu (20.20 ± 2.34 mg/kg), Ni (29.33 ± 2.0mg/kg), Cr (77.97 ± 4.35 mg/kg), Zn (49.27 ± 3.56 mg/kg), Fe (23031 ± 10.56 mg/kg), Mn (158.68± 8.56 mg/kg) ,V (78.21± 5.34 mg/kg), Sn (8.83± 4.85 mg/kg), Cd (12.91± 52 mg/kg) and As (10.11± 2.93 mg/kg). The enrichment factor (0.209±0.004), contamination factor (0.483±0.003) and Pollution Load Index (0.057± 0.004) indicated that soil in the study area is not polluted. The Potential Ecological Risk Index projected low risk effect whereas Hazard Index and Carcinogenic Risk Index indicated no human health risk associated with exposure to these metals. Bioaccessibility of surface soil samples was estimated using the modified *in vitro* physiologically based extraction test (PBET), with the results indicating that the bioaccessibility of the metals were all below 100%. However, to regulate bioaccumulation effect, constant monitoring is required.



**Keywords**: Bioaccumulation, Bioaccessibility, Contamination factor, Carcinogenic Risk Index, Enrichment factor, Pollution Load Index.

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## LIST OF ABBREVIATIONS

ADD – Average Daily Dose

ATSDR – Agency for Toxic Substances and Diseases Registry

CF – Contamination Factor

CRI – Carcinogenic Risk Index

EC – Electrical Conductivity

EF – Enrichment Factor

FPXRF – Field Potable X-Ray Fluorescence

FTIR – Fourier Transform Infrared

GIS – Geological Information Survey

GPS – Global Positioning System

HDPE – High Density Polyethylene

HI – Hazard Index

HQ – Hazard Quotient

MCd – Modified Degree of Contamination

PER – Potential Ecological Risk

PLI – Pollution Load Index

QA/QC – Quality Assurance and Quality Control

$R_fD$ – Reference Dose

USEPA – United States Environmental Protection Authority

XRF – X-Ray Fluorescence

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## DEDICATION

This research work is dedicated to Enyonam, my wife and Jeremy, my precious son.



# CHAPTER ONE

## 1.0 Introduction

## 1.1 Background

There is cumulative awareness that metals present in soil may have negative disquiets on human health and on the environment, demonstrated by the many books and articles that are published on soil metal bioaccessibility and risk assessment (Ljung., 2007). Industrial sites lay open to point source pollution, which often results in elevated soil metal contents within a limited zone. However, a large share of the metals present in soil originates from diffuse emission sources such as long- and short-range atmospheric deposition. This is obvious in urban soil, where there are more diffuse emission sources, for example traffic and building material, than in rural areas, resulting in short-range atmospheric deposition and a more general increase in metal contents (Filippelli et al., 2005).

Metals are largely immobile in the soil system hence an accumulation occurs over intervals which may result in levels that are harmful to humans upon both acute and chronic exposure. Because of the diffuse emission in urban areas and the accumulation of soil metals with time, even residential areas situated away from point source pollution sources may have substantial soil metal levels (Iii., 2016).

Most of the time, children are exposed to metals present in soil because of their hand-to-mouth behaviour, which puts them in more frequent contact with soil than most adults. Children practice both deliberate ingestion of soil and involuntary ingestion through mouthing dirty hands and objects (Diacomanolis et al., 2016). Children are also more vulnerable than adults to any potential negative health effects of metal ingestion. While their smaller body mass increases the relative exposure to a given quantity of

contaminants (per kg body mass), they also have a higher gastrointestinal absorption of metals (Mielkel and Reagan., 2014). Moreover, because their nervous system is not fully developed, they are more sensitive to neurotoxic metals such as Pb and Hg (Hack et al., 2002).

The potential risk from soil metal intake is dependent on the amount of metal ingested and the bioaccessibility of that metal, which in turn depends on variables both in the soil and in the gastrointestinal environment. Metals in soil are in different chemical and physical forms with different solubilities, affecting bioaccessibility (Frohne and Laing., 2016). Metals from anthropogenic emissions are commonly present in a more reactive form than those naturally occurring in minerals. This is because while added metals are sorbed on surfaces in initial stages, metals of natural origin may be incorporated into soil particles, which slows down the desorption process considerably (Michael et al., 1993). The sorption of metals in soil is, however, a scale of different processes, occurring at the same time and at different rates (Sparks., 2005). Soil pH, organic matter and clay content affect the sorption strength of metals. Lowered pH increases the mobility of metals, while presence of organic matter and clay generally lowers the mobility and increases the metal content because more attractive binding sites are provided (Ljung., 2007).

Metals in soil may exist in different forms but the form in which metals exist in soil determines their ability to dissolve in the gastrointestinal system and be accessible for uptake. Low pH's in the stomach renders metals more mobile but then as metals differ in pH-dependence of their solubility, the effect of the low pH differs among elements (Hameed et al., 2013).This has concerns for risk assessment of soil, since the bioaccessible fraction defines the uptake and hence the probable negative health effect. Studies on bioaccessibility have been conducted *in vivo* on test animals, but as these

methods are time-consuming and costly, *in vitro* studies have been developed that mimics the gastrointestinal system. In reality, the *in vitro* system takes into account enzymes and acids present in the stomach and intestine as well as transit times and pH of both sections, and the gastric and intestinal solutions are mixed at body temperature (Hack et al., 2002). While the method does not permit analysis of the fraction that is taken into circulation in the body, it gives an idea of the maximum fraction that is accessible for uptake, *i.e*. the fraction that remains dissolved after dissolution, complexing and re-adsorption (Rodriguez & Basta., 2014).

### 1.2 Problem Statement

Kumasi is the second largest city in Ghana. The metropolis is noted for its well defined human and natural resources. Commercial activities which are sources of heavy metal pollution in urban soil is evident (Engelhardt., 2012; KMA., 2015). Metals do not biodegrade in nature hence the top soil may have higher concentrations derived from anthropogenic activities. This may be due to atmospheric deposition and abundant organic matter. Four years ago, a research group argued the existence of heavy metals in top soils of the metropolis but then, the research was restricted to commercial areas of the metropolis. There is therefore the need to ascertain the concentrations of metals in peri-urban areas and to estimate their potential risk to human health in the metropolis.

### 1.3 Justification

Inhabitants in the metropolis may be exposed to metal contaminants in soil through ingestion, dermal contact and inhalation of dust from top soil in playgrounds, gardens which may be dangerous to human health. Research shows that children ingest very high fraction of soil compared to adults due to outdoor daily activities. Metal contaminants have the propensity to pose serious health effects such as respiratory

diseases, skin diseases and even destruction of delicate internal organs. The need to ascertain the levels of metal concentration in soil from the metropolis and also to perform human risk assessment to predict potential sources as well as the extent of risk in the study area is key.

### 1.4 Aims and Objectives



The main aim of this work was to determine metal concentrations and bioaccessibility fractions in non-commercial areas of the metropolis and also to compare results with results of metal concentrations in commercial areas.

#### 1.4.1 Specific objectives

The specific objectives were to:

- determine the levels of arsenic, lead, cadmium, mercury, iron, nickel, cobalt, chromium, copper, iron ,manganese and zinc in the top soil of non – commercial areas of Kumasi .
- determine bioaccessible fraction of selected metals to human systems .
- assess the potential risks associated with exposure to the metals detected.

# CHAPTER TWO

## 2.0 Literature Review

### 2.1 Metals in soil

The earth crust serves as a natural repository of metals. Mineralogical and adsorptive properties help to determine metal content in rocks. The masses of metals in ore deposits are small compared to amounts in rock species. The metal content in different regions of the environment differ due to spatial variation of background concentration (Nazir et al., 2015).

Biological importance of metals is used to categorize metallic elements as either heavy metals or essential metals. Heavy metals which include Cd, Cu ,Cr ,Co ,Fe ,Hg , Mn ,Mo ,Ni , Pb ,Zn are defined by metallic properties (conductivity, stability and ductility) as cations with atomic number greater than 20 with density not less than 5.6 $kgdm^{-3}$ (Lanphear et al., 2014).

The fate and distribution of metals in the environment depends on the properties of the metals which includes the forms they exist. In the environment, metals exist mostly in inorganic (ions or salts) and organic forms (Paterson., 1996). The ability of metals to spread and to be used is explained by their stability in the environment, their ubiquitous nature, toxicity and their ability to persist in the environment (Beighton., 2013).

Top soils record higher concentrations of metals. High levels of metals in soil may be derived from human activities such as vehicles and industrial exhaust as well as emissions and waste disposal. Natural weathering processes can release metals from their parent materials increasing concentrations in soil (Schroder et al., 2004). However metals released from such natural processes deposits on soil surfaces are relatively low concentrations (Caussy et al., 2003).

## 2.2 Sources of metals in soil

Urban centres have suffered from large amounts of contaminants especially heavy metals due to rural urban drift. It receives tons of contaminants annually from anthropogenic activities as a result of urban cities relatively dense populated (Caussy et al., 2003).

Pb, Fe, Zn, Cr and Cd are the most frequently reported heavy metals due to their potential hazards and occurrence in contaminated soils. Soils acts a carrier of contaminants and also the secondary potential source of metals in the environment hence remains an important source for the assessment of man- made contaminants (Wu et al., 2015).

Industrial and human activities generally contribute to the increased levels of the metal in urban soil. These activities include improper disposal of waste, fossil fuel combustion, automobile exhausts, mining activities, sewage sludges, the use of inorganic pesticides (herbicides, wood preservatives) as well as metal processing leads to metal accumulation in various layers of urban soil.

## 2.3 Occurrence and Transport of Metals in Soil

Anthropogenic activities release great amount of metal contaminants into soil which are responsible for increasing levels of pollution in the environment (Frohne and Laing., 2016). The degree of toxicity depends on the forms in which these metals exist. Metals such as mercury and Lead exist in organometallic form which is more poisonous than their inorganic forms. Persistence in the environment results in bioaccumulation through the food chain and consequently posing their toxic effects on humans and the environment (Tong et al., 2000).

Bioaccumulation of toxic metals results in transport of these metals from their point of contamination to different locations of the environment. The existence of toxic metals in soil does not account for its toxicity to living organisms and the environment (Caussy et al., 2003).

Hence it is key to know the medium of transportation of metals in the environment (Nazir et al., 2015).



In an ecosystem, transport of metals are governed by natural organic matter content ,redox condition, availability of water, air, climate (temperature & precipitation),dilution, desorption, adsorption, evaporation and soil pH (Caussy et al., 2003).

Transportation of toxic metals through aqueous medium is controlled by soil pH. pH is a key parameter which helps in the determination of metal movement due to hydrolysis. At low pH , most metals are available in aqueous media and as a result more mobile than in alkaline or neutral condition (Mielkel and Reagan., 2014). pH of aqueous solution of metals is buffered to a more basic condition due to carbonate solubility and bicarbonate buffering (Caussy et al., 2003). This is evident when aqueous solution metals percolates soil rich in limestone ($CaCO_3$) (Mielkel and Reagan., 2014). A pH of six (6) or less is attained when water percolates soil rich in granite minerals or sandy deposits. Metal transportation in soil is also controlled by the availability of organic matter content. Organic matter rich in humic acid eventually decreases soil pH and that may lead to increase in mobility of metal ions (Wu et al., 2015) .

Erosion or as wind-blown dust is another possible rout of toxic metals transportation in soil surface. Vaporization as another route of transport controls the mobility of volatile metals, especially mercury, even metalloids such as arsenic and antimony, from soil

and surface waters to the atmosphere (Dope et al., 2016). This is an important transport mechanism during forest fires. When the metals are transferred to the atmosphere, their residence time vary depending on reactivity and state of the metals. In the atmosphere the metals may be transformed through chemical reactions which may result in precipitation. Precipitation of the metals can either wet or dry deposition over water or land (Walraven et al., 2015).



**2.4 Biological and Economic Benefits of Metals**

Metals unveil biological effects that can be beneficial or harmful depending on the concentration the living organisms are exposed to (Walraven et al., 2015). The body requires a number of essential metals for its proper function. Metals such as Fe, Cu, Co, Mn, Zn, and Cr are known to be essential elements for humans with their deficiency states associated with major clinical abnormalities. Some metals play most important roles in active centers of metallo-enzymes in the human biological system. Other metals, such as chromium (III) and vanadium, are metabolized within the body to form low molecular weight compounds that regulate glucose metabolism (Luo et al., 2012). Human deficiency in chromium disrupts glucose metabolism which causes obesity, diabetes, and cardiovascular disease, as well as impairment of the reproductive system. Research shows that a diet lacking the essential metal selenium is a potential cause for heart attack (Reeder et al., 2006).

Metals also have unique benefits in the fields of agriculture, industry, and medicine (Caussy et al., 2003). Metals such as mercury, arsenic, copper, and tin are used in the production of biocides such as pesticides and herbicides. Some are also used in the production of fertilizers for effective agricultural activities. Industrially, metals are used to produce paints and aerosols. Hg is globally used as a catalyst in the production of chlorine gas and caustic soda, and as an amalgamator in the extraction of gold, and in

batteries and electrical switches (Tong et al., 2000). Although banned in many countries (e.g., Norway, Sweden and Denmark), Hg is still used worldwide as amalgams in dental fillings (USEPA., 2007). In the medical field metals are used to manufacture metal supplements used to cater for the deficiency of essential metals required in humans and animals. Numerous uses of metals, makes metals economically important and can contribute significantly to economic growth (Peijnenburg et al., 2007).



**2.5 Exposure Pathways of Heavy Metals**

Exposure pathways of toxic metals to humans are described by many researchers because of its importance in heavy metal contamination and also the major health effects associated with human exposure to the metal contaminants. Exposure for each metal occurs through several exposure pathways that depend on the particular contaminated media of air, soil, water, or food and on the target population (Caussy et al., 2003).

The exposure pathways include ingestion through the gastrointestinal tract, inhalation through the respiratory tract, and dermal contact (Glennon et al., 2014; Luo et al., 2012; Qing et al., 2015; Reeder et al., 2006). The physical form or the state of the metal contaminant dictates the extent of the exposure. Metals can be in the form of solid, liquid, or gas (Reeder et al., 2006). The potential primary exposure pathway for arsenic pollution from airborne particles such as mineral dust is inhalation. Direct contact (ingestion) may be a potential significant pathway of exposure to heavy metals especially for young children of age two to six. Children also have the ability to absorb higher percentages of metals through the digestive system into the blood stream than adults, which makes children susceptible to adverse health effects (Tsuka et al., 2012). Many researches on models of different exposure pathways for children have been

designed and also the studies reported that ingestion as a pathway for exposure of soil metal contaminants such as lead, by a child's daily intake represent between 72 and 91 % (Clark et al., 2008; Hamel et al., 1998b).

Whatever the source of the heavy metal contamination, chronic exposure to soil associated with unsafe heavy metal contamination is not desirable because of the risk associated with the exposure to metals by living organisms (Schulin et al., 2009). A lot of studies have shown that people of lower socio-economic status may be highly exposed to conditions that increase their risk of developing health problems associated with exposure to heavy metal contamination. The condition people may be exposed to include poor diet and insufficient quantities of food, and also living in high density and low quality housing (Hameed et al., 2013).

The risk of exposure to heavy metals in soils is estimated by calculating for hazard quotients which is then used to calculate hazard index (HI). Hazard quotient is the ratio of the average daily dose of a toxic substance to its reference dose, as predetermined by government environmental regulatory agencies (Frohne and Laing., 2016). The hazard index calculated from the hazard quotient is used to assess the risk posed by more than one exposure pathway and also helps to determine risk associated with a particular metal (Swarnalatha et al., 2015). The hazard index is the sum of hazard quotients calculated for all toxic metals an individual is exposed to, from all possible pathways. A hazard index greater than one (HI > 1) for soil metals contaminants in a community indicates that the inhabitants are at risk for negative health effects at some point in their lifetime (Swarnalatha et al., 2015).

## 2.6 Bioavailability and Bioaccessibility

Metals vary greatly in their reactivity and bioavailability or ability to enter organism and cause toxicity (Poggio et al., 2009b). Studies indicate that only a fraction of the ingested contaminants, known as bioaccessible fraction, could be finally absorbed and the remaining fraction is excreted (Reeder et al., 2006). After the ingestion and subsequent absorption, a fraction of the metal contaminant accumulates systematically in the blood or tissues of the living organism. A fraction of the accumulated metal then becomes bioavailable to the various target organs and in effect has the potential to produce toxic effects to organisms (Caussy et al., 2003; Hamel, Buckley, & Lioy, 1998; Peijnenburg & Jager., 2003). It is therefore important to assess the bioavailability of the metal contaminant to determine the potential health effects associated with the ingestion of the metal contaminated soil.

The amount of metal absorbed is dependent on the individual, the form of the metal within the soil, and the soils physical characteristics. Also absorbed fraction depends partly on the intrinsic absorptive capacity of the organ as well as on host factors. Though cation-exchange capacity can influence bioavailability in soils; pH is also an important factor controlling partitioning in metal ions. Organic carbon rich in humic acids is the most importance medium for interactions of metal ions (Caussy et al., 2003; Reeder et al., 2006).

Metal bioaccessibility is the fraction of the metal contaminant that dissolves in the digestive system and is assumed to be available for absorption (Ruby et al., 1999; Peijnenburg et al., 2007). Bioavailability and bioaccessibility often determine whether the concentration at which a metal contaminant is present will have effects on organisms or not.

## 2.7 Toxicity and Health Effects of Heavy Metals

Toxicity and negative health effects associated with heavy metals in soils is of much concern to researchers and regulatory agencies (Peijnenburg et al., 2007; Sliggers and Jager., 1993). Although essential metals are known to exert biological functions in human circulatory system, high doses of these same metal elements can cause serious toxic effects (Caussy et al., 2003). Other metals such as mercury, lead, cadmium, and arsenic are not known to exert biological functions or be essential for any animal or humans (Walraven et al., 2015). Certain amounts of a metal or metal compound released into the gastrointestinal tract after exposure to heavy metals get absorbed, accumulate and then becomes available in the human circulatory system and eventually poses toxic treat to humans (Frohne and Laing., 2016). Some metals like cadmium accumulate in the human body for a long period of time meaning negative effects may appear only after a long period of chronic exposure. Exposure history is an important factor in evaluating the toxicity of a metal (Nazir et al., 2015). The toxicity can be classified in acute toxicity and chronic toxicity. Acute toxicity is associated with short term exposure to a toxicant while chronic toxicity is associated with long term exposure which is the type most relevant to environmental toxicants (Qing et al., 2015; Reeder et al., 2006).

The main toxicity targets include skin (As), nervous system (Pb, Hg, As), blood (Pb, As), kidney (Pb, Hg, Cd), lung (Cd), and cancer (As, Cd, Cr). The toxicological effects associated with environmental exposures which cause adverse health effects in the long run can be described in terms of biochemical variables, neurological endpoints, intelligence, verbal ability, activity disorders, and DNA damage (Laird et al., 2014; Wu et al., 2015). The toxic effect associated with metal contaminants is metal dependent. And so, each metal has a significant disease causing effects, which is partly dependent

on the specific metal and since the potential health impacts associated with each metal are enormous: lead affects almost every organ and system in humans (developmental, cardiovascular, reproductive, neurological, ocular, hematological, and renal; inorganic arsenic is a known human carcinogen; while chronic exposure to cadmium can result in kidney disease, brittle bones and decreased lung function) it has always been a concern for researchers as reported by the Agency for Toxic Substances and Diseases Registry (ATSDR., 2015). Also exposure to environmental metal contaminants have been associated with serious health effects in terms of biochemical variables, intelligence, verbal ability, long-term memory activity disorders, and damage to DNA in humans (Wu et al., 2015).

# CHAPTER THREE

## 3.0 Materials and Method

### 3.1 Study area

Kumasi is a city in Ashanti region and is among the largest metropolitan areas in Ghana. The metropolis which is between latitude 6.35º – 6.40º and longitude 1.30º –1.37º is a commercial, industrial and cultural capital of Asanteman. The metropolis is approximately 500 kilometers north from the equator and 200 kilometers north of the Gulf of Guinea. Kumasi features a tropical wet and dry climate, with relatively constant temperatures throughout the year and two different rainy seasons, a longer rainy season from March through July and a shorter rainy season from September to November. The metropolis serves as major commercial centre with commercial activity being centered on wholesaling and retailing with both financial and non-banking financial institutions also offering ancillary services for residents of the metropolis (Engelhardt., 2012; KMA., 2015). Since the metropolis provides a platform for numerous industrial activities, there is a likelihood of soil metal contamination through anthropogenic activities (Darko et al., 2017).

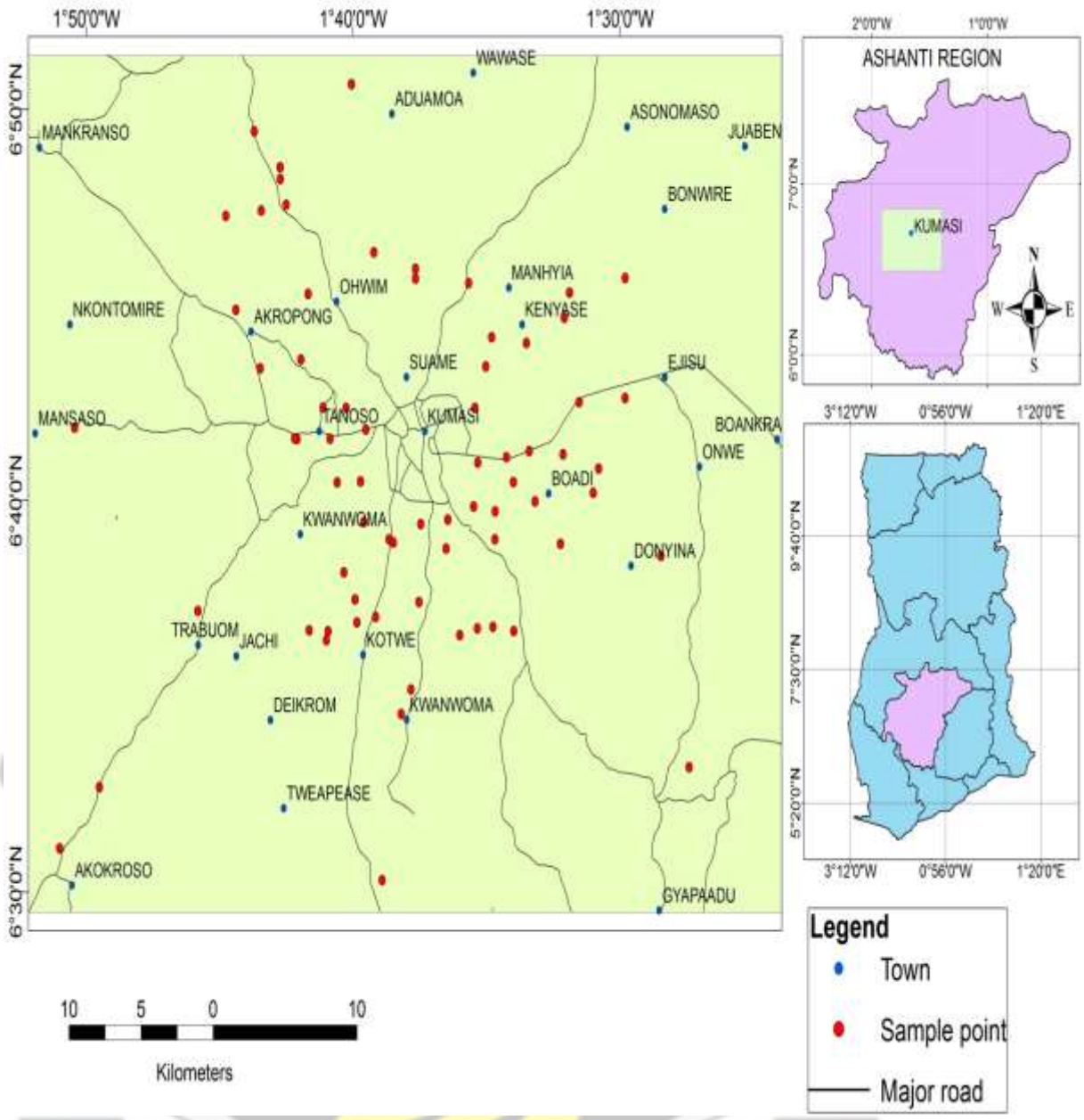



**Figure 3.1: Map of Kumasi showing sampling locations**



### 3.2 Health and Safety

A check of sampling sites was undertaken before the actual field sampling to help in the identification of the various hazards, easily accessible routes, as well as implement and abate measures to control those hazards. The measures include parking in

designated parking places, taking samples from sites without heavy traffic first and wearing personal protective clothing.

### 3.3 Soil Sampling

There were 73 sampling sites included in the study area. The sites were located in a systematic grid net map using a regular 2 km × 2 km over the survey (ArcGIS). The point of intersection of the various longitude and latitude coordinates on the grid map was selected as the specific sampling points. At site locations where sampling was not possible due to interference such as tarred roads, rivers, and houses, sampling was done by shifting or moving to a different location within the same sample cell (Darko et al., 2017).

Soil samples were taken from the top 0 - 10 cm depths at all locations using a plastic trowel to avoid metal contamination from the trowel. The top soil especially 0 - 10 cm was assumed to be the layer human beings are most exposed to during their daily activities and likely to provide human exposure risk estimates. Specific sampling codes were given to each sampling point, ["Kumasi Sample Number (KSN) 01 to Kumasi Sample Number (KSN) 75"] and the position of sampling sites was recorded using a hand-held global positioning system (GPS). Soil sampling was carried out in December, 2016.

Soil samples were transferred into sealed, labeled polyethylene bags. Cross contamination of digging equipment was avoided after each sample collection by scrubbing the trowel with a tissue paper, using an Aquet detergent solution (pH 5-9) and distilled water for rinsing after the collection of each sample.

### 3.4 Sample Preparation and Analysis

#### 3.4.1 Drying and Sieving

The soil samples were air dried at room temperature to ensure that they were moisture free. Each of the dried soil samples was sieved to <250 µm using USA Standard Testing Sieve ASTM E11 and packed into coded polyethylene bags.

#### 3.4.2 Screening Analysis

Approximately 20% of the soils sample were selected for detailed laboratory analysis including PBET. The sieved samples were split into two portions: one set of the samples was analyzed for metal concentrations using a Niton field portable x-ray fluorescence analyzer (FPXRF) while the second set was subjected to the bioaccessibility assay using an *in vitro* method (Dodd et al., 2013; Koch et al.,2013). Laboratory quality assurance/quality control included replicates (10%), procedural blanks and standard reference materials.

The optimization of the XRF to generate useable data were conducted as part of this project. Soil pH and electrical conductivity were also determined with a portable pH/EC meter.

### 3.5 Extraction for Bioaccessibility

#### 3.5.1 Soil Digestion for metal determination

The sieved soil samples were analyzed for total metals after modified aqua regia digestion. A mass of 0.5 g sample was added to 3 mL of 1:1:1 HCl-$HNO_3$-$H_2O$ mixture. The mixture was, digested at 95 °C for 1 hour on a heating block. The sample was made to volume with dilute HCl and analyzed by ICP-MS (US EPA., 2007).

### 3.5.2 Extraction

The extraction protocol was based on the Standard Operating Procedure for an *In Vitro* Bioaccessibility Assay for Lead in Soil, EPA Method 9200.2-86 (US EPA., 2007). QA/QC included a procedure blank and a laboratory control sample. The sieved soil sample was weighed by difference (1.00 ± 0.05 g) into a 125 mL acid cleaned HPDE bottle. An aliquot of 100 ± 0.5 mL of extraction fluid was measured and added to the bottle. This yielded a sample mass to fluid ratio of 1:100.The pH of the soil/extraction fluid mixture was measured. The extraction solution consisted of 30 g/L glycine (Calbiochem) adjusted to a pH of 1.5 with concentrated HCl (Fisher Scientific, trace metal grade). The bottle was then sealed and placed into the extractor in batches of eight and rotated end-over-end in a 37± 2 $^{o}$C water bath for 1h. After the extraction was completed, the bottles were removed. Each extract was drawn directly into a disposable 20 mL plastic syringe with a luer slip (National Scientific). A 0.45 µm cellulose acetate filter (25 mm diameter, Cole Palmer) was attached to the syringe and the extract was filtered into a clean 20 mL polyethylene scintillation vial (Wheaton). The filtered extract was stored at 4 $^{o}$C and subsequently analyzed for metals by ICP-MS (US EPA., 2007).

### 3.5.3 Analysis for Metals in Extracts

Metal analysis was conducted with an Agilent Model 7500ce Collision Cell ICP-MS based on United States Environmental Protection Agency (US EPA) SW846 Method 6020A, Inductively Coupled Plasma - Mass Spectrometry, Revision 1 (USEPA., 2007).

### 3.5.4 Bioaccessibility calculation

Bioaccessibility was calculated for As, Cr, Cd, Co, Cu,Fe, Pb, Ni and Zn using the formula adapted from the USEPA standard operating method for accessing in-vitro extraction test as follows:

$$Bioaccessibility, \% = \frac{(concentration\ in\ extract, \mu g/L) \times (volume\ of\ extract, L)}{(conentration\ in\ soil, mg/kg) \times (mass\ of\ soil\ used, g)} \times 100$$

(Darko et al., 2017).

### 3.6 Analysis for Total Metal Concentration

Soil samples were screened using a Niton XL3t GOLDD+X-ray fluorescence analyzer. XRF analysis followed the United States Environmental Protection Agency (USEPA) method 6200 Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment (USEPA., 2007b). The XRF was calibrated and system check was completed before it was used for the metal concentration analysis.

During the analysis, an aliquot of the sieved sample was placed in a small (approximately 30 mm) polyethylene container so it was three quarters full. A Mylar film was placed over the cup and an open cap was secured to seal the soil in the Mylar. The sample was then placed in the XRF shroud and the scan was conducted on each sample for a total duration of 180 seconds.

### 3.7 Soil pH and Electrical Conductivity

The soil pH and soil electrical conductivity (EC) were also determined using a pH meter and probe of model HANNA HI 9829 (Multi-Parameter). The pH and EC analysis was

performed by dissolving 20 g of the dry soil in 40 mL of distilled water (that is 1:2 ratio of dry soil to distilled water).

### 3.8 Analysis for Total Organic Content

Soil samples were analyzed for total organic carbon (TOC) using loss on ignition (LOI) method. The LOI is a semi-quantitative method for the determination of organic matter which calculates the difference between the initial and final weights of a sample after heating (Schumacher, 2002). Conversion factors were then applied to account for the ratio of carbon in organic matter to account for the total organic carbon. A reproducibility study and method which indicates organic carbon combust at 550 $^{o}$C is outlined by Heiri, Lotter & Lemcke (2001) and was used for this analysis.

About 1 g of the soil sample was weighed directly into the crucible and placed in a pre-heated oven at 105 $^{o}$C for two hours. The samples were cooled to room temperature in a desiccator before weighing. Samples were then placed in Thermolyne muffle furnace, pre-heated to 550 $^{o}$C for four hours. After four hours, samples were removed from the furnace and cooled to room temperature in a desiccator and weighed. Replicates measurement were carried out to ensure reproducibility of results.

Total Organic Content of soil samples calculated from the formula

$$TOC = \frac{Mo}{Md} \times 100\%$$

*where Mo is the mass of organic matter*

*Md is the mass of dry soil sample*

(Schumacher., 2014)

### 3.9 Quality Assurance and Quality Control

#### 3.9.1 Soil Sampling and Handling

Quality assurance (QA) and quality control (QC) procedures used during soil collection, and handling procedures included:

- Soil sample containers used were supplied by the laboratory to minimize sample container contamination;
- Soil samples collected were placed directly in the laboratory supplied containers in the field and sample number was placed on each bag;
- Equipment and materials that contacted soil (i.e., shovels) were decontaminated between sample collection to minimize the possibility of cross contamination;
- New latex or nitrile gloves were used for each sampling event to minimize potential cross-contamination;
- Duplicates were extracted from within and between different batches to ensure batch quality control.

### 3.10 Estimation of Contamination

Determining the level of pollution by a given heavy metal requires that the pollutant concentration be compared with a reference material, which would then be used as a benchmark for representation of data. The processing, analyzing and communicating of raw environmental data as well as distinguishing the source of contaminants require the use of pollution indices. Various methods for quantifying the degree of metal enrichment in soils and sediments have been suggested (Chen et al., 1997; Fergusson., 1990; Qing et al., 2015; Wong et al., 2006). Pollution impacts range from 'low' to 'high' intensity have been proposed to convert the calculated results into the bands of pollution. The level of heavy metal contaminants in soils was evaluated using the

enrichment factor (EF), contamination factor (CF), modified degree of contaminations (MCd), and potential ecological risk (PER) (Qing et al., 2015; Wu et al., 2015).

### 3.10.1 Enrichment Factor

Enrichment factor (EF) is used in assessing the degree of heavy metal pollution from anthropogenic sources. It can also be used to differentiate the source of metal pollution whether it is anthropogenic or naturally occurring. Normalization of measured heavy metal such as iron is usually done by the enrichment factor. This is due to the relatively high natural concentrations of iron and is therefore not expected to get a large amount enriched from anthropogenic sources in soils and sediments (Swarnalatha et al., 2015). The EF is calculated as in equation (1).

$$EF = \frac{Ms \times Fer}{Mr \times Fes} \qquad (1)$$

Where: *Ms* and *Fes* are heavy metal and Fe concentrations in the soil sample respectively, *Mr* and *Fer* are the concentrations of the heavy metal and Fe in a reference material. EF >1 means the metal concentration in the soil sample is enriched relative to the average shale values and the source may be anthropogenic. EF < 1 indicates that the metal concentration is not enriched and may be from natural source. EF=1 indicates that the metal concentration and its reference value are the same.

### 3.10.2 Contamination Factor

Contamination factor (CF) is the ratio of metal concentration in the soil sample to the background metal concentration of the corresponding metal (Hakanson., 1980). The CF accounts for the metal enrichment in the soil and it was calculated using equation (3).

$$CF = \frac{Ms}{Mr} \qquad (2)$$

Where: *Ms* and *Mr* are the mean concentrations of the metal contaminants in the soil samples and background reference material respectively. The CF was calculated and based on the magnitude was classified as either low (CF≤1), moderate (1-3), considerable (3-6), or very high ( CF≥6) (Chen et al., 2015; Hakanson., 1980; Wu et al., 2015).



### 3.10.3 Pollution Load Index

To estimate the overall pollution status for a sample, the pollution load index (PLI) of metal contaminants was calculated. The PLI for a particular sample location can be calculated from the CF of each of its constituent samples (Chen et al., 2015; Qing et al., 2015) as in equation (4).

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CFn)^{1/n} \quad (3)$$

Where: *CF* represents the contamination factor of the corresponding metal, n represents a specific metal's contamination factor. The PLI values are classified as unpolluted (PLI≤1), moderately polluted (1-3), highly polluted (3-5), or very highly polluted (PLI>5) (Qing et al., 2015).

### 3.10.4 Modified Degree of Contaminations

Degree of contamination (Cd) and modified degree of contamination (mCd) can be used to describe the toxicity of a metal contaminant. The degree of contamination is based on the calculation of the CF for each pollutant as in equation (5) and is a measure of the degree of overall contamination in surface layers (Swarnalatha et al., 2015).

$$Cd = \sum_{i=1}^{n} CF \quad (4)$$

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

Modified degree of contamination (*mCd*) is the ratio of the sum of all the contamination factors for a given set of soil metal contaminants to the number of analyzed contaminants. It is calculated as shown in equation (6).

$$mCd = \frac{Cd}{n} \quad (5)$$

Where: *Cd* is the degree of contamination and *n* is the number of analyzed metals. The *mCd* is classified as shown in Table 3.1 (Swarnalatha et al., 2015).

**Table 3.1: Modified degree of contamination and its description**

| mCd values | Contamination description |
|---|---|
| mCd < 1.5 | Nil 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 |

### 3.10.5 Potential Ecological Risk

The potential ecological risk (PER) index was used to assess the degree of heavy metal pollution in soils based on the toxicity of heavy metals and the response of the environment. The *PER* was calculated as the sum of individual risk index (*RI)* (Hakanson., 1980) as follows:

$$PER = \sum_{i}^{n} RI \quad (6)$$

$$RI = Trf \times CF \quad (7)$$

Where: *Trf* is toxic response factor for a given heavy metal. Toxic response factor for metals are in the order Zn=1, Cr=2, Co=Cu=Pb=5, Ni=6, As=10, and Cd=30. *CF* represent contamination factor of a single metal pollutant. The degree of ecological risk can be classified as; RI < 40 (low risk), 40 ≤ RI < 80 (moderate risk), 80 ≤ RI < 160 (considerable risk), 160 ≤ RI < 320 (high risk), and RI ≥ 320 (very high risk) (Qing et al., 2015; Wu et al., 2015).



### 3.10.6 Human Health Risk Assessment

Exposure to metal contaminants in the urban top soil poses serious risk to human health and can be non-carcinogenic and or carcinogenic. Humans are exposed to the metal contaminants through three exposure pathways: ingestion, dermal contact and inhalation. Sensitive population especially children are the most vulnerable to risk. The risk assessment was done based on the model of USEPA (USEPA 1989., 2001). The models express human health risk as a numeric quantity and as a result are more easily comprehended. The susceptibility of children and adults was separately considered.

The assessment of non-carcinogenic risk requires the determination of the average daily doses (ADDs) (mg/kg/day) of toxic metals through ingestion (ADDing), dermal contact (ADDderm), and inhalation (ADDinh) for both adults and children. The average daily doses represent the daily exposure levels of specified parameters for humans without any appreciable risk of their deleterious effects during a lifetime. The average daily doses for both children and adults were calculated as follows:

$$ADDing = Msoil \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (8)$$

$$ADDinh = Msoil \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (9)$$

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

(USEPA ., 2012).

Where: *ADDing*, *ADDderm*, and *ADDinh* are the daily doses of metals (mg/kg/day) through ingestion, dermal contact, and inhalation respectively. The factors or parameters used in the model applied to calculate the average daily dose and risk are given in Table 3.2.

**Table 3.2: Parameters used in the Exposure model for health risk assessment**

| **Parameter** | **Unit** | **Children** | **Adults** |
|---|---|---|---|
| Heavy metal concentration in soil (*Msoil*) | mg/kg | | |
| Ingestion rate of soil (*IngR*) | mg/day | 200 | 100 |
| Exposure frequency (*EF*) | days/year | 350 | 350 |
| Exposure duration (*ED*) | years | 6 | 24 |
| Body weight (*BW*) | kg | 15 | 55.9 |
| Average time (*AT*) | days | 365 ED | 365 ED |
| Inhalation rate of soil (*InhR*) | $m^3$/day | 7.63 | 12.8 |
| Particle emission factor (*PEF*) | $m^3$/kg | $36\times10^9$ | $1.36\times10^9$ |
| Exposed skin surface area (*SA*) | $cm^2$ | 1600 | 4350 |
| Skin adherence factor (*AF*) | mg/cm/day | 0.2 | 0.7 |
| Dermal absorption factor (*ABF*) | constant | 0.001 | 0.001 |

Reference: (EPA., 1989, 2001; Qing et al., 2015; Swarnalatha et al., 2015; US EPA., 2009)

Hazard quotients (HQ) were calculated from the ADD values. The values from the HQs were used to estimate the hazard index (HI) which are used to assess risk of the metals (Swarnalatha et al., 2015). The *HQ* is the ratio of the *ADD* of a heavy metal to its reference dose ($R_fD$) for the same exposure pathway. That is

$$HQ = \sum \frac{ADD}{RfD} \quad (11)$$

The reference dose is the maximum daily dose of a metal from a specific exposure pathway for both children and adults which is believed not to lead to an appreciable risk of deleterious effects to sensitive individuals during a lifetime. HQ>1, indicates the potential of a metal to adversely affect human health by non-carcinogenic effects. HQ<1, indicates that there will be no adverse health effects (Qing et al., 2015; Swarnalatha et al. 2015).

Due to exposure from the three exposure pathways, evaluating the total potential of non-carcinogenic risks posed by more than one pathway, the hazard index (HI) was introduced. The *HI* is the sum of the *HQ* values from all applicable pathways. That is;

$$HI = \sum HQ, \text{ or } HI = HQ \text{ (ingestion)} + HQ \text{ (dermal)} + HQ \text{ (inhalation)} \quad (12)$$

HI < 1, indicates no risk of non-carcinogenic effects, and HI > 1, indicates a probability of adverse health effects occurring.

Carcinogenic risk is estimated as the probability of an individual developing cancer, over a lifetime as a result of exposure to a potential carcinogenic hazard (Qing et al., 2015; Swarnalatha et al., 2015; Wu et al., 2015).

The Carcinogenic risk was estimated as;

$$Carcinogenic\ Risk\ (RI) = \sum ADDc \times SF \quad (13)$$

Where; *ADDc* is average daily dose for carcinogenic metals, and *SF* is slope factor. The *SF* value represents the probability of developing cancer per unit exposure level (mg/kg/day). *SF* values are available in literature for only carcinogenic metals like Ni, Pb, Cd, and As. And as result carcinogenic risk was found for these metals only. The values of $R_fD$ and *SF* are also in Table 3.3.

The *RI* is classified as RI < $1 \times 10^{-6}$ (negligible and therefore acceptable), RI above $1 \times 10^{-4}$ (likely to cause cancer). The acceptable range of carcinogenic risk according to USEPA is in the range of $1 \times 10^{-6}$ to $1 \times 10^{-4}$ (USEPA., 1989).

**Table 3.3: Reference dose ($R_fD$) (µg/kg/day) and Slope factors (SF) in (mg/kg/day) for estimating carcinogenic risk**

| Metal | Cr | Co | Ni | Cu | Zn | Pb | As | Cd |
|---|---|---|---|---|---|---|---|---|
| $R_f$Ding | 3 | 0.3 | 20 | 40 | 300 | 1.4 | 0.3 | 0.5 |
| $R_f$Dderm | 0.015 | 0.06 | 5.4 | 12 | 60 | 0.42 | 0.123 | 0.005 |
| SFing | | | 0.91 | | | 0.042 | 1.50 | 15 |
| SFderm | | | 0.91 | | | 0.042 | 3.66 | 15 |

$R_f$Ding reference dose for ingestion, $R_f$Dderm reference dose for dermal contact and SFing slope factor for ingestion, SFderm slope factor for dermal contact (USEPA., 1989 ; Swarnalatha et al., 2015).

# CHAPTER FOUR

## 4.0 Results and Discussion

### 4.1 Soil pH and Conductivity

pH results of samples in the study were in a range of 6.5 and 8.5 in deionized water. pH of most soil samples were slightly neutral to basic ranging from 7.01 to 8.5. Sample sites KSN3, KSN5, KSN14, KSN33, KSN44, KSN45 and KSN49 ranged from 6.5 to 6.9. Soil samples of lower pH values were from locations where vehicular activities were very high. The account for acidity of soil samples may be spillage of acidic solution (from batteries) in the soils of study area. Spillage of acidic solution can have an effect on the water table and plant growth since cation mobilization is high in acidic media. Soil pH also has effects on solubility and metal retention in soil. In general lower solubility and higher retention is observed at higher pH. Comparing pH result of this study to Darko (2017) based on commercial areas in the Kumasi metropolis, soil samples from commercial areas were more acidic compared to samples across non-commercial areas. This may be due to pronounced anthropogenic activities at commercial areas. Electrical conductivity (EC) of soil samples analyzed gave minimum and maximum values of 153 μS/cm and 8990 μS/cm respectively with an average of 1133.205 μS/cm which probably indicates soil across non-commercial suburb of Kumasi metropolis have high levels of inorganic ions including metals. Total organic content gave positive weak correlation with As and Fe ($0.24 \geq 0.50$, $p < 0.05$) and very weak positive correlation with Cu (0.21, $p < 0.05$). Correlation analysis also shows that TOC has strong positive correlation with Mn and Ni ($0.50 \geq 0.59$, $p<0.05$) this could probably mean TOC has an influence on metal concentration.

### 4.2 Heavy Metal Concentration using XRF

The concentration of all metals analyzed in soil samples from study area are indicated in Table 4.1. Concentration of heavy metals (As, Pb, Cu, Ni, Cr, Zn, Fe, Mn, V, Sn and Cd) in top soil of non-commercial suburb across Kumasi metropolis at different sampling points, descriptive statistics ,the Dutch and Canadian guidelines are summarized in Table 4.1. Fe recorded the highest concentration value of 166298 mg/kg with a mean concentration of 23064 mg/kg. Mean concentrations of the metals were in the order;

Sn< As< Cd<Pb< Cu< Ni< Zn< Cr< V< Mn< Fe.

**Table 4.1: Descriptive Statistics of Metal Concentration (mg/kg) using XRF and Physicochemical Parameters (n=73)**

| Metal | Maximum | Minimum | Average | Standard Deviation | CCME (CCME,2007) | Dutch Target VROM,2000 |
|---|---|---|---|---|---|---|
| As | 55.18 | 2.54 | 10.117 | 11.486 | 12 | 29 |
| Pb | 55.65 | 7.500 | 18.596 | 18.760 | 140 | 85 |
| Cu | 41.27 | 9.79 | 20.198 | 9.119 | 63 | 36 |
| Ni | 55.85 | 20.01 | 29.327 | 10.128 | 45 | 35 |
| Cr | 275.7 | 9.67 | 77.928 | 74.107 | 64 | 100 |
| Zn | 419.23 | 13.1 | 49.273 | 58.993 | 200 | 140 |
| Fe | 166298 | 3031 | 23031 | 28465.4 | - | - |
| Mn | 969.43 | 34.15 | 158.680 | 133.547 | - | - |
| V | 202.48 | 10.96 | 78.217 | 41.146 | - | - |
| Cd | 27.79 | 7.68 | 12.914 | 5.470 | 10 | 0.8 |
| Sn | 22.53 | 4.27 | 8.832 | 4.619 | - | - |
| EC | 8990 | 153 | 1133.205 | 1393.39 | - | - |
| pH | 8.5 | 6.5 | 7.5 | 0.144 | - | - |

### 4.2.1. Vanadium

Fertilizer application happens to be the main source of V introduction to surface soil. V in surface soil has high mobility in neutral to alkaline solution (Wu et al., 2015). Levels of V in soils samples were in the range of 10.96 mg/kg - 202.48 mg/kg with a mean concentration of 78.22 mg/kg. The mean concentration of V (78.22 mg/kg) at non-commercial areas were very low compared to levels recorded by Darko's study (17310 mg/kg) (Darko et al., 2017). This may be due to less anthropogenic activities at non-commercial areas compared to commercial zones. Whereas Kenyase, Aduamoa, and Denkyemmoso recoreded low levels of V, Kotwi and Mansaso recorded higher levels. Levels of V may be attributed to dumping of solid waste and sludge in these locations (Dope et al., 2016).

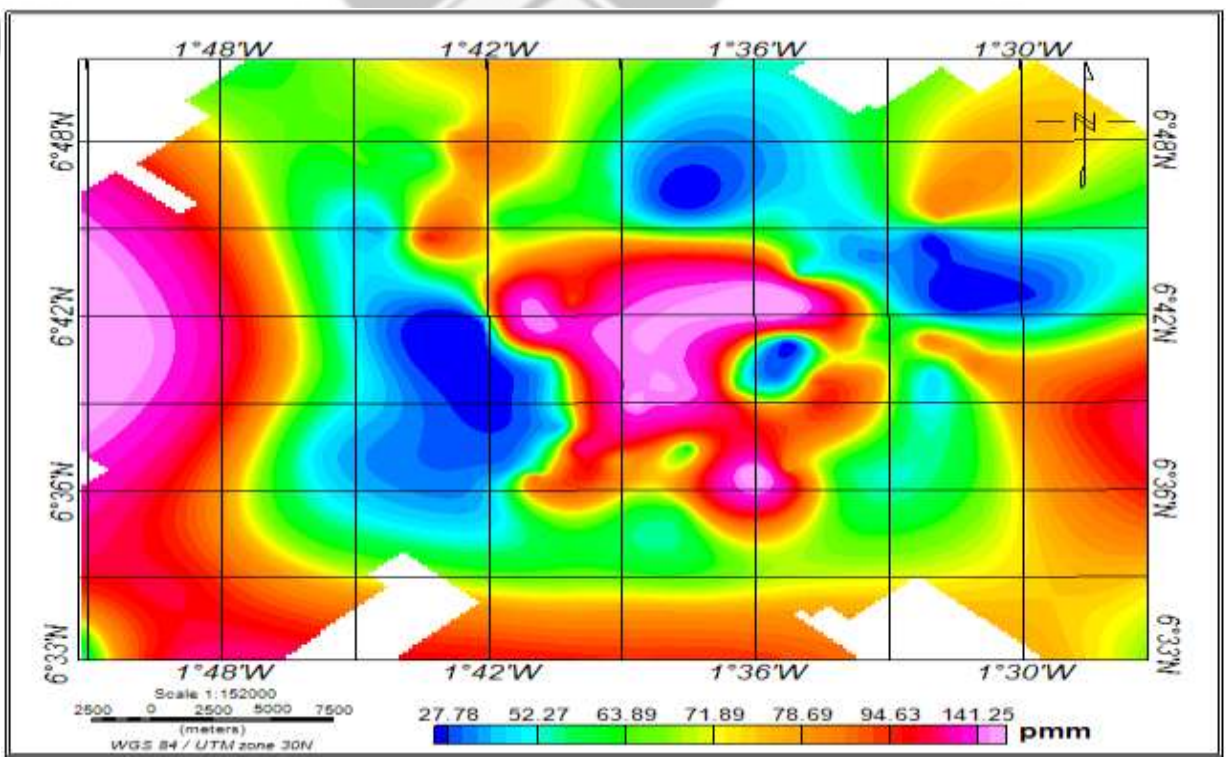



**Figure 4.2: Concentration distribution of Vanadium at Peri-Urban centres of Kumasi.**

### 4.2.2. Arsenic

Although the maximum and minimum recorded values of arsenic during the study were 55.18 mg/kg and 2.54 mg/kg with a mean concentration of 10.12 mg/kg. Whereas Kotei, Jachie Pramso, Agric Nzema and Owabi Forest Reserve recorded very low levels, Odium, Daaban, Sokoban and Atasomanso recorded higher values. The presence of arsenic in non-commercial locations of the metropolis maybe from anthropogenic sources which include the use of arsenic containing herbicides and pesticides, leaching of wood preservatives as well as waste management from feed (Caussy et al., 2003).

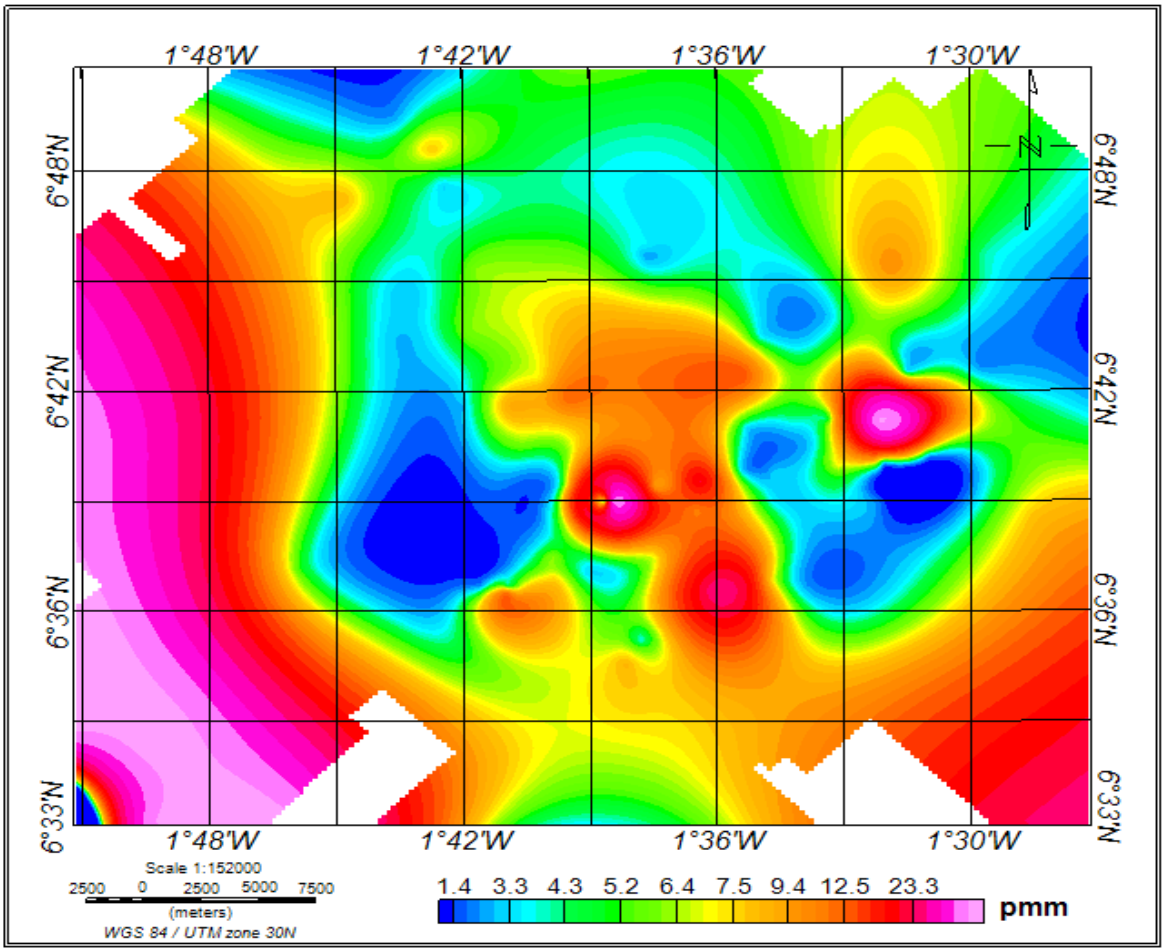



**Figure 4.3: Concentration distribution of Arsenic at Peri-Urban centres of Kumasi.**

### 4.2.3 Copper

Copper levels in soils samples were in the range of 25.08 mg/kg - 41.27 mg/kg with a mean concentration of 20.36 mg/kg. The concentration of copper in analyzed soil sample did not exceed the Canadian and Dutch guidelines of 63 mg/kg and 36 mg/kg respectively. The mean concentration of copper (20.85 mg/kg) at non-commercial areas were very low compared to levels recorded at commercial centres (39.85 mg/kg) (Darko et al., 2017). This may be due to less anthropogenic activities at non-commercial areas compared to commercial zones. But then levels may be attributed to livestock manure introduction to soil, dumping of solid waste and sludges. Asokore Mampong and Tanoso recorded higher levels of copper compared to other sampling sites during the study. Agricultural and domestic use of pesticides and fungicides in these locations could probably be the source of Copper (Hameed et al., 2013).

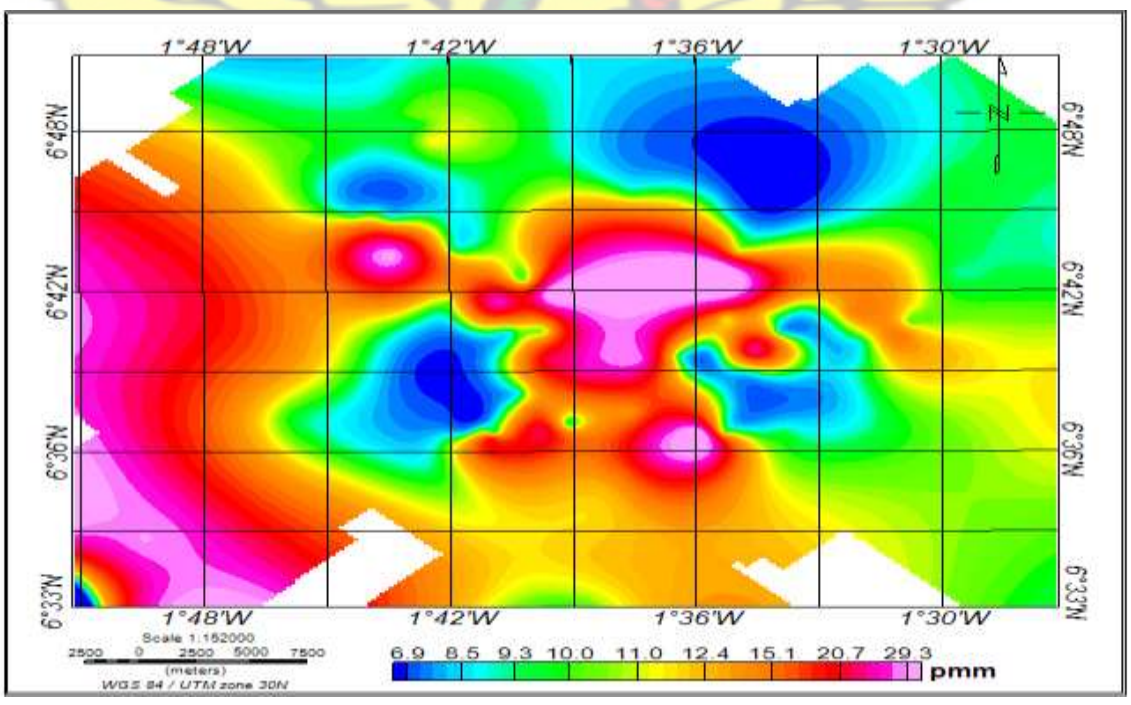



**Figure 4.4: Concentration distribution of Copper at Peri-Urban centres of Kumasi.**

### 4.2.4 Zinc

Levels of Zn in soil samples were in the range 13.1 - 419.23 mg/kg with a mean concentration of 49.702 mg/kg. The concentration of Zn in analyzed soil sample did not exceed the Canadian and Dutch guidelines of 200 mg/kg and 140 mg/kg respectively. The mean concentration of Zn (49.702 mg/kg) at non-commercial areas were very low compared to levels recorded by Darko's study (176.40 mg/kg) (Darko et al., 2017). Zn concentration in urban soils from non-commercial areas could result from anthropogenic inputs relating to vehicular emission. Sampling sites KSN1, KSN2 and KSN5 (Sepe, Asabi and Asokore Mampong) recorded high levels of Zn. Aside vehicular activities which could contribute to high levels, wood processing activity within the same areas could also have contributed to recorded high levels. Sample sites KSN 76 (Pankrono) recorded the lowest value of Zn. This area appears to be a new settlement with less anthropogenic activities (Hameed et al., 2013).

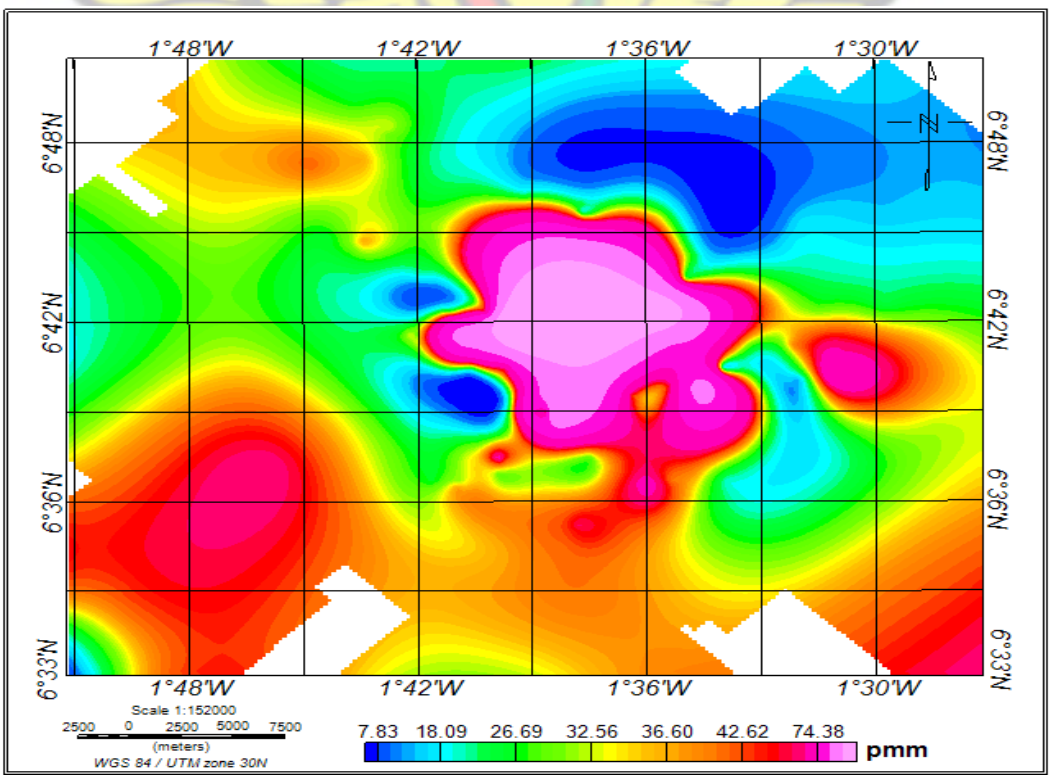



**Figure 4.5: Concentration distribution of Zn at Peri-Urban centres of Kumasi.**

### 4.2.5 Manganese

The concentration of Mn in soil samples from the study area ranged from 34.15 mg/kg to 969.43 mg/kg with a mean concentration of 162.03 mg/kg. Although Mn was detected in the study area, recorded levels at commercial areas of the metropolis were much higher (1473.13 mg/kg) compared to results of present study (Darko et al., 2017). Mn exists naturally in soil and is largely distributed in soil sediments and water. Samples from Chirapatere, Pankrono and Amanfrom recorded lower levels of Mn. Mn in these areas may be due to wastewater and sewage sludge discharge (Lanphear et al., 2014).

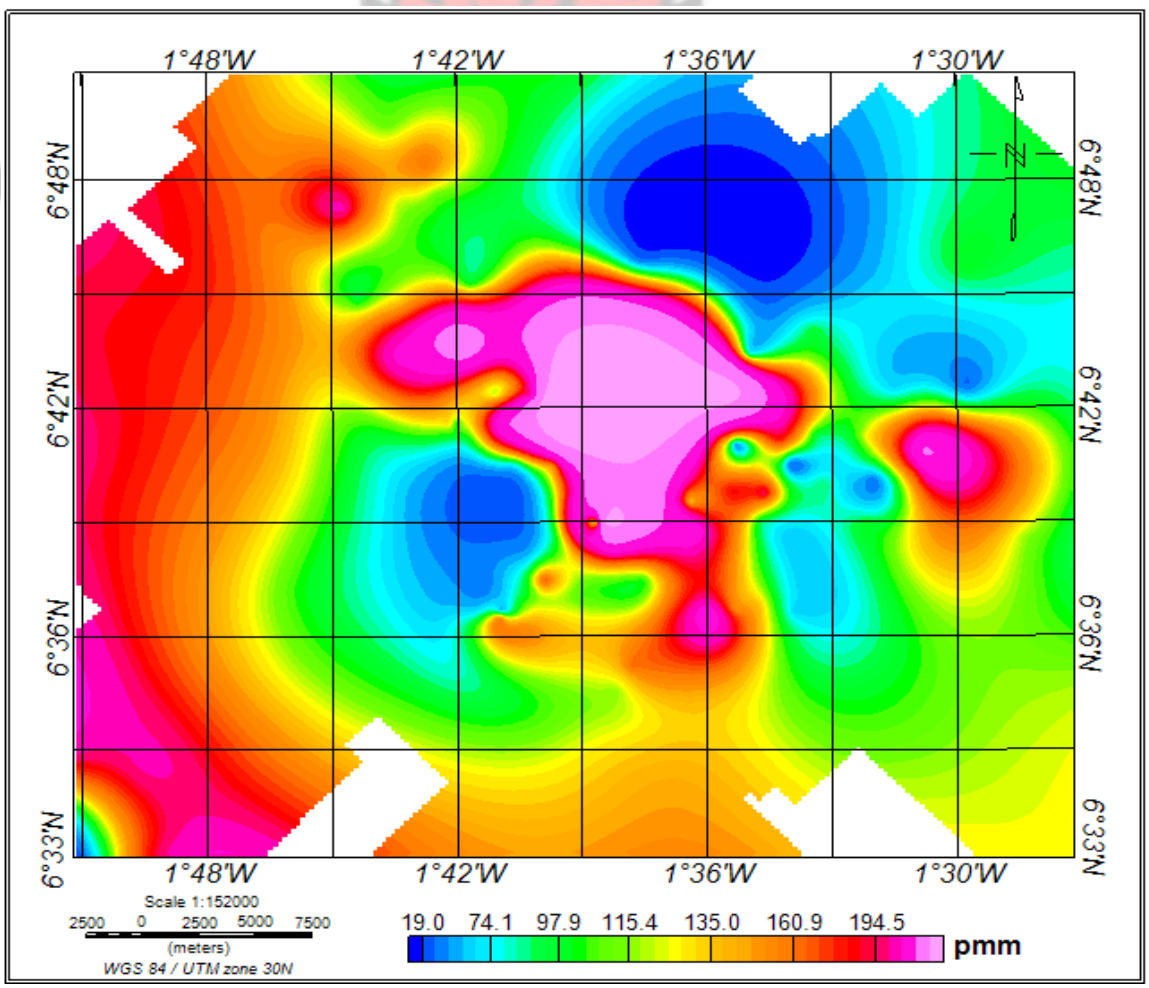



**Figure 4.6: Concentration distribution of Mn at Peri-Urban centres of Kumasi.**

### 4.2.6 Lead

Pb recorded mean value of 18.59 mg/kg with maximum and minimum values of 55.65 mg/kg and 7.5 mg/kg respectively. Although Pb is highly bioavailable, it has low mobility rate (Michael et al., 2015).Toxic effect of Pb results from long residential time on soil surface. Soil samples from sites KSN 5, KSN 32, KSN 37and KSN 44 recorded very low levels of Pb whereas the remaining analyzed soil samples were below detection limits. Soil samples from KSN 32 (Atasomanso) very close to Sir-Max hotel recorded very low levels of Pb (7.5 mg/kg) whereas sampling sites KSN 44 recorded the highest level of 55.65 mg/kg. Recorded levels of Pb in the study area were below Canadian and Dutch guidelines (140 mg/kg and 85 mg/kg respectively).

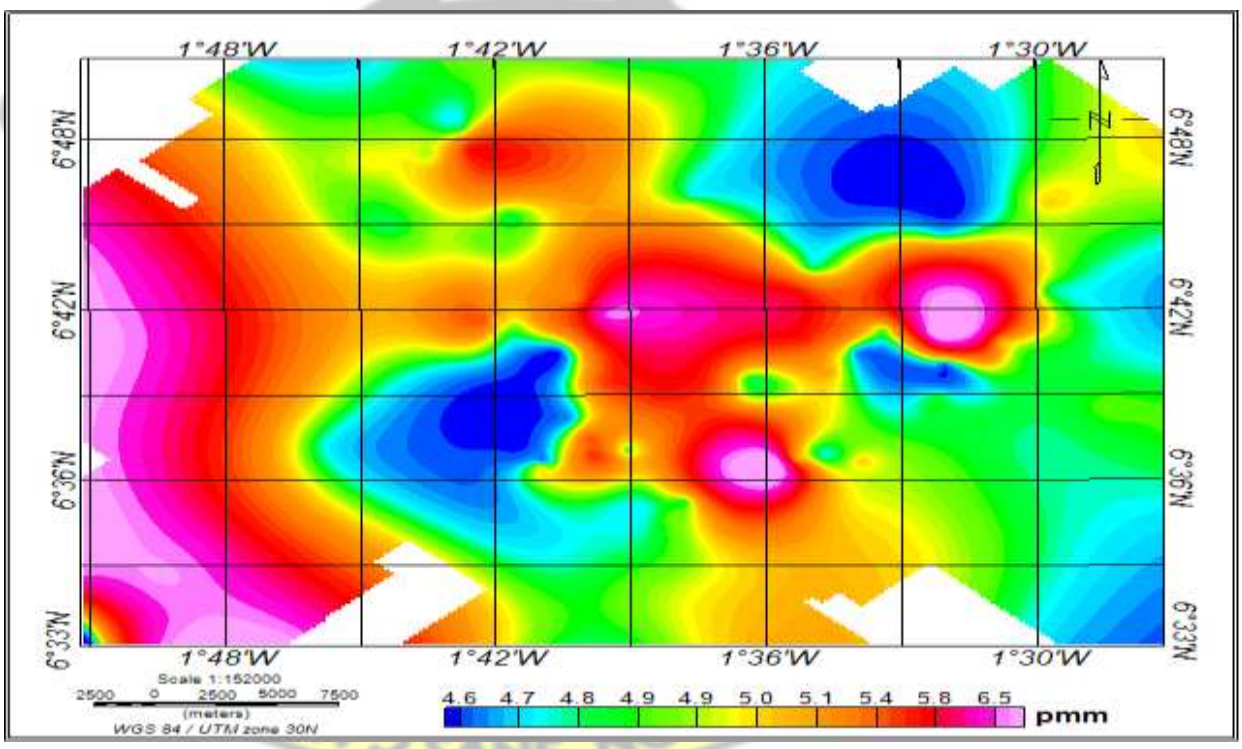



**Figure 4.7: Concentration distribution of Pb at Peri-Urban centres of Kumasi.**

### 4.2.7 Cadmium

Cd recorded 7.68 mg/kg and 27.7 mg/kg as minimum and maximum concentration respectively with a mean concentration of 12.91 mg/kg. Whereas KSN 8 (Anwomaso) recorded the lowest level of Cd , KSN 54 (Agricultural Station) recorded the highest of Cd. Recorded levels of Cd from present study exceeded levels recorded during previous study on commercial activities or areas of the metropolis (Darko et al., 2017). Recorded levels of Cd equally exceeded both Canadian and Dutch guidelines of 10 mg/kg and 0.8 mg/kg respectively. Waste disposal and incineration was very common in the study area and could be the probable cause of recorded levels (Lanphear et al., 2014).

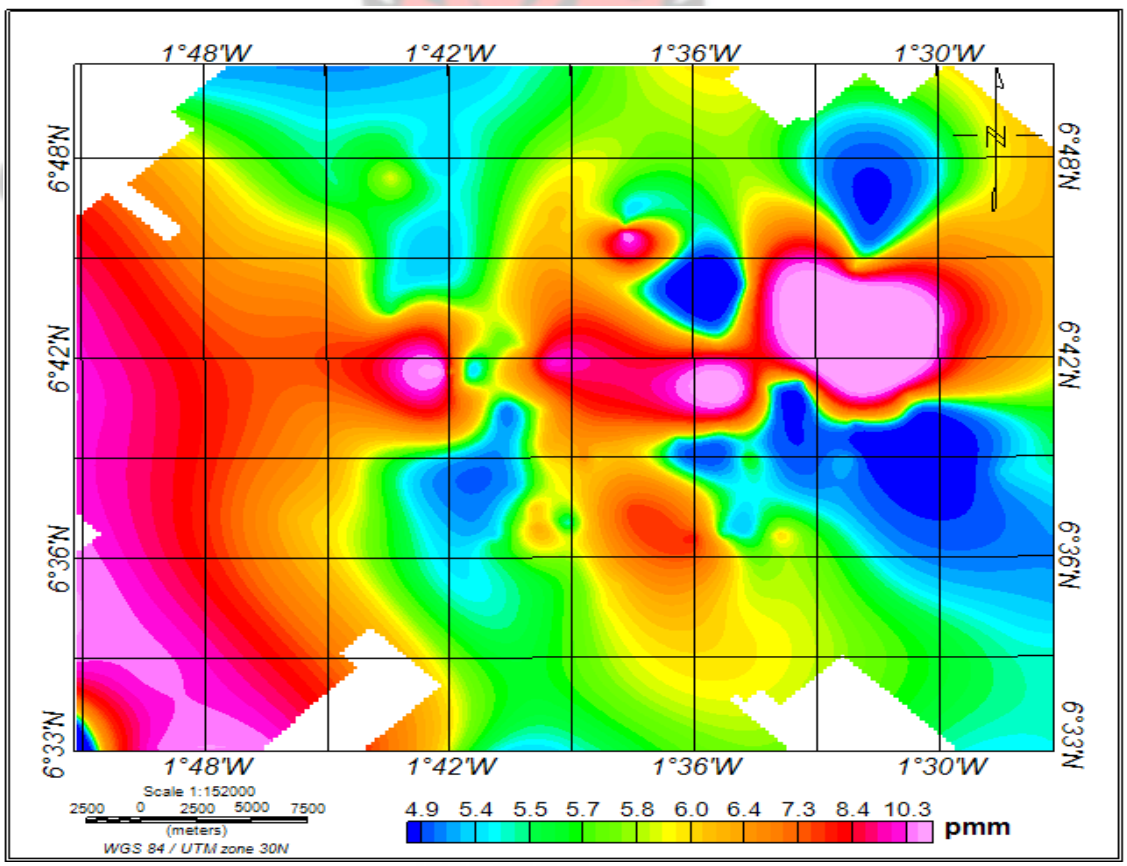



**Figure 4.8: Concentration distribution of Cd at Peri-Urban centres of Kumasi metropolis**

### 4.2.8 Chromium

Chromium levels ranged from 9.67 mg/kg to 275 mg/kg with an average of 78.18 mg/kg whereas that of commercial areas recorded 125.12 mg/kg (Darko et al., 2017). Chromium is a low mobility element which is toxic to biological systems. Its abundance is mainly from anthropogenic sources such as production of ceramics, tanning and wood preservatives (Hameed et al., 2013). Levels of Chromium were higher at sampling sites KSN 31 (Sokoban Panin) and less pronounced at sampling sites KSN 44, KSN45,KSN46 and KSN7 ( Edwenase, Owabi Forest reserve and Pankrono). KSN 31 (Sokoban Panin) is a locality known for wood processing hence incineration of waste materials after wood processing activity could be the probable cause of recorded levels (Hameed et al., 2013). Chromium levels however exceeded both Canadian and Dutch guidelines of 64 mg/kg and 100 mg/kg.

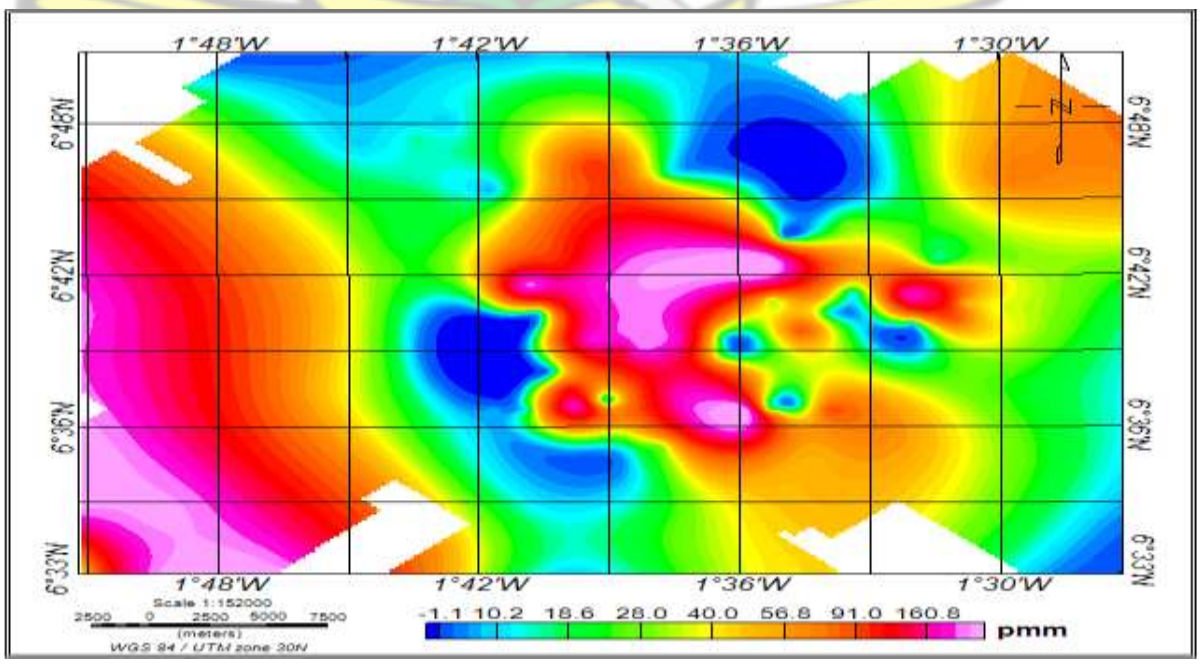



**Figure 4.9: Concentration distribution of Cr at Peri-urban centres of Kumasi.**

### 4.2.9 Iron

The abundance of iron in urban soils is from anthropogenic and natural sources. Iron was the highest recorded metal in all soils samples from the study area. From the study, Fe ranged from 3031 mg/kg to 166298 mg/kg with a mean concentration of 23064 mg/kg compared to mean concentration of 45246.15 mg/kg from previous study on commercial areas of the metropolis (Darko et al., 2017) . Soil samples from sampling sites KSN58, KSN67 and KSN68

(Daku,Abuakwa and Asenemanso) recorded higher levels whereas samples from Apeadu, Buokrom , Amanfrom recorded lower values (Hameed et al., 2013).

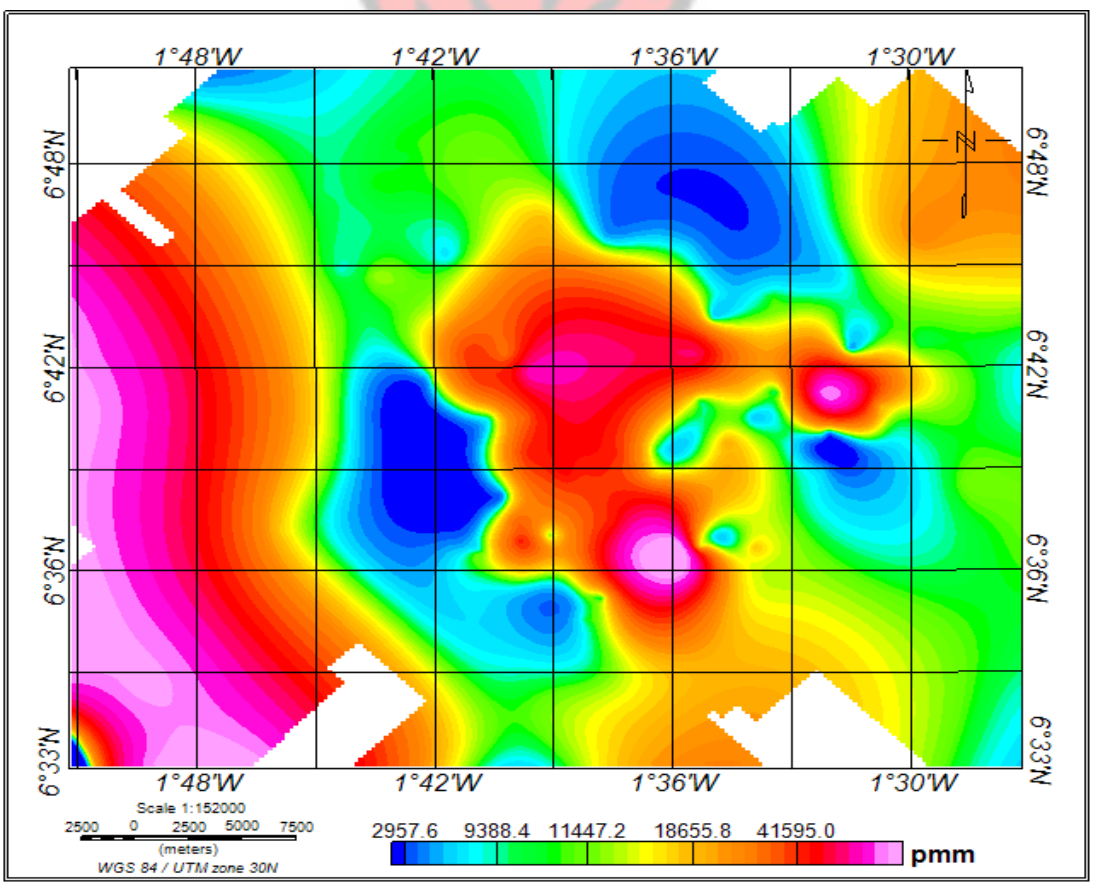



**Figure 4.10: Concentration distribution of Fe at Peri-Urban centres of Kumasi metropolis**

### 4.2.10 Nickel

Concentration of Ni in the study area ranged from 20.01 mg/kg - 55.85 mg/kg with a mean concentration of 29.33 mg/kg . Anthropogenic activities such as the disposal of batteries may be the probable source of Ni in the study area (Darko et al., 2017). The toxicity of Ni on human health can causes respiratory diseases (Beighton 2013). Ni was of high abundance in sampling sites around the Airport and Asokore Mampong zone whereas lower levels were recorded at Pankrono, Ampabame and Kwadaso.

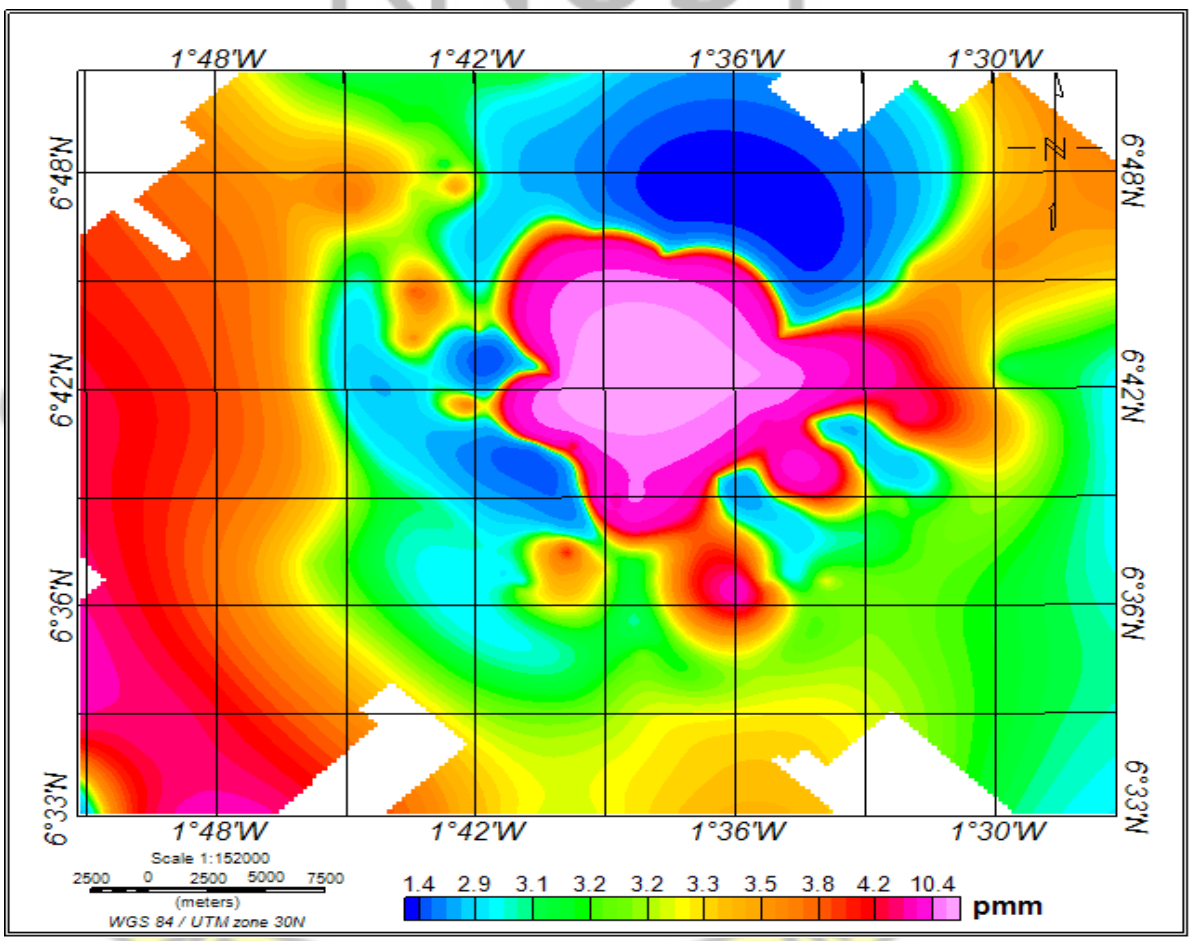



**Figure 4.11: Concentration distribution of Ni in Kumasi metropolis**

### 4.2.11 Tin

Levels of Sn in metropolis were in the range of 4.27 mg/kg - 22.53 mg/kg with mean concentration of 8.834 mg/kg. The mean concentration of Sn (8.834 mg/kg) at non-

commercial areas was high compared to levels recorded by Darko's study (3.69 mg/kg) (Darko et al. 2017). Deduako recorded the lowest level of Sn whereas Abonwinsna recorded the highest level of Sn in the study area. Agricultural activities were very common in these locations hence waste of agrochemicals could be the probable source of Sn in the study area (Filippelli et al., 2005).

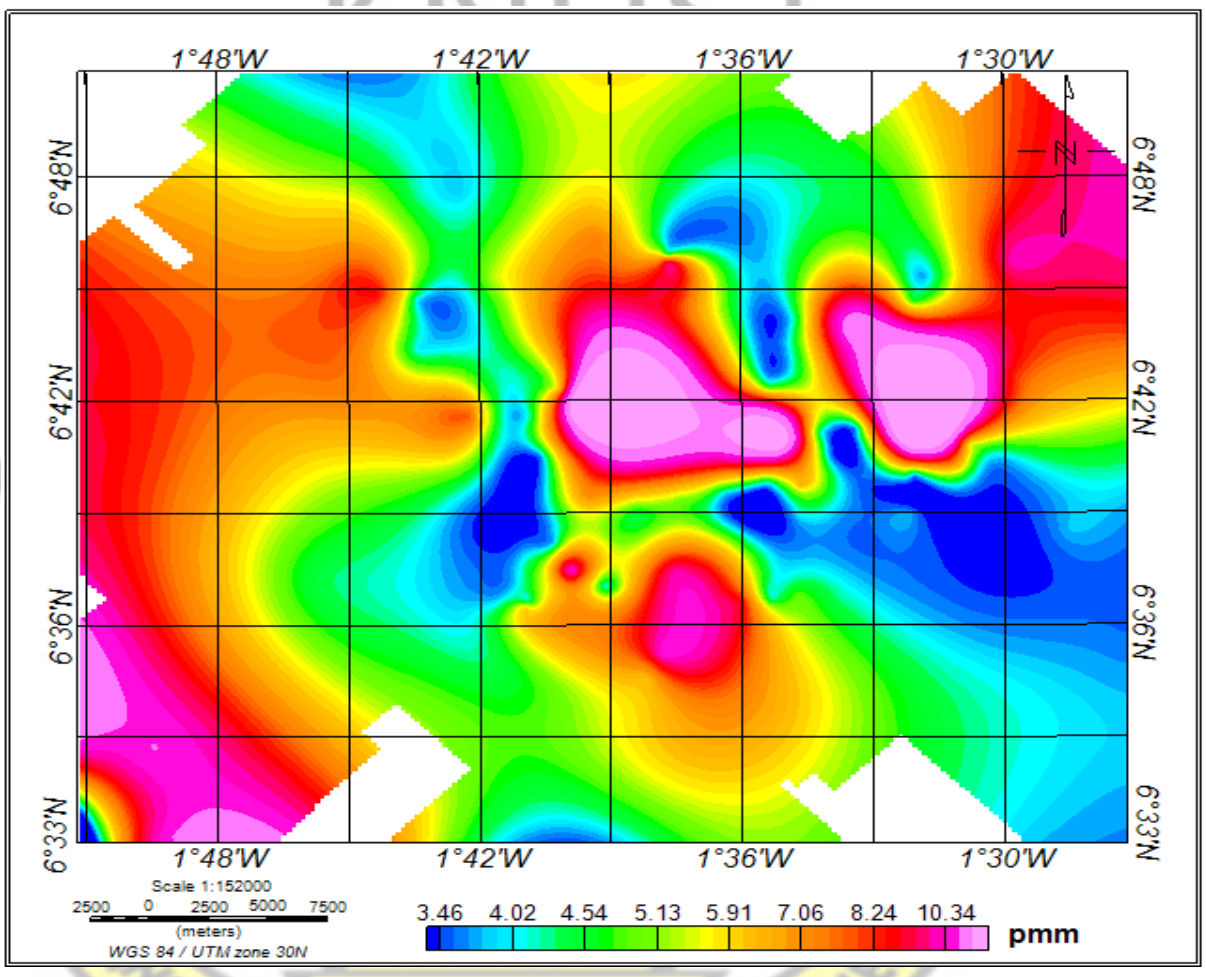



Figure 4.12: Concentration distribution of Sn at Peri-Urban centres of Kumasi.

### 4.3 Data Comparison with Commercial areas of Kumasi metropolis

The concentration of metals in top soil across commercial and non- commercial hub of Kumasi metropolis are indicated in Table 4.3

**Table 4.2: Concentrations of heavy metals across Urban and Peri-Urban soils of Kumasi metropolis.**

| Metal | Present Study | Commercial areas (Darko et al. 2017) | CCME (CCME,2007) | Dutch Target VROM,2000 |
|---|---|---|---|---|
| As | 55.18 | 36.33 | 12 | 29 |
| Pb | 55.65 | 268.35 | 140 | 85 |
| Cu | 41.27 | 307.88 | 63 | 36 |
| Ni | 55.85 | 102.41 | 45 | 35 |
| Cr | 275.7 | 649.53 | 64 | 100 |
| Zn | 419.23 | 783.44 | 200 | 140 |
| Fe | 166298 | 166409.83 | - | - |
| Mn | 969.43 | 1473.13 | - | |
| V | 202.48 | 426.12 | - | |
| Cd | 27.79 | 25.62 | 10 | 0.8 |
| Sn | 22.53 | 71.36 | - | - |

Table 4.2 shows the concentration of heavy metals found in urban soils across commercial and non-commercial hubs of Kumasi metropolis. Except for As and Cd, the concentration of all other metals (Pb, Cu, Ni, Cr, Zn, Mn, V and Sn) were very low compared to concentrations recorded from commercial areas of the metropolis (Darko et al., 2017). Fe concentrations across commercial and non - commercial hubs of the metropolis were similar. The concentration of As and Cd found in top soil across non-commercial suburbs were 1.5 and 1.1 folds higher than concentration of selected metals found across commercial areas of Kumasi metropolis. High levels of Cd in peri- urban

areas of the metropolis could be attributed to usage of phosphate fertilizers in farming (Beighton., 2013).

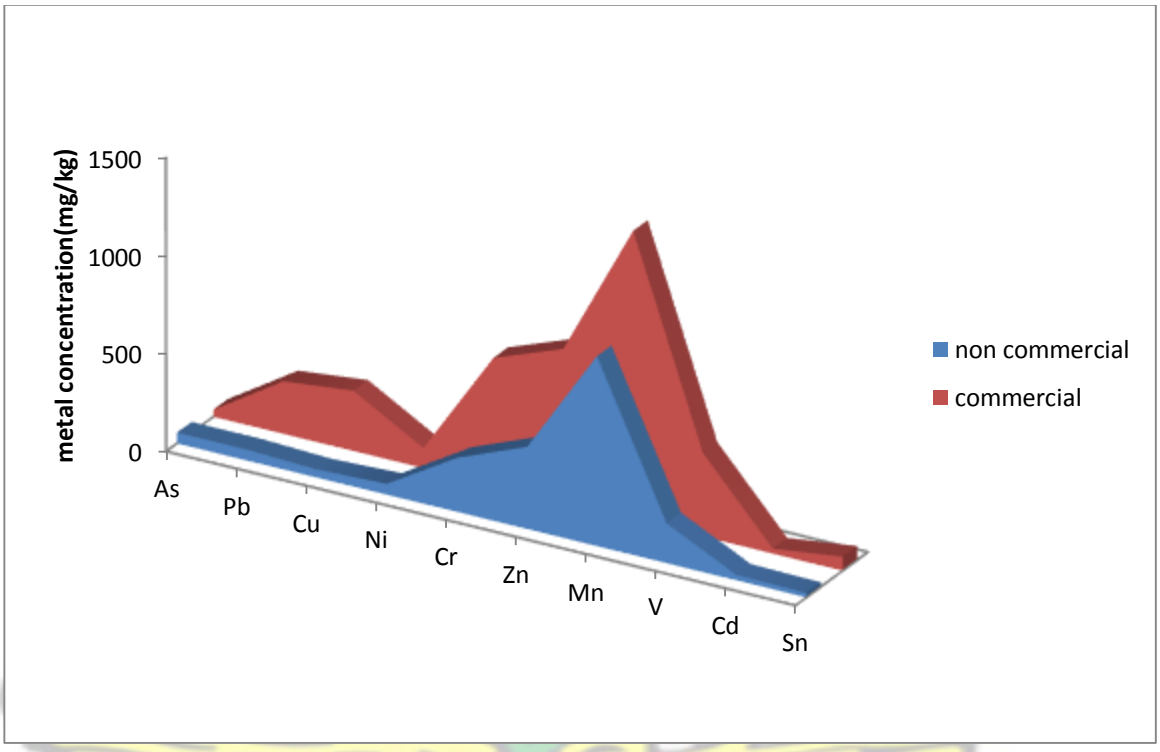



**Figure 4.13: Metal concentration across commercial and non-commercial hub of Kumasi metropolis.**

### 4.4 Comparison between ICP-MS and FP-XRF data

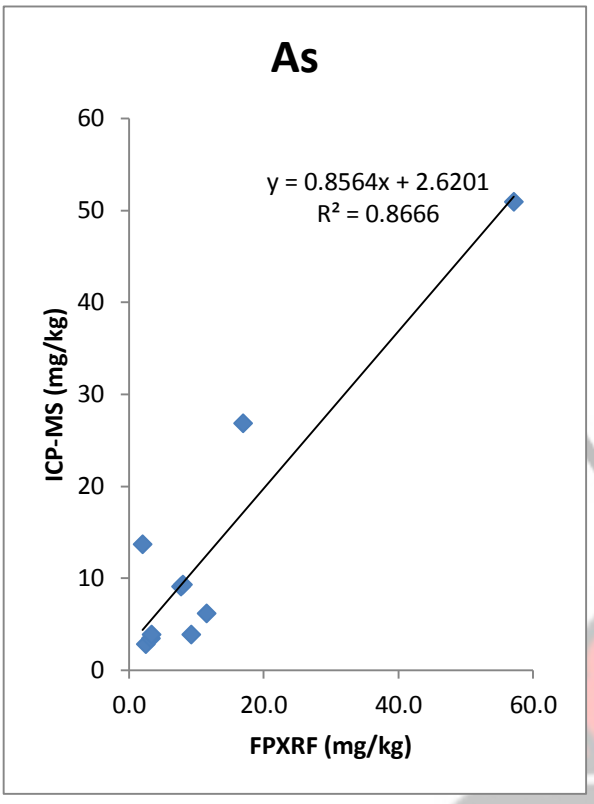
A comparison of the Field Portable X-Ray Fluorescence (FP-XRF) data to the ICP-MS results showed a linear correlation between the two methods for majority of the metals. The Pearson Correlation coefficient ($p < 0.001$) for As, Cr, Fe and Mn were 0.9309, 0.6705, 0.866 and 0.6155 respectively. .The $R^2$ values for As, Cr, Fe and Mn were between 0.3789 and 0.8666 indicating a good compatibility of the confirmatory laboratory data to the XRF data. The slopes of the regression lines for As, Cr, Cu, Fe, Mn and Ni were between 0.3541 and 3.0705 suggesting little data correction would be needed to match the FP-XRF data to confirm laboratory data. Correction of the FP-XRF data would be required in order to match the confirmatory data for Pb due to low

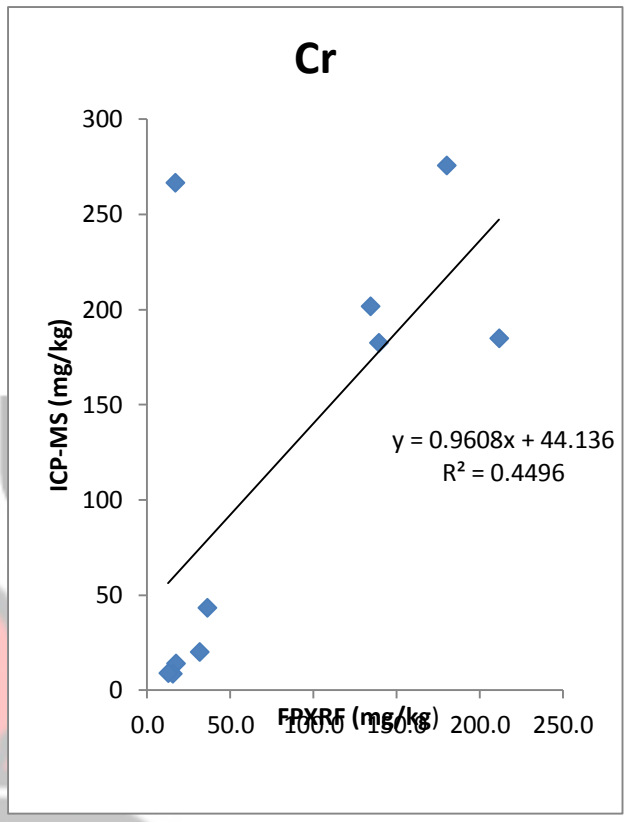
$R^2$ value of 0.0513 and slope of 0.1364 .The detection limit of Pb for the FP-XRF (15 mg/kg) was high compared to that of the ICP-MS (0.2 mg/kg) which may account for the poor comparability. From the data obtained, FP-XRF is a useful analytical instrument for screening a large number of samples of soil for most metals prior to the use of a more sensitive analytical instrument.

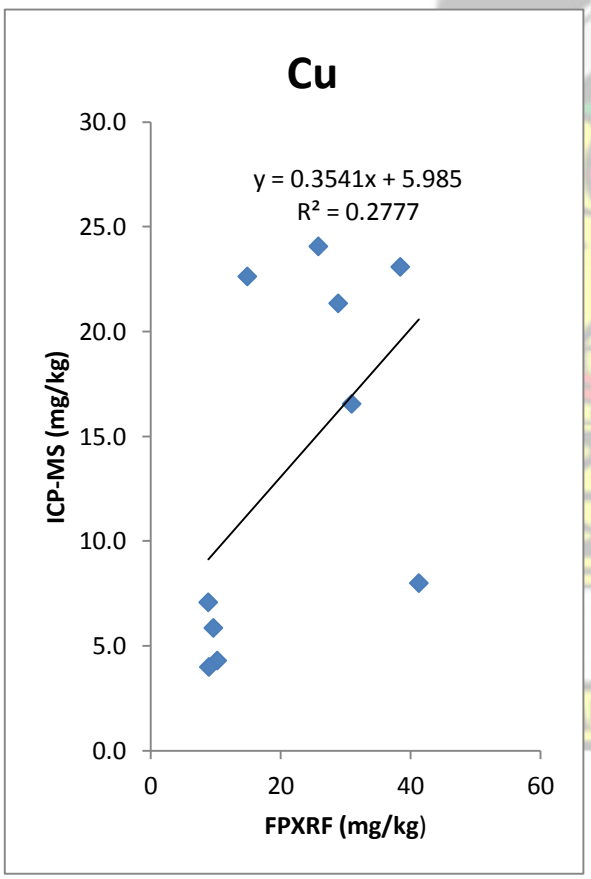


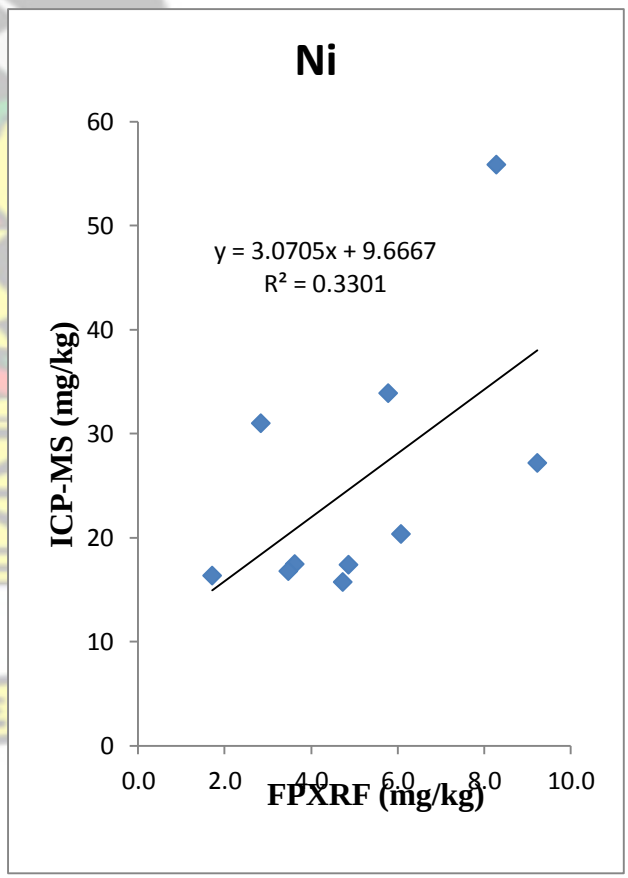
**Table 4.3: Regression parameters for comparability**

| Element | Coefficient of determination | Y- Intercept | Slope |
|---|---|---|---|
| **As** | 0.8666 | 2.6201 | 0.8564 |
| **Cr** | 0.4496 | 44.136 | 0.9608 |
| **Cu** | 0.2777 | 5.985 | 0.3541 |
| **Fe** | 0.7506 | -93.892 | 1.5037 |
| **Ni** | 0.3301 | 50.254 | 3.0705 |
| **Mn** | 0.3789 | 50.254 | 0.9538 |
| **Pb** | 0.0513 | 4.2911 | 0.1364 |
| **V** | 0.2922 | 9.533 | 0.3461 |


As
y = 0.8564x + 2.6201
R² = 0.8666
ICP-MS (mg/kg)
FPXRF (mg/kg)
0
10
20
30
40
50
60
0.0
20.0
40.0
60.0


Cr
y = 0.9608x + 44.136
R² = 0.4496
ICP-MS (mg/kg)
FPXRF (mg/kg)
0
50
100
150
200
250
300
0.0
50.0
100.0
150.0
200.0
250.0


Cu
y = 0.3541x + 5.985
R² = 0.2777
ICP-MS (mg/kg)
FPXRF (mg/kg)
0.0
5.0
10.0
15.0
20.0
25.0
30.0
0
20
40
60


Ni
y = 3.0705x + 9.6667
R² = 0.3301
ICP-MS (mg/kg)
FPXRF (mg/kg)
0
10
20
30
40
50
60
0.0
2.0
4.0
6.0
8.0
10.0

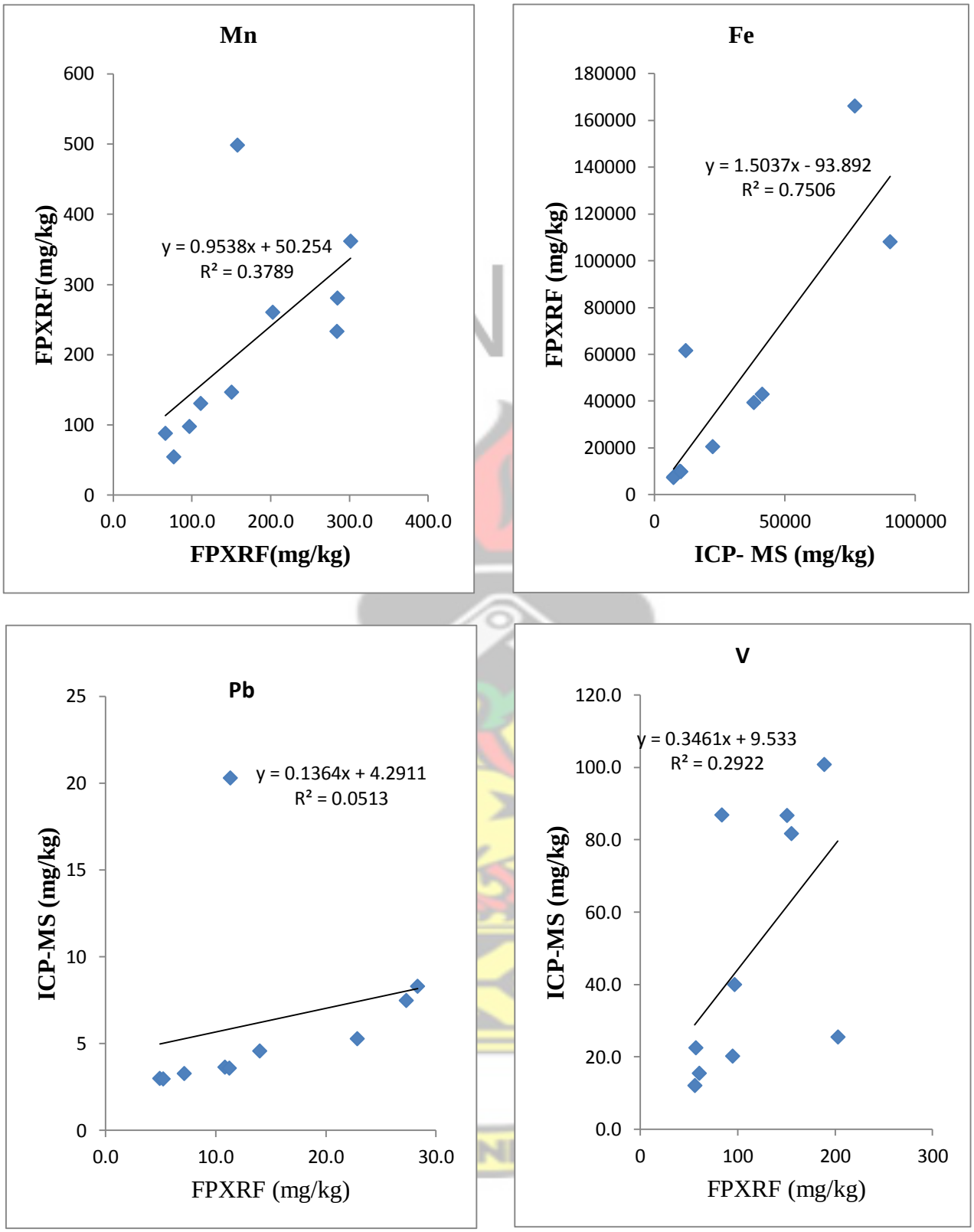



**Figure 4.14 Comparison between data from ICP –MS and Field Portable X- ray Fluorescence (FPXRF).**

### 4.5 Estimation of Contamination

Several contamination and pollution assessment tools were used to evaluate the level of surface soil contamination. In this study, Enrichment factor (EF) was used to determine whether source of metal contamination was either anthropogenic or by natural process. Several authors have effectively used Fe to normalize heavy metal contaminants hence Fe was used as a normalizer in this study to differentiate natural sources from anthropogenic components.

EF > 1 indicates that metal concentration is enriched and may be from anthropogenic sources whereas an EF < 1 indicates metal source to be natural. From the analysis, most of the metals recorded EF values less than one (EF<1) suggesting soil metal contamination may be from natural process. Fe recorded EF value of 1. This suggests soil metal contamination may be from either anthropogenic or natural sources.

As (0.06), Pb (0.025), Cu(0.07), Ni (0.28),Cr(0.65),Zn(0.14), Mn (0.04),V (0.48), Sn (0.00), Cd (0.00) were all less than one (1) and could be described as not anthropogenically impacted.

Contamination factor (CF) was used to reflect metal's enrichment in the soil. CF is rated from 1 - 6 indicating low contamination to very high contamination. This basically depends on magnitude of contamination. CF of As, Pb, Cu, Ni, Cr, Hg, Zn, Mn, Sn and Cd were all less than one (CF <1) meaning the study area is less contaminated by the above metals with the exception of Fe which recorded a CF of 2.125 indicating moderate contamination.

Pollution Load Index (PLI) measures the pollution level of an area. PLI values were in the range 0.07-0.63 which clearly shows very low degree of pollution. Figure 4.15 illustrates the PLI Grid map of selected metals from the study area.

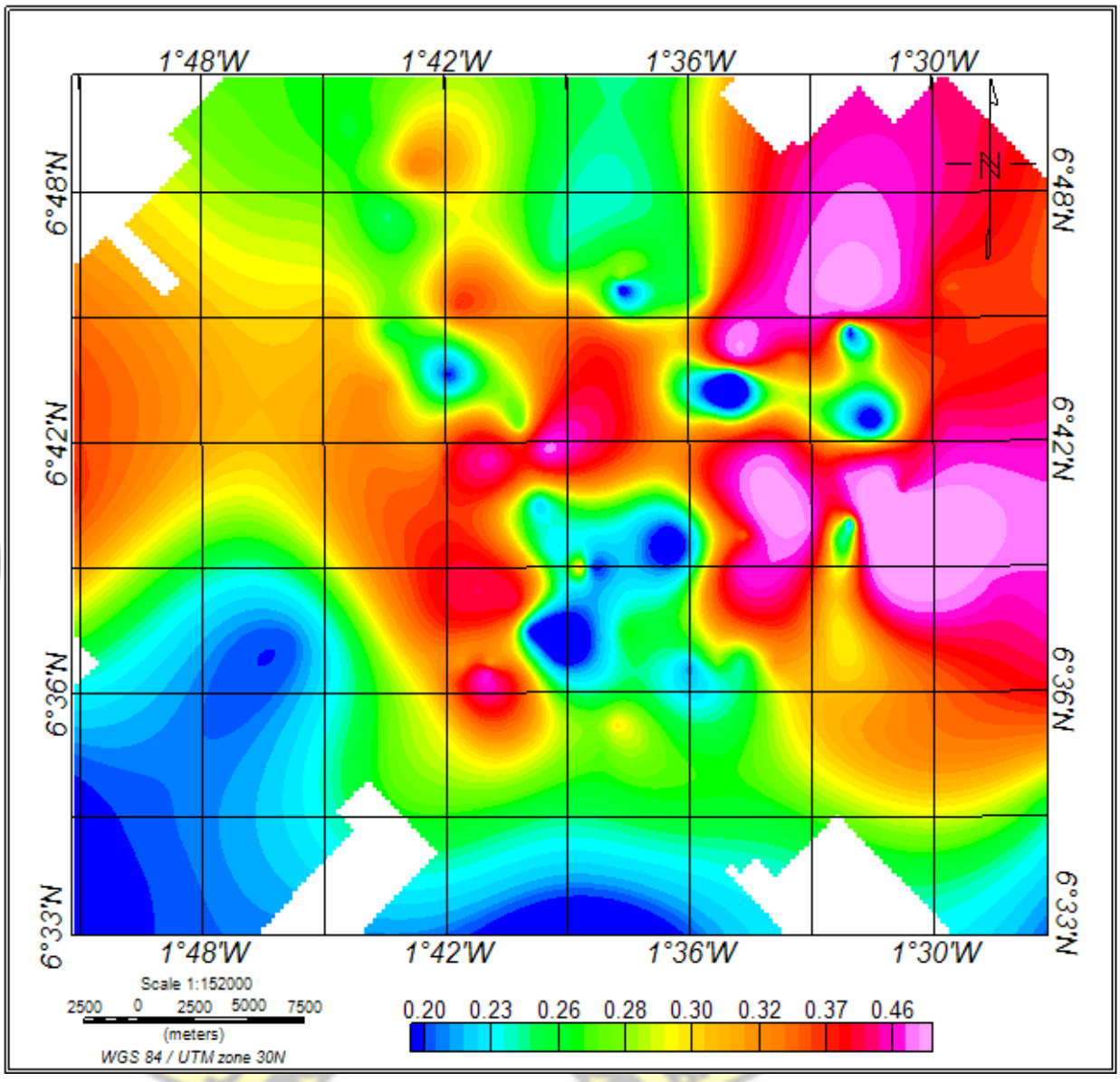



**Figure 4.15: Pollution Load Index of study area.**

The degree of metal contamination in the study area was equally assessed using Modified Degree of Contamination (mCd). Results indicated that all the samples sites recorded nil to very low degree of contamination since all Cd values recorded were less than 1.5 (mCd < 1.5).

Risk Index analysis (RI) recorded values ranging from 0.00 to 2.85 with a Potential Ecological Risk Index (PERI) value of 4.97. Metal contamination values demonstrate a low ecological risk effect.

The Igeo ranged from -3.109 to 11.068 with a mean value of 0.178.The minimum and maximum recorded values of heavy metals were as follows; As (-3.410-1.031) with a mean of -0.850, Pb (-0.475- 0.044) with a mean of -0.008, Cu (-3.423-0.00) with a mean of -0.871,Ni (-1.169 -0.312) with a mean of -0.107, Cr (-5.218-0.00) with a mean of -2.517,Zn (-2.599-2.483 ) with a mean of -1.023, Fe (8.757 -14.535) with a mean of 11.068, Mn (-5.222-0.00) with a mean of -3.109, V (-4.153- 0.054) with a mean of -1.526, Sn (-0.076-2.27 with a mean 0.148 and for Cd (0.00 -5.948) with a mean value of 0.6522. The mean Igeo indicates the study area is unpolluted with As, Pb, Cu, Ni, Cr, Zn, Mn, V, Sn and Cd it is, however, extremely polluted with Fe.

**Table 4.4: Concentration of Heavy Metals on Peri- urban topsoil elsewhere.**

| | As | Cu | Pb | Cr | Ni | Mn | Zn | Fe | V | Cd | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mufuliva Kafue (Evaristo et al., 2013) | | 219 | 0.06 | 0.34 | 12.8 | | | | | | |
| Multan (Shazia et al., 2014) | | 74.63 | 45.37 | 177.75 | | | | | | 23.1 | |
| Nairobi (Muntune et al., 2013) | | 3.59-75.37 | 0.57-20.0 | 0.03-1.4 | | | 14.62-198.3 | | | 0-2.6 | |
| Bamenda (Asongwe et al., 2011) | | | 30.64 | 35.73 | | | | | | 0.45 | |
| Tabriz (Taghpour et al., 2011) | | 101.25 | 10.86 | 87.40 | 38.73 | | 98.27 | | | 1.69 | |
| Mexico (Morton-Bermea et al., 2009) | | 100.8 | 140.5 | 117 | 39.8 | | 306.7 | | | | |
| Alicante (Spain) (Mico et al., 2006) | | 23 | 23 | 27 | 21 | | 53 | | | 0.3 | |
| Trace (Turkey) (Sun et al., 2010) | | 20 | 33 | | | | 45 | | | 0.2 | |
| Bangkok (Wilcke et al., 1998) | | 41.7 | 24.8 | 26.24 | 24.8 | | 118 | | | | |
| Kumasi (Present study) | 55.18 | 41.27 | 55.65 | 275.7 | 55.85 | 202.48 | 1473.1 | 166298 | 202 | 27.7 | 22.5 |

**4.6 Comparison with other cities**

Table 4.4 shows concentrations of heavy metals found in peri-urban topsoils in some cities. Compared with a similar work (Taghpour et al., 2011) in the city of Tabriz in Iran noted for industrial and commercial activities similar to the Kumasi study area, the concentrations of Pb, Cr and Cd found in Kumasi, Ghana, were higher. However, Cu levels in the Tabriz exceeded recorded levels at study area.



**4.7 Human Health Assessment**

Human health risk assessment of metal contaminants was analyzed by calculating the Hazard Index and Carcinogenic Risk Index (Swarnalatha et al., 2013b, 2015). Whereas Carcinogenic Risk Index of Fe, Mn, Cu and Zn could not be calculated since literature values of slope factors for these metals are not in existence , the carcinogenic risks for the metals (As, Cr and Ni) were calculated. Among them, the carcinogenic risk of As for all three exposure modes were estimated in the model, while the carcinogenic risks for Cr and Ni were considered only through inhalation (sample particle size of > 250 μm). The overall risk estimation was by summing the individual cancer risk across all exposure pathways (Chen et al., 2015; Swarnalatha et al., 2015)

Average carcinogenic risk values for adults and children were $1.94 \times 10^{-9}$, $1.38 \times 10^{-9}$ respectively.

Majority of the carcinogenic risk were between $1 \times 10^{-10}$ and $1 \times 10^{-9}$. According to Fryer et al. (2006), risk exceeding $1 \times 10^{-4}$ were observed as unacceptable, whilst risks below $1 \times 10^{-6}$were not considered to pose significant health effects, and risk lying in the range of $10^{-6}$–$10^{-4}$ are generally regarded as a tolerable degree (Chen et al., 2015). Carcinogenic risk levels of heavy metals in top soil across non- commercial hub of Kumasi metropolis were considered not to pose significant health effect. The

carcinogenic risk for children recorded during the study was less compared to that of adults .This may be due to shorter exposure duration.

Oral bioaccessibility study of the selected metals was suggested to help quantify the risk level of these metals to human systems. This was to know the amount of total metal concentration ingested which is available for absorption and their effect on the human system. Bioaccessibility study of As ,Cr, Fe, Pb, Mn, Ni and V recorded were (0.6-35.6)% ,(0.8- 9.2)%, (60.8)%, (0.1-5.8)%, (11.5-110.4)%, (14.6-99.2)%, (22.3-111.8)% and (1.1-15.2)% respectively. Bioaccessibility in KSN 21 (Kyirapatere) exceeded 100%. Sample heterogenicity and analytical constraint could be a probable cause.

**Table 4.5: Mean enrichment factor, mean contamination factor of metals at non-commercial areas of Kumasi metropolis, risk index, hazard index-children, hazard index-adult and carcinogenic risk index**

| METAL | EF | CF | RI | $HI_{Adult}$ | $HI_{children}$ | $CRI_{Adult}$ | $CRI_{children}$ |
|---|---|---|---|---|---|---|---|
| As | 0.06 | 0.443 | 4.43 | 1.34E-08 | 1.20E-08 | 3.20E-09 | 2.40E-09 |
| Pb | 0.025 | 0.013 | 0.65 | 2.30E-09 | 1.40E-09 | | |
| Cu | 0.07 | 0.1 | 0.535 | 2.00E-09 | 1.30E-09 | | |
| Ni | 0.28 | 0.174 | 2.8 | 4.02E-08 | 2.40E-08 | 2.30E-09 | 1.50E-09 |
| Cr | 0.64 | 0.249 | 1.594 | 3.20E-08 | 1.50E-08 | 3.00E-10 | 2.50E-10 |
| Zn | 0.14 | 0.993 | 0.993 | 1.50E-09 | 1.04E-09 | | |
| Fe | 1 | 2.125 | 2.34 | 2.50E-08 | 1.05E-08 | | |
| Mn | 0.04 | 0.1773 | 0.1778 | 2.30E-09 | 1.30E-09 | | |
| V | 0.48 | 0.604 | 0.78 | 7.80E-09 | 5.30E-09 | | |
| Sn | 0 | 0.1337 | 4.011 | 3.40E-08 | 2.01-8 | | |
| Cd | 0 | 0.3028 | 1.02 | 5.30E-09 | 3.20E-09 | | |

# CHAPTER FIVE

## 5.0 CONCLUSION

This study confirmed the presence of heavy metals (As, Pb, Cu, Ni, Cr, Zn, Fe, Mn, V, Sn and Cd) in surface soil from non-commercial areas in the Kumasi metropolis but the concentrations of metals in top soil from non - commercial suburbs of the metropolis were low compared to concentrations recorded at commercial hubs. Contamination estimation tools such as Enrichment factor (EF), Contamination factor (CF), Pollution Load Index (PLI), Modified Degree of Contamination (mCd) and Geo-accummulation (Igeo) index were used to assess soil pollution and contamination in the study area. The EF for most of the soil metals were less than one with the exception of Fe which recorded an EF of 1.0 meaning metals content of soil in the study area were due to natural processes and not from anthropogenic sources. Contamination factor results indicated that the study area could be rated low in terms of soil contamination with As, Pb, Ni, Cr, Zn, Mn, Cu, V, Sn, Cd with low degree of contamination of Fe.

PLI results show the degree of metal pollutant in soils of study area was low. Modified Degree of Contamination was nil to very low degree of contamination. The Potential Ecological Risk Index was rated low to ecological risk whereas Hazard and Carcinogenic Risk Index calculated indicated no human health risk associated with exposure to these metals at the present concentration. A good correlation was found between the results obtained from ICP-MS and FPXRF. FPXRF could be a good instrument for fast measurements of heavy metals in soils from the metropolis. Oral bioaccessibility of the selected metals quantified the risk level of some metals to humans when ingested.

A bioaccessibility study of surface soil samples was estimated using the modified *In Vitro* Physiologically Based Extraction Test (PBET) where bioaccessibility of metals

analyzed were below 100%. Surface soil from non-commercial areas of Kumasi metropolis could be rated as very low in terms of contamination based on metals analyzed.



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## APPENDICES

**APPENDIX A1: Sample Coordinates-KUMASI**

| SAMPLE NUMBER | LATITUDE | LONGITUDE |
|---|---|---|
| KSN1 | 6.723791 | -1.5836 |
| KSN2 | 6.674488 | -1.56651 |
| KSN3 | 6.755216 | -1.53132 |
| KSN4 | 6.761349 | -1.49666 |
| KSN5 | 6.70615 | -1.59042 |
| KSN6 | 6.73375 | -1.55828 |
| KSN7 | 6.744496 | -1.53466 |
| KSN8 | 6.70858 | -1.52533 |
| KSN9 | 6.710343 | -1.49666 |
| KSN10 | 6.68276 | -1.58861 |
| KSN11 | 6.6851 | -1.57082 |
| KSN12 | 6.68772 | -1.55654 |
| KSN13 | 6.686366 | -1.53544 |
| KSN14 | 6.680267 | -1.51312 |
| KSN15 | 6.664119 | -1.59122 |
| KSN16 | 6.662098 | -1.5778 |
| KSN17 | 6.666298 | -1.55284 |
| KSN18 | 6.6.664109 | -1.53395 |
| KSN19 | 6.669957 | -1.51655 |
| KSN21 | 6.650087 | -1.57793 |
| KSN22 | 6.736213 | -1.57998 |
| KSN23 | 6.648237 | -1.53707 |
| KSN24 | 6.643049 | -1.47428 |
| KSN25 | 6.612128 | -1.58894 |
| KSN26 | 6.612908 | -1.57916 |
| KSN27 | 6.611166 | -1.56619 |
| KSN28 | 6.553032 | -1.45668 |
| KSN29 | 6.658561 | -1.60737 |
| KSN30 | 6.646193 | -1.60843 |
| KSN31 | 6.60928 | -1.59995 |
| KSN32 | 6.656701 | -1.62432 |
| KSN33 | 6.623462 | -1.62538 |
| KSN34 | 6.586179 | -1.63049 |
| KSN35 | 6.575692 | -1.63654 |
| KSN36 | 6.650092 | -1.64404 |
| KSN37 | 6.648793 | -1.64143 |
| KSN38 | 6.617118 | -1.65252 |
| KSN39 | 6.504982 | -1.64845 |
| KSN40 | 6.614819 | -1.66421 |
| KSN41 | 6.624462 | -1.66539 |

| | | |
|---|---|---|
| KSN42 | 6.657467 | -1.65996 |
| KSN43 | 6.674842 | -1.66189 |
| KSN44 | 6.696878 | -1.6586 |
| KSN45 | 6.706159 | -1.6709 |
| KSN46 | 6.754656 | -1.6947 |
| KSN47 | 6.803564 | -1.71204 |
| KSN48 | 6.808575 | -1.7122 |
| KSN49 | 6.823933 | -1.72823 |
| KSN50 | 6.792542 | -1.70842 |
| KSN51 | 6.759184 | -1.5944 |
| KSN52 | 6.706188 | -1.68536 |
| KSN53 | 6.692938 | -1.68097 |
| KSN54 | 6.674394 | -1.67654 |
| KSN55 | 6.636063 | -1.67228 |
| KSN56 | 6.61102 | -1.68221 |
| KSN57 | 6.607189 | -1.68324 |
| KSN58 | 6.61137 | -1.69402 |
| KSN59 | 6.61961 | -1.76356 |
| KSN61 | 6.692825 | -1.70158 |
| KSN62 | 6.726693 | -1.69907 |
| KSN63 | 1.744907 | -1.72403 |
| KSN64 | 6.790105 | -1.724 |
| KSN65 | 6.787855 | -1.746 |
| KSN66 | 6.747841 | -1.7398 |
| KSN67 | 6.722922 | -1.72461 |
| KSN68 | 6.693151 | -1.70303 |
| KSN69 | 6.544558 | -1.82504 |
| KSN70 | 6.518503 | -1.84985 |
| KSN71 | 6.69771 | -1.84054 |
| KSN72 | 6.772342 | -1.65358 |
| KSN73 | 6.843959 | -1.66759 |
| KSN74 | 6.761193 | -1.62754 |
| KSN75 | 6.76528 | -1.62759 |

**APPENDIX A2: pH and electrical conductivity**

| SAMPLE CODE | pH | Electrical conductivity *(µS/cm)* |
|---|---|---|
| KSN1 | 8 | 356 |
| KSN2 | 6.92 | 885 |
| KSN3 | 6.56 | 4858 |
| KSN4 | 7.57 | 476 |
| KSN5 | 6.89 | 789 |
| KSN6 | 7.53 | 2534 |
| KSN7 | 7.98 | 365 |
| KSN8 | 7.45 | 787 |
| KSN9 | 7.89 | 645 |
| KSN10 | 6.89 | 799 |
| KSN11 | 7.48 | 924 |
| KSN12 | 7.7 | 475 |
| KSN13 | 7.94 | 2534 |
| KSN14 | 6.89 | 475 |
| KSN15 | 7.09 | 897 |
| KSN16 | 7.35 | 454 |
| KSN17 | 7.6 | 576 |
| KSN18 | 7.9 | 798 |
| KSN19 | 7.32 | 244 |
| KSN21 | 7.84 | 586 |
| KSN22 | 7.45 | 1576 |
| KSN23 | 7.02 | 574 |
| KSN24 | 7.5 | 588 |
| KSN25 | 7.89 | 355 |
| KSN26 | 7.45 | 896 |
| KSN27 | 7.83 | 576 |
| KSN28 | 7.23 | 8990 |
| KSN29 | 7.59 | 364 |
| KSN30 | 7.84 | 787 |
| KSN31 | 7.98 | 687 |
| KSN32 | 7.77 | 788 |
| KSN33 | 6.91 | 334 |
| KSN34 | 7.29 | 789 |
| KSN35 | 7.55 | 789 |
| KSN36 | 8.2 | 789 |
| KSN37 | 7.45 | 325 |
| KSN38 | 7.83 | 788 |
| KSN39 | 7.78 | 1224 |
| KSN40 | 7.84 | 153 |
| KSN41 | 7.83 | 784 |

| | | |
|---|---|---|
| KSN42 | 7.55 | 688 |
| KSN43 | 7.68 | 897 |
| KSN44 | 6.5 | 666 |
| KSN45 | 6.9 | 907 |
| KSN46 | 7 | 465 |
| KSN47 | 8.5 | 688 |
| KSN48 | 7.9 | 465 |
| KSN49 | 7.46 | 897 |
| KSN50 | 6.99 | 253 |
| KSN51 | 6.78 | 678 |
| KSN52 | 6.9 | 888 |
| KSN53 | 7.34 | 834 |
| KSN54 | 7.81 | 576 |
| KSN55 | 7.34 | 645 |
| KSN56 | 7.48 | 798 |
| KSN57 | 7.57 | 4474 |
| KSN58 | 7.83 | 1224 |
| KSN59 | 7.99 | 804 |
| KSN61 | 7.67 | 1274 |
| KSN62 | 8.34 | 2848 |
| KSN63 | 7.5 | 5852 |
| KSN64 | 7.83 | 597 |
| KSN65 | 7.82 | 945 |
| KSN66 | 7.45 | 1253 |
| KSN67 | 7.45 | 385 |
| KSN68 | 7.36 | 784 |
| KSN69 | 7.94 | 1774 |
| KSN70 | 7.83 | 1284 |
| KSN71 | 7.82 | 798 |
| KSN72 | 7.47 | 586 |
| KSN73 | 7.98 | 785 |
| KSN74 | 7.23 | 354 |
| KSN75 | 7.89 | 3745 |
| **AVERAGE** | 7.53589 | 1133.205 |

## APPENDIX A3: Metal Concentrations of XRF

| Sample Code | Pb | Ni | Cr | | Zn | Fe | Mn | V | Sn | Cd | As | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN1 | 3.64 | 16.57 | 8.86 | | 29.56 | 8031 | 74.22 | 53.33 | 3.89 | 5.44 | 3.86 | 12.2 |
| KSN2 | 3.39 | 15.35 | 12.41 | | 15.87 | 6849 | 31.97 | 70.39 | 3.7 | 5.14 | 2.64 | 8.47 |
| KSN3 | 3.36 | 15.16 | 23.25 | | 17.12 | 8318 | 64.5 | 79.69 | 3.78 | 5.31 | 9.95 | 8.69 |
| KSN4 | 3.56 | 17.38 | 67.99 | | 14.61 | 23773 | 100.4 | 70.78 | 10.06 | 6.43 | 4.24 | 9.62 |
| KSN5 | 20.29 | 30.99 | 266.41 | | 238.89 | 61640 | 498.4 | 202.48 | 4.62 | 6.35 | 13.71 | 41.3 |
| KSN6 | 3.44 | 17.59 | 29.36 | | 18.87 | 10824 | 96.89 | 36.8 | 12.73 | 14.22 | 2.76 | 9.96 |
| KSN7 | 3.39 | 15.78 | 19.54 | | 18.44 | 6842 | 73.28 | 22.32 | 4.36 | 6.02 | 7.93 | 9.19 |
| KSN8 | 3.94 | 23.13 | 15.36 | | 28.03 | 5617 | 66.38 | 10.96 | 17.85 | 27.79 | 3.1 | 13.7 |
| KSN9 | 3.09 | 16.42 | 29.42 | | 23.81 | 10202 | 35.01 | 26.67 | 8.32 | 9.14 | 2.43 | 9.32 |
| KSN10 | 4.2 | 19.46 | 31.89 | | 83.32 | 9729 | 39.82 | 13.92 | 18.09 | 15.35 | 3.23 | 11.5 |
| KSN11 | 3.33 | 23.92 | 60.77 | | 67.38 | 16242 | 181.1 | 87.19 | 4.22 | 5.82 | 3.9 | 11.1 |
| KSN12 | 3.05 | 16.88 | 8.9 | | 32.1 | 9515 | 91.79 | 62.3 | 3.92 | 5.39 | 4.65 | 9.08 |
| KSN13 | 4.59 | 27.21 | 184.58 | | 39.94 | 108137 | 130.9 | 83.77 | 21.21 | 14.18 | 50.95 | 14.9 |
| KSN14 | 3.72 | 17.75 | 44.95 | | 52.46 | 18613 | 307.7 | 68.97 | 5.32 | 6.4 | 11.11 | 9.87 |
| KSN15 | 3.49 | 17.6 | 30.56 | | 44.16 | 8178 | 185.3 | 34.23 | 4.4 | 6.11 | 3.28 | 9.82 |
| KSN16 | 8.46 | 17.77 | 87.55 | | 158.35 | 19859 | 202.1 | 91.84 | 6.48 | 5.74 | 3.28 | 25.3 |
| KSN17 | 3.01 | 15.35 | 9.93 | | 30.29 | 10042 | 91.8 | 76.93 | 3.68 | 5.14 | 7.22 | 8.61 |
| KSN18 | 2.77 | 15.8 | 7.61 | | 13.1 | 3031 | 34.15 | 46.1 | 3.8 | 5.27 | 2.2 | 8.67 |
| KSN19 | 3.44 | 24.68 | 85.78 | | 70.52 | 19268 | 179.9 | 87.13 | 6.06 | 5.75 | 2.73 | 15.4 |
| KSN21 | 3.65 | 17.45 | 43.29 | | 106.49 | 20679 | 87.99 | 96.72 | 4.18 | 5.69 | 3.44 | 9.6 |
| KSN22 | 3 | 16.57 | 8.82 | | 26.43 | 8305 | 58.02 | 58.42 | 4.27 | 5.38 | 2.91 | 9.07 |
| KSN23 | 3.21 | 16.45 | 8.71 | | 14.69 | 7299 | 101.9 | 49.92 | 3.93 | 5.39 | 2.6 | 9.08 |
| KSN24 | 3.11 | 16.79 | 20.02 | | 32.53 | 11870 | 119.3 | 100.28 | 3.91 | 5.39 | 8.13 | 11.4 |
| KSN25 | 3.26 | 17 | 11.63 | | 39.18 | 10885 | 147.8 | 81.95 | 3.95 | 5.45 | 20.56 | 9.25 |
| KSN26 | 3 | 16.36 | 9.03 | | 36.74 | 7787 | 136.1 | 73.92 | 4.94 | 5.36 | 7.54 | 8.97 |
| KSN27 | 3.3 | 17.21 | 89.99 | | 20.42 | 17924 | 64.6 | 57.41 | 4.37 | 6.03 | 2.64 | 9.7 |
| KSN28 | 3.06 | 16.26 | 9.67 | | 43.96 | 9892 | 123.6 | 76.03 | 3.93 | 5.48 | 20.28 | 10.3 |
| KSN29 | 3.18 | 16.61 | 13.49 | | 44.75 | 9870 | 134 | 61.9 | 3.95 | 5.42 | 21.43 | 9.03 |
| KSN30 | 3.58 | 17.32 | 28.55 | | 55.43 | 18554 | 288.6 | 106.43 | 4.02 | 5.5 | 11.4 | 12.7 |
| KSN31 | 5.3 | 55.85 | 275.7 | | 57.75 | 166298 | 260.7 | 188.71 | 8.59 | 7.86 | 26.87 | 38.4 |
| KSN32 | 7.5 | 33.92 | 182.38 | | 143.71 | 42988 | 361.9 | 150.4 | 5.27 | 6.14 | 9.34 | 28.8 |
| KSN33 | 3.5 | 20.47 | 167.24 | | 28.3 | 45421 | 104.9 | 60.54 | 10.06 | 7.68 | 6.78 | 14.4 |
| KSN34 | 3.12 | 17.05 | 27.22 | | 48.3 | 9962 | 162.4 | 57.63 | 10.68 | 6.08 | 3.68 | 15.9 |
| KSN35 | 3.2 | 16.9 | 19.12 | | 41.17 | 10717 | 117 | 55.21 | 6.31 | 5.94 | 8.54 | 12.6 |
| KSN36 | 4.01 | 20.41 | 136.21 | | 43.25 | 55340 | 122.5 | 172.36 | 4.86 | 6.65 | 3.14 | 26.1 |
| KSN37 | 11.37 | 19.68 | 181.96 | | 183.8 | 43410 | 456.7 | 144.56 | 4.41 | 6.06 | 44.45 | 24 |
| KSN38 | 3.36 | 16.43 | 9.91 | | 31.67 | 11567 | 110.5 | 77.92 | 3.97 | 5.45 | 3.49 | 9.15 |
| KSN39 | 3.29 | 16.8 | 13.74 | | 33.34 | 10055 | 146.7 | 94.82 | 3.97 | 5.5 | 3.92 | 10.2 |
| KSN40 | 3.5 | 33.96 | 187.14 | | 29.12 | 44721 | 118.6 | 102.34 | 6.94 | 6.27 | 7.55 | 22.4 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN41 | 4.07 | 34.2 | 119.36 | | 55.09 | 32099 | 170.4 | 119.2 | 10.59 | 6.11 | 6.23 | 16.5 |
| KSN42 | 3.67 | 19.71 | 174.86 | | 27.36 | 45411 | 140.4 | 108.52 | 7.14 | 6.26 | 6.07 | 22.4 |
| KSN43 | 3.98 | 18.83 | 144.71 | | 57.59 | 33365 | 164.9 | 127.09 | 8.88 | 6.04 | 5.88 | 10.6 |
| KSN44 | 55.65 | 23.53 | 177.05 | | 419.23 | 79014 | 969.4 | 140.6 | 22.53 | 10.08 | 12.62 | 34.1 |
| KSN45 | 3.74 | 18.46 | 107.72 | | 47.45 | 29814 | 214 | 94.53 | 5.75 | 5.91 | 7.09 | 9.96 |
| KSN46 | 2.99 | 16.39 | 8.36 | | 30.85 | 7906 | 97.64 | 60.47 | 5.4 | 5.45 | 6.19 | 8.97 |
| KSN47 | 3.09 | 23.31 | 9.42 | | 29.17 | 10441 | 153.4 | 79.9 | 3.95 | 5.42 | 6.03 | 9.37 |
| KSN48 | 3.2 | 16.93 | 12.09 | | 32.48 | 10710 | 158.9 | 71.17 | 3.91 | 5.46 | 7.8 | 10.5 |
| KSN49 | 3.15 | 16.61 | 9.27 | | 26.15 | 9637 | 112.1 | 69.65 | 3.96 | 5.43 | 2.52 | 9.01 |
| KSN50 | 3.53 | 20.96 | 13.02 | | 28.02 | 10648 | 109 | 86.27 | 3.92 | 5.45 | 3.22 | 11.5 |
| KSN51 | 2.92 | 15.91 | 8.91 | | 31.93 | 7464 | 33.8 | 53.01 | 3.88 | 5.39 | 3.95 | 8.74 |
| KSN52 | 3.44 | 18.25 | 101.4 | | 26.99 | 41114 | 118.1 | 153.72 | 4.19 | 5.83 | 5.93 | 17.2 |
| KSN53 | 8.31 | 20.38 | 201.46 | | 145.45 | 39508 | 280.9 | 154.72 | 4.3 | 5.94 | 9.11 | 25.8 |
| KSN54 | 3.02 | 15.38 | 10.9 | | 26.41 | 9661 | 74.52 | 59.13 | 3.72 | 5.16 | 5.71 | 8.73 |
| KSN55 | 2.9 | 15.82 | 7.88 | | 23.75 | 4321 | 56.9 | 45.36 | 3.84 | 5.35 | 2.54 | 8.81 |
| KSN56 | 2.96 | 15.74 | 8.85 | | 30.98 | 7484 | 54.44 | 55.76 | 3.9 | 5.37 | 3.92 | 8.84 |
| KSN57 | 3.21 | 20.01 | 19.34 | | 37.43 | 11659 | 160.3 | 86.81 | 6.11 | 5.55 | 13.33 | 20.3 |
| KSN58 | 3.01 | 15.86 | 8.41 | | 26.24 | 6173 | 64.16 | 38.97 | 3.85 | 5.33 | 2.34 | 8.45 |
| KSN59 | 3.23 | 16.3 | 53 | | 49.28 | 16162 | 103.8 | 47.46 | 4.44 | 6.19 | 4.88 | 9.49 |
| KSN61 | 3.47 | 16.78 | 28.4 | | 27.02 | 12450 | 97.62 | 60.22 | 5.73 | 5.83 | 2.67 | 9.48 |
| KSN62 | 3.3 | 16.94 | 35.84 | | 21.77 | 14487 | 363.6 | 72.11 | 4.14 | 5.78 | 5.92 | 9.24 |
| KSN63 | 3.83 | 16.96 | 22.35 | | 36.74 | 12484 | 139.9 | 95.95 | 3.99 | 5.49 | 2.99 | 9.22 |
| KSN64 | 3.23 | 16.8 | 15.48 | | 36.66 | 10748 | 121.3 | 55.53 | 4.28 | 5.9 | 4.86 | 9.38 |
| KSN65 | 3.69 | 21.7 | 9.31 | | 40.75 | 9685 | 210.3 | 64.35 | 5.68 | 5.53 | 8.07 | 9.79 |
| KSN66 | 3.06 | 16.37 | 21.72 | | 25.9 | 9214 | 95.72 | 42.53 | 8.75 | 6.03 | 4.52 | 9.12 |
| KSN67 | 3.58 | 17.4 | 19.94 | | 21.29 | 9969 | 233.3 | 57.1 | 4.03 | 5.55 | 2.82 | 30.9 |
| KSN68 | 3.62 | 18.42 | 37.87 | | 33.6 | 6280 | 130.2 | 15.28 | 7.63 | 11.63 | 2.88 | 10.9 |
| KSN69 | 4.55 | 25.81 | 226.48 | | 42.95 | 111226 | 210.6 | 107.05 | 11.24 | 10.77 | 55.18 | 29.6 |
| KSN70 | 3.34 | 17.7 | 101.64 | | 19.23 | 18534 | 86.53 | 69.61 | 4.56 | 5.79 | 3.64 | 9.73 |
| KSN71 | 4.21 | 37.72 | 167.84 | | 21.73 | 96991 | 192.4 | 175.47 | 8.74 | 9.55 | 39.11 | 25.9 |
| KSN72 | 3.29 | 17.75 | 100.62 | | 19.97 | 18201 | 95.58 | 56.84 | 7.28 | 6.12 | 4.77 | 9.85 |
| KSN73 | 3.07 | 20.61 | 9.17 | | 23.83 | 9769 | 103.5 | 72.95 | 5.58 | 5.48 | 5.35 | 8.91 |
| KSN74 | 3.29 | 17.15 | 37.29 | | 18.92 | 8338 | 81.84 | 27.16 | 9.77 | 11.67 | 2.59 | 9.55 |
| KSN75 | 3.11 | 16.04 | 16.43 | | 24.72 | 5698 | 36.96 | 17.33 | 4.28 | 5.94 | 3.59 | 8.94 |

**APPENDIX A4: Table showing Enrichment Factor**

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | As | Pb | Cu | Ni | Cr | | Zn | Fe | Mn | V | Sn | Cd |
| KSN1 | 0.06 | 0 | 0.06 | 0.28 | 0.73 | | 0.09 | 1 | 0.04 | 0.88 | 0 | 0 |
| KSN2 | 0.12 | 0.02 | 0.07 | 0.3 | 0.64 | | 0.24 | 1 | 0.02 | 0.82 | 0 | 0 |
| KSN3 | 0.08 | 0.01 | 0.1 | 0.21 | 0.72 | | 0.29 | 1 | 0.06 | 0.79 | 0 | 0 |
| KSN4 | 0 | 0 | 0.2 | 0.49 | 0.6 | | 0.05 | 1 | 0.05 | 0.88 | 0 | 0 |
| KSN5 | 0.27 | 0.02 | 0.14 | 0.23 | 0.52 | | 0.05 | 1 | 0.04 | 0.79 | 0 | 0 |
| KSN6 | 0 | 0.04 | 0.23 | 0.28 | 0.89 | | 0.13 | 1 | 0.05 | 0.79 | 0 | 0 |
| KSN7 | 0.06 | 0.08 | 0.05 | 0.14 | 0.7 | | 0.17 | 1 | 0.05 | 0 | 0 | 0 |
| KSN8 | 0.09 | 0.07 | 0.07 | 0.28 | 0.71 | | 0.08 | 1 | 0.06 | 0.8 | 0 | 0 |
| KSN9 | 0 | 0.05 | 0 | 0.21 | 0.49 | | 0 | 1 | 0.03 | 0.95 | 0 | 0 |
| KSN10 | 0 | 0.02 | 0.04 | 0.34 | 0.63 | | 0.25 | 1 | 0.05 | 1.15 | 0 | 0 |
| KSN11 | 0.09 | 0 | 0.05 | 0 | 0.45 | | 0.16 | 1 | 0.02 | 0.81 | 0 | 0 |
| KSN12 | 0 | 0.01 | 0.04 | 0.48 | 0.49 | | 0 | 1 | 0.02 | 0.87 | 0 | 0 |
| KSN13 | 0 | 0.01 | 0.07 | 0.44 | 1.11 | | 0.13 | 1 | 0.02 | 0 | 0 | 0 |
| KSN14 | 0.13 | 0 | 0.07 | 0.48 | 1.05 | | 0.06 | 1 | 0.05 | 0.81 | 0 | 0 |
| KSN15 | 0.14 | 0.01 | 0.13 | 0.64 | 0.74 | | 0.04 | 1 | 0.05 | 1.18 | 0 | 0 |
| KSN16 | 0.08 | 0.02 | 0.05 | 0 | 0.43 | | 0.06 | 1 | 0.06 | 0 | 0 | 0 |
| KSN17 | 0.09 | 0.06 | 0.07 | 0.52 | 0.77 | | 0.02 | 1 | 0.1 | 1.64 | 0 | 0 |
| KSN18 | 0.01 | 0 | 0.04 | 0.53 | 1.33 | | 0 | 1 | 0.03 | 0.83 | 0 | 0 |
| KSN19 | 0 | 0.02 | 0.1 | 0.29 | 0.02 | | 0.08 | 1 | 0.09 | 1.3 | 0 | 0 |
| KSN21 | 0.06 | 0 | 0.07 | 0.54 | 0.07 | | 0.31 | 1 | 0.05 | 0.6 | 0 | 0 |
| KSN22 | 0.15 | 0.01 | 0.07 | 0.66 | 0.9 | | 0.09 | 1 | 0 | 0 | 0 | 0 |
| KSN23 | 0 | 0.07 | 0.06 | 0.6 | 0.4 | | 0.39 | 1 | 0.06 | 0 | 0 | 0 |
| KSN24 | 0.1 | 0 | 0.04 | 0 | 0.73 | | 0.07 | 1 | 0.06 | 1.62 | 0 | 0 |
| KSN25 | 0 | 0.05 | 0.12 | 0 | 0.63 | | 0.28 | 1 | 0.06 | 0.57 | 0 | 0 |
| KSN26 | 0.1 | 0.02 | 0 | 0.48 | 0.87 | | 0.14 | 1 | 0.02 | 1.47 | 0 | 0 |
| KSN27 | 0.06 | 0 | 0.11 | 0.59 | 0.78 | | 0 | 1 | 0.08 | 0.43 | 0 | 0 |
| KSN28 | 0.08 | 0.04 | 0.09 | 0 | 0.69 | | 0.07 | 1 | 0 | 0 | 0 | 0 |
| KSN29 | 0.2 | 0.04 | 0.24 | 0.51 | 0.71 | | 0.01 | 1 | 0.07 | 0 | 0 | 0 |
| KSN30 | 0.09 | 0.03 | 0.04 | 0.53 | 1.12 | | 0.12 | 1 | 0.05 | 0.95 | 0 | 0 |
| KSN31 | 0.1 | 0.08 | 0 | 0.68 | 1.17 | | 0.35 | 1 | 0 | 0 | 0 | 0 |
| KSN32 | 0.05 | 0 | 0 | 0.36 | 0.6 | | 0 | 1 | 0.09 | 0.46 | 0 | 0 |
| KSN33 | 0.11 | 0.01 | 0.12 | 0 | 0.52 | | 0.22 | 1 | 0 | 0 | 0 | 0 |
| KSN34 | 0.04 | 0.06 | 0 | 0.41 | 0.81 | | 0 | 1 | 0.13 | 0.45 | 0 | 0 |
| KSN35 | 0 | 0.03 | 0.51 | 0.7 | 0.34 | | 0.22 | 1 | 0 | 0.97 | 0 | 0 |
| KSN36 | 0.11 | 0.02 | 0.04 | 0.29 | 0.99 | | 0.33 | 1 | 0.07 | 0.82 | 0 | 0 |
| KSN37 | 0 | 0.1 | 0.09 | 0 | 2.7 | | 0.1 | 1 | 0.08 | 0 | 0 | 0 |
| KSN38 | 0.12 | 0.05 | 0 | 0.3 | 0.5 | | 0.08 | 1 | 0.05 | 1 | 0 | 0 |
| KSN39 | 0.14 | 0.01 | 0.05 | 0.72 | 0.2 | | 0.29 | 1 | 0.1 | 0.94 | 0 | 0 |
| KSN40 | 0 | 0 | 0.07 | 0 | 0.71 | | 0.38 | 1 | 0 | 0.68 | 0 | 0 |
| KSN41 | 0 | 0 | 0.05 | 0 | 3 | | 0.08 | 1 | 0.1 | 0.94 | 0 | 0 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN42 | 0.16 | 0.04 | 0.03 | 0 | 0.9 | | 0.27 | 1 | 0.05 | 0.01 | 0 | 0 |
| KSN43 | 0.14 | 0 | 0 | 0.22 | 0.59 | | 0.33 | 1 | 0 | 0 | 0 | 0 |
| KSN44 | 0.08 | 0.03 | 0.16 | 0 | 0.06 | | 0.05 | 1 | 0.02 | 0.6 | 0 | 0 |
| KSN45 | 0 | 0.01 | 0 | 0.28 | 0.63 | | 0.08 | 1 | 0.08 | 0.62 | 0 | 0 |
| KSN46 | 0.21 | 0.05 | 0.09 | 0.6 | 0.96 | | 0.08 | 1 | 0.08 | 0 | 0 | 0 |
| KSN47 | 0 | 0 | 0.03 | 0 | 0.49 | | 0.03 | 1 | 0.06 | 0 | 0 | 0 |
| KSN48 | 0 | 0 | 0.05 | 0.58 | 0.5 | | 0.6 | 1 | 0 | 0 | 0 | 0 |
| KSN49 | 0.36 | 0.06 | 0.03 | 0.49 | 0.57 | | 0 | 1 | 0.02 | 0.79 | 0 | 0 |
| KSN50 | 0 | 0.01 | 0.1 | 0.3 | 0.65 | | 0.1 | 1 | 0.02 | 0.65 | 0 | 0 |
| KSN51 | 0.09 | 0.01 | 0 | 0.43 | 0.61 | | 0.16 | 1 | 0.02 | 0 | 0 | 0 |
| KSN52 | 0.13 | 0.01 | 0.17 | 0.27 | 0.89 | | 0.02 | 1 | 0 | 0 | 0 | 0 |
| KSN53 | 0 | 0.04 | 0 | 0.26 | 0.2 | | 0.03 | 1 | 0 | 0.77 | 0 | 0 |
| KSN54 | 0 | 0 | 0.21 | 0.24 | 0.64 | | 0.02 | 1 | 0.04 | 0 | 0 | 0 |
| KSN55 | 0 | 0.02 | 0.08 | 0.41 | 0.9 | | 0.16 | 1 | 0.04 | 3.42 | 0 | 0 |
| KSN56 | 0 | 0 | 0 | 0.38 | 0.2 | | 0.77 | 1 | 0.05 | 0 | 0 | 0 |
| KSN57 | 0.02 | 0.23 | 0.09 | 0 | 0 | | 0.13 | 1 | 0.03 | 0 | 0 | 0 |
| KSN58 | 0.08 | 0 | 0.04 | 0 | 0.56 | | 0.11 | 1 | 0.06 | 0.59 | 0 | 0 |
| KSN59 | 0.04 | 0.04 | 0.03 | 0 | 0.82 | | 0.48 | 1 | 0 | 0 | 0 | 0 |
| KSN61 | 0.04 | 0.04 | 0.04 | 0.29 | 0.69 | | 0.1 | 1 | 0.01 | 0 | 0 | 0 |
| KSN62 | 0 | 0 | 0 | 0.35 | 0.89 | | 0.14 | 1 | 0.03 | 0 | 0 | 0 |
| KSN63 | 0.03 | 0.01 | 0 | 0 | 0.4 | | 0.16 | 1 | 0.03 | 0.02 | 0 | 0 |
| KSN64 | 0 | 0.02 | 0.13 | 0.03 | 0 | | 0.01 | 1 | 0.03 | 0.68 | 0 | 0 |
| KSN65 | 0.03 | 0.02 | 0.07 | 0.29 | 0.46 | | 0.04 | 1 | 0 | 0 | 0 | 0 |
| KSN66 | 0.05 | 0.05 | 0.1 | 0.43 | 0.62 | | 0.1 | 1 | 0.06 | 0 | 0 | 0 |
| KSN67 | 0.04 | 0 | 0.05 | 0 | 0.76 | | 0.09 | 1 | 0.01 | 0 | 0 | 0 |
| KSN68 | 0.06 | 0.02 | 0.05 | 0 | 0 | | 0.52 | 1 | 0.03 | 0.01 | 0 | 0 |
| KSN69 | 0 | 0.04 | 0 | 0.01 | 0.66 | | 0 | 1 | 0 | 0 | 0 | 0 |
| KSN70 | 0 | 0 | 0 | 0.43 | 0.97 | | 0.03 | 1 | 0.06 | 0 | 0 | 0 |
| KSN71 | 0.06 | 0.03 | 0.07 | 0.62 | 0 | | 0.11 | 1 | 0.02 | 0 | 0 | 0 |
| KSN72 | 0 | 0 | 0.05 | 0 | 0.2 | | 0.09 | 1 | 0 | 0 | 0 | 0 |
| KSN73 | 0 | 0 | 0 | 0.01 | 0 | | 0.12 | 1 | 0.14 | 0 | 0 | 0 |
| KSN74 | 0.1 | 0.03 | 0.03 | 0.01 | 0 | | 0.03 | 1 | 0 | 0 | 0 | 0 |
| KSN75 | 0.04 | 0 | 0.06 | 0.07 | 0.01 | | 0 | 1 | 0.08 | 0 | 0 | 0 |
| **MEAN** | **0.062** | **0.026** | **0.07** | **0.281** | **0.648** | | **0.142** | **1** | **0.042** | **0.484** | **0** | **0** |

## APPENDIX A5: GEO-ACCUMULATION INDEX

**GEO-ACCUMULATION INDEX (I-geo)**

| Sample | As | Pb | Cu | Ni | Cr | Zn | Fe | Mn | V | Sn | Cd |
|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN1 | -2.80629 | 0 | 3.11017 | 0 | | -1.343244 | 10.16303 | -4.10255 | -1.87045 | 0 | 0 |
| KSN2 | 0 | 0 | 0 | 0 | -4.85842 | -2.240588 | 9.933389 | 0 | -1.47003 | 0 | 0 |
| KSN3 | -1.44019 | 0 | 0 | 0 | -3.95269 | -2.131207 | 10.21396 | -4.30505 | -1.291 | 0 | 0 |
| KSN4 | 0 | 0 | 0 | 0 | -2.40464 | -2.359934 | 11.72867 | -3.66724 | -1.46206 | -1.160633 | 0 |
| KSN5 | 0 | 0 | -1.34722 | -0.53812 | -0.434345 | -1.671383 | 13.10319 | -1.35515 | -0.054305 | 0 | 0 |
| KSN6 | 0 | 0 | 0 | 0 | -3.61607 | -1.990796 | 10.59358 | -3.71801 | -2.4057 | 0 | -4.981853 |
| KSN7 | -1.76757 | 0 | 0 | 0 | -4.20349 | -2.024051 | 9.931727 | -4.12093 | -3.12707 | 0 | 0 |
| KSN8 | 0 | 0 | 0 | 0 | -4.55075 | -1.419189 | 9.647276 | -4.2636 | -4.15315 | 0 | -5.948497 |
| KSN9 | 0 | 0 | 0 | 0 | -3.61313 | -1.655323 | 10.50814 | 0 | -2.87018 | -0.886659 | -4.344197 |
| KSN10 | 0 | 0 | 0 | 0 | -3.49682 | -0.151772 | 10.43976 | 0 | -3.80824 | -2.007196 | -5.092107 |
| KSN11 | -2.79141 | 0 | 0 | -0.91171 | -2.56657 | -0.154570 | 11.17908 | -2.8154 | -1.16124 | 0 | 0 |
| KSN12 | -2.53766 | 0 | 0 | 0 | 0 | -1.224317 | 10.40761 | -3.79602 | -1.64617 | 0 | 0 |
| KSN13 | -0.916123 | -0.12639 | 0 | 0 | -0.96375 | -0.909056 | 13.91412 | -3.2844 | -1.21897 | -2.236748 | -4.977789 |
| KSN14 | 1.2811 | 0 | 0 | 0 | 3.00162 | 0.515672 | 11.37565 | -2.05076 | -1.49943 | 0 | 0 |
| KSN15 | 0 | 0 | 0 | 0 | -3.55828 | -0.764150 | 10.18941 | -2.78284 | -2.51014 | 0 | 0 |
| KSN16 | 0 | 0 | 0 | 0 | -2.03982 | -1.078154 | 11.46911 | -2.65743 | -1.08628 | -0.526069 | 0 |
| KSN17 | -1.90289 | 0 | 0 | 0 | 0 | 1.308049 | 10.48531 | -3.79586 | -1.34186 | 0 | 0 |
| KSN18 | 0 | 0 | 0 | 0 | 0 | -2.517323 | 8.757031 | -5.22247 | -2.08064 | 0 | 0 |
| KSN19 | 0 | 0 | -2.77314 | -0.86658 | -2.06928 | -0.088858 | 11.42551 | -2.82555 | -1.16223 | 0 | 0 |
| KSN21 | -2.97248 | 0 | 0 | 0 | -3.05589 | -0.505755 | 11.52751 | -3.85701 | -1.01159 | 0 | 0 |
| KSN22 | -3.21387 | 0 | 0 | 0 | 0 | -1.504714 | 10.21141 | -4.45784 | -1.73894 | -0.075609 | 0 |
| KSN23 | 0 | 0 | 0 | 0 | 0 | -2.352056 | 10.02502 | -3.64555 | -1.96578 | 0 | 0 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN24 | -1.73163 | 0 | -3.20455 | 0 | -4.16848 | -1.205119 | 10.72666 | -3.41844 | -0.95944 | 0 | 0 |
| KSN25 | -0.39312 | 0 | 0 | 0 | -4.95207 | -0.936773 | 10.60167 | -3.10927 | -1.25066 | 0 | 0 |
| KSN26 | 0 | 0 | 0 | 0 | 0 | -1.029539 | 10.11855 | -3.22776 | -1.39944 | 0 | 0 |
| KSN27 | 0 | 0 | 0 | 0 | -2.00016 | -1.876907 | 11.32124 | -4.30282 | -1.76410 | 0 | 0 |
| KSN28 | -0.41290 | 0 | -3.35669 | 0 | -5.21834 | -0.770699 | 10.46361 | -3.36733 | -1.35883 | 0 | 0 |
| KSN29 | 0 | 0 | 0 | 0 | -4.73803 | -0.745002 | 10.46042 | -3.25073 | -1.65546 | 0 | 0 |
| KSN30 | -1.24393 | 0 | -3.04976 | 0 | -3.65643 | -0.436223 | 11.37105 | -2.14357 | -0.87357 | 0 | 0 |
| KSN31 | 0 | 0 | -1.45084 | -0.31632 | -0.38496 | -0.377069 | 14.53502 | -2.28987 | -0.04736 | 0 | 0 |
| KSN32 | -1.53146 | 0 | -1.86525 | -0.40779 | -0.98105 | -0.938197 | 12.58326 | -1.81675 | -0.37467 | 0 | 0 |
| KSN33 | -1.99366 | 0 | -2.86926 | 0 | -1.10608 | -1.406088 | 12.66267 | -3.60327 | -1.68751 | 0 | 4.093109 |
| KSN34 | 0 | 0 | -2.72783 | 0 | -3.72526 | -0.634867 | 10.47348 | -2.97332 | -1.75858 | 0 | 0 |
| KSN35 | 0 | 0 | -3.06119 | 0 | -4.23484 | -0.865297 | 10.57918 | -3.44555 | -1.82047 | 0.487715 | 0 |
| KSN36 | 0 | 0 | -2.00993 | 0 | -1.40216 | -0.794190 | 12.94765 | -3.38023 | -0.17805 | 0 | 0 |
| KSN37 | 0.719224 | 0.475499 | -2.12988 | 0 | -0.98438 | -1.293174 | 12.59735 | -1.48115 | -0.43181 | 0 | 0 |
| KSN38 | 0 | 0 | 0 | 0 | 0 | -1.243773 | 10.68939 | -3.52786 | -1.32341 | 0 | 0 |
| KSN39 | -2.78403 | 0 | -3.36516 | 0 | -4.71154 | -1.169636 | 10.48727 | -3.11995 | -1.04021 | 0 | 0 |
| KSN40 | 0 | 0 | -2.23204 | -0.40609 | -0.94388 | -1.364880 | 12.6403 | 3.426262 | 0.930115 | 0 | 0 |
| KSN41 | 0 | 0 | -2.67335 | -0.39593 | -1.59268 | -0.445100 | 12.16184 | -2.90342 | -0.71009 | 0 | 0 |
| KSN42 | -2.15319 | 0 | -2.22689 | 0 | 1.041864 | -1.454822 | 12.66236 | -3.18278 | -0.84551 | 0 | 0 |
| KSN43 | 0 | 0 | -3.31234 | 0 | -1.31483 | -0.381072 | 12.21767 | -2.95101 | -0.61762 | -0.980635 | 0 |
| KSN44 | -1.09725 | 0 | -1.62212 | 0 | -1.02384 | -2.482779 | 13.46144 | -0.39529 | -0.47188 | 0 | -4.485427 |
| KSN45 | 1.929102 | 0 | 0 | 0 | -1.74071 | -0.660482 | 12.05553 | -2.57508 | -1.04463 | -0.353637 | 0 |
| KSN46 | 0 | 0 | 0 | 0 | 0 | -1.281620 | 10.14032 | -3.70688 | -1.68918 | -0.263034 | 0 |
| KSN47 | 0 | 0 | 0 | -0.94898 | 0 | -1.362405 | 10.54159 | -3.05475 | -1.28721 | 0 | 0 |
| KSN48 | 0 | 0 | -3.32193 | 0 | -4.89611 | 1.207339 | 10.57827 | -3.00458 | -1.45413 | 0 | 0 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN49 | 0 | 0 | 0 | 0 | 0 | -1.520079 | 10.42605 | -3.50815 | -1.48528 | 0 | 0 |
| KSN50 | -3.06783 | 0 | 0 | 0 | -4.7892 | -1.420433 | 10.56985 | -3.54757 | -1.17654 | 0 | 0 |
| KSN51 | -2.77303 | 0 | 0 | 0 | 0 | -1.231978 | 10.05734 | 0 | -1.87914 | 0 | 0 |
| KSN52 | -2.18686 | 0 | -2.61243 | 0 | -1.82794 | -1.474465 | 12.51897 | -3.43217 | -0.34317 | 0 | 0 |
| KSN53 | -1.56744 | 0 | -2.02551 | -1.14277 | -0.83758 | -0.955560 | 12.46148 | -2.18257 | -0.33381 | 0 | 0 |
| KSN54 | 0 | 0 | 0 | 0 | -5.04563 | -1.505806 | 10.42957 | -4.09673 | -1.72151 | 0 | 0 |
| KSN55 | -3.41006 | 0 | 0 | 0 | 0 | -1.658963 | 9.268761 | -4.48592 | -2.10398 | 0 | 0 |
| KSN56 | 0 | 0 | 0 | 0 | 0 | -1.275553 | 10.0613 | -4.54969 | -1.80617 | 0 | 0 |
| KSN57 | -1.01828 | 0 | 0 | -1.16924 | -4.21834 | -1.002695 | 10.70083 | -2.99138 | -1.16754 | 0 | 0 |
| KSN58 | 0 | 0 | 0 | 0 | 0 | -1.515122 | 9.783366 | -4.31268 | -2.32304 | 0 | 0 |
| KSN61 | -2.46801 | 0 | 0 | 0 | -2.76393 | -0.605888 | 10.7955 | -3.61834 | -2.03869 | 0 | 0 |
| KSN62 | 0 | 0 | 0 | 0 | -3.66403 | -1.472862 | 11.0141 | -3.70718 | -1.69516 | 0 | 0 |
| KSN63 | 0 | 0 | 0 | 0 | -3.32835 | -1.784549 | 10.79941 | -1.80995 | 1.435202 | 0 | 0 |
| KSN64 | 0 | 0 | 0 | 0 | -4.00965 | 1.029539 | 10.58337 | -3.18813 | -1.02312 | 0 | 0 |
| KSN65 | -2.47393 | 0 | 0 | 0 | -4.53952 | -1.032683 | 10.43316 | -3.39444 | -1.81213 | 0 | 0 |
| KSN66 | -1.74232 | 0 | -3.42294 | -1.05223 | 0 | -0.880090 | 10.36127 | -2.60005 | -1.59946 | -0.335966 | 0 |
| KSN67 | -2.57856 | 0 | 0 | 0 | -4.05092 | 1.533938 | 10.47491 | -3.73553 | -2.19692 | 0 | 0 |
| KSN68 | 0 | 0 | 0 | 0 | -4.17426 | -1.816716 | 9.808182 | -2.45018 | -1.77191 | 0 | 0 |
| KSN69 | 0 | 0 | 0 | 0 | -3.24887 | -1.158429 | 13.95475 | -3.29125 | -3.67376 | -1.320645 | -4.580949 |
| KSN60 | -1.03118 | -0.044305 | -1.82477 | 0 | -0.66861 | -0.804232 | 11.36948 | -2.59813 | -0.86519 | 0 | 0 |
| KSN70 | 0 | 0 | 0 | 0 | 0 | -1.963531 | 13.75718 | -3.88115 | -1.48611 | 0 | -4.407504 |
| KSN71 | 0 | 0 | -2.02104 | 0.254606 | -1.10091 | -1.787202 | 11.34338 | -2.72809 | -0.15225 | 0 | 0 |
| KSN72 | -2.50090 | 0 | 0 | 0 | -1.83908 | -1.909056 | 10.44559 | -3.73764 | 1.778534 | -0.310344 | 0 |
| KSN73 | 0 | 0 | 0 | 0 | 0 | -1.654111 | 10.21715 | -3.62252 | -1.41849 | 0 | -4.696736 |
| KSN74 | 0 | 0 | 0 | 0 | -3.27114 | -1.986978 | 9.667792 | -3.96155 | -2.84392 | 0 | 0 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN75 | -2.9109 | 0 | 0 | 0 | -4.45359 | -1.6012119 | 10.38439 | -5.10839 | -3.49213 | 0 | 0 |
| **Mean** | **-0.850** | **-0.008** | **-0.871** | **-0.107** | **-2.237** | **-1.023** | **11.068** | **-3.109** | **-1.526** | **0.148** | **0.65216** |
| **min** | **-3.410** | **-0.475** | **-3.423** | **-1.169** | **-5.218** | **-2.517** | **8.757** | **-5.222** | **-4.153** | **-0.076** | **0.000** |
| **max** | **1.031** | **0.044** | **0.000** | **0.312** | **0.000** | **2.483** | **14.535** | **0.000** | **0.054** | **2.237** | **5.948** |



## APPENDIX A6 : RISK INDEX

# RISK INDEX

| Sample | As | Pb | Cu | Ni | Cr | | Zn | Fe | Cd |
|---|---|---|---|---|---|---|---|---|---|
| KSN1 | 2.14 | 0.00 | 10.72 | 0.00 | 0.05 | 0.00 | 0.59 | 0.00 | 0.00 |
| KSN2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.32 | 0.00 | 0.00 |
| KSN3 | 5.53 | 0.00 | 27.64 | 0.00 | 0.14 | 0.00 | 0.34 | 0.00 | 0.00 |
| KSN4 | 2.36 | 0.00 | 11.78 | 0.00 | 0.05 | 0.00 | 0.29 | 0.00 | 0.00 |
| KSN5 | 7.62 | 0.85 | 38.08 | 4.23 | 0.22 | 0.00 | 0.47 | 0.00 | 0.00 |
| KSN6 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.38 | 0.00 | 1422.00 |
| KSN7 | 4.41 | 0.00 | 22.03 | 0.00 | 0.11 | 0.00 | 0.37 | 0.00 | 0.00 |
| KSN8 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.56 | 0.00 | 2779.00 |
| KSN9 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.48 | 0.00 | 914.00 |
| KSN10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.77 | 0.00 | 1535.00 |
| KSN11 | 2.17 | 0.00 | 10.83 | 0.00 | 0.05 | 0.00 | 0.65 | 0.00 | 0.00 |
| KSN12 | 2.58 | 0.00 | 12.92 | 0.00 | 0.06 | 0.00 | 0.48 | 0.00 | 0.00 |
| KSN13 | 28.31 | 0.00 | 141.53 | 0.00 | 0.71 | 0.00 | 0.40 | 0.00 | 1418.00 |
| KSN14 | 6.17 | 0.00 | 30.86 | 0.00 | 0.15 | 0.00 | 0.50 | 0.00 | 0.00 |
| KSN15 | 1.82 | 0.00 | 9.11 | 0.00 | 0.05 | 0.00 | 0.40 | 0.00 | 0.00 |
| KSN16 | 1.82 | 0.35 | 9.11 | 1.76 | 0.03 | 0.00 | 0.37 | 0.00 | 0.00 |
| KSN17 | 4.01 | 0.00 | 20.06 | 0.00 | 0.10 | 0.00 | 0.56 | 0.00 | 0.00 |
| KSN18 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.62 | 0.00 | 0.00 |
| KSN19 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.14 | 0.00 | 0.00 |
| KSN21 | 1.91 | 0.00 | 9.56 | 0.00 | 0.06 | 0.00 | 0.21 | 0.00 | 0.00 |
| KSN22 | 1.62 | 0.00 | 8.08 | 0.00 | 0.04 | 0.00 | 0.35 | 0.00 | 0.00 |
| KSN23 | 1.44 | 0.00 | 7.22 | 0.00 | 0.04 | 0.00 | 0.29 | 0.00 | 0.00 |
| KSN24 | 4.52 | 0.00 | 22.58 | 0.00 | 0.11 | 0.00 | 0.56 | 0.00 | 0.00 |
| KSN25 | 11.42 | 0.00 | 57.11 | 0.00 | 0.29 | 0.00 | 0.78 | 0.00 | 0.00 |
| KSN26 | 4.19 | 0.00 | 20.94 | 0.00 | 0.10 | 0.00 | 0.73 | 0.00 | 0.00 |
| KSN27 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.44 | 0.00 | 0.00 |
| KSN28 | 11.27 | 0.00 | 56.33 | 0.00 | 0.28 | 0.00 | 0.88 | 0.00 | 0.00 |
| KSN29 | 11.91 | 0.00 | 59.55 | 0.00 | 0.30 | 0.00 | 0.91 | 0.00 | 0.00 |
| KSN30 | 6.33 | 0.00 | 31.67 | 0.00 | 0.16 | 0.00 | 0.51 | 0.00 | 0.00 |
| KSN31 | 14.93 | 0.00 | 74.64 | 0.00 | 0.37 | 0.00 | 0.61 | 0.00 | 0.00 |
| KSN32 | 5.19 | 0.31 | 25.94 | 1.56 | 0.13 | 0.00 | 0.28 | 0.00 | 0.00 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| KSN3 | | | 18.8 | | 1.3 | | 0.5 | 0.0 | 768.0 |
| 3 | 3.77 | 0.00 | 3 | 0.00 | 9 | 0.00 | 7 | 0 | 0 |
| KSN3 | | | 10.2 | | 0.2 | | 0.9 | 0.0 | |
| 4 | 2.04 | 0.00 | 2 | 0.00 | 3 | 0.00 | 7 | 0 | 0.00 |
| KSN3 | | | 23.7 | | 0.1 | | 0.8 | 0.0 | |
| 5 | 4.74 | 0.00 | 2 | 0.00 | 6 | 0.00 | 2 | 0 | 0.00 |
| KSN3 | | | | | 1.1 | | 0.8 | 0.0 | |
| 6 | 0.00 | 0.00 | 0.00 | 0.00 | 4 | 0.00 | 7 | 0 | 0.00 |
| KSN3 | 24.6 | | 123. | | 1.5 | | 3.6 | 0.0 | |
| 7 | 9 | 0.47 | 47 | 2.37 | 2 | 0.00 | 8 | 0 | 0.00 |
| KSN3 | | | | | 0.0 | | 0.6 | 0.0 | |
| 8 | 1.94 | 0.00 | 9.69 | 0.00 | 0 | 0.00 | 3 | 0 | 0.00 |
| KSN3 | | | 10.8 | | 0.1 | | 0.6 | 0.0 | |
| 9 | 2.18 | 0.00 | 9 | 0.00 | 1 | 0.00 | 7 | 0 | 0.00 |
| KSN4 | | | 20.9 | | 1.5 | | 0.5 | 0.0 | |
| 0 | 4.19 | 0.00 | 7 | 0.00 | 6 | 0.00 | 8 | 0 | 0.00 |
| KSN4 | | | 17.3 | | 0.9 | | 1.1 | 0.0 | |
| 1 | 3.46 | 0.00 | 1 | 0.00 | 9 | 0.00 | 0 | 0 | 0.00 |
| KSN4 | | | 16.8 | | 1.4 | | 0.5 | 0.0 | |
| 2 | 3.37 | 0.00 | 6 | 0.00 | 6 | 0.00 | 5 | 0 | 0.00 |
| KSN4 | | | 16.3 | | 1.2 | | 1.1 | 0.0 | |
| 3 | 3.27 | 0.00 | 3 | 0.00 | 1 | 1814.00 | 5 | 0 | 0.00 |
| KSN4 | | | 35.0 | 11.5 | 1.4 | | 8.3 | 0.0 | 1008. |
| 4 | 7.01 | 2.32 | 6 | 9 | 8 | 0.00 | 8 | 0 | 00 |
| KSN4 | | | 19.6 | | 0.9 | | 0.9 | 0.0 | |
| 5 | 3.94 | 0.00 | 9 | 0.00 | 0 | 0.00 | 5 | 0 | 0.00 |
| KSN4 | | | 17.1 | | 0.0 | | 0.6 | 0.0 | |
| 6 | 3.44 | 0.00 | 9 | 0.00 | 0 | 2138.00 | 2 | 0 | 0.00 |
| KSN4 | | | 16.7 | | 0.0 | | 0.5 | 0.0 | |
| 7 | 3.35 | 0.00 | 5 | 0.00 | 0 | 0.00 | 8 | 0 | 0.00 |
| KSN4 | | | 21.6 | | 0.1 | | 0.6 | 0.0 | |
| 8 | 4.33 | 0.00 | 7 | 0.00 | 0 | 0.00 | 5 | 0 | 0.00 |
| KSN4 | | | | | 0.0 | | 0.5 | 0.0 | |
| 9 | 0.00 | 0.00 | 0.00 | 0.00 | 0 | 0.00 | 2 | 0 | 0.00 |
| KSN5 | | | | | 0.1 | | 0.5 | 0.0 | |
| 0 | 1.79 | 0.00 | 8.94 | 0.00 | 1 | 0.00 | 6 | 0 | 0.00 |
| KSN5 | | | 10.9 | | 0.0 | | 0.6 | 0.0 | |
| 1 | 2.19 | 0.00 | 7 | 0.00 | 0 | 0.00 | 4 | 0 | 0.00 |
| KSN5 | | | 16.4 | | 0.8 | | 0.5 | 0.0 | |
| 2 | 3.29 | 0.00 | 7 | 0.00 | 5 | 0.00 | 4 | 0 | 0.00 |
| KSN5 | | | 25.3 | | 1.6 | | 2.9 | 0.0 | |
| 3 | 5.06 | 0.35 | 1 | 1.73 | 8 | 0.00 | 1 | 0 | 0.00 |
| KSN5 | | | 15.8 | | 0.0 | | 0.5 | 0.0 | |
| 4 | 3.17 | 0.00 | 6 | 0.00 | 9 | 0.00 | 3 | 0 | 0.00 |
| KSN5 | | | | | 0.0 | | 0.4 | 0.0 | |
| 5 | 1.41 | 0.00 | 7.06 | 0.00 | 0 | 0.00 | 8 | 0 | 0.00 |
| KSN5 | | | 10.8 | | 0.0 | | 0.6 | 0.0 | |
| 6 | 2.18 | 0.00 | 9 | 0.00 | 0 | 0.00 | 2 | 0 | 0.00 |
| KSN5 | | | 37.0 | | 0.1 | | 0.7 | 0.0 | |
| 7 | 7.41 | 0.00 | 3 | 0.00 | 6 | 0.00 | 5 | 0 | 0.00 |
| KSN5 | | | | | 0.0 | | 0.5 | 0.0 | |
| 8 | 0.00 | 0.00 | 0.00 | 0.00 | 0 | 0.00 | 2 | 0 | 0.00 |
| KSN6 | | | 13.5 | | 0.4 | | 0.9 | 0.0 | |
| 1 | 2.71 | 0.00 | 6 | 0.00 | 4 | 0.00 | 9 | 0 | 0.00 |
| KSN6 | | | | | 0.2 | | 0.5 | 0.0 | |
| 2 | 0.00 | 0.00 | 0.00 | 0.00 | 4 | 0.00 | 4 | 0 | 0.00 |
| KSN6 | | | 16.4 | | 0.3 | | 0.4 | 0.0 | |
| 3 | 3.29 | 0.00 | 4 | 0.00 | 0 | 0.00 | 4 | 0 | 0.00 |
| KSN6 | | | | | 0.1 | | 0.7 | 0.0 | |
| 4 | 0.00 | 0.00 | 0.00 | 0.00 | 9 | 0.00 | 3 | 0 | 0.00 |
| KSN6 | | | 13.5 | | 0.1 | | 0.7 | 0.0 | |
| 5 | 2.70 | 0.00 | 0 | 0.00 | 3 | 0.00 | 3 | 0 | 0.00 |
| KSN6 | | | 22.4 | | 0.0 | | 0.8 | 0.0 | |
| 6 | 4.48 | 0.00 | 2 | 0.00 | 0 | 0.00 | 2 | 0 | 0.00 |
| KSN6 | | | 12.5 | | 0.1 | | 0.5 | 0.0 | |
| 7 | 2.51 | 0.00 | 6 | 0.00 | 8 | 0.00 | 2 | 0 | 0.00 |
| KSN6 | | | | | 0.1 | | 0.4 | 0.0 | |
| 8 | 0.00 | 0.00 | 0.00 | 0.00 | 7 | 0.00 | 3 | 0 | 0.00 |
| KSN6 | | | | | 0.3 | | 0.6 | 0.0 | 1077. |
| 9 | 0.00 | 0.00 | 0.00 | 0.00 | 2 | 0.00 | 7 | 0 | 00 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **KSN60** | 30.66 | 0.00 | 153.28 | 0.00 | 1.89 | 0.00 | 0.86 | 0.00 | 0.00 |
| **KSN70** | 2.02 | 0.00 | 10.11 | 0.00 | 0.85 | 0.00 | 0.38 | 0.00 | 955.00 |
| **KSN71** | 21.73 | 0.00 | 108.64 | 0.00 | 1.40 | 0.00 | 0.43 | 0.00 | 0.00 |
| **KSN72** | 2.65 | 0.00 | 13.25 | 0.00 | 0.84 | 1518.00 | 0.40 | 0.00 | 0.00 |
| **KSN73** | 2.97 | 0.00 | 14.86 | 0.00 | 0.00 | 0.00 | 0.48 | 0.00 | 1167.00 |
| **KSN74** | 0.00 | 0.00 | 0.00 | 0.00 | 0.31 | 0.00 | 0.38 | 0.00 | 0.00 |
| **KSN75** | 1.99 | 0.00 | 9.97 | 0.00 | 0.14 | 0.00 | 0.49 | 0.00 | 0.00 |



## APPENDIX A7: CONTAMINATION FACTOR

| | CONTAMINATION FACTOR | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | As | Pb | Cu | Ni | Cr | Zn | Fe | Mn | V | Sn | Cd |
| KSN1 | 0.214 | 0.000 | 0.174 | 0.000 | 0.000 | 0.591 | 1719.76 | 0.087 | 0.410 | 0.000 | 0.000 |
| **KSN2** | 0.000 | 0.000 | 0.000 | 0.000 | 0.052 | 0.317 | 1466.694 | 0.000 | 0.541 | 0.000 | 0.000 |
| **KSN3** | 0.553 | 0.000 | 0.000 | 0.000 | 0.097 | 0.342 | 1781.109 | 0.076 | 0.613 | 0.000 | 0.000 |
| **KSN4** | 0.236 | 0.000 | 0.000 | 0.000 | 0.283 | 0.292 | 5090.662 | 0.118 | 0.544 | 3.353 | 0.000 |
| **KSN5** | 0.762 | 0.169 | 0.590 | 1.033 | 1.110 | 4.778 | 13199.12 | 0.586 | 1.558 | 0.000 | 0.000 |
| **KSN6** | 0.000 | 0.000 | 0.000 | 0.000 | 0.122 | 0.377 | 2317.805 | 0.114 | 0.283 | 4.243 | 0.000 |
| **KSN7** | 0.441 | 0.000 | 0.000 | 0.000 | 0.081 | 0.369 | 1465.004 | 0.086 | 0.172 | 0.000 | 0.000 |
| **KSN8** | 0.000 | 0.000 | 0.000 | 0.000 | 0.064 | 0.561 | 1202.848 | 0.078 | 0.084 | 5.950 | 0.000 |
| **KSN9** | 0.000 | 0.000 | 0.000 | 0.000 | 0.123 | 0.476 | 2184.522 | 0.000 | 0.205 | 2.773 | 0.000 |
| **KSN10** | 0.000 | 0.000 | 0.000 | 0.000 | 0.133 | 1.666 | 2083.396 | 0.000 | 0.107 | 6.030 | 0.000 |
| **KSN11** | 0.217 | 0.000 | 0.000 | 0.797 | 0.253 | 1.348 | 3478.004 | 0.213 | 0.671 | 0.000 | 0.000 |
| **KSN12** | 0.258 | 0.000 | 0.000 | 0.000 | 0.000 | 0.642 | 2037.478 | 0.108 | 0.479 | 0.000 | 0.000 |
| **KSN13** | 2.831 | 0.000 | 0.000 | 0.000 | 0.769 | 0.799 | 23155.77 | 0.154 | 0.644 | 7.070 | 0.000 |
| **KSN14** | 0.617 | 0.000 | 0.000 | 0.000 | 0.187 | 1.049 | 3985.681 | 0.362 | 0.531 | 1.773 | 0.000 |
| **KSN15** | 0.182 | 0.000 | 0.000 | 0.000 | 0.127 | 0.883 | 1751.118 | 0.218 | 0.263 | 0.000 | 0.000 |
| **KSN16** | 0.182 | 0.071 | 0.000 | 0.000 | 0.365 | 3.167 | 4252.411 | 0.238 | 0.706 | 2.160 | 0.000 |
| **KSN17** | 0.401 | 0.000 | 0.000 | 0.000 | 0.000 | 0.606 | 2150.227 | 0.108 | 0.592 | 0.000 | 0.000 |
| **KSN18** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.262 | 648.9636 | 0.040 | 0.355 | 0.000 | 0.000 |
| **KSN19** | 0.000 | 0.000 | 0.219 | 0.823 | 0.357 | 1.410 | 4125.831 | 0.212 | 0.670 | 2.020 | 0.000 |
| **KSN21** | 0.191 | 0.000 | 0.000 | 0.000 | 0.180 | 2.130 | 4428.073 | 0.104 | 0.744 | 0.000 | 0.000 |
| **KSN22** | 0.162 | 0.000 | 0.000 | 0.000 | 0.000 | 0.529 | 1778.413 | 0.068 | 0.449 | 1.423 | 0.000 |
| **KSN23** | 0.144 | 0.000 | 0.000 | 0.000 | 0.000 | 0.294 | 1562.865 | 0.120 | 0.384 | 0.000 | 0.000 |
| **KSN24** | 0.452 | 0.000 | 0.163 | 0.000 | 0.083 | 0.651 | 2541.777 | 0.140 | 0.771 | 0.000 | 0.000 |
| **KSN25** | 1.142 | 0.000 | 0.000 | 0.000 | 0.048 | 0.784 | 2330.837 | 0.174 | 0.630 | 0.000 | 0.000 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN26 | 0.419 | 0.000 | 0.000 | 0.000 | 0.000 | 0.735 | 1667.548 | 0.160 | 0.569 | 1.647 | 0.000 |
| KSN27 | 0.000 | 0.000 | 0.000 | 0.000 | 0.375 | 0.408 | 3838.161 | 0.076 | 0.442 | 0.000 | 0.000 |
| KSN28 | 1.127 | 0.000 | 0.146 | 0.000 | 0.040 | 0.879 | 2118.126 | 0.145 | 0.585 | 0.000 | 0.000 |
| KSN29 | 1.191 | 0.000 | 0.000 | 0.000 | 0.056 | 0.895 | 2113.448 | 0.158 | 0.476 | 0.000 | 0.000 |
| KSN30 | 0.633 | 0.000 | 0.181 | 0.000 | 0.119 | 1.109 | 3972.985 | 0.339 | 0.819 | 0.000 | 0.000 |
| KSN31 | 1.493 | 0.000 | 0.549 | 1.862 | 1.149 | 1.155 | 35609.81 | 0.307 | 1.452 | 2.863 | 0.000 |
| KSN32 | 0.519 | 0.063 | 0.412 | 1.131 | 0.760 | 2.874 | 9205.118 | 0.426 | 1.157 | 1.757 | 0.000 |
| KSN33 | 0.377 | 0.000 | 0.205 | 0.000 | 0.697 | 0.566 | 9726.036 | 0.123 | 0.466 | 3.353 | 0.000 |
| KSN34 | 0.204 | 0.000 | 0.226 | 0.000 | 0.113 | 0.966 | 2133.133 | 0.191 | 0.443 | 3.560 | 0.000 |
| KSN35 | 0.474 | 0.000 | 0.180 | 0.000 | 0.080 | 0.823 | 2294.784 | 0.138 | 0.425 | 2.103 | 0.000 |
| KSN36 | 0.000 | 0.000 | 0.372 | 0.000 | 0.568 | 0.865 | 11850.12 | 0.144 | 1.326 | 0.000 | 0.000 |
| KSN37 | 2.469 | 0.095 | 0.343 | 0.000 | 0.758 | 3.676 | 9295.495 | 0.537 | 1.112 | 0.000 | 0.000 |
| KSN38 | 0.194 | 0.000 | 0.000 | 0.000 | 0.000 | 0.633 | 2476.953 | 0.130 | 0.599 | 0.000 | 0.000 |
| KSN39 | 0.218 | 0.000 | 0.146 | 0.000 | 0.057 | 0.667 | 2153.148 | 0.173 | 0.729 | 0.000 | 0.000 |
| KSN40 | 0.419 | 0.000 | 0.319 | 1.132 | 0.780 | 0.582 | 9576.336 | 0.140 | 0.787 | 2.313 | 0.000 |
| KSN41 | 0.346 | 0.000 | 0.235 | 1.140 | 0.497 | 1.102 | 6873.377 | 0.200 | 0.917 | 3.530 | 0.000 |
| KSN42 | 0.337 | 0.000 | 0.320 | 0.000 | 0.729 | 0.547 | 9723.921 | 0.165 | 0.835 | 2.380 | 0.000 |
| KSN43 | 0.327 | 0.000 | 0.151 | 0.000 | 0.603 | 1.152 | 7144.574 | 0.194 | 0.978 | 2.960 | 39.373 |
| KSN44 | 0.701 | 0.464 | 0.487 | 0.000 | 0.738 | 8.385 | 16919.52 | 1.141 | 1.082 | 7.510 | 0.000 |
| KSN45 | 0.394 | 0.000 | 0.000 | 0.000 | 0.449 | 0.949 | 6384.094 | 0.252 | 0.727 | 1.917 | 0.000 |
| KSN46 | 0.344 | 0.000 | 0.000 | 0.000 | 0.000 | 0.617 | 1692.901 | 0.115 | 0.465 | 1.800 | 86.629 |
| KSN47 | 0.335 | 0.000 | 0.000 | 0.777 | 0.000 | 0.583 | 2235.762 | 0.181 | 0.615 | 0.000 | 0.000 |
| KSN48 | 0.433 | 0.000 | 0.150 | 0.000 | 0.050 | 0.650 | 2293.338 | 0.187 | 0.547 | 0.000 | 0.000 |
| KSN49 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.523 | 2063.687 | 0.132 | 0.536 | 0.000 | 0.000 |
| KSN50 | 0.179 | 0.000 | 0.000 | 0.000 | 0.054 | 0.560 | 2279.987 | 0.128 | 0.664 | 0.000 | 0.000 |
| KSN51 | 0.219 | 0.000 | 0.000 | 0.000 | 0.000 | 0.639 | 1598.281 | 0.000 | 0.408 | 0.000 | 0.000 |
| KSN52 | 0.329 | 0.000 | 0.245 | 0.000 | 0.423 | 0.540 | 8803.942 | 0.139 | 1.182 | 0.000 | 0.000 |
| KSN53 | 0.506 | 0.069 | 0.368 | 0.679 | 0.839 | 2.909 | 8459.987 | 0.330 | 1.190 | 0.000 | 0.000 |
| KSN54 | 0.317 | 0.000 | 0.000 | 0.000 | 0.045 | 0.528 | 2068.737 | 0.088 | 0.455 | 0.000 | 0.000 |
| KSN55 | 0.141 | 0.000 | 0.000 | 0.000 | 0.000 | 0.475 | 925.2655 | 0.067 | 0.349 | 0.000 | 0.000 |
| KSN56 | 0.218 | 0.000 | 0.000 | 0.000 | 0.000 | 0.620 | 1602.666 | 0.064 | 0.429 | 0.000 | 0.000 |
| KSN57 | 0.741 | 0.000 | 0.290 | 0.667 | 0.081 | 0.749 | 2496.668 | 0.189 | 0.668 | 2.037 | 0.000 |
| KSN58 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.525 | 1321.837 | 0.075 | 0.300 | 0.000 | 0.000 |
| KSN61 | 0.271 | 0.000 | 0.000 | 0.000 | 0.221 | 0.986 | 2666.004 | 0.122 | 0.365 | 0.000 | 0.000 |
| KSN62 | 0.000 | 0.000 | 0.000 | 0.000 | 0.118 | 0.540 | 3102.171 | 0.115 | 0.463 | 1.910 | 0.000 |
| KSN63 | 0.329 | 0.000 | 0.000 | 0.000 | 0.149 | 0.435 | 2673.242 | 0.428 | 0.555 | 0.000 | 0.000 |
| KSN64 | 0.000 | 0.000 | 0.000 | 0.000 | 0.093 | 0.735 | 2301.454 | 0.165 | 0.738 | 0.000 | 0.000 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| KSN65 | 0.270 | 0.000 | 0.000 | 0.000 | 0.065 | 0.733 | 2073.889 | 0.143 | 0.427 | 0.000 | 0.000 |
| KSN66 | 0.448 | 0.000 | 0.140 | 0.723 | 0.000 | 0.815 | 1973.079 | 0.247 | 0.495 | 1.893 | 0.000 |
| KSN67 | 0.251 | 0.000 | 0.000 | 0.000 | 0.091 | 0.518 | 2134.782 | 0.113 | 0.327 | 2.917 | 0.000 |
| KSN68 | 0.000 | 0.000 | 0.442 | 0.000 | 0.083 | 0.426 | 1344.771 | 0.274 | 0.439 | 0.000 | 0.000 |
| KSN69 | 0.000 | 0.000 | 0.000 | 0.000 | 0.158 | 0.672 | 23817.11 | 0.153 | 0.118 | 3.747 | 0.000 |
| KSN60 | 3.066 | 0.000 | 0.423 | 0.000 | 0.944 | 0.859 | 3968.675 | 0.248 | 0.823 | 1.520 | 0.000 |
| KSN70 | 0.202 | 0.000 | 0.000 | 0.000 | 0.424 | 0.385 | 20768.97 | 0.102 | 0.535 | 2.913 | 0.000 |
| KSN71 | 2.173 | 0.000 | 0.370 | 1.257 | 0.699 | 0.435 | 3897.522 | 0.226 | 1.350 | 2.427 | 0.000 |
| KSN72 | 0.265 | 0.000 | 0.000 | 0.000 | 0.419 | 0.399 | 2091.831 | 0.112 | 0.437 | 1.860 | 95.018 |
| KSN73 | 0.297 | 0.000 | 0.000 | 0.687 | 0.000 | 0.477 | 1785.497 | 0.122 | 0.561 | 3.257 | 0.000 |
| KSN74 | 0.000 | 0.000 | 0.000 | 0.000 | 0.155 | 0.378 | 1220.075 | 0.096 | 0.209 | 0.000 | 0.000 |
| KSN75 | 0.199 | 0.000 | 0.000 | 0.000 | 0.068 | 0.494 | 2004.955 | 0.043 | 0.133 | 1.533 | 0.000 |



## APPENDIX A8:Total Organic Content

| TOTAL ORGANIC CONTENT | |
|---|---|
| SAMPLE Code | Percentage/ % |
| KSN2 | 7.8 |
| KSN5 | 10.2 |
| KSN13 | 5.5 |
| KSN18 | 2.5 |
| KSN21 | 7.05 |
| KSN23 | 24 |
| KSN27 | 3.9 |
| KSN31 | 32 |
| KSN32 | 0.45 |
| KSN36 | 2.1 |
| KSN39 | 9 |
| KSN44 | 7.5 |
| KSN46 | 5.4 |
| KSN53 | 7.9 |
| KSN56 | 1.5 |
| KSN59 | 15.2 |
| KSN64 | 9.3 |
| KSN67 | 8.3 |
| KSN70 | 2.4 |
| KSN73 | 15 |