UNIVERSITY OF CAPE COAST

ASSESSMENT OF HEAVY METALS AND METALLOID IN SOILS, SEDIMENTS AND WATER FROM PRISTINE AND MAJOR MINING AREAS IN GHANA – DATA TO AID GEOCHEMICAL BASELINE SETTING

BY

GEORGE YAW HADZI

Thesis submitted to the Department of Chemistry of the School of Physical Sciences, College of Agriculture and Natural Sciences, University of Cape Coast, in partial fulfilment of the requirements for the award of Doctor of Philosophy degree in Chemistry

OCTOBER 2017

DECLARATION

Candidate's Declaration

I hereby declare that this thesis is the result of my own original research and that no part of it has been presented for another degree in this university or elsewhere.

Candidate's Signature .... Date 18/05/2018

Name: GEORGE YAW HADZI

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with the guidelines on supervision of thesis laid down by the University of Cape Coast

Principal Supervisor's Signature .... Dtae 18/5/18

Name: PROF. DAVID KOFI ESSUMANG

Co-Supervisor's Signature .... Date 18/05/18

Name: PROF. SHILOH KWABENA DEDEH OSAE

ABSTRACT

The distribution, risks and geochemical baseline analysis of the heavy metals in soils, sediments and water in pristine and major mining areas in Ghana were investigated. The surface soils, sediment and water were pulverized, acid digested, and analyzed for the major and minor elements using (ICP-QQQMS). The average metals and metalloid (As, Cd, Pb and Zn) concentrations from the mining sites were higher than the pristine sites ($p>0.05$) with many of the metals not detected in pristine water samples. The natural geogenic metals however, showed varied concentrations in both the pristine and the mining areas. The total heavy metals concentrations from the study ranged from 0.01±0.01 (Cd) to 86859.36±47.07 (Fe) in the soils and sediments and 0.002±0.00 (As) to 0.929±0.06 mg/L (Fe) in the waters. With the exception of Al, Fe, Mn and As, the metals levels in the water samples were generally found to be below the WHO, EC and USEPA guideline limits. For the soils and sediments, the concentrations of Cd, Pb and Zn were below the guideline limits. However, As showed exceptionally high concentrations in samples from the mining areas, especially those from Obuasi and Kwabeng mining areas, indicating a potential biological effects. Elevated human health risk indices ($>10^{-4}$) were obtained for As and Cr with the severity of the metals and metalloid in the soils and sediment ranked as As >Cr> Pb> Cd. The multi-criteria ranking, employing PROMETHEE and GAIA, indicated that the pristine sites have low degree of contamination which is suitable for setting the geochemical baseline values for the metals and metalloid in the pristine areas. The proposed geochemical baseline values will be applied for speedy identification of sites that could be affected by heavy metals contamination.

KEY WORDS

Contamination

Geochemical baseline

Health risk

Heavy Metals

Mining

Pristine

ACKNOWLEDGEMENTS

First and foremost, I would like to express my gratitude to my two supervisors; Prof. D. K. Essumang and Prof. Shiloh K. D. Osae for their patience, guidance and invaluable contributions in all aspects of this Thesis Work and whose supervisory style was central to the completion of this research:

I would like to especially thank Prof. Godwin Ayoko of Queensland University of Technology (QUT) – Australia for accepting my candidature and providing me with excellent supervisory support throughout my sample analysis. Furthermore, my sincere gratitude goes to Karren, Sunny, Shane, Aarshi, Irina, James and David of the Central Analytical Research Facility (CARF) of QUT for the provision of resources and immense support for this project. Access to CARF was supported by generous funding from QUT's Science and Engineering Faculty (SEF). I am very thankful to some PhD students of QUT; Alfred, Godfred, Mawutorli and Gustav for their contributions towards this work. I must not also forget my very good friend Kwabena who volunteered as my escort to all the forest reserves and other sampling sites. My sincere thank also goes to the University of Cape Coast and the Government of Ghana for granting me financial assistance in every facets of this project and not forgetting Mr Agyemang of Agric Technology Center. To my brothers and sisters for your interest and inputs in my life and this work has been invaluable to my educational success.

Finally, I thank the lecturers and colleague Teaching Associates (TAs) and the entire staff of Department of Chemistry, for their diverse contributions towards this project. Thank you for everything, everyone.

DEDICATION

To my lovely mother, Christine Afua Asamoah and my beautiful wife, Noelle Ablah Nazzar

TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS

ANOVA	Analysis of Variance
CA	Cluster Analysis
CEC	Cation Exchange Capacity
PCA	Principal Component Analysis
PEL	Probable effect level
TEC	Threshold Effect Concentration
BCR	Bureau Community of Reference
CF	Contamination Factor
CRM	Certified Reference Material
EF	Enrichment Factor
GAIA	Geometrical Analysis for Interactive Aid
HCA/CA	Hierarchical Cluster Analysis
ICP-MS	Inductively Couple Plasma, Mass Spectrometry
Igeo	Geo-accumulation Index
ISQGs	Australian Interim Sediment Quality Guidelines
LOD	Limit of Detection
LOQ	Limit of Quantification
MCd	Hakanson's modified degree of contamination index
MPI	Modified Pollution Index
NPI	Nemerow Pollution Index
PROMETHEE	Preference Ranking Organization METHod for Enrichment of Evaluations
RSD	Relative Standard Deviation
USEPA:	United States Environmental Protection Agency

WHO:	World Health Organization
ATSDR:	Agency for Toxic Substance and Disease Registry
NRC	National Research Council.

CHAPTER ONE

INTRODUCTION

Chapter One captures the introduction and the background of heavy metals such as their definition, physical properties, nature and biological activities and thier fate in the environment. The problem statement gives insight into how mining has contributed to heavy metals pollution of our soils, sediments and water in some mining areas of Ghana. The problem statement further indicates the need for setting geochemical guideline values which would serve as basis for the development of control standards as an instrument for assessing the effects of contaminants in Ghanaian environment.

The justification section under the chapter illucidates some prolems caused by heavy metals contamination both in Ghana and worldwide such as the Minamata disease and other devastitations suffered by countries due to organic mercury contamination. The chapter also raises some specific objectives and hypothesis for the study.

Background to the Study

Environmental Pollution is the introduction of contaminants into the natural environment by man resulting in instability and creating some imbalances in physical, chemical and biological dynamics of the environment (Goudie, 2013).

Ghana, like many other countries, has a long history of metal pollution largely emanating from industrial effluent discharges, domestic and agricultural activities. Ghana is currently battling with the ultimate challenge of sustaining economic development activities that are managed at levels that promote human health and environmental protection (Hilson, 2006). Soils and water bodies are contaminated in Ghana as a result of run-offs carrying fertilizers and agrochemical residues from farmlands and various materials from sewage sludge (Amantoge, 2012). However, one of the predominant industrial activities that contribute to metal pollution in the Ghanaian environment is improper disposa of wastes from mining activities (Obiri, 2007). Both surface and underground mining still remain one of the main anthropogenic sources of heavy metals in the Ghanaian environment. Gold mining is widespread and according to Naylor (2007), it contributes about 44% of Ghana's export earnings. The large-scale extraction of gold occurs predominantly in the Western, Brong Ahafo, Eastern and Ashanti regions of Ghana, and is accompanied by arsenic, mercury, and sulphur contamination of surface and groundwater bodies, soil and even air causing acid rain and degradation to the surrounding environment and impacts on human health (Amonoo-Neizer & Amekor, 1993).

In Ghana both local and foreign investor companies have equal right to engage in mineral exploration. In 2000, a total of 224 local and foreign companies have obtained mineral right for gold exploration as well as 600 registered small-scale miners. At the same time, the illegal miners sector locally referred to as "galamsey operators" dominated the small-scale gold sector with an estimated number of 200,000 people in 2004, a situation which was seen as alarming compared with about 60,000 people as at 1997 (Owusu-Koranteng, 2008)

The extent of environmental and health impacts resulting from mining activities depend on the method employed in the extraction of the mineral from its ores. In Ghana, the most commonly approach adopted by many mining companies is the use of cyanide while the illegal miners resorted to the use of mercury for gold extraction (Obri, 2007; Armah, Obiri, Yawson, Pappoe, & Akoto, 2010). The use of cyanide in gold extraction lately has become unattractive as a result of several cyanide spillages witnessed which has caused significant damages to the environment. According to Amegbey and Adimado (2003), the number of cyanide spillages cases that were reported between 1989 and 2003 in Tarkwa and Obuasi alone were eleven (11).

A separate investigative report issued by WACAM, indicated that the number of officially reported cyanide spillages increased from eight (8) between 1989 and 2002 to about thirteen (13) as at 2006. This situation had led to the pollution of water bodies like streams and rivers and over 52% of the population in those mining areas still lacks potable water (Andrews, 2016: Owusu Koranteng, 2008). Regardless of the fact that gold is the main contributor to Ghana's economy, accounting for 38% of total stock and 95% of total mineral exports (Aryee, 2001), small scale mining as well as improper regulation of large scale mining pose enormous environmental challenges such as land degradation, subsidence due to both surface and underground mining and water pollution all of which can result to ill health (Manaf, 1999; Hilson, 2002; Akabzaa, Banoeng-Yakubu, & Seyire, 2005).

The environmental destruction caused by the unplanned and sometimes dangerous and irrational methods used by small-scale miners in Ghana has been an issue of great concern. The Ad-hoc nature of the operations has resulted in a myriad of primary and secondary problems. Of much importance include atmospheric pollution, water pollution, land degradation and deforestation (Amegbey & Adimado, 2003; Amankwah & Buah, 1998).

Wastes from mining processes such as tailing, can result in the introduction of toxic metals into the environment. The waste rocks for instance are known to contain arsenic (As), cadmium (Cd), lead (Pb) and other toxic metals (Chapman, 1997: Donato *et al.*, 2007).

The presence of these metal pollutants from mining activities in the environment increases the influx of metals, which can be transported by wind and water and may become available to plants and animals. Eventually, the metals attain higher concentrations and accumulate in large quantities in different crops and plant parts, and finally pose serious health hazard to humans and animals through bio-magnification (Ray, 1990). It must however, be noted that heavy metals such as Cr, Mn, Co, Cu, Fe and Zn play important biochemical roles in the life processes of many organisms, and their presence in trace amounts are essential (Viarengo, 1985). However, at high concentrations toxic effects are observed. For example, Fe is required for the production of red blood cells but at high concentrations Fe and Mn can cause pathological effects such as the iron oxides deposition which results in Parkinson's disease (Matusch *et al.,* 2010; Altamura & Muckenthaler, 2009). Excess Cu had been associated with liver damage and Zn may produce adverse nutrient interactions with Cu. Also, Zn reduces immune function and the levels of high density lipoproteins (Spears, 2000). Ni helps form enzymes that are needed in the formation of nucleic acids and DNA, but at high concentration it can cause gastrointestinal distress, increase red blood cells and reduce lung functions (Lu, Probst, & Liao, 2005).

There are reports which indicate increased concentrations of heavy metals and other pollutants in water bodies around mining communities in

Ghana. Reports from studies have shown that from 1947 to 1992, mine effluents had been discharged without restriction and treatment into water bodies, soil and air, thereby resulting in the degeneration of the environment (Serfor-Armah, Nyarko, Osae, Carboo, & Seku, 1997; Tufour, 1997; Tsidzi, 1993). Meanwhile recent studies on heavy metals have demonstrated elevated body loadings of the metals and persistent toxic substances in children and e-waste workers, respectively (Huo *et al.,* 2007; Bi, Kong, Hu, & Cui, 2007). Heavy metals have therefore been classified among the most dangerous groups of anthropogenic environmental pollutants due to their toxicity and persistence in the environment (Nyarko *et al.,* 2008; Carreras, Wannaz, & Pignata, 2009).

Recent studies on heavy metals in developing countries, indicate major problems which have arisen such as ground water contamination with As in Bangladesh (Alam, Snow, & Tanaka, 2003) and heavy metals (Cd, Pb, Cu, and Zn) contamination of drinking water sources in Bolivia, Hong Kong, and Berlin (Ho, Chow, & Yau,2003; Miller, Hudson-Edwards, Lechler, Preston, & Macklin, 2004).

In the past, mining was only seen in the southern part of Ghana, but currently, metal and gold exploration is increasing across the country, especially in the Upper East Region (Cobbina, Nkuah, Tom-Dery, & Obiri, 2013). Due to mismanagement of wastes produced from these mining activities, pollutants seen as metals can now be found at elevated levels in the environment. For instance, Iron and manganese have been measured in elevated concentrations in water samples around mining areas at Tarkwa (Armah & Gyeabour, 2013; Armah, Luginaah, & Obiri, 2012), which has resulted in the closure of hundreds of wells in favour of surface waters which are likely to be contaminated with harmful microorganisms (Pelig-Ba, Parker, & Price, 2004).

Heavy metals can induce adverse effects on humans and wildlife even at trace levels (Babalola *et al.,* 2010). River sediments serves as basic components of our environment provide foodstuffs for bentic organisms' and also serves as a sink and reservoir for a variety of contaminants. It has been recognized that sediments absorb persistent and toxic chemicals to levels many times higher than the water column concentration (Casper, Mehra, Farago, & Gill, 2004: Linnik & Zubenko, 2000). Heavy metals released from anthropogenic sources into the aquatic environment, may bind or adsorb onto particulate matter depending on the river morphology and hydrological conditions, the associated contaminants can settle along the watercourse and become part of the bottom sediments, often at many kilometers downstream from the chemical sources (Vigano *et al.,* 2003; Wildi *et al.,* 2004).

The recent and past mining related studies in Ghana conducted on environmental samples like water, air, soil and sediment and on biota such as fish, urine, blood and nails, indicated high levels of Hg, As, Fe, Mn, Pb, Cd and Cu (Babut *et al.*, 2003). Findings by WACAM in 2009 also show that most of the water bodies in Tarkwa and Obuasi for instance, have elevated levels of As, Mn, Cd, Fe, Cu, Hg, Zn and Pb which were all above The World Health Organisation (WHO) and Ghana Environmental Protection Agency's (EPA-Ghana) permissible limits.

Despite the large body of literature that is available on heavy metal pollution in Ghana, the results are not in a common data base to elicit a coherent account on the scope and levels of heavy metal pollution in

Ghanaian. It is therefore necessary to investigate and obtain scientific evidence on the levels, distribution and Risk assessment of heavy metals in Ghanaian environment by analyzing samples from pristine environments and major mining areas.

Statement of the Problem

Gold mining is central to Ghana's socio-economic gains over 1000 years and its processes had contributed immensely to soil and water contamination by heavy metals in the mining areas (Hilson, 2006). The open cast method of mining, as well as the commercial mining contribute to the degradation and introduction of toxic chemicals into the environment (Obiri, 2007).

Reports have shown that even though, Ghana earns about 40% of gross foreign exchange and generates about 5.7% of Gross Domestic Product (GDP) from the mining sector, the gains are achieved at a great environmental cost as the exploitation of gold and other minerals puts stress on water, soil, vegetation and poses human health hazards (Bhattacharya, Routh, Jacks, Bhattacharya, & Mörth, 2006; Aryee, 2001, Obiri *et al.*, 2016).

Gold mining is associated with the release of toxic chemicals at high levels and Hg, and As are among the reported cases of contamination. Mining related activities contribute to contamination of land through seepage of acid water from gold mine dumps, which result in increasing sulphates and a lowering of soil pH. High levels of arsenic comparable to other arsenic-endemic areas of the world were found in the urine of inhabitants of Tarkwa (Asante *et al.*, 2007; Obiri, Dodoo, Okai-Sam, & Essumang, 2006), while arsenic and mercury have been reported in surface soil and cassava (*Manihot esculenta*) around Dunkwa (Golow & Adzei, 2002).

Among the major metal pollutants sources in Ghanaian environment, pollutants emanating from mining activities especially from surface mining ranked very high (Obiri, 2007). The issue of metal contamination from mining activities has become so devastating to the extent that three environmental pressure groups namely Wassa Association of Communities affected by Mining (WACAM), The National Coalition on Mining (NCOM) and Third World Network-Africa (TWN-Af) have expressed serious concerns over the magnitude of land degradation and water pollution that occur in mining communities in Ghana (Hilson, 2006). In some mining communities, the spent rocks from surface mining operations are deposited on agricultural lands which deprive the people, who are predominantly farmers, of their livelihood (Hilson, 2006).

The heavy metals in sediments from waste damps and deforested lands pollute rivers that serve as main sources of drinking water during heavy rainfall. As a result, high levels of metals were determined in water bodies around the mining areas, for instance, Smedley (1996), reported as high as 350 mg/L of Arsenic in rivers affected by surface mining contamination in the Obuasi area of Ghana as a result of acid mine drainage (AMD) and tailings leakages (Asklund & Eldvall, 2005). Since local inhabitants largely depend on local water and food crops, for their livelihood, ingestion of Arsenic is inevitable and may pose a risk to their health. These activities have serious health implications and deprive the people in these communities of basic human needs like good quality drinking water (Owusu-Kwateng 2008; Smedley 1996; Akabzaa, Banoeng-Yakubo, & Seyire, 2007).

In order to protect both health and the environment, it is necessary to regulate the amount of these harmful pollutants that are released without causing unacceptable harm to health and the environment. Regulation in this way involves setting control standards (geochemical baseline) on the potentially harmful pollutants which can be released into the environment (Santos-Francés, Martinez-Graña, Alonso Rojo, & García Sánchez, 2017; DeSombre, 2007).

Many studies on heavy metals in soils, sediments and water have been conducted and many great results have been published in the literatures, however, only a few of the researches have assessed the potential human health risk (Nkoom, Cobbina, & Kumi, 2013; Foli & Nude, 2012: Akabzaa *et al.,* 2007: Armah *et al.,* 2011). Ghana currently has no national baseline values for regulating heavy metals in soils, sediments and water assessment and as a result, regulators for the past years have relied on international guidelines to select baseline values for decision-making. Meanwhile, not all the different methods used in deriving these international baseline standards will be appropriate for use in Ghana's context.

Moreover, research is now moving towards site specific quality guideline setting (Kwok *et al.*, 2008; Burton, 2002). When data on heavy metals are available, they should be compared with control standards to reflect maximum tolerable risk of exposure. Unfortunately; such standards are not in place in Ghana. When there are no standards, government policies tend to neglect the environmental media (soil, water and sediment) pollutants involved which may lead to a divergence between risk as established by governments and actual risks (Toccalino and Norman, 2006). There is therefore a need to develop control quality baseline values which will serve as an instrument for appraisals the degree of pollution and risk assessment without which researchers are unable to consistently assess the effects of contaminants on the Ghanaian environment.

This baseline standard will not only protect people and the environment but also secure a consistent approach and decision-making process throughout the country. With the above background in mind, the objectives of this study are; to investigate (1) the distribution and seasonal variation of heavy metals in soils, sediments and water from pristine and major mining areas in Ghana (2) to evaluate the pollution and potential health impacts of these metals on the general population in the mining areas, (3) to recommend geochemical baseline thresholds which will help in the prioritization of pollution control and health intervention policies to protect local population.

Objectives for the Study

General Objective

The main objective of this study is to determine the levels and distribution of heavy metals (As, Cd, Hg, Zn, Co, Cu, Mn, Fe, Al, V, Cr, and Pb) in soils, sediments and water from Pristine and Major mining areas in in Ghana and to use the results to set geochemical baseline values for the metal.

Specific Objectives

This study addresses the following specific objectives;

- To measure the levels and distribution of As, Cd, Hg, Zn, Cr, Cu, Mn, Co, Fe, and Pb in surface soils, sediments and surface water samples from pristine and major mining areas in Ghana.
- To characterize the sources of heavy metals in soil, sediment and water samples from pristine and mining areas in Ghana.
- To compare metal concentrations from this study with results from previous studies (Secondary data) at similar locations in order to establish possible trends;
- To verify the health hazards associated with exposure to the toxic metals by performing risk and hazard assessment analyses on the results so as to substantiate causal relationship between contamination and illness.
- To come up with authentic results on the geochemical background levels of the toxic metals so as to assist in the development and implementation of policy based on sound scientific data.

Justification

The international Scientific Literature has referred to heavy metals as elements that can cause adverse effects to humans, animals and ecosystems due to their bioavailability and toxicity in various environmental compartments (Walker, Sibly, Hopkin, & Peakall, 2012). Several measures have been taken at global, regional and national level in order to control the pollution from heavy metals, particularly Cd and Pb. The first internationally binding instrument to deal with problems of air pollution on a broad regional basis is represented by the 1979 Geneva Convention on Long Range Transboundary Air Pollution (LRTAP) (Altshuller, 1979). The aim of the Protocol was to reduce emissions from heavy metals caused by anthropogenic activities that are subject to long-range transboundary atmospheric transport and are likely to have serious adverse effects on human health and the environment. Further measures were taken following the adoption of the treaty at regional level and include the European Union strategies on air quality, mercury and waste treatment (Strincone, Fino, Cattani, Catrambone, & Pirrone, 2013).

Despite the enormous health issues associated with pollution, many developing countries like Ghana either have not developed environmental pollution control measures, or have not provided adequate implementation structures to ensure that policies are effective (Armah & Gyeabour, 2013). Ghana is endowed with abundant natural resources, which have played very important roles in the agricultural, industrial, economic and social development efforts of the country. However, as a result of incessant exploitation of these natural resources to meet the legitimate socio-economic aspirations of the people, adequate care has often not been taken to guard against the depletion and mismanagement of the resources (Hilson, 2006). Consequently, this process of unsustainable development has caused irreparable damage resulting in deforestation, land degradation, air and water pollution. Ghana's first Environmental Policy which was enacted in 1995, identified a restructured lead agency (Hilson, 2002) to drive the process towards sustainable development. However, the principal challenge confronting the environmental management process in Ghana is ineffective enforcement of the policies and laws that exist to achieve the desired result.

In the Obuasi mining district, evidence of land contamination in association with gold mining and municipal waste discharge activities have been observed and indications of heavy metal contamination of streams, sediments, and biota were high (Golow, Schlueter, Amihere-Mensah, Granson, & Tetteh, 1996; Amonoo-Neizer, Kambo-Dorsa, & Nyamah, 1995).

Heavy metals contamination can result in several diseases and deformities; for instance, in 1950's fish contamination by large amounts of organic mercury led to severe nerve damage of new born babies from pregnant women in Japan, which was referred to as Fetal Minamata Disease (Harada, 1995). In Iraq, children born to mothers who consumed grain contaminated with organic mercury walk at later age compared to children whose mothers were not exposed to mercury contaminated grains. Also in Faroe Islands, mercury contamination caused by eating contaminated whale meat by pregnant women, led to lower score on brain function test than those women who did not consume mercury contaminated meat (Mahaffey, 2005). Within the European community, 13 elements have been identified as being of highest concern, some of which are essential for humans in minute amounts (Co, Cu, Cr, Ni) while others are carcinogenic or toxic, affecting, among others, the central nervous system (Hg, Pb, As), the kidneys or liver (Hg, Pb, Cd, Cu) or skin, bones, or teeth (Ni, Cd, Cu, Cr) (Bonner and Bridges, 2016). According to the World Health Organization estimates, by 2020, 70% of worldwide cancer cases will occur in developing countries. Despite the statistical limitation due to scarcity of reliable data in Ghana, available data indicate that cancer has emerged as an important cause of morbidity and mortality in Ghana (WHO, 2008). In 2008, GLOBOCAN, an International Agency for Research on Cancer estimates that 16,600 cases of cancer occur annually in Ghana, yielding an age-standardized rate of 109.5 cases per 100,000 persons. The increasing scourge of cancer epidemiology among Ghanaian in recent years may be associated with continual release of heavy metals from mining activities into water, soil and other environmental receptors. A recent media report by MyJoyOnline on the 23rd of July 2015 indicated that Ghana Water Company has identified As and Hg as potential cancer causing chemicals released into Pra River by illegal gold miners. In South Africa and Mozambique, between 1964 and 1996, mining activity and exposure to mining dust were closely associated with lung, liver, esophageal and lymphatic cancers (McGlashan, Harington, & Chelkowska, 2003).

In Ghana, Epidemiological studies on heavy metals exposure in mining communities around Tarkwa by Obri *et al.*, in 2010, revealed that residents suffered from skin, lung, liver, and blood cancers due to ingestion of elevated levels of arsenic in water and food crops. Earlier work by Obiri *et al.*, (2006) in some mining communities also showed 10,000-fold likelihood of residents suffering from cancer or cancer related diseases due to heavy metals exposure. Many other studies have related heavy metal levels with cancer occurrence (Cobina *et al.*, 2013; Armah & Gyeabour, 2013; Obiri *et al.*, 2016).

The Commission on Human rights and Administrative Justice in its recent report on mining and its associated heavy metal contamination in Ghana has indicated that malaria, tuberculosis, skin cancer and stomach ache are some of the commonest diseases reported at health centers around mining communities. The commission therefore, recommended a further study on samples from different environmental receptors in order to establish the veracity of the chemical toxicity claims. A more recent report by regional hospital authorities around the major mining areas revealed that the hospitals are recording increasing cases of kidney infection from persons linked to artisanal and illegal mining (Obiri, 2007; Cobbina *et al.*, 2013; Rajaee, 2015). Although signs of contamination have become obvious overtime, the geochemical implications of these contaminations in stream sediments, as well as the severity of such contaminations have not been thoroughly evaluated using relevant evaluation indices in order to assist environmental managers and the relevant stakeholders plan to avert any future epidemics.

Hypotheses for the Study

The study seeks to test the following hypotheses in attempts to achieve the specific objectives stated:

H_1: The levels of heavy metals in the present study do differ significantly from that in literature around the same study areas and that of WHO and USEPA set standards and for that matter do trigger health related illnesses.

H_2: There are statistical differences in the concentrations of the heavy metals from the mining and pristine areas.

H_3: The levels of the heavy metals have high probability of occurrence to threaten the health of residents living around the mining communities.

H_4: The results of the metals from pristine areas are low enough to allow for setting geochemical base-line values for the pollutants.

H_5 The heavy metals levels from pristine and the mining sites are influenced by physico-chemical parameters such as pH, Conductivity, Organic matter and soil texture.

H_6: Risk and hazard indices from the results would be within or lower than the USEPA threshold limits for the pristine samples and above for the mine samples, making it necessary to establish causal relationship between metal contamination and illness from the mining areas.

Organization of the Study

The study is organized into five chapters. Chapter one is introduction, which covers the background of the study, problem statement, objectives of the study, Justification of the study, Scope of the study and hypothesis of the study. Chapter two focuses on literature review. Issues reviewed among others include Heavy metals contamination: a global problem; properties of heavy metals in soils, water and sediments; Sources of metals in the environment; Impact of heavy metals on soils and water; Health risk and and pollution indices for analysis of heavy metals. The elements considered in this work are inorganic form of heavy metals and Arsenic except a few which normally have metal–alkyl bonds, and which have environmental implications.

The present work is also not primarily a work of toxicology although the toxicity properties of the elements are discussed under this chapter. The present work is a consideration of the inputs (natural and anthropogenic) that results in the introduction of heavy metals in the natural environment (e.g. sediment, water and top soil), their properties, behaviour, and their ultimate fate in the environment.

Chapter Three provides the methodology of the study. It deals with study area; sampling technique; sample collection and instrumental analysis; analysis of results by statistical tools such as excel and SPSS, calculation of risk assessment and pollution indices.

Chapter Four includes results and discussion of heavy metals concentrations; effect of physico-chemical parameters such as pH, conductivity, texture and cation exchange capacity on metal levels in soil, sediment and water; correlations; Principal component analysis; cancer and non-cancer risk assessment and hazard estimation.

Chapter five provides the summary of the work, conclusions and recommendations for further study.

Chapter Summary

The release of high levels toxic chemicals such as Hg and As, into the Ghanaian environment as a result of gold mining has been captured and reported under this chapter. Mining related activities contribute to contamination of land through seepage of acid water from gold mine dumps, which result in the lowering of soil pH. A more recent report by some regional hospital authorities around the major mining areas which has resulted in increasing cases of kidney infection from persons linked to artisanal and illegal mining (Obiri, 2007; Cobbina *et al.*, 2013) was also captured under the chapter.

The enormous health issues associated with pollution in many developing countries like Ghana which necessitate the development of environmental pollution control measures (Armah & Gyeabour, 2013) and in this case the proposal of geochemical baseline values to ensure that policies are effective have also been captured under the chapter.

CHAPTER TWO

LITERATURE REVIEW

Introduction

A heavy metal is a member of a loosely defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. The term heavy metal has been called a "misinterpretation" in an IUPAC technical report due to the contradictory definitions and its lack of a "coherent scientific basis" (Duffus, 2002).

The term "heavy metals" refers to any metallic chemical element that has a relatively high density (superior to 5 g/cm^3) and is toxic or carcinogenic even at low concentration such as Hg, Cd, As and Cr (Lenntech, 2004). "Heavy metals" is a general term, which applies to the group of metals and metalloids with atomic density greater than 4.5 to 5 g/cm^3, or 5 times or more, greater than water (Lars, 2003; Duffus, 2003). However, to be regarded as heavy metal has little to do with density but concerns chemical properties.

A pollutant is any substance in the environment, which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and may eventually cause death. Such a substance may be present in the environment beyond a certain tolerable limit in air, water or soil, which may be poisonous or toxic and will cause harm to living things in the polluted Environment (Khudzari, Wagiran, Hossain, Ibrahim, & Agam, 2011).

Heavy metals are classified among the most dangerous groups of anthropogenic environmental pollutants due to their toxicity and persistence in the environment (Nyarko *et al.*, 2008; Carreras *et al.*, 2009). Although adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues to be on the rise. For example, mercury is still used in gold mining in many parts of of the world (Hylander and Meili, 2003). Arsenic is still common in wood preservatives, and tetraethyl lead in the past was used as a common additive to petrol, although this use has decreased dramatically in the developed countries, it is still predominant in developing countries (Lars, 2003)

Sources and Distribution of Heavy Metals

Major metal sources to water and land include diverse manufacturing, mining, combustion, and pesticide activities. Heavy metals contamination assessment of an environment involves two considerations (Brady, Ayoko, Martens, & Goonetilleke, 2015). The first consideration is the source, which is the physical location from which the heavy metal originates (such as a factory or wastewater treatment plant). The second is the mechanism of distribution and deposition; that is how a heavy metal is transported from the source to its final location (Brady *et al.*, 2015).

The total contents of heavy metal(loid)s in a soil are the sum of the concentrations of elements derived from minerals in the geological parent material on which the soil has developed (lithogenic source) and inputs from a wide range of possible anthropogenic sources (Alloway, 2013). Common sources of heavy metals in soils include atmospheric deposition of aerosol particles (<30 mm diameter), raindrops containing heavy metals, direct applications of agricultural fertilisers, agrichemicals and various organic materials including sewage sludges, livestock manures, food wastes and composts (Alloway, 2013).

Soil contamination can occur either by a point source whereby the contaminant comes from a single, identifiable origin and affects a relatively restricted area (Pulford and Flowers, 2006; Vamerali *et al.*, 2010). Examples of a point source pollution include an abandoned metal working facilities, accidental release or spillage of contaminants, and inappropriate municipal and industrial waste disposal are frequently associated with localized contaminated soils (Vamerali, Bandiera, & Mosca, 2010). Another type of soil contamination is the diffuse source in which the contaminants do not come from one specific source and its effects are usually seen over a large area (Pulford & Flowers, 2006).

Point sources of heavy metals contamination are generally considered to be completely anthropogenic in nature such as industrial processing of ores and metals (Ahdy & Youssef, 2011), Others include, leaching from waste disposal areas and fertilizers (Ahdy & Youssef, 2011; Deng, Zhang, Wang, Chen, & Xu, 2010); and discharge or leakage of human sewage (Deng *et al.*, 2010).

Lithogenic sources of heavy metals are linked to diffuse deposition mechanisms, such as atmospheric deposition, including; Geologically weathered rocks and soils (Ahdy & Youssef, 2011), The major diffuse sources for anthropogenic heavy metals include; Vehicle emissions (Ahdy & Youssef, 2011; Li, Poon, & Liu, 2001), and Atmospheric release of pollutants by industry (Ahdy and Youssef, 2011; Mitra *et al.*, 2012).

applications of agricultural fertilisers, agrichemicals and various organic materials including sewage sludges, livestock manures, food wastes and composts (Alloway, 2013).

Soil contamination can occur either by a point source whereby the contaminant comes from a single, identifiable origin and affects a relatively restricted area (Pulford and Flowers, 2006; Vamerali *et al.*, 2010). Examples of a point source pollution include an abandoned metal working facilities, accidental release or spillage of contaminants, and inappropriate municipal and industrial waste disposal are frequently associated with localized contaminated soils (Vamerali, Bandiera, & Mosca, 2010). Another type of soil contamination is the diffuse source in which the contaminants do not come from one specific source and its effects are usually seen over a large area (Pulford & Flowers, 2006).

Point sources of heavy metals contamination are generally considered to be completely anthropogenic in nature such as industrial processing of ores and metals (Ahdy & Youssef, 2011), Others include, leaching from waste disposal areas and fertilizers (Ahdy & Youssef, 2011; Deng, Zhang, Wang, Chen, & Xu, 2010); and discharge or leakage of human sewage (Deng *et al.*, 2010).

Lithogenic sources of heavy metals are linked to diffuse deposition mechanisms, such as atmospheric deposition, including; Geologically weathered rocks and soils (Ahdy & Youssef, 2011), The major diffuse sources for anthropogenic heavy metals include; Vehicle emissions (Ahdy & Youssef, 2011; Li, Poon, & Liu, 2001), and Atmospheric release of pollutants by industry (Ahdy and Youssef, 2011; Mitra *et al.*, 2012).

Atmospheric deposition and flowing water are the main pathways for diffuse soil contamination (Vamerali *et al.*, 2010). In industrialized areas, most heavy metals originate from industrial activities, although some originate from transportation and other anthropogenic sources which then find their way to marine and terestrial environments through water runoff or direct atmospheric deposition. Terrestrial environments have a largr range of contaminant sources which are diverse and complex (Figure 1).

Aquatic ecosystem has experienced pollution of contaminants from diverse sources and heavy metals are among the most toxic and persistent pollutants in freshwater systems (Figure 1) Much research and monitoring efforts have been conducted to determine sources, transport, and fate of these metals in the aquatic environment. However, studies have shown that contamination artifacts have seriously compromised the reliability of many past and current analyses (Taylor & Shiller, 1995) and in some cases, metals have been measured at 100 times above the true concentration (Windom, Byrd, Smith & Huan, 1991).

River bodies are the main inland water resources for domestic, industrial and irrigational purposes and often carry large municipal sewage, industrial wastewater discharges and seasonal run-offs from agricultural lands which accompany loads of pollutants with the possibility of the presence of poisonous substances in water bodies (Pradhan, Shirodkar, & Sahu, 2009). The problem of water from streams and rivers is more a case of quality than quantity. To be wholesome, water must be free from poisonous substances like heavy metals.

High Mn contamination in drinking water also affects the intellectual functions of 10-year-old children (Wasserman *et al.*, 2006). Similarly, the Ni-sulfate and Ni-chloride ingestion can cause severe health problems, including fatal cardiac arrest (Knight, Kaiser, Lalor, Robotham, & Witter, 1997). According to the World Health Organization and International Agency for Research on Cancer evaluation conclusions, arsenic and other heavy metals exposure through water bodies is causally related to cancer in the lungs, kidney, bladder and skin (IARC & WHO, 2004).

The most common mechanisms of deposition for heavy metals in an environmental media will include; atmospheric deposition, industrial discharge, surface runoff (including stormwater and agricultural runoff), river runoff and offshore weathering of soils and sediments (Choi, Kim, Hong, & Chon, 2012; Bradham & Wentsel, 2010).

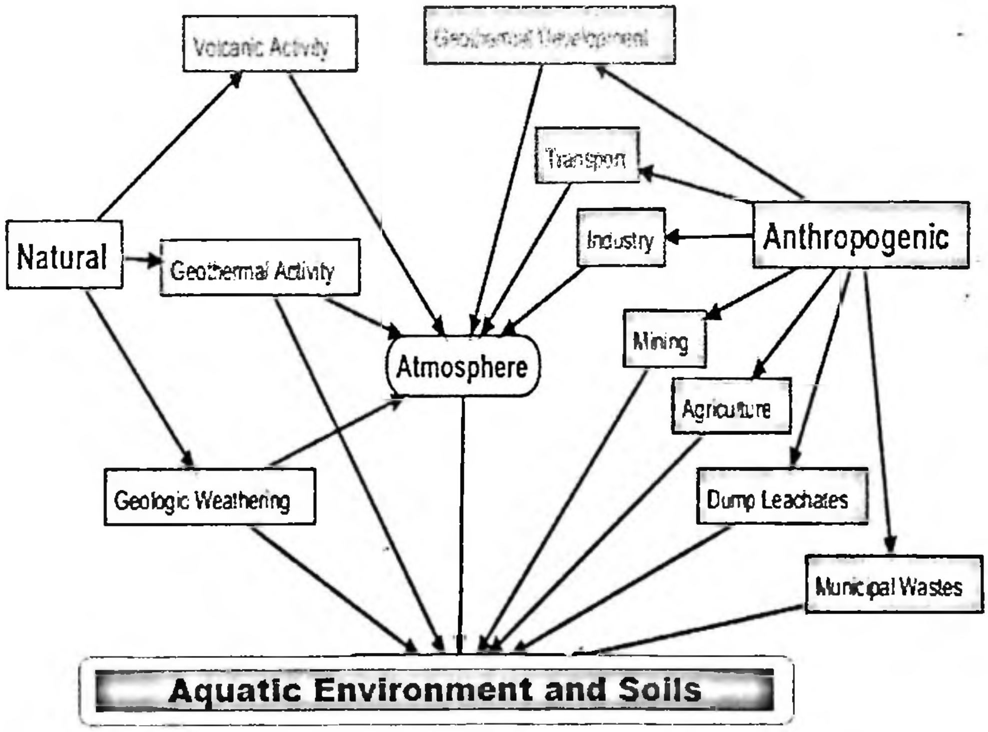


Figure 1: Common sources of heavy metals.
Source: Foster and Charlesworth (1996) and Brady *et al.*, (2015)

Mining Processes and Industrial Wastes

Mining and milling of metal ores which is the major source of soil contamination of heavy metals coupled with industries have bequeathed many countries, the legacy of wide distribution of metal contaminants in soil (Fornes, García-de-la-Fuente, Belda, & Abad, 2009). Mining processes do not involve extraction of preferred metals but also generates immense quantities of tailings, a by-product of metal extraction. The mining process eventually results in the direct discharge of tailings into natural depressions, including onsite wetlands causing elevated concentrations of the metals (DeVolder *et al.*, 2003).

The World Health Organization (2001), reported the failure of a tailings dam at Nakhon Si Thammarat, Thailand in 1993 which had caused serious As contamination of topsoil and groundwater over a 40 km^2 area. The contamination was estimated to last for 40-50 years. Moreover, the As levels in the contaminated topsoil were reported 20 to 100 times higher than the guideline value set by local authorities, while the levels in the groundwater wells were reported to run 50-100 times higher than the guideline value recommended by the WHO for drinking water (WHO, 2001).

Extensive mining of Pb and Zn ore and smelting have resulted in contamination of soil that poses risk to human and ecological health. The reclamation methods used on these sites are lengthy and expensive and may not completely restore soil productivity. Soil heavy metal environmental risk to humans is related to bioavailability. Assimilation pathways include the consumption of plant material grown on contaminated soil or the direct ingestion of, contaminated soil (Basta & Gradwohl, 1998).

Pesticides

Many of the common pesticides legitimately used in the past like DDT on agriculture and horticulture contained substantial amounts of heavy metals. For instance, in the recent past, about 10% of the chemicals that have been approved for use as insecticides and fungicides in the UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride (Jones & Jarvis, 1981). Lead arsenate was used in fruit orchards for many years to control some parasitic insects.

Arsenic containing compounds were also used extensively to control cattle ticks and to control pests in banana in New Zealand and Australia, timbers have been preserved with formulations of Cu, Cr, and As (CCA), and there are now many derelict sites where soil concentrations of these elements greatly exceed background concentrations (Wuanal & Okieimen, 2011). Such contamination has the potential to cause problems, particularly if sites are redeveloped for other agricultural or nonagricultural purposes. Compared with fertilizers, the use of such materials has been more localized, being restricted to particular sites or crops (Zhao & Kaluarachchi, 2002).

Heavy Metals Occurrence and Health Effects

Heavy metals occur as natural constituents of the earth crust as unlike organic pollutants, they are persistent environmental contaminants which cannot be degraded or destroyed but can only be converted into a stable form or removed. To a small extent, they enter the body system through food, air, and water and bio-accumulate over a period of time (Lenntech, 2004;

UNEP/GPA, 2004). In rocks, they exist as their ores in different chemical forms, from which they are recovered as minerals.

Heavy metal ores include sulphides, such as iron, arsenic, lead, lead-zinc, cobalt, gold silver and nickel sulphides; oxides such as aluminum, manganese, gold, selenium and antimony. Some exist and can be recovered as both sulphide and oxide ores such as iron, copper and cobalt. Ore minerals tend to occur in combination whereby metals that exist naturally as sulphides would mostly occur together, likewise for oxides. Therefore, sulphides of lead, cadmium, arsenic and mercury would naturally be found occurring together with sulphides of iron (pyrite, FeS_2) and copper (chalcopyrite, $CuFeS_2$) as minors, which are obtained as by-products of various hydrometallurgical processes or as part of exhaust fumes in pyrometallurgical and other processes that follow after mining to recover them. During mining processes, some metals are left behind as tailings scattered in open and partially covered pits; some are transported through wind and flood, creating various environmental problems (Habashi, 1992).

Heavy metals are basically recovered from their ores by mineral processing operations (Lenntech, 2004; UNEP/GPA, 2004; United States Department of Labor (USDOL, 2004). The following paragraphs explain the occurrence, exposure and health effects of most common heavy metals found at contaminated sites based on abundance (USEPA, 1996).

Mercury

Mercury occurs naturally in the earth's crust. Although it may be found in air, water and soil, mercury is mostly present in the atmosphere as a gaseous element. Mercury's major natural source results from the degassing of the

Other anthropogenic sources of Hg will include, underground mining, mining quarrying, opencast and, production of phytopharmaceutical products and biocides, pharmaceutical industry, landfills, urban waste treatment plants and industrial waste-water treatment plants. (E-PRTR, 2010). Exposure to mercury may mainly occur as a consequence of the deposition from air into water or into soil. By natural biological processes certain microorganisms can change mercury into methyl mercury.

General population is exposed to methyl mercury through the food chain; fish and shellfish are the main source of exposure through the ingestion pathway (USEPA, 2009; Neustadt, 2011). Inhalation of mercury vapor is another possible exposure pathway which occurs when elemental mercury or products that contain elemental mercury break and release mercury into air, in remarkable indoor spaces without enough ventilation. Nevertheless, the main exposure pathway is through food chain and not by inhalation (EPA, 2009). High level of mercury can cause brain damages, heart, kidneys and affect the immunologic system. Fish consumption does not constitute the main cause of health problems as mercury quantity is not high. Nevertheless, high levels of methyl mercury in the bloodstream of little children may affect nervous system, affecting the normal thinking and learning (EPA, 2009).

Lead

Lead is a naturally occurring bluish gray heavy metal usually found as a mineral combined with other elements, such as sulphur (PbS, $PbSO_4$), or oxygen ($PbCO_3$), and ranges from 10 to 30mg kg^{-1} in the earth's crust (USDHHS, 1999). Typical mean Pb concentration for surface soils worldwide averages 32mg kg^{-1} and ranges from 10 to 67mg kg^{-1} (Kabata Pendias &

Pendias, 2001). Lead ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals. Lead is found in air, water, foodstuff, soil and dust either from natural or anthropogenic sources. Ionic lead, Pb(II), lead oxides and hydroxides, and lead metal oxyanion complexes are the general forms of Pb that are released into the soil, groundwater, and surface waters. In the past most of the lead emissions to the environment was due to petrol but impact has decreased drastically in the last few years, in developed countries and has seen an improvement in developing countries due to the introduction of unleaded petrol.

Lead can be found in several categories of use: manufacture of lead storage batteries, solders, bearings, cable covers, ammunition, alloys and pigments. The most significant anthropogenic lead sources result basically from the same sources as for Cd and Hg (E-PRTR, 2010; Manahan, 2011). Inhalation and ingestion are the two routes of lead exposure, and the effects from both are the same and can occur from both anthropogenic and natural sources. Lead bio-accumulates in the body organs, which may lead to poisoning (plumbism) or even death.

The gastrointestinal tract, kidneys, and central nervous system are also the sites affected by the presence of lead. Children exposed to lead are at risk of impaired brain development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at the highest risk (UNEP, 2008, NSC, 2009). Airborne Pb may be deposited on soil, water and crops and also be transported through run offs.

Acute exposure to lead's high levels may cause vomiting, diarrhea, convulsions, coma or even death. Chronic exposure, even to small amounts of lead, can be hazardous, especially to children under 6 years' old who are particularly vulnerable to lead exposure; low levels of exposure to lead can cause neurodevelopment effects in children. Other effects to generic exposed receptors include cardiovascular, renal, gastrointestinal, hematological and reproductive effects. In adults' inorganic lead does not penetrate the blood brain barrier but this barrier is less developed in children.

A high gastrointestinal uptake of Pb and a permeable blood-brain barrier make children critical receptors to Pb and consequent severe brain damages (UNEP, 2008; Udedi, 2003). Organic lead is able to penetrate body and cell membranes, some forms of organic lead penetrate the skin easily and cross blood-brain barrier in adults and in this way adults can also suffer brain damage related to acute poisoning from organic lead compounds.

Arsenic

Arsenic is a widely distributed metalloid that occurs in a wide variety of minerals, mainly as As_2O_3. It is recovered from processing of ores containing mostly Cu, Pb, Zn, Ag and Au. Arsenic is found in rock, soil, water and air and countries like Bangladesh, Chile and China have experienced the presence of inorganic arsenic in groundwater drinking water whereas organic arsenic compounds (such as arsenobetaine) are primarily found in fish, which may give rise to human exposure (WHO, 2001; Smith, 1992). Smelting of non-ferrous metals and the production of energy from fossil fuel are the two major industrial processes that lead to arsenic contamination of air, water and soil, smelting activities being the largest single anthropogenic source of atmospheric pollution41. Other sources of contamination are the manufacture and use of arsenical pesticides and wood preservatives.

Arsenic is transported only over short distances in groundwater and surface water due to their ability to bind strongly to soil particles. Water concentrations are usually <10 µg/l, although higher concentrations may occur near anthropogenic sources (WHO, 2001; Ogunkunle, Fatoba, Ogunkunle, & Oyedeji, 2013).

Absorption of arsenic in inhaled airborne particles is highly dependent on the solubility and the size of particles. Soluble arsenic compounds are easily absorbed from the gastrointestinal tract. However, inorganic arsenic is extensively methylated in humans and the metabolites are excreted in the urine (WHO, 2001).

Arsenic absorbed in the body undergoes some accumulation in soft tissue organs such as the liver, spleen, kidneys, and lungs, but the major long-term storage site for arsenic is keratin-rich tissues, such as skin, hair, blood, nails and urine, making the measurement of arsenic in these biological specimens useful for estimating total arsenic burden and have been used as biomarkers of exposure (Jarup, 2003). Inorganic arsenic is acutely toxic and intake of large quantities leads to gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems, and eventually death. Ingestion of inorganic arsenic may induce peripheral vascular disease, which in its extreme form leads to gangrenous changes (black foot disease, only reported in Taiwan). Chronic exposure to arsenic results in unusual patterns of skin hyperpigmentation, peripheral nerve damage manifesting as numbness, tingling, and weakness in the hands and feet, diabetes, and blood vessel damage resulting in a gangrenous condition affecting the extremities (Col, Çöl, Soran, Sayli, & Oztürk, 1999).

Populations exposed to arsenic *via* drinking water show excess risk of mortality from lung, bladder and kidney cancer. However, consumption of certain seafood may confound estimation of inorganic arsenic exposure. Arsenic is associated with skin damage, increased risk of cancer, and problems with circulatory system (Ogunkunle *et al.*, 2013; WHO, 2001).

Chemical and Physical Properties of Soil and Sediment

The chemical and physical properties of soil such as pH, CEC, organic matter content, mineral phases, oxides and inorganic ligands play major roles in controlling the mobility of heavy metals in soil. Chemical processes that take place on the oxide surfaces, for example, not only influence the behaviour of heavy metals, but also the bioavailability of nutrients in soils (Ponthieu, Juillot, Hiemstra, Van Riemsdijk, & Benedetti, 2006). Organic matter has been regarded as the most important soil constituent in lowering the concentration of free metal ions in the soils and soil solutions (Covelo Vega, & Andrade, 2008). However, the distribution of heavy metals in soil depends on the nature of their interaction with organic matter.

The effects of Dissolved Organic Matter (DOM) by addition of Cd and Zn sorption by acidic sandy loam, calcareous clay loam and calcareous sandy loam soils were investigated (Wong, Zhou, & Selvam, 2007) and the observation was that there were greater inhibitory effects on Zn sorption than on Cd. They further observed that the high mobility of metals in acidic sandy loam could be attributed to the low pH, while low clay content was thought to be the main reason that fewer metals were retained by calcareous sandy loam. They reported that the application of DOM not only reduced metal uptake by soil, but also increased metal mobility in soil due to the formation of soluble DOM-metal complexes.

The fate and mobility of heavy metals in soil are greatly influenced by the chemical behaviour of the metals (Alvarez, Mochon, Sánchez, & Rodríguez, 2002), as well as the chemical and physical properties of the soil (Alloway, 2001). However, adsorption reactions through the formation of complexes with the surfaces of organic matter, oxides and clays, and precipitation reactions leading to the formation of insoluble precipitates such as hydroxides, carbonates and phosphates, are the two major mechanisms involved in the retention of heavy metals by soils (Evans, 1989).

Cation Exchange Capacity Application and Principle

Soils are made up of sand, organic matter, silt and clay particles. Sandy soils have CEC between 1-5meq/100g. Clay soils such as smectite and illite can have CECs between 25-100meq/100g. Increasing the clay content of a low holding capacity for cations compared to clayey and silty soils. Clay and silt particles have negatively charged sites sandy soil will help increase its CEC (Brown & Lemon, 2016). CEC refers to the capacity of soil material to exchange cations such as metals with the soil solution (Hansen, 2001; Alloway, 1992).

In general, the higher the CEC of the soil, the greater the amount of metal ion that can be bound onto soil material. In soil systems, the electropositively charged elements can be attracted to negatively charged surfaces of organic matter, clay particles and Fe and Al oxides, which can be used to determine the CEC (Evans, 1989). Soil quality indicators that directly monitor the soil are grouped into physical, chemical and biological indicators.

Some soil chemical properties such as pH, EC, plant nutrient availability, CEC etc. are the indicators of soil quality (Chandra & Singh, 2009). These chemical properties of soils play an important role in determining the retention and availability of nutrients in soils. The nutrient supply in soil depends on the level of organic matter, $CaCO_3$ content, degree of microbial activity, change in pH, types and amount of clay and status of soil moisture (Zende, 1984).

Exchangeable Cations and Cation Exchange Capacity (CEC)

The phenomenon of ion exchange is of great importance in soil chemistry. The soil properties are greatly affected by exchangeable cations (Bear, 1976). The nutrient uptake by plants is governed by ion exchange phenomenon.

The exchangeable cations present in agricultural soils are Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+. Their relative absorption affinities on soil are in the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+ = NH_4^+ > Na^+$ (Hausenbuiller, 1976). That is to say that among all cations, Ca^{2+} has maximum replacing capacity while Na^+ has minimum. This is because Ca^{2+} has greater valency and a smaller hydrated radius than that of Na^+. As a result of this, the proportion of these ions on colloidal surfaces constantly changes depending upon the ions added from the dissolving minerals, fertilizers, gypsum etc. Losses by plant absorption or by leaching also change cation proportions (Miller & Donahue, 1992).

Determination of Cation Exchange Capacity

A common method for determining CEC uses 1 M ammonium acetate (NH_4OAc) at pH 7 (neutral NH_4OAc) and is a standard method used for soil surveys by the Natural Resource Conservation Service (Carter, 1993). An advantage of CEC measured at a constant pH of 7 is elimination of CEC variability due to differences in soil pH (Table 1). Thus, comparisons of CEC can occur across varied soil types and lime applications. The limitation of the neutral NH_4OAc method is that it may not provide a realistic depiction of the actual CEC at the natural pH of the soil, particularly with soils having considerable pH-dependent charge and a soil pH that is significantly different from 7.

An unbuffered salt extract can be used to determine CEC at the natural pH of soil (Pansu & Gautheyrou, 2006). Summation of equivalent charge concentrations of basic cations (calcium, magnesium, potassium, and sodium) and acidic cations (aluminum, iron, and manganese) extracted with an unbuffered salt is referred to as effective CEC ation exchange capacity can be determined by neutral NH_4OAc, or by indirect estimation from routine soil test results.

The concentrations of bases extracted are similar to concentrations of exchangeable bases. The sum of equivalent charges from exchangeable bases and acidity from routine analysis provides a value for CEC that is similar to CEC from the neutral NH_4OAc method. Two problems with this method of estimating CEC occurs with the presence of soluble salts from fertilizers or solubilization of calcium or magnesium carbonates. Bases extracted from soluble salts or carbonates are not exchangeable bases and thus will result in false high estimates for CEC.

Table 1: Cation Exchange Capacity for Soils and Soil Textures

Soil State	CEC (meq/100g)
Sands	1-5
Fine sandy loams	5-10
Loams and silt loams	5-15
Clay Loam	15-30
Clays	Over 30
Organic matter	200 – 400

Source: Miller and Donahue (1992)

Effect of pH and CEC on Metal Mobility

The CEC for a number of soils depends on the pH of the soil and this is due mostly to the Hofmeister series or lyotrophic series (which is the classification of ions in order of their ability to salt out or salt in proteins), and it describes the relative strength of various cations' adsorption to colloids. The order of cations is usually given as generally as: $Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$.

Increase in soil acidity generally leads to a decrease in soil pH, and as a result, more H^+ ions are attached to the colloids. The other cations from the colloids are then pushed into the soil water solution. Inversely, when soils become more basic (pH increases), the available cations in solution decreases because there are fewer H^+ ions to push cations into the soil solution from the colloids and this leads to an increase in soil CEC (Havlin, Tisdale, Nelson, & Beaton, 2011).

Effect of Organic Matter on Heavy Metals Availability

Organic matter in soils and sediments occur in almost all terrestrial and aquatic environments. A large variety of organic materials are contained in soils and sediments ranging from simple sugars and carbohydrates to the more complex proteins, fats, waxes, and organic acids (Schnitzer, 1978). Organic matter, like clay particles has negatively charged sites which attract and hold on to cations. They are reported to have CEC as high as 250meq/100g. The negatively charged particles in organic matter are as a result of the dissociation of organic acids and this dissociation depends on the soil pH and hence, when a soil has a high CEC resulting from organic matter content, it is said to be pH dependent. A better way of increasing a soil CEC is to increase its organic matter content. This method may be slow but very reliable (AFSS, 2007).

The organic materials in soil increase the CEC through an increase in available negative charges. As such, organic matter build-up in soil usually positively impacts soil fertility. However, organic matter CEC is heavily impacted by soil acidity as acidity causes many organic compounds to release ions to the soil solution. Organic matter contributes substantially to the CEC of soil and thus to the retention of exchangeable cations. Organic matter makes a great impact on CEC because of humification, the formation of humus (complex organic polymers) from raw organic materials such as fulvic acids, humic acids or humin (from organic matter) produces organic colloids of high specific surface area. The organic matter content of a soil increases with increasing decomposition based on the level of temperature available (Franzmeier, Lemme, & Miles, 1985).

Some soil chemical properties such as pH, EC, plant nutrient availability, CEC etc. are the indicators of soil quality (Chandra & Singh, 2009). These chemical properties of soils play an important role in determining the retention and availability of nutrients in soils. The nutrient supply in soil depends on the level of organic matter, $CaCO_3$ content, degree of microbial activity, change in pH, types and amount of clay and status of soil moisture (Zende, 1984).

Exchangeable Cations and Cation Exchange Capacity (CEC)

The phenomenon of ion exchange is of great importance in soil chemistry. The soil properties are greatly affected by exchangeable cations (Bear, 1976). The nutrient uptake by plants is governed by ion exchange phenomenon.

The exchangeable cations present in agricultural soils are Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+. Their relative absorption affinities on soil are in the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+ = NH_4^+ > Na^+$ (Hausenbuiller, 1976). That is to say that among all cations, Ca^{2+} has maximum replacing capacity while Na^+ has minimum. This is because Ca^{2+} has greater valency and a smaller hydrated radius than that of Na^+. As a result of this, the proportion of these ions on colloidal surfaces constantly changes depending upon the ions added from the dissolving minerals, fertilizers, gypsum etc. Losses by plant absorption or by leaching also change cation proportions (Miller & Donahue, 1992).

Determination of Cation Exchange Capacity

A common method for determining CEC uses 1 M ammonium acetate (NH_4OAc) at pH 7 (neutral NH_4OAc) and is a standard method used for soil surveys by the Natural Resource Conservation Service (Carter, 1993). An advantage of CEC measured at a constant pH of 7 is elimination of CEC variability due to differences in soil pH (Table 1). Thus, comparisons of CEC can occur across varied soil types and lime applications. The limitation of the neutral NH_4OAc method is that it may not provide a realistic depiction of the actual CEC at the natural pH of the soil, particularly with soils having considerable pH-dependent charge and a soil pH that is significantly different from 7.

An unbuffered salt extract can be used to determine CEC at the natural pH of soil (Pansu & Gautheyrou, 2006). Summation of equivalent charge concentrations of basic cations (calcium, magnesium, potassium, and sodium) and acidic cations (aluminum, iron, and manganese) extracted with an unbuffered salt is referred to as effective CEC ation exchange capacity can be determined by neutral NH_4OAc, or by indirect estimation from routine soil test results.

The concentrations of bases extracted are similar to concentrations of exchangeable bases. The sum of equivalent charges from exchangeable bases and acidity from routine analysis provides a value for CEC that is similar to CEC from the neutral NH_4OAc method. Two problems with this method of estimating CEC occurs with the presence of soluble salts from fertilizers or solubilization of calcium or magnesium carbonates. Bases extracted from soluble salts or carbonates are not exchangeable bases and thus will result in false high estimates for CEC.

Table 1: Cation Exchange Capacity for Soils and Soil Textures

Soil State	CEC (meq/100g)
Sands	1-5
Fine sandy loams	5-10
Loams and silt loams	5-15
Clay Loam	15-30
Clays	Over 30
Organic matter	200 – 400

Source: Miller and Donahue (1992)

Effect of pH and CEC on Metal Mobility

The CEC for a number of soils depends on the pH of the soil and this is due mostly to the Hofmeister series or lyotrophic series (which is the classification of ions in order of their ability to salt out or salt in proteins), and it describes the relative strength of various cations' adsorption to colloids. The order of cations is usually given as generally as: $Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$.

Increase in soil acidity generally leads to a decrease in soil pH, and as a result, more H^+ ions are attached to the colloids. The other cations from the colloids are then pushed into the soil water solution. Inversely, when soils become more basic (pH increases), the available cations in solution decreases because there are fewer H^+ ions to push cations into the soil solution from the colloids and this leads to an increase in soil CEC (Havlin, Tisdale, Nelson, & Beaton, 2011).

Effect of Organic Matter on Heavy Metals Availability

Organic matter in soils and sediments occur in almost all terrestrial and aquatic environments. A large variety of organic materials are contained in soils and sediments ranging from simple sugars and carbohydrates to the more complex proteins, fats, waxes, and organic acids (Schnitzer, 1978). Organic matter, like clay particles has negatively charged sites which attract and hold on to cations. They are reported to have CEC as high as 250meq/100g. The negatively charged particles in organic matter are as a result of the dissociation of organic acids and this dissociation depends on the soil pH and hence, when a soil has a high CEC resulting from organic matter content, it is said to be pH dependent. A better way of increasing a soil CEC is to increase its organic matter content. This method may be slow but very reliable (AFSS, 2007).

The organic materials in soil increase the CEC through an increase in available negative charges. As such, organic matter build-up in soil usually positively impacts soil fertility. However, organic matter CEC is heavily impacted by soil acidity as acidity causes many organic compounds to release ions to the soil solution. Organic matter contributes substantially to the CEC of soil and thus to the retention of exchangeable cations. Organic matter makes a great impact on CEC because of humification, the formation of humus (complex organic polymers) from raw organic materials such as fulvic acids, humic acids or humin (from organic matter) produces organic colloids of high specific surface area. The organic matter content of a soil increases with increasing decomposition based on the level of temperature available (Franzmeier, Lemme, & Miles, 1985).

Adsorption, Complexation and Chelation of Metals to Organic Matter

Organic matter causes litter to accumulate which usually contribute to the binding of metals by adsorption, complexation and chelation (Du Laing, Rinklebe, Vandecasteele, Meers, & Tack, 2009). Moreover, dissolved organic ligands, such as low to medium molecular weight carboxylic acids, cause amino acids and fulvic acids to form soluble metal complexes. The net effect of the presence of organic matter can either be a decrease or an increase in metal mobility. An enhanced mobilisation of metals as dissolved organic complexes was observed for Ni (Wells, Kozelka, & Bruland, 1998), for Pb, Cu and Zn, and for Hg, Cr, Cu and As, but not for Cd and Zn (Kalbitz & Wennrich, 1998). Charlatchka and Cambier (2000), found that Pb was especially complexed by organic acids in flooded soils. In the reverse reaction, high molecular weight organic matter compounds in the solid soil phase was observed to reduce the metal availability (Gambrell, 1994).

Acid Mine Drainage

The release of dissolved metals from active and past mining operations is dependent on Acid Mine Drainage (AMD) which is the key factor in predicting how much metals that can be transferred into the environment (Solomons, 1995). In the mining environment, the AMD can be generated from a number of sources including waste rock dumps, ore stock piles, tailings deposits and from mine pits. The requirement for AMD is the generation of acid at a faster rate than it can be neutralised by any alkaline materials in the waste, access to atmospheric oxygen and water, and the rate of precipitation higher than evaporation.

The most common mineral causing AMD is pyrite, but other metal sulphides will also contribute (Solomons, 1995). It is generated when pyrite (FeS_2) and other sulphide minerals in the aquifer in the present and former mining sites are exposed to air and water in the presence of oxidizing bacteria, such as Thiobacillus ferrooxidans, and oxidised to produce metal ions, sulphate and acidity (Ogwuegbu & Muhanga, 2005).

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \tag{1}$$

$$2FeSO_4 + 2H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + SO_2 + 2H_2O \tag{2}$$

$$Fe_2(SO4)_3 + 2FeAsS + 9/2O_2 + 3H_2O \longrightarrow 2H_3AsO_4 + 4FeSO_4 + S \tag{3}$$

When AMD occurs, the mine sites are leached and carried by acidic water downstream. Bacteria can then act on the acidic water and methylate some of the metals to yield organic forms, such as monomethylmercury and dimethylcadmium. This conversion is effected by bacteria in water, in the presence of organic matter, according to the following simplified equation. M + organic matter H_2O, bacteria CH_3M and $(CH_3)_2$ M. In the non-biological conversions, the following reactions have been identified for mercury:

$$Hg^{2+} \xrightarrow[\text{(Eutropic condition)}]{H_2S} \underset{\text{less soluble}}{HgS} \xrightarrow{\text{aeration}} \underset{\text{more soluble}}{Hg_2SO_4} \longrightarrow \underset{\text{methyl mercury}}{CH_3Hg^+} \tag{4}$$

These organic forms have been reported to be very toxic and adversely affect water qualities by seepage to pollute underground water sources. Low pH values do not need to be established for metals to be released from mine wastes at adverse concentrations because, near neutral pH (pH 6-7) have been established for some metals, such as Zn, Cd, and As (INECAR, 2000; Lenntech, 2004).

Biological Importance of Heavy Metals

Certain metals are nutritionally essential to humans and play a key role in physiological or biochemical processes (NAS/IOM, 2003; IPCS, 2001; WHO, 1998). Some heavy metals (like Fe, Zn, Cu, Mn, Cr and Co) have been proven to be essential to humans (have threshold limit) (Toffaletti, 2005) and their daily medicinal and dietary allowances had been recommended (NAS/IOM, 2003). Some metals are deemed probably nutritionally essential (Ni, V and Sb) and others are deemed to have no known biological importance (no threshold limit) (As, Cd, Au, Pb, Hg, Si) (Table 2) and consumption even at very low concentrations can be toxic (European Union, 2002; Young, 2005)

Elements essential to other organisms may not be essential to humans and vice versa. Adverse nutritional effects can occur for the essential metals if they are not available in sufficient amounts and result in nutritional deficits which can cause adverse effects and increase the vulnerability of humans to other stressors, including those associated with other metals (Bradham & Wentsel, 2010). Dietary intakes need to be maintained at regulatory limits, as excesses will result in poisoning or toxicity, which is evident by certain reported medical symptoms that are clinically diagnosable (Young, 2005).

Zinc is an important element that balances copper in the body and serves as a co-factor for dehydrogenating enzymes and in carbonic anhydrase (Holum, 1983). Deficiency of Zn in the body can cause anaemia and retardation of growth and development (Maret & Sandstead, 2006). However, Zinc deficiency in the diet may be more detrimental to human health than too much zinc in the diet (Tchounwou, Yedjou, Patlolla, & Sutton, 2012).

Arsenic has been reported to be a trace element of nutritional importance to humans but its functions in the biological system is not clear (Holum, 1983). Any level of concentration of silver in drinking water has some environmental and human health concern as stated by WHO (Sass, Heine, & Hwang, 2016). Hence dietary intakes of non-essential metals, even at very low concentrations can be very harmful because they bio-accumulate.

Table 2: Selected Heavy Metals and their importance to Human Health

	Toxic Metals	Probably Essential	Proven Essential
Trace elements (mg/kg)			Fe, Zn and Cu
Ultratrace elements (ug/kg)	As, Cd, Au, Pb, Hg and Si	Ni, V, Sb	Mn, Co, Se, Mo, Cr

Source: Bradham and Wentsel (2010) and Toffaletti (2005)

Health Risks of Heavy Hetals

Heavy metals can be classified as either essential micronutrients (ppb concentrations or lower) or non-essential to health and wellbeing which can have toxic effects, sometimes even at very low concentrations (Toffaletti, 2005). The metals without any biological importance can be either benign (have no detrimental effect) or can be toxic, even at low concentrations (mercury or cadmium). Generally, the common pathways of toxicity on the human body by heavy metals include, but are not limited to, Renal tubular damage, Gastro-intestinal erosion; and Neurological damage (Gaw, Packard, & Shepherd, 1999).

A more detailed analysis of their toxicological effect on target organs is shown in Table 3, which displays the heavy metals attack on human body in a number of ways with most of these metals affecting two or more organs. Although the most important environmental implication of metal contamination is their ecological toxicological effects, heavy metals also pose health risks, which are dependent on several factors, such as their acute (short term) and chronic (long term) toxicity; biodegradability and their bioavailability (Brady *et al.*, 2015).

Table 3: Table of selected Heavy Metals and their Target Organs

	Target Organs							
Metal	Liver	Kidneys	Lungs	G.I. Tract	Heart	Bones	Testes	Brain
Arsenic	X	X	X					
Cadmium	X	X		X	X	X	X	
Chromium	X			X				
Copper				X				
Iron	X				X			
Lead		X				X		X
Manganese	X	X						X
Mercury	X	X						X
Nickel	X	X	X					X
Vanadium	X							
Zinc				X				

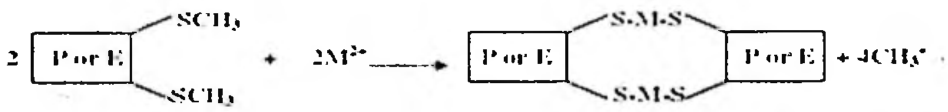
Source: Toffaletti (2005) and Bradham and Wentsel (2010)

Mechanism of Heavy Metals Toxicity

Several metals are toxic to human exposure through occupational sources, environmental contamination, water and food. Upon chronic exposure, most of these metals accumulate in the body throughout the individuals' life time and their biological effect contributes to short lifespan of organs such as the kidney, lung and consequently result in their early failure (Barregård *et al.*, 1999)

The mechanism by which thiol-binding metals exert a toxic activity on cells and organisms is in general terms described as the consequence of "interaction with and inhibition of essential thiol groups of enzymes and proteins", although the systemic toxicity of the metal is very different (Kinraide & Yermiyahu, 2007). Mercury exhibit much more toxicity among the thiol binding metals in their water-soluble salt forms as indicated by the low DL50 values; $HgCl_2$ (oral, rat): 3.7 micromoles/kg; $CdCl_2$ (oral, rat): 473 micromoles/kg; $Pb(OAc)_2$ (oral, dog): 914 micromoles/kg; $ZnCl_2$ (oral, rat): 2381 micromoles/kg (Rubino, 2015).

(5)



(6)

Where: (A) = Intramolecular bonding; (B) = Intermolecular bonding; P = Protein; E = Enzyme; M = Metal

The toxic effects of heavy metals are due to their interference with the normal body biochemistry of the normal metabolic processes. When heavy metals are ingested into the human system, they are converted to their stable oxidation state upon interaction with the acidic medium of the stomach (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, As^{3+}, Hg^{2+} and Ag^{+}) and interact with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds. The metals show the highest toxicity in their most stable oxidation states because they are able to form a very stable biotoxic compounds with the body's bio-molecules, which become difficult to be dissociated. The equations above (Equation 5 and 6) show their reactions during bond formation with the thiol groups (-SH) of cysteine and sulphur groups of methionine ($-SCH_3$) (Ogwuegbu & Ijioma, 2003).

The hydrogen atoms of the methyl groups in this case are replaced by the toxic metal and the enzyme is thus inhibited from functioning, whereas the protein–metal compound acts as a substrate and reacts with a metabolic enzyme. In a scheme shown below (equation 7), the enzyme (E) react with substrate (S) in either the lock-and-key pattern or the induced-fit pattern. In both cases, a substrate fits into an enzyme in a highly specific fashion, due to the enzymes chirality to form an enzyme–substrate complex (E-S*) as follows (Holum, 1983).

$$E + S \longrightarrow E\text{-}S \longrightarrow E - S^{*} \longrightarrow E - P \longrightarrow E + P \text{ -----(7)}$$

(E = Enzyme; S = Substrate; P = Product; * = Activated Complex)

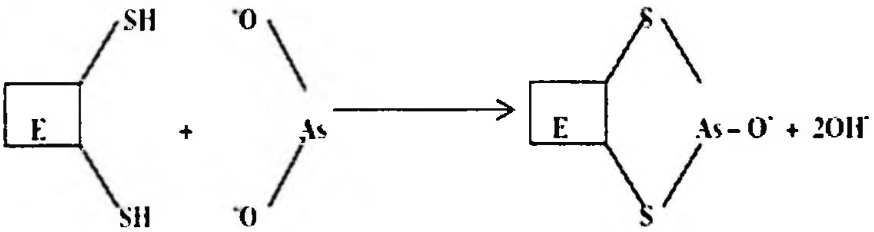
While at the E-S, E–S* and E-P states, an enzyme cannot accommodate any other substrate until it is freed. Sometimes, the enzymes for an entire sequence coexist in one multi-enzyme complex consisting of three or four enzymes. The product from one enzyme reacts with a second enzyme in a chain process, with the last enzyme yielding the final product as follows:

$$A \xrightarrow{E1} B \xrightarrow{E2} C \xrightarrow{E3} D \xrightarrow{E4} F \text{ (E1 to E4 are enzymes) ......(8)}$$

The final product (F) goes back to react with the first enzyme thereby inhibiting further reaction since it is not the starting material for the process.

Hence, the enzyme E1 becomes incapable of accommodating any other substrate until F leaves and F can only leave if the body utilizes it. If the body cannot utilize the product formed from the heavy metal – protein substrate, there will be a permanent blockage of the enzyme E1, which then cannot initiate any other bio-reaction of its function. Therefore, the metal remains embedded in the tissue, and will result in bio-dysfunctioning to various gravities (Holum, 1983). Furthermore, a metal ion in the body's metallo-enzyme can be conveniently replaced by another metal ion of similar size. Thus Cd^{2+} can replace Zn^{2+} in some dehydrogenating enzymes, leading to cadmium toxicity. In the process of inhibition, the structure of a protein molecule can be mutilated to a bio-inactive form, and in this case the enzyme can be completely destroyed. For example, toxic As^{3+} occurs in herbicide, fungicides and insecticides, and can attack –SH groups in enzymes to inhibit their bioactivities as shown below (Ogwuegbu & Ijioma, 2003)

The most toxic forms of these metals are their ionic species in their most stable oxidation states. For example, Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+} and As^{3+}. In their most stable oxidation states, they form very stable biotoxic compounds with the body's bio-molecules, which become difficult to get dissociated, due to their bio-stabilities, during extraction from the body by medical detoxification therapy.



(9)

Background of Heavy Metals in Risk Assessment

Heavy metals are associated with a variety of health effects that are reviewed in detail in EPA's Integrated Risk Information System (IRIS) Toxicology Reviews, the Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profiles, the World Health Organization's International Programme for Chemical Safety (WHO/IPCS) Environmental Health Criteria Documents, and metal toxicology reviews (Lukaski, 1999). Heavy metals have specific characteristics that should be considered in all risk assessments. These principles for metals risk assessment apply in various ways to human health risk assessments, depending on the scale of the assessment (site specific, regional, or national). In the performance of human health risk for heavy metals, the application of metals specific characteristics such as the background levels exposure, mixtures exposure and effects, essentiality effects and forms of metals Exposure (bioavailability), should be considered (Bradham & Wentsel, 2010).

Bioavailability

Bioavailability refers to the portion of the total contaminant in soil, sediment or water that is available for physical, chemical, and biological modifying influences (Lanno, 2003) and it also represents the total metal available at a given time in a system that is potentially able to contact or enter an organism. The term bioaccessible fraction (BF) refers to the amount that actually interacts at the organism's contact surface and is potentially available for absorption or adsorption (if bioactive upon contact) by the organism. The concept of metal bioavailability includes metal species that are bioaccessible and are absorbed or adsorbed with the potential for distribution, metabolism, elimination, and bioaccumulation in the organism.

Metal bioavailability is specific to the metal salt and particulate size, the receptor and its specific pathophysiological characteristics, the route of entry, duration and frequency of exposure, dose, and the exposure matrix. The metal salt is influenced by properties of the environment such as pH, particle size, moisture, redox potential, organic matter, cation exchange capacity, and acid volatile sulfides. CEC has been recently reported as an important factor modifying zinc bioavailability in soils, and presumably been important for other cationic metals as well. However, CEC is strongly dependent on the type and amount of organic material (OM) and oxyhydroxides present in the soil, and is strongly pH dependent (Table 4). Surface charge on OM and oxyhydroxides increases with pH, thereby increasing their sorptive capacity for metals (thus decreasing metal bioavailability).

The metal form is impacted by properties of the environment such as pH, particle size, moisture, redox potential, organic matter, cation exchange capacity, and acid volatile sulfides. It is important that the Exposure Analysis describes the same bioavailable fraction of the metal(s) of concern as that used when estimating the reference value (e.g., the RfD) such as the use of default assumption that the metal in the environmental samples is the same as that tested.

Table 4: Qualitative Bioavailability of Metal Cations in Soils to Plants and Soil Invertebrates

	Soil type		
Soil pH	Low organic matter (< 2%)	Medium organic matter (2 to <6%)	High organic matter (6 to 10%)
4 < Soil pH < 5.5	Medium	Low	Very low
5.5 < Soil pH < 7	High	Medium	Low
7 < Soil pH < 8.5	Very high	High	Medium

Source: Frische *et al.*, (2003)

Susceptible Populations

In risk assessment, the populations subgroups are taken into consideration especially those that may be at greater risk of toxic metals than the general population (USEPA, 2006). There are a number of host factors that can modify or influence susceptibility of metals response to an agent. Factors include life stage, life style, gender, reproductive status, nutritional state, pre-existing health conditions or disease, and genetic polymorphisms. Individuals with chronic liver or kidney disease may have a lower threshold for effects because these are two of the major target organs of metal toxicity. Several well-known, heritable genetic alterations affect people's ability to regulate Cu or Fe, resulting in various deficiency or toxicity problems (WHO/IPCS, 2002).

Demographics

Differences in lifestyle influence metal exposure and as a result different life style of the population of concern need to be clearly investigated. For example, the use of dietary supplements and other consumer products containing essential elements has increased. In addition, folk remedies such as colloidal silver "cure-alls" and folk remedies containing lead tetroxide may contain high levels of metals (McKinney, 1999). Smoking provides significant exposure to some metals (e.g., Cd) and can potentiate the effects of exposures from other sources, and excessive alcohol consumption can exacerbate metal effects.

Concurrent Damage or Disease

People who suffer from allergies and those with pre-existing medical conditions may generally, have higher-than-average biological sensitivity to environmental stressors. For example, diseases or treatments that damage the kidney or liver may increase sensitivity to metals that target these organs. Damage to the lung from smoking can potentiate effects of simultaneously or subsequently inhaled metals, particularly those that act directly on the lung (e.g., Be, Cd, Cr, and Ni). Skin abrasions or other irritations also can alter exposures to and subsequent effects of metals.

Human Health Risk Assessment

Human health risk assessment is defined as the characterization of the potential adverse health effects of humans as a result of exposures to environmental hazards (USEPA, 2013). It is further described as the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future (USEPA, 2004). This process employs the tools of science, engineering, and statistics to identify and measure a hazard, determine possible routes of exposure, and finally use that information to calculate a numerical value to represent the potential risk (Lushenko, 2010).

Hazard Identification

Hazard identification involves the determination of whether a chemical is or is not causally linked to particular health effects. It purposely evaluates the weight of evidence for adverse effects in humans based on assessment of all available data on toxicity and mode of action. Hazard identification addresses two primary questions: - whether an agent may pose a health hazard to humans and under what circumstance an identified hazard may be expressed. Often, multiple end-points are observed following exposure to a given chemical. The critical effect, which is usually the first significant adverse effect that occurs with increasing dose, is determined.

Dose-response

The Dose-response stage involves the determination of the relationship between extent of exposure and the probability of occurrence of the health effects in question. It is a process of characterizing the relationship between the dose of an agent administered or received and the incidence of an adverse health effect. For most types of toxic effects such as organ-specific, neurological/behavioural, immunological, non-genotoxic carcinogenesis, reproductive or developmental, it is generally considered that there is a dose or concentration below which adverse effects will not occur (i.e., a threshold). For other types of toxic effects, it is assumed that there is some probability of harm at any level of exposure (i.e., non-threshold). The non-threshold assumption is generally applied for mutagenesis and genotoxic carcinogenesis.

Exposure Assessment

Exposure assessment can be deemed a comparable step in the process toward the hazard identification and dose-response assessment which has the aim of determining the nature and extent of contact with chemical substances experienced or anticipated under different conditions. In Exposure Assessment, the risk of the toxic agent is quantified to the total exposure of the toxic agent in the environment based on the amount taken into the body, including any combination of the oral, inhalation, and dermal routes of exposure. For some assessments specific to a single exposure route, exposure may be expressed as an environmental concentration.

Exposure assessment requires the determination of the emissions, pathways and rates of movement of a substance and its transformation or degradation, in order to estimate the concentrations to which human populations or environmental spheres (water, soil and air) may be exposed (Table 5). Depending on the purpose of an exposure assessment, the numerical output may be an estimate of the intensity, rate, duration or frequency of contact exposure or dose. Three main exposure routes are determined in exposure assessment namely; dermal, oral and respiratory.

For risk assessments based on dose-response relationships, the output usually includes an estimate of dose. It is important to note that the internal dose, not the external exposure level, determines the toxicological outcome of a given exposure. The term "worst case exposure" has historically meant the maximum possible exposure, or where everything that can plausibly happen to maximize exposure happens.

The worst case represents a hypothetical individual and an extreme set of conditions; this will usually not be observed in an actual population (US EPA, 1992) and for that matter, in most risk assessments the "weakest link" is the exposure assessment (Bridges, 2003). The use of biomarkers may provide the information about the pollution (Kakkar & Jaffery, 2005). On the other hand, pollution often occurs in hotspots due to point sources and it is inadequate to assume that the whole population is exposed to the same, maybe average, contaminant level. By maintaining the spatial distribution of soil contaminant levels and receptors, it is possible, via the source-pathway-receptor paradigm to calculate a more realistic contaminant intake and hence the risks (Gay & Korre, 2006).

Table 5: Exposure Parameters used for the Health Risk Assessment through different Exposure Pathways for Soil

Parameter	Unit	Child	Adult
Body weight (BW)	kg	15	70
Exposure frequency (EF)	days/year	350	350
Exposure duration (ED)	years	6	30
Ingestion rate (IR)	mg/day	200	100
Inhalation rate (IRair)	m^3/day	10	20
Skin surface area (SA)	cm^2	2100	5800
Soil adherence factor (AF)	mg/cm^2	0.2	0.07
Dermal Absorption factor (ABS)	none	0.1	0.1
Dermal exposure ratio (FE)	none	0.61	0.61
Particulate emission factor (PEF)	m^3/kg	1.3×10^9	1.3×10^9
Conversion factor (CF)	kg/mg	10^{-6}	10^{-6}
Average time (AT)			
For carcinogens	days	365 × 70	365 × 70
For non-carcinogens	days	365 × ED	365 × ED

Source: USEPA (2004); Department of Environmental Affairs (2010); Bartholomew, Steele, Moustaki and Galbraith (2008).

Dermal Exposure

The absorption of heavy metals through the skin is limited because the dermal route of exposure is of less concern during a health risk assessment. However, some metals such as Ni and Cr, have the potential to induce toxic and sensitization effects directly on the skin (USEPA, 1992). Dermal exposure can also lead to intakes via other routes, such as oral exposure via hand-to-mouth transfer or ocular contact. Potential sources of dermal uptake that should be considered during risk assessment include small particles in contact with the skin; metal exposure during bathing, showering, and swimming (NAS/NRC, 2002); and the uptake of metals through damaged skin (e.g., irritated skin, sunburn). Dermal contact with metals in soil also represents a potential route of exposure, but the relatively low lipid solubility of most metals limits absorption through the skin (Paustenbach, 2000; Hostynek, Hinz, Lorence, & Guy, 1998).

Heavy Metals Conceptual Model

The generic conceptual model shows the relationships that exist between heavy metals sources, exposure, and effects of metals to human and ecological receptors. The relationships are complex and more often specific to a particular site, environmental condition, and receptor organism. Heavy metals are naturally occurring substances that undergo extensive biogeochemical cycling, transition functions between environmental loadings, media concentrations, exposed receptors, and the final organismal or ecosystem responses which are affected by natural processes to a much greater extent than those that occur with xenobiotic organic contaminants.

The generic conceptual model (Figure 2) shows the interrelationship between the heavy metals or metal compounds of interest and the health risk assessment process. It represents the actual and potential, direct and indirect relationships between stressors in the environment and exposed humans or ecological entities. The conceptual model depicts possible pathways from sources of heavy metals and typical ways in which risk is assessed and identifies areas where metal-specific issues require additional consideration.

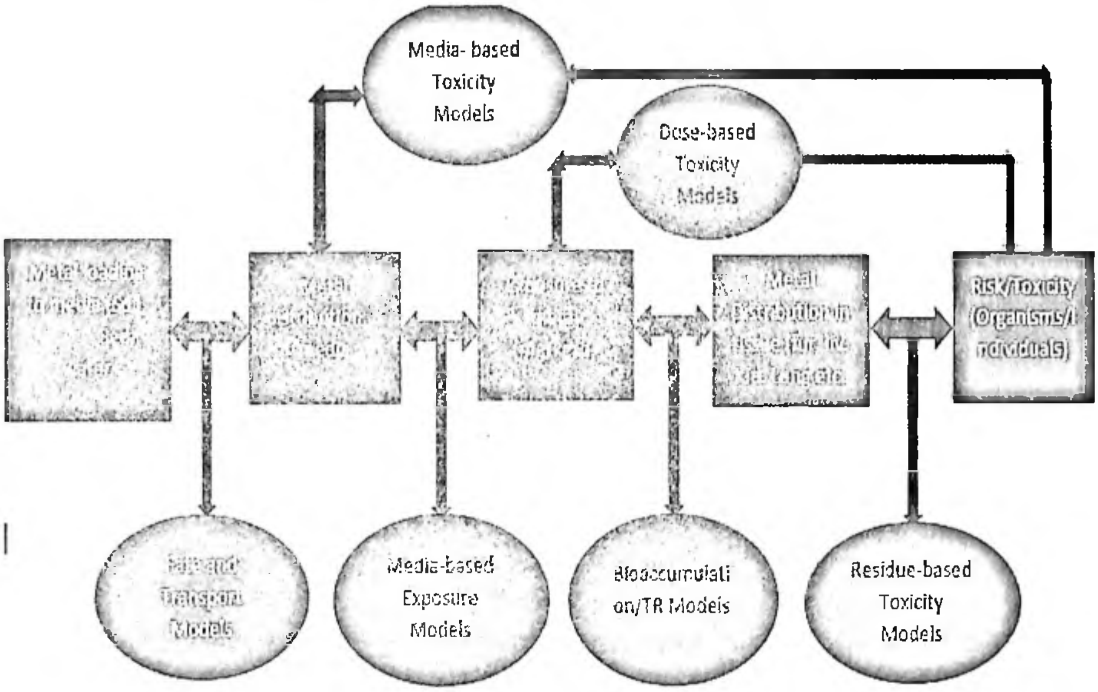


Figure 2: The Generic Conceptual Model for Heavy Metals Risk Assessment.

Risk Characterization

Risk Characterization is the final step in the risk assessment process and was designed to support risk managers and contractors by providing, in plain language, the essential scientific evidence and rationale about risk that they need for decision-making. In this phase, all the information from hazard identification, dose-response, and exposure steps (Figure 3), are summarized and interpreted by quantitatively comparing exposures with doses that are associated with potential health effects in order to determine the actual likelihood of risk to exposed populations (USEPA, 1999).

The term "risk management" encompasses all of those activities required to reach decisions on whether an associated risk requires elimination or necessary reduction. Risk management strategies/or options can be broadly classified as regulatory, non-regulatory, economic, advisory or technological, which are not mutually exclusive. Key decision factors such as the size of the population, the resources, costs of meeting targets and the scientific quality of risk assessment and subsequent managerial decisions vary enormously from one decision context to another.

It is also recognized that risk management is a complex multidisciplinary procedure which is seldom codified or uniform. It is frequently unstructured, but can respond to evolving input from a wide variety of sources. Increasingly, risk perception and risk communication are recognized as important elements, which must also be considered for the broadest possible public acceptance of risk management decisions (WHO, 2000; Paustenbach, 2002).

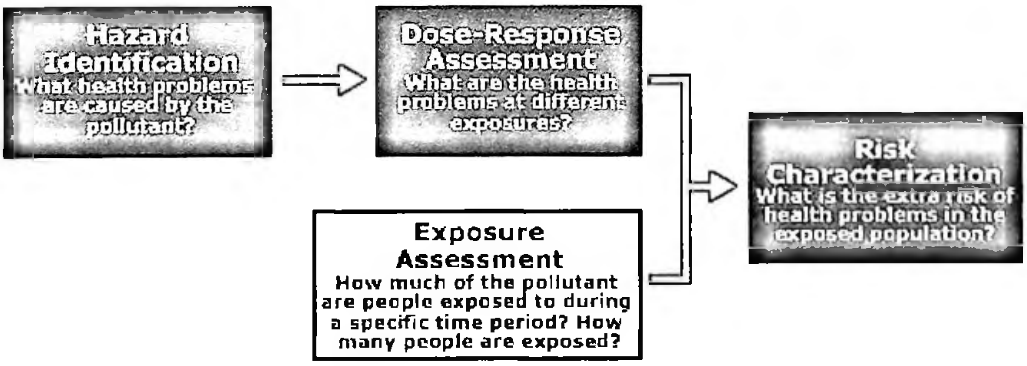


Figure 3: The 4 step Risk Assessment Process.
Source: USEPA (2004)

Gold Mining and the State of Heavy Metals pollution in Ghana

History

Ghana, a West African country (one of the world's most important gold mining regions for centuries) is currently the most significant gold producing country in West Africa (Hilson, 2002). Tarkwa and Prestea were the areas where large scale gold mining activities were concentrated by early European merchants in the late 19th century. A massive increase in gold production was experienced due to gold rush in the 20th century after the gold mining industry collapsed and reached a 50-year low in 1982.

In 1983 the government of Ghana Introduced the Economic Recovery Programme (ERP) under the guidance of WHO. After this the mining industry had seen a phenomenal growth and the gold production had increased by 700% (Hilson, 2002). Both small-scale and large-scale mining were operating in Ghana and about 237 (154 Ghanaian and 83 foreign) enterprises were seeking for gold and another 18 were operating gold mines (Hilson, 2002). Large-scale mining in Tarkwa region was conducted as surface mining.

The most common technique for treatment of non-sulphidic palaeoplacer ore was Cyanidation (Akosa *et al.*, 2002; Kuma & Younger, 2004). The management of waste from large scale mining companies was done in accordance to approved environmental plans. The waste rock heaps were stabilized and re-vegetated. Tailing slurries were channeled into tailing dams that were also re-vegetated. Small-scale mining in Ghana is defined as "mining by any method not involving substantial expenditure by any individual or group of persons not exceeding nine in number or by a co-operative society made up of ten or more persons" (Hilson, 2002). In Tarkwa, gold mining activities can be found all over the area, both in the forest and along the rivers. It is practiced in about 20,000 small-scale mines in the Wassa West district throughout the year.

Among these small-scale miners about 90% were illegal. Currently, 168 small-scale mining concessions are valid in the region (Asklund & Eldvall, 2005; Balfors, Jacks, Singh, Bhattacharya, & Koku, 2007). The most common ore processing techniques that are used by the small-scale miners are handpicking, amalgamation, cyanidation, flotation, electroextraction, and roasting of ore (Akosa *et al.*, 2002). Tarkwa area for instance has three main gold deposits. Placer or alluvial deposit, non-sulphidic paleoplacer or free milling ore and oxidised ore (Kortatsi, 2004).

Impact of Gold Mining and Heavy Metal Pollution

Heavy metals exist as natural constituents of the earth crust and are persistent environmental contaminants (cannot be degraded or destroyed) but can only be transformed (Lenntech, 2004). They occur naturally and are often bound up in inert compounds. As a result of anthropogenic activities such as mining, however, their concentrations have increased several-fold in the environment (Mason *et al.*, 2012; Obiri, Dodoo, Essumang, Armah, 2010). A number of gold enriched areas such as Tarkwa and Obuasi have historically been known to be gold mining towns, and mining of gold by large and small scale miners (including illegal galamsey operators) has been on the increase. However, the knowledge of metals pollution levels such as copper, zinc, iron and manganese in soils, water and sediments where these mining activities occur and surrounding areas is fairly limited (Koranteng – Addo E.J., Owusu – Ansah, Boamponsem, Bentum, & Arthur 2011).

Despite the fact that Large and small-scale mining contributed hugely to the economy of Ghana over the years, it has also negatively impacted the environment and human health (Aryee, 2003). The major environmental impact associated with gold mining is the continuous release of harmful and toxic substances such as Hg, Pb, Cd, As, among others (Hilson, 2001; Paruchuri *et al.*, 2010).

During mining, it is common practice for waste material (tailings) to be removed and piled in large mounds at the mining site. These piles of tailings often contain heavy metals found in the ore and in many instances, also contain mercury waste that was used during the amalgamation of gold (Okang'Odumo *et al.*, 2014). In such instances, these tailings are exposed to the elements and can be easily weathered, releasing toxic metals into the soil, adjacent water bodies and, ultimately, groundwater through acid mine drainage (AMD) (Asklund & Eldvall, 2005).

Report from a study conducted on seven abandoned open mine pits in the Tarkwa gold mining area suggested that the level of heavy metals (Fe, Cu and Mn) pollution from seven abandoned mine pits may be a threat to the health of the inhabitants of the study area and therefore requires remedial action (Koranteng – Addo E.J. *et al.*, 2011). Additionally, a study conducted in Tarkwa gold mining area recorded contamination of Hg (up to 2.3±0.5 mg/L) and As (up to 1.3±1.1) in streams and rivers (Kwadwo *et al.*, 2007). It was reported that an estimated 5 tonnes of Hg was released from gold mining operations in Ghana each year (Hilson, 2001). High concentrations of Hg have been reported in sediments and fish in the vicinity of small-scale mining areas which employ amalgamation as the main technique. The values reported from fish fillets in these areas exceeds the recommended guideline limits of the United States Food and Drug Agency (Babut *et al.*, 2003).

Review of a number of recent literatures on heavy metals contamination, revealed that studies of soil, sediment and water heavy metal pollution related to mining activities had been carried out in Ghana in the past 10 years (2007–2017). For instance, Obiri *et al.*, (2016) reported that the concentrations of As, Mn, Pb, Hg Cd in soils and sediments around mining areas were higher than the recommended WHO, GEPA and USEPA permissible values.

There were worries of communities around the mining areas as to whether the mining activities may be causing serious metal pollution to the water resources by contaminants such as arsenic, lead, cadmium, mercury, and cyanide. A number of studies have linked heavy metals pollution of some surface and groundwater bodies in Ghana to gold mining activities (Kuma & Younger, 2004; Manu, Twumasi, & Coleman, 2004; Obiri, 2007; Rajaee *et al.*, 2015). Studies have shown that metal levels in surface and groundwater exceeded WHO guidelines for drinking water in many mining areas in Ghana (Kortatsi, 2004; Kuma & Younger, 2004). For Instance, Mercury is commonly used in mining for gold extraction, especially among small and artisanal mining industries. The white-silvery substance which can be easily assessed in shops around the mining areas is applied mostly by mixing the liquid mercury in open pans filled with ore in order to amalgamate the gold particles. The miners then suspend this gold-mercury amalgam over an open fire to burn off the mercury and retrieve the raw gold. The activities of getting the raw gold are unfortunately carried out in the presence of both adults and children workers leading to exposure of even miners to this carcinogenic substance. The recent report by regional hospital authorities around the major mining areas revealed that the hospitals are recording increasing cases of kidney infection from persons linked to artisanal and illegal mining (Obiri, 2007; Cobbina *et al.*, 2013; Rajaee, 2015).

A recent study on metal contamination of river bodies around Nangodi and Tinga mining communities in Northen Ghana showed Hg, As, Pb, Zn, and Cd exceeding WHO stipulated limits and hence, direct drinking of water could be deleterious to consumers (Cobbina *et al.*, 2013). Other studies have shown increasing evidence linking toxicants such as Hg, Pb, As, and Cd to the incidence of cognitive impairments, especially in children, cancers of all sorts and deficiencies of some essential nutrients in the human body (Koger, Schettler, & Weiss, 2005; Obiri *et al.*, 2010; Arora *et al.*, 2008). High concentrations of lead, arsenic, and other heavy metals can affect the nervous system and kidneys, and may cause reproductive disorders, skin lesions, endocrinal damage, and vascular diseases (WHO, 2011).

Heavy Metal Pollution and Cancer

Although, current evidence in literature may not be sufficient to establish causal-effect association between chronic environmental exposure to heavy metals and cancer, researchers globally continue to find a strong association between heavy metals and occurrence of cancer. Jaafar and co-workers reported cases of 3 patients who developed symptoms of skin cancer following chronic exposure to arsenic-contaminated well water in Malaysia (Jaafar, Gabriel-Robez, Vignon, Flori, & Rumpler, 1994).

In an American study, Carrigan and co-workers found a strong correlation between pancreatic cancer and chromium, selenium and molybdenum (Carrigan *et al.*, 2007). In a similar study in an Egyptian population, serum cadmium levels were assessed in 31 newly diagnosed cancer patients. Compared to controls, the study found high cadmium levels in pancreatic patients who were exposed to the cadmium-polluted environment (Kriegel *et al.*, 2006). A more recent study in Egypt concluded a causal association between high levels of cadmium and copper in the body and breast cancer (El-Harouny, El-Morsi, Ahmed, & El-Atta, 2011). Similarly, Alatise and Schrauzer (2010), demonstrated a correlation between body levels of lead and volumes of tumor in breast cancer patients in a Nigerian population.

In Ghana, a study carried out by Obiri and co-workers (2006), evaluated cancer risks in Ghanaian population who consume food crops cultivated in mining communities, where agricultural soil has shown high levels of heavy metals. In their report, this population showed 10,000-fold likelihood to suffer from cancer and/or cancer related diseases compared to controls. Similarly, cancer causing heavy metals such as Hg (trace to 0.012 mg/L) and As (0.034–0.7 mg/L) contamination were recorded in human urine in Tarkwa, a gold mining town (Kwadwo *et al.*, 2007).

Methods for Determination of Metals in Soils, Sediments and Water

The mobility and bioavailability of heavy metals in sediments depend strongly on the mineralogical and chemical forms in which they occur, thus the mode of occurrence of a metal (Baeyens, Monteny, Leermakers, & Bouillon, 2003) and the form in which that metal is present (Sundaray, Nayak, Lin, & Bhatta, 2011) is important in the understanding the process of the potential ecological impacts of contamination on a sediment and its associated water body (Zhong, Zhou, Zhu, & Zhao, 2011).

Heavy metals mobility depends on their ways of binding and the determination of specific chemical species or binding focus can be very complex and hardly possible. For that reason, it is necessary to study different forms of heavy metal mobility (Beltrán de la Rosa, Santos, Beltrán, & Gómez-Ariza, 2010) and bioavailability rather than the total metals concentration in order to obtain an indication of the bioavailability of metals (Ahdy & Youssef, 2011; Lee, Kang, Jo, & Choi, 2012; Shikazono, Tatewaki, Mohiuddin, Nakano, & Zakir, 2012). Also, the metal load in sediments/soils results from both natural and anthropogenic sources and thus makes it a daunting task in identifying and determining the origin of heavy metals present in sediments (Idris, Eltayeb, Potgieter-Vermaak, Van Grieken, & Potgieter, 2007).

The sequential extraction method was developed by Tessier, Campbell and Bisson (Tessier, Campbell, & Bisson, 1979) to determine speciation of metals in sediments (Tessier *et al.*, 1979; Coetzee, 1993). The method provides information on the fractionation of metals in different lattices of the solid sample which serves as a good compromise to give information on environmental contamination risk (Margui, Salvadó, Queralt, & Hidalgo, 2004). Extraction involving strong acid digestion method has been used in the determination of total heavy metals in sediments. However, this method was observed to be misleading when assessing environmental effects due to the potential for an overestimation of exposure risk. Moreover, in order to eliminate the mobility of heavy metals in sediments, various sequential extraction procedures have been developed (Salmons & Forsstner, 1980; Li &

Thornton, 2001) with the number of extraction steps varying from 3 to 6 (Ure, Quevauviller, Muntau, & Griepink, 1993).

There are a number of available extraction techniques that employ different reagents and experimental conditions to examine the distribution of heavy metals in sediments and soils. However, the 5-step Tessier *et al.*, (Tessier *et al.*, 1979) and the 6-step extraction method by Kerstin and Fronstier (Kersten & Frostner, 1986) were often widely used as shown in Table 6.

The diversity of procedures and lack of uniformity in different protocols, triggered the development of Community Bureau of Reference (Bureau Communautaire de Référence or BCR) method (Mossop & Davidson, 2003) which seek to examine multiple soil and sediment fractions in which metals may be sequestered (Ure *et al.*, 1993). This method harmonized differential extraction schemes for sediment analysis and was applied and accepted by a large group of specialists (Salmons, 1993; Fiedler *et al.*, 1994). The method is based on a three stage extraction (Table 7), it is widely adapted and augmented with the use of techniques such as ultrasonic or microwaves (Arain *et al.*, 2008).

Table 6: Sequential Extraction Method

Fraction	Reagents and Conditions
Exchangeable	1 M $MgCl_2$ at pH 7
Carbonate	1 M CH_3COONa buffered to pH 5 with CH_3COOH
Reducible	0.04 M $NH_2OH.HCl$ in 25% CH_3COOH heated to 95 °C
Oxidisable (Organics and sulphides)	30 % H_2O_2 adjusted to pH 2 with 0.02 M HNO_3 heated to 85 °C. Treatment with 3.2 M CH_3COONH_4 in 20 % HNO_3
Residual	Dissolution in HF and $HClO_4$ at 95 °C

Source: Tessier *et al.*, (1979)

Table 7: BCR Sequential Extraction Schema

Fraction	Reagents	Conditions
Carbonates	0.11M acetic acid	Shaken at 30 RPM at room tempt. for 16 hrs
Reducible	0.5 M $NH_2OH.HCl$ buffered to pH 1.5 with HNO_3	Shaken at 30 RPM at room temperature for 16 hours
Oxidisable	10 mL H_2O_2; 1 M CH_3COONH_4 buffered to pH 2 with HNO_3	H_2O_2 added slowly followed by CH_3COONH_4, shaken at 30 RPM at room tempt. for 16 hrs

Source: Cuong and Obbard (2006)

Exchangeable Fraction

The Exchangeable fraction comprise of weakly bound metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchangeable processes. Adsorption-desorption reactions can occur in this fraction which will lead to remobilization of metals especially when the pH of the exchange solution is too alkaline (Ahnstrom &

Parker, 1999), requiring careful buffering of the extracting pH to 7. Exchangeable fraction generally accounted for less than 2% of the total metals in soils presents and is also known as non-specifically adsorbed fraction, it can be released by the action of cations such as K, Ca, Mg or (NH_4) displacing metals weakly bond electrostatistically organic or inorganic sites (Beckett, 1989).

The exchangeable fraction involves ion exchange between the cation of choice (usually Mg^{2+}, but Al^{3+}, Na^+ or NH_4^+ have been used) and metal ions adsorbed to iron and manganese oxides and hydroxides in clay particles (Singh, Müller, & Singh, 2002)

The Carbonate Fraction

Carbonate is a major adsorbent for many metals when there is reduction of Fe-Mn oxides and organic matter in the aquatic system. The carbonate fraction has been identified as easily digested with acid solutions with a pH <5 which results in the conversion into metal ions, carbon dioxide and water during the digestion process. Extraction of metals from carbonates phases enhances the leaching of metals specifically sorbed to organic and inorganic substrates (Tessier *et al.*, 1979). The fraction is sensitive to pH changes, and metal release is achieved through dissolution of a fraction of the solid material at pH close to 5.0 (Gleyzes, Tellier, & Astruc, 2002).

The Reducible Fraction

It is considered as the last of the fractions which have heavy metals from anthropogenic sources (Martin, Nirel, & Thomas, 1987). This fraction is referred to as sink for heavy metals. Scavenging by these secondary oxides, present as coating on mineral surfaces or as fine discrete particles which can occur as a combination of the precipitation, adsorption, surface complex formation and ion exchange (Hall & Pelchat, 1999). The reducible fraction is considered to be the last of the fractions which has heavy metals from anthropogenic sources (Martin *et al.*, 1987). The reducible fraction reacts with hydroxylamine hydrochloride ($NH_2OH.HCl$) buffered with acetic acid at elevated temperatures to reduce and solubilise heavy metals in their ionic form which are bound to the iron and manganese oxides. However, to achieve the desired results, the systems need to be buffered to minimize precipitation of these metals after oxidization.

The Organic and Sulphide Fraction

Heavy metals association with organic material such as living organisms and detritus occur through some primary sources such as bioaccumulation or complexation process. In aquatic systems, organic substances tend to have high degree of selectivity for individual ions in the order, Hg > Cu > Pb > Zn > Ni > Co (Filgueiras, Lavilla, & Bendicho, 2002) compared to monovalent ions with organic matter. In the organic fraction, metallic pollutants that are adsorbed in this phase are assumed to stay in the soil for longer periods but may be immobilized by decomposition process (Kennedy, Sanchez, Oughton, & Rowland, 1997). The organic fraction contains metals that can be solubilised only with the use of an oxidising agent which make them unavailable to the ecosystem under normal conditions. Generally oxidising agents, such as H_2O_2/CH_3COONH_4 or H_2O_2/HNO_3 are used to solubilise metals bound to the iron and manganese oxides within this fraction (Martin *et al.*, 1987; Tessier *et al.*, 1979). Under oxidizing conditions, degradation of organic matter can lead to the release of soluble trace metals bound to this component.

The extracts obtained during this step are metals bound to sulphides (Marin *et al.*, 1997). The organic fraction released in the oxidisable step is considered not to be bioavailable because it is beleived to be associated with stable high molecular weight humic substances that release small amount of metals in a slow manner (Filgueiras *et al.*, 2002). These systems however, need to be buffered to minimize precipitation of these metals after oxidization.

Residual Fraction

Residual phase serves as a useful tool in the assessment of the long-term potential risk of heavy metal or toxic metals entering the biosphere. Digestion using strong acids such as nitric acid, hydrochloric acid or mixture (aqua regia) which do not dissolve the silicate matrix have been commonly used to leach out the recalcitrant metals that are bound in the silicate lattice and are otherwise not available to the ecosystem. The recovery of these elements is dependent on how severe the treatment is done. For instance, the total metal recovery is usually achieved by the use of HNO_3 (Tam & Wong, 2000) or HCl/HNO_3 (Cox & Preda, 2005), which leach the metals from the mineral lattice; or combinations of $HF/HClO_4$ or HNO_3/HF (Jones & Turki, 1997; Martin *et al.*, 1987), which completely dissolves the silicate lattice.

Residual phase gives an estimate of the maximum amount of elements that are potentially mobilisable with changes in environmental conditions. ISO 11466 (ISO, 1995) aqua regia digestion procedure is the well-known procedure with a legal backing in some European countries and had been used for the standard reference material of soil and sediments. Moreover, primary and secondary minerals containing metals in the crystalline lattice constitute the bulk of this fraction. Its destruction is achieved by digestion with strong acids, such as HF, $HClO_4$, HCl and HNO_3.

Mining activities and Heavy Metals Quality Guidelines in Ghana

Ghana is primarily an agricultural nation that has stressed economic development before its 1957 independence from England. The focus on economic development has been only marginally successful but has come at enormous environmental cost. For instance, sedimentation and contamination with heavy metals such as As and Hg used in gold extraction are associated with mining practices. The mining activities which result in major cyanide spillages around the major mining areas and its surrounding communities are a few among several reported cases of environmental pollution caused by mining (EPA-Ghana, 2007).

Gold mining in Ghana has played a central role in the socio-economic and political life of the country for the past 1000year (Hilson, 2006). The gold bearing ores obtained from the Biriman and Tarkwanian rock system consists of oxides mainly as iron oxides -haematite (Fe_2O_3) and Magnetite (Fe_3O_4), sulphides – mainly as pyrites and arsenopyrites, and transition ores (Obri, *et al.*, 2006). Some of the challenges residents living around mining communities face are; pollution of river bodies, streams, soil and air, inability of residents to tell the implications of metal pollutants on their health due to soil, water and air contamination and finally, their inability to link toxic chemicals exposure such as As, Hg, Pb and Cd to disease prevalence in the mining communities. Lack of understanding of the relationship between various types of diseases suffered by residents in the mining communities and the concentration of toxic chemicals in surface water, soils and sediments have prevented residents in the mining communities from assessing the connections between the concentrations of toxic chemicals and related disease prevalence.

It is in this regard that this objective of setting geochemical baseline and guideline values for heavy metals (as recommendation to policy and decision makers) in the Ghanaian soil, sediment and water based on sound human health and ecological risk assessment to be investigated in this study become essential and urgent.

Geochemical Background and Baseline Values Determination

Background level is a term used to differentiate between the concentration of a natural element and the concentration of an anthropogenic influence in a particular environmental sample (Matschullat, Ottenstein, & Reimann, 2000; García Sánchez, Alonso-Rojo, & Santos-Francés, 2010). The concentration of heavy metals in a natural soil background depend on the soils composition processes and the geological substrates (Kabata Pendias & Pendias, 2001; Alloway, 2013). In 1993, the term geochemical baseline was officially presented under the International Geological Correlation Program as the Global Geochemical Baselines which was defined as the natural variation in the concentration of an element in the surface environment at a determined place and time. This definition encompasses the natural geographic concentrations and the defuse anthropogenic contributions in soils or sediments (Santos-Francés *et al.*, 2017; Dung, Cappuyns, Swennen, & Phung, 2013).

Setting of geochemical background values for toxic metals always comes with certain terminologies such as the threshold and baseline values which are often used interchangeably with ‘‘geochemical background’’ even though this approach has faced many criticisms due to the different meanings (Reimann, Filzmoser, & Garrett, 2005; Gałuszka & Migaszewski, 2011). The word ‘‘threshold’’ indicates the outer limit of background variation (Garrett 1991) while ‘‘baseline’’ refers to the present concentration in order to be able to quantify future concentration changes (Reimann & Garrett, 2005). The difficulty of establishing a natural background level is due to the complications of finding a pristine environment composing of virgin soil/sediments since soils/sediments without any type of contamination are almost impossible to find due to atmospheric deposition of long distance trace elements and human activity (Albanese, De Vivo, Lima, & Cicchella, 2007).

The calculation of the background level should therefore show an average value and a range of concentrations of heavy metals for a specific area and at a specific time, as well as considering the diffuse entry of these elements into soils (Adriano, 2001). The calculation of the geochemical baseline is therefore more useful, since it takes into consideration certain human impact on the environment that already exists (Chen, Ma, & Harris, 1999; Wei & Wen, 2012).

Estimation of the geochemical background level of soils and sediments involves two main methods and they are: the statistical method (indirect, theoretical) and empirical (direct, geochemical). Besides these methods, the integrated methods which combine both the statistical and empirical methods are mentioned and used by a number of authors (Gałuszka, 2007; Qi, Leipe, Rueckert, Di, & Harff, 2010). The integrated methods which are used in our current work use samples collected in pristine areas which are supposedly considered as not affected by industrial or mining activities and the analytical results are subjected to statistical calculations. Since there are variabilities in soil trace element concentration which most often makes the use of normative values of environmental legislation of other countries or regions inappropriate, it is always advisable to determine the geochemical baseline locally and separately for each metals in different geological regions to avoid the limit values for contaminated media being lower than the background levels calculated for an extensive area (Rojo, Frances, Garcia-Sanchez, & Alvarez-Ayuso, 2004).

Estimation of environmental geochemical baselines is key in assessing the current state of the environment and providing guidelines and quality standards in environmental legislation and policy-making, especially in the evaluation of contaminated soils and in environmental risk assessment (Baize & Sterckeman, 2004) because it allows the development of a frame of reference to help properly control the environmental changes generated during and after the mining activity. It is therefore necessary to conduct a baseline study to check explorative or mining activity in question which is significantly affecting the environment.

Integrated Method for Geochemical Background Determination

The integrated method is a method that combines the statistical and geochemical methods (Gałuszka, 2007; Gałuszka & Migaszewski 2011). In the application of this method, the samples are collected in pristine areas and the analytical results are subjected to statistical analyses. The samples from which background values can be derived are usually collected from certain locations from the source of pollution such as deep core or non-polluted sites.

The integrated method has a number of advantages in that the data are less affected by differences in site sampling because of the representativeness of the samples for the study area and that the data processing is also less complex due to the fact that a restricted amount of data is obtained with this method which (Gałuszka, 2007). The method also was supported and applied in data analysis by a number of authors (Pe´rez-Sirvent, Martı´nez-Sa´nchez, Garcı´a-Lorenzo, Molina, & Tudela, 2009; Qi *et al.*, 2010; Bini, Sartori, Wahsha, & Fontana, 2011). The integrated method was also considered to be an effective tool to show pedogenetic trends in relation to background concentrations of heavy metals. The only challenge which has remained a difficult task because of the influence of long–range transport of atmospheric deposition of heavy metals on soils/sediemnts is how to identify a real pristine area, which is a requirement for the integrated method (Pacyna & Pacyna, 2001; Peirson & Cawse, 1979). The requirement for adequate reference materials for reliable determination of geochemical background has been addressed in detail by Desaules (2012).

Pollution Indices for Assessing Sediment Contamination by Heavy Metals

There are numerous pollution assessment procedures being developed for assessing sediment contamination which take into consideration the effects of various types of anthropogenic activities such as agriculture, industry and transportation. Several of the methods are based on the total concentration of the elements whilst some are based on the available or the reactive pool of the elements (Dung *et al.*, 2013). Generally, the methods for the assessment could be a single or multiple element indices that are used to qualify the enrichment of soils and sediments by an element of interest.

Pollution indices provide a more detailed picture (for example, providing information about metal behaviour in areas with complex sediment behaviours) of enrichment of an element at a sampling site than a concentration-based SQG. As a result, pollution indices are considered throughout the literature as complimentary or even superior to the SQGs currently in use around the world.

The need for historical data which is generally not available is the greatest challenge in determining the enrichment of an element of interest in a sample. To overcome this challenge, it is important for some background data be collected as a sample or as a set of samples taken from the catchment of the waterway of interest, or by the use of the average crustal composition for the continent of interest (de Caritat & Cooper, 2011; Wedepohl, 1995) Another method is by using the average composition of sedimentary rocks, such as shale (Dung *et al.*, 2013), which can then act as useful analogue of unpolluted and historical sediments. The various equations can be referred to under the methodology.

Modified Degree of Contamination and Modified Pollution Index

There are several single element pollution indices that can be applied to a data in the determination of sediment quality. However, the use of a single element pollution indices come with some limitations, notable among them are; they can only be applied to single elements which may undermine the complex nature of heavy metals in urban and industrial environments where a mixture of contaminants intrinsically exists. Also the issue of pollution indices accounting for the background concentrations and the complex, non-conservative behaviour of sediments was not taken into account. Accounting for the limitations of single element pollution indices eventually led to the development of multiple element indices which were reported in research literatures for the assessment of sediment and soil quality (Hakanson, 1980; Nemerow, 1991; Brady *et al.*, 2015).

The modified degree of contamination (mCd) (Equation 10) and pollution index (PI) by Hakanson (1980) and Nemerow (1991) are the two most common and widely used pollution indices in recent years. The mCd uses contamination factors for individual sites, and taking their average, it is possible to assess the quality of sediments based on a set of elements (Abrahim & Parker, 2008, Brady *et al.*, 2015). However, the mCd has certain limitations like other single element pollution indices (such as the incorporation of background concentrations and the complex, non-conservative behaviour of sediments) which was not taken into account in the derivation of the mCd. As a result, a more recently modified pollution index (MPI) (Equation 11) was developed by Brady *et al.*, (2015), which is an improvement of the pollution index by Nemerow (1991) and uses enrichment factors in place of contamination factors in its pollution index estimation. The merits of this new index is that; apart from providing solutions to most of the limitations of single element pollution indexing, it also has another advantage of adjusting the sediment qualification threshold to give a more accurate qualification of sediment contamination and avoid the unlikely overstating of sediment contamination contrary to the trigger value of 3 used by Nemerow for PI (Brady *et al.*, 2015).

$$mCd = \frac{\sum_{i=1}^{n} Cf^{i}}{n} \qquad (10)$$

$$\mathrm{MPI} = \sqrt{\frac{(\mathrm{EF})^2 + (\mathrm{EFmax})^2}{2}} \quad (11)$$

Where mCd is the modified degree of contamination, C_f^i is the contamination factor of the metals, 'n' is the number of selected elements, $\overline{\mathrm{EF}}$ is the average of all the single pollution indices of the heavy metals and EF (max) is the maximum value of the single pollution indices of all the heavy metals. For the description of degree of contamination, the terminologies in Table 8 were used.

Table 8: Sediment/Soil Threshold values/ranges according to Pollution Index

Class	Sediment Qualification	Igeo (Muller , 1969)	EF (Qingjie *et al.*, 2008)	mCd (Hakanson, 1980)	MPI (Brady *et al.*, 2015)
0	No pollution	≤ 0	EF < 1	mCd < 1.5	MPI < 1
1	Minor Pollution	0-1	1 < EF < 3	1.5 < mCd < 2	1 < MPI < 2
2	Moderate pollution	1-2	3 < EF < 5	$2 \leq$ mCd < 4	2 < MPI < 3
3	Moderately-severe pollution	2-3	5 < EF < 10	$4 \leq$ mCd < 8	3 < MPI < 5
4	Severe pollution	3-4	10 < EF < 25	$8 \leq$ mCd < 16	5 < MPI < 10
5	Very Severe polluted	4-5	25 < EF <50	$16 \leq$ mCd 32	MPI > 10
6	Extremely severe polluted	≥ 5	EF > 50	mCd > 32	-

Modified Ecological Risk Index (MRI)

The Potential Ecological Index (RI) was developed by Hakanson, (1980) to determine quantitatively the pollution status of heavy metals in sediment/soil of a specific site. RI is accepted widely, and used for quantitative assessment of ecological risk of heavy metals. The application of contamination factor in the calculation of RI (Equation 12) comes with some limitations because it does not take into consideration inputs from lithogenic and sedimentary sources of the element of interest which pose serious concern on the significant sedimentation input from creeks, a common phenomenon especially in the estuarine environments.

To effectively estimate the RI which will take into consideration impact from terrestrial and sedimentary inputs, the Modified Ecological Risk Index (MRI) (Equation 13) was developed by Brady *et al.*, (2015) which proposed the use of enrichment factor in place of the contamination factor in the calculation of RI (Table 9). Furthermore, the development of the MRI using the enrichment factors as a single element index was observed to be the most preferred method for assessing contamination at a site from large complex data set (Duodu, Goonetilleke, & Ayoko, 2016). It also accounts for lithogenic sources of heavy metals and changes in the background concentration as well as the non-conservative behaviour of sediments that occur in estuarine environments (Brady *et al.*, 2015). The Equation 12 can now be re-written as Equation 13.

$$\mathrm{RI} = \sum_{i=1}^{n} E_i = \sum_{i=1}^{n} Tri \times Cfi \tag{12}$$

$$MRI = \sum_{i=1}^{n} Er^i = \sum_{i=1}^{n} Tr^i \times Ef^i \tag{13}$$

Where RI is the sum of potential ecological risk factor for heavy metals in the sediment, Cf^i is the contamination factor, E^i is the potential ecological risk factor, MRI is the modified potential ecological risk index, Ef^i, is the enrichment factor of the elements, TR is the toxic-response factor for certain metals

Table 9: Grading Standards of Potential and Modified Ecological Risk Index

E^i (HÅKANSON, 1980)	Ecological grade	RI or MRI (Brady *et al.*, 2015)	Ecological grade
Ei < 40	low ecological risk	MRI < 150	low ecological risk
40 < Ei < 80	moderate risk	150 < MRI < 300	moderate risk
80 < Ei < 160	considerable risk	300 < MRI <600	considerable risk
160 < Ei < 320	high risk	-	-
Ei > 320	very high risk	MRI > 600	very high risk index

Multivariate Techniques in Soil/Sediment Assessment

Pearson Correlation Coefficients

The application of Pearson correlation coefficient technique to an analytical data was commonly used by geochemists to determine whether or not two elements in a sample are related by mathematically determining the correlation of variation between elements of interest. Examination of the results matrix by relating the experimental data to Pearson correlation indices (presented in Table 10), it is possible to determine to what extent elements are correlated to each other.

Table 10: Pearson Correlation Index

Correlation	Negative	Positive
None	-0.09 to 0.00	0.00 to 0.09
Small	-0.30 to -0.10	0.10 to 0.30
Medium	-0.50 to -0.30	0.30 to 0.50
Strong	-1.00 to -0.50	0.50 to 1.00

PCA/HCA Analysis

Principal Component Analysis (PCA) and Cluster Analysis (CA) are two chemometric techniques which are complementary in the analysis of data and are sometimes used in conjunction with Pearson correlation matrices to establish similarities between elements and sampling sites. They are commonly used to determine the relationships between heavy metals and other environmental contaminants. The PCA method was used by Muniz *et al.,* (2004), as a complimentary technique to Pearson correlation to assess how the different sampling sites were related to redox conditions (EC) and Dissolved Oxygen (DO) compared to heavy metals and organic matter. A study by Nasrabadi, Bidhendi, Karbassi and Mehrdadi (2010), based on similarity using CA helped identify three distinct groups of heavy metals.

This technique has advantages over other methods (such as pollution indices) in that it produces a graphical representations of the relationships between variables as either PCA scatter plots, loadings plots, biplots (PCA) or dendrograms (HCA). HCA dendrograms and PCA loadings plots provide similar information/groupings of elements based on similarities.

In a loadings plot, Principal Components (PCs) are plotted against each other. Elements which are related are located in clusters in the PCA loadings plot. These clusters of elements have similar sources. In an environmental context, groupings of elements on the loadings plot can be used to identify sources of elements, such as marine sediments, based on a grouping consisting of Mn and As (Hu, Yu, Zhao, & Chen, 2011).

Source profiles identify the contributing elements from a source and the source profiles are generally presented as a bar graph. The elements with the greatest contribution from a source have the largest bars and this information can be used to "fingerprint" the source. Fingerprinting of the source requires some knowledge of the relationships between elements and distinctive relationships, such as V and Ni, which are related to shipping fuels (Lewan & Maynard, 1982). Once the source has been fingerprinted, the contribution of that source can then be determined, through the contributions plot, which plots the contribution of each source at each sampling site to the total metals concentration.

Multicriteria Technique for Ranking Metals at the Sampling Sites

PROMETHEE and GAIA

The PROMETHEE (Preference ranking organization method for enrichment evaluation) and GAIA (Geometrical analysis for interactive aid) are a related set of multiple criteria decision-making (MCDM) methods proposed around 1985 (Brans & Vincke, 1985) which have seen use in a wide variety of fields, from business, to science, to sports management (Behzadian, Kazemzadeh, Albadvi, & Aghdasi, 2010) and has seen some use in an environmental context for ranking contamination of sampling sites (Yatsalo *et al.*, 2007). PROMETHEE is a non-parametric ranking decision making tool which is used to rank objects in order of preference, while GAIA is the visual representation of the PROMETHEE results, showing the data on a plane similar to a PCA loadings plot but contains a decision axis (π) which is used to indicate the variables which are more preferred for making a decision (Brans & Mareschal, 2005; Khalil, Goonetilleke, Kokot, & Carroll, 2004), with the length of the π axis representing the strength of the decision axis, and a longer π representing stronger decision making power (Brans & Mareschal, 2005).

ICP-MS Analysis

The Principle

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique used for elemental determinations which was commercially introduced in 1983 and has gained general acceptance in many laboratories. ICP/MS technique has many advantages over other speciation techniques like optical spectrometric, inductively coupled plasma atomic emission spectroscopy and atomic absorption spectroscopy which are less sensitive and do not provide simultaneous multi elemental detection respectively as compared to ICP-MS.

An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer.

Detection capabilities of ICP/MS varies with the sample matrix, which may affect the degree of ionization that will occur in the plasma or allow the formation of species that may interfere with the analyte determination.

Once the elements in the sample are converted into ions, they are then brought into the mass spectrometer via the interface cones. The interface region in the ICP-MS transmits the ions traveling in the carrier gas sample stream at atmospheric pressure (1-2 torr) into the low pressure region of the mass spectrometer (<1 x 10-5 torr).

Typical quadrupole mass spectrometers used in ICP-MS have resolutions between 0.7 - 1.0 amu. This is sufficient for most routine applications. However, there are some instances where this resolution is NOT sufficient to separate overlapping molecular or isobaric interferences from the elemental isotope of interest.

The ICP-MS detection capability of multielemental ultratrace elements makes it the most powerful technique (Beauchemin, 2010). Speciation analysis using ICP-MS has become common practice in recent years for ultra-sensitive detection of trace metal- and metalloid-containing compounds (Rosen & Hieftje, 2004). ICP/MS has been cited in many literatures to have extensive use for industrial analysis of metals, chemicals and advanced synthesized materials (Fischer, Hinds, Nelms, Penny, & Goodall, 2002), for environmental analysis (Fritsche & Meisel, 2004) and clinical and biological materials, food and beverages (Taylor, Branch, Halls, Patriarca, & White, 2003; Trandafir *et al.*, 2012). ICP-MS gives sensitive detection limits and satisfactory and reliable recovery and accuracy with multi-elements and the technique has the ability to determine low-concentrations (range: ppb = parts per billion = µg/L) and ultra-low-concentrations of elements (range: ptt = parts per trillion = ng/L). ICP-MS specifically is able to filter ions on their mass-to-charge ratio and this allows the technique to supply isotopic information and can measure isotope ratios of elements (Tseng, de Diego, Martin, Amouroux,

& Donard, 1997), since different isotopes of the same element have different masses.

Analysis of Heavy Metals with ICP/MS

Mass spectrometry with inductively coupled plasma (ICP-MS) is a multi-element technique for analyzing liquid samples, characterized by high selectivity, sensitivity and detection limits much lower than other multi-element techniques. Identification and quantification of different heavy metals in soil and sediment mixture using ICP-MS has been recognized by researchers for its unique analytical capabilities throughout the world (Fernandez, Monna, Labanowski, Loubet, & Van Oort, 2008; Kuang, Zhu, Xi, & Li, 2013). It is a powerful technique for trace analysis of elements and is preferred for ultratrace levels due to its higher sensitivity (Yang & Low, 2009; Hoffman, Lüdke, & Scholze, 1997).

The total analysis of heavy metals such as V, Cr, Mn, Co, Ni, Zn and Pb, in sediments and soils, is commonly done to evaluate the degree of contamination of aquatic and terrestrial environments. Analytical methods for the elemental analysis of soil and sediments normally require the partial or total extraction of the sample matrix. Recoveries and precision of pseudo-total and total digestion methods may vary with many factors, including the mineral composition and origin of the soil, the digestion method, as well as the elements of interest. The determination of some elements in soil is challenging and may require the development of various specific methods for a complete multi-element analysis (Kubravova, 1997).

There was therefore an increasing interest of researchers to find an alternative and/or complementary solid sampling techniques that will provide a direct analysis of solid matrices. Soils represent a matrix with inherent heterogeneity and variable mineral composition leading to analytical complexity. Sample digestion often remains a key step in the determination of the "total" element mass concentrations in soils and sediments. A safe dissolution method that provides an analytical recovery of at least approximately 90% of elements is required. Various digestion methods are used to determine the mass concentration of trace elements in solid matrices (Chen & Ma, 2001).

Chapter Summary

This research was initiated as a direct response to the increased soil, water and sediment contamination by heavy metals in Ghana, and a number of cases related to this problem has been discussed under this chapter. The chapter discussed how solid wastes (tailings) containing carcinogenic heavy metals from mining activities is becoming a major issue in Ghana and how high levels of these toxic metals contained in mine wastes are released into the environment through anthropogenic deposition, surface water run-off, acid mine drainage and tailings leakages with serious health implications for human populations residing along the gold mine areas. The chapter also discussed heavy metals chemistry toxicity, exposure assessment, possible mechanisms for its metabolic pathways so as to understand the origin of metal causing diseases and susceptibility to human carcinogenesis based on USEPA (1997, 2006). The chapter further reviewed current pollution and ecological risk indices as well as Human health risk indices that were used in the quantification of pollution and risks examined in this study. The chapter finally examined the geochemical baseline estimation methods of which the integrated mrthod was chosen as the best method for the calculation.

CHAPTER THREE

METHODOLOGY

Introduction

Effective methods for analyzing and quantifying heavy metals in Ghanaian soils, sediments and water from the four major mining areas and some pristine environments and the eventual setting of a geochemical baseline values for quality guidelines in these environmental receptors is the primary focus of this study. Mining and industrial processing are among the main sources of heavy metal contamination in the environment (Jian-Min, Zhi, Mei-Fang, & Cong-Qiang, 2007). As a result of mining and other industrial processes, soils and water bodies are inundated daily with anthropogenic pollutants from industrial, domestic and agricultural chemicals which are ultimately absorbed by aquatic plants and animals. Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage posing threat to human health and sustainable food supply due to bio-magnifications over a period of time.

There is therefore a need to continually assess and monitor the levels of heavy metals in the environment due to anthropogenic activities, including mining, for evaluation of human exposure and for sustainable environment (Koranteng – Addo *et al.*, 2010). This chapter therefore, describes the fieldworks, procedures for sample collection, sample preparation, sample treatment and analysis carried out to evaluate the levels and distribution of heavy metals in soils, sediments and waters in the four major mining areas and some pristine environments. The chapter will also examine the protocols for the estimation of human health risk, single and multiple-element pollution indices and potential ecological risk for heavy metals in soils, sediments and water.

Study Area Description

The study area covered agricultural lands around major mining areas and some River/Stream bodies in major mining areas and some pristine environments in 8 regions of Ghana (Figure 4) with the land area covering between 138 and 2,950km^2 (Table 11). The rivers sampled are; Oda river, Nyam river, Bosomkese forest river, Subri river, Ankasa river, Bonsa river Atewa forest river and Birim river, Kalakpa river, Kakum river and Mole river.

Ghana is underlain partly by what is known as the Basement Complex. The geology of the mining areas is mainly composed of a wide variety of Precambrian igneous and metamorphic rock which mainly covers about 54% of the southern and the Western part of the country. It consists mainly of gneiss, phyllites, schists, magmatites, granite-gneiss and quartites. Other mining areas in the other parts of the country are underlain by Palaeozoic consolidated sedimentary rocks referred to as the Voltarian Formation consisting of sandstones, shale, mudstone, sandy and pebbly beds and limestones (Gyau-Boakye & Dapaah-Siakwan, 1999). A Global Positioning System (GPS) device was used to map out the sampling sites.

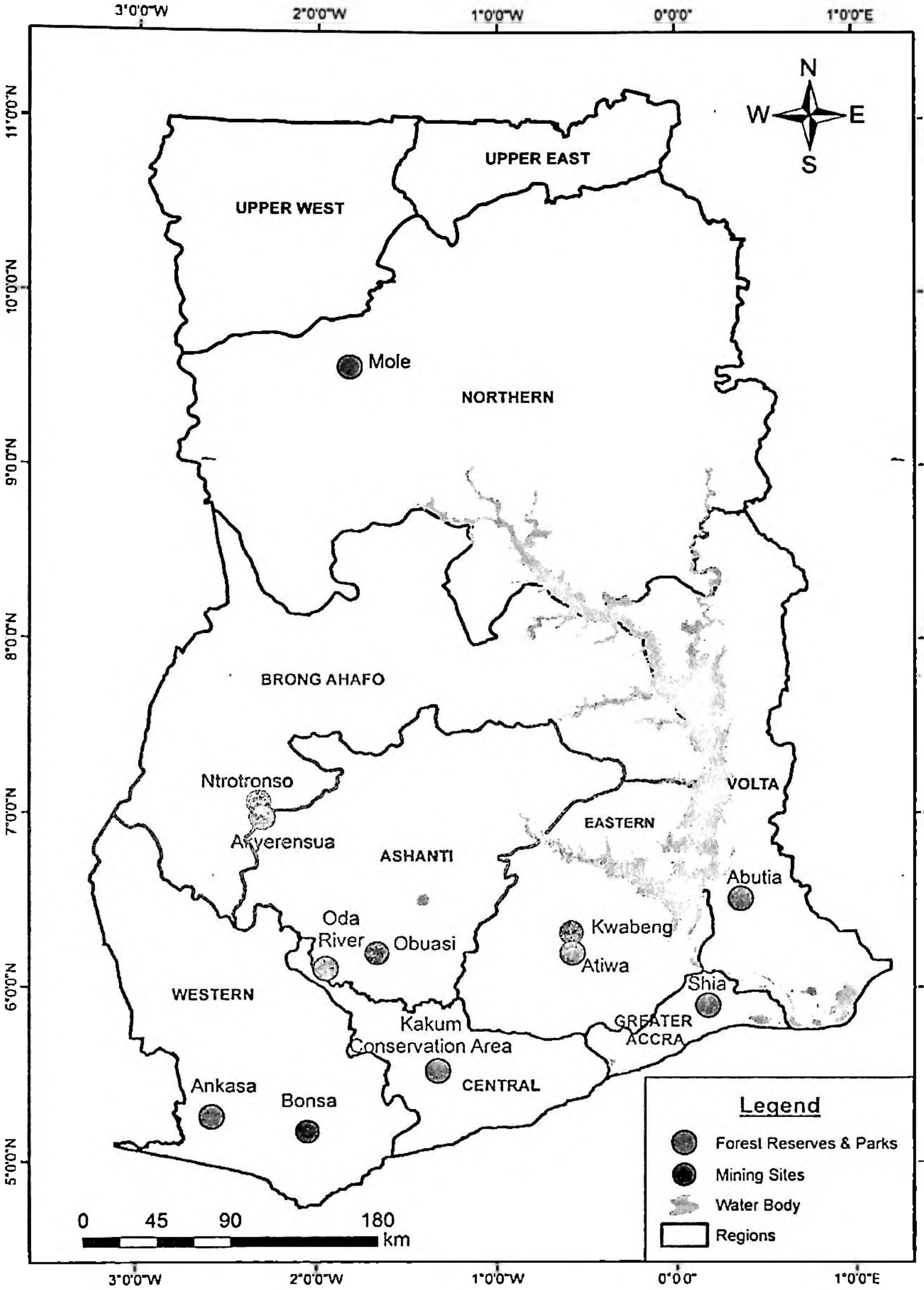


Figure 4: Map of Ghana, Indicating the Sampling Towns around the Pristine and Mining Areas.

Physiography and Selection of the Study Area

The selection of the study areas was based on the fact that there is a commercial gold mining within the selected mining areas and that there is a pristine environment (forest reserves) close to the same area. The study was conducted in Eight (8) forest reserves (pristine environment) and four mining areas (assumed polluted environment) in Eight (8) regions of Ghana namely; Oda River Forest Reserve and AngloGold Ashanti mining area around Obuasi Municipality of Ashanti region. Bosomkese Forest Conservation and Newmont mining area around Kenyase in the Asutifi district of Brong Ahafo region, Ankasa Forest Conservation and Goldfields mining area of Tarkwa Municipal area in the Western region and Atewa Range and Kwabeng mines of Atewa district in the Eastern region of Ghana. The coordinates of the sampling areas are shown in Table 11.

Oda river is located in the south-western part of the Ashanti Region. It shares boundaries with Bosomtwe District in the north, Adansi; North in the south, Bosome-Freho District to the East and Amansie-Central and Amansie; west to the west. Bosomkese forest reserve is located about 28 km East of Sunyani, Ghana and covers a total area of 138 km^2. It is located within the semi-deciduous South East forest zone (Swanes, 1996) and has a mean annual precipitation of between 900 mm to 1500 mm. Atewa is one of Ghana's two upland evergreen forest reserves and thus assumes a great role on the landscape as repository of biodiversity, forests and wildlife. The Range measures about 23,663 ha and is part of an ecosystem known as the Upper Guinea Forest. Atewa has long been recognized as a nationally important reserve because its mountains contain the headwaters of three river systems, the Ayensu, Densu and Birim river. The Ankasa Conservation Area lies in Southwest Ghana on the border with the Ivory Coast. Covering 509 km^2, this protected area falls within an ancient rainforest and is the most biodiverse in Ghana. Its maximum elevation is 150 m at Brasso Hill in the National Park, though most lies below 90 m. The climate of the Conservation Area is characterized by a distinctive bi-modal rainfall pattern with an average annual rainfall is 1,700 to 2,000 mm.

Table 11: Description of Sample Location and Area Coordinates

Site	**Region**	**Location**	**Area**	**Latitude**	**Longitude**
Oda River	Ashanti	Bekwai*	633 km^2	6° 51'N 6° 30'N	1°00 W and 1° 35W
Nyam River	Ashanti	Obuasi	162.4 km^2	5.35N and 5.65N	6.35N and 6.90N
Bosomkese	Brong Ahafo	Bosomkese*	138 km^2	6^0 N -70 N 45'N	10 30 W-30¯ 10'W
Subri River	Brong Ahafo	Kenyasi (Ntrotroso)	307 km^2	2°46'38.33"W	6°46'22.31"N
River Bonsa	Western	Tarkwa	2354 km^2	400'N and 500 40'N	1045'W 20 10'W
Ankasa Conservation	Western	Ankasa (Elubo)*	509 km^2	N 5° 16' 35.69"	W 2° 34' 59.81"
Atewa Range	Eastern	Atewa*	2,950 km^2	O° 3' W and O° 50	6° 10' N and 6° 30'
Birim River	Eastern	Kwabeng	3875 km^2	O° 20'W, 1° 15'W	5° 45'N, 6°35'N
Mole Park	Northern	Damango*	4,577 km^2	9° 11' and 10° 10' N	1° 22' and 2° 13' W
Kakum Conservation	Central	Kakum*	375 km^2	5°25'N 1°19'W	5.417°N 1.317°W
ShaiHills Resource reserve	Greater Accra	Doyumu (Tema)*	51 km^2	O° 01'E, 5° 56' N	O° 06'E, 5° 56'N
Kalakpa Resource reserve	Volta Region	Abutia*	325 km^2	6° 28' 49.12" N	0° 28' 35.57" E

Asterisk represent the pristine area (forest reserves and wildlife conservations)

Sampling Plan

Information supporting the sampling plan was collected during August through September, 2014. The information was collected at the Department of Geography, University of Cape Coast, Council for Scientific and Industrial Research (CSIR) and Ghana Forestry Commission (Wildlife Division). Research Articles and other materials on similar sampling sites were reviewed to have insight into the dynamics of heavy metals contamination and the physico-chemical parameters influencing metal availability of the areas. Review was also done so as not to conflict this study with previous studies in the area by Nkoom *et al.*, (2013), Bhattacharya *et al.*, (2012) and Kortatsi, (2004). More information concerning water sources close to major mining areas, in different communities and soil contamination data were collected. During the field study the sampling plan was revised according to local conditions and situation.

Field Methods

The fieldwork was conducted during October/November, 2014 (wet season) and January/February, 2016 (dry season). Soils, sediments and water samples were collected in the study districts with the help of the District Assemblies. The district offices of the Forestry Commission (Wildlife Division) supported us with forest guards who escorted us throughout the sample collection. This enabled us to visit remote parts of the forests and expand the scope of our sampling. Our sampling locations are marked on the location map (Figure 4).

Siol and Sediment Sample Collection

The sampling sites in the mining areas were selected based on their proximity to a gold mine and human settlement. Sample collection was undertaken in January 2016 with an auger in the dry season. A total of 96 composite soil samples at depths of between 0-20cm and 20-40cm were collected from both mining and pristine sites. Samples from Obuasi (AOB), Tarkwa (WTB) and Kenyasi (BAM) were collected close to major commercial gold mining sites while the Kwabeng (EAM) samples were collected close to a small scale mining site. Additionally, soil samples were taken from eight (8) forest reserves/conservations as: Shai Hills (GSH), Kalakpa (VKPA), Mole (NM), Kakum (CK), Oda River (ODA), Ankasa (ANK), Bosomkese (BB) and Atiwa (EA) as pristine, which are supposedly free from human activities and agrochemical inputs.

Each chosen site was sampled by dividing the locations into grids using handmade poles on one side and well positioned trees perpendicular to the poles on the other side. Labels of S1, S2, S3, S4 etc. were used to identify the quadrants formed (Carter, 1993). Soil samples were taken at depths of 0-20 and 20-40cm at 5 randomly selected quadrants. Ten (10) soil samples from each of the 5 randomly selected quadrants at the respective depths were taken with a pre-calibrated 1-metre auger. The soil samples from each of the corresponding same depths of the five quadrants were composited into one sample to represent the sampling point. In all, eight (8) composite samples with their respective depths were collected per sampling site.

For the sediment, each of the rivers was sampled 100m apart from downstream to upstream. At each point, five (5) discrete sediment samples were collected using augur and composited into a single sample. Samples were put in a well labeled polypropylene zip-loc bags and transported to the Chemistry Department of University of Cape Coast laboratory where the samples were further processed before eventually being sent to the Central Analytical Research Facility (CARF) laboratory of Queensland University of Technology for sample preparation and analysis.

Soil and Sediment Sample Preparation

The soils and sediment samples were air-dried at room temperature for a month (4 weeks). Wearing polyethylene gloves, organic debris and other unwanted large particles were hand-picked from each sample. The dried sub samples were then disaggregated using porcelain mortar and pestle (Figure 5), and were sieved through a 2 mm sieve to remove larger pieces of debris, such as pieces of shell and rocks before being sieved to 90 µm to remove smaller pieces of shell debris and sandy material (see Figure 6).

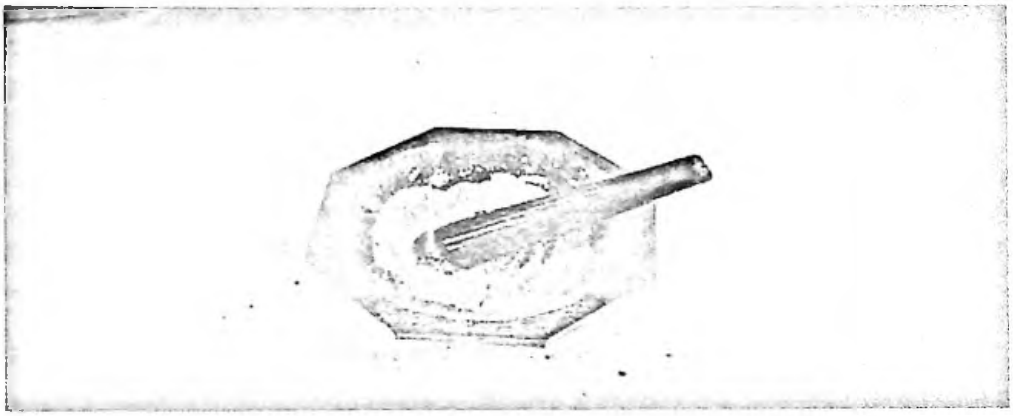


Figure 5: Grinding of Soil and Sediment Samples in Porcelain Motor.

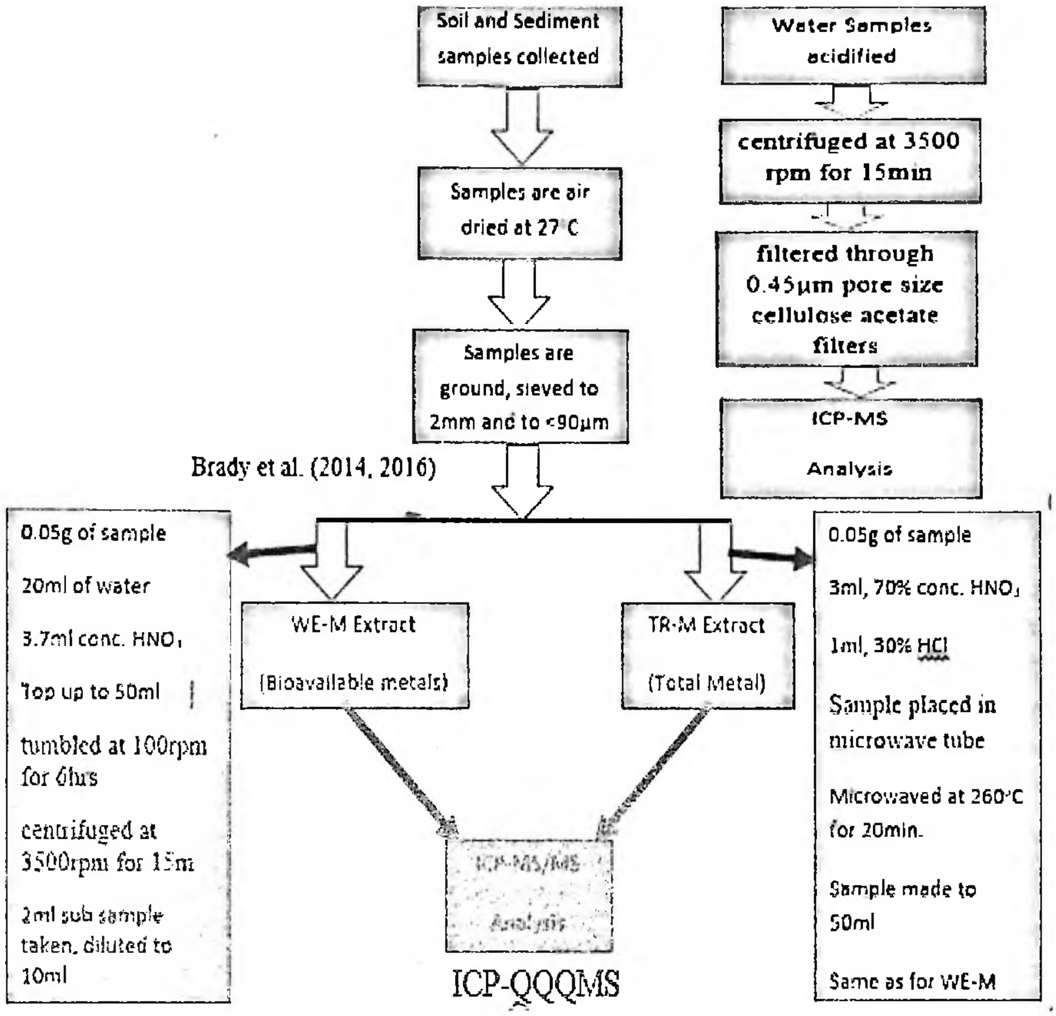


Figure 6: Schematic Diagram Showing how Samples were Treated and Tnalysed.

Water Sample collection and Treatment

The rivers in the mining areas were selected based on their proximity to a gold mine and human settlement. Sample collection was undertaken in October/November, 2014 (wet season) and January/February, 2016 (the dry season). A total of 44 composite water samples were collected from the rivers in the mining and the pristine areas.

At each sampling site, 8 discrete water samples were collected and composited to give a representative sample at that point of the river. The samples were collected 100m apart at 4 different points from downstream to upstream of the rivers. The samples were collected in 1.5 L plastic bottles prewashed with detergent and 1:1 concentrated nitric acid/distilled water solution and eventually rinsed with only distilled water. Those samples meant for metal analysis were acidified to pH 2 with concentrated nitric acid before being transported to the laboratory. The samples were stored in a refrigerator at 4 °C upon arrival in the Chemistry Department, University of Cape Coast laboratory for further analysis (Clescerl, Greenberg, & Eaton, 1999; Naveedullah *et al.*, 2014).

Centrifuge tubes and Glassware Cleaning Process

All glassware containers used in the analytical determinations were immersed in a warm liquid soap bath for two days. They were then rinsed with Ultra-Pure Water (18 MΩ resistivity) and left immersed in 5% HNO_3 at room temperature for three days. The flasks were again rinsed three times with Ultra-Pure Water and afterwards immersed 5% HNO_3 bath at 90 °C for 24 h. They were further rinsed with Ultra-Pure Water several times and placed overnight in a clean oven at 60 °C, then removed from the oven and allowed to cool down. The centrifuge tubes were first rinsed three times in Ultra-Pure Water, and then immersed in 5% once distilled HNO_3 and left on a hot plate at 120 °C for two days. The tubes were rinsed three times again with Ultra-Pure Water, and then immersed in 3% HCl and left on a hot plate at 120 °C for another two days (Figure 7). After this, the tubes were again rinsed three times again with Ultra-Pure Water and dried in a laminar flow fume cupboard.

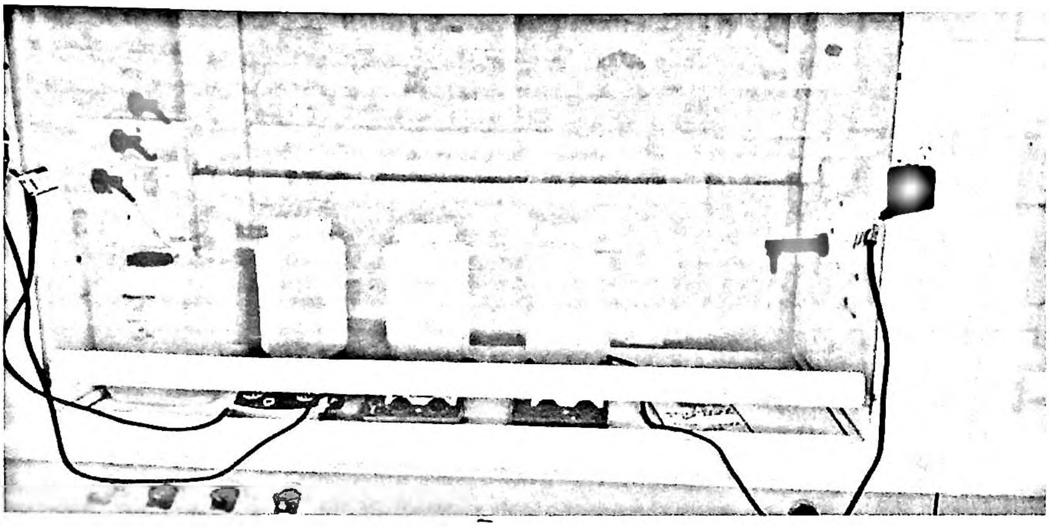


Figure 7: Centrifuge Tubes on Hot Plates at 120 ^{O}C.

Measurement of Soil and Sediment Particle Size

50g oven dried fine earth fraction of the soil and sediment sample, which has passed through a 2mm sieve was weighed into a 250 mL beaker. 100 mL of 5% calgon (sodium hexametaphosphate) solution was added followed by 100 mL of distilled water. The content of the beaker was mixed with stirring rod and was left to settle for 30 min. The content was then shaken with a mechanical shaker for 12 h (overnight) after which it was transferred into a 1.0 L measuring cylinder and topped up to the mark with distilled water. The hydrometer was removed and the top of the cylinder was covered with the hand and shaken end over end several times until all soils and sediments were in suspension. The hydrometer was lowered slowly into suspension until it started floating. The first reading on the hydrometer was taken after 40 sec after the cylinder is set down and this measures the percentage of silt and clay in the suspension.

The second reading was taken after 3 h and this measures the percentage of clay in the suspension. The hydrometer was removed and the temperatures of the suspensions, t1 and t2, were respectively recorded during the 40 sec and 4 h hydrometer readings. The content of the cylinder after the 3 hours was emptied onto a 47-µm sieve. The sand retained on the sieve was then put into a 100 mL beaker, washed and dried at 105 °C for 24 h, after which the dry weight of the sand was recorded (FAO, 1974; Day, 1965, Bouyoucos, 1951). A blank sample hydrometer reading at 40 sec and 4 h were also taken for the 5% calgon solution topped up to 1.0 L. The particle size distribution was then determined using the relations below;

Temperature of the suspensions at t1 and t2 = 29 °C

$$\%\text{Clay and Silt} = \frac{40\ seconds\ reading - correction\ for\ temperature}{oven\ dry\ mass\ of\ soil\ or\ sediment\ sample} \times 100\% \quad (14)$$

$$\%\text{Clay} = \frac{3hour\ reading - correction\ for\ temperature}{oven\ dry\ mass\ of\ soil\ or\ sediment\ sample} \times 100\% \quad (15)$$

$$\%\text{Silt} = \%(Clay\ and\ Silt) - \%\ Clay \quad (16)$$

$$\%\text{Sand} = \frac{oven\ dry\ weight\ of\ particles\ retained\ on\ the\ 47\mu m\ sieve}{oven\ dry\ mass\ of\ soil\ or\ sediment\ sample} \times 100\% \quad (17)$$

Temperature effect on density of the soil particles was accounted for using the relation provided by Day (1965): for every 1 °C increase in temperature, above 19.5 °C, there is an increase of 0.3 in the density of the particles in suspension.

Hence, increase in weight = (t2 – t1) × 0.3 = (29 – 29) × 0.3 = 0

Correction for temperature = blank hydrometer reading – increase in weight of particles

= blank hydrometer reading – 0

Hence, Correction for temperature = blank hydrometer reading

For each soil and sediment sample, the percentages of sand, silt and clay were used to assign a textural class using the United States Department of Agriculture textural triangle. Average proportions of the soil types in each soil core were determined and the corresponding average textural class was determined.

pH and EC Determination of Soil, Dater and Dediment Samples

The pH of the fine earth fraction (< 2mm) of each air-dried soil sample was determined in distilled water (1:1 soil to water ratio (w/v)), (McLean, 1982) by the use of a pre-calibrated JENWAY 3310 and JENWAY 3510 pH meter. 20 g of each air-dried soil and sediment sample was weighed into a 50 ml beaker and 20 ml of distilled water added to it. This was allowed to stand for 30 minutes and stirred occasionally with a glass rod. The pH meter was calibrated with pH 3.0, 7.0 and 10.0 buffer standards before use. The pH was then read by inserting the electrodes of the pH meter into the partly settled suspension. The pH in 1.0 M KCl solution of the soil samples was similarly determined using a 1:1 soil to water ratio (ISO 10390, 1994).

The electrical conductivity (EC) of the water and the suspended soil and sediment samples was similarly measured by inserting directly the electrodes of the JENWAY meter into the water and the soil and sediment suspension.

Soil and Sediment Organic Carbon Determination

Total organic carbon content of soil and sediment was measured using the method proposed by Walkley and Black (1934). An amount of 0.5 g of air dried soil and sediment sample were weighed into a 500 mL Erlenmeyer flasks and 10ml of 1 N potassium dichromate was added followed by 20 mL of concentrated sulfuric acid (H_2SO_4). The content of the flask was initially swirled gently to disperse the soil and later swirled more vigorously for 1 min and allowed to stand for 30 min on a white tile. The unreduced $K_2Cr_2O_7$ remaining in solution after the oxidation of the oxidizable organic material in the soil and sediment sample was titrated with 0.5 N ferrous ammonium sulphate solution after adding 10 mL of 85 % orthophosphoric acid and 1 mL of barium diphenylamine sulphonate indicator from a dirty brown colour to a bright green end point. A standardization titration of $K_2Cr_2O_7$ with ferrous ammonium sulphate was done and the amount of oxidizable organic carbon calculated by subtracting the moles of unreduced $K_2Cr_2O_7$ from that of $K_2Cr_2O_7$ present in the standardized titration.

The amount (in moles) of oxidizable organic carbon was converted to mass (in grams) by multiplying it by 12 (molar mass of C). Then, the mass was expressed as a percentage of 0.5 g (mass of soil used) to obtain percentage oxidizable organic carbon [hus, $\%OC = n[OC] \times M[C] \times 100\% m[C]$] where OC = oxidised organic carbon. This was finally converted to percentage total organic carbon by multiplying by a constant factor (1.33) on the assumption that only 75 % of total organic carbon is oxidizable (FAO, 1974).

The percent organic matter (%OM) content was obtained by assuming that only 58% of the organic matter contains carbon which implies; $\%OM = 1/0.58 \times \%OC$.

Determination of Cation Exchange Capacity

5 g of well ground fraction of the dried soil and sediment sample was weighed into a 100 mL beaker and 30 mL of 1.0 M ammonium acetate at pH 7.0 added.

The content was transferred into a 50 mL centrifuge tube and tumbled for 1 h. The suspension was centrifuged and the clear supernatant solution decanted into a 100 mL volumetric flask. After decanting the clear supernatant solution, another 30ml of 1.0 M ammonium acetate at pH 7.0 was added to the same content, tumbled for another 1 h and centrifuged. The decanted solution was combined with the first one and kept for the determination of exchangeable bases.

The soil mass was then leached with methanol to wash off the non-adsorbed NH_4^+. The NH_4^+ saturated soil was further leached with four 30 mL portions of acidified 1.0 M KCl. The ammonium ion concentration (mol/L) in the KCl filtrate was determined by titrating the solution with 0.01 M HCl and the CEC (cmol/kg) of the soil estimated for the results (Horneck, Hart, Topperand, & Koespell, 1989; Schollenberger & Simon, 1945). Two blank tests were also carried out for quality control purposes, in which the same procedure was followed without the soil/sediment to ensure accuracy and to detect any contamination during the analytical procedure. The Cation Exchange Capacity is calculated by summing up all the exchangeable bases (K^+, Na^+, Ca^{2+}, Mg^{2+}).

For the exchangeable bases, Na and K concentrations (cmol/kg) were read on Flame Photometer, and Ca and Mg concentrations (mg/Kg) were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP/OES). The values were then converted into cmol/kg as follows (Summer & Miller, 1996);

Exchangeable base (cmol/kg) = Extractable base (mg/Kg)/miliequivalent weights as follows;

Exchangeable Ca (cmol/Kg) = Extractable Ca (mg/Kg)/200

Exchangeable Mg (cmol/Kg) = Extractable Mg (mg/Kg)/120

Digestion and Analysis of Water samples

Water samples were directly subjected to analysis after acidifying with 1ml HNO_3 (70%), centrifuged at 3500 rpm for 15 min and finally filtered through 0.45 µm pore size cellulose acetate filters. All samples were analyzed using Agilent 8800 Triple Quadrupole Inductively Coupled Plasma Emission Spectrometer (ICP-QQQMS) in the Central Analytical Research Facility (CARF) laboratory of Queensland University of Technology, Australia for heavy metals; lead Pb, Zn, Cd, Mn, Fe, Cu, Hg, Co, Cr, Al and As. To ensure reliability of the analytical method, quality control (QC) and blank samples were acid digested and subsequently analyzed for appropriate metals through the same procedure. The analytes were acquired using He mode. Arsenic was acquired in MS/MS mass-shift mode using O_2 reaction gas.

Physico-chemical Analysis of Water

The physico-chemical measurements were conducted using The American Public Health Association (APHA, 2005 method for preparation and analysis of water samples. The pH was determined alongside the temperature using a pre-calibrated JENWAY 3310 and JENWAY 3510 pH meter. Conductivity was measured using a pre-calibrated PHYWE 13701.93 and WAGTECH 4510 conductivity meter. The turbidity was measured with JENWAYturbidimeter.

Digestion and Analysis of Soil and Sediment Samples

Weak Acid Extractable Metals

Weak acid extractable metals were obtained by following the method outlined by Brady, Ayoko, Martens and Goonetilleke (2014). A 0.05 g of soil and sediment sample was placed into a pre-weighed clean and dry 50 mL centrifuge tube. Approximately 20 mL of UPW (18 MΩ resistivity) was added before a 3.7 mL aliquot of double distilled, concentrated nitric acid was added and diluted to 50 mL with UPW, sealed and reweighed to determine the dilution factor. The samples were then placed in an end-over-end tumbler and tumbled at 100 rpm for six hours. The samples were finally centrifuged at 1900 g for 10 min before a 2 mL sub sample was taken, diluted to 10 mL and analyzed in ICP-MS using an Agilent 8800 ICP-Triplequad MS (ICP-QQQ) for Pb, Zn, Cd, Mn, Fe, Cu, Hg, Co, Cr, Al and As.

Total Recoverable Metal Analysis (aqua regia digestion)

Similarly, the method by Brady *et al.* (2014, 2016) was used to obtain the total recoverable metals. A 0.05 g of sample was weighed into a pre-cleaned Teflon microwave tube, and 3 mL double distilled, 70 % concentrated nitric acids, as well as 1 mL double distilled concentrated hydrochloric acid were added. The ratio of acids was selected carefully in order to minimize the formation of insoluble chlorides of Pb and Hg. Each time, six samples were placed in the microwave tube, together with a blank. The samples were then microwaved using a milestone ultrawave with a ramp up to 260 °C over 20 min, followed by a 40 min hold at 260 °C to complete extraction. Samples were quantitatively transferred into a cleaned pre-weighed 50 mL falcon tube and diluted to 50 mL with UPW (18 MΩ resistivity), and reweighed to establish the sample dilution factor. The samples were then centrifuged at 1900 g for 10 min before a 2 mL subsample was taken and diluted to 10mL for analysis in ICP-MS/MS using an Agilent 8800 ICP-Triplequad MS (ICP-QQQ).

Physico-chemical measurements were conducted with the pH determined using a pre-calibrated JENWAY 3310 and JENWAY 3510 pH meter. Conductivity was measured using a pre-calibrated PHYWE 13701.93 and WAGTECH 4510 conductivity meter.

Reagents

Analytical reagent–grade acids: HNO_3 (70 %) and HCl (33 %) were distilled twice in Analab Sub-Boiling Distillation System at 70 °C. Ultra-pure water with a resistivity of 18.0 $M\Omega cm^{-1}$, was obtained from a MilliQ Water purification system (Millipore, Billerica, MA, USA). Calibration Solution was prepared from Choice Analytical ICV-1 Solution A Standard. Agilent Technologies Multi Element Standard 2A was analysed as unknown to control the accuracy of analysis.

Quality Control (QC)

Strict quality assurance and quality control measures were adopted to ensure reliability of the results. All reagents and chemicals used were of high purity. Twice distilled analytical reagent–grade acid HNO_3 (70 %) was used. Ultra-pure water (resistivity of 18.0 $M\Omega cm^{-1}$ was obtained from a MilliQ Water purification system (Millipore, Billerica, MA, USA). Besides, samples were analyzed in triplicates and after every 5 samples, a calibration standard was analyzed to check the response and efficiency of the analytical instrument alongside the blank, which was used to constantly check for contamination.

Centrifuge tubes were soaked in 3% analytical grade HCl for two days and then 5% once distilled HNO_3 for two days, rinsed three times in UPW and dried in a laminar flow fume cupboard.

To ensure reliability of the analytical method, quality control (QC) and blank samples were acid digested and subsequently analyzed for appropriate metals through the same procedure. Most of the analytes were acquired using He mode with the exception of elements that do not suffer from polyatomic interferences in any common matrices (e.g. ^{65}Cu: ^{32}S $^{16}O_2$ $^{1}H^+$, ^{40}Ar, $^{25}Mg^+$, ^{40}Ca, $^{16}O^{1}H^+$, ^{36}Ar, $^{14}N_2$ $^{1}H^+$). The LOD and LOQ were calculated by employing the method prescribed by Skoog, Holler, & Crouch (2007). To calculate the LOD, the standard deviation of the blank values was multiplied by three and dividing the value by the slope of the calibration curve. Similarly, the LOQ was calculated by multiplying the standard deviation by ten and then dividing this value by the slope of the calibration curve. The precision was calculated as a percentage relative standard deviation (%RSD) of seven replicate samples of the prepared standard, and was found to be less than 20% except Fe. The limit of detection (LOD) for each element was calculated using Equation 18 and 19.

$$\text{LOD} = \frac{3 \times SD}{m} \tag{18}$$

$$\text{LOQ} = \frac{10 \times SD}{m} \tag{19}$$

Where, SD is the standard deviation of the blank readings and m represents the gradient of the calibration curve for each element.

Recovery and Reproducibility

Reagents and Standards

Stream sediment reference material, STSD-1 (National Research Council of Canada, Ottawa, Canada) was used for the optimization and evaluation of the analytical performance of the digestion method. A Calibration Solution prepared from Choice Analytical ICV-1 Solution and a Standard Agilent Technologies Multi Element Reference Standard 2A, was analyzed as unknown to check the accuracy of analysis. Drift corrections were carried out using Rh In and Re as internal standards. Ultrapure water (UPW) (with resistivity of 18.0 MΩcm-1 (Merck Millipore, Australia) were used for cleaning and digestion. STSD-1 was used to evaluate the performance of the digestion method.

Reference Sample Preparation for ICP-MS Analysis

In order to validate the method for the determination of the heavy metals concentration a Stream Sediment Reference Material, STSD-1 was used. For the digestion of this reference material, 3 drops of Milli Q Water were first added to a 15 mL PTFE vials to reduce electrostatic effect. 0.05 g of the reference materials was weighed into a pre-cleaned Teflon microwave tube, and 3 mL double distilled, 70% concentrated nitric acids and 1ml double distilled concentrated hydrochloric acid were added (3 mL HNO_3 70% and 1 mL HCl 33%). The sample vials were closed by putting on covers. The vials were then placed in a sample holder and were put in an ultrasonic bath for a few minutes to complete sample homogenization. Six such Teflon tubes were inserted in the UntraWAVE device and the whole system was set in an oven at 260 °C over 20 min, followed by a 40 min hold at 260 °C for the extraction to be completed. A colorless solution resulted and ultra-pure water was added up to 50 mL. The sample was transferred to a centrifuge tube and centrifuged at 1900 g for 15 min. Aliquots of the sample was taken and analysed. Calibration standard solutions and internal standards were prepared by successive dilution of a high purity ICP-multielement calibration standard. Ultra-pure de-ionized water ($18\ M\Omega cm^{-1}$) from a Milli-Q analytical reagent grade water purification system (Millipore) and ultra-pure HNO_3 70 % were used.

ICP-MS Analysis

The heavy metals analysis was conducted by using inductively coupled plasma quadrupole mass spectrometer (ICP-QQQMS). Samples were analysed by using calibration solution prepared from Choice Analytical ICV-1 Solution and a Standard Agilent Technologies Multi Element Reference Standard W-2a (dolerite). The calibration solution prepared from Choice Analytical ICV-1 Solution and a Standard Agilent Technologies Multi Element Reference Standard 2A was used as internal standards for instrument drift correction. Natural sediment STSD^{-1} was analysed as unknowns to assess the accuracy of the measurement. Elements that suffer from polyatomic interferences (e.g. ^{65}Cu: $^{32}S\ ^{16}O_2\ ^{1}H^+$, ^{40}Ar, $^{25}Mg^+$, ^{40}Ca, $^{16}O^{1}H^+$, ^{36}Ar, $^{14}N_2\ ^{1}H^+$) were acquired in He mode. However, elements that do not suffer from polyatomic interferences in common matrices were acquired with no added reaction gas. The operating conditions for the instrument are: Cell Gas flow rates: 5 mL/min; Carrier Gas Flow: 1.05 l/min; KED Voltage: 5 V; ICP RF Power: 1550 W; Octopole bias (V): -18, Octopole RF (V); 190: Spray Chamber t (C); 2: Sample depth (mm); 8. The percent recovery of the metals was calculated from the Agilent

Technologies Multi Element Reference Standard and STSD-1 reference standards.

Data and Statistical Analysis

Data from the study were analyzed using IBM SPSS Statistics version 22 and the Excel Analysis ToolPak. Relationships among the considered variables were tested using correlation analysis with statistical significance set at $p < 0.05$. Hierarchical Cluster Analysis (HCA), which begins with the most similar pair of objects and forming higher clusters stepwise, was employed to produce a dendrogram that provide a visual summary of the clustering process unsupervised pattern recognition technique. Basic statistics such as mean and standard deviation were computed along with the multivariate statistics. Factor analysis (FA) and principal component analysis (PCA) were computed to identify significant principal components in the data as well as possible loadings. The PCA was carried out by the Promax normalized rotation method for the results (Bartholomew *et al.*, 2008; USEPA, 1989).

PROMETHEE and GAIA

PROMETHEE, a multicriteria outranking method, was employed to rank objects (sites) on the basis of range of variables and GAIA to add descriptive complement to the PROMETHEE outrankings. PROMETHEE and GAIA are multicriteria decision making tools which were used in the ranking of the sites in order of least contaminated site to the most contaminated site. PROMETHEE and GAIA analysis of the contaminant metals of interest (Al, Fe, Cr, V, Co, Ni, Cu, Zn, As, Pb, Hg and Cd) was performed using Decision Lab software (Anonymous, 1999). The programme used a V-shaped preference function which is available in the Decision Lab Software for the

PROMETHEE analysis, with the maximum concentration of each contaminant heavy metal used as a threshold and a complete ranking of the sites was determined from the most preferred to the least preferred or in other words, least pollute and most polluted. GAIA was used for the display of the PROMETHEE analysis results in the form of a PCA biplot.

Assessment of Heavy Metal Contamination

To evaluate the degree of contamination in the surface soils and sediments of pristine and mining sites in the study areas, the Enrichment Factor, modified degree of contamination, the modified pollution index by Brady *et al.*, (2015) and Index of geo-accumulation (Igeo) were employed.

Contamination Factor

The levels of contamination of soils and sediments by heavy metals were estimated using contamination factor as expressed in Equation 20.

$$CF = Cns/Cnb \qquad (20)$$

Where Cns is the concentration of the heavy metal in soil/sediment sample, Cnb is the background heavy metal concentration which is defined by Bettinentti, Giarei and Provini (2003), and Wedepohl (1995). The following terminologies were used to describe the contamination factors: $CF < 1$, low contamination factor $1 < CF < 3$, moderate contamination factor; $3 < CF < 6$, considerable contamination factor; $CF > 6$, very high contamination factor. In this study, the Average Shale Values proposed by Wedepohl, for Pb, Zn, Cu, Cd, Ni, As, Cr, Mn, Co and Hg were used as the geochemical background values for the metals as 17, 52, 14.3, 0.1, 18.6, 2, 35, 527, 11.6 and 0.056 respectively (Wedepohl, 1995)

Enrichment Factors

The assessment of the metal and the level of contamination in soils require pre-anthropogenic knowledge of metal concentrations to act as pristine values. The enrichment factor (EF) is the ratio between the element concentration and the conservative element concentration in the sample and the element concentration and the conservative element concentration in the background reference values. The Enrichment Factor (EF) of metals is a useful indicator reflecting the status and degree of environmental contamination (Feng, Han, Zhang, & Yu, 2004). The enrichment factor close to unity (EF = 1) indicates, that the element considered did originate from the soil. The EF were determined for all elements normalized against iron (Fe) concentration, with enrichment factors greater than one (1) is considered anthropogenic (metal addition) and requiring further investigation (Equation 21) (Álvarez-Vázquez, Bendicho, & Prego, 2013).

$$EF = \frac{\left(\frac{Cn}{\mathrm{Fe}}\right) \quad sample}{(\frac{Cn}{Fe}) background} \qquad (21)$$

Where (Cn/Fe) sample, is the empirical content of metals in the sample, function of its Fe content and (Me/Fe) background is the natural background value of metal to Fe ratio. In this study, the Average Composition of Shales Values proposed by Wedepohl (1995), (Pb = 17, Cd = 0.1, Zn = 52, Cu = 14.3, Ni = 18.6, Co = 11.6, Fe = 30890, Mn = 527, Cr = 35, As = 2) were employed as the background value for the calculation of EF. Iron was selected for normalization study because it has a relatively high natural concentration (Abrahim & Parker, 2008), and therefore not expected to be substantially enriched from anthropogenic sources. Chen, Kao, Chen, and Dong (2007) suggested the description of EF values as follow; EF < 2 indicates no enrichment, EF = 2 to 3 is minor enrichment, EF = 3 to 5 is moderate enrichment, EF = 5 to 10 is moderately severe enrichment, EF = 10 to 25 is severe enrichment, EF = 25 to 50 is very severe enrichment and EF > 50 is extremely severe enrichment (Mmolawa, Likuku, & Gaboutloeloe, 2011; Pekey, 2006).

Index of Geo-accumulation

The geo-accumulation index (Igeo) enables the assessment of environmental contamination and was proposed by Müller, (Müller, 1969). The method can be used to assess contamination status of soils though it was initially designed for river bottom sediments (Loska, Wiechuła, & Korus, 2004). In this study, the Igeo was employed to examine soils contamination from mining and pristine sites using the Equation 22.

$$Igeo = \log_2\left(\frac{Cn}{1.5B_n}\right) \tag{22}$$

where Cn is the measured concentration of heavy metal found in the soil (mg/kg), and Bn is the geochemical background value of the heavy metals found in Average Composition of Shales proposed by Wedepohl, (1995). The constant 1.5 is used due to potential variations in the baseline data (Loska *et al.*, 2004; Solgi, Esmaili-Sari, Riyahi-Bakhtiari, & Hadipour, 2012). The geo-accumulation index consists of 7 classes or grades whereby the highest class 6 reflects a 100-fold enrichment above the background values (Forstner, Ahlf, Calmano, & Kersten, 1990) and is described as follows; Igeo ≤ 0, Practically uncontaminated; 0 < Igeo < 1, Uncontaminated to moderately contaminated; 1 < Igeo < 2, Moderately contaminated; 2 < Igeo < 3, Moderately to heavily contaminated; 3 < Igeo < 4, Heavily contaminated; 4 < Igeo < 5, Heavily to extremely contaminated; 5 > Igeo, Extremely contaminated.

Modified Pollution Index

The modified degree of contamination (mCd) (Equation 4)) and pollution index (PI) by Hakanson (1980) and Nemerow (1991), are the two most common and widely used pollution indices in recent years. The mCd uses contamination factors for individual sites, and taking their average, it is possible to assess the quality of sediments based on a set of elements (Abrahim & Parker, 2008, Brady *et al.*, 2015). However, the mCd has certain limitations like other single element pollution indices (such as the incorporation of background concentrations and the complex, non-conservative behaviour of sediments) which was not taken into account in the derivation of the mCd. (Equation (11). As a result, a more recently modified pollution index (MPI) (Equation (12) was developed by Brady *et al.* (2015), which is an improvement of the Nemerow pollution index (1991), and uses enrichment factors in place of contamination factors in its pollution index estimation.

Ecological Risk Assessment

Modified Ecological Risk Index

The application of contamination factor in the calculation of ecological risk index (RI) (Equation 13) comes with limitations because it does not take into consideration inputs from lithogenic and sedimentary sources of the element of interest which pose serious concern on the significant sedimentation input from creeks, a common phenomenon especially in the estuarine environments. To effectively estimate the RI which will take into consideration impact from terrestrial and sedimentary inputs, the Modified Ecological Risk Index (MRI) (Equation 14) was developed by Brady *et al.*, (2015) which proposed the use of enrichment factor in place of the contamination factor in the calculation of RI. Furthermore, the development of the MRI using the enrichment factors as a single element index was observed to be the preferred index for assessing contamination at a site from large complex data set. It also accounts for lithogenic sources of heavy metals and changes in the background concentration as well as the non-conservative behaviour of sediments/soils that occur in estuarine and terrestrial environments (Brady *et al.*, 2015). The Equation 13 can now be re-written as Equation 14.

The TR in the equation, is the toxic-response factor for certain metals (Hg = 40, Cd = 30, As = 10, Cu = Pb = 5, Cr = 2 and Zn = 1) (HĀKANSON, 1980). The grading standards of RI are maintained for MRI as shown in Table 9 (Suresh, Sutharsan, Ramasamy, & Venkatachalapathy, 2012; Duodu *et al.*, 2016).

Questionnaire and statistical analyses

A standardized questionnaire was constructed to obtain site-specific parameters for risk assessment calculation. The door-to-door survey method was conducted with open response in selected communities around the mining areas.

Questions on the ingestion rate, age, gender and body weight were asked and the responses documented. The survey included 20 respondents from each mining area selected, resulting in a total of 80 participants (33 males and 47 females). From the survey, the average ingestion rate of water was set at 2.2 L, Average body weight for male and female was set at 65.5 kg for adults and Exposure duration was set at 35.9 years for resident adults. Other parameters for adults and children were taken from other sources (USEPA, 2004; USEPA, 1989; Bartholomew *et al.*, 2008).

With the exception of IR, ED and BW, which were obtained through standardized questionnaire survey and the Ghana Statistical Service (Ghana Statistical Service, 2010), the rest were default values in the Risk Integrated Software for clean-up of hazardous waste sites (RISC 4.02) developed by BP for the Superfund sites (Spence, 2001). The average life expectancy for resident adult in Ghana is 62 years (i.e., 60 years for men and 63 years for women) (Ghana Statistical Service, 2010), however in this study, an average lifetime expectancy of 70 years was used as life expectancy for the residents around the sampling sites so as to be consistent with similar studies carried out in Ghana (Armah & Gyeabour, 2013; Obiri *et al.*, 2016).

The sampling point mapped coordinates were collected and converted into shape-files after which separated maps were created for arsenic, cadmium, lead and zinc concentrations using the ArcGIS 10.1 programme.

Human Health Risk Assessment

The health risk assessment for heavy metals in surface soils from mining and the pristine areas was estimated through ingestion and dermal contact based on the USEPA risk assessment method (USEPA, 2004; USEPA, 1989; Bartholomew *et al.*, 2008; Obiri *et al.*, 2016; Armah *et al.*, 2013). The default values from the Risk Integrated Software for clean-up of hazardous waste sites (RISC 4.02) were used for each toxicant. In the exposure assessment, the average daily dose (ADD) (Equation 23) for the ingestion of heavy metals in soil, sediment and water was calculated using the following equations from USEPA protocol 1989 and 2004.

$$\text{ADDing} = \frac{Cx \times Ir \times Ef \times Ed}{Bwt \times At} \times \text{Cf} \tag{23}$$

Where, Cx is the concentration of toxicant metals in the soil samples (mg/kg), Ir is the ingestion rate per unit time (kg/day), Ed is the exposure duration (years), Ef is the exposure frequency (days/year), Bwt is the body weight of receptor (kg), and At is the average lifetime (years) which is equal to the life expectancy of a resident of Ghana. Cf represents a unit transfer factor, which is $\times 10^{-6}$ for soil/sediment. For the conversion factor from year to days, 365 was used. In addition, ADDing is the quantity of heavy metals ingested per kilogram of body weight.

In this study, surface soil ingestion and dermal contact were considered the main pathways for the metal risk assessment because members of the communities may come into contact with the toxic metals in the surrounding soils through ingestion or dermal contact. Average daily dose for dermal contact of metals in soil, sediments and water was calculated using the Equation 24.

$$\text{ADDderm} = \frac{Cx \times Sa \times Pc \times Af \times Fe \times Ef \times Ed \times Cf}{\text{Bwt} \times \text{At} \times 365} \tag{24}$$

Where, Sa is the total skin surface area (cm^3), Cf is the volumetric conversion factor for water ($1L/1000cm^3$), Af is the soil adherence factor (mg/cm^2), Pc is the chemical-specific dermal permeability constant (cm/h), Ef is the exposure frequency (days/years), Ed is the exposure duration (years), Lt is the human lifetime (defined as 70 years) and Bwt is body weight, Fe Dermal exposure ratio (no unit).

The hazard assessment was performed by comparing the calculated contaminant dose with the reference dose (RfD) to develop the Hazard Quotient (HQ) using Equation 25.

$$\mathrm{HQ} = \frac{ADD}{\mathrm{RfD}} \tag{25}$$

Where HQ represents the hazard quotient via ingestion or dermal contact (no units) and RfD is the oral/dermal reference dose (mg/L/day).

Finally, the carcinogenic risks (CRs) (Equation 26) of the metals were estimated so as to assess the probability of an individual developing a cancer over a lifetime as a result of exposure to a potential carcinogenic metal. The slope factor (SF) is a toxicity value that quantitatively defines the relationship between dose and response. The range for carcinogenic risk acceptable by the USEPA is $1\text{x}10^{-6}$ to $1\text{x}10^{-4}$.

$$\mathrm{CRing} = ADDing \times SFing \tag{26}$$

Where CRing represent carcinogenic risk due to ingestion and SF is the slope factor (mg/kg)/ day. To demonstrate the lifetime carcinogenic risk that the local population experience, the CR values were calculated for As, Cd, Cr, Ni and Pb. In this study, both oral and dermal reference doses (RfDoral/dermal) were employed for the respective toxic metals. The slope factor values for the metals are 1.5 (mg/kg)/day, 6.1×10^{2} (mg/kg)/day, 5.0×10^{2} (mg/kg)/day 1.7 (mg/kg)/dayand 8.5 (mg/kg)/day respectively. And the Dermal Permeability Co-efficient (cm/h) for the elements are; As, Hg, Cr, Cd, Mn, Fe, Cu (1×10^{-3}), Pb (1×10^{-4}) and Co (4×10^{-4}). Exposure parameters used for the health risk assessment of the soils, sediments and water can be referred to in Table 5 in Chapter two. All parameters were calculated by the use of IBM SPSS Statistics 21 version and Excel Analysis ToolPak.

Chapter Summary

Chapter Three examines the methods available for analyzing and quantifying heavy metals in soils, sediments and water. It examines the methods used in setting a geochemical base-line values for quality guidelines. The field work was conducted in Four major mining areas and Eight pristine environments which were carefully selected to give a nationwide representative sample size. The chapter also examines how soils, sediments and water sample were collected from their respective sites. Sample processing, treatment, digestion/extraction and the use of ICP/MS to analyse these samples were also discussed. Some physico-chemical parameters such as soil and sediment particle size analysis, pH, %OC, CEC, EC were also measured. Quality control measures were taken under this Chapter to ensure precision, accuracy and reproducibility of the analysis. Parameters considered are LOD, LOQ, and Recovery studies. The chapter finally examines the current methods for calculating pollution and ecological risk indices. The USEPA method for calculating human health risks was used alongside our own survey results.

CHAPTER FOUR

RESULTS AND DISCUSSION

Introduction

Several parameters have been taken into consideration and evaluated for the validation of the analytical methods for quantitative determination of metals in soils, sediments and water namely: linearity, the minimum detection limit, the minimum limit of quantification, repeatability and accuracy.

The inherent heterogeneity and variable mineral composition which characterize soil/sediment matrixes had led to analytical complexity. This challenge has been recognized by the soil/sediment researchers and consequently, acceptable precision and accuracy for digestion methods have been reported as typically < 20 % (Chen & Ma, 2001; Ene *et al.*, 2010). Also, the behaviour of sediments in the environment is complicated by a number of simultaneous processes that can occur to increase the risk of heavy metal contamination in sediments (Liu *et al.*, 2003).

A safe dissolution method that provides an analytical recovery of at least approximately 90 % of elements is usually required (Voica, Dehelean, Iordache, & Geana, 2012). Various digestion methods are used to determine the concentration of trace elements in solid/sediment matrices (Chen & Ma, 2001).

Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique preferred for trace and ultratrace analysis of elements due to its higher sensitivity, high selectivity and with detection limits much lower than other multi-element techniques (Yang & Low, 2009; Gilon, 2005).

Heavy Metal Levels and Distribution in the Soils, Sediments and Water

The determination of heavy metals such as V, Cr, Mn, Co, Ni, Zn and Pb in soil and sediment is challenging and require the development of various specific methods for a complete multi-element analysis. The degree of contamination of aquatic and terrestrial environments is commonly determined by employing analytical protocols for the elemental analysis of soil and sediments which normally require partial or total breakdown of the sample matrix. Recoveries and precision of the digestion methods vary with many factors, including the mineral composition and origin of the soil and sediment. The following subsections examine the performance of the analytical method and the instrument by assessing the Quality control results.

Quality Control Results

In order to evaluate the overall performance of the analytical method employed in the study such as the digestion procedure, clean-up and the instrumental analysis, the analytical procedure was validated using a Calibration Solution prepared from Choice Analytical ICV-1 Solution and a Standard Agilent Technologies Multi Element Reference Standard 2A. The Standard Agilent Technologies Multi Element Reference Standard 2A was analyzed as unknown to control the accuracy of analysis and to determine the instrumental drift. The calibration solutions were prepared for three sets of elements. The first solution comprised of Al, Fe, Ni, Cu, As and Pb. The second comprised of Cr, Mn, Co, Zn, Cd and V, and the third solution contains only Hg. Using the calibration solutions, calibration curves: $y = ax + b$, were determined, where y is the signal intensity and x is the concentration of the given analyte in the calibration solution. The linearity of the calibration curve (Figure 8) was considered acceptable because the regression coefficient $R^2 > 0.999$ (Voica *et al.*, 2012).

The recovery results obtained from the analysis are shown in Table 13. The means of the measured and the certified values were compared by applying ANOVA single factor test to the data with the confidence interval set at 95 %. The test output indicates that there was no significant difference between the two set of data (*p*-value = 0.905) and hence the measured values were statistically the same as their respective certified values.

The certified soil/sediment reference material (STSD-1) was further used to assess the variation and effectiveness of the extraction method and the result also showed that there was no significant difference between the certified and the measured values (*p*-value = 0.994) as shown in Table 13. The accuracy of the analytical procedure was, therefore, deemed very good for the quantification of all the metals under study.

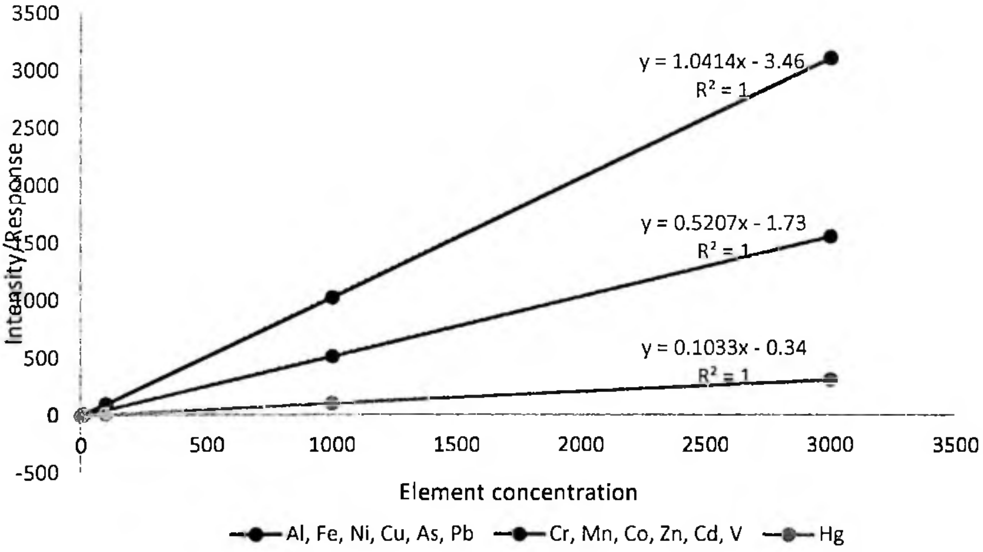


Figure 8: Linear Calibration Curves of Three Sets of Calibration Standard Solutions of Heavy Metals.

Accuracy and Precision/Reproducibility

The limit of quantification (LOQ) and method limit of detection (LOD) (Table 12) for the individual heavy metals ranged from 0.003 to 0.058 µg/g and 0.01 to 0.192 µg/g respectively. The regression coefficient (R^2) of the three set of heavy metals multi-element mix calibration gave a perfect linear curve (i.e., $R^2 = 1$).

Table 12: Limit of Detection and Limit of Quantification for the heavy metals.

Element	SD_{blank}	$3*SD_{blank}$	Gradient	LOD	LOQ
Al	0.020	0.061	1.041	0.058	0.192
Fe	0.019	0.057	1.041	0.055	0.183
Mn	0.001	0.003	0.521	0.006	0.010
As	0.003	0.009	1.041	0.009	0.029
Cd	0.001	0.003	0.521	0.006	0.010
Co	0.001	0.003	0.521	0.006	0.010
Cr	0.001	0.003	0.521	0.006	0.010
Cu	0.001	0.003	1.041	0.003	0.010
Hg	0.001	0.003	0.103	0.029	0.010
Ni	0.001	0.003	1.041	0.003	0.010
Pb	0.001	0.003	1.041	0.003	0.010
Zn	0.001	0.003	0.521	0.006	0.010
V	0.001	0.003	0.521	0.006	0.010

SD = Standard Deviation

The recovery of heavy metals obtained using Agilent mixed reference standard - 2A ranged from 98.4 -103.4 %. Seven replicates were run on both calibration and extraction standards. The relative standard deviation (RSD) for the analyzed metals were found to be below 3 %. The low RSD values indicate that the precision of the calibration method did not vary significantly during the analysis and for that matter showed high analytical efficiency (Table 13).

The accuracy was determined by testing STSD-1 certified reference standard (Table 13). The recovery study showed high recovery values ranging from 92.3 to 100.4 %. The extraction efficiencies of the UltraWave digestion instrument were typically > 92 % for both elements associated with anthropogenic activities (As, Cd, Cu, Hg, Pb, Zn), and lithogenic elements (Al, Cr, Fe, Ni, Co and Mn).

Table 13: Analytical Performance of ICP/MS Instrument and the Extraction method. n=7

	STSD-1 reference standard					Agilent reference standard - 2A	
Element	Certified Value (µg/g)	±SD	Measured Value (µg/g)	±SD	Recovery (%)	RSD	%Recovery
Al	66200	3200	65221	1466	98.50	0.64	98.41
Fe	40900	600	41,051	761	100.40	2.43	98.38
Mn	440.00	19.00	436.60	3.90	99.20	0.45	100.32
As	26.20	1.50	24.94	0.10	95.30	2.57	103.35
Cd	2.11	0.20	2.09	0.03	99.10	0.69	101.59
Co	11.50	0.30	10.74	0.30	93.40	0.79	101.49
Cr	90.70	4.60	87.21	6.10	96.20	0.72	103.38
Cu	310.00	12.00	298.20	22.20	96.20	0.81	101.30
Hg	3.04	0.20	2.81	0.50	92.30	<0.00	<0.00
Ni	39.50	2.30	36.31	0.20	91.90	0.79	99.69
Pb	183.00	8.00	173.10	1.00	94.60	0.67	99.43
Zn	364.00	23.00	362.40	0.80	99.60	1.43	99.75
V	133.00	5.00	132.30	1.60	99.50	0.71	99.65

SD = Standard Deviation

Soil Textural Class

The texture of the individual soil depths for each sampling site is presented in Tables 14 and 15. From the textural analysis, the clay content ranged from 10.78 to 59.24 %, the silt content ranged from 6.08 to 50.47 % and the sand content ranged from 8.09 to 76.22 %. The 0-20 cm depth in most sites showed increasing sandy loan content but decreasing clay content while the 20-40 cm depth in most sites showed increasing clay content. However, the texture contents were relatively uniform with depth from the sites except in sites CK (6.08, 14.45) and GSH (7.01, 11.80). The texture ranged from a sandy clay loam, sandy loam to clay loam except sites EAM in the mining area (49.52 %) and site EA in the pristine site (59.24 %) that showed high clay content.

The Particle size distributions in the soils from the pristine and their corresponding mining areas are similar which indicate that, weathering processes for the respective soils from the various regions of Ghana do not differ significantly. Three sites (WTB, EA and VKP) recorded high percentage of clay content suggesting the ability of the soil samples to retain substantial amount of the heavy metals. The clay content of the remaining 87.50 % sites is generally low suggesting that the soil particles from these sites have minimal retention ability to retain heavy metals since adsorption reactions through the formation of complexes with the surfaces of organic matter, oxides and clays are the major mechanisms involved in the retention of heavy metals in soils (Evans, 1989).

Physicochemical Characteristics of the Soils

The mean soil pH values from mining soils ranged from 4.9 to 6.9 while the pH of pristine soils ranged from 5.7 to 7.1 as shown in Tables 14 and 15. The World Health Organization (WHO)'s accepted range for soil pH is 6.5-8.5. The pH of all soil samples was within the normal range except for sites AOB (pH 4.9-5.9) and EAM (pH 4.8-5.9) from the mining sites which were below WHO's limit. The relatively low pH values of mine soils may be due to the weathering of sulfide minerals as a result of mineral processing for gold. However, there is no statistical difference between the soils pH values ($p > 0.05$) of the various sites.

Similar pH values from different soil samples were reported by Deshmukh, (2012) and Daji, (1996). Applying McLean's (1982), description of pH acidity to the results show that about 8.33 % of the soil samples were strongly acidic with pH values ranging from 4.0 to 5.0 ($4.0 \leq pH \leq 5.0$). The remaining soil samples from the sites representing 87.50 % were slightly acidic with a PH range of 5.5 to 6.0 ($5.5 \leq pH \leq 6.0$) except site WA. It can therefore be stated that the study sites are composed mainly of acidic soils. However, at the 20-40 depth, soil samples from site WA representing 4.17 % were around neutral with a pH range of 6.7 to 7.0 (6.7-7.1) range. pH is an important factor that influence the mobility and regulates the solubility of heavy metals in soil and most metals tend to be available in acidic medium because acidic soils aid desorption of metals into soil solution (Havlin *et al.*, 2011).

The % Organic Carbon (OC) content in this study ranged from 0.49 to 2.85 % from the mining sites and 0.35 to 2.44 % from the pristine sites, as shown in Tables 14 and 15. For almost all the sites, the OC content of the 0-20cm depth was higher than that of 20-40 cm depth. This can be attributed to the organic materials such as dead animals, plant materials in the top layer of most soils. In the temperate climate, about 2 % soil OC which represent about 3.4 % OM content has been suggested as a threshold value for aggregate stability for maintaining a stable structure, (Howard & Howard, 1990; Huber *et al.*, 2008). The results from all the sites in this study are within the suggested threshold value of 2 % OC except values from sites WTB (2.88) and GSH (2.44) which showed %OC values slightly above the suggested threshold value. The % OC at sites AOD (1.37) and EAM (1.16) were above 1 while sites EA (1.85) and VKP (1.95) were very close to 2. The moderate levels of organic carbon content for majority of the sites imply that the soils properties would not be significantly influenced except in areas where there is significant anthropogenic addition of heavy metals to the soils.

The EC values ranged from 340 to 1130 µS/cm in the mining sites and 130 to 420 µS/cm in the pristine sites. The WHO normal range for electrical conductivity of water is 400-600µS/cm. The electrical conductivity of most of the samples from the pristine sites were below the WHO permissible limits (Hasan *et al*, 2012). EC values from the mining sites were within the permissible limits except samples from AOB and EAM sites which recorded values above the permissible limits recording 890 and 1130 µS/cm respectively. The higher EC values obtained from the mining sites may be due to the introduction of metals by anthropogenic mining activities.

The cation exchange capacity (CEC) for all the soils in the mining areas was in the range of 1.84 – 8.89 (Table 14) with all the surface soils having CEC less than 9 cmol/kg. The CEC of the soils from the pristine areas ranged from 1.29 – 17.31 (Table 15). The Highest CEC values in the pristine areas were obtained at site EA (17.31 cmol/kg for 20-40 cm and 16.52 cmol/kg for 0-20 cm depth) which is in conformity with the high clay content obtained from site EA (texture 59.24 and 57.12 respectively). The rating of the CEC values based on the textural class indicate that the CEC levels at all sites were low (below the textural CEC range) except soils from site BB which showed CEC value of 12.36 cmol/kg at 0-20 cm depth above the recommended CEC range of 5-10 meq/100 g and CEC value of 9.85 cmol/kg at 20-40 cm depth. The low CEC values imply that all the soil samples from the pristine and the mining sites have low capacity to retain and supply nutrient and other cations.

Table 14: Physico-chemical Properties for Soils from the Mining Areas

Site	Depth (cm)	%Particle size by weight			TexT. class	pH	%OC	CEC
Mining		Clay	Silt	Sand			g/kg	(cmol/kg)
AOB	0-20	24.98	20.04	54.99	SCL	4.9-5.7	2.11	6.63
	20-40	27.74	37.23	45.03	CL	5.1-5.9	1.51	8.35
BAM	0-20	16.35	25.16	58.49	SL	6.4-6.6	2.03	4.63
	20-40	33.01	28.63	38.36	CL	6.5-6.8	0.49	3.19
EAM	0-20	17.78	10.2	72.02	LS	4.8-.5.6	1.16	7.69
	20-40	34.69	50.47	14.85	CL	5.0-5.7	0.66	8.89
WTB	0-20	49.52	34.46	16.02	C	6.3-6.7	2.85	7.99
	20-40	32.33	16.65	51.02	SCL	6.5-6.9	0.98	1.84

Table 15: Physico-chemical Properties for Soils from the Pristine Areas

Site	Depth (cm)	%Particle size by weight			TexT. class	pH	%OC	CEC
Pristine		Clay	Silt	Sand			g/kg	(cmol/kg)
AOD	0-20	25.85	28.16	45.99	SCL	6.4-6.8	1.37	2.42
	20-40	22.15	30.05	47.8	SCL	6.6-6.8	0.72	2.12
BB	0-20	10.78	37.03	52.19	SL	6.2-6.5	0.98	12.36
	20-40	12.03	34.92	53.05	SL	6.5-6.9	0.7	9.85
EA	0-20	59.24	32.67	8.09	C	5.7-6.5	1.85	16.52
	20-40	57.12	34.2	8.68	C	5.9-6.6	1.73	17.31
CK	0-20	17.7	6.08	76.22	LS	6.3-6.7	0.91	10.73
	20-40	23.27	14.45	62.28	SCL	6.4-6.6	0.55	1.36
GSH	0-20	30.57	7.01	62.41	SCL	6.7-6.9	2.44	9.51
	20-40	26.16	11.8	62.03	SCL	6.5-6.6-	1.41	8.24
NM	0-20	16.84	21.46	61.7	SL	6.5-6.9.	0.96	4.73
	20-40	13.84	18.47	67.69	SL	6.6-6.8	0.92	4.29
VKP	0-20	39.93	26	34.07	CL	6.1-6.3	1.94	12.02
	20-40	50.06	23.68	26.26	C	6.3-6.7	1.95	18.21
WA	0-20	18.65	11.45	69.9	SL	6.5-6.9	0.93	1.33
	20-40	32.64	18.7	48.65	SC	6.7-7.1	0.95	1.29

CL = clay loam; C = clay; SCL = sandy clay loam; SC = sandy clay; %OC = percent organic carbon in g/kg; CEC = cation exchange capacity in cmol/kg.

Physico-chemical Characteristics of the Sediment

Chemical parameters such as electrical conductivity, pH and percent organic carbon content were measured in this study in the sediment samples

(Table 16). The pH values of the sediments for the dry and wet seasons ranged from 6.8 to 7.4 and 6.7 to 7.5 respectively while the pH of the pristine sediments for the dry and wet seasons ranged from 6.9 to 8.0 and 7.0 to 7.7 respectively. Apart form the accepted WHO pH range, a pH range of 6.5 to 7.5 of the saturation extract is considered as the pH range in which most of the soil nutrients are available in the correct amounts for plants uptake. The pH of all samples were within the accepted WHO range in the two seasons for the sediment from the pristine and mining areas. The relatively low pH values of mine sediments may be attributed to the weathering of sulfide minerals as a result of mineral processing for gold (Obiri, 2007; Jung, 2001). And the high pH (around 7.0 to 7.3) values may be due to the reaction with carbonates and cyanides from gold mining activities (Jung, 2001) However, there is no statistical difference between the soils pH values ($p > 0.05$) from the various sites (Deshmukh, 2012; Daji, 1996).

The electrical conductivity (EC) in the saturated extract was used as an index for grading the metal content in the sediment samples (McLean, 1982). The EC of the sediments for the dry ad wet seasons ranged from 274 to 383 and 294 to 420 μS/cm respectively in the mining areas and 98 to 285 and 120 to 265 μS/cm respectively in the pristine areas. The electrical conductivity of most of the sediment samples for both dry and wet seasons from the pristine and the mining areas were below the permissible limits of 400-600 μS/cm (Hassan *et al.*, 2012; WHO, 2004). The relatively high EC recorded for the sediments from the mining sites may be due to the introduction of cations into the rivers through weathering, runoffs and other anthropogenic depositions from mining activities (Ahdy & Youssef, 2011). Organic matter influence heavy metal adsorption in soils due to high CEC of organic materials at near neutral pH. High organic matter content is favorable for heavy metal sorption in sediments (Kabata-Pendias, 2007). The % OC content in the soils for the dry and wet seasons samples ranged from 0.73 to 1.54 and 0.49 to 1.51 respectively in the mining sites, whereas from the pristine sites, it ranged from 0.19 to 1.32 and 0.16 to 0.98 respectively which are within the 2% threshold limit. (Howard & Howard, 1990).

Table 16: Physico-chemical Parameters for Sediments in the Pristine and Mining Sites

	Dry Season			Wet Season		
Site	pH	EC µS/cm	%OC	pH	EC µS/cm	%OC
Mining						
AOB	6.7-6.9	311	1.54	6.7-6.8	420	1.11
BAM	7.0-7.2	274	1.24	7.1-7.3	316	1.51
EAM	6.8-7.3	383	1.13	6.9-7.1	294	1.03
WTB	7.0-7.4	294	0.73	7.2-7.5	410	0.49
Pristine						
AOD	7.3-7.4	186	0.34	7.1-7.3	254	0.16
BB	7.1-7.5	176	0.74	7.5-7.7	265	0.85
EA	7.6-8.0	285	1.32	7.0-7.4	315	0.98
CK	7.3-7.4	98	0.19	7.3-7.5	120	0.54
NM	6.9-7.3	111	0.45	7.1-7.4	189	0.37
VKP	7.4-7.6	136	1.06	7.3-7.6	210	0.72
WA	7.0-7.1	122	0.88	7.3-7.5	150	0.98

Physico-chemical Characteristics of the Water Samples

High pH of water results in a bitter taste for drinking water (Obiri *et al.*, 2010). The pH of the water samples from all the pristine samples fell within the WHO range for both seasons (6.5-8.5). The pH of the water samples from the mine sites was below the WHO lower limit of 6.5 with River Nyam recording a pH as low as 3.5 and 4.3 in the dry and the wet seasons respectively. The low pH of the water samples from the mine sites may account for the relatively high heavy metal concentrations measured at site AOB (Tarras-Wahlberga, Flachier, Lane, & Sangfors, 2001).

WHO acceptable range for electrical conductivity of water is 400-600 μS/cm (WHO, 2004). All conductivities obtained in both seasons for the pristine water samples were below the acceptable range. However, the conductivities of the samples from the mine sites in the dry and wet seasons were above the acceptable limit. It was realized that the conductivity values were higher during the wet season which can be attributed to dissolved materials from weathering and runoffs. Turbidity values of water samples from pristine and the mining sites in the dry and wet seasons ranged from 0 - 9 and 3 – 27 NTU and 0 - 39 and 3 - 92 NTU respectively. The WHO guideline for turbidity in drinking water is 5 NTU. The high turbidities (3 to 92) particularly in samples from the mining sites can be attributed to the activities of small scale and illegal mining operators along the rivers. Low turbidity could also indicate low levels of disease causing organisms such as bacteria, viruses, and parasites. (Akoto & Adiyiah, 2007).

The results for the physico-chemical analysis of the water samples for the two seasons are shown in Tables 17 and 18. The maximum TDS was recorded for both seasons in River Nyam (AOB) in the mining areas and it ranged from 46.3-47.7 mg/L and 38.6-39.1 mg/L respectively. The high TDS of the water samples in the mining areas could be attributed to the draining of mine wastes which contains elevated levels of cations.

Table 17: Physico-chemical Parameters for Water from Pristine and Mining Sites (dry season)

Sites	pH Range	Cond. Range	Turbidity NTU	Temp. Range (°C)	TDS Range (mg/L)
Mining					
AOB	3.5-3.6	6440-6560	9-22	28.1-28.5	38.6-39.1
BAM	5.3-5.9	300-320	3-21	28.6-28.9	6.1-6.4
EAM	5.3-5.5	1130-1150	12-27	28.0-28.7	5.7-5.9
WTB	5.1-5.4	950-1010	5-15	28.3-28.6	2.7-2.7
Pristine					
EA	6.2-6.4	450-490	1-6	28.0-28.2	2.0-2.1
WA	6.1-6.4	50-60	0-4	28.6-28.9	0.3-0.5
BB	6.4-6.5	170-180	3-9	27.4-27.9	1.0-1.3
AOD	6.2-6.3	210-220	5-7	28.2-28.4	1.6-1.7
VKP	6.3-6.4	50-60	1-6	28.5-28.7	0.5-0.6
NM	6.1-6.9	70-80	2-9	28.0-28.1	0.4-0.5
CK	6.6-6.8	40-050	0-1	28.0-28.3	0.7-0.8

Table 18: Physico-chemical Parameters for Water from Pristine and Mining Sites (wet season)

Sites	pH Range	Cond. (μS/cm) Range	Turbidity NTU	Temp. Range (°C)	TDS Range (mg/L)
Mining					
AOB	4.3-5.5	2790-2890	7-92	28.1-28.4	46.3-47.7
BAM	6.9-7.2	2070-2079	6-52	28.1-28.5	5.4-7.5
EAM	5.7-7.0	442-1890	21-50	28.4-28.7	6.2-6.9
WTB	7.0-7.4	470-478	3-15	28.2-28.4	4.3-5.1
Pristine					
EA	6.8-7.8	485-519	0-1	28.1-28.5	2.7-3.5
WA	5.6-6.4	242-272	1-4	28.0-28.4	0.7-1.1
BB	6.7-6.8	626-938	21-39	28.0-28.4	1.5-1.8
AO	6.2-6.6	228-258	6-8	28.0-28.3	3.2-3.6
VKP	6.5-6.8	89-96	3-8	28.1-28.5	0.6-0.8
NM	6.3-6.9	75-94	1-5	28.4-28.7	1.3-1.9
CK	6.5-6.8	60-82	2-4	28.0-28.4	1.2-1.6

Concentration of Heavy Metals in Water from the Pristine and Mining areas

The results of the heavy metal concentrations in surface waters are presented in Tables 20 and 21. The mean concentration of the heavy metals in the water samples during both seasons from the mining and the pristine rivers are generally low when compared with the various guidelines values (Table 19) except River Nyam and River Subri which showed high levels of As and Mn respectively. The rivers can thus be said to be safe for drinking and for aquatic life except for As and Mn. Hg and Cd were not detected in the two seasons samples. In general, high concentrations of heavy metals were found in the mining sites compared with those from the pristine sites in both seasons.

The maximum mean concentrations of 13.85±4.57, 20.36±5.60, 2.67±1.29, 0.09±0.03, 0.25±0.18, 0.11±0.01, 0.23±0.03, 0.08±0.01, 0.04±0.01, 0.02±0.01 and 0.03±0.05 mg/L for Al, Fe, Mn, Cr, Cu, Zn, As, Pb, V, Co and Ni respectively were all recorded in the dry season from the mining areas. The maximum concentration of the metals measured in the mining areas correlates with the relatively low water pH recorded from the mining areas and the high EC, TDS and %OC content measured from the mining areas in the two seasons.

The maximum As concentrations was recorded in Nyam river (AOB) in both the dry and wet seasons whilst the maximum concentration of Mn in river Subri (BAM) was also recorded in the dry season. The high levels of the metals in River Nyam and River Subri is not surprising since the two rivers run through major mining areas with number of mine tailings and waste dumps. The maximum concentrations of Al, Fe and Zn were recorded in the water samples from river Birim (EAM) in the dry season at the mining areas.

The maximum values for most metals were above the guideline limits for drinking water (Table 19).

To further elucidate the variation of the heavy metals in the water samples across the sampling areas, Figure 9, was designed to show site specific concentrations of Zn, As, Pb and Cr at the various sample locations from Pristine and the mining areas. The figure showed Pb, Cr and Zn having the highest concentration in River Birim (EAM) while the highest As concentration was recorded in River Nyam (AOB).

In assessing the heavy metal contaminations from the various sites, the levels were compared with the maximum permitted values of EC (1998), WHO (2004), USEPA (2009) and USEPA (2006) (Table 22) and previous studies from similar areas and other rivers from other countries and it was found that the metal concentrations from this study were relatively lower ($p < 0.05$) (Nkoom *et al.*, 2013; Ansa-Asare & Asante, 2000; Cobbina *et al.*, 2013; Akoto & Adiyiah, 2007). Similar low concentrations of Cd, Hg, As, Mn, Cu and Zn were reported in river Samre in the Wassa Amenfi West District in the Western Region and Nangodi and Tinga drinking water sources in Northern region of Ghana (Nkoom *et al.*, 2013; Cobina *et al.*, 2013).

Similar study conducted in the Eastern Region (Kibi, Obronikrom, Bunso and Apapam) reported average Pb values to be 25 mg/L at Obronikrom, 18 mg/L at Kibi and 6 mg/L each at Bunso and Apapam. In the case of As, the mean values were 180 mg/L (Obronikrom) and 46 mg/L each (Kibi-Deaf and Bunso) (Asamoah, 2012). The average concentrations of As and Pb reported in this study are comparable to the concentrations reported in other studies of water samples from gold mining areas in Ghana (Obiri *et al.*, 2016; Cobbina *et* *al.*, 2013; Rajaee *et al.*, 2015). In a separate study, Cobbina *et al.*, (2013), found relatively low concentrations of heavy metals in surface water and borehole samples from Tinga, in the Bole-Bamboi District of Ghana. According to Bowen (1979), fresh water contains 0.1, 3.0, 3.0 and 15 mg/l of Cd, Cu, Pb and Zn, respectively. However, metal levels in this study are by far less than the fresh water values reported by Bowen (1979).

Aladesanmi, Adeniyi, & Adesiyan (2014), in similar study reported concentrations of Cd below detection limits, and levels of Pb, Cr, Co and Cu ranging from 0.003 to 0.009 mg/L which are lower than the values obtained from this study. Despite the low levels of the metals, some of the rivers (AOB, BAM and EAM) especially during the dry season recorded quite high levels above the guideline limits (Table 19) (e.g. As at AOB = 0.23 mg/kg and Mn at BAM = 2.67 mg/kg). The metals could also build up if extensive use of pesticides in farm lands at the vicinity of the rivers and illegal mining activities continue along the rivers.

Table 19: Maximum Permitted Metal Concentrations (mg/L) for water

Water Quality Guidelines	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Co
EC(1998)	0.01	0.05	2	0.2	0.05	0.02	0.01	0.1	-
WHO (2004)	0.01	0.05	2	-	0.4	0.07	0.01	-	-
USEPA (2009)	0.01	0.1	1.3	0.3	0.05	-	0.015	5	0.11
USEPA (2006)	0.34	-	0.013	1	-	0.47	-	0.12	-

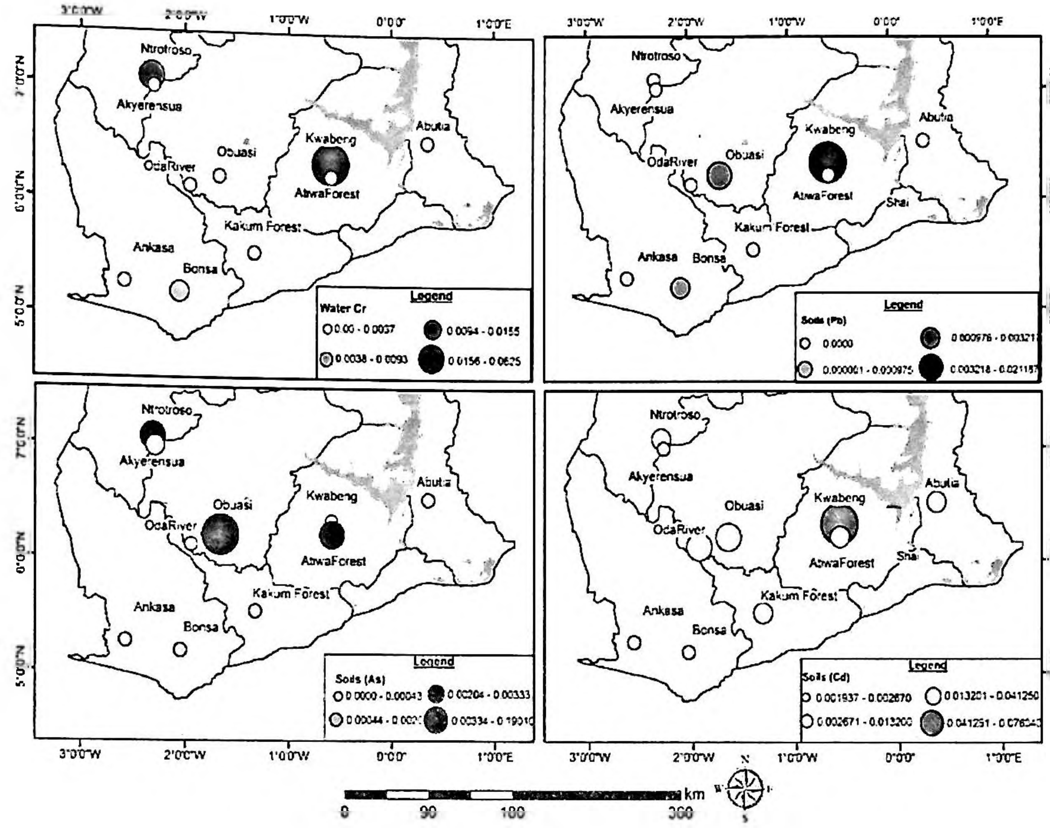


Figure 9: The Concentrations of Zn, As, Pb and Cr in Water at the various Sites (designed from Ghana map using ArcGIS 10.1 programme).

Table 20: Concentration of Heavy Metals (mg/L) in Surface Water from the Pristine and Mining areas

Sites	**WET SEASON (2014)**										
	Al	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
Mines											
AOBW	0.725±0.37	0.005±0.01	0.023±0.00	1.901±1.55	3.152±0.87	0.009±0.01	0.010±0.01	0.015±0.01	0.041±0.02	0.190±0.03	0.003±0.00
BAMW	0.718±1.18	0.009±0.00	0.016±0.03	2.231±1.36	7.104±2.31	0.007±0.01	0.015±0.02	0.005±0.01	0.013±0.02	0.003±0.01	-
EAMW	10.524±2.65	0.051±0.00	0.063±0.02	1.187±0.03	12.791±2.05	0.040±0.00	0.018±0.01	0.080±0.00	0.076±0.02	-	0.021±0.00
WTBW	0.412±0.06	0.004±0.00	0.009±0.01	0.232±0.00	1.508±0.08	-	0.010±0.00	0.007±0.00	0.002±0.00	-	-
Pristine											
EAW	0.060±0.01	-	-	0.064±0.03	0.439±0.03	-	0.010±0.01	-	0.011±0.02	0.003±0.00	-
WAW	0.098±0.00	-	0.004±0.01	0.020±0.00	0.794±0.25	-	-	-	-	-	-
BBW	0.062±0.03	-	-	1.122±0.11	0.837±0.06	-	-	-	-	0.002±0.00	-
AODW	0.101±0.06	0.010±0.01	-	0.044±0.05	0.255±0.13	-	0.007±0.01	0.008±0.00	0.041±0.01	-	-
VKPW	0.063±0.01	0.003±0.00	-	-	0.904±0.12	-	-	0.004±0.00	0.007±0.01	-	-
NMW	0.069±0.03	-	-	0.009±0.01	0.525±0.32	-	-	-	0.025±0.01	-	-
CKW	0.041±0.01	-	-	0.015±0.02	0.109±0.15	-	-	-	0.007±0.03	-	-

Table 21: Concentration of Heavy Metals (mg/L) in Surface Water from the Pristine and Mining areas

Sites	DRY SEASON (2016)										
	Al	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
Mines											
AOBW	2.453±0.83	0.080±0.00	0.006±0.00	1.827±1.48	3.862±1.55	0.008±0.01	0.011±0.00	0.016±0.01	0.078±0.02	0.226±0.03	0.002±0.00
BAMW	0.684±0.24	0.006±0.01	0.003±0.01	2.667±1.29	6.758±1.76	0.006±0.01	0.005±0.00	0.004±0.01	0.043±0.02	0.010±0.01	0.002±0.00
EAMW	13.847±4.57	0.077±0.02	0.088±0.03	1.213±0.03	20.355±5.60	0.044±0.00	0.024±0.00	0.092±0.02	0.111±0.01	0.007±.00	0.024±0.00
WTBW	1.922±0.65	0.003±0.00	0.014±0.01	0.230±0.00	2.371±1.16	0.003±0.00	0.005±0.00	0.245±0.18	0.053±0.03	0.006±0.00	0.026±0.05
Pristine											
EAW	0.067±0.01	-	-	0.064±0.03	0.463±0.02	-	-	-	0.044±0.02	0.007±0.00	-
WAW	0.111±0.00	-	-	0.019±0.02	0.715±0.00	-	-	0.008±0.02	0.037±0.01	0.005±0.00	-
BBW	0.142±0.02	-	-	0.042±0.01	0.929±0.06	-	-	0.089±0.03	0.044±0.01	0.003±0.00	0.010±0.02
AODW	0.038±0.03	0.010±0.00	-	0.016±0.02	0.157±0.07	-	0.004±0.00	0.006±0.00	0.029±0.01	-	-
VKW	0.030±0.02	-	-	-	0.594±0.18	-	-	0.004±0.00	0.006±0.01	-	-
NMW	0.047±0.02	-	-	-	0.371±0.28	-	-	-	0.021±0.02	-	-
CKW	0.022±0.01	-	-	0.010±0.01	0.074±0.01	-	-	-	0.006±0.01	-	-

Concentrations of Heavy Metals in Sediment (weak acid digestion)

The mean concentrations of heavy metals in sediments extracted with 1.0MHNO_3 solution during the wet and the dry seasons are shown in Tables 23 and 24. The maximum concentrations of As, Zn, Cu, and Pb were found in the mining areas especially around Obuasi (AOB) and Ntotroso (BAM) with as high as 166.38±11.91, 20.88±3.04, 11.33±0.39 and 5.49±0.14 mg/kg respectively during the wet season and 180.88±12.78, 22.46±5.44, 10.83±1.37 mg/kg respectively during the dry season. The highest concentrations of As, Zn, Pb and Cu were measured from the pristine site EAD to be 30.99±2.18 mg/kg. The maximum mean concentrations of Cd for the wet and dry seasons were recorded from the mining areas as; 0.08±0.03 and 0.06±0.01 mg/kg respectively.

The remaining metals such as Al, Fe, V, Cr, Co and Ni were fairly distributed in the mining and pristine sites and their concentrations ranged from 411.99±27.98 - 2255.02±20.22, 1388.04±16.93 - 5753.43±84.23, 3.19±0.30 - 17.51±0.86, 3.29±0.82 - 6.26±0.27, 1.99±0.63 - 11.45±0.61, 2.12±0.02 - 4.24±0.32 and 0.04±0.03 - 0.06±0.01 mg/kg respectively in the mining sites. For the pristine sites, the concentrations ranged from 237.37±12.43 - 2345.84±38.86, 292.56±13.55 - 12612.14±59.53, 0.55±0.40 - 47.67±1.72, 0.16±0.21- 45.95±5.43, 0.33±0.05 - 61.21±5.99 and 0.34±0.02 - 102.18±0.77 mg/kg respectively. Elements such as V, Cr, Mn, Cu and Ni were faily high at the Kalakpa (VKP) Forest Conservation which may be attributed to inputs from river flows associated with watershed's geology (Álvarez-Vázquez, 2013). Table 22 shows the geochemical background data for sediment quality guidelines and toxicological reference values for safe limit of heavy metals in sediment (Wedepohl, 1995; USEPA, 1997).

Comparing the metal levels in this study with the quality guidelines revealed that the concentrations of the available metals in the mining and the pristine samples during the wet and dry seasons were below the reference limits except As (166.38) from Obuasi mines (AOB), Cu (25.72, 21.15) from Atiwa (EA) and Kalakpa (VKP) forest reserves. Other metals are Ni (102.18) from Kalakpa forest reserve, Mn (1292.85) from Kalakpa forest reserve (VKP) and Kwabeng mines (EAM) which were above some of the guideline levels especially the Average composition of shale values and EPA, ecological screening values during the wet seasons and As (180.88±12.78 mg/kg, 4.13±0.84 mg/kg) respectively at sites AOB and EA. Furthermore, Cu (14.86±0.55, 30.99±2.18, and 22.02±1.51 mg/kg) respectively at sites BAM, EA and VKP, Ni (114.33±9.59 mg/kg) at site VKP Mn (741.45±72.48 and 707.45±16.33 mg/kg) respectively at sites EAM and VKP, Cr (46.61±4.75 mg/kg) at site VKP, Ni (114.33±9.59 mg/kg) at site VKP and Co (13.04±2.19, 14.25±1.56 and 66.91±6.35 mg/kg) respectively at sites EAM, EA and VKP for the dry season.

The enrichment of all the natural geogenic elements (Al, Fe, Cr, Ni, CO, Mn and Cu) at site VKP may be attributed to inputs from river flows associated with watershed's geology (Álvarez-Vázquez, 2013). The anthropogenic elements (As, Cd, and Pb) were detected in all the mining sites in both seasons but were not detected in most of the pristine sites especially during the dry season.

Table 22: Mean sediment Values (mg/kg) for Geochemical Baseline, Sediment Guidelines and Toxicological Reference Values

Elements	Fe	Pb	Zn	Cu	Cd	Ni	As	Cr	Mn	Co	Hg	V	Al
USEPA Ecological Screening Values		30.2	124	18.7	1	15.9	7.24	52.3					
Mean composition of Shales (Wedepohl, 1995)	3890	17	52	14.3	0.1	18.6	2	35	527	11.6	0.06	53	77440
Canadian ISQG	TEC	35	123	35.7	0.60	18	5.9	37.3					
	PEL	91.3	315	197	3.53	35.9	17	90					

TEC= Threshold effect concentration; PEL= Probable effect level; ISQG = Interim sediment quality guideline. Wedepohl (1995); USEPA (1995).

Table 23: Mean Concentrations (mg/kg) of the Metals in Sediments in the Wet Season (bioavailable metals in 2016)

	WET SEASON										
	Mining				Pristine						
Elements	AOBD	BAMD	EAMD	WTBD	AODD	EAD	BBD	CKD	MMD	VKPD	WAD
Al	713.69±46.59	2255.02±20.22	1677.59±62.14	411.99±27.98	296.09±26.56	465.68±10.75	1862.18±32.21	749.18±43.01	1736.29±16.76	2345.84±38.86	237.37±12.43
V	3.19±0.30	17.51±0.86	13.75±0.05	4.87±0.51	1.20±0.01	6.48±0.74	41.14±4.14	8.24±0.43	7.28±0.27	47.67±1.72	0.55±0.40
Cr	3.29±0.82	6.26±0.27	5.24±0.26	5.13±0.73	0.46±0.05	2.13±0.63	15.24±1.17	2.14±0.03	3.42±0.27	45.95±5.43	0.16±0.21
Mn	121.81±10.20	361.19±12.04	688.58±61.55	208.97±18.44	11.79±2.02	96.13±3.45	645.03±19.10	230.69±21.02	227.96±15.33	1292.85±97.41	50.85±3.77
Fe	4434.76±40.18	5753.43±84.23	3868.39±41.02	1388.04±16.93	456.04±35.03	2273.88±165.02	12612.14±59.53	3650.86±43.31	2835.19±15.04	6816.19±10.71	292.56±13.55
Co	1.99±0.63	9.97±0.55	11.45±0.61	5.14±0.26	0.33±0.05	3.92±0.19	13.83±1.66	3.95±0.34	5.79±0.81	61.21±5.99	0.43±0.37
Ni	2.12±0.02	3.72±0.23	4.24±0.32	3.05±0.74	0.34±0.02	2.56±0.42	10.70±0.82	1.45±0.05	3.25±0.19	102.18±0.77	ND
Cu	11.33±0.39	11.09±0.66	6.06±0.29	3.92±0.95	1.75±0.09	6.14±0.52	25.72±3.26	4.69±0.86	5.86±0.45	21.15±0.81	0.15±0.07
Zn	20.88±3.04	10.51±0.54	8.28±0.56	9.83±0.86	2.86±0.41	7.96±0.38	12.52±0.56	5.77±0.01	3.34±0.79	7.05±0.69	0.29±0.11
As	166.38±11.91	1.91±0.80	4.23±0.28	1.02±0.18	0.51±0.22	0.56±0.07	2.33±00.70	0.62±0.50	ND	0.11±0.04	0.04±0.01
Cd	0.04±0.04	0.05±0.03	0.06±0.01	0.04±0.03	0.02±0.01	0.03±0.04	0.03±0.02	0.03±0.01	ND	0.02±0.03	0.01±0.01
Pb	5.49±0.14	6.63±0.61	5.64±0.41	1.18±0.41	0.89±0.02	1.57±0.46	3.97±0.78	3.13±0.45	3.60±0.89	5.95±0.34	0.35±0.08

Table 23: Mean Concentrations (mg/kg) of the Metals in Sediments in the Wet Season (bioavailable metals in 2016)

	WET SEASON										
	Mining				Pristine						
Elements	AOBD	BAMD	EAMD	WTBD	AODD	EAD	BBD	CKD	MMD	VKPD	WAD
Al	713.69±46.59	2255.02±20.22	1677.59±62.14	411.99±27.98	296.09±26.56	465.68±10.75	1862.18±32.21	749.18±43.01	1736.29±16.76	2345.84±38.86	237.37±12.43
V	3.19±0.30	17.51±0.86	13.75±0.05	4.87±0.51	1.20±0.01	6.48±0.74	41.14±4.14	8.24±0.43	7.28±0.27	47.67±1.72	0.55±0.40
Cr	3.29±0.82	6.26±0.27	5.24±0.26	5.13±0.73	0.46±0.05	2.13±0.63	15.24±1.17	2.14±0.03	3.42±0.27	45.95±5.43	0.16±0.21
Mn	121.81±10.20	361.19±12.04	688.58±61.55	208.97±18.44	11.79±2.02	96.13±3.45	645.03±19.10	230.69±21.02	227.96±15.33	1292.85±97.41	50.85±3.77
Fe	4434.76±40.18	5753.43±84.23	3868.39±41.02	1388.04±16.93	456.04±35.03	2273.88±165.02	12612.14±59.53	3650.86±43.31	2835.19±15.04	6816.19±10.71	292.56±13.55
Co	1.99±0.63	9.97±0.55	11.45±0.61	5.14±0.26	0.33±0.05	3.92±0.19	13.83±1.66	3.95±0.34	5.79±0.81	61.21±5.99	0.43±0.37
Ni	2.12±0.02	3.72±0.23	4.24±0.32	3.05±0.74	0.34±0.02	2.56±0.42	10.70±0.82	1.45±0.05	3.25±0.19	102.18±0.77	ND
Cu	11.33±0.39	11.09±0.66	6.06±0.29	3.92±0.95	1.75±0.09	6.14±0.52	25.72±3.26	4.69±0.86	5.86±0.45	21.15±0.81	0.15±0.07
Zn	20.88±3.04	10.51±0.54	8.28±0.56	9.83±0.86	2.86±0.41	7.96±0.38	12.52±0.56	5.77±0.01	3.34±0.79	7.05±0.69	0.29±0.11
As	166.38±11.91	1.91±0.80	4.23±0.28	1.02±0.18	0.51±0.22	0.56±0.07	2.33±00.70	0.62±0.50	ND	0.11±0.04	0.04±0.01
Cd	0.04±0.04	0.05±0.03	0.06±0.01	0.04±0.03	0.02±0.01	0.03±0.04	0.03±0.02	0.03±0.01	ND	0.02±0.03	0.01±0.01
Pb	5.49±0.14	6.63±0.61	5.64±0.41	1.18±0.41	0.89±0.02	1.57±0.46	3.97±0.78	3.13±0.45	3.60±0.89	5.95±0.34	0.35±0.08

Table 24: Mean Concentrations (mg/kg) of the Metals in Sediments in the Dry Season (bioavailable metals in 2014)

DRY SEASON											
	Mining				Pristine						
Elements	AOBD	BAMD	EAMD	WTBD	AODD	EAD	BBD	CKD	MMD	VKPD	WAD
Al	705.1±46.72	2199.00±212.13	1745.50±60.33	402.60±31.76	301.60±20.08	1839.00±35.96	474.45±39.04	301.95±77.06	1811.95±171.26	2317.00±30.97	247.65±13.46
V	2.82±0.64	18.04±1.24	13.62±3.93	4.81±0.54	ND	41.89±5.07	6.31±0.31	1.22±0.06	7.87±1.69	46.61±4.75	ND
Cr	4.22±0.72	8.13±0.25	6.65±1.72	6.27±1.77	ND	16.99±2.57	2.32±0.62	1.61±0.03	4.27±0.23	52.52±3.22	ND
Mn	128.08±11.08	290.50±1.13	741.45±72.48	215.92±18.71	13.06±2.14	707.45±16.33	97.55±4.41	14.33±32.81	257.41±18.80	1503.93±121.19	53.19±9.31
Fe	4821.50 ±437.46	6630.23 ±173.14	4481.51 ±468.82	1530.53 ±24.95	475.41 ±16.41	13845.21 ±176.78	2439.13 ±168.24	464.92±42.41	3324.51 ±189.58	7557.04±11.82	301.11±3.17
Co	1.81±0.19	10.87±0.11	13.04±2.19	5.57±0.18	ND	14.25±1.56	4.01±0.79	ND	6.87±0.61	66.91±6.35	ND
Ni	3.47±0.70	4.94±0.15	4.89±0.85	4.33±1.19	ND	10.74±0.16	2.74±0.78	ND	3.69±0.84	114.33±9.59	ND
Cu	11.79±2.07	14.86±0.55	6.52±0.43	10.58±3.87	1.78±00.11	30.99±2.18	6.43±1.19	1.39±0.89	6.69±0.82	22.02±1.51	ND
Zn	22.46±5.44	11.26±0.45	11.47±2.03	10.82±2.17	3.33±0.37	14.76±1.71	8.47±0.64	ND	4.37±0.98	9.09±1.87	1.21±0.32
As	180.88±12.78	0.53±0.75	0.51±0.31	ND	0.74±0.04	4.13±0.84	ND	ND	0.78±0.10	ND	ND
Cd	0.06±0.04	0.05±0.02	0.08±0.03	0.06±0.01	0.04±0.02	0.05±0.01	0.05±0.03	0.03±0.02	0.02±0.01	0.04±0.03	0.02±0.01
Pb	8.19±1.14	10.83±1.37	7.54±4.17	1.27±1.28	2.98±0.44	6.32±6.29	5.01±1.78	3.06±0.17	6.01±3.59	5.81±1.22	0.67±0.94

ND =Not detected

Heavy Metals Concentration in Sediments (aqua regia digestion)

Aqua regia digestion method has the potential to extract between 70 and 90 % of the total contents of heavy metals and as a result, the method has been widely used to estimate the amount of heavy metals in soils and sediments (Ure, 1990). The aqua regia digestion method in this study gave the maximum concentration of As at site AOB in the dry and wet seasons to be 409.95±19 mg/kg and 397.08±7.65 mg/kg respectively. Similar high levels of As, Cu, Pb and Zn were reported in earlier studies around this site (AOB) (Antwi-Agyei, Hogarh, & Foli, 2009; Amonoo-Neizer & Amekor, 1993; Asiam, 1996; Smedley, 1996; Smedley *et al.*, 1996; Ahmad & Carboo, 2000) Mercury was not detected in samples collected in both wet and dry seasons. In the mining area, samples from Kwabeng mines (EAM) recorded the highest concentration of V (114.20±7.51 mg/kg), Mn (1174.05±24.37 mg/kg), Fe (56394.25±400.66 mg/kg), Co (30.41±0.88 mg/kg), Ni (38.64±2.43 mg/kg) and Zn (67.54±9.05 mg/kg) for the wet season, and for the dry seasons, the results were 115.66±21.12 mg/kg, 1179.30±69.13 mg/kg, 57860±37.62 mg/kg, 32.19±5.76 mg/kg, 47.18±3.88 mg/kg and 72.94±5.01 mg/kg respectively.

The levels of Al (64338.44 mg/kg), Cr (134.13 mg/kg) and Pb (14.43 mg/kg) were high in samples from site WTB mining area, during the wet season whiles Al (63130 ±6161.28 mg/kg) and Pb were high at WTB in the dry season. The maximum concentration of Fe (66365±14.50 mg/kg) was recorded at site EAM and the highest concentration of Cr (194.75±0.28 mg/kg), recorded at site BAM in the dry season. Most of the anthropogenic metals like As, Pb, Cd and Hg were dominant in the mining areas than in the pristine areas (EA, BB and AOD) where illegal mining activities are known to be taking place.

In the pristine areas, Al, Fe, Zn and Cu showed maximum concentrations in samples from site EA in the wet season whiles Al, Fe and Zn showed maximum concentration at site EA during the dry season. As and Cd showed maximum concentration at site BB which is located at Newmont mining area. Other metals like V, Cr, Mn, Co, Pb and Ni showed recorded metal concentrations at site VKP in both seasons as shown in Tables 25 and 26.

The surface soil texture of samples from sites VKP is clay loam and subsoil is purely clayey. The soil texture of samples from site EA is purely clayey and might be responsible for the high metals concentration in the soils at these sites. (Evans, 1989). The results from this study were also compared with different quality guidelines as shown in Table 22.

It was observed that the concentrations of Pb, Cd and Zn were below the guidelines limit from the pristine and the mining areas in the wet and the dry seasons. Arsenic concentrations from the mining sites were above the Canadian TEC and average shales composition limits (Table 22) in both seasons. Arsenic concentrations from the pristine sites were below the guideline limits except the levels from site EA. The levels of Cu in the sediment samples from the mining sites were above the guideline limits except at site WTB. The levels of Cu in the sediment samples from the pristine sites were below the guideline limits except those from sites EA, NM and VKP. The levels of Ni in the mining samples were above the permissible limits in the pristine and minining sites for both seasons except the levels at site AOB which were lower than the guideline limits.

The levels of Mn and Co in the mining samples were below the permissible levels except from site EAM which were above the permissible levels as 1174.05 and 30.41 mg/kg respectively in both seasons. The levels of Cr from pristine and the mining sites were above the EPA Ecological Screening Values and Canadian TEC permissible limits except the levels from sites EA and WA in the wet season and sites AOD and WA respectively in the dry season. The results of a single factor ANOVA computed using the average values of the heavy metals from the pristine and the mining areas indicate that there was a significant difference between the metals concentrations ($P < 0.05$).

Table 25: Mean Concentrations (mg/kg) of the Metals in Sediments in the Wet Season (total metals in 2016)

	WET SEASON										
	Mining				Pristine						
Metals	AOBD	BAMD	EAMD	WTBD	AODD	EAD	BBD	CKD	MMD	VKPD	WAD
Al	25445.39 ±110.54	47792.56 ±33.31	42469.29 ±421.94	64338.44 ±632.97	10490.38 ±410.73	14474.78 ±558.72	97999.93 ±28.51	9213.07 ±30.14	55181.59 ±6.32	39417.21 ±76.36	5277.57 ±18.69
V	38.93 ±1.87	83.09 ±4.98	114.21 ±7.51	85.22 ±1.96	17.21 ±2.58	28.31 ± 2.58	198.28 ±14.46	12.82 ±2.36	77.30 ±7.75	229.11 ±1.12	3.17 ±0.86
Cr	59.46 ±2.96	119.62 ±9.73	134.02 ±10.95	134.13 ±3.61	38.16 ±1.68	30.61 ±3.95	170.80 ±2.21	24.43 ±0.15	74.22 ±4.42	2224.95 ±3.62	7.09 ±1.57
Mn	150.62 ±11.53	271.07 ±28.13	1174.05 ±24.37	149.22 ±14.53	167.55 ±16.57	172.59 ±16.02	892.61 ±54.34	39.03 ±3.79	588.52 ±21.58	4568.79 ±54.64	72.92 ±2.98
Fe	18246.82 ±125.85	36076.53 ±332.84	56394.25 ±400.66	42067.55 ±43.39	4958.55 ±52.76	9183.79 ±251.11	73753.64 ±39.15	3264.38 ±13.19	28869.06 ±35.67	65176.78 ±93.56	1824.69 ±16.15
Co	4.47 ±1.25	12.12 ±1.12	30.41 ±0.88	7.09 ±1.02	3.52±0.59	6.67 ±0.78	30.45 ±1.88	1.38 ±0.22	17.52 ±1.13	167.11 ±1.08	1.12 ±0.07
Ni	12.17 ±0.26	23.79 ±0.81	38.64±2.43	27.30 ±3.95	6.03±0.58	9.87±0.55	63.86 ±5.66	3.88 ±0.55	28.32 ±2.70	570.49 ±20.76	1.11 ±0.39
Cu	19.43 ±1.99	28.09 ±1.87	35.19±2.18	16.32 ±0.11	6.55 ±0.34	12.51 ±0.14	66.37 ±3.64	4.54 ±0.36	23.76 ±0.34	65.90 ±3.85	0.38 ±0.14
Zn	39.36 ±3.63	31.82 ±4.57	67.54±9.05	27.76 ±2.50	13.87 ±1.44	27.55 ±2.50	83.69 ±3.93	8.15 ±0.37	32.29 ±3.54	46.28 ±4.37	10.61 ±1.60
As	397.08 ±7.65	9.63±1.33	35.01±2.54	4.84 ±0.29	1.95±0.03	0.97 ±0.04	42.86 ±1.10	1.32 ±0.04	3.61 ±0.48	1.88 ±0.75	0.03 ±0.01
Cd	0.06±0.02	0.04±0.02	0.05±0.02	0.05 ±0.03	0.03±0.01	0.04 ±0.01	0.08 ±0.07	0.02 ±0.01	0.01 ±0.01	0.05 ±0.02	0.01 ±0.01
Pb	7.93 ±0.36	10.17 ±0.80	10.30 ±0.82	14.43 ±1.50	2.43 ±0.02	3.68 ±0.89	10.87 ±1.25	2.32 ±0.74	10.81 ±0.69	12.31 ±1.99	1.75 ±0.15
Hg	0.15±0.01	0.03±0.01	0.06±0.01	ND	0.02±0.01	ND	0.07±0.02	ND	ND	ND	ND

Table 26: Mean Concentrations (mg/kg) of Heavy Metals in Sediments in the Dry Season (total metals in 2014)

DRY SEASON											
	Mining				Pristine						
Metals	AOBD	BAMD	EAMD	WTBD	AODD	EAD	BBD	CKD	NMD	VKPD	WAD
Al	24830.46 ±11.59	7646.53 ±48.83	4307.16 ±71.11	63130.24 ±62.28	19015.15 ±19.40	38900.83 ±14.42	9352.50 ±11.60	95345.12 ±48.85	56620.76 ±58.60	39665.91 ±350.18	5268.54 ±29.43
V	36.06 ±8.97	135.05 ±2.19	115.655 ±21.12	85.975 ±40.10	18.66 ±1.80	53.23 ±1.87	25.785 ±2.68	193.9 ±0.85	74.805 ±5.33	233.85 ±15.32	2.41 ±0.65
Cr	62.73 ±14.34	194.75 ±0.28	137.75 ±9.81	134.95 ±15.43	29.21 ±2.55	66.395 ±2.74	34.095 ±2.35	168.75 ±4.60	76.895 ±6.22	2332.4 ±24.93	7.681 ±1.10
Mn	152.58 ±19.67	458 ±1.70	1179.3 ±69.13	151.37 ±15.09	56.93 ±5.15	578.25 ±18.46	178.25 ±56.92	871.6 ±3.82	579.3 ±58.47	4734.05 ±56.49	74.24 ±8.69
Fe	19065.15 ±13.72	66365.11 ±14.57	57860.25 ±37.62	41880.57 ±43.40	5166.50 ±42.41	22505.18 ±87.74	9821.54 ±11.10	74485.75 ±26.94	29265.28 ±25.39	67715.34 ±39.52	1895.40 ±14.25
Co	4.47 ±1.34	20.81 ±0.23	32.19 ±5.76	7.03 ±0.97	3.128 ±0.99	13.075 ±0.16	7.491 ±0.31	30.955 ±0.13	18.29±1.39	184.34 ±20.40	1.453 ±0.03
Ni	14.26 ±2.14	17.12 ±2.45	47.18 ±3.88	31.41 ±33.45	7.91±1.79	13.94 ±1.18	74.52 ±0.88	6.15 ±1.71	24.47±2.79	478.05 ±35.82	1.35 ±0.13
Cu	68.75 ±6.98	50.14 ±0.43	35.99 ±9.47	16.17±7.03	6.87±0.57	17.08 ±0.14	14.025 ±2.0	69.035 ±1.11	23.284±3.31	69.22 ±14.16	0.265 ±0.21
Zn	42.66 ±3.10	47.86 ±0.17	72.94 ±5.01	28.95±2.59	12.95 ±0.37	41.54 ±0.34	29.82 ±3.40	88.99 ±7.72	33.03±2.22	45.57 ±0.69	11.13 ±82.04
As	409.95 ±19.16	15.78 ±5.13	35.90 ±54.70	1.852±0.56	2.39±0.49	3.16 ±0.77	9.658 ±2.03	37.14 ±3.13	6.49±90.58	11.24 ±1.94	4.45 ±0.58
Cd	0.08±0.03	0.05 ±0.02	0.06±0.01	0.07±0.01	0.06±0.01	0.05 ±0.01	0.06±0.03	0.05 ±0.02	0.05±0.01	0.05 ±0.02	0.06 ±0.02
Pb	11.26±0.60	18.14 ±0.87	15.50±0.11	24.51±1.06	5.23±0.41	4.55 ±0.83	6.64±0.43	4.41 ±1.60	13.53±0.74	14.57 ±2.17	3.14 ±0.64

Table 26: Mean Concentrations (mg/kg) of Heavy Metals in Sediments in the Dry Season (total metals in 2014)

	DRY SEASON										
	Mining				Pristine						
Metals	AOBD	BAMD	EAMD	WTBD	AODD	EAD	BBD	CKD	NMD	VKPD	WAD
Al	24830.46	7646.53	4307.16	63130.24	19015.15	38900.83	9352.50	95345.12	56620.76	39665.91	5268.54
	±11.59	±48.83	±71.11	±62.28	±19.40	±14.42	±11.60	±48.85	±58.60	±350.18	±29.43
V	36.06	135.05	115.655	85.975	18.66	53.23	25.785	193.9	74.805	233.85	2.41
	±8.97	±2.19	±21.12	±40.10	±1.80	±1.87	±2.68	±0.85	±5.33	±15.32	±0.65
Cr	62.73	194.75	137.75	134.95	29.21	66.395	34.095	168.75	76.895	2332.4	7.681
	±14.34	±0.28	±9.81	±15.43	±2.55	±2.74	±2.35	±4.60	±6.22	±24.93	±1.10
Mn	152.58	458	1179.3	151.37	56.93	578.25	178.25	871.6	579.3	4734.05	74.24
	±19.67	±1.70	±69.13	±15.09	±5.15	±18.46	±56.92	±3.82	±58.47	±56.49	±8.69
Fe	19065.15	66365.11	57860.25	41880.57	5166.50	22505.18	9821.54	74485.75	29265.28	67715.34	1895.40
	±13.72	±14.57	±37.62	±43.40	±42.41	±87.74	±11.10	±26.94	±25.39	±39.52	±14.25
Co	4.47	20.81	32.19	7.03	3.128	13.075	7.491	30.955		184.34	1.453
	±1.34	±0.23	±5.76	±0.97	±0.99	±0.16	±0.31	±0.13	18.29±1.39	±20.40	±0.03
Ni	14.26	17.12	47.18	31.41		13.94	74.52	6.15		478.05	1.35
	±2.14	±2.45	±3.88	±33.45	7.91±1.79	±1.18	±0.88	±1.71	24.47±2.79	±35.82	±0.13
Cu	68.75	50.14	35.99			17.08	14.025	69.035		69.22	0.265
	±6.98	±0.43	±9.47	16.17±7.03	6.87±0.57	±0.14	±2.0	±1.11	23.284±3.31	±14.16	±0.21
Zn	42.66	47.86	72.94		12.95	41.54	29.82	88.99		45.57	11.13
	±3.10	±0.17	±5.01	28.95±2.59	±0.37	±0.34	±3.40	±7.72	33.03±2.22	±0.69	±82.04
As	409.95	15.78	35.90			3.16	9.658	37.14		11.24	4.45
	±19.16	±5.13	±54.70	1.852±0.56	2.39±0.49	±0.77	±2.03	±3.13	6.49±90.58	±1.94	±0.58
Cd		0.05				0.05		0.05		0.05	0.06
	0.08±0.03	±0.02	0.06±0.01	0.07±0.01	0.06±0.01	±0.01	0.06±0.03	±0.02	0.05±0.01	±0.02	±0.02
Pb		18.14				4.55		4.41		14.57	3.14
	11.26±0.60	±0.87	15.50±0.11	24.51±1.06	5.23±0.41	±0.83	6.64±0.43	±1.60	13.53±0.74	±2.17	±0.64

Concentrations of the Metals in Soils with 1.0M HNO_3

The mean concentrations of heavy metals in soils extracted with dilute acid (1.0M HNO_3) solution for the dry and wet seasons are shown in Tables 30 and 31. The bioavailable metals (As, Pb, Cd and Zn) were fairly distributed in the pristine and the mining areas across the dry and wet seasons. However, the metals exhibit different enrichment levels (Tables 29 and 30) at the sites in the two seasons, with the natural geogenic metals (Al, V, Cr, Mn, Fe, Cu Co and Ni) showing much enrichment in the pristine areas while the anthropogenic metals (As, Cd, Pb and Zn) showing much enrichment at the mining sites. The maximum concentrations of the natural geogenic metals were found in the pristine sites, especially those elements from site VKP.

It was observed that almost all the natural geogenic metals had their maximum values recorded from site VKP except Fe which had its highest concentration recorded from site EA. It was also observed that the natural geogenic metals were mostly enriched in the 20-40 cm depth layer of the soils except Fe which was enriched in the 0-20 cm depth layer of the soils. The high values of the geogenic metals recorded from site EA and particularly from site VKP can be attributed to the soils physico-chemical properties such as % OC, pH and soil texture (Table 14). The maximum concentrations of the anthropogenic metals (Cu, Zn, As, Cd and Pb) were found in the mining sites, especially from site AOB (Tables 28-31). It was observed that the anthropogenic metals were enriched in the mining sites with almost all the metals recording their highest concentrations from site AOB. The high levels of the heavy metals from site AOB in the mining areas can be related to the soil physico-chemical properties at that site (Table 18). Table 27 shows the various guidelines for safe limit for heavy metals in soils (FAO/ISRIC, 2004; USEPA, 2010; Wedepohl, 1995). Comparing the results with the permissible limits revealed that the concentrations of the dilute acid extractable metals in the mining and the pristine samples in the dry and wet seasons were below the reference limits, except As at site AOB whose values exceeded the guideline limits. The high level of As in samples from site AOB can be attributed to both the commercial and illegal mining activities around the site which had been acknowledged by some previous studies (Antwi-Agyei, 2009: Obiri, 2007).

The high levels of As in the mining areas can lead to chronic exposure to this metal. Meanwhile, arsenic is acutely toxic and intake of large quantities which was observed at the sites can lead to gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems, and eventually death (Col *et al.*, 1999).

Table 27: Recommended Guideline Values for Heavy Metals in Soils (mg/kg)

Metals	Pb	Cd	Hg	Cu	Co	Zn	Cr	Ni	Mn	As
FAO/ISRIC, 2004	150	5	-	100	50	500	250	100		
USEPA, 2010	300	3.0	1.5	50		200			80	
Average Shale Values (Wedepohl, 1995)	17	0.1	0.06	14.3	19	52	90	18.6	850	1.6

Table 28: Mean Concentrations (mg/kg) of the Metals in Mine Soils during the Dry Season (Bioavailable metals in 2014)

Site	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Mining	0-20cm											
AOBS	794.25±106.26	3.52±0.13	3.69±0.27	227.15±10.61	4909.5±103.74	3.51±0.19	6.7±0.81	47.86±0.51	6778	260.15±14.31	0.11±0.02	8.73±0.10
EAMS2	2041±26.87	18.96±2.83	7.08±0.44	489.75±7.42	5568.5±13.44	10.12±0.38	3.68±0.18	8.56±0.23	10.76±0.59	1.32±0.02	0.13±0.12	8.61±0.28
BAMS3	517.45±21.57	1.84±0.04	0.84±0.01	141.7±7.21	738.2±70.85	2.14±0.06	1.76±0.15	3.32±0.05	4.62±0.21	0	0.05±0.06	4.58±0.33
WTBS	618.35±52.59	0.94±0.15	2.82±0.17	38.01±6.14	1270±119.13	0.37±0.03	0.86±0.09	1.26±0.12	1.43±0.31	0	0.02±0.02	2.49±0.54
Mining	20-40cm											
AOBS2	637.25±26.86	2.91±0.21	3.56±0.08	137.44±12.01	3610±223.45	2.99±0.09	4.27±0.32	21.07±4.18	15.58±3.09	182.15±16.51	0.07±0.01	5.71±0.51
EAMS2	2353±202.23	20.59±2.55	8.28±0.29	585±12.99	6929±137.62	12.01±1.52	4.17±0.16	9.48±1.01	12.04±0.24	0	0.05±0.03	4.14±3.59
BAMS3	509.7±67.59	1.58±0.02	0.78±0.13	112.77±12.32	705.55±10.91	2.02±0.41	1.24±0.16	3.14±0.01	3.69±0.58	0	0.04±0.01	2.02±0.16
WTBS2	1215.5±125.56	1.29±0.11	4.07±0.25	4.89±0.38	1583.5±133.04	0.28±0.04	0.15±00.01	91.91±9.38	6.21±0.65	0	0.03±0.05	2.54±0.60

Table 29: Mean Concentrations (mg/kg) of the Metals in Pristine Soils during the Dry Season (Bioavailable metals in 2014)

Site & Depth	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Pristine	0-20cm										
AODS	1100.35±258.12	1.71±0.37	1.79±0.01	88.12±11.52	2122±222.25	2.34±0.30	0.74±0.08	5.51±0.24	4.12±00.24	0.04±0.02	2.41±0.59
EAS2	2673.5±204.76	22.27±1.26	9.99±1.70	782.5±2.40	8477±216.79	17.93±1.32	10.62±1.57	19.99±3.28	18.92±0.86	0.05±0.08	3.55±4.02
BBS3	1076.3±114.93	13.32±3.63	3.02±0.08	366.75±51.12	4235.5±373.64	7.37±0.95	3.44±0.86	9.38±1.70	8.12±0.28	0.03±0.01	3.22±2.74
WAS	1449±178.16	0.059±50.01	1.59±0.11	7.1695±1.72	1838.5±197.69	0	0.3835±0.02	1.02±0.01	2.209±0.43	0.03±0.03	2.321±0.18
GSHS	1854±50.91	10.06±00.12	2.53±0.10	118.55±16.05	1008.95±39.67	6.11±0.44	3.7±0.25	3.41±00.72	3.41±0.27	0.06±0.03	1.72±1.07
NMS	956.5±21.01	3.48±0.39	1.15±0.45	241±11.16	1746.7±125.66	3.22±0.06	3.12±0.14	212.48±29.19	16.51±2.57	ND	3.02±2.81
CKS	1763.5±172.46	1.05±0.13	3.82±0.18	9.87±2.38	1645.5±157.08	0.5055±0.12	1.17±0.05	4.02±0.34	2.21±0.52	ND	6.98±1.43
VKPS	3628.5±115.20	31.63±4.08	64.91±3.46	794.55±14.06	6021±178.73	28.565±3.41	60.74±13.73	23.05±2.94	8.42±1.42	0.04±0.07	6.33±0.70
Pristine	20-40cm										
AODS2	1844.5±14.85	0.45±0.03	2.8375±0.02	10.26±.45	1843.5±62.93	0.1905±0.02	0.5±0.16	2.46±0.13	0.99±0.04	0.03±0.01	3.91±0.24
EAS2	2393.5±136.88	17.33±5.45	8.08±1.05	534.6±142.55	6235.5±398.32	13.59±2.11	7.19±0.71	18.18±2.36	17.58±2.18	0.06±0.03	5.28±0.32
BBS2	1218.5±197.69	13.91±0.17	3.59±0.21	266.1±5.09	4079.5±352.25	5.99±0.13	3.68±00.18	6.52±0.38	8.04±0.52	0.02±0.01	2.72±0.24
WAS2	1597±164.04	0.56±0.15	2.10±0.25	5.17±0.27	1925.5±125.16	0.13±0.07	0.48±0.07	0.66±0.34	1.25±0.17	0.04±0.02	4.93±0.19
GSHS2	2357.5±604.17	30.55±5.61	3.75±0.95	415.05±18.66	1931.7±141.81	16.17±1.76	10.52±3.17	12.16±2.12	6.21±1.16	ND	3.31±0.13
NMS2	1458±167.28	4.83±00.83	1.46±0.4	232.15±10.34	2095±151.86	3.93±0.12	1.58±0.27	3.98±0.36	3.19±0.39	ND	3.85±0.39
CKS2	1693.5±146.37	1.98±0.03	2.13±0.15	102.76±13.55	965.95±14.90	2.17±0.2	0.36±0.12	5.44±1.44	2.95±00.92	ND	10.65±1.51
VKPS2	3757.5±104.39	37.81±0.06	86.67±8.24	836.55±34.53	5929.5±118.16	36.67±6.73	96.45±14.01	21.81±50.96	7.308±0.65	0.05±0.02	3.67±0.67

Table 30: Mean Concentrations (mg/kg) of the Metals in Mine Soils during the Wet Season (Bioavailable metals in 2016)

Site & Depth	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Mining	0-20cm											
AOB	833.54 ±20.85	3.99±0.74	2.56±0.05	220.47±9.81	4694.71±98.37	3.62±.17	4.82±0.12	46.53±4.71	23.75±0.75	241.75 ±14.22	0.05±0.03	6.59±0.47
EAM	1259.27 ±14.34	9.17±1.08	3.716±0.10	237.75±9.08	3162.18±38.66	5.03±0.66	1.52±0.52	4.93±0.73	10.67±1.34	4.05±0.26	0.10±0.04	5.76±0.23
BAM	511.33 ±16.04	2.48±0.22	0.76±0.04	140.51±6.16	699.89±72.29	2.27±0.11	2.19±0.81	3.22±0.13	8.56±0.14	0.35±0.01	0.04±0.00	2.85±.0.07
WTB	624.43 ±54.43	1.81±0.05	1.59±00.31	37.46±3.23	1230.36±11.39	0.43±0.00	ND	0.92±0.06	0.60±0.02	0.24±0.00	0.01±0.00	1.01±0.25
Mining	20-40cm											
AOB2	663.44 ±28.51	3.38±0.33	2.41±0.20	133.74±8.66	3405.15±22.18	2.49±0.38	3.12±0.01	20.23±4.06	14.72±2.19	167.29 ±2.21	0.05±0.01	4.64±0.40
EAM2	2293.74 ±20.36	20.26±2.47	6.94±0.42	509.12±32.58	5791.40±78.83	10.46±1.63	3.33±0.01	9.29±0.59	4.89±0.92	3.68±0.06	0.05±0.05	3.96±0.37
BAM2	449.26 ±14.08	2.22±0.41	0.46±0.03	108.13±4.39	607.53±16.63	1.92±0.51	1.04±0.22	2.48±0.16	2.81±0.37	0.24±0.12	0.03±0.01	2.44±0.51
WTB2	717.71 ±52.81	1.73±0.28	2.73±0.57	9.22±0.47	1048.15±87.09	0.23±0.20	0.28±0.08	0.65±0.11	0.82±0.16	0.25±0.02	0.01±0.00	1.21±0.08

Table 31: Mean Concentrations (mg/kg) of the Metals in Pristine Soils during the Wet Season (Bioavailable metals in 2016)

Site & Depth	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Pristine	0-20cm											
AOD	1081.58±54.16	1.87±0.56	1.90±0.00	82.15±10.45	1869.33±54.68	2.21±0.18	0.65±0.03	2.72±0.71	2.24±0.70	1.25±0.52	0.02±0.01	1.72±0.31
EA	2708.94±31.03	23.18±3.69	8.19±0.76	723.41±30.39	7599.86±164.53	16.36±1.11	9.24±0.45	18.83±0.83	16.52±0.93	0.86±0.00	0.03±0.00	5.25±0.3
BB	834.31±45.73	7.84±2.06	1.42±0.14	158.77±18.07	1188.19±17.37	4.45±0.48	2.23±0.76	4.45±0.24	4.17±0.83	0.29±0.02	0.02±0.02	1.78±0.51
WA	1462.71±15.07	0.92±0.07	1.65±0.14	6.51±1.21	1707.05±32.22	0.13±0.05	0.35±0.02	0.47±0.07	1.84±0.31	0.27±0.05	0.02±0.00	2.01±0.27
GSH	1676.95±11.69	9.92±1.02	2.21±0.16	195.38±10.38	800.45±8.34	7.04±1.01	4.45±0.47	2.37±0.17	3.45±0.37	ND	ND	1.22±0.01
NM	890.77±13.84	3.73±0.48	1.41±0.33	225.75±9.98	1596.92±12.20	2.96±0.16	2.63±0.74	2.87±0.65	3.17±0.16	0.05±0.07	ND	2.61±0.15
CK	1708.64±67.18	2.03±0.19	3.12±0.18	8.59±0.74	1482.30±39.05	0.15±0.01	0.57±0.06	3.14±1.08	1.09±0.14	ND	ND	4.82±0.34
VKP	3637.79±11.48	33.65±3.65	55.90±3.86	710.06±15.09	5169.35±16.30	26.31±0.66	55.23±3.17	21.79±2.51	6.89±0.37	0.11±0.3	0.02±0.02	5.37±0.37
Pristine	20-40cm											
AOD2	1822.71±20.24	0.89±0.00	2.65±.04	9.15±0.16	1611.83±23.37	0.11±0.00	0.07±0.03	2.00±0.11	1.62±0.00	0.76±0.02	ND	2.71±0.12
EA2	2512.85±26.05	18.62±0.49	7.34±0.83	500.97±13.44	5959.62±80.74	13.18±1.08	7.28±0.12	13.06±2.57	17.01±2.55	2.21±0.30	0.04±0.01	4.67±0.24
BB2	1206.86±27.75	11.87±2.12	3.03±0.17	231.88±7.50	3588.38±32.34	5.38±0.16	3.09±0.14	6.13±0.36	7.01±0.54	0.12±0.02	ND	2.18±0.13
WA2	1605.66±11.32	1.18±0.02	1.44±0.02	4.48±0.54	1713.99±17.42	0.09±0.06	0.07±0.02	0.24±0.02	0.41±0.18	0.20±0.03	0.01±0.00	2.05±0.13
GSH2	2189.33±74.17	27.69±2.62	3.28±0.65	285.25±26.46	1693.50±12.20	12.71±1.09	8.35±0.66	7.67±0.38	3.14±0.15	0.03±.03	0.06±0.01	1.14±0.02
NM2	1325.61±15.86	4.64±0.35	1.48±0.06	210.02±12.41	1744.79±13.69	3.52±0.15	2.29±0.18	3.39±0.55	2.10±0.01	ND	ND	3.60±0.36
CK2	1523.27±14.23	2.48±0.04	2.34±0.29	90.26±11.71	803.98±9.85	2.11±0.19	1.01±0.23	4.84±0.37	1.25±0.18	0.02±0.02	ND	5.49±1.86
VKP2	3907.02±115.55	40.38±3.78	78.52±2.73	805.68±34.46	5609.65±11.52	34.32±1.74	91.59±3.09	21.19±1.36	7.09±0.64	0.11±0.03	0.03±0.00	3.66±0.36

Heavy Metal Concentrations in Soils by Aqua Regia

The total recoverable metals (Tables 32-35) for the dry and wet seasons were fairly distributed in the pristine and the mining areas. The highest mean concentrations of the geogenic metals metals (Al, V, Cr, Mn, Fe, Co and Ni) were found in the pristine sites, with majority of the elements recorded in site VKP with concentrations 82284.96±27.43, 177.36±8.71, 2298.50±41.71, 3478.15±31.59, 86859.36±47.07, 128.97±3.01 and 533.64±7.74 mg/kg respectively in the wet season and 80720±143.40, 176.7±7.82, 2400±86.71, 3456.5±116.95, 87060±161.34, 134.83±8.01 and 6322.5±92.74 mg/kg respectively in the dry season. For the total recoverable metals, it was observed that Cr, Mn and Co had their maximum values recorded from site VKP while V and Fe recorded their highest concentration at site EA.

Concentrations of Zn, As, Pb and Cr in soils from the Pristine and the mining sites are displayed on map showing metal levels (Figure 10).

The high values of the natural geogenic metals recorded from site EA and VKP can be attributed to the soils physico-chemical properties such as % OC, pH and soil texture (Table 15). Also, the high levels of the metals at site VKP in the pristine areas may be due to inputs from river flows associated with watershed's geology (Álvarez-Vázquez, 2013).

The maximum concentrations of the anthropogenic metals (Cu, Zn, As, Cd and Pb) were found in both the mining (AOB and BAM) and the pristine (EA) sites, with concentrations of 65.03±1.43, 108.66±4.83, 379.89±20.85, 0.15±0.02 and 15.37±1.75 mg/kg respectively in the wet season and

135.98±7.57, 116.8±0.85, 405.8±22.01, 0.21±0.07 and 18.90±2.12 mg/kg respectively in the dry season.

In the mining areas samples from site AOB recorded the highest metal concentrations for most of the metals including As. The high As levels in the mining areas especially at site AOB which is dominated by both commercial and illegal mining activities confirms the report that contaminated soils such as mine-tailings were potential source of As exposure (Liu *et al.*, 2005).

Research reports have also shown that heavy metals in soils which were covered with mine tailings greatly exceeded the maximum allowable concentration with As showing increase of 24-fold (WHO, 2001). Similar high levels of As, Cu, Pb and Zn were reported by some earlier researchers around Obuasi mining areas (AOB) of Ghana (Antwi-Agyei *et al.*, 2009; Amonoo-Neizer *et al.*, 1995; Asiam, 1996; Smedley, 1996; Smedley *et al.*, 1996; Ahmad & Carboo, 2000; Kumi-Boateng, 2007). In general, natural geogenic elements are more enriched in the 20-40 cm depth layer of the soil than the 0-20 cm depth while the anthropogenic metals are more enriched in the 0-20 cm depth than the 20-40 cm depth.

The results were also compared with various guidelines (Table 27) for safe limit for heavy metals in soils (FAO/ISRIC, 2004; USEPA, 2010 and Wedepohl, 1995). The concentrations of Al from the pristine and the mining areas during the study seasons were below the average shale values except at site CK (80720±143.40, 82284.96±27.43 mg/kg) where the concentration was above the guideline limit. The concentrations of Cd and Pb in the pristine and the mining sites at 0-20 cm and 20-40 cm depth were below all the recommended guideline values (Table 29). The concentrations of V at sites

AOB, EAM, BB, EA, GSH and VKP at 0-20 and 20-40 cm depth were above the guideline limits (Table 27). The level of Cr at all sites at 0-20 and 20-40 cm were above the guideline limits except sites WA and NM. The concentration of Mn was above the USEPA guideline limit in the pristine and the mining areas. However, only sites EAM, EA, BB, GSH and VKP recorded Mn levels above the Average Shale levels. The concentration of Ni was substantially higher than the guideline limits of both FAO/ISRIC, (2004) and Wedepohl, (1995). The concentration of Cu was generally above the Shale values at 0-20 and 20-40 cm depth except sites WTB, GSH, AOD and WA. Comparing the concentrations of Cu with FAO/ISRIC (2004), and USEPA (2010), only the concentrations of Cu at sites AOB and VKP at 0-20 and 20-40 cm depth were above the guideline limits (Table 27). The concentrations of Zn at all sites in the pristine and mining sites were below the Average shale values except those from sites AOB, EAM, EA and GSH which had values above the shale guideline limits. However, when the concentration of Zn was compared with FAO/ISRIC (2004) and USEPA (2010), values, the levels in layers 0-20 and 20-40 cm depth, were far below the recommended guidelines.

The results were also compared with the world average heavy metals concentrations reported by Bowen (1979) to be 0.35, 30, 35 and 90 mg/kg for Cd, Cu, Pb and Zn respectively. The results showed that the concentrations of Cd, Pb and Zn from this study were below the world average concentrations from all the sites in the pristine and the mining area except the concentration of Zn from site BB. The concentrations of Pb from all sites were below the worldwide average Pb concentration of 32 mg/kg (Kabata-pendias, 2007).

Table 32: Mean Concentrations (mg/kg) of the Metals in Mine Soils during the Dry Season (total metals, 2014)

Site	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Mining	0-20cm											
AOB	38900 ±562.85	54.185±0.25	70.63±5.10	270±10.84	24970±71.98	7.73±0.70	5665.5±16.90	121.27±0.66	51.43±2.68	405.8±22.01	0.08±0.03	10.75±14.35
EAM	59500 ±44.55	114.75±0.83	99.32±0.87	881.95±8.98	47265±28.14	22.67±0.24	4947±81.53	32.66±3.02	72.54±1.60	18.99±0.35	0.10±0.01	13.35±1.06
BAM	17075 ±141.42	25.01±1.34	34.38±3.37	202.55±12.91	9495±16.47	4.77±0.62	5200.5±31.11	28.95±0.89	19.68±0.75	0.21±0.02	0.07±0.03	18.90±2.12
WTB	16985.5 ±134.27	21.29±0.56	44.45±2.55	103.33±5.59	9707.5±63.81	2.24±0.16	5300.5±12.94	3.89±0.61	14.82±5.28	4.01±00.62	0.11±0.04	4.00±0.43
Mining	20-40cm											
AOB	28545 ±109.39	40.61±6.65	55.35±8.95	166.27±10.16	18550±93.90	5.87±0.13	5713.5±15.62	32.55±1.11	35.4±1.96	341.15±30.01	0.07±0.05	13.10±1.13
EAM	72735 ±579.83	144.95±1.17	118.95±0.23	1225.5±30.76	60070±341.53	29.46±0.13	4991.5±26.51	44.5±1.54	81.48±0.93	28.73±0.88	0.09±0.03	10.31±0.65
BAM	16540 ±218.49	26.24±1.33	34.59±1.20	179.85±5.30	9098.5±224.60	5.56±0.62	5924.5±29.06	7.95±0.99	18.68±1.07	2.55±0.60	0.02±0.01	7.45±0.54
WTB	24265 ±179.11	29.64±4.52	63.08±4.61	64.34±2.12	13886±116.16	1.97±0.29	4937.5±61.44	4.01±0.01	17.69±0.55	3.04±0.17	0.03±0.01	5.65±0.11

Table 33: Mean Concentrations (mg/kg) of the Metals in Pristine Soils during the Dry Season (total metals, 2014)

Site	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Pristine	0-20cm											
AOD	21489.5±259.09	36.01±0.62	36.6±0.54	130.90±11.62	14090±425.78	8.28±0.06	5440.5±48.15	6.66±0.36	16.11±1.70	19.1±0.89	0.05±0.02	4.96±0.49
EA	51970±108.75	174.1±7.96	179.75±4.53	1308±55.51	77935±106.66	40.62±5.13	4891.5±92.34	67.17±2.16	111.6±8.10	52.51±1.75	0.21±0.07	11.41±0.75
BB	32710±295.28	58.66±3.75	69.77±0.97	629.05±4.55	23380±121.97	16.46±0.93	5373±32.52	21.98±1.50	35.62±4.90	0.98±0.02	0.06±0.03	4.85±0.63
WA	53640±373.35	19.245±1.47	18.97±2.87	30.62±2.70	10612±59.75	1.59±0.07	5017±14.77	2.95±0.39	18.65±0.37	5.31±0.36	0.05±0.01	10.95±1.01
GSH	54290±374.67	84.8±1.92	87.74±1.39	1468.5±14.85	60750±52.75	33.79±1.39	5965±39.60	7.49±0.69	54.45±2.95	1.38±0.18	0.04±0.02	1.98±0.12
NM	18945±104.76	26.21±2.01	27.89±4.35	310.1±31.27	11760±228.95	5.23±0.20	6322.5±92.74	6.23±0.62	17.80±0.29	3.95±0.06	ND	6.08±0.44
CK	80720±143.40	57.06±2.43	60.73±0.59	51.63±3.12	31895±80.10	4.06±0.34	4230±34.19	24.53±1.70	31.11±32.57	3.85±0.28	ND	18.35±1.19
VKP	45865±373.35	148.3±1.97	1344.25±69.25	1235.8±43.03	55765±177.90	55.99±0.05	5194±95.17	69.88±1.64	51.23±1.61	ND	0.05±0.03	9.74±1.02
Pristine	20-40cm											
AOD	42265±158.88	50.41±0.24	49.83±0.45	33.79±0.08	21340±165.69	1.43±0.32	4753.5±14.85	9.96±1.27	15.12±1.34	23.03±1.10	0.02±0.01	6.33±0.57
EA	56565±244.83	176.7±7.82	208.65±12.66	1250±29.70	87060±161.34	43.3±0.47	5252±175.58	62.88±4.53	116.8±0.85	62.48±1.63	0.09±0.02	11.42±1.30
BB	34100±141.44	64.29±7.59	75.325±8.70	538.15±12.48	25065±298.10	15.77±1.27	5874±23.52	25.22±1.15	35.79±2.68	5.17±0.34	0.06±0.01	6.25±0.37
WA	55995±158.86	20.16±1.98	20.14±1.60	28.1±2.02	10930±194.97	1.69±0.07	4379.5±41.72	1.24±0.23	17.52±0.64	5.98±00.34	0.03±0.02	12.55±1.23
GSH	61750±222.41	123.06±9.21	98.93±2.29	1574±91.92	67445±89.59	42.69±1.59	4605.5±21.41	32.09±3.98	60.92±4.64	ND	0.09±0.03	3.42±0.57
NM	32280±209.03	47.95±3.61	47.62±2.75	383±19.51	20205±132.22	8.59±0.64	5361.5±103.35	135.98±7.57	30.85±1.64	10.06±1.34	0.03±0.01	7.25±0.15
CK	55015±253.35	44.16±3.74	49.45±7.02	208.56±19.69	22340±102.05	9.97±0.00	3316±71.59	30.77±4.45	31.02±1.69	0.77±0.00	0.02±0.01	5.51±0.22
VKP	46200±200.44	172.7±6.47	2400±86.71	3456.5±116.95	68055±194.90	134.83±8.01	5915.5±26.33	64.66±1.25	59.47±3.13	ND	0.05±0.02	9.48±1.03

Table 34: Mean Concentrations (mg/kg) of the Metals in Mine Soils during the Wet Season (total metals in 2016)

Site	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Mining 0-20cm												
AOB	38227.87±5.11	56.41±1.12	65.33±5.16	265.61±1.02	22916.98±6.15	6.67±0.37	17.98±2.96	64.93±2.69	47.35±2.48	379.89±20.85	0.07±0.01	10.43±0.37
EAM	58620.81±17.68	114.95±3.66	99.19±3.06	894.95±11.98	46389.58±42.20	22.29±0.62	29.41±0.08	31.31±0.87	67.81±1.72	25.39±0.21	0.05±0.00	12.88±0.01
BAM	17462.05±8.47	27.34±0.25	32.66±1.16	201.28±1.08	8755.95±37.64	4.26±0.03	7.23±0.22	8.25±0.13	17.23±0.23	2.00±0.10	0.07±0.02	15.78±0.13
WTB	17214.01±13.78	22.32±1.19	61.26±3.11	103.25±5.14	9364.96±63.12	1.88±0.10	10.41±0.19	4.35±0.46	14.05±0.29	1.85±0.27	0.10±0.01	4.29±0.02
Mining 20-40cm												
AOB	28996.21±9.63	43.34±1.66	53.31±1.81	167.66±3.90	17248.17±80.11	5.60±0.33	14.93±0.51	32.73±2.08	34.51±1.06	327.15±9.01	0.06±0.02	8.07±0.67
EAM	73946.77±93.07	146.47±3.91	119.46±2.51	1242.63±51.26	59006.95±79.06	28.52±1.19	36.42±0.69	42.81±0.79	76.01±0.05	19.34±0.62	0.05±0.00	10.75±0.26
BAM	16787.16±79.46	25.60±0.40	31.52±0.71	160.36±0.18	8539.20±13.96	4.46±0.09	5.99±0.12	7.29±0.09	16.39±0.84	0.95±0.01	0.01±0.01	6.34±0.30
WTB	24095.39±17.69	29.68±1.68	58.65±3.08	64.94±1.15	13182.72±11.21	1.82±0.34	6.59±0.30	4.42±0.21	26.83±2.23	1.53±0.02	0.01±0.02	3.37±0.26

Table 35: Mean Concentrations (mg/kg) of the Metals in Pristine Soils during the Wet Season (total metals in 2016)

Site	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
Pristine 0-20cm												
AOD	34086.21±17.51	39.39±1.73	33.25±0.17	128.57±2.63	13092.11±68.93	4.34±0.47	5.55±0.63	6.87±0.09	14.90±0.48	15.82±0.80	0.02±0.01	4.78±0.11
EA	62577.64±15.46	172.96±3.67	175.93±4.30	1303.74±20.43	77662.48±11.74	38.41±0.91	74.67±1.87	65.03±1.43	103.49±1.96	62.00±0.27	0.15±0.02	11.29±0.17
BB	11990.60±12.48	39.93±00.14	34.56±0.46	524.17±1.84	14917.84±15.78	12.40±0.00	16.43±0.01	16.93±0.34	20.02±1.04	1.37±0.03	0.04±0.00	4.55±0.73
WA	52179.04±40.54	18.02±0.88	17.76±0.12	31.24±0.77	9957.01±67.73	1.17±0.03	4.53±0.02	2.75±0.00	17.02±0.33	1.47±0.01	0.03±0.01	9.79±0.03
GSH	55307.79±20.71	94.50±0.66	86.21±0.68	1478.27±5.32	61283.89±11.43	31.44±0.71	32.20±00.00	9.26±0.58	51.42±0.95	0.56±0.02	0.06±0.00	2.64±0.10
NM	18773.83±33.29	29.83±1.31	25.57±0.22	299.61±4.79	11283.54±89.20	5.079±0.17	7.61±0.07	6.27±0.05	17.09±0.60	2.06±0.09	ND	5.84±0.32
CK	82284.96±27.43	59.03±2.84	55.65±4.70	52.82±0.74	30815.99±53.49	3.55±0.34	16.85±0.25	24.65±0.50	29.37±1.66	2.17±0.38	ND	15.37±1.75
VKP	46747.88±69.60	152.46±0.90	1280.70±0.14	1237.78±0.24	55184.56±51.22	52.59±0.02	259.97±0.08	59.69±0.11	50.64±0.19	1.52±0.01	0.04±0.00	10.52±0.10
Pristine 20-40cm												
AOD	51981.86±74.39	54.02±1.23	44.72±0.24	34.36±0.58	20911.01±23.93	1.09±0.14	4.71±0.32	6.19±0.11	12.80±0.42	15.29±0.30	0.01±0.04	5.21±0.22
EA	57185.53±54.84	177.36±8.71	209.30±9.84	1260.36±16.78	86859.36±47.07	41.29±0.22	63.07±1.18	60.69±0.96	108.66±4.83	54.35±0.35	0.13±0.03	10.89±0.63
BB	32841.40±42.81	68.46±2.61	68.12±0.94	513.21±3.91	24268.79±36.23	15.03±0.14	23.22±0.75	25.07±0.07	32.94±0.63	1.45±0.08	0.05±0.00	6.18±0.40
WA	54860.85±26.87	18.70±0.54	19.19±0.56	28.78±0.85	10439.41±29.30	1.13±0.10	4.93±0.46	1.48±0.19	16.62±0.64	1.41±0.05	0.03±0.00	11.09±0.67
GSH	61055.36±48.97	131.71±5.33	95.59±5.06	1549.29±17.71	65380.20±10.36	39.95±2.02	44.87±0.22	31.95±0.35	57.57±1.61	0.50±.05	0.07±0.00	2.36±0.14
NM	32458.56±25.58	50.41±0.77	43.23±1.03	362.68±2.67	18465.62±11.82	7.86±0.18	12.40±0.19	10.50±0.70	22.25±0.0.37	3.29±0.17	0.01±0.02	8.88±0.66
CK	54647.81±43.25	46.46±1.51	44.68±0.67	198.68±3.16	21371.59±17.63	5.99±2.41	14.27±.94	30.31±3.14	29.76±1.21	0.99±0.02	0.01±0.00	5.21±0.53
VKP	48489.06±82.43	175.59±1.42	2298.50±41.71	3478.15±31.59	69047.78±32.17	128.97±3.01	533.64±7.74	65.28±0.60	61.92±1.24	1.39±0.17	0.04±0.01	8.50±0.31

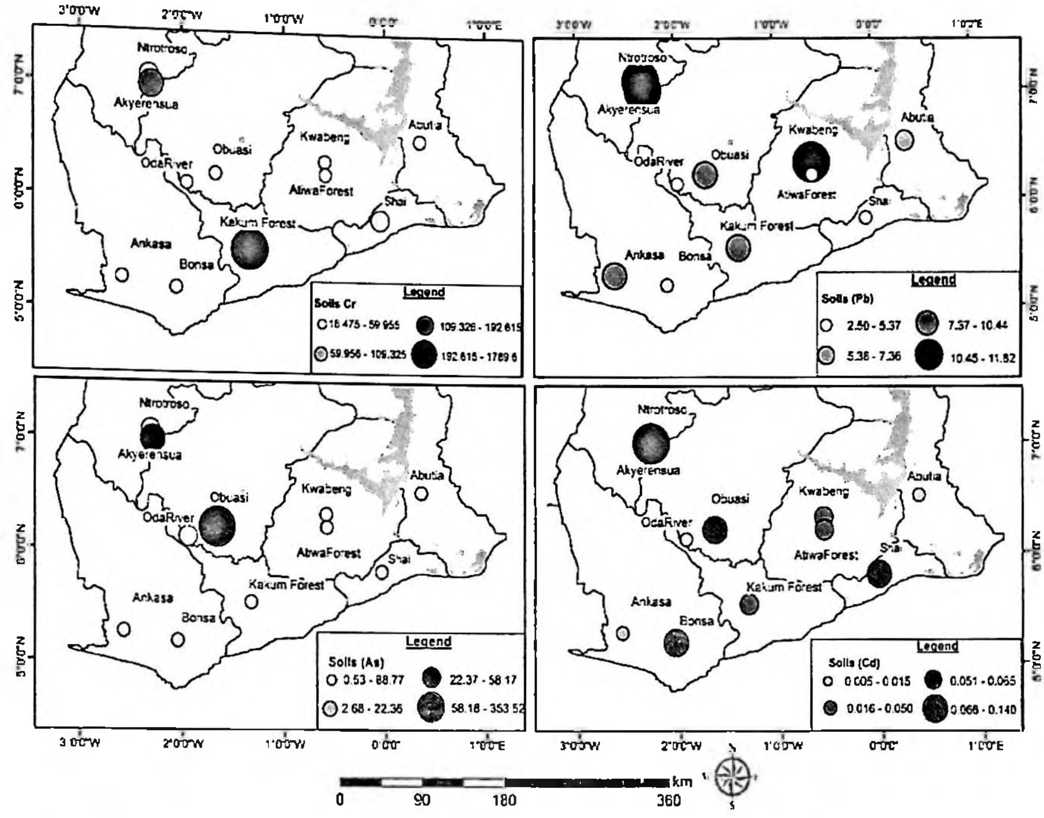


Figure 10: Concentrations of Zn, As, Pb and Cr in Surface Soils from the Pristine and the Mining areas.

Statistical Analysis of Heavy Metals in Soils and Sediments Water

Statistical analysis of metals in the water samples

The statistical analysis was conducted to identify possible correlations and variabilities in the heavy metal levels in rivers from the mining and the pristine sites. The Cluster analysis was employed with two main groups of metals. Cluster 1 comprised of V, Co, Cr, Ni, Pb, Cu, Zn and As with some association with Mn and Cluster 2 comprised of Fe and Al also with some association with Mn. The occurrence of metals such as Pb, Co, Zn, Cu, As and Cr indicate anthropogenic activities around the study sites as shown in Figure 11. The PCA analysis also identified two main components which were significant with eigenvalues greater than 1.0. Both components accounted for 88.6 % of the total variance (Appendix G). Component 1 accounted for 74.1 %

of the total variance and are associated with V, Fe, Al, Co, Pb, Cu, Zn, Ni and Cr. Components 2 accounted for 14.5 % of the total variance and have high Mn and As loadings as shown in Figure 12 and (Appendix G).

The association of metals in the PCA analysis was confirmed with the correlation results in which As and Mn correlated weakly with all other metals except Fe (0.76) as shown in Table 36. The association of Mn and As could be due to co-precipitation of the two elements in the environment, caused by manganese hydroxides and oxides in clay minerals. (Takamatsu, Kawashima, & Koyama, 1985). Component 1 which explain majority of the total variance (74.1 %) had strong loadings on Fe, Al, Pb, V, Cu, Zn, Co, Ni, and Cr. The presence of metals like Pb, Cu, Co, Ni, Zn and Cr suggest that anthropogenic mining activities in the study areas might have contributed to the strong loading of the metals (Prego & Cobelo-García, 2003).

Component 2 had strong loading of As and moderate loading on Mn suggesting that As and Mn may be emanating from the same source.

Two-way ANOVA results indicate significant difference between the heavy metal concentrations and the various sampling sites studied since the probability associated with the *p*-value for metals (p = 0.05) is less than 0.05 (F=2.89, Fcrit=1.99) and *p*-value (p = 0.015) for the sites is also less than 0.05 (F=2.37, Fcrit=1.94). The statistical study suggests anthropogenic activities as mining may be a major source of metal contamination of the rivers.

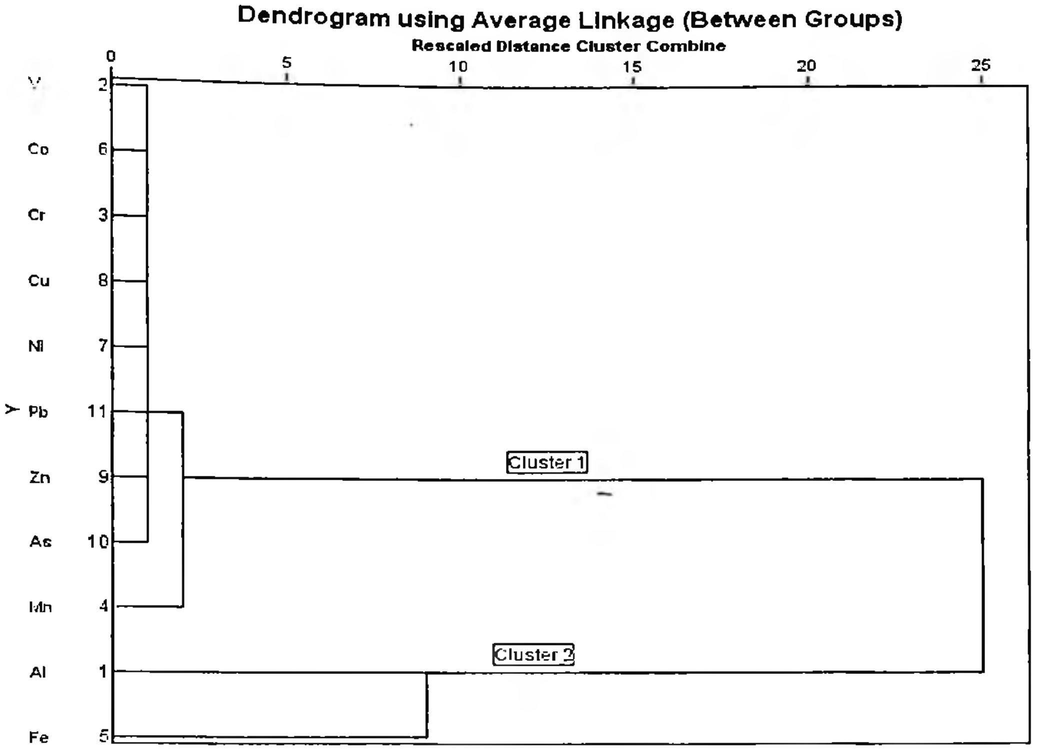


Figure 11: Dendrogram Showing Clustering of Metals in Rivers from Pristine and Mining Sites.

Table 36: Correlation Matrix of Selected Metals in Water samples from Pristine and Mining sites, n=44

Correlations											
	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Pb
Al	1										
V	.921*	1									
Cr	-.053	-.074	1								
Mn	.244	.429	-.063	1							
Fe	.740*	.832*	-.058	.755*	1						
Co	.943*	.953*	-.063	.490	.847*	1					
Ni	.498	.529*	-.110	.437	.543*	.558*	1				
Cu	.965*	.936*	-.055	.259	.709*	.957*	.510*	1			
Zn	.553*	.418	-.041	.010	.331	.415	.272	.441	1		
As	.042	-.039	-.050	.348	.052	.123	.156	.073	-.088	1	
Pb	.967*	.896*	-.058	.159	.658*	.929*	.446	.984*	.440	.040	1

Values with astericks (*) are significant at p=0.05

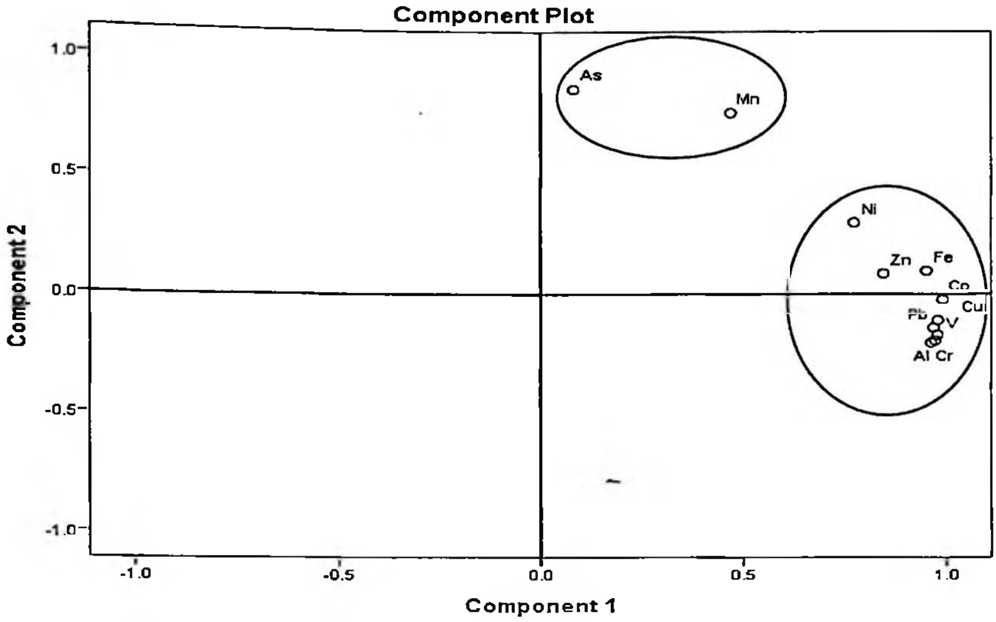


Figure 12: Component Plot showing Metals and metalloid Loadings on Components from pristine and Mining sites.

PROMETHEE and GAIA Analysis of the Metals in Sediment

For meaningful ranking and pattern recognition, all objects (sites) and variables (metals) from this study were subjected systematically to PROMETHEE and GAIA analysis. The PROMETHEE II complete ranking (Figure 13) presented the sites in the order of most preferred to the least preferred as; CK > AOD > NM > EA > VKP > WA > BB > WTB > AOB > BAM > EAM. The order shows that heavy metal concentration from pristine sites are the least contaminated area. The site with the least metal contamination is Kakum river (CK) (pristine site) while the site with the most contaminated river is Birim river (EAM (mining site). On the other hand, the GAIA results showed that approximately 81.9 % of the variance is explained by the first two principal components (PCs).

The GAIA plot (Figure 15) identified groupings of the heavy metals which correlated well with that obtained from the PCA analysis. It can be established that loading vectors for all the metals correlated with one another except As which is almost at 90° to Cr and thus independent of Cr (Keller, Massart, & Brans, 1991; Brans & Mareschal; Espinasse, Picolet, & Chouraqui, 1997). Mn showed close association with As and the same grouping was seen in the cluster analysis. GAIA plot of the sampling sites in Figure 14 showed the decision axis (Pi) pointing towards the pristine sites, confirming that water samples at these sites are the least contaminated and they include WAW, EAW, BBW and AODW. River Birim (EAMW) is the farthest and also opposite to the decision axis which indicates that it is the most contaminated and least preferred river followed by river Nyam (AOBW), river Bonsa (WTBW) and finally river Subri (BAMW) all from mining sites as shown Figure 13. The results also showed that anthropogenic activities such as mining may be contributing to heavy metal contamination of the rivers.

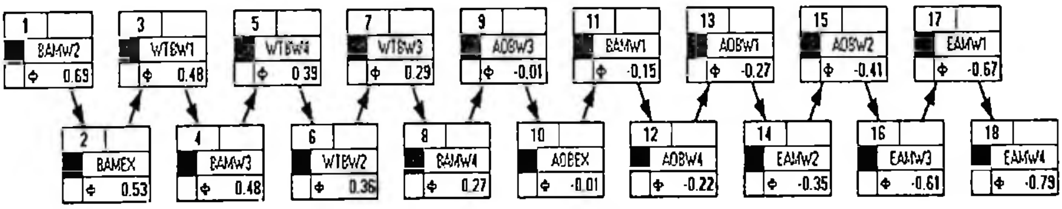


Figure 13: PROMETHEE 2 outranking of Sites based on the Metals Concentration in Water from Mining and Pristine Sites.

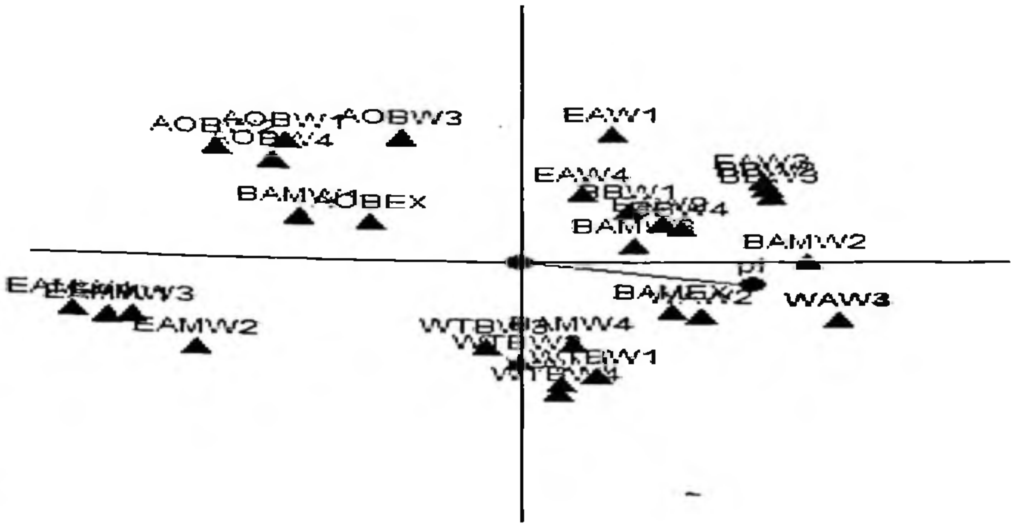


Figure 14: GAIA Plot of Site Distribution based on the Metals Levels in Water samples from Pristine and Mine Sites.

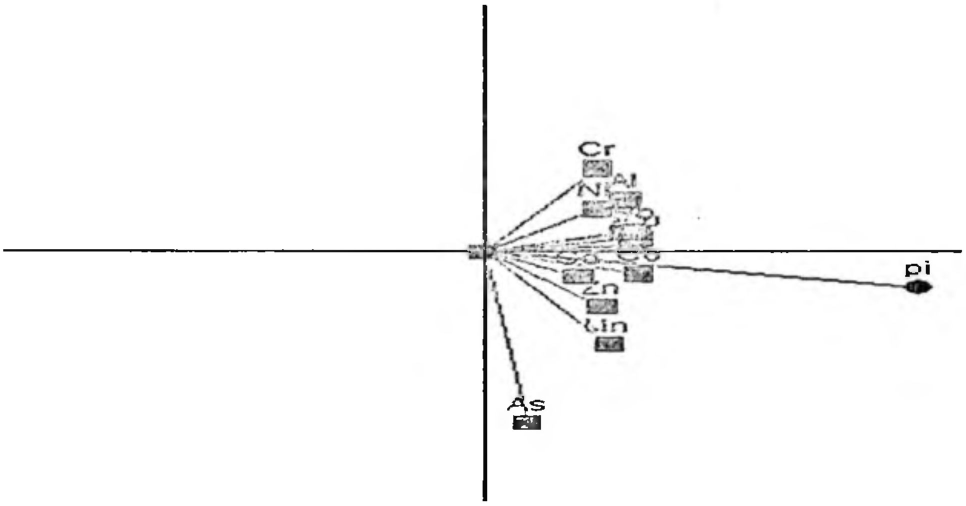


Figure 15: GAIA Plot showing the Metals and Metalloid Deviation from the Decision Axis.

Statistical Analysis of Heavy Metals in the River Sediment

Cluster, principal component and correlation analyses were applied to the data to identify possible patterns and variabilities in heavy metals concentrations in the sediment samples. The cluster analysis, identified two main groups of metals as shown in Figure 16. For the aqua regia extractable metals, Cluster 1 comprised V, Co, Cr, Ni, Pb, Cu, Zn, Mn and As and Cluster

2 comprised Fe and Al. The association of metals such as Pb, Co, Zn, Cu, As and Cr indicate that these metals may have anthropogenic contribution through mining activities around the study areas. Nevertheless, most of the metals in cluster one are predominant at the mining sites. The association of Fe with Al in cluster 2 suggests natural geogenic origin of these metals (Álvarez-Vázquez, 2013).

The principal component analysis (PCA) from the total recoverable metals identified two components as seen with the cluster analysis in Figure 17. Component 1 comprised Al (0.67), V (0.99), Cr (0.77), Mn (0.84), Fe (0.93), Co (0.83), Ni (0.79), Cu (0.96), and Pb (0.76). Component 2 comprised of metal loading of As (0.89) with minor contributions from Zn (0.54), Pb (0.49) and Cd (0.55). The major and the minor enrichment of the metals from the sites show that both the threshold and the non-threshold metals may have more than one source (possibly natural geogenic and anthropogenic sources). The components which were significant with eigenvalues greater than 1 accounted for total percent variance of 78.53 % (Appendix F). The results suggest that the levels of Zn, Pb, Cd and As at the sites may have anthropogenic influence whiles the rest of the metals may be coming from natural sources.

The results from the correlation analysis confirm metals association from the PCA analysis in which Al, V, Cr, Mn, Cu, Fe, Co and Ni correlated strongly with each other but weakly with Zn, As and Cd. Arsenic correlated inversely with all the metals except Zn, Cd and Pb confirming their common anthropogenic origin. It further suggests that As, Zn, Pb and Cd occurrence at the study sites might have arisen through mining activities even though the concentrations of some of the metals were below the recommended guideline limits (Armah *et al.*, 2010).

A Pearson correlation matrix was also performed to establish the relationships of three physico-chemical parameters with the metals in the sediment samples. The association of pH with the total recoverable metals which presented weak but inverse correlation for all metals except Cr and Ni was observed (Table 37). The results show that an increase in pH will cause a corresponding decrease in metal adsorption in the sediment samples. The inverse correlation between pH and Zn, As, Cd and Pb is suggestive of the fact that these metals have common anthropogenic origin because among heavy metals, an increase in pH affects the adsorption of many metals including Cu, Pb, Cd and Zn (Sako, Lopes, & Roychoudhury, 2009; Abd-elfattah & Wada, 1981).

The EC for the total extractable metals and weak acid extractable metals presented weak and inverse correlation for all the metals except As, Cd, Zn, Cu and Pb with total variability in metal concentration explained by 97.0 % (r^2 = 97.0 %, p = 0.39) which confirms the anthropogenic origin of these metals since they are bioavailable and are easily desorbed from soils surface into soil solution (Mclaren, Clucas, Taylor, & Hendry, 2004; Rubio, Nombela, & Vilas, 2000).

The percent OC (%OC) correlated weakly with all the metals with the variability in the metals concentrations explained by 46.5 % (r^2 = 46.5 %, p = 0.65) explaining the variability in the metals concentrations. The %OC for the aqua-regia and weak acid extraction methods presented weak and inverse correlation for all the metals except Ni and Co with total variability in the metals concentrations explained by 99.7 % ($r^2 = 99.7$ %, $p = 0.12$). In all, pH, EC and %OC significantly influence the concentrations of the heavy metals content as shown in Table 16.

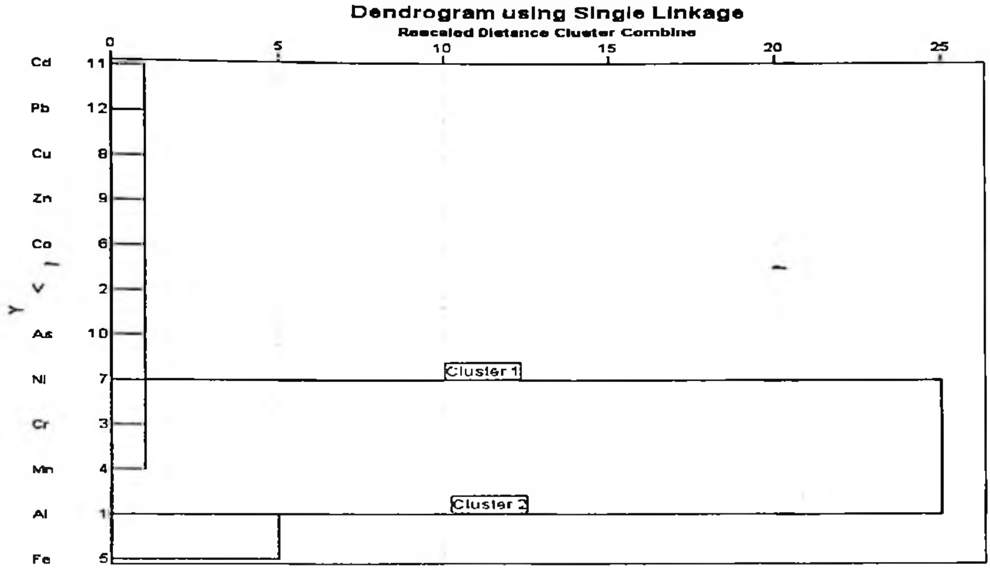


Figure 16: Dendogram showing the Clustering of the Metals in River Sediments from the Pristine and the Mining Areas.

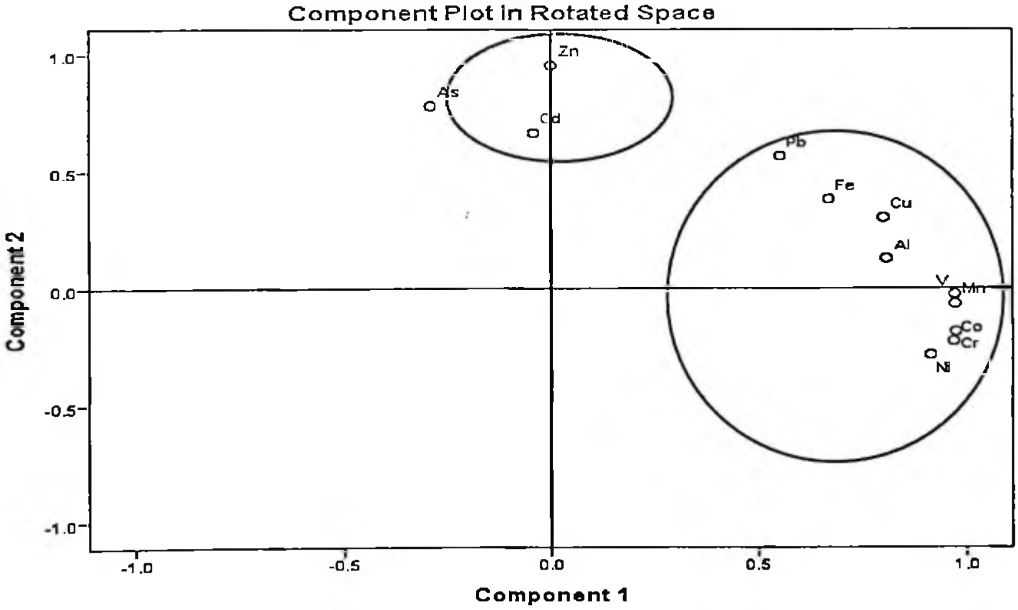


Figure 17: Component Plot of the Metals Loadings from Pristine and Mining Areas.

Table 37: Pearson's Correlation Matrix between pH, EC, %OC and the Heavy Metals in Sediment Samples

	pH	EC	%OC	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
pH	1.000														
EC	-.706	1.000													
%OC	-.230	.430	1.000												
Al	-.312	.459	.157	1.000											
V	-.261	.248	.165	.728	1.000										
Cr	.025	-.214	-.039	.098	.713	1.000									
Mn	-.048	-.118	-.009	.193	.797	.973	1.000								
Fe	-.388	.489	.255	.838	.951	.509	.624	1.000							
Co	-.019	-.150	-.006	.188	.790	.987	.997	.605	1.000						
Ni	.023	-.212	-.039	.126	.736	.999	.980	.532	.992	1.000					
Cu	-.340	.281	.256	.721	.979	.649	.746	.929	.737	.676	1.000				
Zn	-.543	.629	.373	.767	.784	.221	.388	.877	.351	.254	.845	1.000			
As	-.723	.410	.317	-.054	-.117	-.124	-.142	-.073	-.143	-.128	-.010	.169	1.000		
Cd	-.629	.734	.411	.592	.602	.202	.253	.680	.251	.216	.658	.781	.443	1.000	
Pb	-.361	.491	.155	.813	.743	.388	.442	.834	.439	.396	.673	.618	.050	.523	1.000

PROMETHEE and GAIA Analysis of the Heavy Metals in Sediments

The PROMETHEE II complete ranking presented in Figure 18 is in the order of most preferred to the least preferred (most contaminated) as; WA > AOD > CK > BBT > VKP > NM > BAM > WTB > EA > EAM > AOB. The order shows that the sediments from rivers in the pristine areas (WA, AOD, CK, BB, VKP and NM) are less contaminated with heavy metals than sediments samples from the mining areas (AOB, BAM, EAM and WTB). The site with the least metal contamination is site WA (pristine) and the most contaminated sediment is site AOB.

On the other hand, GAIA results showed that approximately 79.40 % of the variance is explained by the first two principal components (PC1 and PC2). The GAIA plot identified groupings of the heavy metals which correlate well with that obtained from the PCA analysis as shown in Figure 20. It can be established that loading vectors for all the metals correlate well with one another except As. Mn showed close association with Co, Ni, Fe, V and Al as shown in the Pearson correlation matrix and cluster Dendrogram in Figure 16 and Table 37. GAIA plot of the sampling sites (Figure 19) showed the decision axis (Pi) pointing towards the pristine dominant sites, suggesting that the sediment samples from pristine sites are least contaminated. Sediment samples from sites AOB, EAM and EA appears to be the most contaminated and least preferred sites. However, those forest reserves which are close to minor and major mining areas and where illegal mining activities take place like sites EA, BB and AOD experienced appreciable loading of the heavy metals. The results also showed that anthropogenic activities such as mining and the use of agro-chemicals may be impacting negatively on heavy metal contamination along the mining areas.

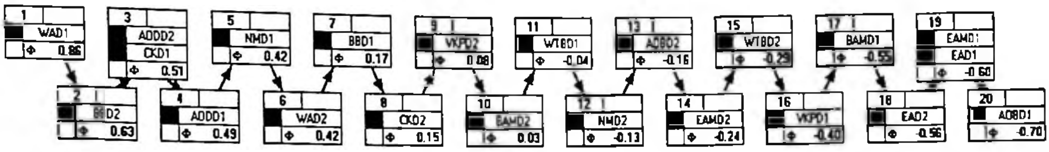


Figure 18: PROMETHEE 2 outranking of Sites based on the Metals Concentration in Soils from Pristine and Mine Sites.

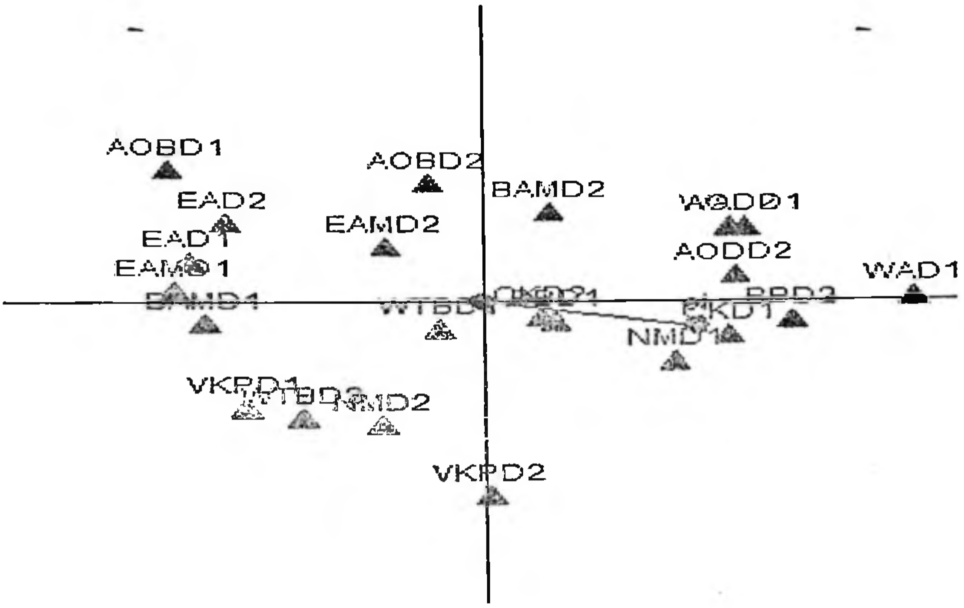


Figure 19: GAIA Plot of site Distribution based on the Metals Concentrations in Soils from Pristine and Mine Sites.

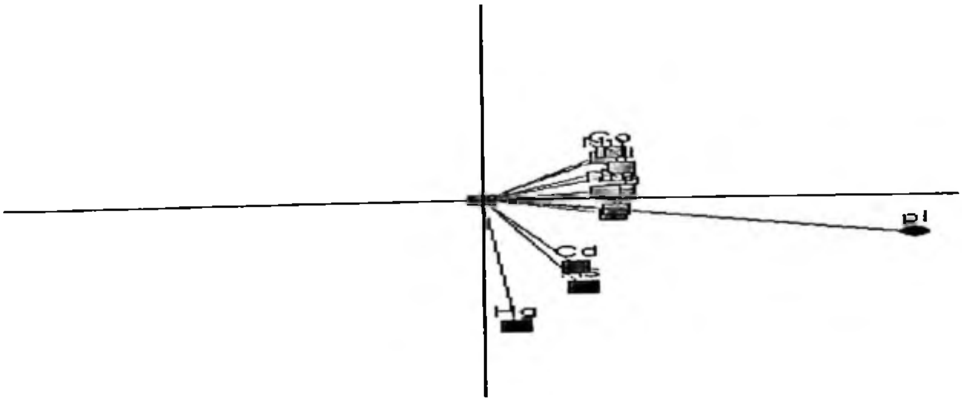


Figure 20: GAIA Plot showing the Metals Deviation from the Decision Axis for Soil Samples from Pristine and Mine areas.

Statistical Analysis of Heavy Metals in Soil samples

The experimental data was analyzed by using Cluster, PCA and correlation to explain as much of the total variance and covariance in the concentrations of the heavy metals measured in soil samples from pristine and the mining areas. The cluster analysis, identified two main groups of metals as shown in Figure 21. Cluster 1 comprised of V, Co, Cr, Ni, Pb, Cu, Zn, Mn and As. Cluster 2 comprised of Al and Fe. The association of metals such as Pb, Co, Zn, Cu, As and Cr suggest that the metals may be released from common anthropogenic sources such as gold mining and farming activities. Nevertheless, most of the metals in cluster one are predominant in the mining sites (Jung and Thornton, 1997). The occurrence of Fe and Al indicates natural geogenic enrichment of these metals (Álvarez-Vázquez, 2013).

The PCA analysis identified two components which were significant with total percent variability of 79.02 % as shown in (Appendix F) and Figure 22. Component 1 accounted for 54.37 % of the total variance and include V, Fe, Al, Mn Co, Ni and Cr. The second component accounted for 24.65 % of the total variance and include Cu, Zn, Cd, Pb and As. Chromium has anthropogenic sources especially in its use in alloys, leather tannings, refractory bricks and pigments. However, this study has indicated that Cr may be naturally enriched in Ghanaian soils especially at site VKP.

The association of the metals from the PCA is similar to the correlation results obtained in which As, Zn, Cu, Cd and Pb showed strong positive correlation indicating their common anthropogenic sources which might have arisen from mining activities (Armah *et al.*, 2010). The concentration of As from site AOB was very high (379.89 mg/kg). High levels of As in soils around site AOB (Obuasi mining area), was reported elsewhere (Antwi-Agyei, 2009). Relatively high levels (25 mg/kg) of As was measured in samples from site BAM. Arsenic correlated inversely (negatively) with all metals except Cu, Zn, Cd and Pb suggesting their common anthropogenic sources.

Correlation of pH with the total recoverable metals presented weak but positive correlation for all metals except As, Cd and Pb (Table 38) which indicates that these metals have common input sources.

The % OC correlated weakly with all the metals. Here also, the pH and EC significantly influence the concentrations of the heavy metals than the % OC content which explains the anthropogenic sources of these metals (As, Cu, Cd, Zn and Pb) since they are bioavailable and are easily desorbed from soils surface into soil solution (Mclaren, 2004; Rubio *et al.*, 2000).

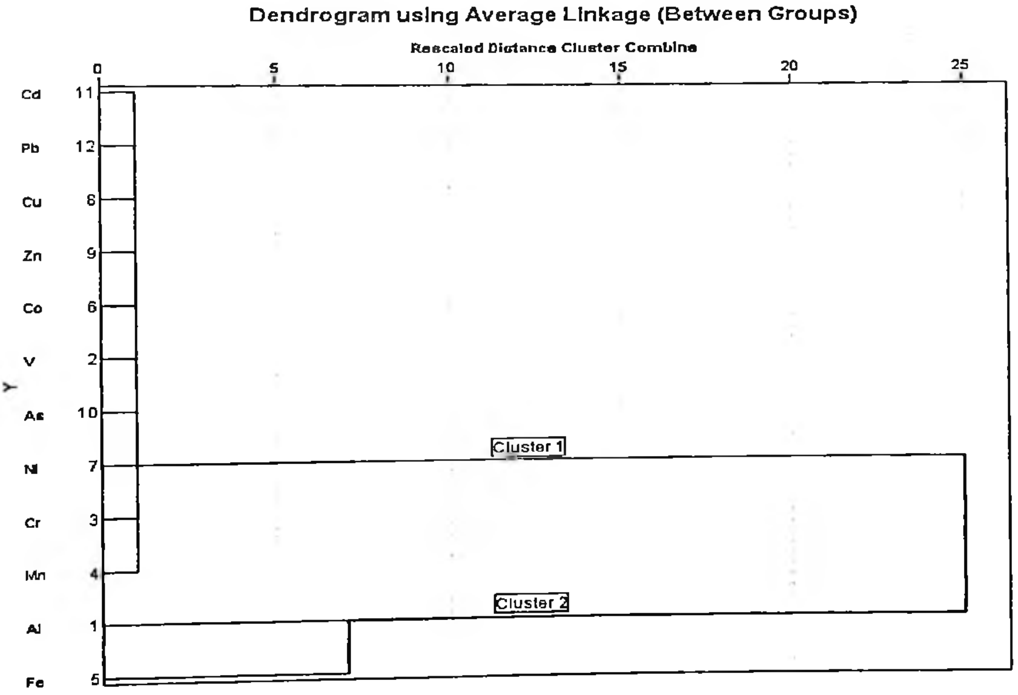


Figure 21: Dendrogram showing Clustering of Metals in Soils from the Pristine and Mining Sites.

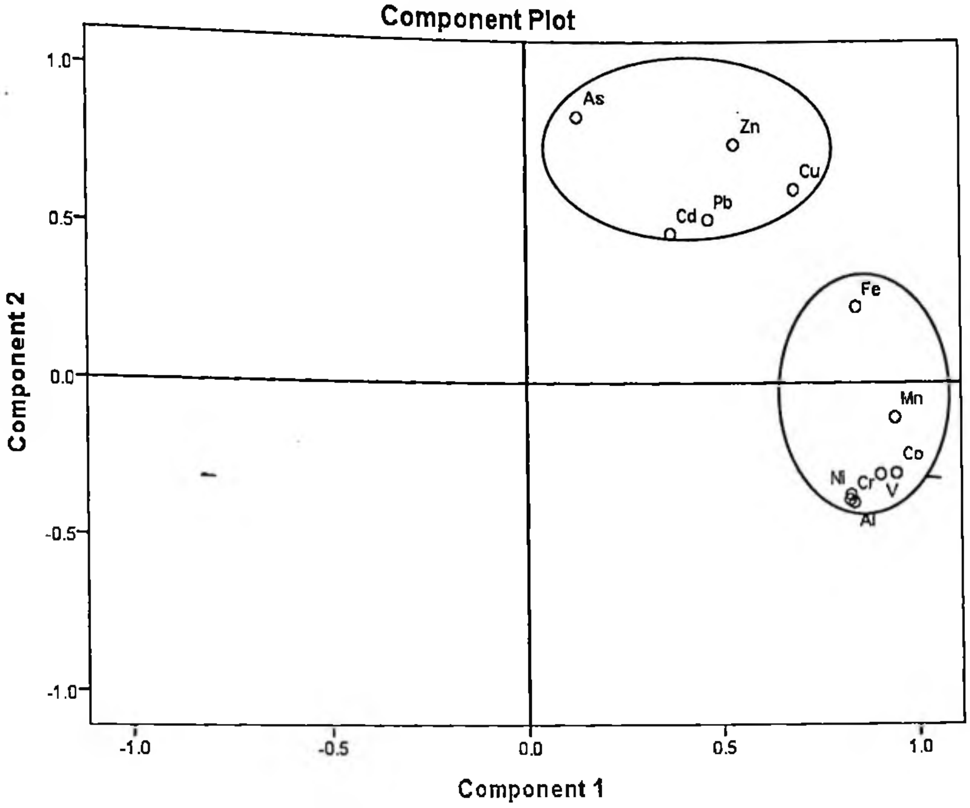


Figure 22: Component Plot of Metal Loadings on Components from Pristine and Mining sites.

Table 38: Pearson's Correlation Matrix between pH, EC, %OC and the Metals in the Soils

	pH	EC	%OC	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
pH	1														
EC	-0.843	1													
%OC	0.051	0.077	1												
Al	0.44	-0.372	0.054	1											
V	0.412	-0.388	0.005	0.567	1										
Cr	0.311	-0.441	0.004	0.116	0.565	1									
Mn	0.397	-0.42	0.01	0.335	0.836	0.792	1								
Fe	0.428	-0.379	0.067	0.626	0.968	0.448	0.807	1							
Co	0.377	-0.45	-0.016	0.287	0.799	0.901	0.973	0.738	1						
Ni	0.316	-0.44	-0.006	0.152	0.612	0.995	0.839	0.504	0.935	1					
Cu	0.015	-0.116	0.083	0.409	0.818	0.546	0.64	0.745	0.666	0.581	1				
Zn	0.245	-0.181	0.007	0.557	0.909	0.281	0.654	0.926	0.583	0.342	0.806	1			
As	-0.589	0.414	0.224	-0.081	-0.036	-0.102	-0.128	-0.045	-0.115	-0.097	0.411	0.15	1		
Cd	-0.115	0.207	0.195	0.129	0.539	0.024	0.34	0.584	0.277	0.079	0.532	0.702	0.264	1	
Pb	-0.268	0.359	-0.08	0.356	0.199	0.1	-0.005	0.136	0.052	0.099	0.336	0.273	0.148	0.177	1

PROMETHEE and GAIA Analysis of the Heavy Metals in Soils

The PROMETHEE II complete ranking presented in Figure 23 has the order of most preferred (least contaminated) to the least preferred (most contaminated) sites as; NM > WA > BAM > WTB > AOD > CK > BBT > GSH > AOB > VKP > EA > EAM. The order shows that heavy metal levels in soils from pristine areas are the most preferred to the levels from the mining areas. The site with the least metal contamination is NM (pristine site) and the most contaminated site is EAM. On the other hand, GAIA showed that approximately 72.83 % of the variance is explained by the first two principal components (PCs). The GAIA plot (Figure 25) identified groupings of the heavy metals which correlate well with that obtained from the PCA analysis (Figure 22). Manganese showed close association with Co, Ni, Fe, V and Al as shown in the Pearson correlation matrix and cluster dendrogram in Figure 21 and Table 38.

GAIA plot of the sampling sites (Figure 24) showed the decision axis (Pi) pointing towards the pristine dominant sites, confirming that the soil samples from these sites are the least contaminated. Soil samples from sites EAM and EA appears farthest and opposite to the direction of the decision axis which indicates that they are the most contaminated and least preferred site followed by site AOB, all from the mining sites as shown in the PROMETHEE ranking analysis (Figure 23). Generally, the PROMETHEE and the GAIA analysis clearly identifies the pristine sites to be the least contaminated, while the mining sites were identified to be the most contaminated with heavy metals. The results also showed that anthropogenic activities such as mining and the use of chemicals on farm lands may be impacting heavily on heavy metal contamination of agricultural lands along the mining areas.

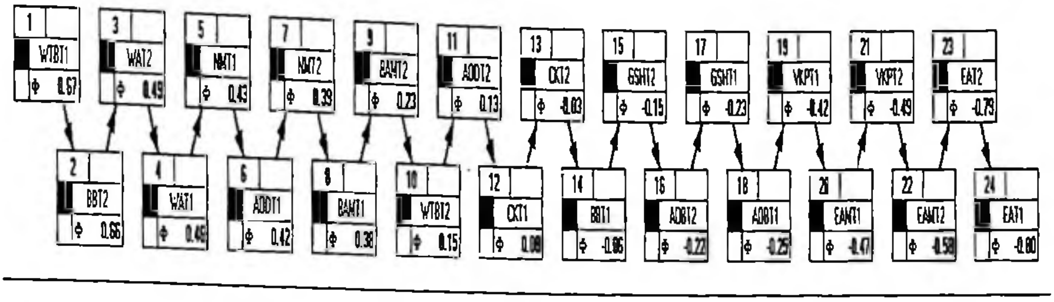


Figure 23: PROMETHEE 2 outranking for Sites based on the Metals Concentration in Soil samples from Pristine and Mine Sites.

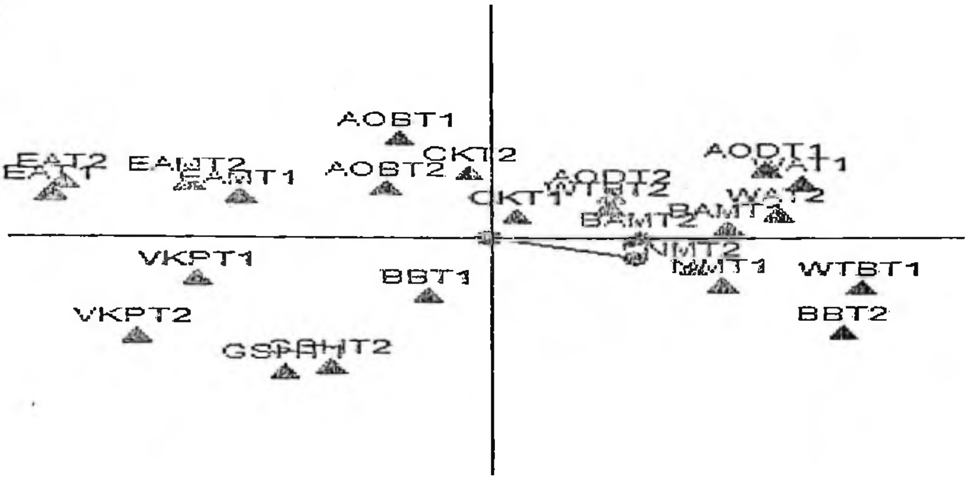


Figure 24: GAIA Plot of site Distribution based on the Metals Concentrations in the Soils from Pristine and Mine sites.

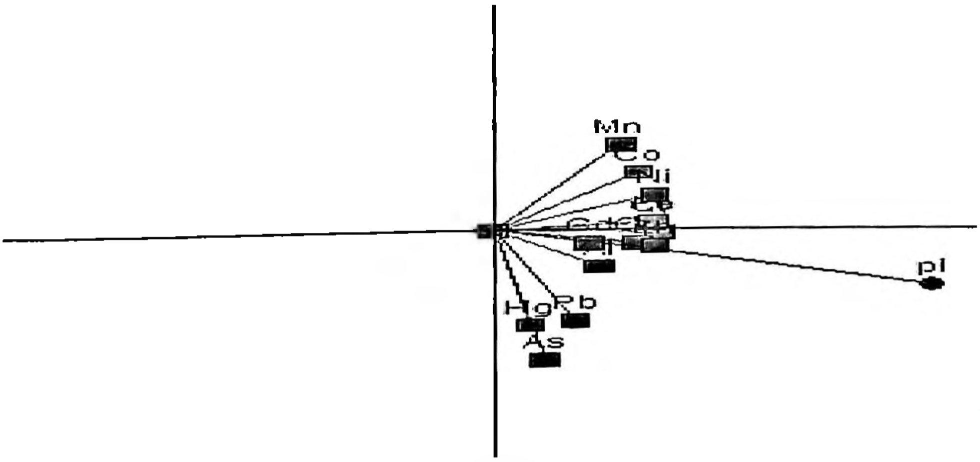


Figure 25: GAIA Plot showing the Metals in relation to the Decision Axis for Soil samples from Pristine and Mine Sites.

Pollution indices for Heavy Metals in the Soils and Sediments

Pollution Indices for the Metals in Sediments

The total recoverable metals were used to compute the pollution indices to obtain an overview of the contamination levels of the heavy metals in the studied sites. The contamination factor (CF) values for the metals were shown in Table 39. The CF values for Pb, Cd, Cu and Zn ranged between 0 and 1 from all the pristine and the mining areas and can be categorized as low contamination of the metals. The CF value for Co, Ni, Mn and Cr ranged from 0 to 1 in the soils from pristine and the mining sites indicating low to moderate contamination except at site VKP where the CF values of the metals ranged from 8 to 9, 8 to 8.5, 5 to 6 and 24 to 25 respectively indicating a high contamination of metals at site VKP.

The CF values for As at sites WTB (3.0), AOD (1.2), BB (0.6), CK (0.8), NM (2.3) and VKP (1.2) ranged between 1 and 3 and can be categorized as moderate contamination. However, the CF values of As at site AOB, BAM, EAM and EA (mostly mining areas) ranged between 6.0 and 248.2 which can be categorized as high to severely high contamination. Mercury recorded CF values between 1 and 2.7 at sites EA, EAM and AOB. Generally, the CF values for most of the metals in the samples from pristine and the mining areas showed low to moderate contamination except Cr, Ni, Co Mn and As which showed moderate to very high contamination at the selected sites. The CF results indicate that contamination of the river sediments from pristine and the mining sites were substantially contributed by Cr and As respectively.

The Modified Degrees of Contamination (mCd) values of the pristine and the mining sites are shown in Table 39. The mCd values of the sites AOB

(25.4), BAM (1.1) and EAM (3.0) indicate slightly to heavily polluted sites except site WTB (0.7) which indicate a non-polluted site. The mCd values of the pristine areas ranged between 0.1 and 5.1 which indicate an unpolluted to moderately-heavily polluted sites. The pollutions levels at sites AOB, EA and VKP, suggests a very serious anthropogenic deposition at these sites. The graphical representation of the results is shown in Figure 26.

Table 39: Contamination Factor (CF) and Modified Degrees of Contamination (mCd) Values of Heavy Metals in Sediments

Site	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Hg	mCd
Mining											
AOB	0.7	0.2	0.2	0.2	0.4	0.4	248.2	0.2	0.4	2.7	25.4
BAM	1.3	0.3	0.6	0.3	0.6	0.3	6.0	0.1	0.5	0.5	1.1
EAM	1.5	1.4	1.6	0.6	0.8	0.7	21.9	0.2	0.5	1.1	3.0
WTB	1.5	0.2	0.4	0.4	0.4	0.3	3.0	0.2	0.7	0.0	0.7
Pristine											
AOD	0.4	0.2	0.2	0.1	0.1	0.1	1.2	0.1	0.1	0.4	0.3
BB	0.3	0.2	0.4	0.1	0.3	0.3	0.6	0.1	0.2	0.0	0.3
EA	1.9	1.1	1.6	0.9	1.5	0.9	26.8	0.3	0.5	1.3	3.7
CK	0.3	0.0	0.1	0.1	0.1	0.1	0.8	0.1	0.1	0.0	0.2
NM	0.8	0.7	0.9	0.4	0.5	0.3	2.3	0.0	0.5	0.0	0.7
VKP	24.7	5.4	8.8	8.4	1.5	0.5	1.2	0.2	0.6	0.0	5.1
WA	0.1	0.1	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.1

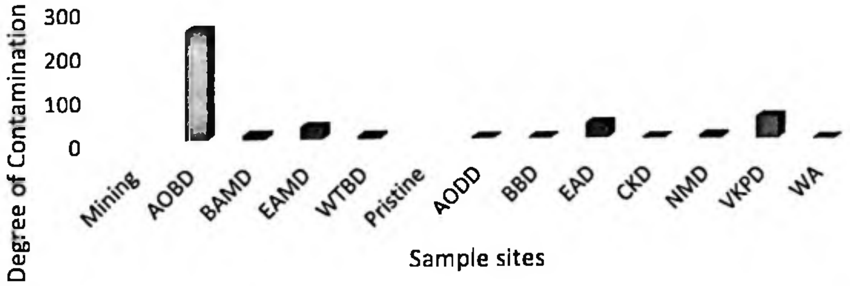


Figure 26: Degree of Contamination of the Metals in Sediment Samples from Pristine and Mining Sites.

Evaluation of Enrichment Factor and Modified Pollution Index of the Metals

The Enrichment factor (EF) values for the heavy metals at the pristine and the mining areas are shown in Table 40. In the mining areas, Zn, Cd and Pb showed no enrichment (EF < 2). Copper showed no enrichment at the mining sites except site AOB (EF = 2.3) where Cu showed minor enrichment. Chromium showed minor enrichment (EF = 2.1 to 2.9) at all the mining sites. Arsenic on the other hand showed no enrichment at site WTB (EF=1.8), moderate enrichment at site BAM (EF=4.1), moderately severe enrichment at site EAM (EF=9.6) and extremely severe enrichment at site AOB (EF=336.1).

In the pristine areas, the threshold heavy metals (Ni, Cu, Co, Zn, and Mn) showed relatively high enrichment. Similar to the mining areas, Zn, Cd and Pb showed no enrichment (EF<2) at all the pristine sites except at site WA which showed minor enrichment for Zn and Cd as 3.5 and 2.0 respectively. Arsenic on the other hand showed no enrichment (EF=0.2 to 1.9) at all the pristine sites except sites AOD, EA and CK where As showed moderately severe enrichment.

For the MPI, sites BAM and WTB experienced moderate pollution while site EAM experienced severe pollution. However, Site AOB experienced an extreme pollution due to the high level of As concentration (239) in the soil from this site. However, the pollution at site VKP was extremely high which was due to the contribution from Cr as a single element (30.1). The high enrichment and for that matter pollution of As and Hg at the mining sites may be due to mining activities and need to be monitored since they are known as human carcinogen and can cause cancer of the skin, lungs, liver and bladder (ATSDR, 2007).

Table 41. Geo-accumulation Indices (Igeo) of the Metals in Sediments from Pristine and Mining Areas

Site	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Hg
Mining										
AOBD	-0.4	-0.9	-0.8	-0.9	-0.5	-0.6	2.2	-0.8	-0.6	-0.7
BAMD	-0.1	-0.7	-0.4	-0.6	-0.4	-0.7	0.6	-1.1	-0.5	-1.4
EAMD	0.0	0.0	0.0	-0.4	-0.3	-0.3	1.2	-0.9	-0.5	-1.1
WTBD	0.0	-0.9	-0.6	-0.6	-0.6	-0.7	0.3	-0.9	-0.3	0.0
Pristine										
AODD	-0.5	-0.9	-0.9	-1.2	-1.0	-1.0	-0.1	-1.2	-1.1	-1.6
BBD	-0.6	-0.9	-0.6	-1.0	-0.7	-0.7	-0.4	-1.0	-0.9	0.0
EAD	0.1	-0.2	0.0	-0.2	0.0	-0.2	1.3	-0.8	-0.4	-1.1
CKD	-0.7	-1.5	-1.3	-1.4	-1.2	-1.2	-0.3	-1.4	-1.1	0.0
NMD	-0.3	-0.3	-0.2	-0.6	-0.5	-0.6	0.2	-1.8	-0.4	0.0
VKPD	1.2	0.6	0.8	0.7	0.0	-0.5	-0.1	-1.0	-0.4	0.0
WA	-1.3	-1.2	-1.4	-2.0	-2.3	-1.1	-1.9	-1.6	-1.2	0.0

Pollution Indices for Heavy Metals in the Soils

To effectively compare whether the sampling sites examined suffer contamination or not, the Enrichment Factor (EF), Modified Pollution Index (MPI) and geo-accumulation index (Igeo). were estimated for the total recoverable metals and the results are shown in Tables 42 and 43.

The Enrichment factor (EF) for the heavy metals in soils from the pristine and the mining areas are shown in Table 42. In the mining areas, Zn, Ni, Co and Mn showed no enrichment (EF<2) at all sites. Copper showed minor to moderately severe enrichment enrichment at sites EAM and AOB. Chromium and As showed moderate enrichment at all sites. Arsenic recorded severe enrichment at site BAM (EF = 5.1 to 8.5) to extremely severe enrichment at site AOB (EF = 256.0 to 292.9) indicating high contamination of the soil samples from site BAM and AOB.

Table 41. Geo-accumulation Indices (Igeo) of the Metals in Sediments from Pristine and Mining Areas

Site	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Pb	Hg
Mining										
AOBD	-0.4	-0.9	-0.8	-0.9	-0.5	-0.6	2.2	-0.8	-0.6	-0.7
BAMD	-0.1	-0.7	-0.4	-0.6	-0.4	-0.7	0.6	-1.1	-0.5	-1.4
EAMD	0.0	0.0	0.0	-0.4	-0.3	-0.3	1.2	-0.9	-0.5	-1.1
WTBD	0.0	-0.9	-0.6	-0.6	-0.6	-0.7	0.3	-0.9	-0.3	0.0
Pristine										
AODD	-0.5	-0.9	-0.9	-1.2	-1.0	-1.0	-0.1	-1.2	-1.1	-1.6
BBD	-0.6	-0.9	-0.6	-1.0	-0.7	-0.7	-0.4	-1.0	-0.9	0.0
EAD	0.1	-0.2	0.0	-0.2	0.0	-0.2	1.3	-0.8	-0.4	-1.1
CKD	-0.7	-1.5	-1.3	-1.4	-1.2	-1.2	-0.3	-1.4	-1.1	0.0
NMD	-0.3	-0.3	-0.2	-0.6	-0.5	-0.6	0.2	-1.8	-0.4	0.0
VKPD	1.2	0.6	0.8	0.7	0.0	-0.5	-0.1	-1.0	-0.4	0.0
WA	-1.3	-1.2	-1.4	-2.0	-2.3	-1.1	-1.9	-1.6	-1.2	0.0

Pollution Indices for Heavy Metals in the Soils

To effectively compare whether the sampling sites examined suffer contamination or not, the Enrichment Factor (EF), Modified Pollution Index (MPI) and geo-accumulation index (Igeo). were estimated for the total recoverable metals and the results are shown in Tables 42 and 43.

The Enrichment factor (EF) for the heavy metals in soils from the pristine and the mining areas are shown in Table 42. In the mining areas, Zn, Ni, Co and Mn showed no enrichment (EF<2) at all sites. Copper showed minor to moderately severe enrichment enrichment at sites EAM and AOB. Chromium and As showed moderate enrichment at all sites. Arsenic recorded severe enrichment at site BAM (EF = 5.1 to 8.5) to extremely severe enrichment at site AOB (EF = 256.0 to 292.9) indicating high contamination of the soil samples from site BAM and AOB.

At the pristine areas, the metals especially the non-threshold metals (Pb, As, Cd) showed relatively lower enrichment. Contrary to the mining sites where Zn, Cd and Pb showed minor enrichment (EF > 2) at most sites, Zn, Cd and Pb showed no enrichment at the pristine sites (EF < 2) indicating metal enrichment due to anthropogenic mining activities. Arsenic on the other hand showed no enrichment at most pristine sites (WA, VKP, GSH and EA) (EF < 2), minor enrichment at sites NM and CK (EF > 2), and moderately severe to severe enrichment at sites AOD and BB (EF = 10 to 19). The impact of mining on enrichment of the metals was realized because more of the metals showed high enrichment indices from the mining sites (Chen *et al.*, 2007; Wedepohl, 1995).

The distribution of the Modified Pollution Index (MPI) values in the mining sites for the total recoverable metals ranged from slightly polluted to severely polluted (MPI = 1.6 to 24.1) with all the sites recording pollution indices greater than 1.5 (MPI > 1.5). From the MPI values, site BAM recorded the least pollution index (MPI = 1.6) with site AOB recording the highest pollution Index (MPI = 24). The severe pollution experienced from site AOB was contributed mainly by As concentration at the site. Apart from site AOB, the rest of the sites experienced moderate to heavy pollution (Brady *et al.*, 2015). The pristine sites show the natural state of the elements with slight disturbances which may be resulting from atmospheric deposition of the metals from anthropogenic sources.

At the pristine areas, the metals especially the non-threshold metals (Pb, As, Cd) showed relatively lower enrichment. Contrary to the mining sites where Zn, Cd and Pb showed minor enrichment (EF > 2) at most sites, Zn, Cd and Pb showed no enrichment at the pristine sites (EF < 2) indicating metal enrichment due to anthropogenic mining activities. Arsenic on the other hand showed no enrichment at most pristine sites (WA, VKP, GSH and EA) (EF < 2), minor enrichment at sites NM and CK (EF > 2), and moderately severe to severe enrichment at sites AOD and BB (EF = 10 to 19). The impact of mining on enrichment of the metals was realized because more of the metals showed high enrichment indices from the mining sites (Chen *et al.*, 2007; Wedepohl, 1995).

The distribution of the Modified Pollution Index (MPI) values in the mining sites for the total recoverable metals ranged from slightly polluted to severely polluted (MPI = 1.6 to 24.1) with all the sites recording pollution indices greater than 1.5 (MPI > 1.5). From the MPI values, site BAM recorded the least pollution index (MPI = 1.6) with site AOB recording the highest pollution Index (MPI = 24). The severe pollution experienced from site AOB was contributed mainly by As concentration at the site. Apart from site AOB, the rest of the sites experienced moderate to heavy pollution (Brady *et al.*, 2015). The pristine sites show the natural state of the elements with slight disturbances which may be resulting from atmospheric deposition of the metals from anthropogenic sources.

Table 42: Enrichment factor (EF) and Modified Pollution Index (MPI) Values for the the Metals in Soils

Site	Depth (cm)	Cr	Mn	Co	Ni	Cu	Zn	Cd	As	Pb	MPI
Mining											
AOB	0-20	2.5	0.7	0.8	1.3	6.1	1.2	0.9	256.0	0.8	21.3
	20-40	2.7	0.6	0.9	1.4	4.1	1.2	1.1	292.9	0.9	24.1
BAM	0-20	1.9	1.1	1.3	1.1	1.5	0.9	0.3	8.5	0.5	1.9
	20-40	1.8	1.2	1.3	1.0	1.6	0.8	0.3	5.1	0.3	1.6
EAM	0-20	3.3	1.3	1.3	1.4	2.0	1.2	2.5	3.5	3.3	2.8
	20-40	3.3	1.1	1.4	1.2	1.8	1.1	0.4	1.7	1.3	2.6
WTB	0-20	5.8	0.6	0.5	1.8	1.0	0.9	3.3	3.1	0.8	4.3
	20-40	3.9	0.3	0.4	0.8	0.7	1.2	0.2	1.8	0.5	2.9
Pristine											
AOD	0-20	2.2	0.6	0.9	0.7	1.1	0.7	0.5	18.7	0.7	2.6
	20-40	1.9	0.1	0.1	0.4	0.6	0.4	0.1	11.3	0.5	1.8
BB	0-20	2.0	1.0	1.3	1.6	1.8	0.8	0.6	12.3	0.3	2.2
	20-40	2.1	0.9	1.3	1.2	1.5	0.7	0.5	9.7	0.2	2.1
EA	0-20	2.0	2.1	2.2	1.8	2.5	0.8	0.8	1.4	0.6	2.1
	20-40	2.5	1.2	1.6	1.6	2.2	0.8	0.6	0.9	0.5	2.0
CK	0-20	1.6	0.2	0.3	0.8	0.6	1.0	0.9	2.3	1.8	1.5
	20-40	1.6	0.2	0.3	0.8	0.3	0.9	0.9	2.1	1.9	1.5
GSH	0-20	1.2	1.4	1.4	0.9	0.3	0.5	0.3	0.1	0.1	1.1
	20-40	1.3	1.4	1.6	1.1	1.1	0.5	0.3	0.1	0.1	1.3
NM	0-20	2.0	1.6	1.2	1.1	1.2	0.9	0.0	2.8	0.9	1.7
	20-40	2.1	1.2	1.1	1.1	1.2	0.7	0.2	2.8	0.9	1.7
VKP	0-20	1.6	0.1	0.3	0.9	1.7	0.6	0.0	1.1	0.9	1.3
	20-40	1.8	0.5	0.7	1.1	3.1	0.8	0.1	0.7	0.4	2.3
WA	0-20	20.5	1.3	2.5	7.8	2.3	0.5	0.2	0.4	0.3	14.8
	20-40	29.4	3.0	5.0	12.8	2.0	0.5	0.2	0.3	0.2	21.2

Geo-accumulation (Igeo) of the Metals

The Igeo values for the total recoverable metals in the soil samples varied from 0.1 to 126.6 in the mining areas and 0.1 to 43.8 in the pristine areas as shown in Table 43. The Igeo for Zn, Cd and Pb were less than 1 (Igeo < 1) at all the sites studied in pristine and the mining areas suggesting no-contamination of the sites by these metals. Mn, Fe, Co and Ni showed moderate contamination at site BAM with the rest of the sites (AOB, EAM and WTB) showing no-contamination mining areas. The Igeo for As at sites EAM and WTB showed no-contamination of the sites, however, Arsenic at sites BAM and AOB indicated extremely severe contamination with site AOB recording an exceptionally high As Igeo value of 109 and 127 for the depths 0-20 and 20-40 cm respectively. The high levels of As in soil samples from site AOB has previously been reported and was attributed to mining activities (Antwi-Agyei *et al.*, 2009)

In the pristine sites, the Igeo for Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb at sites AOD, EA, CK, NM and VKP showed environment that is uncontaminated to moderately contaminated (< Igeo >1). The exceptionally high Igeo values of As at site BB and Cr at site WA could be attributed to illegal mining activities (which was evident during the sampling) and anthropogenic deposition of the metals at the sites (Müller, 1969).

Table 43: Geo-accumulation Indices (Igeo) of the Metals in Soils from the Pristine and Mining Areas

Site	Depth (cm)	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	As	Pb
Mining											
AOB	0-20	1.2	0.3	0.5	0.4	0.6	3.0	0.6	0.5	126.6	0.4
	20-40	1.0	0.2	0.4	0.3	0.5	1.5	0.4	0.4	109.1	0.3
BAM	0-20	1.9	1.1	1.0	1.3	1.1	1.5	0.9	0.3	8.5	0.5
	20-40	2.3	1.6	1.3	1.6	1.3	2.0	1.0	0.3	6.4	0.4
EAM	0-20	0.6	0.3	0.2	0.2	0.3	0.4	0.2	0.5	0.7	0.6
	20-40	0.6	0.2	0.2	0.3	0.2	0.3	0.2	0.1	0.3	0.2
WTB	0-20	1.2	0.1	0.2	0.1	0.4	0.2	0.2	0.7	0.6	0.2
	20-40	1.1	0.1	0.3	0.1	0.2	0.2	0.3	0.1	0.5	0.1
Pristine											
AOD	0-20	0.6	0.2	0.3	0.2	0.2	0.3	0.2	0.1	5.3	0.2
	20-40	0.9	0.0	0.5	0.1	0.2	0.3	0.2	0.1	5.1	0.2
BB	0-20	3.4	1.6	1.7	2.2	2.7	3.1	1.3	1.0	20.7	0.4
	20-40	4.0	1.6	1.9	2.4	2.3	2.8	1.4	0.9	18.1	0.4
EA	0-20	0.7	0.7	0.3	0.7	0.6	0.8	0.3	0.3	0.5	0.2
	20-40	1.3	0.6	0.5	0.9	0.8	1.2	0.4	0.3	0.5	0.2
CK	0-20	0.3	0.0	0.2	0.1	0.2	0.1	0.2	0.2	0.5	0.4
	20-40	0.4	0.0	0.2	0.1	0.2	0.1	0.2	0.2	0.5	0.4
GSH	0-20	1.6	1.9	1.3	1.8	1.2	0.4	0.7	0.4	0.2	0.1
	20-40	1.8	2.0	1.4	2.3	1.6	1.5	0.7	0.5	0.2	0.1
NM	0-20	0.5	0.4	0.2	0.3	0.3	0.3	0.2	0.0	0.7	0.2
	20-40	0.8	0.5	0.4	0.5	0.4	0.5	0.3	0.1	1.1	0.3
VKP	0-20	1.1	0.1	0.7	0.2	0.6	1.2	0.4	0.0	0.7	0.6
	20-40	0.9	0.3	0.5	0.3	0.5	1.4	0.4	0.1	0.3	0.2
WA	0-20	24.4	1.6	1.2	3.0	9.3	2.8	0.6	0.3	0.5	0.4
	20-40	43.8	4.4	1.5	7.4	19.1	3.1	0.8	0.3	0.5	0.3

Ecological risk Assessment of the Heavy Metals in Sediment Samples

Potential ecological risk factors (Ei) of the metals are summarized in Table 44. From the mining areas, a low potential ecological risk factors were recorded for Cu, Zn, Cr, Cd and Pb from all sites (Ei = 0.5 to 32.5). The potential ecological risk for As (3361.1) and Hg (181.4) at site AOB pose very high and high risk respectively. The potential risk posed by As at site BAM and EAM is considered as moderate to considerable risk. In general, As and Hg are the elements which showed potential ecological risk at the four sites studied in the mining areas especially their contributions from sites AOB and EAM. Similar high levels of As and Hg at sites AOB and EAM were recorded for EF, Igeo and CF and the high levels above one (1) in most cases suggest anthropogenic inputs of As and Hg from these sites (Álvarez-Vázquez *et al.*, 2013).

The high ecological risk indices for As, Cd and Hg at sites AOD, BB and EA may be due to illegal mining activities in those forests reserves as reported by Ansa-Asare (2000).

The modified ecological risk indices for the river sediment from the 11 sites showed varied ecological risks indices. Only 2 (AOB and AOD) out of the 11 sites showed significant ecological risk indices. The remaining sites showed low ecological risk values (MRI < 150). The ecological risk of the multi-elements at site AOB pose a very high risk and the ecological risk of the metals at site AOD pose a moderate risk. The high ecological risks observed at sites AOB and AOD were substantially contributed by the high As and Hg individual element concentrations. The results indicate that control measures are needed to mitigate the pollution of As, Hg, and Cd in the mining environments especially at site AOB, EAM and AOD in order to reduce the ecological risk impact of these metals.

Table 44: Potential (Ei) and Modified Ecological Risk Index (MRI) for Heavy Metals in Sediment

	Potential Ecological Index (Ei)							MRI
Site	Cr	Cu	Zn	As	Cd	Pb	Hg	
Mining								
AOB	5.8	11.5	1.3	3361.1	32.5	3.9	181.4	3597.4
BAM	5.9	8.4	0.5	41.2	9.8	2.6	18.3	86.7
EAM	4.2	6.7	0.7	95.9	8.4	1.7	23.5	141.0
WTB	5.6	4.2	0.4	17.8	11.2	3.1	0.0	42.3
Pristine								
AOD	13.6	14.3	1.7	60.9	48.2	4.5	89.0	232.0
BB	5.9	14.7	1.8	16.2	42.1	3.6	0.0	84.3
EA	4.1	9.7	0.7	89.8	9.9	1.3	20.9	136.4
CK	13.2	15.0	1.5	62.5	47.9	6.5	0.0	146.6
NM	4.5	8.9	0.7	19.3	2.6	3.4	0.0	39.3
VKP	60.3	10.9	0.4	4.5	7.0	1.7	0.0	84.8
WA	6.9	2.2	3.5	2.5	60.3	8.7	0.0	84.0

Ecological risk Assessment of the Heavy Metals in Soil samples

The potential ecological risk factors (Ei) of the metals in the soil samples are summarized in Table 45. The calculated ecological risk factors for Cu, Zn, Cr, and Pb were below 40 (Ei < 40) in the pristine and the mining sites except Cr at site WA of depth 0-20 and 20-40 cm which recorded Ei values above 40, indicating a moderate ecological risk. The Ei for Cd at all sites can be considered as posing low ecological risk except the risk factors at sites EAM (75) and WTB (99) at 0-20 cm depth which has the potential of posing moderate risk. In general, As is the only element that showed considerable to high potential ecological risk in the four sites studied in the mining and the pristine areas especially the contributions of As from site AOB.

The high Ei values recorded from sites BB and AOD for As is evident of the anthropogenic activities such as illegal mining in the forest reserves. The high ecological risk indices for As and Cd at sites AOB, EAM, WTB, AOD and BB may be due to illegal mining activities in these forests as reported by Ansa-Asare (2000).

The highest ecological risk indices in the mining areas were recorded at site AOB as 2627.7 (0-20 cm) and 2993.6 (20-40 cm). The remaining sites showed low ecological risk indices (MRI < 150). Even though the potential ecological risks of As and Cd at sites AOB, EAM, WTB and BAM showed moderate ecological risks at various depths for single elements, the combined multi-element indices at these sites suggest low ecological risk. The results indicate that control measures are needed to mitigate the pollution of As and Cd in the mining environments especially at sites AOB and EAM in order to reduce the ecological risk impact of these metals.

Table 45: Potential (Ei) and Modified Ecological Risk Index (MRI) of the Metals in Soils

		Potential Ecological Risk Index (Ei)						MRI
Site	Depth (cm)	Cr	Cu	Zn	Cd	As	Pb	
Mining								
AOB	0-20	5.0	30.5	1.2	27.0	2560.0	4.0	2627.7
	20-40	5.4	20.5	1.2	33.0	2929.0	4.5	2993.6
BAM	0-20	3.8	7.5	0.9	9.0	85.0	2.5	108.7
	20-40	3.6	8.0	0.8	9.0	51.0	1.5	73.9
EAM	0-20	6.6	10.0	1.2	75.0	35.0	16.5	144.3
	20-40	6.6	9.0	1.1	12.0	17.0	6.5	52.2
WTB	0-20	11.6	5.0	0.9	99.0	31.0	4.0	151.5
	20-40	7.8	3.5	1.2	6.0	18.0	2.5	39.0
Pristine								
AOD	0-20	4.4	5.5	0.7	15.0	187.0	3.5	216.1
	20-40	3.8	3.0	0.4	3.0	113.0	2.5	125.7
BB	0-20	4.0	9.0	0.8	18.0	123.0	1.5	156.3
	20-40	4.2	7.5	0.7	15.0	97.0	1.0	125.4
EA	0-20	4.0	12.5	0.8	24.0	14.0	3.0	58.3
	20-40	5.0	11.0	0.8	18.0	9.0	2.5	46.3
CK	0-20	3.2	3.0	1.0	27.0	23.0	9.0	66.2
	20-40	3.2	1.5	0.9	27.0	21.0	9.5	63.1
GSH	0-20	2.4	1.5	0.5	9.0	1.0	0.5	14.9
	20-40	2.6	5.5	0.5	9.0	1.0	0.5	19.1
NM	0-20	4.0	6.0	0.9	0.0	28.0	4.5	43.4
	20-40	4.2	6.0	0.7	6.0	28.0	4.5	49.4
VKP	0-20	3.2	8.5	0.6	0.0	11.0	4.5	27.8
	20-40	3.6	15.5	0.8	3.0	7.0	2.0	31.9
WA	0-20	41.0	11.5	0.5	6.0	4.0	1.5	64.5
	20-40	58.8	10.0	0.5	6.0	3.0	1.0	79.3

Human Health Risk Evaluation

Non-carcinogenic Risk for Water

The Non-carcinogenic risks from exposure to the heavy metals were calculated for child and adult residents by employing the Central Tendency Exposure (CTE) scenario only (average metals concentrations) and also using the default values in the RISC 4.02 software. The hazard quotient (HQ) results for water from this study are summarized in Table 46. Generally, HQ value greater than 1.0 is considered as having the probability of adverse health effects and therefore interpreted as a level of concern (Wihlem, Heinzow, Angerer, & Schulz, 2010; Ekong, Jaar, & Weaver, 2006; USEPA, 1997; USEPA, 2004).

The results from Table 46 showed that even though, there were no much variabilities in the hazard quotients for children and adults from both the mining and the pristine sites, adults generally seem to be at higher non-cancer risks than children. Similar results were obtained by Adamu, Nganje and Edet (2015), in their study on pond and stream waters in Nigeria. The highest HQ value for ingestion of water from the mining sites is 7.44 for As and the lowest values is 2.88×10^{-7} for Cu. The highest HQ recorded in the water samples, from the pristine sites is 2.20 for As and Cu recorded the lowest HQ to be 7.68×10^{-8} in the samples.

The highest HQ for dermal contact in the water from the mining sites is 1.04 recorded for As while Zn (5.62×10^{-7}) recorded the lowest non-cancer risk from the mining areas. Comparing the results from this study with that of USEPA risk assessment guidelines, though a number of the metals in the pristine and mining samples for adults and children have HQs close to 1, only Mn at sites AOB, BAM, EAM and BB and As at site AOB have HQ greater than 1 mostly from the mining sites due to ingestion of water. For Dermal contact, only As has HQ greater than 1 (1.04) at site AOB for children. The graphical representation of the HQ for adult and child residents in the pristine and mining sites is shown in Figures 27 and 28.

Similar values of hazard potentials were reported in the literature (Obiri *et al*., 2016; Armah & Gyeabour, 2013; Nkoom *et al*., 2013; Obiri *et al*., 2010). Overall, the results show that Mn and As pose non-cancer risk in river Nyam (AOB) to resident adults and children (Table 46) while Mn pose a non-cancer risk to residents that consume water from river Subri (BAM) and Birim (EAM) in the mining areas. In the pristine areas, only Mn had HQ greater than 1 in river Bosomkese (BB) for both adults and children residents suggesting a non-carcinogenic risk for dermal contact (Table 47). This implies that adverse health effects from exposure to As and Mn in the rivers are possible.

Table 46: Non-carcinogenic and Carcinogenic Risks for Ingestion of Mine Water by Child and Adult Residents

		Hazard Quotient							Carcinogenic Risk			
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Pb	Cr	Ni	As	Pb
Mining												
AOB	Adult	$4.6 \text{ x}10^{-1}$	3.7	$5.87 \text{ x}10^{-3}$	$1.05 \text{ x}10^{-5}$	$3.74 \text{ x}10^{-3}$	7.4	$3.52 \text{ x}10^{-2}$	$1.35 \text{ x}10^{-1}$	$2.00 \text{ x}10^{-4}$	$3.35 \text{ x}10^{-3}$	$2.99 \text{ x}10^{-4}$
	Child	$1.68 \text{ x}10^{-4}$	3.5	$5.48 \text{ x}10^{-3}$	$2.88 \text{ x}10^{-7}$	$3.49 \text{ x}10^{-3}$	6.9	$3.29 \text{ x}10^{-2}$	$1.26 \text{ x}10^{-1}$	$1.86 \text{ x}10^{-4}$	$3.12 \text{ x}10^{-3}$	$2.79 \text{ x}10^{-4}$
BAM	Adult	$1.25 \text{ x}10^{-4}$	4.4	$8.81 \text{ x}10^{-3}$	$3.50 \text{ x}10^{-6}$	$1.19 \text{ x}10^{-3}$	$1.17 \text{ x}10^{-1}$		$9.39 \text{ x}10^{-2}$	$2.99 \text{ x}10^{-4}$	$5.28 \text{ x}10^{-5}$	
	Child	$1.17 \text{ x}10^{-4}$	4.1	$8.22 \text{ x}10^{-3}$	$9.60 \text{ x}10^{-8}$	$1.11 \text{ x}10^{-3}$	$1.10 \text{ x}10^{-1}$		$8.77 \text{ x}10^{-2}$	$2.79 \text{ x}10^{-4}$	$4.93 \text{ x}10^{-5}$	
EAM	Adult	$4.93 \text{ x}10^{-4}$	2.3	$1.06 \text{ x}10^{-2}$	$5.60 \text{ x}10^{-5}$	$6.94 \text{ x}10^{-3}$		$2.47 \text{ x}10^{-1}$	$3.70 \text{ x}10^{-1}$	$3.59 \text{ x}10^{-4}$		$2.10 \text{ x}10^{-3}$
	Child	$4.60 \text{ x}10^{-4}$	2.2	$9.86 \text{ x}10^{-3}$	$1.54 \text{ x}10^{-6}$	$6.48 \text{ x}10^{-3}$		$2.30 \text{ x}10^{-1}$	$3.45 \text{ x}10^{-1}$	$3.35 \text{ x}10^{-4}$		$1.96 \text{ x}10^{-3}$
WTB	Adult	$7.05 \text{ x}10^{-5}$	$4.54 \text{ x}10^{-1}$	$5.87 \text{ x}10^{-3}$	$4.90 \text{ x}10^{-6}$	$1.83 \text{ x}10^{-4}$			$5.28 \text{ x}10^{-2}$	$2.00 \text{ x}10^{-4}$		
	Child	$6.58 \text{ x}10^{-5}$	$4.24 \text{ x}10^{-1}$	$5.48 \text{ x}10^{-3}$	$1.34 \text{ x}10^{-7}$	$1.70 \text{ x}10^{-4}$			$4.93 \text{ x}10^{-2}$	$1.86 \text{ x}10^{-4}$		

Table 47: Non-carcinogenic and Carcinogenic Risks for Ingestion of Pristine Water by Child and Adult Residents

		Hazard Quotient							Carcinogenic Risk		
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Pb	Cr	Ni	As
Pristine									CR Pristine		
EA	Adult		1.3 x 10^{-1}	5.9 x10^{-3}		1.0 x10^{-3}	1.2 x10^{-1}			2.0 x10^{-4}	5.3 x10^{-5}
	Child		1.2 x 10^{-1}	5.5 x10^{-3}		9.4x10-4	1.1 x10^{-1}			1.9 x10^{-4}	4.9 x10^{-5}
WA	Adult	3.1 x10^{-5}	3.9 x 10^{-2}						2.4 x10^{-2}		
	Child	2.9 x10^{-5}	3.7 x 10^{-2}						2.2 x10^{-2}		
BB	Adult		2.2				7.8 x10^{-2}				3.5 x10^{-5}
	Child		2.1				7.3 x10^{-2}				3.3 x10^{-5}
AOD	Adult		8.6 x 10^{-2}	4.1 x10^{-3}	5.60 x10^{-6}	3.7 x10^{-3}				1.4 x10^{-4}	
	Child		8.1 x 10^{-2}	3.8 x10^{-3}	1.5 x10^{-7}	3.5 x10^{-3}				1.3 x10^{-4}	
VKP	Adult				2.8 x10^{-6}	6.4 x10^{-4}					
	Child				7.7 x10^{-8}	6.0 x10^{-4}					
NM	Adult		1.8 x 10^{-2}			2.3 x10^{-3}					
	Child		1.6 x 10^{-2}			2.1 x10^{-3}					
CK	Adult		2.9 x 10^{-2}			6.4 x10^{-4}					

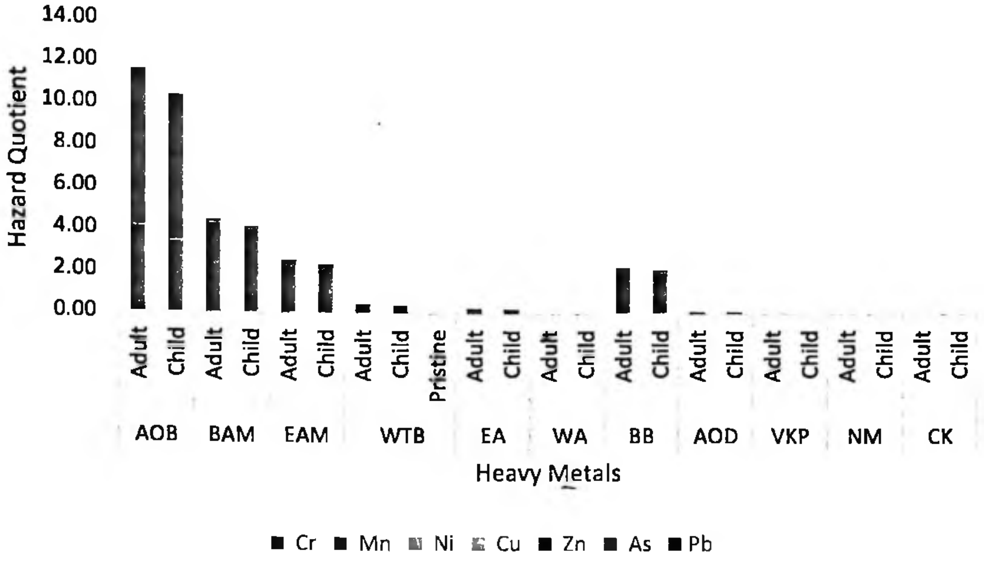


Figure 27: Non-carcinogenic Risk (ingestion) of the Metals in Water for Child and Adult Residents in the Pristine and Mining Areas.

Carcinogenic Risk for Water

For ingestion of water (Table 46), the highest cancer risks due to exposure to the heavy metals were recorded for resident child and adult from river EAM for Cr in the mining areas. In the pristine sites, the highest cancer risk was recorded for Cr in child and adult residents at site WA to be 2.2 x 10^{-2} and 2.4 x 10^{-2} respectively. For dermal contact, similar results were obtained where Cr recorded the highest cancer risk in river EAM and WA for adult and child residents (Table 49). The graphical representation of the CR for adult and child residents in the pristine and mining sites is shown in Figures 29 and 30. The carcinogenic risks for Ni, As and Pb are within the USEPA risk assessment guideline limit (1.0 x 10^{-6} to 1.0 x 10^{-4}) (USEPA, 1997; USEPA, 2004) except for As at site AOB and Pb at site EAM for resident adult and child respectively. This implies that for As and Pb, there is a likelihood that up to 2 to 3 adults, out of one thousand and 1 to 3 children out of one thousand respectively if equally exposed continuously to the As and Pb concentrations over 70 years would contract cancer.

For dermal contact, the carcinogenic risk values for As, Ni, and Pb in the pristine and mining sites for adult and child are within the USEPA risk assessment guidelines limit. The values from this study are comparable with results obtained by other researchers (Obiri *et al.*, 2016; Obri *et al.*, 2010; Iqbal & Shah, 2013).

The high carcinogenic risk values recorded for As and Cr in this study raise carcinogenic concerns for the local residents living around the catchment areas. Inorganic arsenic is a known human carcinogen. High levels of As and Cr can cause cancer of the skin, lungs, liver and bladder. Lower intakes of As may cause nausea and vomiting, abnormal heart rhythm, and damage to blood vessels (ToxFAQs, 2014).

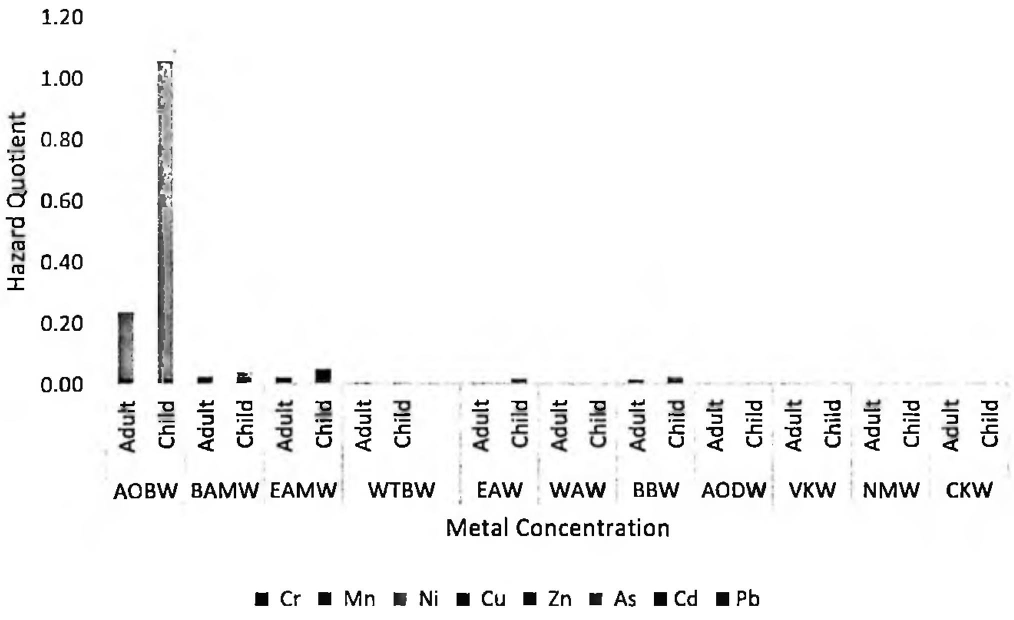


Figure 28: Non-carcinogenic Risk (dermal contact) of the Metals in Water for Child and Adult Residents in the Pristine and Mining Areas.

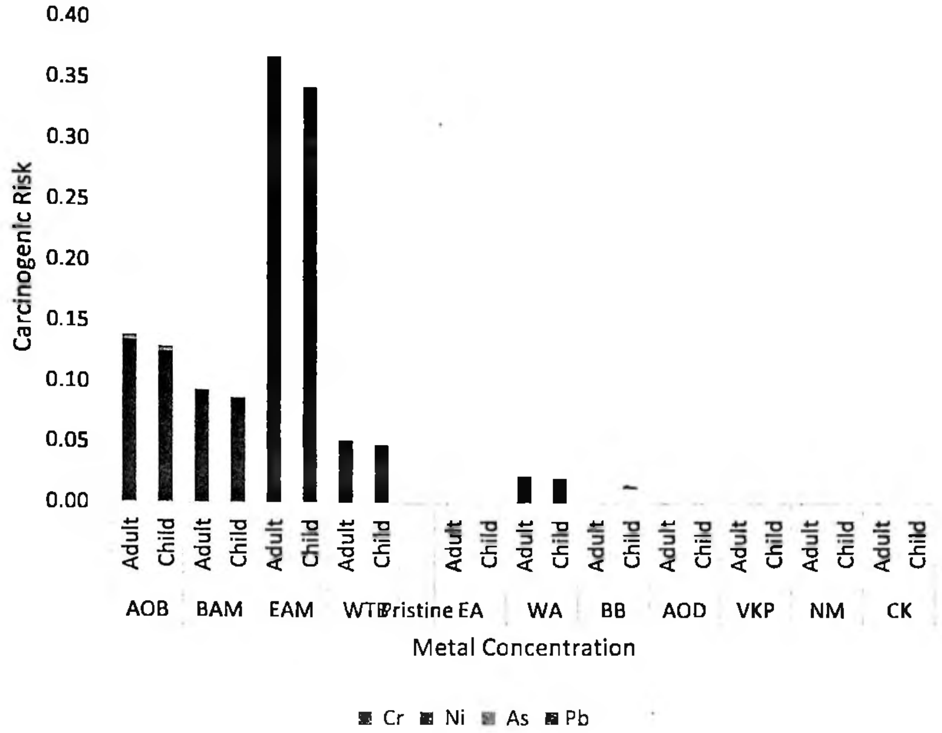


Figure 29: Carcinogenic Risk (ingestion) of the Metals in Water for Child and Adult Residents in the Pristine and Mining Areas.

Table 48: Non-carcinogenic Risk of the Metals for Dermal Contact of Metals in Water by Child and Adult Residents

		Hazard Quotient							
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Mining									
AOBW	Adult	5.2 x10^{-6}	2.0 x10^{-2}	1.7 x10^{-4}	5.5 x10^{-5}	1.2 x10^{-5}	2.2 x10^{-1}		1.0 x10^{-4}
	Child	2.5 x10^{-5}	1.9 x10^{-2}	8.2 x10^{-4}	5.3 x10^{-5}	1.2 x10^{-5}	1.1		4.9 x10^{-4}
BAMW	Adult	3.6 x10^{-6}	2.3 x10^{-2}	2.6 x10^{-4}	1.8 x10^{-5}	3.8 x10^{-6}	3.4 x10^{-3}		
	Child	1.8 x10^{-5}	2.3 x10^{-2}	1.2 x10^{-3}	1.8 x10^{-5}	3.7 x10^{-6}	1.7 x10^{-2}		
EAMW	Adult	1.4 x10^{-5}	1.2 x10^{-2}	3.1 x10^{-4}	2.9 x10^{-4}	2.2 x10^{-5}		7.1 x10^{-3}	
	Child	6.9 x10^{-5}	1.2 x10^{-2}	1.5 x10^{-3}	2.8 x10^{-4}	2.2 x10^{-5}		3.5 x10^{-2}	
WTBW	Adult	2.1 x10^{-6}	2.4 x10^{-3}	1.7 x10^{-4}	2.6 x10^{-5}	5.8 x10^{-7}			
	Child	9.8 x10^{-6}	2.3 x10^{-3}	8.2 x10^{-4}	2.5 x10^{-5}	5.6 x10^{-7}			
Pristine									
EAW	Adult		6.7 x10^{-4}	1.7 x10^{-4}		3.2 x10^{-6}	3.4 x10^{-3}		
	Child		6.4 x10^{-4}	8.2 x10^{-4}		3.1 x10^{-6}	1.7 x10^{-2}		
WAW	Adult	9.1 x10^{-7}	2.1 x10^{-4}						
	Child	4.4 x10^{-6}	2.1 x10^{-4}						
BBW	Adult		1.2 x10^{-2}				2.3 x10^{-3}		
	Child		1.1 x10^{-2}				1.1 x10^{-2}		
AODW	Adult		4.6 x10^{-4}	1.2 x10^{-4}	2.9 x10^{-5}	1.2 x10^{-5}			
	Child		4.4 x10^{-4}	5.7 x10^{-4}	2.8 x10^{-5}	1.2 x10^{-5}			
VKW	Adult				1.5 x10^{-5}	2.1 x10^{-6}			
	Child				1.4 x10^{-5}	2.0 x10^{-6}			
NMW	Adult		9.4 x10^{-5}			7.3 x10^{-6}			
	Child		9.0 x10^{-5}			7.0 x10^{-6}			
CKW	Adult		1.6 x10^{-4}			2.1 x10^{-6}			
	Child		1.5 x10^{-4}			2.0 x10^{-6}			

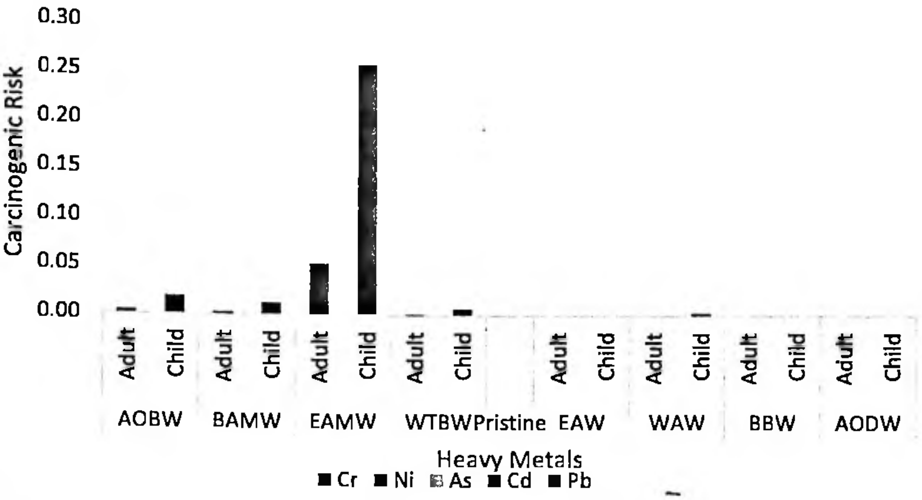


Figure 30: Carcinogenic Risk (dermal contact) of the Metals in Water for Child and Adult Residents in the Pristine and Mining Areas.

Table 49: Carcinogenic risk of the Metals for Dermal Contact of Metals in Water by Child and Adult Residents

		Carcinogenic Risk				
Site	Age	Cr	Ni	As	Cd	Pb
Mining						
AOBW	Adult	3.9 x10^{-3}	5.8 x10^{-6}	9.7 x10^{-5}		8.7 x10^{-7}
	Child	1.9 x10^{-2}	2.8 x10^{-5}	4.7 x10^{-4}		4.2 x10^{-6}
BAMW	Adult	2.7 x10^{-3}	8.7 x10^{-6}	1.5 x10^{-6}		
	Child	1.3 x10^{-2}	4.2 x10^{-5}	7.4 x10^{-6}		
EAMW	Adult	1.1 x10^{-2}	1.1 x10^{-5}		4.4 x10^{-2}	
	Child	5.2 x10^{-2}	5.0 x10^{-5}		2.1 x10^{-1}	
WTBW	Adult	1.5 x10^{-3}	5.8 x10^{-6}			
	Child	7.4 x10^{-3}	2.8 x10^{-5}			
Pristine						
EAW	Adult		5.8 x10^{-6}	1.5 x10^{-6}		
	Child		2.8 x10^{-5}	7.4 x10^{-6}		
WAW	Adult	6.8 x10^{-4}				
	Child	3.3 x10^{-3}				
BBW	Adult			1.1 x10^{-6}		
	Child			4.9 x10^{-6}		
AODW	Adult		4.1 x10^{-6}			
	Child		1.9 x10^{-5}			

Non-carcinogenic Risk for Sediment

The non-carcinogenic health hazards resulting from exposure to Cr, Mn, Ni, Cu, Zn, Cd, Hg and As in sediment by residents around major mining areas using the Central Tendency Exposure (CTE) scenario only for oral ingestion and dermal contact are shown in Tables 50 and 51, while Tables 52 and 53 displays the cancer risk results for oral ingestion and dermal contact for the heavy metals respectively.

The results from Table 49 show that even though the hazard quotients of specific metals for children and adults in the mining and pristine sites did not change much, children in most cases seem to be at higher non-cancer risk compared with adults.

The non-cancer risk for Cr, Cu, Zn, Cd and Hg were low whiles Pb, Ni and Mn showed relatively higher Hazard quotients even though lower than the acceptable limit of 1.0 both in the pristine and the mining sites, suggesting an acceptable risk in majority of the cases. However, HQ values show unacceptable risk for As for resident child in River Nyam (AOB) which is far above the 1.0 guideline limit suggesting a non-cancer risk threat to children living around the mining areas.

The dermal contact of residents with metals in sediments in the pristine and the mining sites for adults and children resulted in the lowest hazard quotient attributed to Cr (1.4×10^{-6}, 1.3×10^{-6}) from river WA while the highest attributed to As (4.5×10^{-1}, 2.2) from river AOB respectively (Table 51).

Comparing the results from this study with that of USEPA risk assessment guidelines, though many of the metals in the pristine and mining samples for adults and children have HQs close to 1.0, it is only As which had HQ greater than 1 (1.04) for resident child from site AOB due to dermal contact of water. The graphical representation of the HQ for adult and child residents in the pristine and mining sites is shown in Figures 31 and 32.

Similar values of hazard quotients were reported elsewhere (Obiri *et al.*, 2016; Armah & Gyeabour, 2013; Obiri *et al.*, 2010). Overall, the results show that As pose non-cancer risk in river AOB to resident children due to ingestion and dermal contact of the metals (Tables 50 and 51). This implies that adverse health effects from exposure to As in the rivers are possible since the sediment is contaminated. For ingestion of sediments by adults and children, the hazard indices of As, Cd, Cu and Hg were higher than values reported from similar study around abandoned Au-Ag mine in Korea (Jung, 2001). Although the HQs are below the acceptable limit of 1.0, the range of HQ values points to the importance of having heavy metals measured in sediments from major mining areas in Ghana.

Table 50: Non-carcinogenic Risk Index for Ingestion of Metals in sediment by Child and Adult Residents

		Hazard Quotient								
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb	Hg
Mining										
AOBD	Adult	2.3×10^{-5}	1.5×10^{-2}	3.6×10^{-4}	6.8×10^{-7}	1.8×10^{-4}	7.8×10^{-1}	3.8×10^{-5}	4.7×10^{-3}	5.5×10^{-4}
	Child	4.4×10^{-5}	2.8×10^{-2}	6.7×10^{-4}	3.7×10^{-8}	3.4×10^{-4}	1.45	7.0×10^{-5}	8.7×10^{-3}	1.0×10^{-3}
BAMD	Adult	4.7×10^{-5}	2.7×10^{-2}	7.0×10^{-4}	9.9×10^{-7}	1.5×10^{-4}	1.9×10^{-2}	2.3×10^{-5}	6.0×10^{-3}	1.10×10^{-4}
	Child	8.7×10^{-5}	5.0×10^{-2}	1.3×10^{-3}	5.4×10^{-8}	2.7×10^{-4}	3.5×10^{-2}	4.2×10^{-5}	1.1×10^{-2}	2.1×10^{-4}
EAMD	Adult	5.3×10^{-5}	1.2×10^{-1}	1.1×10^{-3}	1.2×10^{-6}	3.1×10^{-4}	6.9×10^{-2}	3.0×10^{-5}	6.1×10^{-3}	2.2×10^{-5}
	Child	9.8×10^{-5}	2.2×10^{-1}	2.1×10^{-3}	6.8×10^{-8}	5.8×10^{-4}	1.3×10^{-1}	5.6×10^{-5}	1.2×10^{-2}	4.1×10^{-5}
WTBD	Adult	5.3×10^{-5}	1.5×10^{-2}	8.0×10^{-4}	5.7×10^{-7}	1.3×10^{-4}	9.5×10^{-3}	3.0×10^{-5}	8.5×10^{-3}	-
	Child	9.8×10^{-5}	2.7×10^{-2}	1.5×10^{-3}	3.1×10^{-8}	2.4×10^{-4}	1.8×10^{-2}	5.6×10^{-5}	1.6×10^{-2}	-
Pristine										
AOD	Adult	1.5×10^{-5}	1.7×10^{-2}	1.8×10^{-4}	2.3×10^{-7}	6.4×10^{-5}	3.8×10^{-3}	1.5×10^{-5}	1.4×10^{-3}	7.4×10^{-5}
	Child	2.8×10^{-5}	3.1×10^{-2}	3.3×10^{-4}	1.3×10^{-8}	1.2×10^{-4}	7.2×10^{-3}	2.8×10^{-5}	2.7×10^{-3}	1.4×10^{-4}
BB	Adult	1.2×10^{-5}	1.7×10^{-2}	2.9×10^{-4}	4.4×10^{-7}	1.3×10^{-4}	1.9×10^{-3}	2.5×10^{-5}	2.2×10^{-3}	-
	Child	2.3×10^{-5}	3.2×10^{-2}	5.4×10^{-4}	2.4×10^{-8}	2.4×10^{-4}	3.5×10^{-3}	4.6×10^{-5}	4.1×10^{-3}	-
EA	Adult	6.7×10^{-5}	8.7×10^{-2}	1.9×10^{-3}	2.3×10^{-6}	3.8×10^{-4}	8.4×10^{-2}	4.6×10^{-5}	6.4×10^{-3}	2.6×10^{-4}
	Child	1.3×10^{-4}	1.6×10^{-1}	3.5×10^{-3}	1.3×10^{-7}	7.1×10^{-4}	1.6×10^{-1}	8.7×10^{-5}	1.2×10^{-2}	4.8×10^{-4}
CK	Adult	9.6×10^{-6}	4.5×10^{-1}	1.2×10^{-4}	1.6×10^{-7}	3.7×10^{-5}	2.6×10^{-3}	9.9×10^{-6}	1.4×10^{-3}	-
	Child	1.8×10^{-5}	8.3×10^{-1}	2.1×10^{-4}	8.7×10^{-9}	7.0×10^{-5}	4.8×10^{-3}	1.9×10^{-5}	2.6×10^{-3}	-
NM	Adult	2.9×10^{-5}	5.8×10^{-2}	8.3×10^{-4}	8.3×10^{-7}	1.5×10^{-4}	7.1×10^{-3}	4.7×10^{-6}	6.4×10^{-3}	-
	Child	5.4×10^{-5}	1.1×10^{-1}	1.6×10^{-3}	4.6×10^{-8}	2.8×10^{-4}	1.3×10^{-2}	8.8×10^{-6}	1.2×10^{-2}	-
VKP	Adult	8.7×10^{-4}	3.8×10^{-3}	1.7×10^{-2}	2.3×10^{-6}	2.1×10^{-4}	3.7×10^{-3}	2.9×10^{-5}	7.2×10^{-3}	-
	Child	1.6×10^{-3}	7.1×10^{-3}	3.1×10^{-2}	1.3×10^{-7}	4.0 x10-4	6.9×10^{-3}	5.4×10^{-5}	1.4×10^{-2}	-
WA	Adult	2.8×10^{-6}	7.2×10^{-3}	3.3×10^{-5}	1.3×10^{-8}	4.9×10^{-5}	5.7×10^{-5}	7.0×10^{-6}	1.0×10^{-3}	-
	Child	5.2×10^{-6}	1.3×10^{-2}	6.1×10^{-5}	7.3×10^{-1}	9.1×10^{-5}	1.1×10^{-4}	1.3×10^{-5}	1.9×10^{-3}	-

Table 51: Non-carcinogenic Risk Index for Dermal Contact of Metals in Sediment for Resident Child and Adult.

		Hazard Quotient								
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb	Hg
Mining										
AOB	Adult	1.4 x10^{-5}	1.6 x10^{-3}	2.1 x10^{-4}	7.1 x10^{-5}	1.2 x10^{-5}	4.5 x10^{-1}	2.2 x10^{-5}	2.7 x10^{-4}	3.2 x10^{-4}
	Child	6.5 x10^{-5}	1.5 x10^{-3}	9.9 x10^{-4}	6.8 x10^{-5}	1.1 x10^{-5}	2.17	1.1 x10^{-4}	1.3 x10^{-3}	1.5 x10^{-3}
BAM	Adult	2.7 x10^{-5}	2.8 x10^{-3}	4.1 x10^{-4}	1.1 x10^{-4}	9.3 x10^{-6}	1.1 x10^{-2}	1.3 x10^{-5}	3.5 x10^{-4}	6.4 x10^{-5}
	Child	1.3 x10^{-4}	2.7 x10^{-3}	1.9 x10^{-3}	9.9 x10^{-5}	8.9 x10^{-6}	5.3 x10^{-2}	6.3 x10^{-5}	1.7 x10^{-3}	3.1 x10^{-4}
EAM	Adult	3.1 x10^{-5}	1.2 x10^{-2}	6.6 x10^{-4}	1.3 x10^{-4}	2.0 x10^{-5}	4.0 x10^{-2}	1.7 x10^{-5}	3.5 x10^{-4}	1.3 x10^{-4}
	Child	1.5 x10^{-4}	1.2 x10^{-2}	3.2 x10^{-3}	1.3 x10^{-4}	1.9 x10^{-5}	1.9 x10^{-1}	8.4 x10^{-5}	1.7 x10^{-3}	6.2 x10^{-4}
WTB	Adult	3.0 x10^{-5}	1.6 x10^{-3}	4.6 x10^{-4}	5.9 x10^{-5}	8.1 x10^{-6}	5.5 x10^{-3}	1.7 x10^{-5}	4.9 x10^{-4}	
	Child	1.5 x10^{-4}	1.5 x10^{-3}	2.3 x10^{-3}	5.7 x10^{-5}	7.8 x10^{-6}	2.6 x10^{-2}	8.4 x10^{-5}	2.4 x10^{-3}	
Pristine										
AOD	Adult	8.6 x10^{-6}	1.7 x10^{-3}	1.0 x10^{-4}	2.4 x10^{-5}	4.1 x10^{-6}	2.2 x10^{-3}	8.8 x10^{-6}	8.3 x10^{-5}	4.3 x10^{-5}
	Child	4.2 x10^{-5}	1.7 x10^{-3}	4.9 x10^{-4}	2.3 x10^{-5}	3.9 x10^{-6}	1.1 x10^{-2}	4.2 x10^{-5}	4.0 x10^{-4}	2.1 x10^{-4}
BB	Adult	6.9 x10^{-6}	1.8 x10^{-3}	1.7 x10^{-4}	4.6 x10^{-5}	8.0 x10^{-6}	1.1 x10^{-3}	1.4 x10^{-5}	1.3 x10^{-4}	
	Child	3.4 x10^{-5}	1.7 x10^{-3}	8.1 x10^{-4}	4.4 x10^{-5}	7.7 x10^{-6}	5.3 x10^{-3}	6.8 x10^{-5}	6.1 x10^{-4}	
EA	Adult	3.9 x10^{-5}	9.3 x10^{-3}	1.1 x10^{-3}	2.4 x10^{-4}	2.4 x10^{-5}	4.9 x10^{-2}	2.7 x10^{-5}	3.7 x10^{-4}	1.5 x10^{-4}
	Child	1.9 x10^{-4}	8.9 x10^{-3}	5.2 x10^{-3}	2.3 x10^{-4}	2.4 x10^{-5}	2.4 x10^{-1}	1.3 x10^{-4}	1.8 x10^{-3}	7.2 x10^{-4}
CK	Adult	5.5 x10^{-6}	4.7 x10^{-2}	6.6 x10^{-5}	1.7 x10^{-5}	2.4 x10^{-6}	1.5 x10^{-3}	5.7 x10^{-6}	7.9 x10^{-5}	
	Child	2.7 x10^{-5}	4.6 x10^{-2}	3.2 x10^{-4}	1.6 x10^{-5}	2.3 x10^{-6}	7.2 x10^{-3}	2.8 x10^{-5}	3.8 x10^{-4}	
NM	Adult	1.7 x10^{-5}	6.1 x10^{-3}	4.8 x10^{-4}	8.6 x10^{-5}	9.4 x10^{-6}	4.1 x10^{-3}	2.7 x10^{-6}	3.7 x10^{-4}	
	Child	8.1 x10^{-5}	5.9 x10^{-3}	2.3 x10^{-3}	8.4 x10^{-5}	9.1 x10^{-6}	2.0 x10^{-2}	1.3 x10^{-5}	1.8 x10^{-3}	
VKP	Adult	5.0 x10^{-4}	4.1 x10^{-4}	9.7 x10^{-3}	2.4 x10^{-4}	1.4 x10^{-5}	2.2 x10^{-3}	1.7 x10^{-5}	4.2 x10^{-4}	
	Child	2.4 x10^{-3}	3.9 x10^{-4}	4.7 x10^{-2}	2.3 x10^{-4}	1.3 x10^{-5}	1.0 x10^{-2}	8.1 x10^{-5}	2.0 x10^{-3}	
WA	Adult	1.6 x10^{-6}	7.6 x10^{-4}	1.9 x10^{-5}	1.4 x10^{-6}	3.1 x10^{-6}	3.3 x10^{-5}	4.1 x10^{-6}	5.9 x10^{-5}	
	Child	7.8 x10^{-6}	7.3 x10^{-4}	9.1 x10^{-5}	1.3 x10^{-6}	3.0 x10^{-6}	1.6 x10^{-4}	2.0 x10^{-5}	2.9 x10^{-4}	

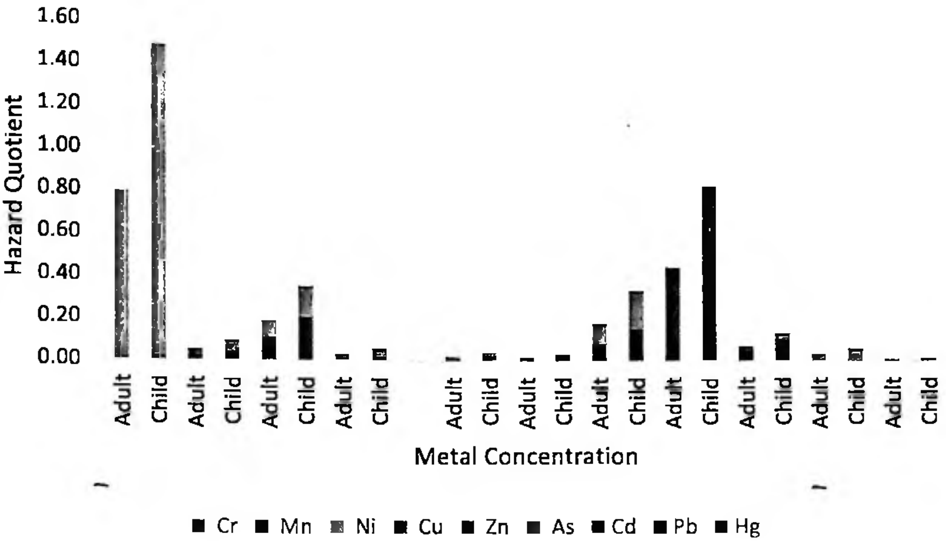


Figure 31: Non-carcinogenic Risk (ingestion) of Metals in Sediment for Child and Adult Residents in the Pristine and Mining Areas.

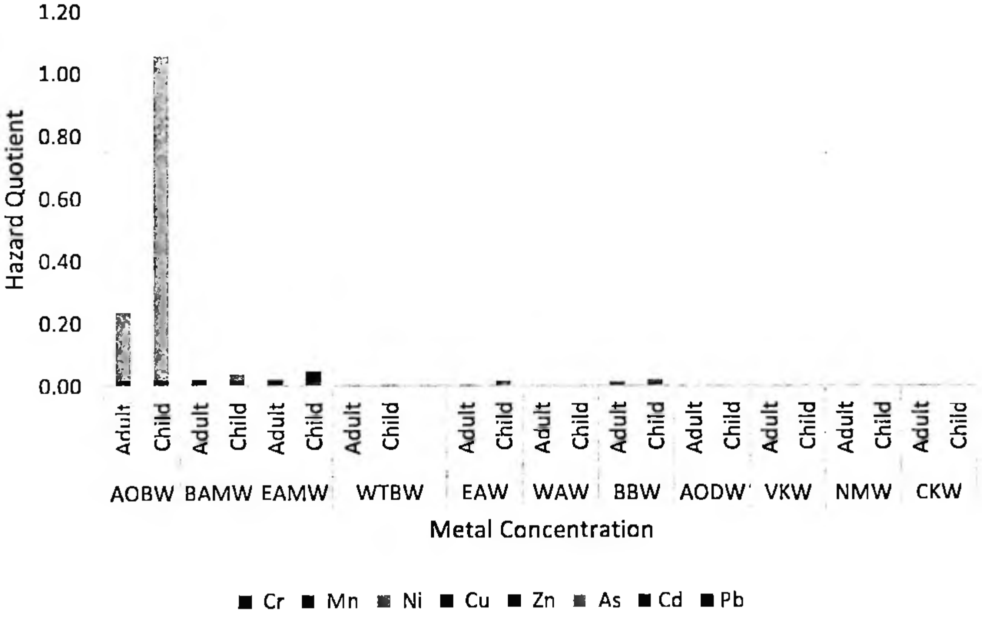


Figure 32: Non-carcinogenic Risk (dermal contact) of Metals in Sediment for Child and Adult Residents in the Pristine and Mining Areas.

Carcinogenic Risk for Sediment

The results of cancer health risk for resident adult and child exposed to As, Cd, Ni, Cr and Pb via oral ingestion and dermal contact of river sediments are presented in Tables 52 and 53. Cancer health risk is defined as the probability of an individual to develop cancer during his or her lifetime due to exposure to harmful chemicals under specific exposure scenarios estimated. The carcinogenic risk (CR) for ingestion and dermal contact was calculated for Cr, Pb, As and Ni and compared with the U.S. EPA Exposure Factors and the International Agency for Research on Cancer (IARC), which have these metals among list of metals that are likely to be carcinogenic through oral ingestion and dermal contact in sediments (ATSDR, 2007; USEPA, 1999).

For child and adult residents, carcinogenic risks for the metals in sediment were determined for As, Cr, Ni, Cd and Pb under the Central Tendency Exposure scenario (CTE) (risk analysis using average concentrations). For ingestion, (Table 53), the highest cancer risk of resident adult and child due to exposure to the heavy metals in sediments were recorded for Cr in river VKP as 3.9 x10^{-2} and 7.4 x10^{-2}, respectively in the mining areas. For the pristine, the highest cancer risk was recorded for adult and child residents from river VKP for Cr as 6.5 x10^{-1} and 1.2 respectively. For dermal contact, similar results were obtained where Cr recorded the highest cancer risk in river EAM (1.1 x10-1) and WTB (1.0 x10^{-1}) for child residents and river AOB (1.0 x10^{-2}) for adult resident in the mining areas (Table 53). The graphical representation of the CR for adult and child residents in the pristine and mining sites is shown in Figures 33 and 34. The carcinogenic risks for As, Ni, Cd and Pb due to ingestion are within the USEPA risk assessment guidelines limit (1.0 x10^{-6} to 1.0 x10^{-4}) (USEPA, 1997; USEPA, 2004) except Cr which pose serious carcinogenic risk threat in the pristine and the mining areas ranging from 2.1 x10^{-3} to 1.2 and 3.3 x10^{-2} to 7.4 x10^{-2} respectively.

implies that for Cr, there is a likelihood that up to 1 to 2 adults, out of one thousand and 3 to 7 children out of one hundred respectively if equally exposed continuously to the specific metals concentration via ingestion in sediment over 70 years would contract cancer. The carcinogenic risk for Cr due to dermal contact in all the sediment samples in the pristine and mining sites are above the USEPA guideline limit for child and adult residents. For the sediment, it was observed from the study that in both children and adults, dermal contact poses higher cancer risks compared with ingestion. The values from this study are comparable with results obtained by other researchers where HQ of Cr exceeded 1.0 and CR exceeded USEPA carcinogenic risk limit of 1.0×10^{-6} to 1.0×10^{-4} (Obiri *et al.*, 2016; Obri *et al.*, 2010; Armah & Gyeabour, 2013).

The high carcinogenic risk values recorded for Cr in this study raise carcinogenic concerns for the local residents living around the catchment areas. Meanwhile, ingestion or dermal contact of chromium can result in several complications, notable among them include: Skin sensitization through chronic skin exposure resulting in skin abnormalities, gastrointestinal complications including diarrhea and vomiting with blood, electrolyte imbalances can result in severe damage to vital organs, increased blood and tissue acidity which can cause vital organs to fail, cancers of the liver and kidney and lung and respiratory tract cancer (ToxFAQs, 2014; Costa & Klein, 2006).

Table 52: Carcinogenic Risk Index for Child and Adult Residents for Ingestion of Sediment

		Carcinogenic Risk				
Site	Age	Cr	Ni	As	Cd	Pb
Mining						
AOBD	Adult	1.8 x10^{-2}	1.2 x10^{-5}	3.5 x10^{-4}	2.3 x10^{-4}	3.9 x10^{-5}
	Child	3.3 x10^{-2}	2.3 x10^{-5}	6.5 x10^{-4}	4.3 x10^{-4}	7.4 x10^{-5}
BAMD	Adult	3.5 x10^{-2}	2.4 x10^{-5}	8.5 x10^{-6}	1.4 x10^{-4}	5.1 x10^{-5}
	Child	6.6 x10^{-2}	4.4 x10^{-5}	1.6 x10^{-5}	2.6 x10^{-4}	9.5 x10^{-5}
EAMD	Adult	3.9 x10^{-2}	3.9 x10^{-5}	3.1 x10^{-5}	1.8 x10^{-4}	5.2 x10^{-5}
	Child	7.4 x10^{-2}	7.2 x10^{-5}	5.8 x10^{-5}	3.4 x10^{-4}	9.6 x10^{-5}
WTBD	Adult	3.9 x10^{-2}	2.7 x10^{-5}	4.3 x10^{-6}	1.8 x10^{-4}	7.2 x10^{-5}
	Child	7.4 x10^{-2}	5.1 x10^{-5}	7.9 x10^{-6}	3.4 x10^{-4}	1.4 x10^{-4}
Pristine						
AOD	Adult	1.1 x10^{-2}	6.0 x10^{-6}	1.7 x10^{-6}	9.2 x10^{-5}	1.2 x10^{-5}
	Child	2.1 x10^{-2}	1.1 x10^{-5}	3.2 x10^{-6}	1.7 x10^{-4}	2.3 x10^{-5}
BB	Adult	8.9 x10^{-3}	9.9 x10^{-6}	8.5 x10^{-7}	1.5 x10^{-4}	1.8 x10^{-5}
	Child	1.7 x10^{-2}	1.8 x10^{-5}	1.6 x10^{-6}	2.8 x10^{-4}	3.4 x10^{-5}
EA	Adult	5.0 x10^{-2}	6.4 x10^{-5}	3.8 x10^{-5}	2.8 x10^{-4}	5.4 x10^{-5}
	Child	9.4 x10^{-2}	1.2 x10^{-4}	7.1 x10^{-5}	5.3 x10^{-4}	1.0 x10^{-4}
CK	Adult	7.2 x10^{-3}	3.9 x10^{-6}	1.2 x10^{-6}	6.1 x10^{-5}	1.2 x10^{-5}
	Child	1.4 x10^{-2}	7.2 x10^{-6}	2.2 x10-6	1.1 x10^{-4}	2.2 x10^{-5}
NM	Adult	2.2 x10^{-2}	2.8 x10^{-5}	3.2 x10^{-6}	2.9 x10^{-5}	5.4 x10^{-5}
	Child	4.1 x10^{-2}	5.3 x10^{-5}	5.9 x10^{-6}	5.4 x10^{-5}	1.0 x10^{-4}
VKP	Adult	6.5 x10^{-1}	5.7 x10^{-4}	1.7 x10^{-6}	1.8 x10^{-4}	6.2 x10^{-5}
	Child	1.2	1.1 x10^{-3}	3.1 x10^{-6}	3.3 x10^{-4}	1.2 x10^{-4}
WA	Adult	2.1 x10^{-3}	1.1 x10^{-6}	2.6 x10^{-8}	4.3 x10^{-5}	8.7 x10^{-6}
	Child	3.9 x10^{-3}	2.1 x10^{-6}	4.8 x10^{-8}	7.9 x10^{-5}	1.6 x10^{-5}

Table 53: Carcinogenic Risk Index for Child and Adult Residents for Dermal Contact of Sediment

Site		Carcinogenic Risk				
		Cr	Ni	As	Cd	Pb
Mining						
AOB	Adult	1.0 x10^{-2}	7.0 x10^{-6}	2.0 x10^{-4}	1.3 x10^{-4}	2.3 x10^{-6}
	Child	4.9 x10^{-2}	3.4 x10^{-5}	9.8 x10^{-4}	6.4 x10^{-4}	1.1 x10^{-5}
BAM	Adult	2.0 x10^{-2}	1.4 x10^{-5}	4.9 x10^{-6}	7.9 x10^{-5}	2.9 x10^{-6}
	Child	9.8 x10^{-2}	6.6 x10^{-5}	2.4 x10^{-5}	3.8 x10^{-4}	1.4 x10^{-5}
EAM	Adult	2.3 x10^{-2}	2.2 x10^{-5}	1.8 x10^{-5}	1.1 x10^{-4}	2.9 x10^{-6}
	Child	1.1 x10^{-1}	1.1 x10^{-4}	8.6 x10^{-5}	5.1 x10^{-4}	1.4 x10^{-5}
WTB	Adult	2.3 x10^{-2}	1.6 x10^{-5}	2.5 x10^{-6}	1.1 x10^{-4}	4.2 x10^{-6}
	Child	1.1 x10^{-1}	7.6 x10^{-5}	1.2 x10^{-5}	5.1 x1^{-4}	2.0 x10^{-5}
Pristine						
AO	Adult	6.5 x10^{-3}	3.5 x10^{-6}	9.9 x10^{-7}	5.3 x10^{-5}	7.0 x10^{-7}
	Child	3.1 x10^{-2}	1.7 x10^{-5}	4.8 x10^{-6}	2.6 x10^{-4}	3.4 x10^{-6}
BB	Adult	5.2 x10^{-3}	5.7 x10^{-6}	4.9 x10^{-7}	8.6 x10^{-5}	1.1 x10^{-6}
	Child	2.5 x10^{-2}	2.8 x10^{-5}	2.4 x10^{-6}	4.2 x10^{-4}	5.1 x10^{-6}
EA	Adult	2.9 x10^{-2}	3.7 x10^{-5}	2.2 x10^{-5}	1.6 x10^{-4}	3.2 x10^{-6}
	Child	1.4 x10^{-1}	1.8 x10^{-4}	1.1 x10^{-4}	7.9 x10^{-4}	1.5 x10^{-5}
CK	Adult	4.2 x10^{-3}	2.2 x10^{-6}	6.7 x10^{-7}	3.5 x10^{-5}	6.7 x10^{-7}
	Child	2.0 x10^{-2}	1.1 x10^{-5}	3.3 x10^{-6}	1.7 x10^{-4}	3.3 x10^{-6}
NM	Adult	1.3 x10^{-2}	1.6 x10^{-5}	1.8 x10^{-6}	1.7 x10^{-5}	3.1 x10^{-6}
	Child	6.1 x10^{-2}	7.9 x10^{-5}	8.9 x10^{-6}	7.9 x10^{-5}	1.5 x10^{-5}
VKP	Adult	3.8 x10^{-1}	3.3 x10^{-4}	9.6 x10^{-7}	1.0 x10^{-4}	3.6 x10^{-6}
	Child	1.82	1.6 x10^{-3}	4.6 x10^{-6}	4.9 x10^{-4}	1.7 x10^{-5}
WA	Adult	1.2 x10^{-3}	6.4 x10^{-7}	1.5 x10^{-8}	2.5 x10^{-5}	5.0 x10^{-7}
	Child	5.8 x10^{-3}	3.1 x10^{-6}	7.2 x10^{-8}	1.2 x10^{-4}	2.4 x10^{-6}

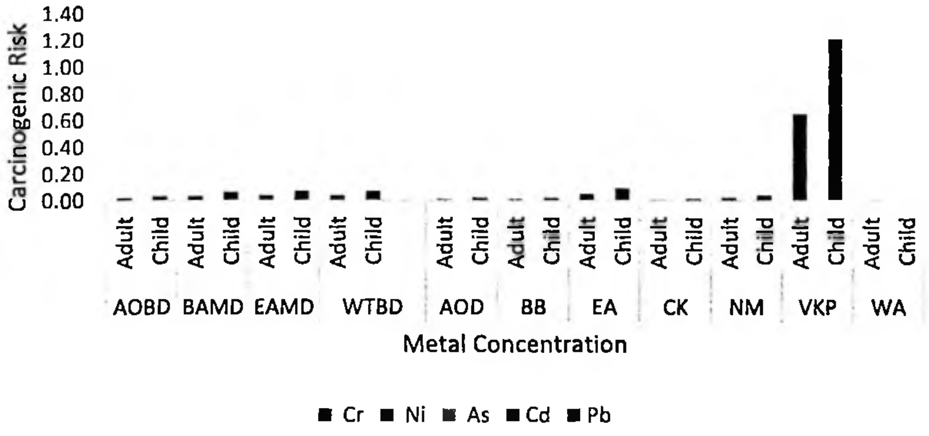


Figure 33: Carcinogenic Risk (ingestion) of Metals in Sediment for Child and Adult Residents in the Pristine and Mining Areas.

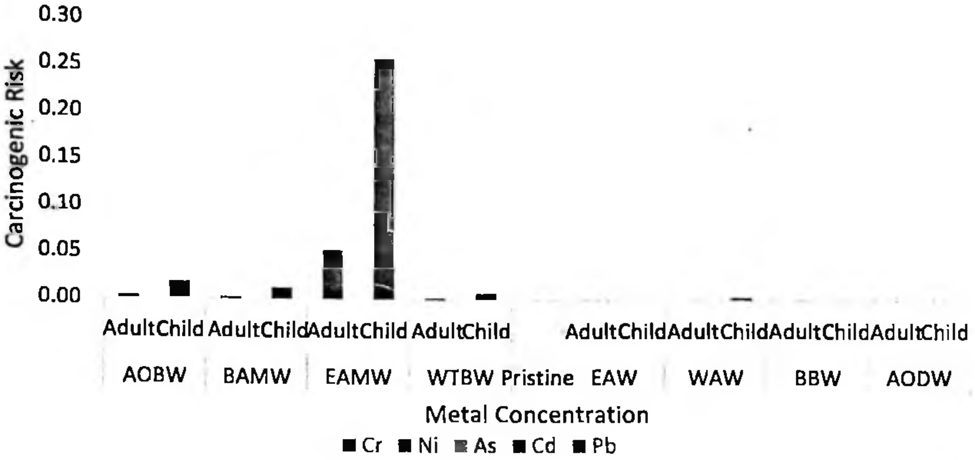


Figure 34: Carcinogenic Risk (dermal contact) of Metals in Sediment for Child and Adult Residents in the Pristine and Mining Areas

Non-carcinogenic Risk of Metals in the Soil

The central Tendency Exposure Scenario (CTE) was used to estimate the non-carcinogenic health hazards indices for Cr, Mn, Ni, Cu, Zn, Cd, Hg and As in soil samples obtained from four major mining areas and seven forest reserve/conservations. The concerned categories are adult and child residents and the hazard quotients were calculated for oral ingestion and dermal contact as shown in Tables 54-57, while Tables 58 and 59 displays the cancer risk results for oral ingestion and dermal contact for the heavy metals respectively.

The Hazard Quotient (HQ) results in Tables 54-57 present the metals in the pristine and the mining sites where all the metals showed a non-cancer risk for ingestion and dermal contact less than 1.0 for adult and child residents. However, child residents are at higher non-cancer risk compared with adults. The HQ of As showed values for resident child higher than 1.0 for ingestion (1.39) and dermal contact (2.07) around Obuasi gold mine (AOB) raising non-carcinogenic risk concern for children living around the mining area. Similar high levels of As in soil was reported in a study where emphasis was particularly given to As due to its reported cases of poisoning and cancer related issues in the region (Antwi-Agyei *et al.*, 2009). The study recorded non-carcinogenic and carcinogenic risk values for As at some mining areas far exceeding 1.0 (HQ) and 1.0 x10^{-4} (CR) upper guideline limit respectively and was indicated as unacceptable (Li, Ma, van der Kuijp, Yuan, & Huang, 2014; Koki, Bayero, Umar, & Yusuf, 2015).

Similar to the trend observed with water and sediment in this study, the HQ for resident child and adult through ingestion of soil poses higher non-cancer risks compared to dermal contact with the soil. Also the HQ for all the metals except Cu is higher for resident child than the adults which can be attributed to shorter duration of exposure for children. Even though the HQ values for all the metals were below 1.0, As, Pb and Mn showed HQ values close to the guideline limit (1.0) suggesting an acceptable non-carcinogenic health risk threat from ingestion and dermal contact of the metals to the residents. Again, though, the HQ for ingestion and dermal contact of the metals were relatively lower, they still represent a large range of risk from 5.3 x10^{-9} (Cu) to 1.4 (As) and 3.9 x10^{-6} (Zn) to 2.1 (As) respectively.

The graphical representation of the HQ for adult and child residents in the pristine and mining sites is shown in Figures 35 and 36. Overall, the results show that As pose non-cancer risk in river AOB to resident child due to ingestion and dermal contact (Tables 54-57). This implies that adverse health effects from exposure to As in the soils are possible. Although the HQs are below the acceptable limit of 1.0, the range of HQ values points to the importance of having heavy metals measured in soils from major mining areas in Ghana.

Table 54: Non-carcinogenic Risk Index for Ingestion of Heavy Metals in Mine Soil by Child and Adult Residents

		Hazard Quotient							
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Mining									
AOB	Adult	2.6 x10^{-5}	2.6 x10^{-2}	5.3 x10^{-4}	2.3 x10^{-6}	2.2 x10^{-4}	7.4 x10^{-1}	4.1 x10^{-5}	6.1 x10^{-3}
	Child	4.8 x10^{-5}	4.9 x10^{-2}	9.9 x10^{-4}	1.3 x10^{-7}	4.1 x10^{-4}	1.39	7.7 x10^{-5}	1.2 x10^{-2}
EAM	Adult	3.9 x10^{-5}	8.8 x10^{-2}	8.6 x10^{-4}	1.1 x10^{-6}	3.1 x10^{-4}	4.9 x10^{-2}	2.9 x10^{-5}	7.6 x10^{-3}
	Child	7.3 x10^{-5}	1.6 x10^{-1}	1.6 x10^{-3}	6.0 x10^{-8}	5.8 x10^{-4}	9.3 x10^{-2}	5.5 x10^{-5}	1.4 x10^{-2}
BAM	Adult	1.3 x10^{-5}	1.9 x10^{-2}	2.1 x10^{-4}	2.9 x10^{-7}	7.9 x10^{-5}	3.9 x10^{-3}	4.1 x10^{-5}	9.3 x10^{-3}
	Child	2.4 x10^{-5}	3.7 x10^{-2}	3.9 x10^{-4}	1.6 x10^{-8}	1.5 x10^{-4}	7.3 x10^{-3}	7.7 x10^{-5}	1.7 x10^{-2}
WTB	Adult	2.4 x10^{-5}	1.0 x10^{-2}	3.1 x10^{-4}	1.5 x10^{-7}	6.4 x10^{-5}	3.6 x10^{-3}	5.9 x10^{-5}	2.5 x10^{-3}
	Child	4.5 x10^{-5}	1.9 x10^{-2}	5.7 x10^{-4}	8.4 x10^{-9}	1.2 x10^{-4}	6.8 x10^{-3}	1.1 x10^{-4}	4.7 x10^{-3}

Table 55: Non-carcinogenic Risk Index for Ingestion of the Metals in Pristine Soil by Child and Adult Residents

		Hazard Quotient							
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Pristine									
AOD	Adult	1.3×10^{-5}	1.3×10^{-2}	1.6×10^{-4}	2.4×10^{-7}	6.8×10^{-5}	3.1×10^{-2}	8.8×10^{-5}	2.8×10^{-3}
	Child	2.4×10^{-5}	2.4×10^{-2}	3.1×10^{-4}	1.3×10^{-8}	1.3×10^{-4}	5.8×10^{-2}	1.6×10^{-4}	5.2×10^{-3}
BB	Adult	6.9×10^{-5}	1.3×10^{-1}	2.2×10^{-3}	2.3×10^{-6}	4.7×10^{-4}	2.7×10^{-3}	1.2×10^{-5}	6.6×10^{-3}
	Child	1.3×10^{-4}	2.4×10^{-1}	4.1×10^{-3}	1.3×10^{-7}	8.8×10^{-4}	5.0×10^{-3}	2.2×10^{-5}	1.2×10^{-2}
EA	Adult	1.4×10^{-5}	5.1×10^{-2}	4.8×10^{-4}	5.9×10^{-7}	9.2×10^{-5}	1.2×10^{-1}	2.4×10^{-5}	2.7×10^{-3}
	Child	2.5×10^{-5}	9.6×10^{-2}	9.0×10^{-4}	3.3×10^{-8}	1.7×10^{-4}	2.3×10^{-1}	4.4×10^{-5}	4.9×10^{-3}
CK	Adult	6.9×10^{-6}	3.1×10^{-3}	1.3×10^{-4}	9.6×10^{-8}	7.8×10^{-5}	2.9×10^{-3}	1.8×10^{-5}	5.8×10^{-3}
	Child	1.3×10^{-5}	5.7×10^{-3}	2.5×10^{-4}	5.3×10^{-9}	1.5×10^{-4}	5.4×10^{-3}	3.3×10^{-5}	1.1×10^{-2}
	Adult	3.4×10^{-5}	1.5×10^{-1}	9.5×10^{-4}	3.2×10^{-7}	2.4×10^{-4}	1.1×10^{-3}	3.5×10^{-5}	9.0×10^{-3}
	Child	6.3×10^{-5}	2.7×10^{-1}	1.8×10^{-3}	1.8×10^{-8}	4.4×10^{-4}	2.1×10^{-3}	6.6×10^{-5}	1.7×10^{-2}
NM	Adult	1.0×10^{-5}	2.9×10^{-2}	2.2×10^{-4}	2.2×10^{-7}	7.8×10^{-5}	4.0×10^{-3}	-	3.4×10^{-3}
	Child	1.9×10^{-5}	5.5×10^{-2}	4.2×10^{-4}	1.20×10^{-8}	1.5×10^{-4}	7.5×10^{-3}	-	6.4×10^{-3}
VKP	Adult	2.2×10^{-5}	5.2×10^{-3}	4.9×10^{-4}	8.6×10^{-7}	1.3×10^{-4}	4.3×10^{-3}	-	1.6×10^{-3}
	Child	4.1×10^{-5}	9.7×10^{-3}	9.2×10^{-4}	4.7×10^{-8}	2.5×10^{-4}	7.9×10^{-3}	-	2.9×10^{-3}
WA	Adult	5.0×10^{-4}	1.2×10^{-1}	7.6×10^{-3}	2.1×10^{-6}	2.3×10^{-4}	2.9×10^{-3}	2.4×10^{-5}	6.2×10^{-3}
	Child	9.4×10^{-4}	2.3×10^{-1}	1.4×10^{-2}	1.2×10^{-7}	4.3×10^{-4}	5.6×10^{-3}	4.4×10^{-5}	1.2×10^{-2}

Table 56: Non-carcinogenic Risk Index for Dermal Contact of Metals in Mine Soil by Child and Adult Residents

		Hazard Quotient							
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Mining									
AOB	Adult	1.5×10^{-5}	2.8×10^{-3}	3.1×10^{-4}	2.4×10^{-4}	1.4×10^{-5}	4.3×10^{-1}	2.4×10^{-5}	3.5×10^{-4}
	Child	7.1×10^{-5}	2.7×10^{-3}	1.5×10^{-3}	2.3×10^{-4}	1.3×10^{-5}	2.1	1.2×10^{-4}	1.7×10^{-3}
BAM	Adult	2.2×10^{-5}	9.3×10^{-3}	4.9×10^{-4}	1.2×10^{-4}	1.9×10^{-5}	2.9×10^{-2}	1.7×10^{-5}	4.4×10^{-4}
	Child	1.1×10^{-4}	8.9×10^{-3}	2.4×10^{-3}	1.1×10^{-4}	1.9×10^{-5}	1.4×10^{-1}	8.2×10^{-5}	2.1×10^{-3}
EAM	Adult	7.4×10^{-6}	2.1×10^{-3}	1.2×10^{-4}	3.0×10^{-5}	5.0×10^{-6}	2.3×10^{-3}	2.4×10^{-5}	5.4×10^{-4}
	Child	3.6×10^{-5}	2.0×10^{-3}	5.9×10^{-4}	2.9×10^{-5}	4.8×10^{-6}	1.1×10^{-2}	1.2×10^{-4}	2.6×10^{-3}
WTB	Adult	1.4×10^{-5}	1.1×10^{-3}	1.8×10^{-4}	1.6×10^{-5}	4.1×10^{-6}	2.1×10^{-3}	3.4×10^{-5}	1.5×10^{-4}
	Child	6.7×10^{-5}	1.1×10^{-3}	8.5×10^{-4}	1.5×10^{-5}	3.9×10^{-6}	1.0×10^{-2}	1.6×10^{-4}	7.0×10^{-4}

Table 57: Non-carcinogenic Risk Index for Dermal Contact of Metals in Pristine Soil by Child and Adult Residents

		Hazard Quotient							
Site	Age	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Pristine									
AOD	Adult	7.5 x10^{-6}	1.3 x10^{-3}	9.4 x10^{-5}	2.5 x10^{-5}	4.3 x10^{-6}	1.8 x10^{-2}	5.1 x10^{-5}	1.6 x10^{-4}
	Child	3.6 x10^{-5}	1.3 x10^{-3}	4.5 x10^{-4}	2.4 x10^{-5}	4.2 x10^{-6}	8.7 x10^{-2}	2.5 x10^{-4}	7.8 x10^{-4}
BB	Adult	3.9 x10^{-5}	1.4 x10^{-2}	1.3 x10^{-3}	2.4 x10^{-4}	3.0 x10^{-5}	1.6 x10^{-3}	6.8 x10^{-6}	3.8 x10^{-4}
	Child	1.9 x10^{-4}	1.3 x10^{-2}	6.1 x10^{-3}	2.3 x10^{-4}	2.9 x10^{-5}	7.5 x10^{-3}	3.3 x10^{-5}	1.9 x10^{-3}
EA	Adult	7.8 x10^{-6}	5.4 x10^{-3}	2.8 x10^{-4}	6.2 x10^{-5}	5.8 x10^{-6}	7.0 x10^{-2}	1.4 x10^{-5}	1.5 x10^{-4}
	Child	3.8 x10^{-5}	5.3 x10^{-3}	1.4 x10^{-3}	5.9 x10^{-5}	5.6 x10^{-6}	3.4 x10^{-1}	6.6 x10^{-5}	7.5 x10^{-4}
CK	Adult	4.0 x10^{-6}	3.2 x10^{-4}	7.7 x10^{-5}	1.0 x10^{-5}	4.9 x10^{-6}	1.7 x10^{-3}	1.0 x10^{-5}	3.3 x10^{-4}
	Child	1.9 x10^{-5}	3.1 x10^{-4}	3.7 x10^{-4}	9.7 x10^{-6}	4.8 x10^{-6}	8.0 x10^{-3}	4.9 x10^{-5}	1.6 x10^{-3}
GSH	Adult	1.9 x10^{-5}	1.5 x10^{-2}	5.5 x10^{-4}	3.4 x10^{-5}	1.5 x10^{-5}	6.3 x10^{-4}	2.1 x10^{-5}	5.2 x10^{-4}
	Child	9.4 x10^{-5}	1.5 x10^{-2}	2.6 x10^{-3}	3.3 x10^{-5}	1.4 x10^{-5}	3.1 x10^{-3}	9.8 x10^{-5}	2.5 x10^{-3}
NM	Adult	5.8 x10^{-6}	3.1 x10^{-3}	1.3 x10^{-4}	2.3 x10^{-5}	4.9 x10^{-6}	2.3 x10^{-3}	-	1.9 x10^{-4}
	Child	2.8 x10^{-5}	3.0 x10^{-3}	6.2 x10^{-4}	2.2 x10^{-5}	4.8 x10^{-6}	1.1 x10^{-2}	-	9.6 x10^{-4}
VKP	Adult	1.3 x10^{-5}	5.5 x10^{-4}	2.9 x10^{-4}	8.9 x10^{-5}	8.5 x10^{-6}	2.5 x10^{-3}	-	8.9 x10^{-5}
	Child	6.1 x10^{-5}	5.3 x10^{-4}	1.4 x10^{-3}	8.7 x10^{-5}	8.3 x10^{-6}	1.2 x10^{-2}	-	4.3 x10^{-4}
WA	Adult	2.9 x10^{-4}	1.3 x10^{-2}	4.4 x10^{-3}	2.2 x10^{-4}	1.5 x10^{-5}	1.7 x10^{-3}	1.4 x10^{-5}	3.6 x10^{-4}
	Child	1.4 x10^{-3}	1.2 x10^{-2}	2.1 x10^{-2}	2.1 x10^{-4}	1.4 x10^{-5}	8.3 x10^{-3}	6.6 x10^{-5}	1.7 x10^{-3}

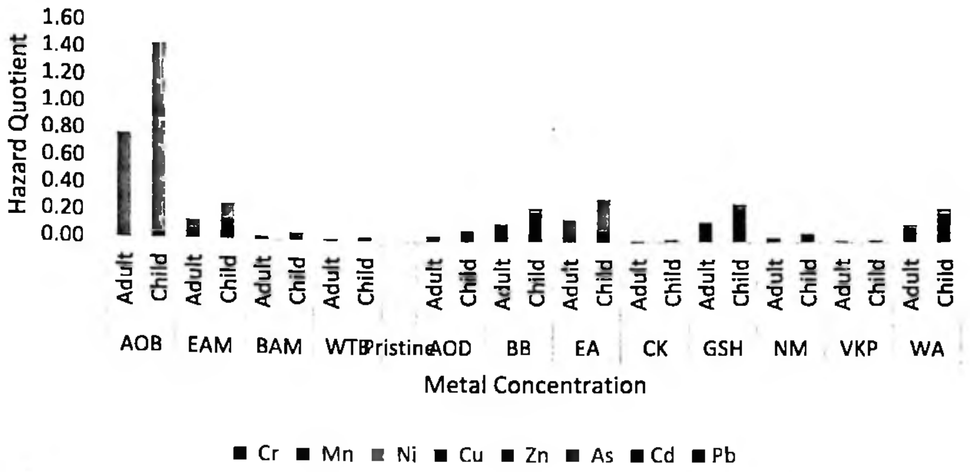


Figure 35: Non-carcinogenic Risk (ingestion) of Metals in Soil for Child and Adult Residents in the Pristine and Mining Areas.

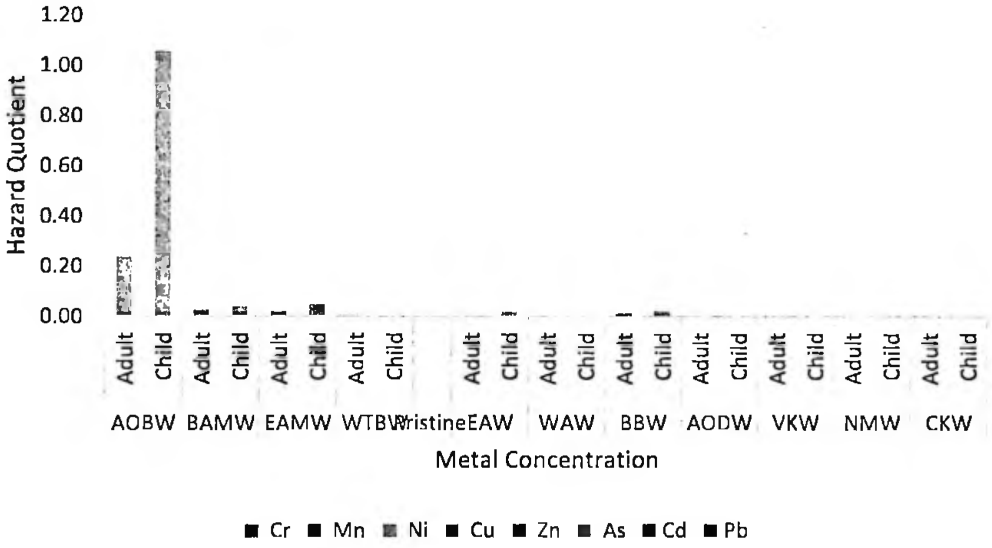


Figure 36: Non-carcinogenic Risk (dermal contact) of Metals in Soil for Child and Adult Residents in the Pristine and Mining Areas.

Carcinogenic Risk for the Metals in Soil

The results of cancer health risk for resident adult and child exposed to As, Cd, Ni, Cr and Pb in soil from the study area via oral ingestion and dermal contact are presented in Tables 58 and 59. The carcinogenic risk (CR) for ingestion and dermal contact was calculated for Cr, Pb, As, Cd and Ni and compared with the U.S. EPA Exposure Factors and the International Agency for Research on Cancer (IARC), which have these metals among list of metals that are likely to be carcinogenic through oral ingestion and dermal contact with soils (ATSDR, 2007; USEPA, 1999).

The highest cancer risk of resident adult and child due to exposure to the heavy metals in soils were recorded for Cr at site WA as 3.8 $\times 10^{-1}$ and 7.0 $\times 10^{-1}$, respectively (Table 58), in the pristine areas. For the dermal contact, similar results were obtained where Cr recorded the highest cancer risk at site WA to be 2.2 $\times 10^{-1}$ for resident adult and 1.1 for resident child. The graphical representation of the CR for adult and child residents in the pristine and mining sites is shown in Figures 37 and 38.

The high carcinogenic risk values recorded for Cr in this study raise carcinogenic concerns for the local residents living around the catchment areas. Meanwhile, ingestion or dermal contact of chromium can result in several complications such as; Skin sensitization through chronic skin exposure resulting in skin abnormalities and gastrointestinal complications. (ToxFAQs, 2014; Costa & Klein, 2006).

Table 58: Carcinogenic Risk Index for Child and Adult Residents for Ingestion of soil

		Carcinogenic Risk				
Site	Age	Cr	Ni	As	Cd	Pb
Mining						
AOB	Adult	1.9 x10^{-2}	1.8 x10^{-5}	3.4 x10^{-4}	2.5 x10^{-4}	5.2 x10^{-5}
	Child	3.6 x10^{-2}	3.4 x10^{-5}	6.2 x10^{-4}	4.7 x10^{-4}	9.7 x10^{-5}
EAM	Adult	2.9 x10^{-2}	2.9 x10^{-5}	2.2 x10^{-5}	1.8 x10^{-4}	6.4 x10^{-5}
	Child	5.4 x10^{-2}	5.5 x10^{-5}	4.2 x10^{-5}	3.3 x10^{-4}	1.2 x10^{-4}
BAM	Adult	9.6 x10^{-3}	7.2 x10^{-6}	1.8 x10^{-6}	2.5 x10^{-4}	7.9 x10^{-5}
	Child	1.8 x10^{-2}	1.4 x10^{-5}	3.3 x10^{-6}	4.7 x10^{-4}	1.4 x10^{-4}
WTB	Adult	1.8 x10^{-2}	1.0 x10^{-5}	1.6 x10^{-6}	3.6 x10^{-4}	2.2 x10^{-5}
	Child	3.4 x10^{-2}	1.9 x10^{-5}	3.0 x10^{-6}	6.7 x10^{-4}	4.0 x10^{-5}
Pristine						
AOD	Adult	9.8 x10^{-3}	5.5 x10^{-6}	1.4 x10^{-5}	5.37 x10^{-4}	2.5 x10^{-5}
	Child	1.8 x10^{-2}	1.0 x10^{-5}	2.6 x10^{-5}	1.0 x10^{-3}	4.5 x10^{-5}
BB	Adult	5.2 x10^{-2}	7.5 x10^{-5}	1.2 x10^{-6}	7.2 x10^{-5}	5.6 x10^{-5}
	Child	9.6 x10^{-2}	1.4 x10^{-4}	2.3 x10^{-6}	1.3 x10^{-4}	1.1 x10^{-4}
EA	Adult	1.0 x10^{-2}	1.6 x10^{-5}	5.5 x10^{-5}	1.4 x10^{-4}	2.3 x10^{-5}
	Child	1.9 x10^{-2}	3.1 x10^{-5}	1.0 x10^{-4}	2.7 x10^{-4}	4.2 x10^{-5}
CK	Adult	5.2 x10^{-3}	4.5 x10^{-6}	1.3 x10^{-6}	1.1 x10^{-4}	4.9 x10^{-5}
	Child	9.7 x10^{-3}	8.4 x10^{-6}	2.4 x10^{-6}	2.0 x10^{-4}	9.1 x10^{-5}
GSH	Adult	2.5 x10^{-2}	3.2 x10^{-5}	4.9 x10^{-7}	2.2 x10^{-4}	7.7 x10^{-5}
	Child	4.7 x10^{-2}	6.0 x10^{-5}	9.2 x10^{-7}	4.0 x10^{-4}	1.4 x10^{-4}
NM	Adult	7.5 x10^{-3}	7.6 x10^{-6}	1.8 x10^{-6}	-	2.9 x10^{-5}
	Child	1.4 x10^{-2}	1.4 x10^{-5}	3.4 x10^{-6}	-	5.4 x10^{-5}
VKP	Adult	1.6 x10^{-2}	1.7 x10^{-5}	1.9 x10^{-6}	-	1.3 x10^{-5}
	Child	3.1 x10^{-2}	3.1 x10^{-5}	3.6 x10^{-6}	-	2.5 x10^{-5}
WA	Adult	3.8 x10^{-1}	2.6 x10^{-4}	1.3 x10^{-6}	1.4 x10^{-4}	5.3 x10^{-5}
	Child	7.0 x10^{-1}	4.8 x10^{-4}	2.5 x10^{-6}	2.7 x10^{-4}	9.8 x10^{-5}

Table 58: Carcinogenic Risk Index for Child and Adult Residents for Ingestion of soil

		Carcinogenic Risk				
Site	**Age**	**Cr**	**Ni**	**As**	**Cd**	**Pb**
Mining						
AOB	Adult	1.9 x10^{-2}	1.8 x10^{-5}	3.4 x10^{-4}	2.5 x10^{-4}	5.2 x10^{-5}
	Child	3.6 x10^{-2}	3.4 x10^{-5}	6.2 x10^{-4}	4.7 x10^{-4}	9.7 x10^{-5}
EAM	Adult	2.9 x10^{-2}	2.9 x10^{-5}	2.2 x10^{-5}	1.8 x10^{-4}	6.4 x10^{-5}
	Child	5.4 x10^{-2}	5.5 x10^{-5}	4.2 x10^{-5}	3.3 x10^{-4}	1.2 x10^{-4}
BAM	Adult	9.6 x10^{-3}	7.2 x10^{-6}	1.8 x10^{-6}	2.5 x10^{-4}	7.9 x10^{-5}
	Child	1.8 x10^{-2}	1.4 x10^{-5}	3.3 x10^{-6}	4.7 x10^{-4}	1.4 x10^{-4}
WTB	Adult	1.8 x10^{-2}	1.0 x10^{-5}	1.6 x10^{-6}	3.6 x10^{-4}	2.2 x10^{-5}
	Child	3.4 x10^{-2}	1.9 x10^{-5}	3.0 x10^{-6}	6.7 x10^{-4}	4.0 x10^{-5}
Pristine						
AOD	Adult	9.8 x10^{-3}	5.5 x10^{-6}	1.4 x10^{-5}	5.37 x10^{-4}	2.5 x10^{-5}
	Child	1.8 x10^{-2}	1.0 x10^{-5}	2.6 x10^{-5}	1.0 x10^{-3}	4.5 x10^{-5}
BB	Adult	5.2 x10^{-2}	7.5 x10^{-5}	1.2 x10^{-6}	7.2 x10^{-5}	5.6 x10^{-5}
	Child	9.6 x10^{-2}	1.4 x10^{-4}	2.3 x10^{-6}	1.3 x10^{-4}	1.1 x10^{-4}
EA	Adult	1.0 x10^{-2}	1.6 x10^{-5}	5.5 x10^{-5}	1.4 x10^{-4}	2.3 x10^{-5}
	Child	1.9 x10^{-2}	3.1 x10^{-5}	1.0 x10^{-4}	2.7 x10^{-4}	4.2 x10^{-5}
CK	Adult	5.2 x10^{-3}	4.5 x10^{-6}	1.3 x10^{-6}	1.1 x10^{-4}	4.9 x10^{-5}
	Child	9.7 x10^{-3}	8.4 x10^{-6}	2.4 x10^{-6}	2.0 x10^{-4}	9.1 x10^{-5}
GSH	Adult	2.5 x10^{-2}	3.2 x10^{-5}	4.9 x10^{-7}	2.2 x10^{-4}	7.7 x10^{-5}
	Child	4.7 x10^{-2}	6.0 x10^{-5}	9.2 x10^{-7}	4.0 x10^{-4}	1.4 x10^{-4}
NM	Adult	7.5 x10^{-3}	7.6 x10^{-6}	1.8 x10^{-6}	-	2.9 x10^{-5}
	Child	1.4 x10^{-2}	1.4 x10^{-5}	3.4 x10^{-6}	-	5.4 x10^{-5}
VKP	Adult	1.6 x10^{-2}	1.7 x10^{-5}	1.9 x10^{-6}	-	1.3 x10^{-5}
	Child	3.1 x10^{-2}	3.1 x10^{-5}	3.6 x10^{-6}	-	2.5 x10^{-5}
WA	Adult	3.8 x10^{-1}	2.6 x10^{-4}	1.3 x10^{-6}	1.4 x10^{-4}	5.3 x10^{-5}
	Child	7.0 x10^{-1}	4.8 x10^{-4}	2.5 x10^{-6}	2.7 x10^{-4}	9.8 x10^{-5}

Table 59: Carcinogenic Risk Index for Child and Adult Residents for Dermal Contact of Soil

		Carcinogenic Risk				
Site	Age	Cr	Ni	As	Cd	Pb
Mining						
AOB	Adult	1.1 x10^{-2}	1.0 x10^{-5}	1.9 x10^{-4}	1.5 x10^{-4}	3.0 x10^{-6}
	Child	5.4 x10^{-2}	5.0 x10^{-5}	9.3 x10^{-4}	7.0 x10^{-4}	1.5 x10^{-5}
BAM	Adult	1.7 x10^{-2}	1.7 x10^{-5}	1.3 x10^{-5}	1.0 x10^{-4}	3.7 x10^{-6}
	Child	8.1 x10^{-2}	8.2 x10^{-5}	6.2 x10^{-5}	5.0 x10^{-4}	1.8 x10^{-5}
EAM	Adult	5.5 x10^{-3}	4.17 x10^{-6}	1.0 x10^{-6}	1.5 x10^{-4}	4.5 x10^{-6}
	Child	2.7 x10^{-2}	2.0 x10^{-5}	4.9 x10^{-6}	6.9 x10^{-4}	2.2 x10^{-5}
WTB	Adult	1.1 x10^{-2}	6.0 x10^{-6}	9.4 x10^{-7}	2.1 x10^{-4}	1.2 x10^{-6}
	Child	5.0 x10^{-2}	2.9 x10^{-5}	4.5 x10^{-6}	9.9 x10^{-4}	5.9 x10^{-6}
Pristine						
AOD	Adult	5.6 x10^{-3}	3.2 x10^{-6}	8.1 x10^{-6}	3.1 x10^{-4}	1.4 x10^{-6}
	Child	2.7 x10^{-2}	1.6 x10^{-5}	3.9 x10^{-5}	1.5 x10^{-3}	6.7 x10^{-6}
BB	Adult	2.9 x10^{-2}	4.3 x10^{-5}	6.9 x10^{-7}	4.2 x10^{-5}	3.3 x10^{-6}
	Child	1.4 x10^{-1}	2.1 x10^{-4}	3.4 x10^{-6}	2.0 x10^{-4}	1.6 x10^{-5}
EA	Adult	5.9 x10^{-3}	9.5 x10^{-6}	3.2 x10^{-5}	8.3 x10^{-5}	1.3 x10^{-6}
	Child	2.8 x10^{-2}	4.6 x10^{-5}	1.5 x10^{-4}	4.0 x10^{-4}	6.3 x10^{-6}
CK	Adult	3.0 x10^{-3}	2.6 x10^{-6}	7.5 x10^{-7}	6.2 x10^{-5}	2.8 x10^{-6}
	Child	1.5 x10^{-2}	1.3 x10^{-5}	3.6 x10^{-6}	3.0 x10^{-4}	1.4 x10^{-5}
GSH	Adult	1.5 x10^{-2}	1.9 x10^{-5}	2.9 x10^{-7}	1.2 x10^{-4}	4.4 x10^{-6}
	Child	7.1 x10^{-2}	8.9 x10^{-5}	1.4 x10^{-6}	5.9 x10^{-4}	2.2 x10^{-5}
NM	Adult	4.3 x10^{-3}	4.4 x10^{-6}	1.1 x10^{-6}	-	1.7 x10^{-6}
	Child	2.1 x10^{-2}	2.1 x10^{-5}	5.1 x10^{-6}	-	8.1 x10^{-6}
VKP	Adult	9.4 x10^{-3}	9.7 x10^{-6}	1.1 x10^{-6}	-	7.6 x10^{-7}
	Child	4.6 x10^{-2}	4.7 x10^{-5}	5.3 x10^{-6}	-	3.7 x10^{-6}
WA	Adult	2.2 x10^{-1}	1.5 x10^{-4}	7.7 x10^{-7}	8.3 x10^{-5}	3.0 x10^{-6}
	Child	1.1	7.2 x10^{-4}	3.7 x10^{-6}	4.0 x10^{-4}	1.5 x10^{-5}

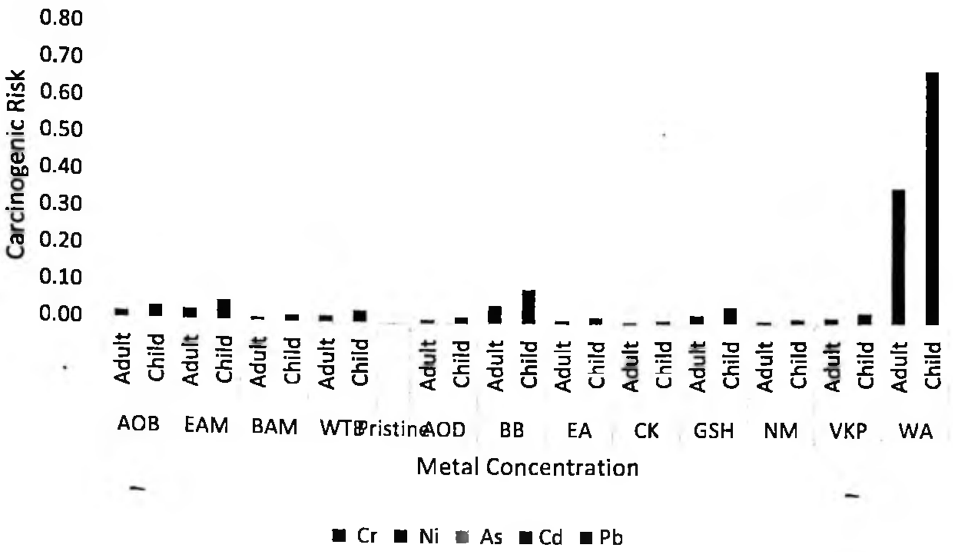


Figure 37: Carcinogenic Risk (ingestion) of Metals in Soil for Child and Adult Residents in the Pristine and Mining Areas.

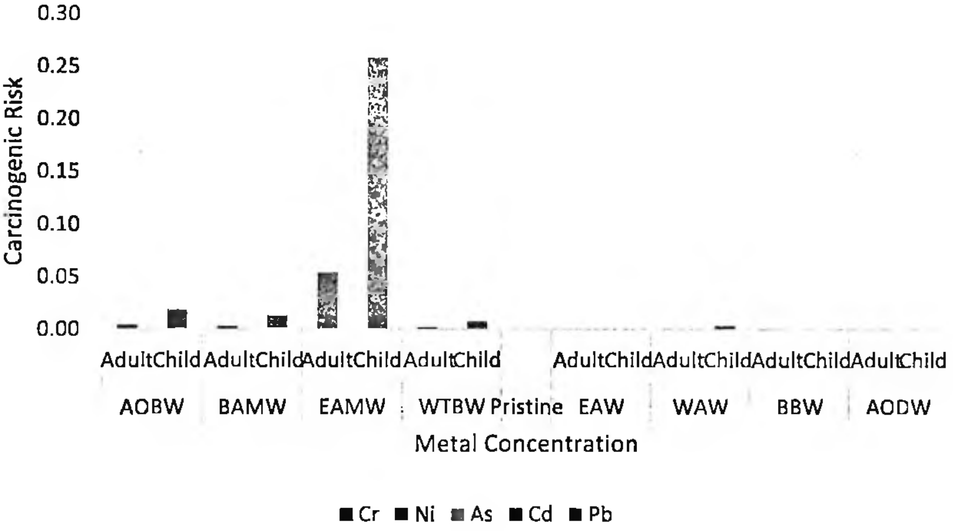


Figure 38: Carcinogenic Risk (dermal contact) of Metals in Soil for Child and Adult Residents in the Pristine and Mining Areas.

Estimation of Geochemical Background and Baseline Values

The study of baseline values is best carried out by first defining the threshold of toxicity for the various heavy metals where the normal values of potentially polluting substances present in natural soils without human influence are calculated, which corresponds to the normal value of an element in a given environment (Santos-Francés *et al.*, 2017; Salminen & Gregorauskiene, 2000; Tack, Verloo, Vanmechelen, & Van Ranst, 1997). According to Reimann *et al.*, (2005), geochemical background concentrations correspond to the values within the range of the arithmetic or geometric mean plus twice the standard deviation (mean ± 2 standard deviation (SDEV)) or (median ± 2 maximum absolute standard deviation (MAD)). This concept comes originally from exploratory geochemistry which defined the outliers as the values falling outside the range (mean ± 2 SDEV) (ISO/DIS, 2002; Hawkes & Webb 1963). When the geochemical baseline values of a region are identified and known, soil/sediment quality standards such as the reference and intervention levels can be established.

The current methodology for assessing environmental quality through the content of the heavy metals in the soils/sediments includes the calculation of several pollution indices such as geo-accumulation index (Igeo), Enrichment factor, Modified Nemerow Pollution Index, Potential Ecological Risk Index (RI), and the Modified Ecological Risk Index for the surface horizons of soils/sediments. Soils and sediment samples are treated using the same method in our study. However, different views are shared by a number of authors as to whether it experimentally prudent to treat the two samples with the same method.

Concentration of Heavy Metals in Soils and Sediments of the Pristine Sites

This section of the study is focused primarily on the understanding the natural metal content of the soils and sediments from the various pristine areas (geochemical background) so as to help estimate the degree of contamination which will further help to compare the state of our environment with that of other countries' regulations worldwide (Santos-Francés *et al.*, 2017; Sterckeman *et al.*, 2006; Pils, Karathanasis, & Mueller, 2004).

In the statistical analysis of the data, the superficial layer (0-20 cm) and the subsurface layer (20-40 cm) were treated separately. The superficial layer (0-20 cm) was taken as the layer that provides information on the levels of pollution caused by the processes of soil formation and by anthropogenic sources, whereas the subsurface layer (20-40 cm) was taken as the layer that represents more lithogenic contributions, since there is little probability of heavy metal contamination through atmospheric deposition and thus was used for the calculation of the natural geological and geochemical background values (Tarvainen & Kallio, 2002).

The average values of the heavy metals obtained from the statistical analysis of the sediments and soils are presented in Tables 60 and 61. The data from this study are compared with literature data from other countries such as the World Mean (Reaves & Berrow, 1984), World Range (Bowen, 1979) and average shale values (Wedepohl, 1995). The average values from the pristine sites for 2014 and 2016 data were calculated and used in the determination of the natural geological values since there were no such previous works done to determine the geological background values at the sites investigated.

Sediment Samples

The background levels of As, Cd and Pb for the sediment samples were below the world average value across all the pristine areas except As at site EA which showed concentration above the world average value as shown in Table 60. The background levels of Cr, Ni, Cu and Zn were below the world average limit at AOD, CK and WA pristine areas. The background levels of Cr and Zn were below the world average while Ni and Cu were above the world average at site BB. In the case of Atiwa range (EA), the background levels for all the metals were above the world average values except Cd and Pb which were below the limit. The background values of Cr content at sites AOD, BB, CK and WA werewithin the world average ranging from 7.39 to 45.41 mg/kg while the Cr content at sites EA, VKP and NM were above the limit, ranging from 75.56 to 2278.68 mg/kg. The background values for Ni at sites AOD, CK and WA were below the world average level whiles the values at sites BB, EA, NM and VKP showed appreciably high Ni levels ranging from 26.40 to 524.28 mg/kg. Sites EA, NM and VKP showed background levels of Cu above the world average value ranging from 23.52 to 67.70 mg/kg. Comparing the background values in this study with the world average and global range values (1 – 1500 mgkg) indicated an abnormally high values across all sample sites for V, Cr, Mn, Fe, Co, Ni and Cu content, at sites EA and VKP. A study conducted by Albanese *et al.*, (2007), to determine the geochemical background and baseline values of some heavy metals in stream sediments of Campania region (Italy), has reported the baseline ranges for As, Cd, Cr, Cu, Pb, Hg and Zn as; 0.08 to 29.3, 0.02 to 1.54, 2 to 71, 5 to 157, 29 to 51, 4 to 67 and 156 to 215 mg/kg respectively. Comparing this work with this report showed that most of the ranges in this study fall within the ranges reported with their maximum concentrations for Zn, Hg, Pb, Cu and Cd higher than those obtained from this study. However, the maximum concentrations for As and Cr were higher than those reported with Cr going as far as 2278.68 mg/kg from this study as against 2-71 mg/kg reported.

The background levels of the heavy metals in the sediment samples were also compared with the average shale concentrations. In summary, the background levels of V, Cr, Mn, Fe, Co, Ni and Cu were substantially high at sites EA and VKP indicating the metals enrichment at these pristine areas whiles the anthropogenic metals (Cd, As, Pb and Hg) showed appreciably high enrichment at site EA. Site EA is one of Ghana's forest conservations which has been invaded by illegal miners over the past years and hence the availability of these metals could be attributed to illegal mining activities. However, the use of agrochemicals in the farm lands around the river plains cannot be excluded as potential metal pollution sources.

Table 60: Statistical Analysis to Determine Geochemical Baseline of the Metals in Sediments at Sites AOD, BB, EA and CK

Site	statistics	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	Hg
	Mean	14752.76	17.94	33.68	112.24	5062.52	3.32	6.97	6.71	13.41	2.17	0.04	3.83	0.02
	Std. Deviation	6027.92	1.02	6.33	78.22	147.05	0.28	1.33	0.23	0.65	0.31	0.02	1.98	
AOD	Minimum	10490.38	17.21	29.21	56.93	4958.55	3.13	6.03	6.55	12.95	1.95	0.03	2.43	
	Maximum	19015.15	18.66	38.16	167.55	5166.50	3.52	7.91	6.87	13.87	2.39	0.06	5.23	
	Geometric Mean	14123.60	17.92	33.39	97.67	5061.45	3.32	6.90	6.71	13.40	2.16	0.04	3.57	0.02
Geochemical Baseline		26179.45	19.97	46.04	254.11	5355.55	3.87	9.57	7.16	14.71	2.78	0.09	7.52	0.02
	Mean	11913.64	27.04	32.35	175.43	9502.67	7.08	42.20	13.27	28.69	5.31	0.05	5.16	
	Std. Deviation	3622.00	1.78	2.46	4.00	450.96	0.58	45.71	1.07	1.61	6.14	0.01	2.09	
BB	Minimum	9352.50	25.79	30.61	172.60	9183.79	6.67	9.87	12.51	27.55	0.97	0.04	3.68	
	Maximum	14474.78	28.30	34.10	178.25	9821.54	7.49	74.52	14.03	29.82	9.66	0.06	6.64	
	Geometric Mean	11635.09	27.01	32.31	175.40	9497.31	7.07	27.12	13.25	28.66	3.06	0.05	4.94	
Geochemical Baseline		18879.09	30.57	37.23	183.39	10399.23	8.23	118.55	15.39	31.87	15.35	0.08	9.13	
	Mean	96672.53	196.09	169.78	882.11	74119.70	30.70	35.01	67.70	86.35	40.00	0.07	7.64	0.07
	Std. Deviation	1877.23	3.10	1.45	14.86	517.68	0.36	40.81	1.88	3.74	4.04	0.02	4.57	
EA	Minimum	95345.12	193.90	168.75	871.60	73753.64	30.45	6.15	66.37	83.70	37.14	0.05	4.41	
	Maximum	97999.93	198.28	170.80	892.61	74485.75	30.96	63.86	69.04	88.99	42.86	0.08	10.87	
	Geometric Mean	96663.41	196.08	169.77	882.04	74118.79	30.70	19.82	67.69	86.30	39.90	0.06	6.92	0.07
Geochemical Baseline		100417.88	202.27	172.67	911.76	75154.15	31.42	101.43	71.46	93.79	47.99	0.11	16.06	0.07
	Mean	24056.95	33.03	45.41	2573.53	12884.78	7.23	8.91	10.81	24.85	2.24	0.04	3.44	
	Std. Deviation	20992.42	28.57	29.67	2821.74	13605.30	8.27	7.11	8.87	23.61	1.30	0.02	1.58	
CK	Minimum	9213.07	12.82	24.43	578.25	3264.38	1.38	3.88	4.54	8.15	1.32	0.02	2.32	
	Maximum	38900.83	53.23	66.40	4568.80	22505.18	13.08	13.94	17.08	41.54	3.16	0.05	4.55	
	Geometric Mean	18931.35	26.12	40.27	1625.39	8571.20	4.25	7.35	8.81	18.40	2.04	0.03	3.25	
Geochemical Baseline		60916.18	83.27	99.62	7268.88	35781.80	20.79	21.58	26.54	65.62	4.64	0.07	6.40	

Table 61: Statistical Analysis to Determine Geochemical Baseline of the Metals in Sediments at Sites NM, WA and WA

Site	Statistics	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
	Mean	55901.18	76.05	75.56	583.91	29067.17	17.91	26.40	23.52	32.66	5.05	0.03	12.17
	Std. Deviation	1017.65	1.76	1.89	6.52	280.17	0.54	2.72	0.34	0.52	2.04	0.03	1.92
NM	Minimum	55181.59	74.81	74.22	579.3	28869.06	17.52	24.47	23.28	32.29	3.60	0.01	10.81
	Maximum	56620.76	77.30	76.90	588.52	29265.28	18.29	28.32	23.76	33.03	6.49	0.05	13.53
	Geometric Mean	55896.54	76.04	75.55	583.89	29066.49	17.900	26.32	23.52	32.66	4.83	0.02	12.09
Geochemical Baseline		57931.84	79.57	79.33	596.93	29626.83	18.99	31.77	24.20	33.70	8.92	0.08	15.94
	Mean	39541.56	231.48	2278.68	2386.54	66446.06	175.73	524.28	67.56	45.93	6.56	0.05	13.44
	Std. Deviation	175.86	3.35	75.98	3319.88	1795.03	12.18	65.37	2.35	0.50	6.62	0.01	1.61
VKP	Minimum	39417.21	229.11	2224.95	39.03	65176.78	167.11	478.05	65.90	45.57	1.88	0.05	12.30
	Maximum	39665.91	233.85	2332.40	4734.05	67715.34	184.34	570.50	69.22	46.28	11.24	0.05	14.570
	Geometric Mean	39541.36	231.47	2278.04	429.85	66433.94	175.51	522.23	67.54	45.92	4.60	0.05	13.39
Geochemical Baseline		39893.08	238.17	2430.00	7069.61	70024	199.88	652.98	72.23	46.93	17.83	0.07	16.60
	Mean	5273.06	2.79	7.39	73.59	1860.05	1.29	1.23	0.32	10.87	2.24	0.04	2.44
	Std. Deviation	6.39	0.54	0.41	0.93	50.00	0.24	0.17	0.08	0.37	3.13	0.04	0.99
WA	Minimum	5268.54	2.41	7.10	72.93	1824.69	1.12	1.11	0.27	10.61	0.03	0.01	1.74
	Maximum	5277.57	3.17	7.68	74.24	1895.40	1.45	1.35	0.38	11.13	4.45	0.06	3.14
	Geometric Mean	5273.05	2.76	7.38	73.58	1859.71	1.28	1.22	0.32	10.87	0.37	0.02	2.34
Geochemical Baseline		5285.82	3.84	8.21	75.43	1959.71	1.75	1.56	0.48	11.60	6.62	0.10	4.32
	World mean			50				25	12	40	20	0.4	15
	World Range			1-1500				1-1500	0.1-250	1-1500	0.1-250	0.01-2	1-1500
	Wedepohl(1995)	77440	53	35	527	30890	11.6	18.6	14.3	52	2	0.1	17

Soil Samples

In relation to the background values obtained in the soil samples from the pristine sites, the following deductions were made; For sites AOD and WA, Cr, Cu, Zn, As, Cd and Pb presented background levels considered to be below those given by the world average while Ni presented a value far above the world average value as shown in Table 62. When this results were compared with the world shale average, it was observed that only Ni and As showed background content above the shale average values at site AOD. In relation to site EA, Cd and Pb showed metal content in soil samples below the world average values while Pb and Al showed levels below the average shale values. The contents of Zn, As, Cd and Pb in soil samples from site BB, were below the world average whiles the levels of Al, V, Ni, Cr, Co and Cu were above the world shale average.

The background levels of As, Cd and Pb in the soil samples were below the world average values in sites GSH and VKP. However, when compared with the average shale values Al, Pb, Cd and As showed background values at site GSH and VKP below the average shale values. When the data was related to the average shale values, only Cr, Ni and Cu showed background values above the average shale values. It was observed that the background concentrations of Ni were abnormally high in all the sites when compared with those obtained by the world average, world rank and average shale values.

A study conducted by Cicchella *et al.*, (2005), to determine the background and baseline concentrations of elements harmful to human health in soils of Napoli (Italy) came up with the maximum baseline ranges for As, Cd, Pb and Hg higher than those obtained from this study.

Comparing results from this study with that reported in Italy showed that most of the ranges in this work fall within the ranges reported with the maximum concentrations for Zn, Pb, Cu and Cd higher than those from our work. However, the maximum concentrations for As, Co and Cr were higher than those reported with Cr recording as high as 2349.25 mg/kg from this study as against 30-50 mg/kg reported.

The background levels of Cr, V, As and Mn at selected sites in this work were identified to be abnormally high. For instance, Cr content in soil samples from site EA was observed to be high to the tune of 208 mg/kg but was seen as abnormally high when exceeding 2300 mg/kg at site VKP.

Table 62: Statistical Analysis and Geochemical Baseline Values of the Metals in the sublayers of Soils

Site	Statistics	Al	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb
AOD	Mean	47123.43	52.22	47.28	34.08	21125.51	1.26	4699.13	8.08	13.96	19.16	0.02	5.77
	Std. Deviation	6870.86	2.55	3.61	0.40	303.34	0.24	76.96	2.67	1.64	5.47	0.01	0.79
	Geometric Mean	46872.31	52.18	47.21	34.07	21124.42	1.25	4698.82	7.85	13.91	18.77	0.01	5.74
	Minimum	42265.00	50.41	44.72	33.79	20911.01	1.09	4644.71	6.19	12.80	15.29	0.01	5.21
	Maximum	51981.86	54.02	49.83	34.36	21340.00	1.43	4753.55	9.96	15.12	23.03	0.02	6.33
	Geochemical Baseline	60614.02	57.29	54.43	34.88	21731.10	1.73	4852.74	13.18	17.19	29.71	0.03	7.33
EA	Mean	56875.27	177.03	208.98	1255.18	86959.68	42.30	5257.54	61.79	112.73	58.42	0.11	11.16
	Std. Deviation	438.78	0.47	0.46	7.33	141.87	1.42	7.83	1.55	5.76	5.75	0.03	0.37
	Minimum	56565.00	176.70	208.65	1250.00	86859.36	41.29	5252.00	60.69	108.66	54.35	0.09	10.89
	Maximum	57185.53	177.36	209.30	1260.36	87060.00	43.30	5263.07	62.88	116.80	62.48	0.13	11.42
	Geometric Mean	56874.42	177.03	208.97	1255.17	86959.62	42.28	5257.53	61.78	112.66	58.27	0.11	11.15
	Geochemical Baseline	57751.98	177.96	209.89	1269.82	87243.37	45.13	5273.19	64.87	124.17	69.77	0.16	11.90
BB	Mean	33470.70	66.38	71.73	525.68	24666.90	15.40	5848.61	25.15	34.37	3.31	0.06	6.22
	Std. Deviation	889.96	2.95	5.10	17.64	563.01	0.52	35.91	0.11	2.02	2.63	0.01	0.05
	Minimum	32841.40	64.29	68.12	513.21	24268.79	15.03	5823.22	25.07	32.94	1.45	0.05	6.18
	Maximum	34100.00	68.46	75.33	538.15	25065.00	15.77	5874.00	25.22	35.79	5.17	0.06	6.25
	Geometric Mean	33464.78	66.34	71.63	525.53	24663.68	15.40	5848.56	25.14	34.34	2.74	0.05	6.21
	Geochemical Baseline	35244.71	72.24	81.83	560.80	25789.69	16.44	5920.38	25.36	38.37	8.00	0.07	6.31
WA	Mean	55427.93	19.43	19.67	28.44	10684.71	1.41	4360.22	1.36	17.07	3.70	0.03	11.82
	Std. Deviation	801.97	1.03	0.67	0.48	346.90	0.40	27.27	0.17	0.64	3.23	0.00	1.03
	Minimum	54860.85	18.70	19.19	28.10	10439.41	1.13	4340.93	1.24	16.62	1.41	0.03	11.09
	Maximum	55995.00	20.16	20.14	28.78	10930.00	1.69	4379.50	1.48	17.52	5.98	0.03	12.55
	Geometric Mean	55425.02	19.42	19.66	28.44	10681.89	1.38	4360.17	1.35	17.06	2.90	0.03	11.80
	Geochemical Baseline	57028.95	21.48	21.00	29.40	11375.69	2.17	4414.72	1.69	18.34	9.37	0.03	13.86

Table 62: Continues

	Mean	61402.68	127.39	97.26	1561.65	66412.60	41.32	4525.19	32.02	59.25	0.48	0.08	2.90
	Std. Deviation	491.18	6.12	2.36	17.47	1460.03	1.94	113.58	0.10	2.37	0.04	0.01	0.76
GSH	Minimum	61055.36	123.06	95.59	1549.29	65380.20	39.95	4444.87	31.95	57.57	0.45	0.07	2.36
	Maximum	61750.00	131.71	98.93	1574.00	67445.00	42.69	4605.50	32.09	60.92	0.50	0.09	3.43
	Geometric Mean	61401.70	127.31	97.25	1561.60	66404.58	41.30	4524.47	32.02	59.22	0.47	0.08	2.85
Geochemical Baseline		62384.07	139.54	101.97	1596.54	69324.64	45.17	4751.64	32.22	63.96	0.55	0.11	4.36
	Mean	32369.28	49.18	45.43	372.84	19335.31	8.23	5436.95	73.24	26.55	6.68	0.02	8.07
	Std. Deviation	126.26	1.74	3.10	14.37	1229.93	0.52	106.70	88.73	6.08	4.79	0.01	1.15
NM	Minimum	32280.00	47.95	43.23	362.68	18465.62	7.86	5361.50	10.50	22.25	3.29	0.01	7.25
	Maximum	32458.56	50.41	47.62	383.00	20205.00	8.59	5512.40	135.98	30.85	10.06	0.03	8.88
	Geometric Mean	32369.16	49.16	45.37	372.70	19315.74	8.22	5436.43	37.79	26.20	5.75	0.02	8.02
Geochemical Baseline		32621.68	52.64	51.58	401.44	21775.60	9.25	5649.83	215.24	38.36	15.33	0.05	10.33
	Mean	54831.41	45.31	47.07	203.62	21855.80	7.98	3265.14	30.54	30.39	0.88	0.02	5.36
	Std. Deviation	259.64	1.63	3.37	6.99	684.77	2.81	71.93	0.33	0.89	0.16	0.01	0.21
CK	Minimum	54647.81	44.16	44.68	198.68	21371.59	5.99	3214.27	30.31	29.76	0.77	0.01	5.21
	Maximum	55015.00	46.46	49.45	208.56	22340.00	9.97	3316.00	30.77	31.02	0.99	0.02	5.51
	Geometric Mean	54831.10	45.30	47.00	203.56	21850.43	7.73	3264.74	30.54	30.38	0.87	0.01	5.36
Geochemical Baseline		55350.38	48.55	53.75	217.53	23219.97	13.36	3408.61	31.19	32.17	1.18	0.03	5.78
	Mean	47344.53	174.15	2349.25	3467.35	68551.39	131.90	5724.57	64.97	60.70	1.34	0.05	8.99
	Std. Deviation	1618.61	2.04	71.77	15.27	702.00	4.14	270.02	0.44	1.73	0.07	0.01	0.69
VKP	Minimum	46200.00	172.70	2298.50	3456.55	68055.00	128.97	5533.64	64.66	59.47	1.29	0.04	8.50
	Maximum	48489.06	175.59	2400.00	3478.15	69047.78	134.83	5915.50	65.28	61.92	1.39	0.05	9.48
	Geometric Mean	47330.69	174.14	2348.70	3467.33	68549.59	131.87	5721.39	64.97	60.68	1.34	0.04	8.98
Geochemical Baseline		50567.91	178.23	2492.24	3497.88	69953.60	140.15	6261.42	65.85	64.15	1.48	0.06	10.36

Geochemical Baseline Study of the Soils and Sediments at the Pristine Areas

To calculate the geochemical baseline values, the heavy metals concentrations in the soils and the sediments from the pristine areas were used which was conducted by adding the geometric mean to twice the standard deviation (Santos-Francés *et al.*, 2017; Dung *et al.*, 2013; ISO/DIS, 2002). Some of the metals in the soil samples from the pristine areas were characterized by high baseline values such as Ni and Cr. The geochemical baseline values from this study were compared with an earlier study by Ackah *et al.*, (2012) around Atiwa and Kwabeng areas (sites EA and EAM) (Table 63) and the results indicate similar geochemical baseline values for Cu, Mn and Fe from the two studies while Ni and Cr levels were far higher than those reported by Akah and co (2012). However, the geochemical background for the anthropogenic metals (Cd, Pb and Zn) were higher than those obtained from this study which can be attributed to the application of agrochemicals on cocoa farmlands which subject soils and sediments to heavy metal contamination.

The geochemical baseline values from this study were also related to the World Mean and Average Shale values which shows that apart from Cr and Ni concentrations being abnormally higher than those obtained by World Mean and Average Shale, the rest of the metals from this study showed geochemical values that are close to the world mean values. However, the content of Al in our soils and sediments samples is low compared with the Average Shale values. Finally, the results from this study were compared with a recent study by Santos-Francés *et al.*, (2017) in soil samples from the Andes Mountain Range in Italy and the results indicate similar baseline values for Zn and Cu and higher baseline values for As, Cd, Pb and Hg than those obtained from this study. However, the baseline values for Ni and Cr were abnormally higher than those obtained from the Andes Mountain Range in Italy. The geochemical baseline values in this study were also related to the guideline values provided by the Ghana Standards Authority in sediment for As (27 mg/kg) and Cd (6 mg/kg) and the results show that the proposed guideline values (As = 14 and Cd 0.08 mg/kg) were far lower than those provided by the GSA 175/WHO. The low geochemical baseline values for the metals indicate an uncontaminated pristine environment, suitable for setting the baseline values for the metals in Ghana

The application of regional geochemical baseline values proposed in our work will allow for speedy identification of sites that could be affected by heavy metals pollution due to mining operations and the current petroleum exploitation in the Western parts of the country.

Table 63: Statistical Analysis of the Metals Levels in Soils and Sediment Samples for Geochemical Baseline Values

	Present work (2014-2016)	Present work (2014-2016)	Ackah, J. E. (2012).	Mean Shale values	World Mean	Soils from Italy
	Soil (mg/kg)	Sediment (mg/kg)	Soil (mg/kg)	Wedepohl, (1995)	Berrow and Reaves (1984)	Santos-Francés *et al.*, (2017)
	Proposed Baseline	Proposed Baseline	Literature (Ghana) Baseline			
	Geochemical	Geochemical	Geochemical			Geochemical
Al	51445.46	44214.76		77440		
V	93.49	93.95		53		
Cr	383.34	410.44	78.99	35	50	8.26
Mn	951.04	2337.16	942.59	527		
Fe	41301.71	32614.47	57821.69	30890		
Co	34.18	40.7		11.6		
Ni	5066.57	133.92	3.81	18.6	25	56.97
Cu	56.2	31.07	33.79	14.3	12	22.2
Zn	49.59	42.6	73.79	52	40	47.42
As	16.92	14.88		2	20	27.5
Cd	0.07	0.08	11.22	0.1	0.4	4.36
Pb	8.78	10.85	18.94	17	15	44.87
Hg		0.07		0.06		4.89

Analysis of Ecological Risks and Pollution Indices

The state of heavy metal contamination in soils and sediments from the pristine areas in this study were evaluated using different qualitative and quantitative single and multiple element pollution indices and ecological risk indices.

Enrichment Factor and Modified Pollution Index

The enrichment of the metals in the soil samples is shown in Table 42. The heavy metals at most of the pristine sites presented an environment which is not enriched with the metals with few of the sites showing moderate enrichment. However, Arsenic at sites AOD and BB and Ni at site WA showed a moderately severe enrichment while Cr showed severe enrichment at site WA. The enrichment of Ni and Cr at sites WA have contributed to the high geochemical background values obtained for Ni and Cr in the study.

Using the Modified Pollution Index to determine pollution levels in the soil samples from the pristine areas showed that a number of samples (24.5 %) were not contaminated, 12 % of the samples were moderately contaminated, and 61.9 % of the samples were severely contaminated, mainly by Cr and Ni from site WA. Similar results were obtained by Santos-Francés *et al.*, (2017) in which Cr was identified as a major contributor to high background level.

In the case of the sediment samples, similar trend of metal distribution in the soil samples were observed in which most of the sites showed minor to moderate pollution of the heavy metals (Table 40). However, the enrichment of Cr and Ni at site VKP showed moderately severe to very severe enrichment which may be responsible for the high geochemical background values observed at these two metals.

The modified pollution indices showed 3.9 % of the samples being slightly polluted, 11.3 % of the samples being moderately polluted, 22.5 % of the samples being moderately-heavily polluted, 14.3% of the samples being severely polluted and 47.9 % of the samples being heavily polluted. The severe and the heavy pollution observed at sites VKP and EA were mainly being caused by the abnormal enrichment of Cr and Ni.

The values reported in a similar study conducted by Ackah *et al.*, (2012), even though was conducted earlier than the current study had geochemical values for most of the heavy metals greater than those obtained in the current study except Cr and Ni and thus the data from this study is best suited for our regional and national standard recommendation. The proposed baseline values can be relied upon since most of the pristine areas considered are natural areas without any type of mining activity and thus the geochemical values can be applied to calculate the degree of soil and sediment contamination.

Geo-accumulation Index (Igeo)

The Igeo for the heavy metals in the soil samples studied are presented in Table 43. The Igeo for most the heavy metals showed practically uncontaminated pristine areas with few of the sites showing uncontaminated to moderately contaminated sites. However, Igeo for Cr (43.8) and Ni (19.1) at site WA and the Igeo for As (18.1) at site BB and AOD were abnormally high representing an environment that is extremely contaminated with these metals. The high accumulation of Cr and Ni at site WA may be due to natural geogenic formation of the metals because Ankasa forest reserve (WA) is known as the most virgin forest of Ghana which is free from any form of

< 150) while the MRI of site AOD (28.7 %) alone can be considered as having moderate ecological risk of contamination. By considering the ecological risk assessment outcomes, it can be concluded that the proposed geochemical baseline values are within a range that depicts natural and uncontaminated environment.

Human Health Risk Analysis

The hazard quotient (HQ) results for the soils and sediments from the study are summarized in Tables 50, 51, 54, 55, 56 and 57. In the pristine areas, all the metals in the soils and the sediment samples have HQ less than 1 for both adults and children residents and for ingestion and dermal contact suggesting no potential non-carcinogenic risk to residents who ingest or come into contact with the soils and the sediments.

The carcinogenic risks (CRs) due to ingestion and dermal contact for As, Ni, Cd and Pb are presented in Tables 51, 52, 53, 58 and 59 which are within the USEPA risk assessment guidelines limit (1.0×10^{-6} to 1.0×10^{-4}). However, Cr showed a carcinogenic risk levels that have the potency to pose serious carcinogenic threat in the pristine areas through ingestion and dermal contact.

The enrichment of Cr at the pristine sites WA and VKP which led to the high carcinogenic risk index may not be due to any anthropogenic activities but rather resulting from natural geogenic processes since these sites are forest reserves void of any human activities like mining and farming. The low hazard and carcinogenic indices for As, Ni, Cd and Pb is indicative of a natural environment that is free from anthropogenic activities and therefore fit for use in setting the geochemical baseline values.

Baseline Study of the Pristine Surface Water

Water quality guidelines play an important role in protecting water uses and in assessing the impact of environmental contaminants on the quality and uses of aquatic resources (Health and Welfare Canada, 1993). The mean values of the heavy metals obtained from the statistical analysis of the water are presented in Table 64. The average values from the pristine sites for 2014 and 2016 were used in the determination of the Baseline values.

The data from this study are compared with other guideline values from other countries such as the European Commission (EC, 1998), World Health Organization (WHO, 2004), USEPA (2006, 2009) and Ghana Standard Authority/WHO (2010). The proposed Baseline values for the metals in this study were lower than the WHO and EC guideline limits except for As and Pb which were either the same or slightly higher than the guideline limits respectively. The USEPA guideline values showed higher metal levels for Cr, Ni, Cu, Zn and As than the proposed values in this study but lower metal levels for Pb, Fe and Mn. Relating the proposed Baseline values in this study to that provided by the Ghana Standards Authority in water suggest that the proposed guideline for As in this study is the same as the one provided by the GSA 175/WHO, but the proposed value for Pb is higher than the one provided by the GSA 175/WHO. The high level of Pb shows a non-static environment and can be attributed to anthropogenic addition of Pb over the years.

Table 64: Mean Concentrations of the Metals in the Pristine Water Samples

Metals	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb
Average Dry (2016)	0.07	0.01	0.01	0.21	0.55	0.01	0.01	0.02	0.01	0.1
Average Wet (2014)	0.07	0.01	0.01	0.03	0.47	0	0.03	0.03	0.01	0.01
Mean	0.07	0.01	0.01	0.12	0.51	0.01	0.02	0.03	0.01	0.06
Std. Deviation	0.00	0.00	0.00	0.13	0.06	0.01	0.01	0.01	0.00	0.06
Geometric Mean	0.07	0.01	0.01	0.08	0.51	0.00	0.02	0.02	0.01	0.03
Minimum	0.07	0.01	0.01	0.03	0.47	0.00	0.01	0.02	0.01	0.01
Median	0.07	0.01	0.01	0.12	0.51	0.01	0.02	0.03	0.01	0.06
Maximum	0.07	0.01	0.01	0.21	0.55	0.01	0.03	0.03	0.01	0.10
Proposed Guideline Values	0.07	0.01	0.01	0.12	0.51	0.005	0.02	0.025	0.01	0.055
EC(1998)			0.05	0.05	0.2	0.02	2	0.1	0.01	0.01
WHO (2004)			0.05	0.4	-	0.07	2	-	0.01	0.01
USEPA (2009)			0.1	0.05	0.3	-	1.3	5	0.01	0.02
USEPA (2006)					1	0.47	0.013	0.12	0.34	-
GSA-175/WHO									0.01	0.01

GSA 175/WHO = Ghana Standard Authority legislative instrument for WHO.

The human health risks values were calculated by using the default values from the USEPA (1989 and 2004) and results from the questionnaire administered and the results obtained were presented in Table 65. The HQ and CR indices of the metals for resident child and adult through ingestion and dermal contact of water did not exceed the USEPA recommended guideline (USEPA, 1997, 2004).

The CR and HQ results also indicate that the risk levels of the metals are fit for setting the proposed guideline limits. The CR and HQ results for the USEPA default values and the administered questionnaire values did not differ significantly ($p > 0.05$) suggesting that any of the methods could be used to assess the risk levels of the metals in the Ghanaian environment.

Table 65: Carcinogenic and Non-carcinogenic Risk for Child and Adult Residents' due to Ingestion of Water

Metals	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**As**	**Pb**
Results from USEPA default values							
HQ Adult	7.8×10^{-8}	2.4×10^{-4}	5.9×10^{-6}	1.4×10^{-8}	1.8×10^{-6}	3.9×10^{-4}	5.9×10^{-4}
HQ Child	7.3×10^{-8}	2.2×10^{-4}	5.5×10^{-6}	3.8×10^{-10}	1.7×10^{-6}	3.7×10^{-4}	5.5×10^{-4}
CR Adult	5.9×10^{-5}		2.0×10^{-7}			1.8×10^{-7}	4.9×10^{-6}
CR Child	5.5×10^{-5}		1.9×10^{-7}			1.6×10^{-7}	4.7×10^{-6}
Results from Administered Questionnaire							
HQ Adult	1.1×10^{-7}	3.3×10^{-4}	8.3×10^{-6}	1.5×10^{-8}	2.6×10^{-6}	5.5×10^{-4}	8.3×10^{-4}
HQ Child	8.0×10^{-8}	2.4×10^{-4}	6.0×10^{-6}	4.2×10^{-10}	1.9×10^{-6}	4.0×10^{-4}	6.0×10^{-4}
CR Adult	8.3×10^{-5}		2.8×10^{-7}			2.5×10^{-7}	7.0×10^{-6}
CR Child	6.0×10^{-5}		2.1×10^{-7}			1.8×10^{-7}	5.1×10^{-6}

Table 66: Carcinogenic and Non-carcinogenic Risk for Child and Adult Residents' for Dermal Contact of Water

Metals	Cr	Mn	Ni	Cu	Zn	As	Pb
Results from USEPA Default values							
HQ Adult	2.3×10^{-7}	1.3×10^{-3}	1.7×10^{-4}	7.3×10^{-5}	5.8×10^{-6}	1.1×10^{-2}	1.7×10^{-3}
HQ Child	1.1×10^{-6}	1.2×10^{-3}	8.2×10^{-4}	7.0×10^{-5}	5.6×10^{-6}	5.5×10^{-2}	8.2×10^{-3}
CR Adult	1.7×10^{-4}		5.8×10^{-6}			5.1×10^{-6}	1.4×10^{-5}
CR Child	8.2×10^{-4}		2.8×10^{-5}			2.5×10^{-5}	6.9×10^{-5}
Results from Administered Questionnaire							
HQ Adult	2.4×10^{-7}	3.1×10^{-4}	1.8×10^{-5}	1.8×10^{-5}	2.4×10^{-6}	1.2×10^{-3}	1.8×10^{-3}
HQ Child	1.1×10^{-6}	1.2×10^{-3}	8.2×10^{-4}	7.0×10^{-5}	5.6×10^{-6}	5.5×10^{-2}	8.2×10^{-3}
CR Adult	1.8×10^{-4}		6.2×10^{-7}			5.4×10^{-7}	1.5×10^{-5}
CR Child	8.2×10^{-4}		2.8×10^{-5}			2.5×10^{-5}	6.9×10^{-5}

Chapter Summary

This study is set out with three main objectives: to assess heavy metals distribution and pollution by using different pollution indices in the pristine and major mining areas; to determine sources of heavy metal pollution using different statistical methods in the selected areas and finally to propose geochemical baseline values for the metals in sediments, water and 20-40cm depth of the soils amples from the pristine areas.

The proposed site-specific geochemical baseline values showed considerably high enrichment for the geogenic metals (Fe, Al, Mn, Ni, Cr, Co, Cu V) while the anthropogenic metals (Zn, As, Hg, Cd and Pb) showed low enrichment when compared with other threshold values (Table 63 & 64).

Those pristine areas that are close to the major mining areas such as site EA, BB and AOD have the highest metal content for the anthropogenic metals. Generally, the enrichment of Cr, Ni and Mn in the pristine areas was higher while the enrichment of As, Zn and Pb were higher in the mining areas. The human health risk assessment conducted by using the USEPA default values and the results of questionnaire survey did not show much variation in the results obtained. The carcinogenic risk study of the metals showed Cr, As and Pb posing a cancer risk through ingestion of water and only Cr posing a carcinogenic risk through dermal contact of water.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Summary

Even though a number of studies have been done on heavy metals pollution in Ghana, this work has immensely contributed to knowledge of assessing heavy metals pollution in mining areas by being the first study to assess heavy metal pollution in all the Four major mining areas in Ghana at the same time over two-years period. The study on the heavy metals and metalloid in the selected pristine and mining areas in Ghana has indicated varied (low to high) concentrations of the metals in the soils, sediments and water samples investigated. The differences in the metal contents of the pristine and the mining areas were significant, which confirm the fact that gold mining activities may be a contributing factor to increased heavy metal contamination in the mining areas studied. However, there was no statistically significant difference between the metal concentrations in the soils, sediments and the water samples collected in 2014 and 2016, though the results obtained during the dry season were slightly higher.

Conclusions

Generally, the outcome of the risk assessment has indicated acceptable risk in both the pristine and the mining areas except for As and Cr in some selected sites. The most significant exposure route is ingestion of the metals in water, soils and sediments from the sites. It is possible to reduce the risk of human exposure to the metal contamination by monitoring the activities of commercial, small scale and illegal mining around the mining areas investigated.

In the case of the soils, the concentrations of the heavy metals from the various pristine sites were found to be either below or within the USEPA and WHO's recommended limits for surface soils except the major elements such as Al, Fe and Mn and thus presents no direct environmental threat, although potentially, they could accumulate and affect the surrounding ecosystems over a period of time. The concentration of As content of the soils was extremely high, at site AOB which confirmed the past evidence based on available data that Obuasi mining area (site AOB) could be one of the regions in the world with very high background levels of As. The Hazard assessment quotients (HQing) for adults and children were found to be below one ($HQ<1.0$) in the pristine and mining sites except As (in the mining sites) indicating no adverse effects as a result of incidental or deliberate ingestion of the soils around the study areas. However, HQing for As was more than one ($HQ>1.0$) in the mine samples which suggests that children from communities which interact (consume) with soils from the mining areas may be at high risk of As associated illnesses.

The carcinogenic risk (CRing) values for Cr, Cd and Pb in the soil samples from the pristine and mining sites for adults and children were below the USEPA recommended range of 1×10^{-6} to 1×10^{-4}. The CR value for As however, exceeded the recommended limit (4.36×10^{-3}) for children at the mining sites suggesting a carcinogenic threat to the local residents. This means that small children would be exposed to high levels of As in soils especially those with soil eating disorders, and, therefore may suffer As related illnesses.

In the case of the sediment samples, the concentrations of the heavy metals in river sediments from the various pristine and mining sites were found to be below the USEPA guideline limits, Average Composition of Shales and Canadian ISQG limits and thus presents no direct environmental threat, although they could mobilize and affect the surrounding ecosystems over a period of time. The concentrations of As, Cu, Ni, Co, and Cr however, exceeded the above guideline levels and thus pose serious threat to the study environments especially in the mining areas. Results from the multivariate and multi-criteria decision making methods suggest that anthropogenic activities may be the major sources of heavy metals contamination in the mining areas which may be emanating from gold mining activities and agro-chemical application on farmlands.

The PCA and GAIA modelling identified two main sources of the heavy metals as anthropogenic related (As, Cd, Zn) and natural geogenic related (Fe, Al, Mn, Ni, Cr, Co, V). Pollution assessment of the heavy metals revealed that the Enrichment Factor of the river sediments is extremely severe for As, very severe for Cr, moderately severe for Cu, minor for Zn and no enrichment for Cd and Pb.

For the ecological risk assessment (Ei and RI) of all sites showed low to moderate ecological risk indexes except site AOB which presented a very high ecological risk index. The extremely high content of As at site AOB was reported in earlier studies around the this study area whereby the site was identified to be one of the regions in the world with very high background levels of As.

In the case of the water samples, the average concentrations of heavy metals in the rivers from mining and pristine sites were within the permissible limits of USEPA, EC and WHO's except for the major elements such as Fe, Al and Mn, which recorded slightly higher concentrations than the guideline limits. Even though, the average metal concentrations were low in some sites, it could be pointed out from the study that continual consumption of water from the river sources could be harmful to consumers since individual site concentrations were far above the USEPA and WHO drinking water guideline limits. The PROMETHEE and GAIA ranking of the sites revealed that most of the metal pollution were found in the mining areas. Finally, the HQ and CR estimation showed that the heavy metals levels studied were within the USEPA's acceptable limit except As, Pb and Cr which were above the permissible limits in the mining sites hence constituted significant environmental threat. The high toxicity of As, Pb and Cr estimated raises carcinogenic concerns for the local residents living around the mining catchment areas.

The data presented in this study shows that gold mining in the four major mining areas in Ghana may severely be impacting on soils, sediments and water quality since the threshold values for most metals exceeded the recommended limits. Even though a number of the heavy metals did not show high levels at some of the mining areas, poor management of tailings, mercury and cyanide can enhance the mobilization of the metals over time at the various sites. The study provided evidence on soils, sediments and water contamination impacts and identified potential thresholds associated with the pollution and its possible socio-economic consequences on people living around the mining areas.

Recommendations

The outcomes of this research work have led to the identification of key areas that require further research because there were questions that either remains unanswered or unasked. These recommendations include:

1. The sampling period for this study was only two years, which provides some information on short term bases. It is recommended that a longer study period of up to five years or longer with regular monitoring of heavy metal pollution be performed to provide more robust temporal data;

2. One outcome of this work was the identification of potential sources of the heavy metals in the pristine and the mining areas. It is recommended that further work be conducted to identify the source/s of these elements in more expanded manner ranging from mine wastes, tailings to agricultural lands in the mining areas.

3. This work did not consider speciation of the heavy metals. Considering that the oxidation states of these elements is related to their toxicity, it is therefore recommended that further works be done to examine the speciation of these elements.

REFERENCES

Abdelfattah, A. L. Y., & Wada, K. (1981). Adsorption of lead, copper, zinc, cobalt, and cadmium by soils that differ in cation□exchange materials. *European Journal of Soil Science*, 32(2), 271-283.

Abrahim, G. M. S., & Parker, R. J. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental monitoring and assessment*, 136(1-3), 227-238.

Ackah, J. E. (2012). Distribution of heavy metals in cocoa farm soils in the western region of Ghana (Doctoral dissertation, University of Ghana).

Adamu, C. I., Nganje, T. N., & Edet, A. (2015). Heavy metal contamination and health risk assessment associated with abandoned barite mines in Cross River State, southeastern Nigeria. *Environmental Nanotechnology, Monitoring & Management*, 3, 10-21.

Agency for Toxic Substances and Diseases Registry (ATSDR), (2007). Toxicological Profile for Arsenic; Draft for Public Comment; U.S. Department of Health and Human Services, Public Health Service: Atlanta, GA, USA,. Available online: http://www.atsdr.cdc.gov/toxprofiles/tp2.html

Agronomic Fact Sheet Series (AFSS) (2007) Cation Exchange Capacity. Retrieved from: http://nmsp.cals.cornell.edu/publications/factsheets/factsheet 22.pdf.

Ahdy, H. H., & Youssef, D. H. (2011). Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt. *Chemistry and Ecology*, 27(5), 427-443.

Ahmad, K., & Carboo, D. (2000). Speciation of As (III) and As (V) in some Ghanaian gold tailings by a simple distillation method. *Water, Air, & Soil Pollution*, 122(3), 317-326.

Ahnstrom, Z. S., & Parker, D. R. (1999). Development and assessment of a sequential extraction procedure for the fractionation of soil cadmium. *Soil Science Society of America Journal*, 63(6), 1650-1658.

Akabzaa, T. M., Banoeng-Yakubo, B. K., & Seyire, J. S. (2007). Impact of mining activities on water resources in the vicinity of the Obuasi mine. *West African Journal of Applied Ecology*, *11*(1).

Akabzaa, T. M., Banoeng-Yakubu, B., & Seyire, J. S. (2005). Heavy metal contamination in some mining areas within the Jimi River basin in Ashanti Region, Ghana. *Journal of Ghana Science Association*, 7(1), 36-45.

Akosa, A. B., Adimado, A. A., Amegbey, N. A., Nignpense, B. E., Carboo, D., & Gyasi, S. (2002). Report submitted by Cyanide investigation committee. Ministry of Environment and Science.

Government of Ghana, 1989. Small-Scale Gold Mining Law. PNDC Law 218.

Akoto, O., & Adiyiah, J. (2007). Chemical analysis of drinking water from some communities in the Brong Ahafo region. *International Journal of Environmental Science & Technology*, 4(2), 211-214.

Aladesanmi, O. T., Adeniyi, I. F., & Adesiyan, I. M. (2014). Comparative assessment and source identification of heavy metals in selected fishpond water, sediment and fish tissues/organs in Osun State, Nigeria. *Journal of Health Pollution*, 4(7), 42-53.

Alam, M. G. M., Snow, E. T., & Tanaka, A. (2003). Arsenic and heavy metal contamination of vegetables grown in Samta village, Bangladesh. *Science of the Total Environment*, 308(1), 83-96.

Alatise, O. I., & Schrauzer, G. N. (2010). Lead exposure: a contributing cause of the current breast cancer epidemic in Nigerian women. *Biological trace element research*, 136(2), 127-139.

Albanese, S., De Vivo, B., Lima, A., & Cicchella, D. (2007). Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Ital.). *Journal of Geochemical Exploration*, 93(1), 21-34.

Alloway, B. J. (1992). Land contamination and reclamation. In: Understanding Our Environment-An Introduction to Environmental Chemistry and Pollution, Harrison, R.M. (Ed.), 2nd Ed. Royal Society of Chemistry, Cambridge, UK.

Alloway, B. J. (2001). Soil pollution and land contamination. In: Pollution: Causes, Effects and Control, Harrison, R.M. (Ed.), 4th Edition, *Royal Society of Chemistry,* Cambridge, UK.

Alloway, B. J. (2013). Sources of heavy metals and metalloids in soils. In Heavy metals in soils (pp. 11-50). Springer Netherlands.

Altamura, S., & Muckenthaler, M. U. (2009). Iron toxicity in diseases of aging: Alzheimer's disease, Parkinson's disease and atherosclerosis. *Journal of Alzheimer's Disease,* 16(4), 879-895.

Altshuller, A. P., Canada. Atmospheric Environment Service, & McBean, G. A. (1979). The LRTAP problem in North America: a preliminary overview. Downsview, Ont.: *Atmospheric Environment Service.*

Alvarez, E. A., Mochon, M. C., Sánchez, J. J., & Rodríguez, M. T. (2002). Heavy metal extractable forms in sludge from wastewater treatment plants. *Chemosphere,* 47(7), 765-775.

Álvarez-Vázquez, M., Bendicho, C., & Prego, R. (2013). Distribution of major and trace elements in coastal sediments and identification of their continental, marine and anthropogenic sources. Mouth, 4, 000.

Amankwah, R. K., & Buah, W. K. (1998). Some metallurgical aspects of smallscale gold mining in Ghana. In Proceedings of the Extraction Metallurgy Africa'98 Conference. South African Institute of Mining and Metallurgy, Johannesburg (pp. 1-4).

Amantoge, A. T. (2012). Drinking Water Suitability from the Karaga Dam in the Northern Region, Ghana (Doctoral dissertation).

Amegbey, N. A., & Adimado, A. A. (2003). Incidents of cyanide spillage in Ghana. *Mineral Processing and Extractive Metallurgy*, 112(2), 126-130.

American Conference of Governmental Industrial Hygienists, (1995). Threshold limit values for chemical substances and physical agents and biological exposure indices. American Conference of Governmental Industrial Hygienists.

Amonoo-Neizer, E. H., & Amekor, E. M. (1993). Determination of total arsenic in environmental samples from Kumasi and Obuasi, Ghana. *Environmental health perspectives,* 101(1), 46–49

Amonoo-Neizer, E. H., Kambo-Dorsa, J., & Nyamah, D. (1995). Effect of mining activities on the quality of waters around the Mining town of Obuasi (Ghana). *Ghana journal of chemistry*, 1, 491-498.

Armah, F. A., Luginaah, I., & Obiri, S. (2012). Assessing environmental exposure and health impacts of gold mining in Ghana. *Toxicological & Environmental Chemistry,* 94(4), 786-798.

Armah, F. A., Obiri, S., Yawson, D. O., Onumah, E. E., Yengoh, G. T., Afrifa, E. K., & Odoi, J. O. (2010). Anthropogenic sources and environmentally relevant concentrations of heavy metals in surface water of a mining district in Ghana: a multivariate statistical approach. *Journal of Environmental Science and Health Part A*, 45(13), 1804-1813.

Armah, F. A., Obiri, S., Yawson, D. O., Pappoe, A. N. M., & Akoto, B. (2010). Mining and heavy metal pollution: assessment of aquatic environments in Tarkwa (Ghana) using multivariate statistical analysis. *Journal of Environmental Statistics*, 1(4), 1-13.

Armah, F. A., Odoi, J. O., Afrifa, E. K. A., Pappoe, A. N. M., Yawson, D. O., & Essandoh, P. K. (2011). Spatial variability of trace metals in surface and groundwater within a Contaminated Mining Environment in Ghana. *Research Journal of Environmental and Earth Sciences*, *3*(5), 546-554.

Arora, M., Kiran, B., Rani, S., Rani, A., Kaur, B., & Mittal, N. (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. *Food chemistry*, 111(4), 811-815.

Aryee, B. N. (2001). Ghana's mining sector: its contribution to the national economy. *Resources Policy*, *27*(2), 61-75.

Aryee, B. N., Ntibery, B. K., & Atorkui, E. (2003). Trends in the small-scale mining of precious minerals in Ghana: a perspective on its environmental impact. *Journal of Cleaner production*, 11(2), 131-140.

Asamoah, E. (2012). The Impact of Small Scale Gold Mining Activities on theWater Quality of River Birim in the Kibi Traditional Area. Master's Thesis, Kwame Nkrumah University of Science and Technology (KNUST), Kumasi, Ghana

Asante, K. A., Agusa, T., Subramanian, A., Ansa-Asare, O. D., Biney, C. A., & Tanabe, S. (2007). Contamination status of arsenic and other trace elements in drinking water and residents from Tarkwa, a historic mining township in Ghana. *Chemosphere,* 66(8), 1513-1522.

Asiam, E. K. (1996). Environmental assessment of gold beneficiation: arsenic audit and impact on the Obuasi environs. *Ghana Mining J*, 2(1), 17-20.

Asklund, R., & Eldvall, B. (2005). Contamination of water resources in Tarkwa mining area of Ghana. A Minor Field Study (Doctoral diss., MSc Thesis Lund Institute of Technology, Sweden, ISRN LUTVDG/TVTG-5042-SE).

ATSDR, (2007). Toxicological profile for arsenic (Update) Agency for Toxic Substances and Disease Registry, Atlanta, *Georgia*. pp. 499.

Babalola, O. O., Okonji, R. E., Atoyebi, J. O., Sennuga, T. F., Raimi, M. M., & Ejim-Eze, E. E. (2010). Distribution of lead in selected organs and tissues of albino rats exposed to acute lead toxicity. *Scientific Research and Essay*, 5(9), 845-848.

Babut, M., Sekyi, R., Rambaud, A., Potin-Gautier, M., Tellier, S., Bannerman, W., & Beinhoff, C. (2003). Improving the environmental management of small-scale gold mining in Ghana: a case study of Dumasi. *Journal of Cleaner Production*, 11(2), 215-221.

Baeyens, W., Monteny, F., Leermakers, M., & Bouillon, S. (2003). Evalution of sequential extractions on dry and wet sediments. *Analytical and Bioanalytical Chemistry*, 376(6), 890-901.

Baize, D., & Sterckeman, T. (2004). Of the necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. *Science of the Total Environment*, 264(1), 127-139.

Balfors, B., Jacks, G., Singh, N., Bhattacharya, P., & Koku, J. (2007). Contamination of water resources in Takwa mining area of Ghana: Linking technical, social-economic and gender dimensions. Scientific Report 2004–2006. TRITA-LWR REPORT 3016, ISBN 978-91-7178-759-0. p. 23

Barregård, L., Svalander, C., Schütz, A., Westberg, G., Sällsten, G., Blohmé, I., ... & Haglind, P. (1999). Cadmium, mercury, and lead in kidney cortex of the general Swedish population: a study of biopsies from living kidney donors. *Environmental Health Perspectives*, 107(11), 867.

Bartholomew, D. J., Steele, F., Moustaki, I., & Galbraith J. (2008). Analysis of multivariate Social Science data. 2nd ed. Raton: CRC press; Jun 4. 384 p

Basta, N. T., & Gradwohl, R. (1998). Remediation of heavy metal-contaminated soil using rock phosphate. *Better Crops*, 82(4), 29-31.

Bear, (1976). Chemistry of the Soils, 2nd edn. Oxford and IBH Publishing Corporation, New Delhi.

Beauchemin, D. (2010). Environmental analysis by inductively coupled plasma mass spectrometry. Mass spectrometry reviews, 29(4), 560-592.

Beckett, P. H. (1989). The use of extractants in studies on trace metals in soils, sewage sludges, and sludge-treated soils. *In Advances in soil science* (pp. 143-146). Springer US.

Behzadian, M., Kazemzadeh, R. B., Albadvi, A., & Aghdasi, M. (2010). PROMETHEE: A comprehensive literature review on methodologies and applications. *European journal of Operational research*, 200(1), 198-215.

Beltrán, R., de la Rosa, J., Santos, J., Beltrán, M., & Gómez-Ariza, J. (2010). Heavy metal mobility assessment in sediments from the Odiel River (Iberian Belt) using sequential extraction. *Environmental Earth Sciences* 61, 1493-1503.

Bettinetti, R., Giarei, C., & Provini, A. (2003). Chemical analysis and sediment toxicity bioassays to assess the contamination of the River Lambro (Northern Italy). *Archives of Environmental Contamination and Toxicology*, 45(1), 0072-0078.

Bhattacharya, A., Routh, J., Jacks, G., Bhattacharya, P., & Mörth, M. (2006). Environmental assessment of abandoned mine tailings in Adak, Västerbotten district (northern Sweden). *Applied Geochemistry*, 21(10), 1760-1780.

Bi, W. X., Kong, F., Hu, X. Y., & Cui, X. (2007). Role of glutathione in detoxification of copper and cadmium by yeast cells having different abilities to express cup1 protein. *Toxicology mechanisms and methods*, 17(6), 371-378.

Bini, C., Sartori, G., Wahsha, M., & Fontana, S. (2011). Background levels of trace elements and soil geochemistry at regional level in NE Italy. *Journal of Geochemical Exploration*, 109(1-3), 125-133.

Bodek, W. J., Lyman, W. F., & Reehl, D. H. (1988). Rosenblatt, in *Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods*, Pergamon Press, Elmsford, NY, USA.

Bonner, F. W., & Bridges, J. W. (2016). Toxicological properties of trace elements. Trace Elements in Health: A Review of Current Issues, 1.

Bouyoucos, G. J. (1951). A recalibration of the hydrometer method for making mechanical analysis of soils. *Agronomy journal*, 43(9), 434-438.

Bowen, H. J. M. (1979). Environmental Chemistry of the Elements; Academic Press: New York, NY, USA.

Bradham, K., & Wentsel, R. (2010). Scientific issues in the US EPA framework for metals risk assessment. *Journal of Toxicology and Environmental Health*, Part A, 73(2-3), 108-113.

Brady, J. P., Ayoko, G. A., Martens, W. N., & Goonetilleke, A. (2014). Temporal trends and bioavailability assessment of metals in the sediments of Deception Bay, Queensland, Australia. *Marine pollution bulletin*, 89(1), 464-472.

Brady, J. P., Ayoko, G. A., Martens, W. N., & Goonetilleke, A. (2015). Development of a hybrid pollution index for heavy metals in marine and estuarine sediments. *Environ. Monit. Assess.* 187 (5), 1–14.

Brady, J. P., Kinaev, I., Goonetilleke, A., & Ayoko, G. A. (2016). Comparison of partial extraction reagents for assessing potential bioavailability of heavy metals in sediments. *Marine pollution bulletin*, 106(1-2), 329-334.

Brans, J. P., & Mareschal, B. (2005). PROMETHEE methods. Multiple criteria decision analysis: state of the art surveys, *Springer*, 163-186.

Brans, J. P., & Vincke, P. (1985). Note—A Preference Ranking Organisation Method: (The PROMETHEE Method for Multiple Criteria Decision-Making). *Management science*, 31(6), 647-656.

Bridges, J. (2003). Human health and environmental risk assessment: the need for a more harmonised and integrated approach. *Chemosphere* 52, 1347-1351.

Brown, K., & Lemon, J. (2016) Fact Sheets Cations and Cation Exchange Capacity. Retrieved from: http://www.soilquality.org.au/factsheets/cation-exchange-capacity.

Burton, J. G. A. (2002). Sediment quality criteria in use around the world. Limnology 3(2): 65–76

Carrera, J., Rodrigo, G., Jaramillo, A., & Elena, S. F. (2009). Reverse-engineering the Arabidopsis thaliana transcriptional network under changing environmental conditions. *Genome biology*, *10*(9), R96.

Carreras, H. A., Wannaz, E. D., & Pignata, M. L. (2009). Assessment of human health risk related to metals by the use of biomonitors in the province of Cordoba, Argentina. *Environ Pollut*; 157: 117–122.

Carrigan, P. E., Hentz, J. G., Gordon, G., Morgan, J. L., Raimondo, M., Anbar, A. D., & Miller, L. J. (2007). Distinctive heavy metal composition of pancreatic juice in patients with pancreatic carcinoma. *Cancer Epidemiology and Prevention Biomarkers*, 16(12), 2656-2663.

Carter, M. R. (1993). Soil sampling and methods of analysis. Boca Raton, FL:Lewis Publishers.

Casper, S. T., Mehra, A., Farago, M. E., & Gill, R. A. (2004). Contamination of surface soils, river water and sediments by trace metals from copper processing industry in the Churnet River Valley, Staffordshire, UK. Environmental *Geochemistry and Health*, 26(1), 59-67.

Chandra, R., & Singh, S. K. (2009). Fundamentals and management of soil quality. Westville Publishing House, New Delhi.

Chapman, P. M., Anderson, B., Carr, S., Engle, V., Green, R., Hameedi, J., ... & Long, E. (1997). General guidelines for using the sediment quality triad. *Marine Pollution Bulletin,* 34(6), 368-372.

Charlatchka, R., & Cambier, P. (2000). Influence of reducing conditions on solubility of trace metals in contaminated soils. *Water, air and soil pollution*, 118(1-2), 143.

Chen, C. W., Kao, C. M., Chen, C. F., & Dong, C. D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere*, 66(8), 1431-1440.

Chen, M., & Ma, L. Q. (2001). Comparison of three aqua regia digestion methods for twenty Florida soils. Soil science society of America Journal, 65(2), 491-499.

Chen, M., Ma, L. Q., & Harris, W. G. (1999). Baseline concentrations of 15 trace elements in Florida surface soils. *Journal of Environmental Quality,* 28(4), 1173-1181.

Choi, K. Y., Kim, S. H., Hong, G. H., & Chon, H. T. (2012). Distributions of heavy metals in the sediments of South Korean harbors. *Environmental geochemistry and health*, 34(1), 71-82.

Clescerl, L. S., Greenberg, A. E., & Eaton, A. D. (1999). Standard methods for the examination of water and wastewater. American Water Works Association Washington, DC. Part 3000.

Cobbina, S. J., Nkuah, D., Tom-Dery, D., & Obiri, S. (2013). Non-cancer risk assessment from exposure to mercury (Hg), cadmium (Cd), arsenic (As), copper (Cu) and lead (Pb) in boreholes and surface water in Tinga, in the Bole-Bamboi District, Ghana. *Journal of Toxicology and Environmental Health Sciences*, 5(2), 29-36.

Coetzee, P. P. (1993). Determination and speciation of metals in sediments of the Hartebeespoort Dam By sequential extraction. Water 19: 291-300.

Çöl, M., Çöl, C., Soran, A., Sayli, B. S., & Oztürk, S. (1999). Arsenic-related Bowen's disease, palmar keratosis, and skin cancer. Environmental Health Perspectives, 107(8), 687.

Costa, M., & Klein, C. B. (2006). Toxicity and carcinogenicity of chromium compounds in humans. *Critical reviews in toxicology*, 36(2), 155-163.

Covelo, E. F., Vega, F. A., & Andrade, M. L. (2008). Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by a Fibric Histosol and its organo-mineral fraction. *Journal of Hazardous Materials*, 159(2), 342-347.

Cox, M. E., & Preda, M. (2005). Trace metal distribution within marine and estuarine sediments of western Moreton Bay, Queensland, Australia: relation to land use and setting. *Geographical Research*, 43(2), 173-193.

Cuong, D.T., Obbard, J.P., 2006. Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Appl. Geochem. 21, 1335–1346.

Daji, J. A. (1996). A text book of soil Science, Media promoters and publishers, Bombay.

Day, P. R. (1965). Particle fractionation and particle-size analysis. In C. A. Black, D. D. Evans, J. L. White, L. E. Ensminger, and F. E. Clark (Eds.), Methods of soil analysis, Part 1 (pp. 545–567). Madison, WI: American Society of Agronomy.

De Caritat, P., & Cooper, M. (2011). National geochemical survey of Australia: data quality assessment. *Geoscience Australia Record*, 21(2), 1-478.

Deng, H. G., Zhang, J., Wang, D. Q., Chen, Z. L., & Xu, S. Y. (2010). Heavy metal pollution and assessment of the tidal flat sediments near the coastal sewage outfalls of shanghai, China. *Environmental Earth Sciences*, 60(1), 57-63.

Department of Environmental Affairs (DEA), (2010). The Framework for the Management of Contaminated Land, South Africa. Available online: http://sawic.environment.gov.za/documents/562.

Desaules, A. (2012). Critical evaluation of soil contamination assessment methods for trace metals. *Sci Total Environ* 426:120–131.

Deshmukh, K. K. (2012). Studies on chemical characteristics and classification of soils from Sangamner area, Ahmednagar district, Maharashtra, India. Rasayan *Journal Chemistry,* 5(1), 74-85.

DeSombre, E. R. (2007). The Global Environment and World Politics 2nd Edition. *Bloomsbury Publishing.*

DeVolder, P. S., Brown, S. L., Hesterberg, D., & Pandya, K. (2003). Metal bioavailability and speciation in a wetland tailings repository amended with biosolids compost, wood ash, and sulfate. *Journal of environmental quality*, 32(3), 851-864.

Donato, A. J., Eskurza, I., Silver, A. E., Levy, A. S., Pierce, G. L., Gates, P. E., & Seals, D. R. (2007). Direct evidence of endothelial oxidative stress with aging in humans. *Circulation research*, 100(11), 1659-1666.

Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., & Tack, F. M. (2009). Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review. *Science of the total environment*, 407(13), 3972-3985.

Duffus, J. H. (2002). " Heavy metals" a meaningless term (IUPAC Technical Report). *Pure and applied chemistry*, 74(5), 793-807.

Dung, T. T. T., Cappuyns, V., Swennen, R., & Phung, N. K. (2013). From geochemical background determination to pollution assessment of heavy metals in sediments and soils. *Reviews in Environmental Science and Bio/Technology*, 12(4), 335-353.

Duodu, G. O., Goonetilleke, A., & Ayoko, G. A. (2016). Comparison of pollution indices for the assessment of heavy metal in Brisbane River sediment. *Environmental Pollution*, 219, 1077-1091.

European Commission, (1998). The quality of water intended to human consumption. Directive 1998/83/EC, Official Journal L330/05.12. 1998. *European Community*, pp. 32–54

Ekong, E. B., Jaar, B. G., & Weaver, V. M. (2006). Lead-related nephrotoxicity: a review of epidemiologic evidence. *Kidney Intern.*, 70(12), 2074-2084.

El-Harouny, M. A., El-Morsi, D. A., Ahmed, B. R. A., & El-Atta, H. M. O. (2011). Chronic toxicity of some heavy metals and breast cancer in Egyptian Females. *J Clinic Toxicol*, 1(2).

Ene, A., Popescu, I. V., Stihi, C., Gheboianu, A., Pantelica, A., & Petre, C. (2010).PIXE analysis of multielemental samples. Rom. *Journ. Phys*, 55(7-8), 806.

Environment Canada, (1995). “Interim Sediment Quality Guidelines (ISQG), Soil and Sediment Quality Section Guidelines Division”, Ecosystem Conservation Directorate, Evaluation and Interpretation Branch, Ottawa

Environmental Protection Agency (EPA), (1995). “Ecological Screening Values”.In: Supplemental Guidance to RAGS: Region 4 Bulletins-

Ecological Risk Assessment, Bull..2, Atlanta,Georgia. E-PRTR, European Pollutant Release and Transfer Register, (2010): http://prtr.ec.europa.eu/

Espinasse, B., Picolet, G., & Chouraqui, E. (1997). Negotiation support systems: a multi-criteria and multi-agent approach. *European Journal of Operational Research,* 103(2), 389-409.

Essumang, D. K., Togoh, G. K., & Chokky, L. (2009). Pesticide residues in the water and fish (lagoon tilapia) samples from lagoons in Ghana. *Bulletin of the Chemical Society of Ethiopia,* 23(1), 19-27.

European Union (2002). Heavy Metals in Wastes, European Commission on Environment (http://ec.europa.eu/environment/waste/studies/pdf/heavy

Evans, L. J. (1989). Chemistry of metal retention by soils: several processes are explained. *Environmental Science & Technology*, 23(9), 1046-1056.

FAO, (1974). The Euphrates Pilot Irrigation Project: Methods of soil analysis. Gabed Soil Laboratory (A laboratory manual). Rome: Food and Agriculture Organization.

FAO/ISRIC, (2004). Guiding principles for the quantitative assessment of soil degradation with a focus on salinization, nutrient decline and soil pollution ftp://ftp.fao.org/agl/agll/docs/misc36e.pdf.

Feng, H., Han, X., Zhang, W., & Yu, L. (2004). A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization. *Marine Pollution Bulletin*, 49(11), 910-915.

Ferlay, J., Shin, H. R., Bray, F., Forman, D., Mathers, C., & Parkin, D. M. (2010). GLOBOCAN 2008, cancer incidence and mortality worldwide:

IARC CancerBase No. 10 [Internet]. Lyon, France: International Agency for Research on Cancer, 2. http://globocan. iarc. fr.

Fernandez, C., Monna, F., Labanowski, J., Loubet, M., & Van Oort, F. (2008). Anthropogenic lead distribution in soils under arable land and permanent grassland estimated by Pb isotopic compositions. *Environmental Pollution*, 156(3), 1083-1091.

Fiedler, H. D., López-Sánchez, J. F., Rubio, R., Rauret, G., Quevauviller, P., Ure, A. M., & Muntau, H. (1994). Study of the stability of extractable trace metal contents in a river sediment using sequential extraction. *Analyst*, 119(6), 1109-1114.

Filgueiras, A. V., Lavilla, I., & Bendicho, C. (2002). Chemical sequential extraction for metal partitioning in environmental solid samples. Journal of Environmental Monitoring, 4(6), 823-857.

Fisher, A., Hinds, M. W., Nelms, S. N., Penny, D. M., & Goodall, P. (2002). Atomic spectrometry update. Industrial analysis: metals, chemicals and advanced materials. *Journal of Analytical Atomic Spectrometry*, *17*(12), 1624-1649.

Foli, G., & Nude, P. M. (2012). Concentration levels of some inorganic contaminants in streams and sediments in areas of pyrometallurgical and hydrometallurgical activities at the Obuasi gold mine, Ghana. *Environmental Earth Sciences*, *65*(3), 753-763.

Fornes, F., García-de-la-Fuente, R., Belda, R. M., & Abad, M. (2009). ‘Alperujo’compost amendment of contaminated calcareous and acidic soils: effects on growth and trace element uptake by five Brassica species. *Bioresource technology*, 100(17), 3982-3990.

Förstner, U., Ahlf, W., Calmano, W., & Kersten, M. (1990). Sediment criteria development: contributions from environmental geochemistry to water quality management.

Foster, I. D. L., & Charlesworth, S. M. (1996). Heavy metals in the hydrological cycle: trends and explanation. *Hydrological processes*, 10(2), 227-261

Franzmeier, D. P., Lemme, G. D., & Miles, R. J. (1985). Organic carbon in soils of north central United States. *Soil science society of America journal*, 49(3), 702-708.

Frische, T., Mebes, K. H., & Filser, J. (2003). Assessing the bioavailability of contaminants in soils: a review on recent concepts. Umweltbundesamt.

Fritsche, J., & Meisel, T. (2004). Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS. *Science of the Total Environment, 325*(1), 145-154.

Gałuszka, A. (2007). A review of geochemical background concepts and an example using data from Poland. *Environmental geology*, 52(5), 861-870.

Gałuszka, A., & Migaszewski, Z. (2011). Geochemical background-an environmental perspective. *Mineralogia*, 42(1), 7-17.

Gambrell, R. P. (1994). Trace and toxic metals in wetlands—a review. *Journal of Environmental Quality*, 23(5), 883-891.

García-Sánchez, A., Alonso-Rojo, P., & Santos-Francés, F. (2010). Distribution and mobility of arsenic in soils of a mining area (Western Spain). *Science of the total environment*, 408(19), 4194-4201.

Garrett, R. G. (1991). The management, analysis and display of exploration geochemical data. Exploration geochemistry workshop, Ottawa Geological Survey of Canada, *Open File* 2390

Gaw, A., Packard, C. J., & Shepherd, J. (Eds.). (1999). Statins: the HMG CoA reductase inhibitors in perspective. CRC Press.

Gay, J. R., & Korre, A. (2006). A spatially-evaluated methodology for assessing risk to a population from contaminated land. *Environmental Pollution,* 142(2), 227-234.

Ghana Government. Ghana Statistical Service; Ghana Demographic and Health Survey, (2010). *Population and housing census*, Accra, Ghana.

Ghana Standard Authority (GSA 175/1) legislative instrument backing to World Health Organisation, (2010). In Guidelines for Drinking Water Quality; Health Organization: Accra, Ghana.

Ghana, EPA. (2007). Annual report: industrial effluent monitoring. Environmental Protection Agency, Accra, Ghana.

Gilon, N. (2005). ICP-AES and ICP-MS laser/spectrometry ablation coupling: a multiple application tool. Can. *J. Anal. Sci. Spectrosc*, 50(5), 240-254.

Gleyzes, C., Tellier, S., & Astruc, M. (2002). Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *TrA Trends in Analytical Chemistry*, 21(6), 451-467.

Golow, A. A., & Adzei, E. A. (2002). Mercury in surface soil and cassava crop near an alluvial goldmine at Dunkwa-on-Offin, Ghana. *Bulletin of environmental contamination and toxicology*, 69(2), 228-235.

Golow, A. A., Schlueter, A., Amihere-Mensah, S., Granson, H. L. K., & Tetteh, M. S. (1996). Distribution of arsenic and sulphate in the vicinity of Ashanti Goldmine at Obuasi, Ghana. *Bulletin of environmental contamination and toxicology*, 56(5), 703-710.

Goudie, A. S. (2013). The human impact on the natural environment: past, present, and future. John Wiley & Sons.

Government of Ghana, (1989). Small-Scale Gold Mining Act; PNDCL 218; Government of Ghana: Accra, Ghana.

Gyau-Boakye, P., & Dapaah-Siakwan, S. (1999). Groundwater: Solution to Ghana's Rural Water Supply Industry? The Ghana Engineer. *Accra, Ghana.*

Habashi, F. (1992). Environmental Issues in the Metallurgical Industry – Progress and Problems, Environmental Issues and Waste Management in Energy and Mineral Production. Balkama, Rotherdam, pp. 1143 - 1153.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water research*, 14(8), 975-1001.

Hall, G. E. M., & Pelchat, P. (1999). Development of a mercury vapour air analyser for measurement of Hg in solution. *Water, Air, & Soil Pollution*, 111(1), 287-295

Hansen, H. C. B. (2001). The filter function. In: Environmental Soil Chemistry, Hansen, H. C. B. (Ed.), Matej Bel University, Banská Bystrica, Slovakia.

Harada, M. (1995). Minamata disease: methylmercury poisoning in Japan caused by environmental pollution. Critical reviews in toxicology, 25(1), 1-24.

Hasan, Z., Anwar, Z., Khattak, K. U., Islam, M., Khan, R. U., & Khattak, J. Z. K.

(2012). Civic pollution and its effect on water quality of river Toi at District Kohat, NWFP. *Research Journal of Environmental and Earth Sciences*, 4(3), 334-339.

Hausenbuiller, (1976). Soil Science: Principles and practices, Washington state University, Pullman, 247.

Havlin, J. L., Tisdale S. L., Nelson W. L., & Beaton J. D. (2011). Soil Fertility and Fertilizers. New Delhi: PHI

Hawkes, H. E., & Webb, J. S. (1963). Geochemistry in Mineral Exploration. *Soil Science*, 95(4), 283.

Health and Welfare Canada, (1993). Guidelines for Canadian drinking water quality. 5th ed. Prepared by the Federal–Provincial Subcommittee on Drinking Water of the Federal–Provincial Advisory Committee on Environmental and Occupational Health.

Hilson, G. (2001). A contextual review of the Ghanaian small-scale mining industry. Mining, Minerals and Sustainable Development 76.

Hilson, G. (2002). An overview of land use conflicts in mining communities. Land use policy, 19(1), 65-73.

Hilson, G. (2002). Harvesting mineral riches: 1000 years of gold mining in Ghana. *Resources Policy*, 28(1), 13-26.

Hilson, G. (2002). The environmental impact of small-scale gold mining in Ghana: identifying problems and possible solutions. *The Geographical Journal*, 168(1), 57-72.

Hilson, G., & Nyame, F. (2006). Gold mining in Ghana's forest reserves: a report on the current debate. *Area*, 38(2), 175-185.

Ho, K. C., Chow, Y. L., & Yau, J. T. S. (2003). Chemical and microbiological qualities of The East River (Dongjiang) water, with particular reference to drinking water supply in Hong Kong. *Chemosphere,* 52(9), 1441-1450.

Hoffmann, E., Lüdke, C., & Scholze, H. (1997). Is laser-ablation-ICP-MS an alternative to solution analysis of solid samples. *Fresenius' journal of analytical chemistry*, 359(4-5), 394-398.

Holum, J. R. (1983). Elements of General and Biological Chemistry, 6th Edition, John Wiley and Sons, N.Y. pp. 324, 326, 353, 469.

Horneck, D. A., Hart, J. M., Topperand, K., & Koespell, B. (1989). Methods of Soil Analysis used in the soil testing laboratory at Oregon State University. *Agricultural Experiment Station SM* 89, 4, 13–35.

Hostynek, J. J., Hinz, R. S., Lorence, C. R., & Guy, R. H. (1998). Human skin penetration by metal compounds. *Drugs and the pharmaceutical sciences*, 91, 647-668.

Howard, P. J. A., & Howard, D. M. (1990). Use of organic carbon and loss-on-ignition to estimate soil organic matter in different soil types and horizons. *Biology and Fertility of soils*, 9(4), 306-310.

Hu, G., Yu, R., Zhao, J., & Chen, L. (2011). Distribution and enrichment of acid-leachable heavy metals in the intertidal sediments from Quanzhou

Bay, southeast coast of China. *Environmental monitoring and assessment*, 173(1), 107-116.

Huber, S., Prokop, G., Arrouays, D., Banko, G., Bispo, A., Jones, R. J. A., ... & Shishkov, T. (2008). Environmental assessment of soil for monitoring: EUR 23490 EN/1. Office for the Official Publications of the European Communities, Luxembourg. Volume I Indicators and Criteria (p. 339).

Huo, X., Peng, L., Xu, X., Zheng, L., Qiu, B., Qi, Z., ... & Piao, Z. (2007). Elevated blood lead levels of children in Guiyu, an electronic waste recycling town in China. *Environmental Health Perspectives*, 115(7), 1113.

Hylander, L. D., & Meili, M. (2003). 500 years of mercury production: global annual inventory by region until 2000 and associated emissions. Science of the Total Environment, 304(1-3), 13-27.

Idris, A. M., Eltayeb, M. A. H., Potgieter-Vermaak, S. S., Van Grieken, R., & Potgieter, J. H. (2007). Assessment of heavy metals pollution in Sudanese harbours along the Red Sea Coast. *Microchemical Journal*, 87(2), 104-112.

Institute of Environmental Conservation and Research (INECAR), (2000). Position Paper Against Mining in Rapu-Rapu, Published by INECAR, Ateneo de Naga University, Philippines (www.adnu.edu.ph/Institutes/pospaper1.asp).

International Standard Organization (1995) Soil quality. Extraction of trace elements Soluble in Aqua Regia, ISO 11466.

IPCS (International Programme on Chemical Safety), (2001). Environmental health criteria 222, biomarkers in risk assessment: validity and validation. United Nations Environment Programme, International Labour Organization, World Health Organization. Available online at http://www.inchem.org/ documents/ ehc/ehc/ehc222.htm.

Iqbal, J., & Shah, M. H. (2013). Health risk assessment of metals in surface water from freshwater source lakes, Pakistan. *Human and Ecological Risk Assessment: An International Journal*, 19(6), 1530-1543.

ISO 10390, (1994). Soil Quality – Determination of pH. Geneva, Switzerland: International Organization for Standardization. Retrieved from http://www.iso.ch on 7th June, 2011

ISO/DIS 19258, (2002). Soil quality. In Guidance on the Determination of Background Values; International Standard Organisation (ISO): Switzerland, Geneva.

Jaafar, H., Gabriel-Robez, O., Vignon, F., Flori, E., & Rumpler, Y. (1994). Supernumerary chromosomes and spermatogenesis in a human male carrier. *Human genetics*, 94(1), 74-76.

Järup, L. (2003). Hazards of heavy metal contamination. *British medical bulletin*, *68*(1), 167-182.

Jian-Min, Z. H. O. U., Zhi, D., Mei-Fang, C. A. I., & Cong-Qiang, L. I. U. (2007). Soil heavy metal pollution around the Dabaoshan mine, Guangdong province, China. *Pedosphere*, *17*(5), 588-594.

Neustadt, N. D., & Pieczenik, S. (2011). Heavy-metal Toxicity—With Emphasis on Mercury. *Integrative Medicine*, 10(5).

Jones, B., & Turki, A. (1997). Distribution and speciation of heavy metals in surficial sediments from the Tees Estuary, north-east England. *Marine Pollution Bulletin*, 34(10), 768-779.

Jones, L. H. P., & Jarvis, S. C. (1981). The fate of heavy metals. The chemistry of soil processes, 599.

Jung, M. C. (2001). Heavy metal contamination of soils and waters in and around the Imcheon Au–Ag mine, Korea. *Applied geochem.*, 16(11), 1369-1375.

Jung, M. C., & Thornton, I. (1997). Environmental contamination and seasonal variation of metals in soils, plants and waters in the paddy fields around a Pb, Zn mine in Korea. *Science of the Total Environment*, 198(2), 105-121.

Kabata Pendias, A. & Pendias, H. (2001). Trace Elements in Soils and Plants; CRC Press Inc.: Boca Raton, FL, USA.

Kabata-Pendias, (2007). Trace elements in soils and plants (3rd ed.) CRC Press; Boca Raton, FL, USA.

Kabata-Pendias, A., & Mukherjee, A. B. (2007). Trace elements from soil to human. Springer Science & Business Media.

Kakkar, P., & Jaffery, F. N. (2005). Biological markers for metal toxicity. *Environmental Toxicology and Pharmacology*, 19(2), 335-349.

Kalbitz, K., & Wennrich, R. (1998). Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Science of the Total Environment*, 209(1), 27-39.

Keller, H. R., Massart, D. L., & Brans, J. P. (1991). Multicriteria decision making: a study. *Chemometrics and Intelligent laboratory systems*, 11(2), 175-189.

Kennedy, V. H., Sanchez, A. L., Oughton, D. H., & Rowland, A. P. (1997). Use of single and sequential chemical extractants to assess radionuclide and heavy metal availability from soils for root uptake. *Analyst*, 122(8), 89R-100R.

Kersten, M., & Förstner, U. (1986). Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. *Water Science and Technology*, 18(4-5), 121-130.

Khalil, W. A. S., Goonetilleke, A., Kokot, S., & Carroll, S. (2004). Use of chemometrics methods and multicriteria decision-making for site selection for sustainable on-site sewage effluent disposal. *Analytica Chimica Acta*, 506(1), 41-56.

Khudzari, J. M., Wagiran, H., Hossain, M. I., Ibrahim, N., & Agam, M. A. (2011). Heavy metals Mn, Fe, Ni, Cu and Zn in human hair samples using energy dispersive X-ray fluorescence analysis. International Journal of Physical Sciences, 6(8), 2090-2094.

Kinraide, T. B., & Yermiyahu, U. (2007). A scale of metal ion binding strengths correlating with ionic charge, Pauling electronegativity, toxicity, and other physiological effects. *Journal of Inorganic Biochem.*, 101(9), 1201-1213.

Knight, C., Kaiser, J., Lalor, G. C., Robotham, H., & Witter, J. V. (1997). Heavy metals in surface water and stream sediments in Jamaica. *Environmental Geochemistry and Health*, 19(2), 63-66.

Koger, S. M., Schettler, T., & Weiss, B. (2005). Environmental toxicants and developmental disabilities: a challenge for psychologists. *American Psychologist*, 60(3), 243.

Koki, I. B., Bayero, A. S., Umar, A., & Yusuf, S. (2015). Health risk assessment of heavy metals in water, air, soil and fish. *African Journal of Pure and Applied Chemistry*, 9(11), 204-210.

Koranteng – Addo, E. J., Owusu – Ansah, E., Boamponsem, L. K., Bentum, J. K., & Arthur, S. (2011). Levels of zinc, copper, iron and manganese in soils of abandoned mine pits around the Tarkwa gold mining area of Ghana. *Adv. Appl. Sci. Res.*, 2 (1):280-288

Koranteng, D. O. (2004). A Statement by WACAM on the cyanide spillage by Bogoso Gold Limited [Internet]. Tarkwa, Ghana: Wassa Association of Communities Affected by Mining; Oct 23 [cited 2017 Jul. 16]. Available from: http://www.miningwatch.ca/statement-wacam-cyanide-spillage.

Kortatsi, B. K. (2004). Hydrochemistry of groundwater in the mining area of Tarkwa-Prestea, Ghana. PhD, University of Ghana, Ghana.

Kriegel, A. M., Soliman, A. S., Zhang, Q., El-Ghawalby, N., Ezzat, F., Soultan, A., ... & Hamilton, S. R. (2006). Serum cadmium levels in pancreatic cancer patients from the East Nile Delta region of Egypt. *Environmental health perspectives*, 114(1), 113.

Kuang, Y., Zhu, X., Xi, D., & Li, J. (2013). J. Soil Sedi. 13, 394–402

Kubravova, I. (1997). Spectrochim. *Acta Part B*, 52, 1469–1481.

Kuma, J. S., & Younger, P. L. (2004). Water quality trends in the Tarkwa gold-mining district, Ghana. *Bulletin of Engineering Geology and the Environment*, 63(2), 119-132.

Kwadwo, A. A., Tetsuro, A., Annamalai, S., Osmund, D. A., Charles, A. B. & Shinsuke, T. 2007. Contamination status of arsenic and other trace elements in drinking water and residents from Tarkwa, a historic mining township in Ghana. *Chemosphere* 66: 1513–1522.

Kwok, K. W., Bjorgesæter, A., Leung, K. M., Lui, G., Gray, J. S., Shin, P. K., & Lam, P. K. (2008). Deriving site-specific sediment quality guidelines for Hong Kong marine environments using field-based species sensitivity distributions. *Environmental Toxicology and Chemistry*, 27(1), 226-234.

Lanno, R. P. (2003). Proceedings from the Pellston Workshop on Assessing Contaminated Soils: From Soil-Contaminant Interactions to Ecosystem Management, Pellston, Michigan, USA, 23-27 September 1998, *Society of Environmental Toxicology and Chemistry* (SETAC).

Lee, P. K., Kang, M. J., Jo, H., & Choi, S. H. (2012). Sequential extraction and leaching characteristics of heavy metals in abandoned tungsten mine tailings sediments. *Environmental Earth Sciences* 66, 1909-1923.

Lenntech, R. (2004). Water Treatment and Air Purification. Available online: http//www.excelwater.com/thp/filters/Water-Purification.htm

Lewan, M. D., & Maynard, J. B. (1982). Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochimica et Cosmochimica Acta*, 46(12), 2547-2560.

Li, X., & Thornton, I. (2001). Chemical partitioning of trace and major elements in soils contaminated by mining and smelting activities. *Applied geochemistry*, 16(15), 1693-1706.

Li, X., Poon, C.-S., & Liu, P. S. (2001). Heavy metal contamination of urban soils and street dusts in Hong Kong. *Applied Geochemistry*, 16(11-12), 1361–1368. Retrieved from http://www.sciencedirect.com/science/article.

Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z., & Huang, L. (2014). A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Science of the Total Environment*, 468, 843-853.

Linnik, P. M., & Zubenko, I. B. (2000). Role of bottom sediments in the secondary pollution of aquatic environments by heavy metal compounds. Lakes & Reservoirs: *Research & Management*, 5(1), 11-21.

Liu, H., Probst, A., & Liao, B. (2005). Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Science of the Total Environment*, 339(1), 153-166.

Liu, W. X., Li, X. D., Shen, Z. G. Wang, D. C., Wai, O.W. H., & Li, Y. S. (2003). Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environmental Pollution*, 121(3), 377–388.

Loska, K., Wiechuła, D., & Korus, I. (2004). Metal contamination of farming soils affected by industry. *Environment international*, 30(2), 159-165.

Lu, J., Getz, G., Miska, E. A., Alvarez-Saavedra, E., Lamb, J., Peck, D., ... & Downing, J. R. (2005). MicroRNA expression profiles classify human cancers. *Nature*, 435(7043), 834-838.

Lukaski, H. C. (1999). Chromium as a supplement. *Annual review of nutrition*, 19(1), 279-302.

Lushenko, M. A. (2010). A risk assessment for ingestion of toxic chemicals in fish from Imperial Beach, California (Doctoral dissertation, San Diego State University).

Mahaffey, K. R. (2005). Mercury exposure: medical and public health issues. Transactions of the American Clinical and Climatological Association, 116, 127.

Manaf, H. (1999). The environmental impact of small scale mining in Indonesia. In Abstract of the 3rd Environmental Cooperation workshop for Sustainable Development on Mining Activities, Cairns.

Manahan, S. E. (2011). Fundamentals of environmental chemistry. CRC press. 2003

Manu, A., Twumasi, Y. A., & Coleman, T. L. (2004). Application of remote sensing and GIS technologies to assess the impact of surface mining at Tarkwa, Ghana. In Geoscience and Remote Sensing Symposium, 2004. IGARSS'04. Proceedings. 2004 IEEE International (Vol. 1). IEEE, Volume 1, pp. 572–574

Maret, W., & Sandstead, H. H. (2006). Zinc requirements and the risks and benefits of zinc supplementation. *Journal of Trace Elements in Medicine and Biology*, 20(1), 3-18.

Margui, E., Salvadó, V., Queralt, I., & Hidalgo, M. (2004). Comparison of three-stage sequential extraction and toxicity charact leaching tests to evaluate metal mobility in mining wastes. *Analytica Chimica Acta,* 524(1), 151-159.

Martin, J. M., Nirel, P., & Thomas, A. J. (1987). Sequential extraction techniques: promises and problems. *Marine Chemistry*, 22(2-4), 313-341.

Mason, R. P., Choi, A. L., Fitzgerald, W. F., Hammerschmidt, C. R., Lamborg, C. H., Soerensen, A. L., & Sunderland, E. M. (2012). Mercury biogeochemical cycling in the ocean and policy implications. *Env. research*, 119, 101-117.

Matschullat, J., Ottenstein, R., & Reimann, C. (2000). Geochemical background–can we calculate it. *Environmental geology*, 39(9), 990-1000.

Matusch, A., Depboylu, C., Palm, C., Wu, B., Höglinger, G. U., Schäfer, M. K. H., & Becker, J. S. (2010). Cerebral bioimaging of Cu, Fe, Zn, and Mn in the MPTP mouse model of Parkinson's disease using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Journal of the American Society for Mass Spectrometry*, 21(1), 161-171.

McGlashan, N. D., Harington, J. S., & Chelkowska, E. (2003). Changes in the geographical and temporal patterns of cancer incidence among black gold miners working in South Africa, 1964–1996. *British journal of cancer*, 88(9), 1361-1369.

McKinney, P. E. (1999). Elemental mercury in the appendix: an unusual complication of a Mexican-American folk remedy. *Journal of Toxicology: Clinical Toxicology*, 37(1), 103-107.

McLaren, R. G., Clucas, L. M., Taylor, M. D., & Hendry, T. (2004). Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 2. Leaching of metals. *Soil Research*, 42(4), 459-471

McLean, E. O. (1982). Soil pH and lime requirement. In A. L. Page (Ed.), Methods of Soil Analysis, Part 2: Chemical and microbiological properties (pp. 199 – 224). Madison, WI: *American Society of Agronomy Inc.*

Miller, J.R., Hudson-Edwards, K.A., Lechler, P.J., Preston, D., and Macklin, M.G. (2004). Heavy metal contamination of water, soil and produce with in riverine communities of the R Pilcomayo basin, Bolivia. *Sci. Total Environ.*, 320, 189–209.

Miller, R. W., & Donahue, R. L. (1992). Soils: An introduction to soils and plant growth, Prentice Hall of India Pvt Ltd, New Delhi.

Mmolawa, K. B., Likuku, A. S., & Gaboutloeloe, G. K. (2011). Assessment of heavy metal pollution in soils along major roadside areas in Botswana. African *Journal of Environmental Science and Technology*, 5(3), 186-196.

Mossop, K. F., & Davidson, C. M. (2003). Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. *Analytica Chimica Acta*, 478(1), 111-118.

Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine river. *Geol. J.* 2 (3), 109-118.

Muniz, P., Danulat, E., Yannicelli, B., Garcí, J., Medina, G., & Bí, M. C. (2004). Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). *Environment International*, 29(8), 1019-1028.

NAS/IOM (National Academy of Sciences/Institute of Medicine), (2003). Dietary reference intakes: guiding principles for nutrition labeling and fortification. Food and Nutrition Board, Institute of Medicine, Washington, DC.

NAS/NRC (National Academy of Sciences/National Research Council), (2002). Bioavailability of contaminants in soils and sediments: processes, tools, and applications. Washington, DC: National Academem Press.

Nasrabadi, T., Bidhendi, G. N., Karbassi, A., & Mehrdadi, N. (2010). Evaluating the efficiency of sediment metal pollution indices in interpreting the pollution of Haraz River sediments, southern Caspian Sea basin. *Environmental monitoring and assessment,* 171(1-4), 395-410.

National Research Council, (2014). Review of EPA's integrated risk information system (IRIS) process. National Academies Press.

Naveedullah, M. Z., Hashmi, C. Y. Shen, H., Duan, D., Shen, C., Lou L., & Chen Y. (2014). "Concentrations and human health risk assessment of selected heavy metals in surface water on the Siling reservoir watershed in Zhejiang Province, China". Polish Journal of Environmental Studies, 23(3), 801-811.

Naylor, R. T. (2007). The alchemy of fraud: Investment scams in the precious-metals mining business. Crime, law and social change, 47(2), 89-120.

Nemerow, N. L. (1991). Stream, lake, estuary, and ocean pollution, New York,

Niencheski, L. F., Windom, H. L., & Smith, R. (1994). Distribution of particulate trace metal in Patos Lagoon Estuary (Brazil). *Mar. Pol. Bull*, 28(2), 96-102.

Nkoom, M., Cobbina, S. J., & Kumi, M. (2013). Assessment of Endocrine Disrupting Trace Metals in River Samre at Samreboi in the Wassa Amenfi West District of the Western Region of Ghana. *Journal of Water Resource and Protection*, 5(10), 983.

NSC, National Safety Council, (2009). Lead Poisoning. http://www.nsc.org/newsresources/Resources/Documents/Lead Poisoning.pdf.

Nyarko, B. J. B., Dampare, S. B., Serfor-Armah, Y., Osae, S., Adotey, D. & Adomako, D. (2008). Biomonitoring in the forest zone of Ghana: the primary results obtained using neutron activation analysis and lichens. *Int J Environ Pollut;* 32(4): 467–476.

Obiri, S. (2007). Determination of heavy metals in water from boreholes in Dumasi in the Wassa West District of western region of Republic of Ghana. *Environmental monitoring and assessment*, 130(1-3), 455.

Obiri, S., Dodoo, D. K., Essumang, D. K., Armah, F. A. (2010). Cancer and non-cancer risk assessment from exposure to arsenic, copper, and cadmium in borehole, tap, and surface water in the Obuasi municipality, Ghana. *Hum. Ecol. Risk Assess.*, *22*, 651–665

Obiri, S., Dodoo, D. K., Okai-Sam, F., & Essumang, D. K. (2006). Cancer health risk assessment of exposure to arsenic by workers of AngloGold Ashanti–Obuasi Gold Mine. *Bulletin of environmental contamination and toxicology*, 76(2), 195-201.

Obiri, S., Dodoo, D. K., Okai–Sam, F., Essumang, D. K., & Adjorlolo-Gasokpoh, A. (2006). Cancer and non-cancer health risk from eating cassava grown in some mining communities in Ghana. *Environmental monitoring and assessment*, *118*(1-3), 37-49.

Obiri, S., Yeboah, P. O., Osae, S., Adu-kumi, S., Cobbina, S. J., Armah, F. A., ... & Quansah, R. (2016). Human Health Risk Assessment of Artisanal Miners Exposed to Toxic Chemicals in Water and Sediments in the PresteaHuni Valley District of Ghana. *International journal of environmental research and public health*, 13(1), 139.

Ogunkunle, C. O., Fatoba, P. O., Ogunkunle, M. O., & Oyedeji, A. A. (2013). Potential health risk assessment for soil heavy metal contamination of Sagamu, South-west Nigeria due to cement production. *International Journal of Applied Science and Technology*, *3*(2).

Ogwuegbu, M. O. C., & Muhanga, W. (2005). Investigation of lead concentration in the blood of people in Copperbelt Province of Zambia. *J Env.*, *1*, 66-75.

Ogwuegbu, M. O., & Ijioma, M. A. (2003). Effects of certain heavy metals on the population due to mineral exploitation. In Int. conference on scientific and environmental issues, University of Ado Ekiti, Ekiti State (8-10).

Okang'Odumo, B., Carbonell, G., Angeyo, H. K., Patel, J. P., Torrijos, M., & Martín, J. A. R. (2014). Impact of gold mining associated with mercury contamination in soil, biota sediments and tailings in Kenya. *Environmental Science and Pollution Research*, 21(21), 12426-12435.

Owusu-Koranteng, D. (2008). Mining Investment & Community Struggles. *Review of African Political Economy*, 35(117), 467-473.

Pacyna, J. M., & Pacyna, E. G. (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ Rev* 9(4): 269–298.

Pansu, M. & Gautheyrou. J. (2006). Handbook of Soil Analysis: mineralogical, organic and inorganic methods. Springer-Verlag, Berlin, Germany.

Paruchuri, Y., Siuniak, A., Johnson, N., Levin, E., Mitchell, K., Goodrich, J. M., ... & Basu, N. (2010). Occupational and environmental mercury exposure among small-scale gold miners in the Talensi–Nabdam District of Ghana's Upper East region. *Science of the Total Environment*, 408(24), 6079-6085.

Paustenbach, D. J. (2000). The practice of exposure assessment: a state-of-the-art review. Journal of Toxicology and Environmental Health Part B: *Critical Reviews*, 3(3), 179-291.

Paustenbach, D. J. (Ed.), (2002). Human and ecological risk assessment: Theory and practice. John Wiley and Sons, New York, NY.

Pe´rez-Sirvent, C., Martı´nez-Sa´nchez, M. J., Garcı´a-Lorenzo, M. L., Molina, J., & Tudela, M. L. (2009). Geochemical background levels of zinc, cadmium and mercury in anthropically influenced soils located in a semi-arid zone (SE, Spain). *Geoderma* 148(3–4):307–317

Peirson, D. H., & Cawse, P. A. (1979) Trace elements in the atmosphere. Phil Trans R Soc Lond B288:41–49.

Pekey, H. (2006). The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Marine Pollution Bulletin, 52(10), 1197-1208.

Pelig-Ba, K. B., Parker, A., & Price, M. (2004). Trace element geochemistry from the Birrimian metasediments of the Northern Region of Ghana. *Water, Air, & Soil Pollution*, 153(1), 69-93.

Pils, J. R. V., Karathanasis, A. D., & Mueller, T. G. (2004). Concentration and distribution of six trace metals in northern Kentucky soils. *Soil & Sediment Contamination*, 13(1), 37-51.

Pinto, M. M. C., Silva, M. M., da Silva, E. A. F., Dinis, P. A., & Rocha, F. (2017). Transfer processes of potentially toxic elements (PTE) from rocks to soils and the origin of PTE in soils: A case study on the island of Santiago (Cape Verde). *Journal of Geochemical Exploration*.

Pollution - Definition from the Merriam-Webster Online Dictionary" (2010). *Merriam-webster.com*. [Retrieved 17-10-2017].

Ponthieu, M., Juillot, F., Hiemstra, T., Van Riemsdijk, W. H., & Benedetti, M. F. (2006). Metal ion binding to iron oxides. *Geochimica Et Cosmochimica Acta*, 70(11), 2679-2698.

Pradhan, U. K., Shirodkar, P. V., & Sahu, B. K. (2009). Physico-chemical characteristics of the coastal water off Devi estuary, Orissa and evaluation of its seasonal changes using chemometric techniques. *Current Science*, 1203-1209.

Prego, R., & Cobelo-Garcıa, A. (2003). Twentieth century overview of heavy metals in the Galician Rias (NW Iberian Peninsula). *Environmental Pollution*, 121(3), 425-452.

Pulford, I., & Flowers, H. (2006). Environmental chemistry at a glance. *Blackwell Pub.*

Qi, S., Leipe, T., Rueckert, P., Di, Z., & Harff, J. (2010). Geochemical sources, deposition and enrichment of heavy metals in short sediment cores from the Pearl River Estuary, Southern China. *J. of Marine Systems*, 82, S28-S42.

Qingjie, G., Jun, D., Yunchuan, X., Qingfei, W., & Liqiang, Y. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences*, 19(3), 230-241.

Rajaee, M., Obiri, S., Green, A., Long, R., Cobbina, S. J., Nartey, V., ... & Basu, N. (2015). Integrated assessment of artisanal and small-scale gold mining in Ghana—Part 2: Natural sciences review. *International journal of environmental research and public health,* 12(8), 8971-9011.

Ray, M. (1990). Accumulation of heavy metals in plants grown in industrial areas. *Indian Biologist*, 22(2), 33-38.

Reaves, G. A., & Berrow, M. L. (1984). Total copper contents of Scottish soils. *European Journal of Soil Science*, 35(4), 583-592.

Reimann, C., & Garrett, R. G. (2005). Geochemical background–concept and reality. *Sci Total Environ* 350(1–3):12–27

Reimann, C., Filzmoser, P., & Garrett, R. G. (2005). Background and threshold: critical comparison of methods of determination. *Science of the Total Environment*, 346(1-3), 1-16.

Rojo, P. A., Frances, F. S., Garcia-Sanchez, A., & Alvarez-Ayuso, E. (2004). Baseline concentrations of heavy metals in native soils of the Salamanca and Valladolid provinces, Spain. *Arid Land Research and Management*, 18(3), 241-250.

Rosen, A. L., & Hieftje, G. M. (2004). Inductively coupled plasma mass spectrometry and electrospray mass spectrometry for speciation analysis: applications and instrumentation. Spectrochimica Acta Part B: *Atomic Spectroscopy*, 59(2), 135-146.

Rubino, F. M. (2015). Toxicity of glutathione-binding metals: a review of targets and mechanisms. Toxics, 3(1), 20-62.

Rubio, B., Nombela, M. A., & Vilas, F. (2000). Geochemistry of major and trace elements in sediments of the Ria De Vigo (NW Spain): an assessment of metal pollution. *Marine pollution bulletin*, 40(11), 968-980.

Sako, A., Lopes, L., & Roychoudhury, N. (2009). Adsorption and surface complexation modelling of palladium, rhodium and platinum in surficial semi-arid soils and sediment. *Applied Geochemistry*, 24, 86–95.

Salminen, R., & Gregorauskien, V. (2000). Considerations regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology. *Applied Geochemistry*, 15(5), 647-653.

Salmons, W. (1993). Adoption of common schemes for single and sequentia l extractions of metals in soil and sediments. *Int J Env. Anal Chem*, 51, 3-4.

Santos-Francés, F., Martinez-Graña, A., Alonso Rojo, P., & García Sánchez, A. (2017). Geochemical Background and Baseline Values Determination and Spatial Distribution of Heavy Metal Pollution in Soils of the Andes Mountain Range (Cajamarca-Huancavelica, Peru). *International Journal of Environmental Research and Public Health*, 14(8), 859

Sass, J., Heine, L., & Hwang, N. (2016). Use of a modified GreenScreen tool to conduct a screening-level comparative hazard assessment of conventional silver and two forms of nanosilver. *Environmental Health*, 15(1), 105.

Schnitzer, M. (1978). Humic substances: Chemistry and reactions. In: Soil Organic Matter, M. Schnitzer and S.U. Khan, Ed. Elsevier Scientific Publishing Co., New York. 8. 1-64.

Schollenberger, C. J., & Simon, R. H. (1945). Determination of exchange capacity and exchangeable bases in soil-ammonium acetate method. *Soil Science*, 59(1), 13-24.

Serfor-Armah, Y., Nyarko, B. J. B., Osae, E. K., Carboo, D., & Seku, F. (1997). Seaweed as bioindicators for monitoring toxic elements pollutants in the marine ecosystem. Progress report, IAEA Research Contract No. GHA/9486/RO, 2–11.

Shikazono, N., Tatewaki, K., Mohiuddin, K. M., Nakano, T., & Zakir, H. M. (2012). Sources, spatial variation, and speciation of heavy metals in sediments of the Tamagawa River in Central Japan. *Environmental geochemistry and health*, 34(1), 13-26.

Singh, M., Müller, G., & Singh, I., (2002). Heavy Metals in Freshly Deposited Stream Sediments of Rivers Associated with Urbanisation of the Ganga Plain, India. *Water, Air and Soil Pollution* 141, 35-54.

Skoog, D. A., Holler, F. J., & Crouch, S. R. (2007). Principles of Instrumental Analysis; Thomson Brooks/Cole: Belmont, CA, USEPA. National Priorities List for Uncontrolled Hazardous Waste Sites. *Federal Register*. 1989; 54(223):48184–48189.

Smedley, P. L. (1996). Arsenic in rural groundwater in Ghana: part special issue: hydrogeochemical studies in sub-Saharan Africa. *Journal of African Earth Sciences*, 22(4), 459-470.

Smedley, P. L., Edmunds, W. M., & Pelig-Ba, K. B. (1996). Mobility of arsenic in groundwater in the Obuasi gold-mining area of Ghana: some implications for human health. *Geological Society, London, Special Publications*, 113(1), 163-181.

Smith, L. A. (1992). Remedial options for metals-contaminated sites. Lewis Publ.

Smith, L. A. Means, J. L. Chen *et al.*, (1995). Remedial Options for Metals Contaminated Sites, Lewis Publishers, Boca Raton, Fla, USA.

Solgi, E., Esmaili-Sari, A., Riyahi-Bakhtiari, A., & Hadipour, M. (2012). Soil contamination of metals in the three industrial estates, Arak, Iran. *Bulletin of environmental contamination and toxicology*, 88(4), 634-638.

Solomons W., (1995). Environmental impact of metals derived from mining activities: Processes, predictions, prevention. D21502 Geesthacht, Germany. Journal of Geochemical Exploration 52 (1995) 5-23.

Spears, J. W. (2000). Micronutrients and immune function in cattle. Proceedings of the nutrition society, 59(4), 587-594.

Spence, L. R. (2001). User Manual for RISC4 Software for Clean-Ups and Human Health Risk Assessment; Unpublished.

Sterckeman, T., Douay, F., Baize, D., Fourrier, H., Proix, N., & Schvartz, C. (2006).

Trace elements in soils developed in sedimentary materials from Northern France. *Geoderma*, 136(3), 912-929.

Strincone, M., Fino, A., Cattani, G., Catrambone, M., & Pirrone, N. (2013). Emissions, air concentrations and atmospheric depositions of arsenic, cadmium, lead and nickel in Italy in the last two decades: A review of recent trends in relation to policy strategies adopted locally, regionally and globally. *In E3S Web of Conferences* (Vol. 1). EDP Sciences.

Sundaray, S. K., Nayak, B. B., Lin, S., & Bhatta, D. (2011). Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments--A case study: Mahanadi basin, India. *J. of Hazardous Materials* 186, 1837-1846.

Suresh, G., Sutharsan, P., Ramasamy, V., & Venkatachalapathy, R. (2012). Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. *Ecotoxicology and Environmental Safety*, 84, 117-124.

Tack, F. M. G., Verloo, M. G., Vanmechelen, L., & Van Ranst, E. (1997). Baseline concentration levels of trace elements as a function of clay and organic carbon contents in soils in Flanders (Belgium). *Science of the Total Environment*, 201(2), 113-123.

Takamatsu, T., Kawashima, M., & Koyama, M. (1985). The role of Mn2+-rich hydrous manganese oxide in the accumulation of arsenic in lake sediments. *Water Research,* 19(8), 1029-1032.

Tam, N. F. Y., & Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution,* 110(2), 195-205.

Tarras-Wahlberg, N. H., Flachier, A., Lane, S. N., & Sangfors, O. (2001). Environmental impacts and metal exposure of aquatic ecosystems in rivers contaminated by small scale gold mining: the Puyango River basin, southern Ecuador. *Science of the Total Environment*, 278(1), 239-261.

Tarvainen, T., & Kallio, E. (2002). Baselines of certain bioavailable and total heavy metal concentrations in Finland. *Applied Geochemistry*, 17(8), 975-980.

Taylor, A. Branch, S. Halls D., Patriarca, M. White, M. (2003). *J. Anal. At. Spectrom*. 18 385-427.

Taylor, H. E., & Shiller, A. M. (1995). Mississippi River methods comparison study: Implications for water quality monitoring of dissolved trace elements. *Environmental science & technology*, 29(5), 1313-1317.

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Heavy metal toxicity and the environment. *In Molecular, clinical and environmental toxicology* (pp. 133-164). Springer Basel.

Tessier, A., Campbell, P. G., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51(7), 844-851.

Toccalino, P. L., & Norman, J. E. (2006). Health-based screening levels to evaluate US Geological Survey ground water quality data. *Risk Analysis*, 26(5), 1339-1348.

Toffaletti, J. G. (2005). Trace Elements. In M. L. Bishop, E. P. Fody & L. E. Schoeff (Eds.), Clinical Chemistry: Principles, Procedures, Correlations (pp. 364-377). Sydney: Lippincott Williams & Wilkins.

ToxFAQs [Internet]. Atlanta, GA: Agency for Toxic Substances and Disease Registry. [date unknown] - [updated 2014 Jun 24; cited 2016 Dec. 20]. Available from: http://www.atsdr.cdc.gov/toxfaqs/index.asp#bookmark01

Trandafir, V. & Nour, M. E. (2012). Ionica, *Polish J of Environ. Studies*. 21: 749-754.

Tseng, C. M., de Diego, A., Martin, F. M., Amouroux, D., & Donard, O. F. (1997).

Rapid determination of inorganic mercury and methylmercury in biological reference materials by hydride generation, cryofocusing, atomic absorption spectrometry after open focused microwave-assisted alkaline digestion. *Journal of Analytical Atomic Spectrometry*, 12(7), 743-750.

Tsidzi, K. E. N., & Adofo, R. A. (1993). Some Environmental Aspects of Mining and Related Activities in Ghana in Proceedings of the National Seminar on Current Development in the Mineral Industry of Ghana. IMME, UST, Kumasi Ghana, 126-131.

Tufour, K. (1997, April). Mining, degradation of forest lands resources and rehabilitation. In Proceedings of the National Symposium on Mining Industry and the Environment, University of Science and Technology, Kumasi (pp. 43-48).

U.S. Environmental Protection Agency (USEPA), (1999). Exposure Factors Handbook, Volume II: General Factors; Exposure Factor Handbook NCEA-W-005.107; Office of Research and Development: DC, USA.

Udedi, S. S. (2003). From guinea worm scourge to metal toxicity in Ebonyi State. *Chem Nigeria New Millenn Unfold*, 2, 13-14.

UNEP, United Nations Environment Programme, (2008). Heavy Metals: http://www.cep.unep.org/publications-and-resources/coastal-issues-links/heavy-metals.

United Nations Environmental Protection/Global Program of Action, (2004). Why The Marine Environment Needs Protection From Heavy Metals, Heavy Metals 2004, UNEP/GPA Coordination Office (http://www.oceansatlas.org/unatlas/uses/uneptextsph/wastesph/2602gpa.)

United States Department of Labor (2004). Occupational Safety and Health Administration (OSHA); Safety and Health Topics: Heavy metals, USDOL Publication, Washington, D.C. (www.osha.gov/SLTC/metals heavy/index.h tml).

Ure, A. M. (1990). Methods of analysis of heavy metals in soils. Heavy metals in soils., 40-80.

Ure, A. M., Quevauviller, P., Muntau, H., & Griepink, B. (1993). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International journal of environmental analytical chemistry,* 51(1-4), 135-151.

USEPA, (1997). Exposure Factors Handbook. Environmental Protection Agency, Office of Research and Development, Washington DC

USDHHS, (1999). *Toxicological profile for lead,* United States Department of Health and Human Services, Atlanta, Ga, USA,

USEPA (Environmental Protection Agency), (1992). Framework for ecological risk assessment. Risk Assessment Forum, Washington, DC; EPA/630/R.

USEPA, (1996). *Report: recent Developments for In Situ Treatment of Metals contaminated Soils,* U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

USEPA, (2004). Risk Assessment Guidance for Superfund Vol. 1 Human Health Evaluation Manual, Part E, Supplemental Guidance from

Dermal Risk Ass.; Office of Emergency and Remedial Response: Washington, DC, USA.

USEPA, (2006). National Recommended Water Quality Criteria. United States Environmental Protection Agency. Office of Water, Office of Science and Technology.

USEPA, (2009). National Primary Drinking Water Regulations. United States Environmental Protection Agency. EPA 816-F-09-004.

USEPA, (2013): Reference dose (RfD): Description and use in health risk assessments, Background Document 1A, Integrated risk information system (IRIS); United States Environmental Protection Agency: Washington, DC, 15 March 2013; http://www epa.gov/iris/rfd.htm.

USEPA, (US Environmental Protection Agency), (2010). Exposure Factors Handbook – General Factors. EPA/600/P-95/002Fa, vol. I. Office of Research and Development. National Center for Environmental. Washington, DC. http://www.epa.gov/ncea/pdfs/efh/front.pdf>.

Vamerali, T., Bandiera, M., & Mosca, G. (2010). Field crops for phytoremediation of metal-contaminated land. A review. *Env. Chemistry Letters,* 8(1), 1-17.

Viarengo, A. (1985). Biochemical effects of trace metals. *Marine Pollution Bulletin, 16*(4), 153-158.

Viganò, L., Arillo, A., Buffagni, A., Camusso, M., Ciannarella, R., Crosa, G., ... & Mingazzini, M. (2003). Quality assessment of bed sediments of the Po River (Italy). *Water research*, 37(3), 501-518.

Voica, C., Dehelean, A., Iordache, A., & Geana, I. (2012). Method validation for determination of metals in soils by ICP-MS. *Rom Rep in Phy*, 64, 221-231.

Walker, C. H., Sibly, R. M., Hopkin, S. P., & Peakall, D. B. (2012). Principles of ecotoxicology. CRC press.

Walkley, A., & Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil science*, 37(1), 29-38.

Wasserman, G. A., Liu, X., Parvez, F., Ahsan, H., Levy, D., Factor-Litvak, P., ... & Cheng, Z. (2006). Water manganese exposure and children's intellectual function in Araihazar, Bangladesh. *Env.l health perspect.*, 114(1), 124-129.

Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica et cosmochimica Acta,* 59(7), 1217-1232.

Wei, C., & Wen, H. (2012). Geochemical baselines of heavy metals in the sediments of two large freshwater lakes in China: implications for contamination character and history. *Environmental geochemistry and health*, 34(6), 737-748.

Wells, M. L., Kozelka, P. B., & Bruland, K. W. (1998). The complexation of dissolved'Cu, Zn, Cd and Pb by soluble and colloidal organic matter in Narragansett Bay, RI. *Marine Chemistry*, 62(3), 203-217.

WHO, (2000). Environmental Health Criteria 214. Human Exposure Assessment. WHO, Geneva.

WHO, (2001). Arsenic and Arsenic Compounds. *Environmental Health Criteria*, vol. 224. Geneva: World Health Organization, WHO, (2004). Guidelines for Drinking Water Quality, 3rd edition. World Health Organization, Geneva.

WHO/IPCS (World Health Organization/International Programme on Chemical Safety), (1998). Copper. Environmental health criteria document no. 200. Geneva, Switzerland.

WHO/IPCS (World Health Organization/International Programme on Chemical Safety), (2002). Copper. *Environmental health criteria document no. 200.* Geneva, Switzerland.

Wildi, W., Dominik, J., Loizeau, J. L., Thomas, R. L., Favarger, P. Y., Haller, L., & Peytremann, C. (2004). River, reservoir and lake sediment contamination by heavy metals downstream from urban areas of Switzerland. *Lakes & Reservoirs: Research & Management*, *9*(1), 75-87.

Wilhelm, M., Heinzow, B., Angerer, J., & Schulz, C. (2010). Reassessment of critical lead effects by the German Human Biomonitoring Commission results in suspension of the human biomonitoring values (HBM I and HBM II) for lead in blood of children and adults. *International journal of hygiene and environmental health*, 213(4), 265-269.

Windom, H. L., Byrd, J. T., Smith, R. G., & Huan, F. (1991). Environ Sci Technol 25:1137.

Wong, J. W. C., Li, K. L., Zhou, L. X., & Selvam, A. (2007). The sorption of Cd and Zn by different soils in the presence of dissolved organic matter from sludge. *Geoderma*, 137(3), 310-317.

World Health Organization (WHO), (2011). Guidelines for Drinking-Water Quality: Recommendations; WHO: Geneva, Switzerland.

World Health Organization, (2008). Cancer control: knowledge into action. WHO Wuana, R. A., & Okieimen, F. E. (2011). Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *Isrn Ecology*, 2011.

Yang, X. J., & Low, G. C. (2009). Validation of a digestion procedure for ICP-AES and dynamic reaction cell ICP-MS for trace elemental analysis in environmental samples. *Environmental Chemistry Letters,* 7(4), 381.

Yatsalo, B. I., Kiker, G. A., Kim, J., Bridges, T. S., Seager, T. P., Gardner, K., ... & Linkov, I. (2007). Application of multicriteria decision analysis tools to two contaminated sediment case studies. *Integrated Environmental Assessment and Management*, 3(2), 223-233.

Young, R. A. (2005). Toxicity Profiles: Toxicity Summary for Cadmium, Risk Assessment Information System, RAIS, University of Tennessee (rais.ornl.gov/tox/profiles/cadmium.shtml).

Zende, G. K. & Kiba, M. M. (1984). Correlation between soil attributes, uptake of nutrients, agronomic characters and cane yield of an adsali crop of sugarcane. *Maharashtra Sugar*,8: 79–89.

Zhao, Q., & Kaluarachchi, J. J. (2002). Risk assessment at hazardous waste-contaminated sites with variability of population characteristics. *Environment international,* 28(1), 41-53.

Zhong, X. L., Zhou, S. L., Zhu, Q., & Zhao, Q. G. (2011). Fraction distribution and bioavailability of soil heavy metals in the Yangtze River Delta—a case study of Kunshan City in Jiangsu Province, China. *Journal of hazardous materials*, 198, 13-21.

APPENDICES

APPENDIX A

CHOICE ANALYTICAL ICV-1 SOLUTION AND A STANDARD AGILENT TECHNOLOGIES MULTI ELEMENT REFERENCE STANDARD W-2A PREPARATION

N	Samp Name	Tube+Lead Wt.g.	Add Al. Wt.g.	Add 1% HNO_3 Wt.g.	Al.Wt.g.	Tot.Sol.Wt.g.	D.F.1	D.F.2	D.F.final
1	Cal.Bl.								
2	Cal.St.1	6.354	6.455	16.46	0.101	10.106	50.39	100.045	5041.267
3	Cal.St.10	6.482	7.486	16.569	1.003	10.087	50.39	10.053	506.553
4	Cal.St.100	6.702	6.903	16.814	0.201	10.112	50.39		50.39
5	Cal.St.1000	6.273	8.28	16.348	2.007	10.075	5.021		5.021
6	Cal.St.3000	6.408	12.634	16.671	6.226	10.263	1.648		1.648
7	Pr.Bl.1								

APPENDIX B

AGILENT TECHNOLOGIES MULTI ELEMENT REFERENCE STANDARD W-2A CALIBRATION RESULTS

		Results				
Elements	Standard	1	2	3	4	5
Al, Fe, Ni, Cu, As, Pb	5151.373	1.022	10.168	102.210	1025.764	3124.751
Cr, Mn, Co, Zn, V	2575.186	0.511	5.084	51.105	512.882	1562.375
Hg	510.985	0.101	1.009	10.141	101.769	310.017

APPENDIX C

STREAM SEDIMENT REFERENCE STANDARD (STSD-1) FOR TESTING THE PERFORMANCE OF THE EXTRACTION METHOD

	STSD-1
Element	Certified value (ug/g)
Si	280000
Al	66200
Fe	40900
Ti	4430
Mn	440
Sr	276
As	26.2
Cd	2.11
Co	11.5
Cr	90.7
Cu	310
Hg	3.04
Ni	39.5
Pb	183
Sb	11.3
Se	0.92
Sn	19.8
Tl	0.6
U	3
V	133
Zn	364

APPENDIX D

PHYSICO-CHEMICAL PROPERTIES FOR SOILS FROM THE MINING AREAS

Site	Depth (cm)	% Particle size by weight			TexT. class	pH	%OC	Exchangeable Cations (cmol/kg)				CEC (cmol/kg)
Mining		Clay	Silt	Sand			g/kg	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	
AOB	0-200cm	24.98	20.04	54.99	SCL	4.9-5.7	2.11	4.36±0.46	1.80±0.38	0.31±0.07	0.16±0.04	6.63
	20-40cm	27.74	37.23	45.03	CL	5.1-5.9	1.51	5.42±0.14	2.49±0.01	0.33±0.02	0.10±0.01	8.35
BAM	0-20cm	16.35	25.16	58.49	SL	6.4-6.6	2.03	3.10±0.01	1.36±1.11	0.03±0.02	0.14±0.01	4.63
	20-40cm	33.01	28.63	38.36	CL	6.5-6.8	0.49	1.95±0.97	0.98±0.38	0.12±0.05	0.13±0.03	3.19
EAM	0-20cm	17.78	10.2	72.02	LS	4.8-.5.6	1.16	3.23±0.54	3.98±0.47	0.37±0.01	0.12±0.09	7.69
	20-40cm	34.69	50.47	14.85	CL	5.0-5.7	0.66	2.41±0.02	5.94±0.02	0.39±0.01	0.14±0.01	8.89
WTB	0-20cm	49.52	34.46	16.02	C	6.3-6.7	2.85	3.25±0.05	4.31±0.15	0.29±0.06	0.12±0.06	7.99
	20-40cm	32.33	16.65	51.02	SCL	6.5-6.9	0.98	0.23±0.01	1.33±0.02	0.21±0.06	0.06±0.06	1.84

APPENDIX E

PHYSICO-CHEMICAL PROPERTIES FOR SOILS FROM THE PRISTINE AREAS

	Depth (cm)	%Particle size by weight			TexT. class	pH	%OC	Exchangeable Cations (cmol/kg)				CEC (cmol/kg)
Pristine site		Clay	Silt	Sand			g/kg	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	
AOD	0-20cm	25.85	28.16	45.99	SCL	6.4-6.8	1.37	0.76±0.23	1.28±0.10	0.32±0.10	0.05±0.06	2.42
	20-40cm	22.15	30.05	47.80	SCL	6.6-6.8	0.72	0.22±0.44	1.49±0.09	0.25±0.15	0.17±0.03	2.12
BB	0-20cm	10.78	37.03	52.19	SL	6.2-6.5	0.98	9.57±1.51	2.52±0.50	0.19±0.04	0.08±0.02	12.36
	20-40cm	12.03	34.92	53.05	SL	6.5-6.9	0.70	7.18±0.16	2.46±0.32	0.12±0.49	0.09±0.10	9.85
EA	0-20cm	59.24	32.67	8.09	C	5.7-6.5	1.85	5.58±0.15	10.48±0.48	0.38±0.02	0.07±0.01	16.52
	20-40cm	57.12	34.20	8.68	C	5.9-6.6	1.73	5.05±0.17	11.92±0.63	0.27±0.01	0.07±0.01	17.31
CK	0-20cm	17.70	6.08	76.22	LS	6.3-6.7	0.91	5.71±0.48	4.54±0.33	0.37±0.01	0.12±0.08	10.73
	20-40cm	23.27	14.45	62.28	SCL	6.4-6.6	0.55	0.29±0.07	0.98±0.11	0.04±0.01	0.05±0.02	1.36
GSH	0-20cm	30.57	7.01	62.41	SCL	6.7-6.9	2.44	5.32±0.05	3.92±0.03	0.23±0.04	0.04±0.03	9.51
	20-40cm	26.16	11.8	62.03	SCL	6.5-6.6-	1.41	5.29±0.62	2.69±0.06	0.14±0.01	0.12±0.09	8.24
NM	0-20cm	16.84	21.46	61.70	SL	6.5-6.9.	0.96	1.62±0.26	2.06±0.24	0.88±0.01	0.17±0.03	4.73
	20-40cm	13.84	18.47	67.69	SL	6.6-6.8	0.92	1.24±0.15	2.76±0.07	0.18±0.01	0.10±0.01	4.29
VKP	0-20cm	39.93	26.00	34.07	CL	6.1-6.3	1.94	9.42±1.08	2.49±0.14	0.02±0.12	0.10±0.01	12.02
	20-40cm	50.06	23.68	26.26	C	6.3-6.7	1.95	1.91±0.47	4.83±1.67	0.18±0.07	0.05±0.08	18.21
WA	0-20cm	18.65	11.45	69.90	SL	6.5-6.9	0.93	0.31±0.27	0.83±0.32	0.09±0.02	0.10±0.03	1.33
	20-40cm	32.64	18.70	48.65	SC	6.7-7.1	0.95	0.25±0.03	0.77±0.04	0.17±0.10	0.11±0.02	1.29

APPENDIX F

ANOVA SINGLE FACTOR RESULTS TO TEST THE SIGNIFICANCE OF METALS LEVELS FROM THE MINING AND PRISTINE AREAS

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	28734.91	1	28734.91	6.77E-05	0.99	4.26
Within Groups	1.02E+10	24	4.25E+08			
Total	1.02E+10	25				

APPENDIX G

FACTOR LOADING FOR SELECTED HEAVY METALS IN SOILS FROM MINING AND PRISTINE SITES

	Component	
Elements	PCA1	PCA2
Al	0.84	
V	0.91	
Cr	0.83	
Mn	0.94	
Fe	0.84	
Co	0.95	
Ni	0.83	
Cu	**0.69**	**0.63**
Zn	**0.54**	**0.78**
As		0.87
Cd	**0.37**	**0.49**
Pb	**0.47**	**0.53**
Eigenvalues	6.53	2.96
% total Variance	54.37	24.65
% cumulative variance	54.37	79.02

APPENDIX H

FACTOR LOADINGS FOR HEAVY METALS IN WATER SAMPLES FROM PRISTINE AND MINING SITES

	Component	
Elements	PCA1	PCA2
Co	0.99	
Cu	0.98	
V	0.98	
Al	0.97	
Pb	0.97	
Cr	0.96	
Fe	0.95	
Zn	0.85	
Ni	0.77	
As		0.87
Mn		0.77
Eigenvalues	8.151	1.59
% total Variance	74.10	14.50
% cumulative variance	74.10	88.60

APPENDIX I

SUMMARY OF ONE-FACTOR ANOVA RESULTS FOR TESTING THE SIGNIFICANT DIFFERENT BETWEEN SAMPLES COLLECTED IN 2014 AND 2016 SEASONS

	ANOVA Results			
	Mining		Pristine	
Water	p-0.718 F-0.134 Fcri.-4.351		p-0.764 F-0.093 Fcri.-1.148	
Sediment TR	p-0.942 F-0.0054 Fcri.-4.279		p-0.829 F-0.0475 Fcri.-4.279	
Sediment WA	p-0.931 F-0.0076 Fcri.-4.301		p-0.984 F-0.00039 Fcri.-4.301	
	0-20cm	20-40cm	0-20cm	20-40cm
Soil TR	p-0.904 F-0.015 Fcri.-4.301	p-0.921 F-0.01 Fcri.-4.301	p-0.936 F-0.0066 Fcri.-4.301	p-0.958 F-0.00279 Fcri.-4.301
	0-20cm	20-40cm	0-20cm	20-40cm
Soil WA	p-0.538 F-0.391 Fcri.-4.301	p-0.873 F-0.0259 Fcri.-4.301	p-0.787 F-0.075 Fcri.-4.325	p-0.866 F-0.029 Fcri.-4.325