ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS (PTEs) DISTRIBUTION AND CONTAMINATION IN ALIZAGA LEAD-ZINC MINING AREA, NASARAWA-EGGON, NORTH-CENTRAL NIGERIA

BY

BELLO, Ozovehe Abdulbasit
MTech/SPS/2018/7686

DEPARTMENT OF GEOLOGY
FEDERAL UNIVERSITY OF TECHNOLOGY
MINNA, NIGERIA

JUNE, 2023

ASSESSMENT OF POTENTIALLY TOXIC ELEMENTS DISTRIBUTION AND CONTAMINATION IN ALIZAGA LEAD-ZINC MINING AREA, NASARAWA-EGGON, NORTH-CENTRAL NIGERIA

BY

BELLO, Ozovehe Abdulbasit
MTech/SPS/2018/7686

A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGERIA, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF TECHNOLOGY IN GEOLOGY (ENVIRONMENTAL GEOLOGY)

JUNE, 2023

DECLARATION

I hereby declare that this thesis titled: **“Assessment of Potentially Toxic Elements (PTEs) Distribution and Contamination in Alizaga Lead-zinc Mining Area, Nasarawa-Eggon, North-Central Nigeria”** is a collection of my original research work and it has not been presented for any other qualification anywhere. Information from other sources (published or unpublished) has been duly acknowledged.

BELLO Ozovehe Abdulbasit
MTech/SPS/2018/7686
FEDERAL UNIVERSITY OF TECHNOLOGY
MINNA, NIGERIA

Signature/Date

CERTIFICATION

The thesis titled: **“Assessment of Potentially Toxic Elements (PTEs) Distribution and Contamination in Alizaga Lead-zinc Mining Area, Nasarawa-Eggon, North-Central Nigeria”** by BELLO, Ozovehe Abdulbasit (MTech/SPS/2018/7686) meets the regulations governing the award of the degree of Master of Technology, of the Federal University of Technology, Minna and it is approved for its contribution to scientific knowledge and literary presentation.

Prof. I. N. Abdullahi ______________________
SUPERVISOR Signature & Date

Dr. (Mrs) S. H. Waziri ______________________
HEAD OF DEPARTMENT Signature & Date

Prof. M. Jiya ______________________
DEAN, SCHOOL OF PHYSICAL SCIENCES Signature & Date

Engr. Prof. O.K. Abubakre ______________________
DEAN, POSTGRADUATE SCHOOL Signature & Date

DEDICATION

This work is dedicated to my late father, Mallam Muhammed Jamiu Bello. He believed so much in the pursuit of knowledge through sincere commitments and focus.

ACKNOWLEDGEMENTS

Praise to Almighty God with whom all things are possible and by His Grace this work completed successfully. The help and support of kind and patient people around me, only some of whom it is possible to mention here, made this research remarkable.

The level of academic standard and problem-solving approach in this research would not have been achieved without the guidance and patience of my principal supervisor, Professor I. N. Abdullahi. His wealth of knowledge and wisdom were helpful to the successful completion of this work. The good advice and support of Dr. Nuhu Waziri and Mr Suleiman Abdullahi as well as other academic and non-academic staff of Geology Department, Federal University of Technology, Minna have contributed immensely to the success of this journey. I am also grateful to my dear friends and colleagues, especially Habib Ibrahim and Nasiru Abdullahi for their advice, useful collaboration with ideas and research materials.

I would like to acknowledge the assistance of Dr. Umar A. Degree and Mr. Enwongulu George, both of Federal University, Lafia for their support during the field work. My gratitude to the management of Vinco Innovation Nigeria Limited, especially their site geologists, Kamal Musa and Nathaniel Adigizi for their support, allowing access to their mining area. Many thanks to the good people of Alizaga village for their kindness and patience while I carried out mapping and sampling on their lands.

My profound gratitude to my beloved wife, Fatima, for her personal support, patience and encouragement at all times. She is indeed dependable, keeping our home strong while I had to travel on so many occasions. My entire family were also very supportive and I appreciate all their efforts.

ABSTRACT

This work is an assessment of concentration and distribution of potentially toxic elements (PTEs) in Alizaga Pb-Zn mining area, North Central Nigeria. It also evaluates the pollution levels, ecological risks and human health risks posed by these PTEs in the area. This study was done by geological mapping and sampling of top soils, stream sediments, rocks and groundwater for chemical analysis. Pollution levels in soils and stream sediments were determined using pollution indices such as geo-accumulation index, pollution load index, modified degree of contamination, enrichment factor and ecological risk factor. Human health risks were determined for both non-carcinogenic and carcinogenic risks using hazard index and incremental lifetime cancer risks respectively. The area is underlain by biotite granite (47%), followed by gneiss (31%), migmatite (11%), ryholite (10%), quartzite (0.9%) and dolerite dykes (0.1%). The results of the chemical analysis revealed a concentration range of 97-83299 mg/kg for lead, 80-55352 mg/kg for zinc, 80-1438 mg/kg for copper, 68-1916 mg/kg for chromium and 0.02-52 mg/kg for cadmium respectively in the top soils. Their corresponding average concentration was also higher when compared to guidelines by Ministry of the Environment, Finland (MEF, 2007). PTEs in stream sediments in the study area revealed a concentration range of 97-58776 mg/kg for lead 80-107491 mg/kg for zinc, 80-2397 mg/kg for copper, 68-137 mg/kg for chromium and 2-93 mg/kg for cadmium respectively. They showed a radial decrease in concentration away from the mines and this was more evident towards the southern part of the study area. Average Concentration of PTEs in groundwater is 0.18 mg/L for lead, 0.34 mg/L for zinc, 0.49 mg/L for chromium, 0.42 mg/L for cadmium and 0.43 mg/L for arsenic. Apart from zinc, these elements have concentration above permissible limits for drinking-water by World Health Organization (2022) and guidelines by Nigeria Standard for Drinking Water Quality (2007). Pollution levels for lead, zinc, copper and cadmium were highest in soils and sediments within the vicinity of the mines but moderate to unpolluted in other areas more than 300 m away from the mines. Whereas chromium contamination was low to unpolluted within the mines, it is polluted in few areas 600-800 m away from the mines. The potential ecological risks posed by the studied PTEs is such that Pb>Zn>Cu>Cd>Cr. Again the highest risk is within the immediate vicinity of the mines while it is considerable to moderate risk in surrounding areas. The risks are lowest in those areas farthest from the mines. Non-carcinogenic health risk exists through soil ingestion especially among children as well as adults within 300 m radius of the mines. In surrounding areas such as farmlands and settlements, only children are currently at risk. The sediments also present no serious current non-carcinogenic risks. However, carcinogenic health risk exist to both children and adult through the consumption of groundwater from shallow wells contaminated by chromium and arsenic. Sustainable mining practices that control dispersion of contaminants in the environment should be encouraged in the area. In addition, sources of contamination by chromium outside the mines should be further investigated. Soil remediation approach such as potential immobilization of PTEs using various amendments to minimize their bioavailability and toxicity can also be practiced.

TABLE OF CONTENTS

Title **Page**

Cover Page
Title Page i
Declaration ii
Certification iii
Dedication iv
Acknowledgements v
Abstract vi
Table of Contents vii
List of Tables x
List of Figures xii
List of Plates xiii
Abbreviation, Glossaries and Symbols xiv

CHAPTER ONE

1.0 INTRODUCTION 1
1.1 Background to the Study 1
1.2 Sources and Occurrence of Potentially Toxic Elements (PTEs) in soil 2
1.2.1 Geogenic sources 3
1.2.2 Anthropogenic sources 5
1.3 Exposure Pathways and Human Health Effects of Contamination by PTEs 7
1.4 Statement of the Research Problem 8
1.5 Justification for the Study 10
1.6 Aim and Objectives of the Study 10
1.7 Scope and Limitation of the Study 11
1.7.1 Location and accessibility 12
1.7.2 Climate and vegetation 12
1.7.3 Relief and drainage 12

CHAPTER TWO

2.0 LITERATURE REVIEW 14
2.1 PTEs Levels and Risk Assessment in Soils 13
2.2 Human Health Risks Assessment 16

2.3 Remediation Approach to PTEs Contamination 18

CHAPTER THREE

3.0 MATERIALS AND METHODS 19
3.1 Preliminary Studies 19
3.2 Field Work 19
3.2.1 Geological Mapping 19
3.2.2 Sampling 19
3.3 Laboratory Analysis 22
3.3.1 X-ray florescence (XRF) analysis 22
3.3.2 Atomic absorption spectroscopy (AAS) analysis 22
3.4 Data Analysis 23
3.4.1 Determination of pollution levels 25
3.4.2 Ecological risk assessment 30
3.4.3 Human health risk assessment 31

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION 35
4.1 Geology of the Area 35
4.1.1 Migmatites 36
4.1.2 Gneiss 36
4.1.3 Biotite granites 37
4.1.4 Quartzites 38
4.1.5 Rhyolites 39
4.1.6 Dolerite dykes 40
4.1.7 Structural Measurement 41
4.2 PTEs concentration in the study environment 42
4.2.1 Rocks 42
4.2.2 Soils 43
4.2.3 Stream sediments 46
4.2.4 Correlation analysis of the PTEs concentration in soils and stream sediments 48
4.2.5 Groundwater 49
4.3 Assessment of Pollution Levels in Soils and Stream Sediments of the Study Area 53

4.3.1 Geo-accumulation factor 53
4.3.2 Contamination factor 61
4.3.3 Enrichment factor 68
4.3.4 Modified degree of contamination 75
4.3.5 Pollution load index 76
4.4 Ecological Risk Assessment 78
4.5 Contribution of Mining and Processing Methods to the Release of PTEs in the Study Area 86
4.6 Human Health Risk Assessment 89
4.6.1 Non-carcinogenic risks 90
4.6.2 Carcinogenic risks 93

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS 95
5.1 Conclusion 95
5.2 Recommendations 97
5.3 Contribution to Knowledge 99
REFERENCES 100

LIST OF TABLES

Table **Page**

1.1 Position of PTEs on the Periodic Table of Chemical Elements 2

3.1 Threshold and Guideline Values for PTEs in Soils 24

3.2 Consensus-Based Sediment Quality Guidelines that Reflects Threshold Effect Concentration and Probable Effect Concentration 24

3.3 Nigerian Standard for Drinking Water Quality (2007) and Permissible Limits by World Health organisation (2022) for Selected PTEs in Groundwater 25

3.4 Classification of Geo-accumulation Factor 26

3.5 Classification of Contamination Factor and Level of Contamination 27

3.6 Classification of Pollution Load Index 27

3.7 Classification of Modified Degree of Contamination 28

3.8 Classification of Enrichment Factor 29

3.9 Indices and Risk Levels of Potential Ecological Risk of PTEs 31

3.10 Summary of Reference Dose (RfD) and Cancer Slope Factor (CSF) of Metals and Metalloid Arsenic Through Oral and Dermal Pathways 34

4.1 PTEs Concentration in rocks of Alizaga. 42

4.2 PTEs Concentration in the soil of the study area 44

4.3 PTEs Concentration in Stream Sediments of the Study Area. 47

4.4 Correlation Matrix of PTEs in Soils and Stream Sediments in the Study Area. 48

4.5 Physical Parameters and PTEs Concentration of Groundwater in the Study Area. 49

4.6 Calculated ADI, HQ and HI by Non-dietary Ingestion of Soil PTEs in Mines Site, Schools, Settlements and Cultivated Lands in the Study Area 91

4.7 Calculated ADI, HQ and HI by Non-dietary Ingestion of Stream Sediments PTEs Close and Away from Alizaga Mines Site 92

4.8 Calculated ADI, HQ and Hazard Index HI by Drinking and Dermal Contact with PTEs in Groundwater of the Study Area. 92

4.9 Calculated Average ILCR for Chromium and Arsenic in Soils, Stream Sediments and Groundwater in the Study Area. 93

LIST OF FIGURES

Figure **Page**

1.1 Potentially Toxic Elements (PTEs) Source in Soil Ecosystem 3
1.2 Location and Topographic Map of the Study Area 11
3.1 Samples Location Map of the Study Area 21
4.1 Geological Map of the Study Area with Cross Section A-B 35
4.2 Rose Diagram of Dominant Joint Direction in Granites and Gneiss of the Study Area. 41
4.3a Scatter plot of Pb concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards. 51
4.3b Scatter plot of Zn concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards. 51
4.3c Scatter plot of Cr concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards 52
4.3d Scatter plot of Cd concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards. 52
4.3e Scatter plot of Cd concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards 53
4.4a(i) Geo-accumulation of Pb in the soil of Alizaga 54
4.4a(ii) Geo-accumulation of Zn in the soil of Alizaga 54
4.4a(iii) Geo-accumulation of Cu in the soil of Alizaga 55
4.4a(iv) Geo-accumulation of Cd in the soil of Alizaga 56
4.4a(v) Geo-accumulation of Cr in the soil of Alizaga 57
4.4b(i) Geo-accumulation of Pb in the stream sediment of Alizaga 58
4.4b(ii) Geo-accumulation of Zn in stream sediments of Alizaga 58
4.4b(iii) Geo-accumulation of Cu in stream sediments of Alizaga 59
4.4b(iv) Geo-accumulation of Cd in stream sediments of Alizaga 60
4.4b(v) Geo-accumulation of Cr in stream sediments of Alizaga 60
4.5a(i) Contamination by Pb in the soil of Alizaga 61
4.5a(ii) Contamination by Zn in the soil of Alizaga 62
4.5a(iii) Contamination by Cu in the soil of Alizaga 63
4.5a(iv) Contamination by Cd in the soil of Alizaga 63
4.5a(v) Contamination by Cr in the soil of Alizaga 64
4.5b(i) Contamination by Pb in the stream sediments of Alizaga 65

Figure		**Page**
4.5b(ii)	Contamination by Zn in the stream sediments of Alizaga	65
4.5b(iii)	Contamination by Cu in the stream sediments of Alizaga	66
4.5b(iv)	Contamination by Cd in the stream sediments of Alizaga	67
4.5b(v)	Geo-accumulation of Cr in stream sediments of Alizaga	67
4.6a(i)	Pb Enrichment in the soils of Alizaga	68
4.6a(ii)	Zn Enrichment in the soils of Alizaga	69
4.6a(iii)	Cu Enrichment in the soils of Alizaga	70
4.6a(iv)	Cd Enrichment in the soils of Alizaga	70
4.6a(v)	Cr Enrichment in the soils of Alizaga	71
4.6b(i)	Pb Enrichment in the stream sediments of Alizaga	72
4.6b(ii)	Zn Enrichment in the stream sediments of Alizaga	72
4.6b(iii)	Cu Enrichment in the stream sediments of Alizaga	73
4.6b(iv)	Cd Enrichment in the stream sediments of Alizaga	74
4.6b(v)	Cr Enrichment in the stream sediments of Alizaga	74
4.7a	Modified degree of contamination by Pb-Zn-Cu-Cr-Cd in Alizaga soil.	75
4.7b	Modified degree of contamination by Pb-Zn-Cu-Cr-Cd in Alizaga stream sediments	76
4.8a	Pollution Load Index by Pb-Zn-Cu-Cr-Cd in Alizaga soils	77
4.8b	Pollution Load Index by Pb-Zn-Cu-Cr-Cd in Alizaga stream sediments.	77
4.9a(i)	Ecological risk by Pb in Alizaga soils	78
4.9a(ii)	Ecological risk by Zn in Alizaga soils	79
4.9a(iii)	Ecological risk by Cu in Alizaga soils	79
4.9a(iv)	Ecological risk by Cr in Alizaga soils	80
4.9a(v)	Ecological risk by Cd in Alizaga soils	81
4.9a(vi)	Potential ecological risk posed by PTEs (Pb, Zn, Cu, Cd and Cr) in Alizaga soils	81
4.9b(i)	Ecological risk by Pb in Alizaga stream sediments	82
4.9b(ii)	Ecological risk by Zn in Alizaga stream sediments	83
4.9b(iii)	Ecological risk by Cu in Alizaga stream sediments	83

4.9b(iv) Ecological risk by Cr in Alizaga stream sediments 84

4.9b(v) Ecological risk by Cd in Alizaga stream sediments 85

4.9b(vi) Potential ecological risk posed by PTEs (Pb, Zn, Cu, Cd and Cr) in Alizaga stream sediments. 85

LIST OF PLATES

Plate		Page
I	Weathered Migmatite Outcrop Intruded by Dolerite Dykes	36
II	Aplite Veins on Grey Coarse-grained Gneiss	37
III	Weathered and Jointed Grey Medium-coarse grained Biotite Granite Outcrop	38
IV	Quartzite Outcrop 15 m Wide and Striking N340º.	38
V	Quartzite Outcrop Excavated for Rock Aggregates.	39
VI	Quartzite Composed Majorly of Quartz Crystals.	39
VII	Highly Weathered Rhyolite with Phenocrysts of Quartz and Feldspars in a Microcrystalline Groundmass	40
VIII	Dolerite Dyke 0.5 m Wide Cross-cuts Highly Weathered and Jointed Coarse Grained Granite Outcrop.	40
IX	Overview of Alizaga Pb-Zn Mining and Processing Area	86
X	Abandoned Surface Pb-Zn Mining pits.	87
XI	Women Involved in Crushing Overburden Rocks into Aggregates	87
XII	Mines Workers Sorting and Washing Pb-Zn Ore.	88
XIII	Mine Waste Water and Tailings from Pb-Zn Ore Sorting and Washings Discharged Directly into Nearby Stream Channel	88
XIV	Women Carrying Out Alluvial Cassiterite Mining on Stream Bichi where Domestic Wastes are also Discharged	88
XV	Pb-Zn Ore Handling by Women at the Sorting Area without Use of Adequate Personal Protective Equipments (PPEs)	89
XVI	Children Play Ground in a Neighbouring Village less than 1 km from Mining Site	90

ABBREVIATION AND SYMBOLS

ADI	Average Daily Intake
AGR	Alizaga Rock samples
AGS	Alizaga Soil samples
AGSS	Alizaga Stream Sediment samples
AGW	Alizaga Water samples
As	Arsenic
ASL	Above Sea Level
ATSDR	Agency for Toxic Substances and Disease Registry
Cd	Cadmium
Cr	Chromium
Cu	Copper
GIS	Global Information System
GPS	Global Position System
HI	Hazard Index
HQ	Hazard Quotient
ILCR	Incremental Lifetime Cancer Risk
MEF	Ministry of the Environment, Finland
mg/kg	milligram per kilogram
mg/l	milligram per litre
NESREA	National Environmental Standard Regulatory and Enforcement Agency
NSDWQ	Nigerian Standard for Drinking Water Quality
Pb	Lead
ppm	parts per million
PTEs	Potentially Toxic Elements
USEPA	United States Environment Protection Agency
WHO	World Health Organisation
Zn	Zn

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background to the Study

Potentially Toxic Elements (PTEs) include heavy metals (such as cadmium, lead, zinc, mercury, cobalt and copper), alkali earth metal (barium), lighter metal (aluminium), metalloid (arsenic) or non-metal (selenium) as indicated in the periodic table (Table 1.1). Their presence in trace levels is a natural phenomenon, but their enhanced concentration is an indicator of contamination load in an area (Krishna and Dasaram, 2021). This means that they can be found naturally but their toxicity does not depend on their presence itself but on their concentrations. In recent years, the environment is highly polluted due to the increase in the population pressure on land, industrialization, use of fertilizers and other human activities on the ecosystem. These release PTEs that can contaminate the environmental matrices such as air, water, soil and sediment (Vineethkumar *et al*., 2020). The PTEs accumulation and enrichment in soil and sediment increase enormously with time and leads to contamination of the adjacent agricultural areas, food crops, and aquatic systems.

PTEs food chain contamination is a serious issue that threatens both animal and human health (Antoniadis *et al*., 2017)**.** An estimated 12.6 million people have died worldwide in recent years from over 100 diseases caused by unhealthy environments such as contaminated soils (WHO, 2016). In 2015, the Institute for Health Metrics and Evaluation and the World Health Organization (WHO) reported 494,550 deaths and a loss of 9.3 million disability-adjusted life years resulting from long-term lead exposure to humans. For example, young children are particularly susceptible to lead poisoning due to ingestion of lead-contaminated soil or dust. Many young children in Nigeria, Senegal, and some other countries have died from exposure to lead-contaminated soil (WHO, 2018; Keller *et al*., 2017). Each year, more than 600,000 children worldwide have mental retardation caused by elevated blood lead levels (O'Connor *et al*., 2018).

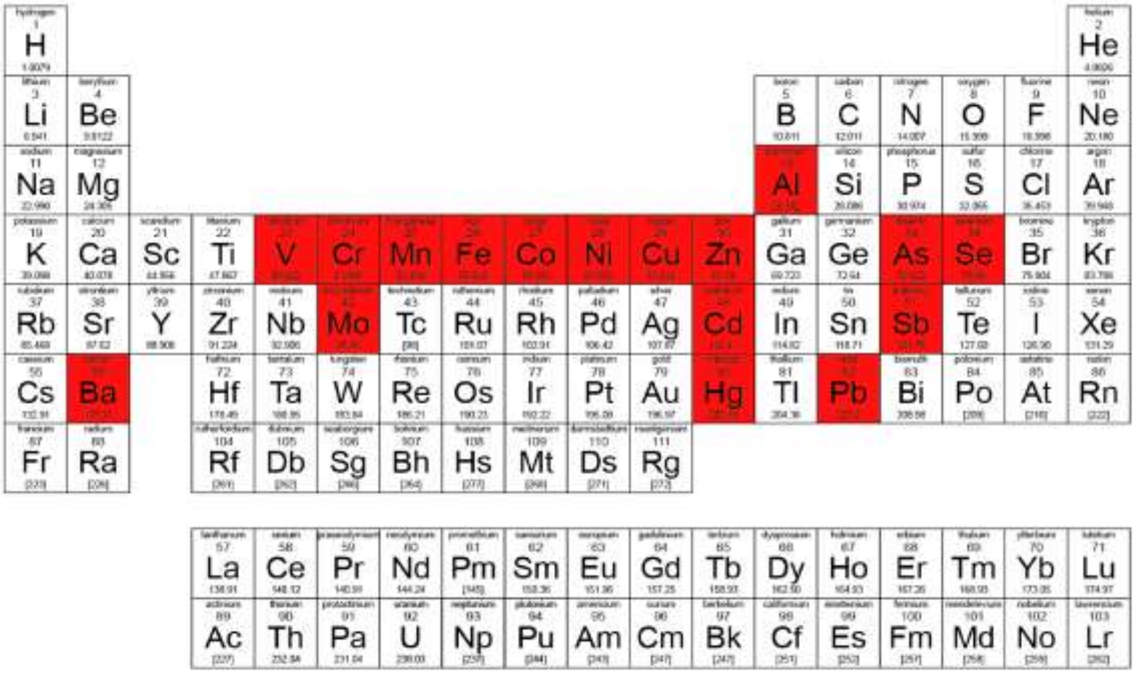

Table 1.1: Position of PTEs on the Periodic Table of Chemical Elements, (Pourret and Hursthouse, 2019)

1.2 Sources and Occurrence of PTEs in Soils

PTEs can occur naturally in soils in varying concentrations depending on geochemical composition of source rocks and natural processes such as weathering, sedimentation and even volcanic eruptions. Meanwhile, anthropogenic activities such as mining and smelting operations, oil and gas production, industrial production, military practices, and agricultural activities can also result in elevated soil PTEs concentrations (Hou and Li, 2017; O'Connor *et al*., 2018).

According to Alloway (2013), soil PTEs concentration equals the sum of inputs from geogenic and anthropogenic sources minus losses due to plant uptake, soil erosion, leaching and volatilization of gaseous forms (Figure 1.1).

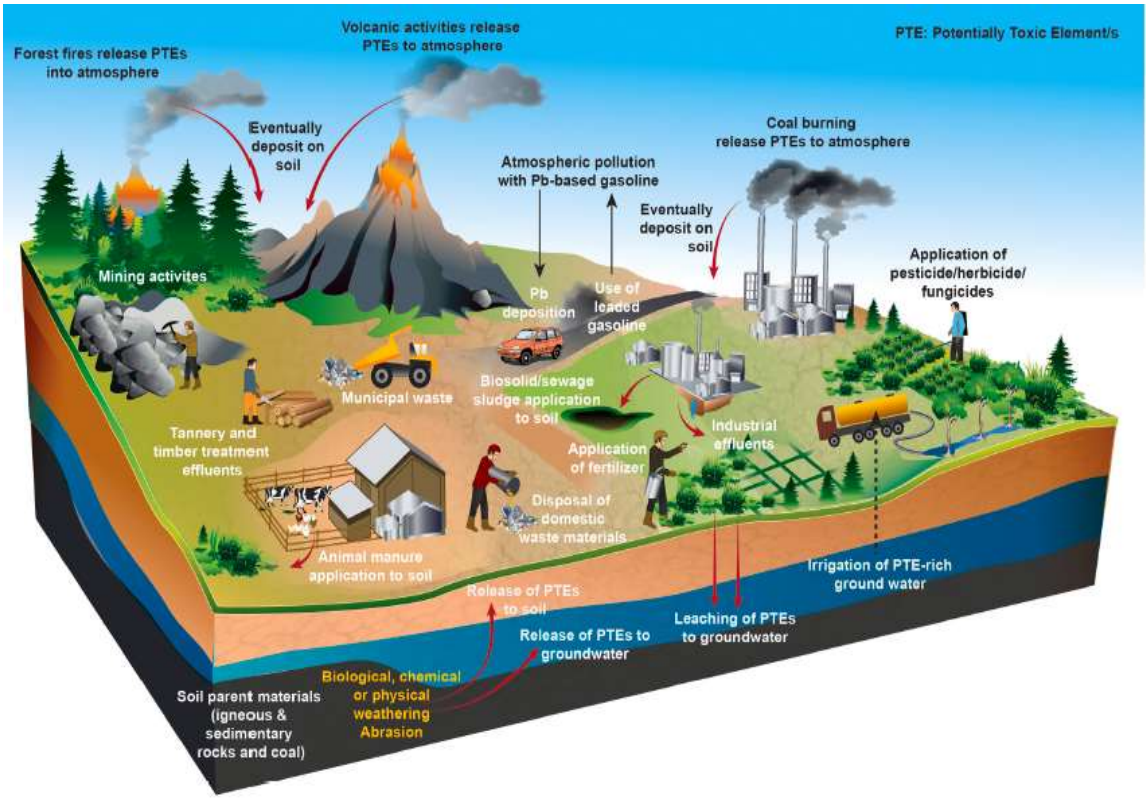

Figure 1.1: PTEs sources in soil ecosystems (Alloway 2013).

1.2.1 Geogenic sources

Geogenic sources are soil parent materials from which PTEs are derived. PTEs can be found in soil formed through geological weathering, volcanic activities or sedimentation (Wong *et al*., 2006). During weathering, some constituent minerals of parent materials are released in soluble forms, with biochemical interactions between weathering products forming secondary minerals. Immobile PTEs and Rare Earth Elements such as Zirconium, Hafnium, Thorium, Niobium, and Scandium are usually either concentrated in resistant phases or strongly adsorbed by secondary minerals, whereas mobile elements such as Barium, Strontium, and Rubidium are derived mainly from leachable minerals such as feldspars, apatite, and micas (Alloway, 2013).

A comparison of PTE concentrations from various soils around the world showed that Manganese (418 mg/kg) and Ba (362 mg/kg) have the highest concentrations, which is consistent with their relative abundance in Earth's upper crust (Alloway, 2013). In volcanic areas, volcanic plumes and ashes are important PTEs sources, with their abundance depending on secondary mineral composition (Adamo *et al*., 2003). People living near volcanic areas may have naturally higher PTEs exposure than those in reference sites. For example, children living near Mt. Etna, Italy, showed elevated intake of Arsenic, Manganese, Uranium and Vanadium (Varrica *et al*., 2014). Geogenic source rock types also significantly influence PTE abundance and distribution in soils. Black shales are known to have enriched organic matter content (usually 10-20%) owing to oceanic anoxic events and contain significantly elevated PTEs concentrations compared to the upper crust (Alloway, 2013).

Apatite [$Ca_5(F,Cl,OH)(PO_4)_3$] is a major phosphate mineral form that can serve as a raw material for phosphorus fertilizer manufacturing. Geochemical studies have shown that several PTEs are enriched in apatite through different mechanisms such as formation of insoluble compounds with lead and surface adsorption or complexation with copper and zinc (Cao *et al*., 2004). This raises the concern of leaching weakly bounded metals in minerals, which subsequently serves as an important source of PTE inputs to soils. Likewise, mineral ores result in higher soil PTE concentrations, whereas elevated concentrations in larger areas can be attributed to mining and smelting activities as anthropogenic sources. Bedrock geological composition provides information on PTEs background levels, which is helpful for identifying excessive PTEs from anthropogenic sources. However, this approach may have limitations in urban contexts where soils may have originated from more than one source and have been redistributed by human activities (Wong *et al*., 2006).

1.2.2 Anthropogenic sources

Anthropogenic sources such as energy production, mining, metal smelting, waste incineration and traffic emissions account for a significant portion of total PTEs inputs to soils (Rinklebe and Shaheen, 2017). Depending on the composition of coal used, its combustion can release various PTEs into the atmosphere (Davis *et al*., 2009). For example, in China, most silver found in urban soil is related to atmospheric deposition of fossil fuel combustion by-products, especially from coal burning (Kuo *et al*., 2006). Moreover, India has been found to be the second largest atmospheric lead emitter in Asia after China because of coal combustion (Das *et al*., 2018).

Elevated PTE concentrations can also be found near urban-rural transition zones or locations where mining and smelting activities take place. Elevated PTEs concentration, predominantly of arsenic, cadmium, silver, and lead, have been found in soils near mining areas in Europe (Toth *et al*., 2016). Mine tailing dam failures have been reported in various places across the world (Hatje *et al*., 2017), which have resulted in contamination of downstream alluvial soil by metal(loid)-containing particles. Elevated soil arsenic content is usually found near antimony and lead-zinc mining areas. Additionally, smelting of lead ores can put arsenic particulates of up to 3% weight into the atmosphere (Taylor *et al*., 2014). In this respect, some recent studies (Rinklebe and Shaheen, 2017) found that high total PTEs concentration have accumulated in the flood plains of the Elbe and Wupper river systems in Germany. These high concentrations were most likely caused by contamination of Wupper River water and sediments by discharge of waste from industrial activities such as textile bleaching, knife manufacturing, electroplating and mining.

In urban soils, the sources of PTEs are usually complex, and include deposition of dust and aerosol particles, industrial activities, fertilizer and compost use in urban gardens, and the use of paints and other protective materials (Luo *et al*., 2012). GIS-based and multivariate statistical analyses have found that cadmium, copper, lead, and zinc are commonly detected in urban soils contaminated by vehicle traffic, paint use, and other industrial discharges (Davis *et al*., 2009; Lee *et al*., 2006; Luo *et al*., 2012), whereas arsenic and silver primarily come from coal burning (Luo *et al*., 2012). Lead is the most distinctive urban soil PTE contaminant coming from paints and vehicle exhausts. In urban areas, dispersion and deposition of metal-containing particulate matter transports and redistributes PTEs. This process is influenced by multiple physical and environmental factors such as urban landscape, wind direction, and urban water runoff.

In agricultural areas, profiles of soil PTEs are more closely related to geogenic sources. However, atmospheric transport and deposition of PTEs from fossil fuel combustion, industrial processes, waste incineration and application of PTEs-containing products such as insecticides, herbicides, fungicides and wood preservatives are also major sources (Alloway, 2013; Chen *et al*., 2008). Additional sources of PTEs contamination include localized events such as flooding that carries PTEs and deposits them on flooded land downstream and corrosion of metals from building materials. Industrial by-products (such as flue gas, dusts and various slags) that are re-used on agricultural lands to reduce burden on landfills could also contribute to elevated soil PTEs levels (Luo *et al*., 2012).

Military activity and shooting sports can also introduce arsenics, copper, manganese, molybdenum, nickel, lead, antimony, and zinc to soil due to oxidation and deterioration of spent ammunition (Alloway, 2013). At a shooting range, lead concentrations could reach as high as approximately 2000μg/g, which stands in stark contrast to a baseline concentration of 70µg/g or less (Murray *et al*., 1997). In Korea, 11,100 mg/kg of total lead, approximately 16 times greater than the permitted 700 mg/kg value was observed in soil at a military shooting range by the Korea Ministry of Environment (Ahmad *et al*., 2012). In the same sites, copper and antimony concentrations were much higher than the acceptable limits of 150 mg/kg and 5 mg/kg respectively (Ahmad *et al*., 2016). In a clay pigeon shooting range in Japan, lead concentrations reached 18,100 mg/kg in the surface soil (Hashimoto *et al*., 2009).

In conclusion, PTEs can reach the soil either from geogenic or anthropogenic sources. However, the potential mobility and associated risk of these elements differ widely based on their source (Shaheen *et al*., 2017). The potential mobility of PTEs in the anthropogenically contaminated soils is much higher than the geogenically contaminated soils. Although naturally occurring PTEs are relatively immobile and rarely toxic, however, they may pose a potential risk to the environment particularly under certain changes of soil pH and redox potential. Soil pollution with anthropogenic PTEs and its remediation has been the focus of increasing research in the last few decades due to their toxic impacts on our ecosystems. Soils that contain elevated levels of PTEs derived from geological sources have received scant attention, even though they provide some fascinating topics to study.

1.3 Exposure Pathways and Human Health Effects of Contamination by PTEs

Humans are exposed to these PTEs through different pathways including ingestion of soils, plants and dusts directly, dust adhering and inhalation (Carla *et al*., 2014). The uptake of PTEs from contaminated soils by plants comprises a major path for these elements to enter the human and animal food chain. They enter the body system when these plants are directly or indirectly consumed, also through air and water and may bio-accumulate over a period of time.

At excess level in the human body, it affects the immune system, basic physiological processes of cell and gene expression and may cause nausea, anorexia, vomiting, gastrointestinal abnormalities, and dermatitis (Chui *et al.,* 2013). For example, low-level cumulative exposure to cadmium has been associated with changes in renal function and bone metabolism (Salt *et al*., 1997). Lead affects and damages body organs and systems such as kidney (Suzuki *et al*., 2009); liver (Sadik, 2008); and change blood composition (Cope *et al*., 2009); damage lungs and reproductive system (Lindemann *et al*., 2008); central nervous system (Su *et al*., 2004); urinary system (WHO, 2018).

Chen (2011) reported that workers who are in close contact with nickel powder are more likely to suffer from respiratory cancer and nasopharyngeal carcinoma. At lower concentration, copper acts as co-factors for various enzymes of redox cycling. However, the higher concentration of copper disrupts the human metabolism leading to anaemia, liver and kidney damage, stomach and intestinal irritation. Arsenic induces skin, liver, lung, colorectal cancers, physical muscular and neurological impairments, the degenerative processes similar to Alzheimer's disease (Suzuki *et al*., 2009). Parkinson's disease, muscular dystrophy and multiple sclerosis may occur when the human population is exposed to PTEs for a long time (Guilarte, 2011),

1.4 Statement of the Research Problem

Contamination by PTEs has been widely reported and has led to growing concerns regarding severe negative effects on living organisms, including humans (Wang *et al*., 2008). Soil contamination by PTEs can lead to low agricultural production and even negatively affect other biological communities if present at anomalously high level. They can enter food chains by enrichment, posing risks to the ecosystem and human health through long-term exposure, even at very low concentrations. For example, elevated concentrations of cadmium, arsenic and lead in the environment are a particular issue in mining regions because of their documented deleterious human health effects such as gastrointestinal and kidney dysfunction, nervous system disorders, skin lesions, vascular damage, immune system dysfunction, birth defects, and cancer (Taylor *et al*., 2014). This is also common in young children who often place objects in their mouths resulting in soil being ingested (Lanphear *et al.*, 1996) and dust being inhaled directly (Laidlaw and Filippelli, 2008).

Elevated concentration of PTEs such as lead, arsenic, chromium and cadmium has both high toxicity and persistence in the environment. Therefore they are expected to be monitored worldwide (Edna *et al*, 2017). For example, in March, 2010, *Medecins san Frontières* (also called doctors without borders is an international humanitarian medical Non-Governmental Organisation) reported over 400 deaths, primarily among children under the age of 5 years in Bukkuyum and Anka LGAs of Zamfara State, Nigeria. This unusually high number of deaths was discovered to be due to lead poisoning from mining and processing of lead sulphide-containing gold deposits in the area.

In Alizaga Pb-Zn mining area, the workers are exposed to these PTEs when it is carried by dust within the vicinity of the mining and processing area. Women and children involved in quarrying of overburden rocks, sorting and handling of mine tailings are also exposed. In addition to this, the settling pond for recycled water used for mineral processing can get into groundwater through infiltration. When adequate care and monitoring are not undertaken by the mining company, this water can also overflow, finding its way into nearest surface water sources.

The mines waste deposited on the adjoining land is being cultivated for food crops such as yams, maize, groundnuts and rice. There is also a possibility of plant uptake of PTEs in soils which may later get into the food chain.

1.5 Justification for the Study

Musa *et al. (*2021) studied the human health risks of heavy metals in the wells and stream water within the vicinity of lead mining area of Nasarawa-Eggon. However, this research will focus on the concentration of PTEs in the soils, stream sediments, rocks and groundwater in Alizaga village of Nasarawa-Eggon. It will reveal the distribution and contamination levels by PTEs around the Pb-Zn mining area. Furthermore, it will also present the level of contamination in surrounding farmlands and settlements. This study will raise more awareness on the risk posed by these PTEs so that appropriate steps can be taken to prevent further contribution by anthropogenic factors and remediation approach taken if the soil is already contaminated.

1.6 Aim and Objectives of the Study

This study is aimed at assessing the concentration and distribution of PTEs in soils, stream sediments, rocks and groundwater of Alizaga Pb-Zn mining area. The Objectives are as follows:

i. Produce an updated geological map of the study area on a scale of 1:15,000.
ii. Determine the PTEs concentrations in soils, stream sediments, groundwater and rocks in the study area and pollution levels using appropriate indices
iii. Determine the potential human health risks posed by PTEs contamination to the inhabitants of the study area.

1.7 Scope and Limitation of the Study

The study focus on the concentration and contamination levels of Potentially Toxic Elements in the soils, stream sediments and groundwater of Alizaga and surrounding environment. The area is bounded by the coordinates (WGS 1984) 8° 40' 38" N to 8° 42' 31" N and 8° 31' 48" E to 8° 33' 45" E, covering a total area of about 13 sq km. Alizaga lead-zinc mining site in centrally located within the study area (Figure 1.2). Data collection involved geological mapping and sampling of the soils, stream sediments, groundwater and rocks. Their concentrations will be used to determine the contamination levels of these PTEs (Pb, Zn, Cu, Cr and As) in the environment of the study area and identify any connection to the Pb-Zn mining activities in the area.

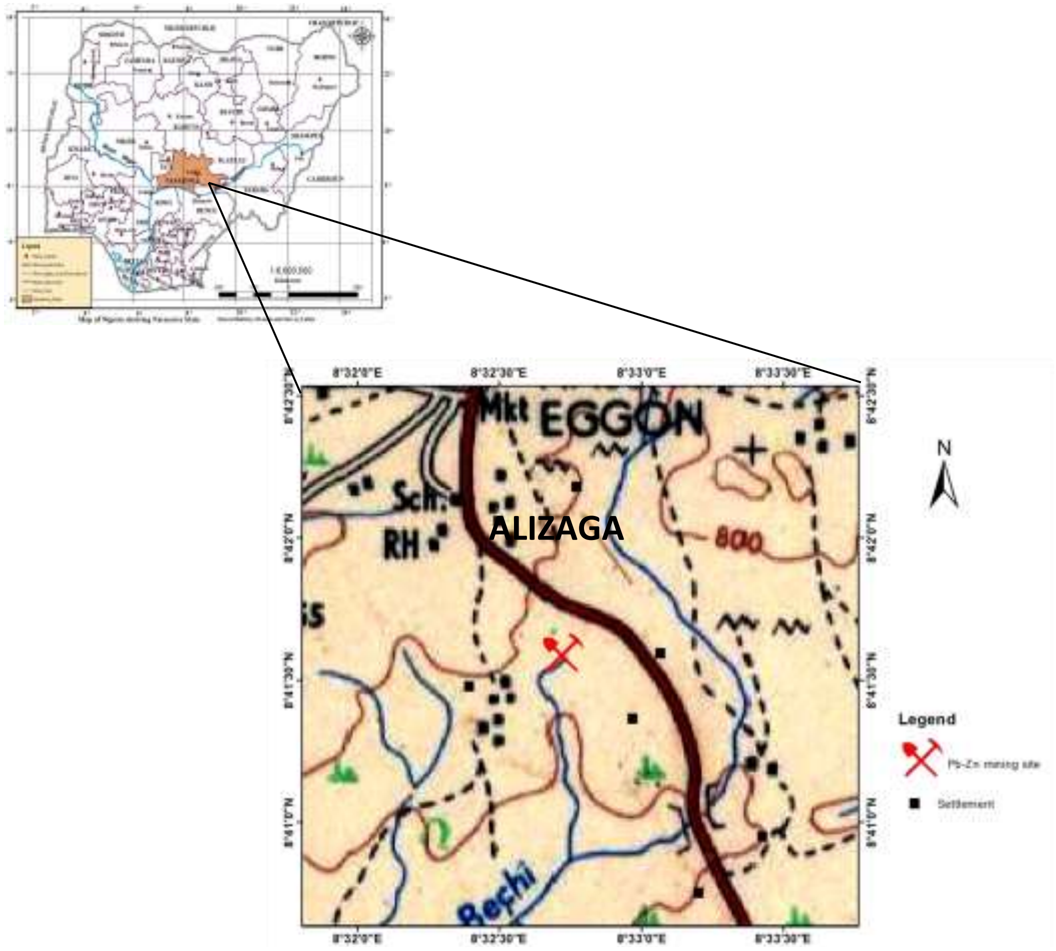

Figure 1.2: Location and Topographic Map of the Study Area (Adapted from Federal Surveys, Nigeria, Wamba Sheet 210 SW)

The limitation in the study is especially on the several uncertainties associated with USEPA (1997) model used for health risks assessment. This can create overestimation or underestimation of the health risks caused by the PTEs in the study area.

1.7.1 Location and accessibility

The study area is located in Alizaga village, Nasarawa-Eggon Local Government of Nasarawa State, North-Central Nigeria (Federal Surveys Nigeria, 1970). The mine site is located about 1 km south of Alizaga village and about 500 m off Akwanga-Lafia road. It is accessible by the Akwanga-Lafia road, which cuts from North to South-East of the study area. There are several other minor road and footpaths in the area, linking villages and farmlands (Figure 1.2).

1.7.2 Climate and vegetation

The climate of Nasarawa-Eggon falls within the tropical savannah climate with two clearly marked seasons, wet and dry. It has a mean minimum and maximum temperature of 15.6ºC and 26.7ºC respectively with an annual rainfall between 1317mm and 1450mm. 1t rains from April to October and the months of December to February experiences the northeast trade winds and thus the dry harmattan. The onset of rains in April ushers in a noticeable decline in temperature. This continues in the cessation period by October ending when a further decline is made possible in November/December by the coming of the harmattan winds (Ayiwulu, 2012).

1.7.3 Relief and drainage

Most of the study area is elevated between 200 to 300 m Above Sea Level, consisting mostly of an East-West trending hilly landscape and characterized by the rocks of the Nigerian Basement Complex. The few drainage channels observed exhibit dendritic drainage pattern which correspond to the structure and relief of the landscape (Ayiwulu, 2012). The area is drained by River Bechi, taking it sources from the high lands in the North and flowing South-West (Figure 1.2)

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 PTEs Levels and Risks Assessment in Soils and Sediments

Pan *et al.* (2018) studied the PTEs levels and risk assessment of soils and sediments in the Upstream River (with focus on Chao and Baimaguan River), Miyun Reservoir, Beijing China. The result of their work showed that the average concentration of the six PTEs (cadmium, zinc, lead, chromium, arsenic and copper) analysed were below the soil environmental quality standards for China, with cadmium being the most serious pollutant in both soils and sediments. They concluded that the historical iron ore mining and agricultural activity were the primary sources of PTEs pollution of soil and sediment in the Chao-Baimaguan River in Miyun District. Human health risk assessment indicated that non-carcinogenic risks all fell below threshold values. The total carcinogenic risks due to chromium and Arsenic were within the acceptable range for both adults and children.

Biasioli *et al*. (2007) presented a comparison of Potentially Toxic Elements contamination in urban soils of three European cities Ljubljana (Slovenia), Sevilla (Spain) and Torino (Italy) using common sampling and analytical protocols. Their results highlighted similarities across the cities, despite their differences in geography, size, climate, etc. PTEs showed a wide range in concentration reflecting a diffuse contamination. Among the ‘‘urban’’ elements, Pb (45%, 43% and 11%) and Zn (20%, 43% and 2%) exceeded the legislation threshold in the soils of Ljubljana, Torino, and Sevilla, respectively. They discovered that distribution of PTEs showed no depth-dependant changes. They also used multivariate statistics to reveal similar associations between PTE in the three cities, with Cu, Pb, and Zn in a group, and Ni and Cr in another, suggesting an anthropogenic origin for the former group and natural one for the latter. In their work, chromium and nickel were unaffected by land use, except for roadside soils, while Cu, Pb and Zn contamination appeared to be more dependent on the distance from emission sources. They concluded that regardless of the location, climate, and size, the ‘‘urban’’ factor integrating type and intensity of contaminant emission and anthropogenic disturbance—seems to prevail in determining trends of PTE contamination.

Adamu *et al*. (2014) also carried out an assessment of Potentially Toxic Metals in soil and sediments of the Keana Brine field in the Middle Benue Trough, North-Central Nigeria where there is long history of mining activities (brine, lead-zinc, barite and limestone). The geochemical data analysis showed that the soil and stream sediments in the area are extremely polluted by Zn, Cr and Ni but remains uncontaminated by Cu, Sr and Sc. They concluded that the continued exposure of inhabitants of this area particularly, those in the mining locations who depend on the soil (for subsistence farming) and water from ponds, wells and boreholes (for drinking, cooking and other domestic uses), would result in various health risks and concerns if not checked or abated.

Nnabo (2015) studied Heavy Metal Distribution and Contamination in Soils around Enyigba Pb-Zn Mines District, South Eastern Nigeria. He presented the physico-chemical analyses of the soil which showed that pH is fairly acidic to neutral (5.3-7.0). This is from the dissolution of the sulphide-containing tailings into the soil. The variations observed for the heavy metals concentration suggest that both geogenic and anthropogenic activities may be responsible for their distribution. He went further to conclude that the risk level of heavy metal leaching and groundwater contamination from the soil is very high with considerable likelihood of heavy metal transport by water percolation through the soils and mine waste. Nnabo’s findings were replicated by Obiora *et al*. (2016). They assessed the level of contamination of soils caused by mining activities in the same area by analyzing Potentially Harmful Elements associated with Pb-Zn mining such as Pb, Zn, As, Cd, Mn, Fe, Se, Sb, Cu and Bi. In their work, the samples analyzed showed elevated concentrations of Pb, Zn, Cd, Cu and Cr when compared with concentrations documented in Canadian Environmental Quality Guidelines (Canadian Council of Ministers of the Environment, 2002). The pollution index also revealed that soil quality all around the mines have deteriorated. The authors concluded that there is need for immediate remedial measures and the miners as well as local communities living around the mines need to be enlightened about the dangers of exposure to these heavy metal contaminants.

More recently, the work of Akintunde *et al*. (2020) was focused on contamination assessment of Potentially Toxic Metals in road-side surface soils along Iwo-Ibadan expressway, Nigeria. They discovered that variation in the elemental levels across the sampling points was a reflection of the variation in traffic density. They also used cluster analysis to indicate that the metals are associated with vehicular emissions. They recommended that strict regulations be put in place against the use of leaded gasoline as vehicular fuels. They also suggested adequate and frequent monitoring of highway contamination by heavy metals as a result of their bioaccumulative tendencies.

2.2 Human Health Risk Assessments

Several researchers in Nigeria have carried out studies on associated health risks by heavy metals and potentially harmful elements. Lar *et al*. (2013) studied the human exposure to lead and other Potentially Harmful Elements (PHEs) such as U, Cd, Se, Zn and As associated with galena mining in New Zurak, Central Nigeria. They presented an assessment of the degree of contamination or toxicity of these elements using Geoaccumulation Index (Igeo) and contamination factor (CF) in the different media sampled – farmland soils, uncultivated lands, mine tailings/dumps, water and vegetables.

Their findings revealed that the mine tailings and dump are highly contaminated with Pb, U, Cd, Se, Zn and As. This have contributed to the enrichment of these elements in the surrounding environment. They advised that mining activities in Zurak should be done in a more environmentally-friendly manner.

On the other hand, Ombugus *et al*. (2021) was interested on evaluating the human health risks of heavy metal in wells and streams water in the vicinity of a lead mining site in Nasarawa State, North Central Nigeria. They concluded that wells and the stream water used by the community around the mining area were contaminated with Cr, Cd and Pb as their concentration were greater than the standard concentration limit set by World Health Organization (WHO, 2011) and Nigeria Environmental Standards and Regulatory Enforcement Agency (Ladan, 2012). They also added that among all the studied metals, Cr and Cd have the highest chances of cancer risks while Pb and Ni have the lowest chances of cancer risks.

Nganje *et al*. (2020) presented a study on the concentration, distribution and health risk from Potentially Toxic Elements in the soil - plant - water system developed on black shales in SE Nigeria. They examined the concentration and distribution of these PTEs such as Cd and Pb in shale and soil-water-plant systems. They discovered that some PTEs such as Mo, Se, Tl, and Zn are highly enriched in the black shales while As, Cd, Cr, Cu and Zn are enriched in soils. Pollution indices revealed various levels of soil, water and crop plants contamination by PTEs. Distribution of PTEs may be attributed to differences in geochemical nature of shale formations and degree of weathering. The concentrations may also be modified by varying degree of pedogenetic processes that may lead to mobility and redistribution of PTEs in soil. Health risk assessment of the population based on the Hazard quotients (HQ) and Health indices (HI), indicated minimal or no risk for drinking water consumption in the area. The cancer risk from Arsenic for individuals exposed through the soil and stream water pathways did not exceed the acceptable risk of 1 in 10,000 set for regulatory purposes. Their study provided data for the development, demobilization and implementation of a monitoring system and management of PTEs from shale bedrock.

2.3 Remediation Approach to PTEs Contamination

In an attempt to evaluate remediation approach to contamination by PTEs, Palansooriya *et al*. (2020) discussed remediation of PTEs contaminated soils through immobilization techniques using different soil amendment methods with respect to type of element, soil, and amendment, immobilization efficiency, underlying mechanisms and field applicability. Soil amendment methods such as manure, compost, biochar, clay minerals, phosphate compounds, coal-fired ash and liming materials are widely used as immobilizing agents for PTEs. They also stated that among these soil amendment methods, biochar has attracted more interest over the past few years because of its promising surface properties. They recommended that integrated application of appropriate amendments can maximize their use and efficiency. These amendments can reduce PTE bioavailability in soils through diverse mechanisms such as precipitation, complexation, redox reactions, ion exchange, and electrostatic interaction. However, they emphasized that soil properties such as soil pH, and clay, sesquioxides and organic matter content, and processes, such as sorption/desorption and redox processes, are the key factors governing the amendments' efficacy for PTEs immobilization in soils.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Preliminary Studies

This includes:

1. Literature Review.
2. Acquisition of materials needed for field work.
3. Acquisition of topographical map of the study area.
4. Use of satellite imageries to study the area.
5. Reconnaissance site visit to compare what is on ground to existing maps.

3.2 Field Work

Field work involved geological mapping and sampling (rock, soil, groundwater and stream sediments samples were taken).

3.2.1 Geological mapping

An enlarged topographical map (1:15,000) was used as base map for the geological mapping. With the use of a Garmin GPS receiver, pencil and compass clinometer, samples location, geological features such as lithological variations and geological structures observed on the field were represented on the map along a profile spacing of 500 m. These data were put together with the use of ArcGIS version 10.7 to produce a geological map.

3.2.2 Sampling

Soils, rocks, stream sediments and groundwater samples were taken during the field work (Figure 3.1).

3.2.2.1 Soils

Sampling guidelines by Carter and Gregorich (2007) was adopted in the work. Systematic soil sampling method using grids of 500m by 500m was used. In each of the sample location, rock pebbles, grasses and roots on the surface were removed and a V-shape was dug to depth of about 20cm using a shovel. Then a plastic spoon was used to take soil sample from this depth. In each grid of 500m by 500m, four soil subsamples were taken and mixed together to produce a composite sample of about 1 kg. They were stored in well labelled polyethylene ziploc bags and sent to laboratory for chemical analysis. A total of 25 soil samples were taken (Figure 3.1).

3.2.2.2 Rocks

Separate rock samples of the different lithologies observed in the area were taken using a geologic hammer. Their mode of occurrence, grain sizes and structural features were noted. A total of seven rock samples were taken.

3.2.2.3 Groundwater

Groundwater samples were collected from seven hand-dug well, one borehole and one underground mine water. New sample bottles (250mL and made of polyethylene) were first rinsed with deionised water before proceeding to the field. At each location, the bottles were rinsed twice with the water to be sampled, before actual collection. Few drops of concentrated nitric acid were immediately added, bottle capped and well labeled. The physical parameters (temperature, pH, total dissolved solids and electrical conductivity) of the water were measured with the use of digital multimeter while also taking note of colour, odour and taste. Also the static water level were measured with the use of a dipmeter. The water samples were stored in a dark bag and sent immediately for laboratory analysis.

3.2.2.4 Stream sediments

Sampling guidelines by Carter and Gregorich (2007) was adopted for stream sediment sampling in this work. Random sampling along River Bechi and its tributaries was done. In each of the sample location, areas of gentle current where sediments can easily deposit were selected. Rock pebbles, roots and grasses were removed and a plastic spoon used to carefully take sediments from the central part of the stream while facing against the flow direction. Four subsamples along 100-200m stretch of the stream were taken to produce composite samples. Excess water is carefully drained out and the sediments stored in a well labelled Polyethylene ziploc bag

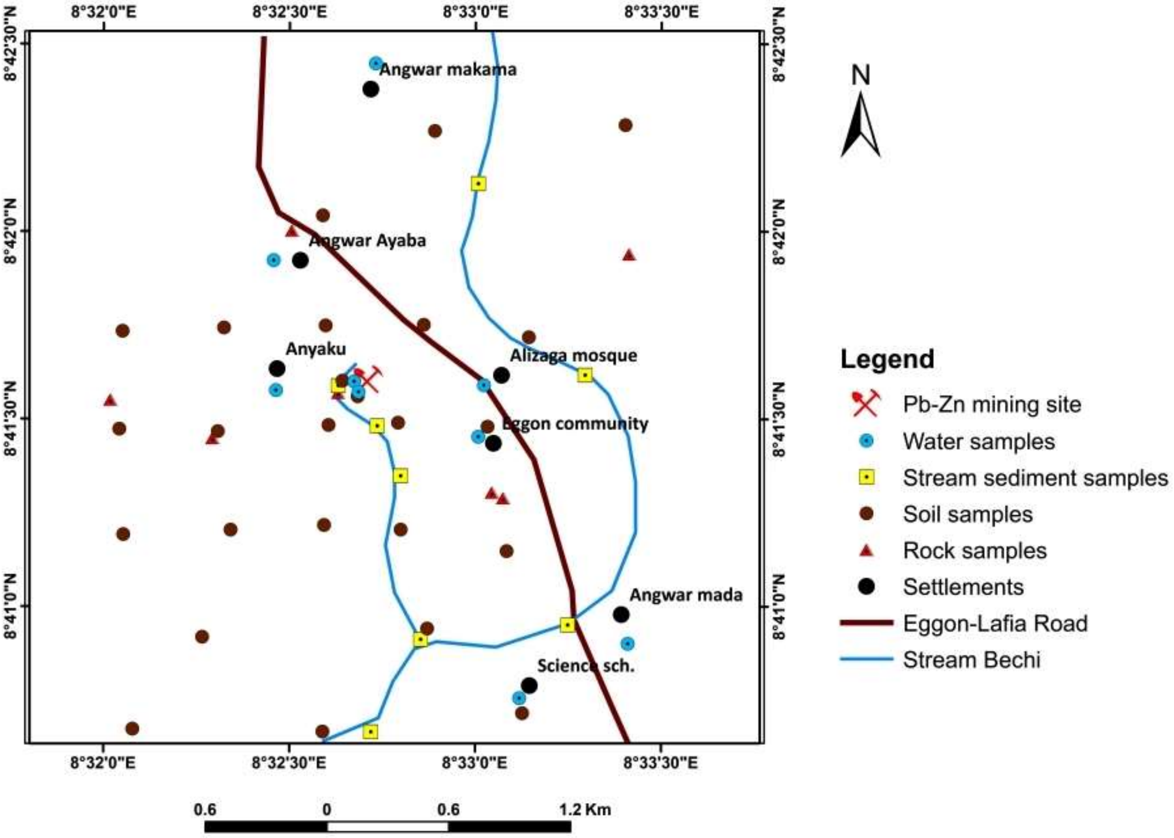

Figure 3.1: Samples location map of the study area.

3.3 Laboratory Analysis

Soil and stream sediments samples were carefully sun dried in a clean area for two days, disaggregated while rock samples were crushed and pulverized. Their representative samples were analysed by X-Ray Florescence (XRF) method at Central instrumentation laboratory, Centre for Dry land Agriculture, Bayero University, Kano. Water samples were analysed by Atomic Absorption Spectroscopy (AAS) method at Muhammadu Buhari TETFUND Centre of Excellence Laboratory, Federal University of Lafia, Nasarawa State.

3.3.1 X-Ray florescence (XRF) analysis

The samples were pulverised with the aid of agate motar and pistol. Then it is sieved through a <60µm nylon mesh and the oversize is ground again until no grain larger than 60µm is left. 2g of each of the sample were weighed, poured into a sample holder (made of propylene, a thermoplastic) and covered with cotton wool to prevent spraying. The sample holders containing the samples were run in a vacuum for 10 minutes and then inserted into an S-2 Ranger (Bruker, UK) XRF Spectrometer for elemental analysis. They were allowed to run in the EDXRF spectrometer for 10 minutes each after which the results were obtained.

3.3.2 Atomic absorption spectroscopy (AAS) analysis

In the laboratory, all glass wares to be used were rinsed with concentrated nitric acid in a sub-boiling system and then with deionized water before use to avoid contamination. Digestion was done by transferring 20ml of each water samples into a clean, dried 250ml beaker containing aqua-regia (HCl and HNO_3) in the ratio 3:1 (that is, 15ml of HCl and 5ml of HNO_3). It was then heated for 15 minutes, transferred to 100mL volumetric flask, diluted to the mark by adding deionized water, filtered through a 0.45µm filter and then stored in a refrigerator until analysis. Standard solutions were also prepared by serial dilution of the 1000 ppm stock solution of each metal to be analysed. Each sample solution was run in triplicate and the results were corrected by subtracting the blank reading from the value of each metal. The instrument setting and operational conditions were done in accordance with the manufacturer's specification.

3.4 Data Analysis

Five PTEs (Pb, Zn, Cu, Cd and Cr), which are commonly found in soils and stream sediments in Pb-Zn mining environment, were selected and their mean concentration compared with standards set in the Finnish legislation for contaminated soil. The Finnish standard values represent a good approximation of the mean values of different national systems in Europe (Carlon *et al*., 2007) and India (Bhatnagar and Awasthi, 2000). They have also been applied in an international context for agricultural soils as well (Van der Voet *et al*., 2013). The Finnish legislation sets concentration levels by each hazardous elements to identify soil contamination and remediation needs. It sets lower and higher concentration levels indicating the need for different actions if exceeded. Higher concentration levels are defined by major land uses, that is for industrial or transport sites. The "threshold value" is equally applicable for all sites and it indicates the need for further assessment of the area (Table 3.1).

The second concentration level is the so-called "guideline value". If this is exceeded, the area has a contamination level which presents ecological or health risks. Different guideline values are set for industrial and transport areas (higher guideline value) and for all other land uses (lower guideline value). In this work, agricultural land was assessed and the threshold and lower guideline values applied for samples. In Table 3.1, the guideline values have been defined on the basis of either ecological risks (e) or health risks (t)

Table 3.1: Threshold and Guideline Values for PTEs in soils

PTEs	Threshold Value (mg/kg)	Lower Guidelines value (mg/kg)	Higher Guideline Value (mg/kg)
Pb	60	200(t)	750(e)
Zn	200	250(e)	400(e)
Cu	100	150(e)	200(e)
Cr	100	200(e)	300(e)
Cd	1	10(e)	20(e)

(Extract from Ministry of the Environment Finland MEF, 2007)
(e) stands for ecological risks and (t) for health risks

Assessment of PTEs in stream sediments was made by comparing mean concentrations of selected elements with Consensus-Based Freshwater Sediment's Quality Guidelines published by USEPA (2002). In Figure 3.2, Threshold Effect Concentrations (TEC) are concentrations below which harmful effects are unlikely to be observed while Probable Effect Concentrations (PEC) are concentrations above which harmful effects are likely to be observed.

Table 3.2: Consensus-Based Sediment Quality Guidelines that Reflects Threshold Effect Concentration and Probable Effect Concentrations

PTEs	Threshold Effect Concentration (TEC) (mg/kg)	Probable Effect Concentration (PEC) (mg/kg)
Pb	35.80	128.00
Zn	121.00	459.00
Cu	31.60	149.00
Cr	43.40	111.00
Cd	0.99	4.98

(Extract from USEPA, 2002)

Mean concentration of these PTEs in ground water (shallow wells, borehole and mine waste water) were also compared with local and international standards (Figure 3.3).

Table 3.3: Nigerian Standard for Drinking Water Quality (2007) and Permissible Limits by World Health Organization (2022) for selected PTEs in Groundwater

PTEs	Nigerian Standard for Drinking Water Quality (2007) (mg/L)	World Health Organization (WHO, 2022) (mg/L)
Pb	0.01	0.01
Zn	5	3
Cr	0.05	0.05
Cd	0.01	0.01
As	0.2	0.01

3.4.1 Determination of Pollution Levels

While soils and sediments guidelines provide values that allow for quantification of pollution, further comparisons are required to make an overall assessment of the degree of PTEs contamination in the studied area. Five pollution indices (both single and integrated) were used as a tool to indicate the level of contamination by PTEs accumulation in the study area. They are: Geo-accumulation Index (Igeo), Contamination Factor (CF), Pollution Load Index (PLI), Modified Degree of Contamination (mCd) and Enrichment Factor (EF). (Ferreira *et al*., 2022).

3.4.1.1 Geo-accumulation index (Igeo)

Geo-accumulation index is generally used to determine the anthropogenic contamination in soils or sediments as introduced by Muller (1979). This index is used to evaluate the contamination levels by comparing present concentrations with a referenced background levels. Igeo is expressed using the following Muller equation.

$$\mathrm{I}_{\mathrm{geo}} = log_2 \frac{\mathrm{Cn}}{1.5\ \mathrm{Bn}} \tag{3.1}$$

Where;

Cn is the measured concentration of the given heavy metal examined in the soils or sediment.

Bn is the geochemical background value of the element.

1.5 is incorporated in the relationship to account for possible variation in background data (the background matrix correction factor) owing to lithogenic effects, according to Loska *et al.* (1997). The Igeo values is helpful to divide soils into grades (0 to 6) based on the increasing numerical value of the index and ranges from unpolluted to extremely polluted. The standard Igeo values (according to Muller, 1979) are presented in table 3.4.

Table 3.4: Classification of Index of Geo-accumulation (Igeo).

Igeo Value	Grade	Classification
≤0	0	Unpolluted
0-1	1	Unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	Moderately polluted to strongly polluted
3-4	4	Strongly Polluted
4-5	5	Strongly Polluted to extremely polluted
>5	6	Extremely polluted

3.4.1.2 Contamination Factor (CF)

Contamination Factor is used to assess the level of soil contamination, taking into account the content of heavy metals from the surface of the soil and values of pre-industrial reference levels. It is calculated by the following formula by Hakanson (1980).

$$\mathrm{CF} = \frac{C_{\mathrm{metal}}}{C_{\mathrm{background}}} \qquad (3.2)$$

Where;

CF is Contamination Factor

C_{metal} is metal concentration in polluted soil/sediments

$C_{background}$ is background value of the metal

Background concentrations of soil/sediment were adopted from the work of Bowen (1979), where he determined the background concentration of elements in selected components of the environment (Pb=35ppm, Zn=90ppm, Cu=30ppm, Cr=70ppm, Cd=0.35ppm and Al=71000ppm).

Contamination Factor and level of contamination by Muller (1979) is shown in Table 3.5.

Table 3.5: Classification of Contamination Factor and Level of Contamination

Contamination Factor	**Level of Contamination**
CF < 1	Low contamination
1 ≤ CF <3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF ≥ 6	Very High contamination

3.4.1.3 Pollution load index (PLI)

This is used for the determination of entire pollution level in the soil. It provides an easy way to prove the deterioration of the soil conditions as a result of the accumulation of PTEs (Tomlinson, 1980). Generally, the PLI is calculated by obtaining the n-root from the n-CFs measured. This is expressed by Tomlinson *et al.* (1980) in equation (3).

$$\mathrm{PLI} = \sqrt[n]{\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \ldots \mathrm{CF}_n} \qquad (3.3)$$

Where;

n = number of metals

Table 3.6 is the classification of pollution load index by Tomlinson *et al*. (1980)

Table 3.6: Classification of Pollution load Index

Pollution Load Index	**Pollution Level**
PLI ≤ 1	No metal pollution
PLI > 1	Metal pollution exist

3.4.1.4 Modified degree of contamination (mCd)

The modified degree of contamination is used for the assessment of overall metal contamination in the samples. It is used for better assessment value and can be calculated using the following relation by Muller (1979):

$$\mathrm{mC_d} = \frac{\sum \mathrm{CF}}{\mathrm{n}} \qquad (3.4)$$

Where;

CF is the Contamination Factor and n is the number of analyzed trace elements. Table 3.7 is the classification of modified degree of contamination according to Abrahim and Parker (2008).

Table 3.7: Classification of Modified Degree of Contamination

Modified degree of contamination	**Contamination status**
$mC_d < 1.5$	Nil to a very low degree of contamination
$1.5 \leq mC_d < 2$	Low degree of contamination
$2 \leq mC_d < 4$	A moderate degree of contamination
$4 \leq mC_d < 8$	A high degree of contamination
$8 \leq mC_d < 16$	A very high degree of contamination
$16 \leq mC_d < 32$	An extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

3.4.1.5 Enrichment Factor (EF)

This is used to evaluate the level of soil contamination and seeks to know the possible natural or anthropogenic input and impact in soils and sediments. That is, it is used to differentiate between the elements originating from anthropogenic activities and those from natural sources. Enrichment Factor of PTEs in the samples can be calculated using the formula originally introduced by Buat-Menard and Chesselet (1979):

$$\mathrm{EF} = \frac{\left(\frac{\mathrm{C_n}}{\mathrm{C_{ref}}}\right)\mathrm{sample}}{\left(\frac{\mathrm{B_n}}{\mathrm{B_{ref}}}\right)\mathrm{background\ value}} \tag{3.5}$$

Where;

EF is the Enrichment Factor

(C_n/C_{ref}) is the ratio of the concentration of the examined element to the concentration of the reference element in the examined environment.

(B_n/B_{ref}) is the ratio of the background value of the examined element to that of the background value of the reference element.

According to Loska *et al*. (1997), an element can be considered as a reference element if it occurs in significant in the environment but has no interaction or resistance towards an examined element. A reference element is often a conservative one, unchanged by anthropogenic influences. The most used reference elements include Sc, Mn, Ti, Al, Fe and Zn. In this assessment, aluminum (Al) was used as the immobile element to differentiate between natural and anthropogenic component. It is a normalizing element assumed not to be consequentially enriched owing to local contamination (Sutherland, 2000). Table 3.8 gives the classification of enrichment factor according to Barbieri (2016) and Mei *et al*. (2011).

Table 3.8: Classification of Enrichment Factor

Enrichment Factor	**Soil/Sediment Quality**
EF < 2	Deficiency to minimal enrichment
2 < EF < 5	Moderate enrichment
5 < EF < 20	Significant enrichment
20 < EF < 40	Very high enrichment
EF > 40	Extremely high enrichment

EF values lower than and around 1.0 indicates that the element in the sample originated predominantly from the crustal/background material and/or weathering process. EF values greater than 1.0 displays anthropogenic origin of the element. As the EF values increases, the contribution of the anthropogenic origins also increases (Sutherland, 2000).

3.4.2 Ecological risk assessment

The method introduced by Hakanson (1980) was adopted in this work to assess the ecological risks posed by PTEs pollution in the topsoil and stream sediments of the study area. He developed the following quantitative approach, and this method was used in many other studies to assess ecological risks of PTEs in soils and stream sediments. The potential ecological risk factor of a given contaminant [EI(i)] is defined by Hakanson (1980) as:

$$\mathrm{EI(i)} = \mathrm{Ti} \times \frac{\mathrm{Ci}}{\mathrm{Co}} \tag{3.6}$$

Where,

Ti is the toxic-response factor of the PTEs (Cd = 30, As = 10, Pb = Cu = 5, Cr = 2, Zn = 1)

Ci represents PTEs concentration in the topsoil

Co is the referenced background concentration of elements in soil according to Bowen (1979).

The potential ecological risk index (RI) is the sum of the individual potential risk factors E(i). It is expressed in equation (7) according to Hakanson (1980).

$$\mathrm{RI} = \sum_{\mathrm{i=1}}^{\mathrm{n}} \mathrm{Ti} \tag{3.7}$$

There are four and five risk levels (Hakanson, 1980) of RI and E(i) respectively (Table 3.9).

Table 3.9: Indices and Risk Levels of Potential Ecological Risk by PTEs Contamination

E(i)-value	E(i)-Risk level	RI value	RI risk level
E(i) < 40	Low risk	RI < 110	Low risk
40 ≤ E(i) < 80	Moderate risk	110 ≤ RI < 200	Moderate risk
80 ≤ E(i) < 160	Considerable risk	200 ≤ RI < 400	Considerable risk
160 ≤ E(i) < 320	High risk	RI ≥ 400	Very high risk
E(i) ≥ 320	Very high risk		

3.4.3 Human health risk assessment

Human health risk assessment was carried out with respect to exposure assessment, non-carcinogenic and carcinogenic risk assessment of selected PTEs in the soil, stream sediments and water in the study area using predetermined parameters and models by United States Environmental Protection Agency (USEPA 1989).

3.4.3.1 Exposure assessment

In general, individuals are exposed to contaminants through three pathways: ingestion, inhalation and dermal contact, which can be determined according to the Exposure Factors Handbook (USEPA, 1997). However, for PTEs in soil, stream sediments and water, ingestion and dermal absorption were considered the main exposure pathways (Fryer *et al.,* 2006). Thus, these two exposure pathways were selected for health risk assessment in this study. Exposure areas for soils in the study area were grouped into three;

i. In mine site (mining and processing area and mine roads)
ii. Settlements and
iii. Cultivated lands.

Exposure areas for stream sediments were grouped into two;

i. Those close to the mines (within 200 m radius)

ii. Those away from the mines (more than 200m away)

The Average Daily Intake (ADI) of chemicals from soils, stream sediments and water were calculated using the following equations by USEPA (2014):

$$\mathrm{ADI}_{\mathrm{non-dietary(soil/sediment)}} = \frac{\mathrm{Cs} \times \mathrm{IR}_{\mathrm{ing}} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times 10^{-6} \quad (3.8)$$

$$\mathrm{ADI}_{\mathrm{dermal\ (water)}} = \frac{\mathrm{Cw} \times \mathrm{SA} \times \mathrm{PC} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{CF}}{\mathrm{BW} \times \mathrm{AT}} \quad (3.9)$$

$$\mathrm{ADI}_{\mathrm{non-dietary\ (water)}} = \frac{\mathrm{Cw} \times \mathrm{IR}_{\mathrm{ing}} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \quad (3.10)$$

Where;

Cs is the average chemical concentration of the PTEs in soil/sediments (mg kg^{-1})

$\mathrm{IR}_{\mathrm{ing}}$ is the ingestion rate (mg/day). Soil/sediment is 100 mg/day for adults and 200 mg/day for children. Water is 1L/day for children and 2L/day for adults;

EF is the exposure frequency, 350 days/year;

ED is the exposure duration, 30 years for adults and 6 years for children;

SA is the exposed area. Soil/stream sediments (5700cm^2 for adults and 2800cm^2 for children; Water (18200cm^2 for adults and 12000cm^2 for children)

SAF is the Soil Adherence Factor. 0.07 mg/cm^2 for adults and 0.2 mg/cm^2 for children;

ABS is the dermal absorption factor. Average value of 0.001 was used for all elements considered in this study;

BW is body weight, 70 kg for adults and 20 kg for children;

AT is the averaging time, determined for non-carcinogens as ED × 365 days and for the carcinogens (As and Cr) as 70 (lifespan) × 365 days;

Cw is the chemical concentration of the PTEs in soil/sediments (mg L^{-1});

PC is chemical specific permeability constant (cm/h). 0.001cm/h was used for this study;

ET is exposure time. 2.6 hours/day;

CF is volumetric conversion factor for water (1L/1000cm^3=0.001)

Default values, based on assumptions outlined by USEPA (2011) from the Risk Integrated Software for Clean-up (also known as RISC 4.02) of hazardous waste sites, were used for the parameters in equations (8-10).

3.4.3.2 Non-carcinogenic risk assessment

The hazard quotient (HQ) is traditionally used to describe non-carcinogenic risk, which is calculated as the ratio of the average daily dose and the reference dose (RfD) for a given substance (USEPA, 2011). The equation is defined as follows:

$$\mathrm{HQ} = \frac{\mathrm{ADI}}{RfD} \qquad (3.11)$$

where;

RfD is the reference dose of the i-th PTE (mg/kg day^{-1}) (Table 3.8), which is the maximum allowable level of the PTE that causes no harmful effects on human health. To assess the overall non-carcinogenic effects of multiple chemicals, the sum of HQ values for all chemicals is expressed as HI, following the equation:

$$\mathrm{HI} = \sum \mathrm{HQ_i} = \sum \frac{\mathrm{ADI_i}}{\mathrm{RfD_i}} \qquad (3.12)$$

If the HI value is less than 1, the exposed individual is unlikely to experience obvious adverse health effects. On the other hand, if the HI value exceeds 1, there is a chance that non-carcinogenic effects may occur, with a probability that tends to increase as HI increases.

3.4.3.3 Carcinogenic risk assessment

This is defined as the incremental probability of an individual to develop any type of cancer throughout their lifetime due to 24 hours per day exposure to a given daily amount of carcinogenic hazards for 70 years (Gržetić and Ghariani, 2008). According to USEPA (2011), the carcinogenic risk for an individual over a lifetime was calculated according to the following equation:

$$\mathrm{ILCR} = \mathrm{ADI} \times \mathrm{CSF} \tag{3.13}$$

Where;

ILCR is the incremental lifetime cancer risk or probability of an individual developing cancer.

Table 3.10: Summary of reference dose (RfD) and cancer slope factor (CSF) of metals and the metalloid As through oral, dermal and inhalation pathway

Elements	Oral RfD[a.b] (mg.kg^{-1}.day^{-1})	Dermal RfD[b,c] (mg.kg^{-1}.day^{-1})	Oral CSF[b,c] (mg.kg^{-1}.day^{-1})	Dermal CSF[b,c] (mg.kg^{-1}.day^{-1})
Pb	3.50×10^{-3}	5.24×10^{-4}	NA	NA
Cd	1.00×10^{-3}	3.00×10^{-3}	5.01×10^{-1}	2.00×10^{1}
Cr	1.50×10^{0}	NA	5.00×10^{-1}	NA
Cu	4.00×10^{-2}	5.40×10^{-3}	1.70×10^{0}	4.25×10^{1}
Zn	3.00×10^{-1}	1.20×10^{-2}	NA	NA
As	3.00×10^{-4}	8.00×10^{-4}	1.50×10^{0}	3.66×10^{0}

[a]United States Environmental Protection Agency (USEPA, 1997); [b]United States Environmental Protection Agency (USEPA,2002); [c]Ferreira and Miguel (2005).

CSF, as listed in Table 3.10, is the carcinogenicity slope factor (per mg/kg$^{-\mathrm{day}}$) defined as the risk generated by a lifetime average amount of one mg/kg/day of carcinogenic chemical and it is contaminant specific. Risks between 1.0×10^{-4} and 1.0×10^{-6} are generally considered acceptable while those exceeding 1.0×10^{-4} are considered to represent a lifetime carcinogenic risk to the human body (USEPA, 1989).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Geology of the Area

The geological mapping revealed that the study area is underlain by Basement Complex rocks of Nigeria. The dominant rock type is biotite granite (47%), followed by gneiss (31%), migmatite (11%), ryholite (10%), quartzite (0.9%) and dolerite dykes (0.1%). Lead and zinc mineralisation is hosted within the quartzite (as patches), striking N340°, up to 15m wide and disseminated in parts of the adjoining biotite granite (Figure 4.1). The dominant joint direction in the area is NE-SW.

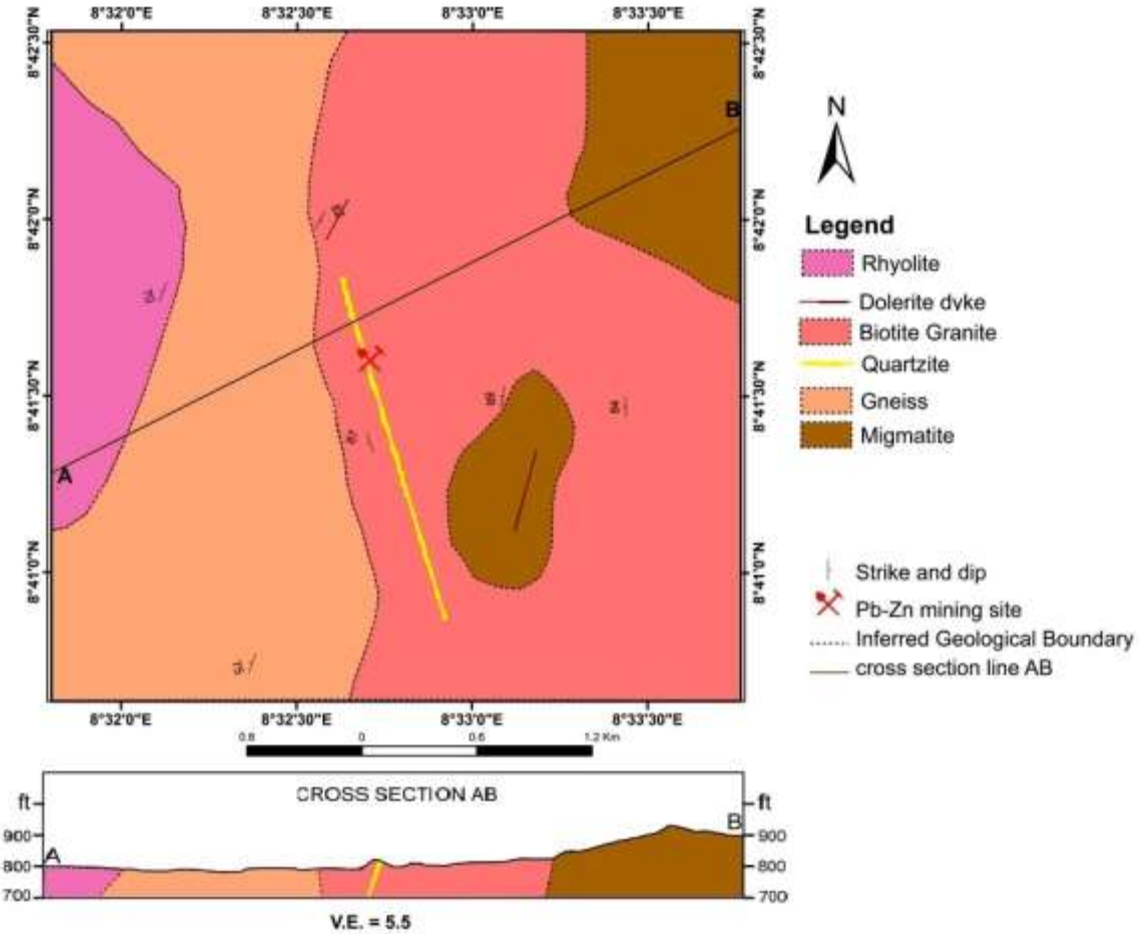

Figure 4.1: Geological map of the study area with cross section A-B.

4.1.1 Migmatite

Migmatites were observed in the north-eastern and central part of the study area having a relatively NNE-SSE trend. They occur as medium-grained rocks comprising both igneous rocks of granitic composition and high grade, foliated metamorphic rocks. The migmatites are highly fractured with prominent joints on the NE-SW direction. Also associated with the migmatites is dolerite dykes; 0.5-1m wide and striking NE direction (Plate I).

Plate I: Weathered migmatite outcrop intruded by dolerite dyke, 0.8m thick, striking relatively NE direction. Location coordinates (N 08° 40' 54.1", E 08° 32' 45.7", 196m ASL).

4.1.2 Gneiss

About 25-30% of the study area is underlain by gneiss outcropping at the central portion trending N-S direction. The rocks are medium to coarse grained texture and leucrocratic-melanocratic in colour (Plate II). They are slightly foliated at the southern area but highly foliated towards the north. This foliation, also called gneissose foliation, is characterized by a banded appearance caused by segregation of ferromagnesian minerals from quartzo-feldspathic minerals in a discontinuous bands or lenses (Silas, 2019). Just like the migmatite, the gneiss is highly jointed, majorly along NE direction. The aplite vein (striking N58^o) cross cutting the gneiss have been displaced by N334^o fault (Plate II). This is a sinistral strike slip fault.

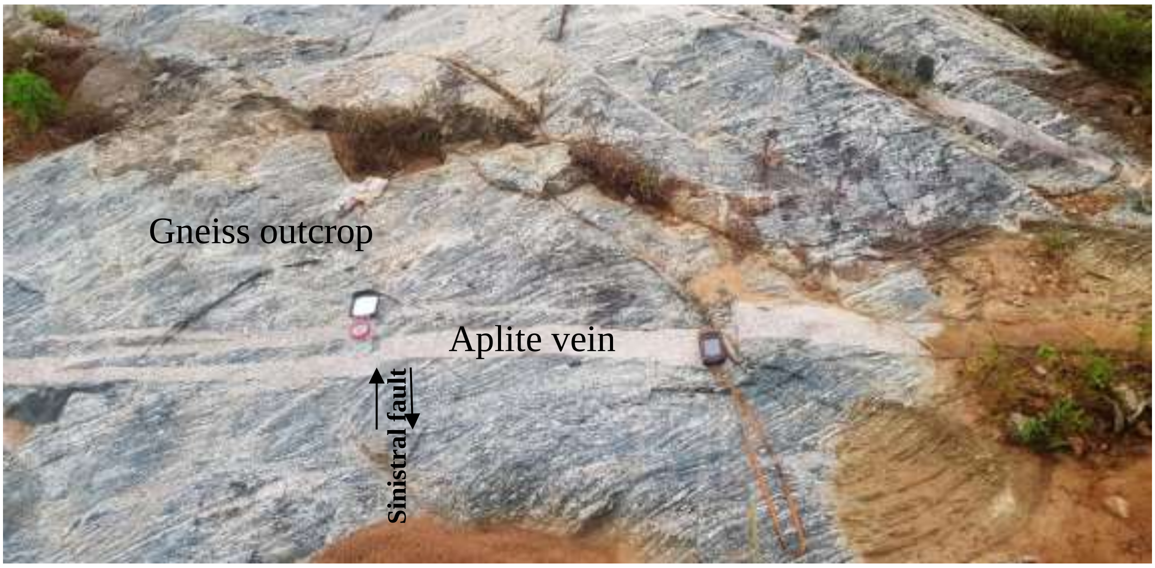

Plate II: Aplite veins (displaced by a strike slip sinistral fault) on grey coarse-grained gneiss. Location coordinates (N 08° 41' 38.6", E 08° 32' 31.0", 238m ASL).

4.1.3 Biotite Granite

Over 50% of the study area is underlain by biotite granite. They are highly weathered, fractured (with dominant NW-SE joint direction) and occur as medium to coarse-grained rocks (Plate III). It is commonly grey in colour but towards the southern part of the area, it occurs as pink granite. The quartzite ridge containing the Pb-Zn ore deposit is hosted by the biotite granite, competent enough to support underground mining practiced by a Chinese mining company in the area. On outcrop scale, they are composed of quartz, feldspar, biotite with minute hornblende. In some areas, the granites have undergone chloritic alteration, expressed by the greenish striations on its surface

Plate III: Weathered and jointed (marked by yellow lines) medium-coarse grained biotite granite outcrop. Location coordinates (N 08° 41' 04.0", E 08° 33' 02", 210m ASL).

4.1.4 Quartzite

This exists on the central part of the study area as a ridge striking N340° and dipping 87°W. It is 10-50m wide outcropping intermittently along the strike direction. It is exposed about 1.5 km strike length within the study area (Plate IV and V). It is highly fractured majorly along NNE-SSW and NNW-SSE direction.

Plate IV: Quartzite outcrop (15m wide) striking N340°. Location coordinates (N 08° 40' 57.3", E 08° 32' 50.0", 222m ASL)

Plate V: Quartzite outcrop excavated for rock aggregates.
Location coordinates (N 08° 40' 56.4", E 08° 32' 45.2", 223m ASL)

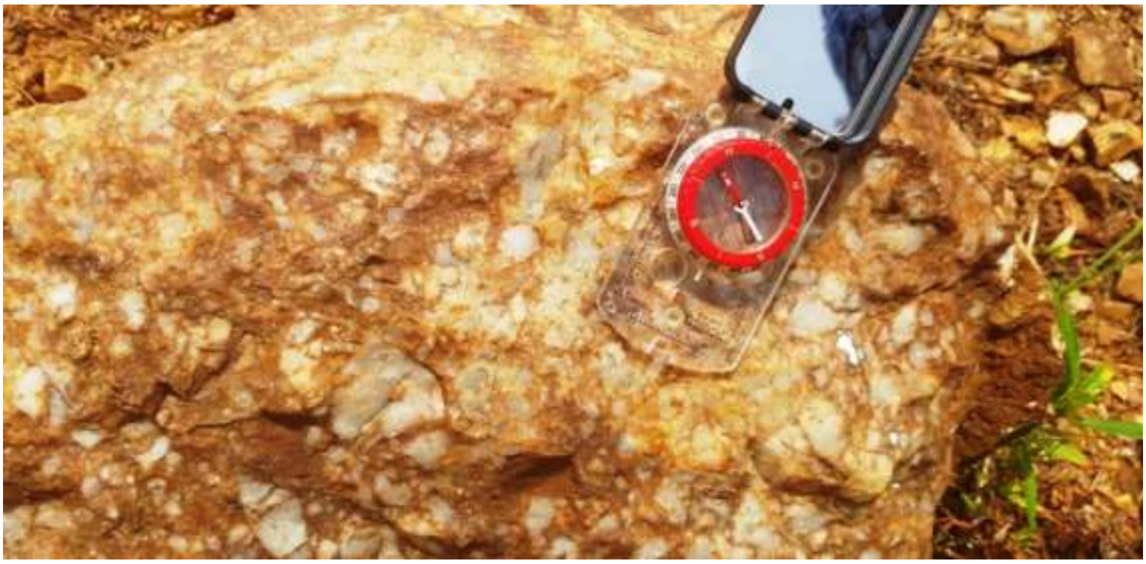

Plate VI: Quartzite is composed majorly of quartz crystals.

4.1.5 Rhyolite

Outcrops of rhyolite are exposed on a ridge at the north western part of the study area. It is porphyritic, with phenocrysts of quartz and feldspar in a glassy to microcrystalline groundmass (Plate VII). It is highly weathered with superficial clay deposited around the outcrop.

Plate VII: Highly weathered rhyolite with phenocrysts of quartz and feldspar in a microcrystalline groundmass.
Location coordinates (N 08° 41' 16.7", E 08° 32' 53.2", 223m ASL).

4.1.6 Dolerite

Plate VIII: Dolerite dyke 0.5m wide cross cuts highly weathered and jointed granite outcrop. (Location coordinates: N08° 42' 02.4", E08° 32' 33.9", 281m ASL)

Dolerite dykes (0.5-1 m wide, striking NE-SW) were observed as intrusions on the migmatites and biotite granites in the study area (Plates I and VIII respectively). They are melanocratic in colour and medium-fine grained in texture. Mineralogically, it is composed of pyroxene, plagioclase and few quartz grains.

4.1.7 Structural measurement

Apart from joints observed on most of the outcrops in the area, strike-slip sinistral faults displacing aplite veins were observed on the gneiss outcrops in the study area (Plate II). However, the most prominent joint direction on the granite and gneiss in the area is NE-SW trend (Figure 4.2). This supports the structural measurement by Silas (2019) close to the area.

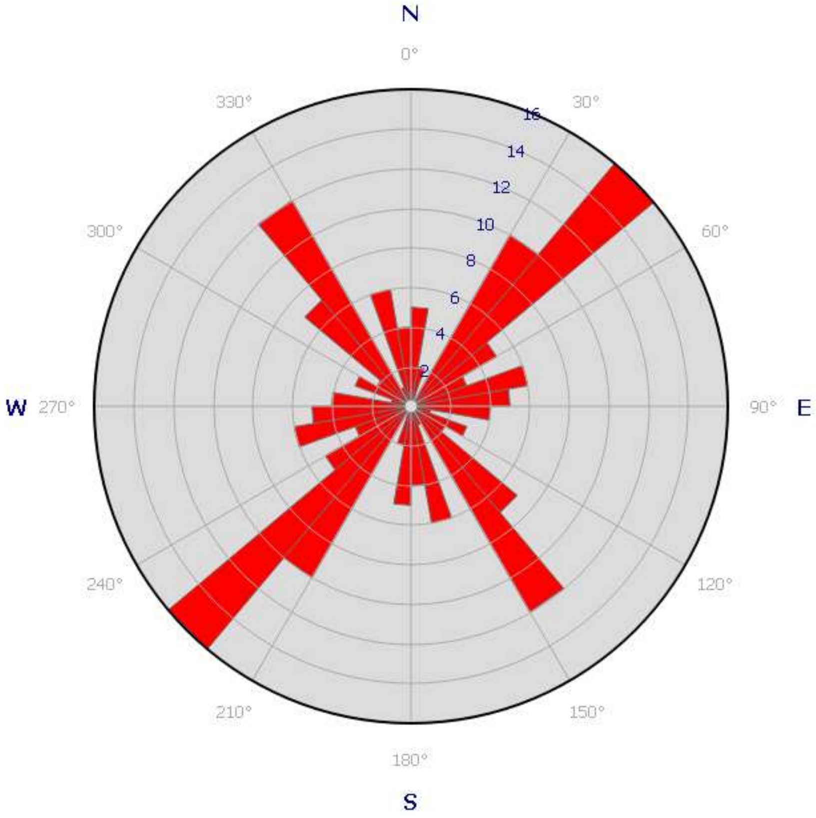

Figure 4.2: Rose diagram of the dominant joint direction in the granites and gneiss of the study area.

4.2 PTEs Concentration in the Study Environment

Concentration (ppm) of selected PTEs (Pb, Zn, Cu, Cd, Cr and As) which are commonly found in Pb-Zn mining environment were determined in the soils, stream sediments, groundwater and rocks of the study area.

4.2.1 Rocks

High concentration of Pb and Zn were detected in quartzite and biotite granites (Table 4.1) because of their mineralisation in veins and dissemination respectively. While Pb is undetected in dolerite dyke in the area, Zn concentration is widely distributed in the rocks of the study area. The presence of Pb, Zn, Cu and Cr in considerable high concentration in some of the rocks away from the mines is an indication of a geogenic source. Weathering and erosion processes may have caused dispersion into soils leading to contamination especially close to the mines.

Table 4.1: PTEs Concentration in Rocks of Alizaga

Sample ID	**COORDINATES**		**LITHOLOGY**	**PTEs Concentration (ppm)**				
				Pb	**Zn**	**Cu**	**Cr**	**Cd**
AGR 001	8° 41' 34.17" N	8º 32' 37.81" E	Quartzite with spots of sulphides	778	321	<DL	<DL	0.29
AGR 002	8° 41' 17.33" N	8º 33' 04.43" E	Medium grained dolerite dyke	<DL	402	160	342	0.48
AGR 003	8° 41' 33.04" N	8º 32' 01.06" E	Weathered Rhyolite	487	884	80	68	0.30
AGR 004	8° 41' 26.91" N	8º 32' 17.53" E	Coarse grained gneiss	97	321	<DL	<DL	<DL
AGR 005	8° 42' 00.14" N	8º 32' 30.35" E	Medium grained granite with chloritic alterations	487	402	<DL	68	<DL
AGR 006	8° 41' 18.24" N	8º 33' 02.63" E	Coarse grained biotite granite	97	161	<DL	<DL	<DL
AGR 007	8° 41' 56.36" N	8º 33' 24.74" E	Medium-coarse grained biotite granite	1168	1526	<DL	68	0.50

<DL means concentration below the detection limit of the analytical method used

4.2.2 Soils

Except for Cr concentration, Pb, Zn, Cu and Cd were very high within the vicinity of the mines about 300 m radius. Pb and Zn are widely distributed in the soils, within and away from the mining site.

i. Lead

Pb concentration ranges from 12651-83299 mg/kg in the soils within 300 m radius of the mines. This is where galena (PbS) is mined, sorted and sometimes washed. The top soil here have been covered by galena and associated tailings in most parts. This is responsible for the high concentrations recorded in soil. In other parts of the study area, including cultivated farmlands, schools and settlements, Pb concentration ranges from 97-3114 mg/kg and an average concentration of 605 mg/kg. The average concentration is higher when compared to any of the referenced values by (Bowen, 1979) and Ministry of the Environment, Finland (MEF, 2007). They are also higher when compared with the work of Obiora *et al.* (2016) where they assessed the level of contamination of soils caused by mining activities in Ameka, Enyigba and Alibaruhu Pb-Zn mining district, SE Nigeria. Their results indicated Pb concentration of 2509 mg/kg and 114.5 mg/kg close and away from the mining district respectively. Lead is non-essential for plants and animals and it is toxic by ingestion, being a cumulative poison (MacFarlane and Burchett, 2002).

ii. Zinc

Zn concentration ranges from 7230-55352 mg/kg within 300 m radius of the mines and 80-3213 mg/kg with an average of 451 mg/kg outside of the mine (Table 4.2). These concentrations are higher when compared to the referenced values (Bowen, 1979 and MEF, 2007).

Table 4.2: PTEs Concentration in Soil of the Study Area

	Sample ID	**LOCATION NAME**	**LOCATION COORDINATES**		**PTEs CONCENTRATION(mg/kg)**				
					Pb	**Zn**	**Cu**	**Cr**	**Cd**
Samples 300m Radius of the Mines	AGS 001	Mine site road	8° 41' 36.1" N	8° 32' 38.6" E	12651	7230	160	<DL	2.37
	AGS 002	Around the processing area	8° 41' 33.6" N	8° 32' 41.1" E	83299	55352	1438	68	52.06
	Average Concentration within the mining area				**47975**	**31291**	**799**	**68**	**27.21**
Samples outside of 500m Radius of the Mines	AGS 003	Settlement	8° 41' 29.4" N	8° 32' 47.6" E	195	80	<DL	<DL	0.09
	AGS 004	Eggon com sec sch.	8° 41' 28.8" N	8° 33' 02.0" E	3114	884	80	68	0.43
	AGS 005	Cultivated land	8° 41' 08.9" N	8° 33' 05.1" E	97	241	<DL	<DL	0.34
	AGS 006	Cultivated land	8° 41' 12.3" N	8° 32' 48.0" E	2141	3213	80	<DL	0.35
	AGS 007	Cultivated land	8° 41' 29.0" N	8° 32' 36.3" E	1752	241	80	68	0.04
	AGS 008	Cultivated land	8° 41' 28.0" N	8° 32' 18.5" E	195	321	<DL	<DL	0.15
	AGS 009	Cultivated land	8° 41' 28.4" N	8° 32' 02.6" E	584	562	80	68	0.23
	AGS 010	Cultivated land	8° 41' 11.5" N	8° 32' 03.2" E	389	321	80	137	0.48
	AGS 011	Cultivated land	8° 41' 12.3" N	8° 32' 20.6" E	195	161	<DL	<DL	0.03
	AGS 012	Cultivated land	8° 41' 13.0" N	8° 32' 35.7" E	389	241	80	1916	1.78
	AGS 013	Cultivated land	8° 40' 56.4" N	8° 32' 52.3" E	681	402	80	205	0.27
	AGS 014	quartzite quarry	8° 40' 55.1" N	8° 32' 16.0" E	876	80	80	68	0.22
	AGS 015	Cultivated land	8° 40' 40.4" N	8° 32' 04.8" E	195	161	80	137	0.37
	AGS 016	Cultivated land	8° 40' 40.0" N	8° 32' 35.5" E	487	723	<DL	68	0.02
	AGS 017	Cultivated land	8° 40' 43.0" N	8° 33' 07.7" E	292	321	<DL	<DL	0.06
	AGS 018	Settlement	8° 42' 02.6" N	8° 32' 35.4" E	195	161	<DL	68	0.12
	AGS 019	Cultivated land	8° 41' 44.1" N	8° 32' 03.1" E	292	402	80	68	0.62
	AGS 020	Settlement	8° 41' 44.6" N	8° 32' 19.5" E	584	402	80	274	0.77
	AGS 021	Cultivated land	8° 41' 45.0" N	8° 32' 35.9" E	389	402	80	137	0.43
	AGS 022	Cultivated land	8° 41' 45.1" N	8° 32' 51.7" E	487	562	160	274	0.88
	AGS 023	Cultivated land	8° 42' 16.1" N	8° 32' 53.5" E	97	161	80	<DL	0.31
	AGS 024	Cultivated land	8° 42' 17.0" N	8° 33' 24.3" E	195	161	80	68	0.07
	AGS 025	Cultivated land	8° 41' 43.1" N	8° 33' 08.7" E	97	161	80	<DL	1.86
	Minimum concentration out of the mines				97	80	80	68	0.02
	Maximum concentration out of the mines				83299	55352	1438	1916	52
	Average concentration out of the mines				605	451	85	242	0.43
	Background Concentration (Bowen, 1979)				35	90	30	70	0.35
	Threshold Value (MEF, 2007)				60	200	100	100	1
	Lower Guideline Value (MEF, 2007)				200	250	150	200	10
	Higher Guideline Value (MEF, 2007)				750	400	200	300	20

<DL means concentration below the detection limit of the analytical method used.

They are also higher when compared with the study by Obiora *et al.* (2016) in Ameka, where their result of Zn concentration in soil were 583.13mg/kg and 442.5 mg/kg close and away from the mining area respectively. Although Zn is an essential growth element for plants and animals, it can be toxic at concentration above 250 mg/kg for agricultural soil or 400 mg/kg for industrial soil (MEF, 2007).

iii. Copper

Average concentration of Cu in the present study is 799 mg/kg and 85 mg/kg within 300 m radius of the mines and away from the mines respectively (Table 4.2). This is also higher when compared to background values by Bowen (1979) and guideline values by Ministry of the Environment, Finland MEF (2007). It is also higher when compared to similar work by Obiora *et al.* (2016) in Enyigba, where their results showed an average concentration of 63.7 mg/kg for Cu close to the mining district. Copper and chromium pollution in soil could result from weathering of parent rocks containing copper and chromium bearing minerals as well as application of agro-chemicals such as fungicides and pesticides. Exposure to high concentration of these metals can result in serious health consequences such as lung carcinoma and transitory fever (Pascual *et al*., 2004).

iv. Chromium

Interestingly, average concentration of Cr in the soil of the present study is higher away from the mining area than within the mines. In this work, average Cr concentration is 68 mg/kg and 242 mg/kg within and away from the mining area respectively. This is similar to the work by Obiora *et al.* (2016) in Alibaruku Pb-Zn mining district, where average concentration of Cr in soils close and away from the mines were 87.56 mg/kg and 95.33 mg/kg respectively. In Table 4.2, the average concentration of Cr within 300 m of the mines in the current study is lower when compared to referenced guidelines Bowen (1979) and MEF (2007). However, outside of the mines, average concentration of Cr is only lower than the higher guideline value of 300 mg/kg for industrial sites (MEF, 2007). This means that, although there is need to monitor Cr concentration in the study area, they are mostly below contamination limits, especially within the mines.

v. Cadmium

Average Cd concentration in the soil of the present study is 27 mg/kg and 0.43 mg/kg within and away from the mines respectively. The corresponding Cd concentration in the work of Obiora *et al.* (2016) is lower (3.47 mg/kg) closer to the mines but higher (1.97 mg/kg) away from the mines. Average Cd concentration within 300 m radius of the mines site is higher than the referenced standards (Bowen, 1976 and MEF, 2007). This showed higher contamination level of Cd within 300 m radius of the mines. However, average Cd concentration away from the mines is lower than the threshold, lower guidelines and higher guidelines values respectively (MEF, 2007). This is also showed no recorded current Cd contamination outside of the mines.

Generally, the concentrations of studied PTEs in the present study are in the order Pb>Zn>Cu>Cr>Cd within the mining site and Pb>Zn>Cr>Cu>Cd away from the mining site. Apart from Cd, the average concentration of the PTEs is higher (Table 4.2) when compared to guidelines by Ministry of the Environment, Finland (MEF, 2007) and Background concentration in soils by Bowen (1979).

4.2.3 Stream sediments

The concentration of PTEs in stream sediments showed a decreasing value away from the mines. The highest concentration of PTEs was detected in samples AGSS 007 and AGSS 008 (Table 4.3). They were taken from the stream sediments 100 m and 200 m respectively away from the processing area where tailing were directly discharged.

Table 4.3: PTEs Concentration in Stream Sediments of Alizaga.

Sample ID	LOCATION COORDINATES		PTE Concentration (mg/kg)				
			Pb	**Zn**	**Cu**	**Cr**	**Cd**
AGSS 001	8° 41' 03.4" N	8° 33' 09.5" E	195	161	80	137	<DL
AGSS 002	8° 41' 36.3" N	8° 33' 15.0" E	195	161	<DL	<DL	<DL
AGSS 003	8° 42' 07.6" N	8° 32' 51.7" E	195	161	<DL	<DL	<DL
AGSS 004	8° 40' 55.3" N	8° 32' 42.8" E	3114	964	80	68	2
AGSS 005	8° 40' 41.8" N	8° 32' 23.5" E	97	80	<DL	68	<DL
AGSS 006	8° 41' 20.7" N	8° 32' 39.8" E	97	241	<DL	<DL	2
AGSS 007	8° 41' 29.1" N	8° 32' 36.7" E	7493	3856	240	68	3
AGSS 008	8° 41' 35.3" N	8° 32' 37.9" E	58776	107491	2397	68	93
Maximum			58776	107491	2397	137	93
Minimum			97	80	80	68	2
Average Concentration close to mines			33135	55674	1319	68	48
Average Concentration >300m away from the mines			648	295	80	137	2
Threshold Effect Concentration (TEC)			35.80	121.00	32.60	43.40	0.99
Probable Effect Concentration (TEC)			128.00	459.00	149.00	111.00	4.98

<DL means concentration below the detection limit of the analytical method used.

Average concentration for the selected PTEs (Pb, Zn, Cu, Cr and Cd) from stream sediment samples (AGSS 007 and AGSS 008) within 300m of the mines are higher than the Threshold Effect Concentration and Probable Effect Concentration) by USEPA (2002) referenced in this work (Table 4.3). This means that harmful effects are likely to be observed by these concentrations. Away from the mines (> 300m), average Pb concentration in the stream channel samples is also above the referenced concentrations (USEPA, 2002) and as a result harmful effects are likely to be observed. However, average Zn, Cu, Cr and Cd concentration of stream sediments samples taken more than 300m away from the mines is above Threshold Effect Concentration but below Probable Effect Concentration by USEPA (2002). This means that, even as these concentrations are below where harmful effects are likely to be observed, there is still need for continuous monitoring because of their considerable levels.

4.2.4 Correlation Analysis of the PTEs Concentration in Soils and Stream Sediments

The correlation matrix among the studied PTEs showed a relationship among them. Pb-Zn-Cu-Cd have a significant positive correlation (Table 4.4). This suggests that the elements in association simultaneously increase or decrease in concentrations in the soils, and the release of a particular element in the association may also cause the release of the other. It could also mean a shared pollution sources leading to the release of the elements.

Table 4.4: Correlation matrix of PTEs in soils and stream sediments in the study area.

		Pb	**Zn**	**Cu**	**Cr**	**Cd**
Soils	**Pb**	1.0000				
	Zn	0.9987	1.0000			
	Cu	0.9872	0.9875	1.0000		
	Cr	-0.0579	-0.0586	-0.0150	1.0000	
	Cd	0.9920	0.9936	0.9903	-0.0186	1.0000
		Pb	**Zn**	**Cu**	**Cr**	**Cd**
Stream sediments	**Pb**	1.0000				
	Zn	0.9955	1.0000			
	Cu	0.9988	0.9977	1.0000		
	Cr	0.1711	0.1492	0.1893	1.0000	
	Cd	0.9953	0.9998	0.9973	0.1443	1.0000

However, a weak negative correlation was observed between Cr and other PTEs (Pb, Zn, Cu and Cd) (Table 4.4). This may be due to contribution from other anthropogenic source such as domestic waste disposal and use of agricultural chemicals such as pesticides and herbicides. The results of the stream sediments also showed a strong positive correlation between Pb-Zn-Cu-Cd while Cr showed a weak positive correlation.

4.2.5 Groundwater

PTEs in the soil and stream sediments were also detected in the groundwater (wells and underground mine). In Table 4.5, average pH (6.0) of shallow wells is acidic to slightly acidic and below the recommended standard of 6.5-8.5 by WHO (2022) and NSDWQ (2007). However, groundwater from deep borehole (about 150m) sited at the mines and underground mines have neutral pH values (7.39 and 7.28 respectively).

Table 4.5: Physical Parameters and PTEs Concentration of Groundwater in the study Area

SAMPLE ID	LOCATION NAME	Physical Parameters				PTEs Concentration (mg/L)				
		Temp °C	**pH**	**TDS (ppt)**	**EC (mSm-^{1})**	**Pb**	**Zn**	**Cr**	**Cd**	**As**
AGW 001	Angwar Ayaba	29.1	5.95	0.05	0.09	0.25	0.34	0.32	0.36	0.3
AGW 002	Anyaku	28.4	5.54	0.1	0.17	0.23	0.32	0.4	0.82	0.86
AGW 003	Eggon community	28.2	5.86	0.04	0.07	0.33	0.63	0.69	0.12	0.78
AGW 004	Science sch.	29.3	5.42	0.04	0.07	0.23	0.22	0.58	0.67	0.41
AGW 005	Angwar Mada	29	6.36	0.06	0.1	0.13	0.08	0.41	0.3	0.25
AGW 006	Alizaga mosque	28.9	6.25	0.11	0.19	0.05	0.33	0.27	0.2	0.3
AGW 007 (Control)	Angwar makama-	28.3	6.27	0.3	0.52	0.02	0.47	0.73	0.48	0.14
AGW 008	Mine waste water	33.9	7.28	0.83	0.83	0.08	8.17	0.34	0.14	0.47
AGW 009	Site borehole	32.6	7.39	0.33	0.57	0.08	0.64	0.22	0.15	0.28
Average in shallow wells		**28.74**	**6.0**	**0.1**	**0.17**	**0.18**	**0.34**	**0.49**	**0.42**	**0.43**
NSDWQ (2007)		**27-33**	**6.5-8.5**			**0.01**	**5**	**0.05**	**0.01**	**0.2**
WHO (2022)		**27-33**				**0.01**	**3**	**0.05**	**0.01**	**0.01**

<DL means concentration below the detection limit of the analytical method used

In table 4.5, Pb concentrations in groundwater from shallow wells in the study area are higher than those from the deep borehole sited at the mines and the underground mines. This also corresponds to slightly acidic pH values in shallow wells which facilitate the release of Pb in an oxidising surface environment. In the present study, the average Pb concentration of 0.18 mg/L in shallow wells and 0.08 mg/L in mine waste water and site borehole are lower when compared to the work of Ombugus *et al.* (2021) where they evaluated the human health risks of heavy metal in wells and streams water in the same region. In their work, the average Pb concentration in shallow wells and mine waste water were 0.31 mg/L and 21.5 mg/L respectively. This is also lower for average Zn concentration in the shallow wells (0.34mg/L) and in mine waste water (8.17 mg/L) when compared to 1.31 mg/L and 6.60 mg/L by Ombugus *et al.* (2021) respectively.

Average concentration of Cr in shallow wells and that in mine waste water is 0.49 mg/L and 0.34 mg/L respectively. This is higher when compared to results of previous work where 0.25 mg/L and 0.003 mg/L were recorded respectively. However, average concentration of Cd in shallow wells and mine waste water (0.42 mg/L and 0.14 mg/L respectively) is lower when compared to the work by Ombugus *et al*. (2021) in the same region (0.93 mg/L and 0.68 mg/L respectively). Although Arsenic was not detected in the shallow wells samples of their study, it was detected in the mine waste water (0.001 mg/L). When compared to the present study, higher average concentrations of 0.43 mg/L and 0.47 mg/L were recorded for shallow wells and mine waste water respectively. This is a result of concern considering the high toxicity of arsenic.

Generally, average concentration of PTEs in shallow wells is such that Cr>As>Cd>Zn>Pb while Zn>As>Cr>Cd>Pb in site borehole and mine waste water. Apart from the control sample from Angwar Makama (1.7km north and uphill of the mines), water samples from the study area have Pb and As concentration above guidelines by WHO (2022) and NSDWQ (2007) for driking-water. However, zinc concentration in most of the water samples is below the recommended standards.

The scatter plot in Figure 4.4(a-e) compares each PTEs studied to recommended standards for drinking-water by WHO (2022) and NSDWQ (2007). Pb concentrations in the all the water samples taken are above referenced standards. Only the control sample from Angwan Makama has Pb concentration just close to the standards. Zn concentration is below the reference values (except for the mine waste water). However, chromium, cadmium and arsenic concentration is above the reference standards. Although, control sample from Agwan Makama have arsenic concentration below NSDWQ (2007) but above WHO (2022) permissible limit.

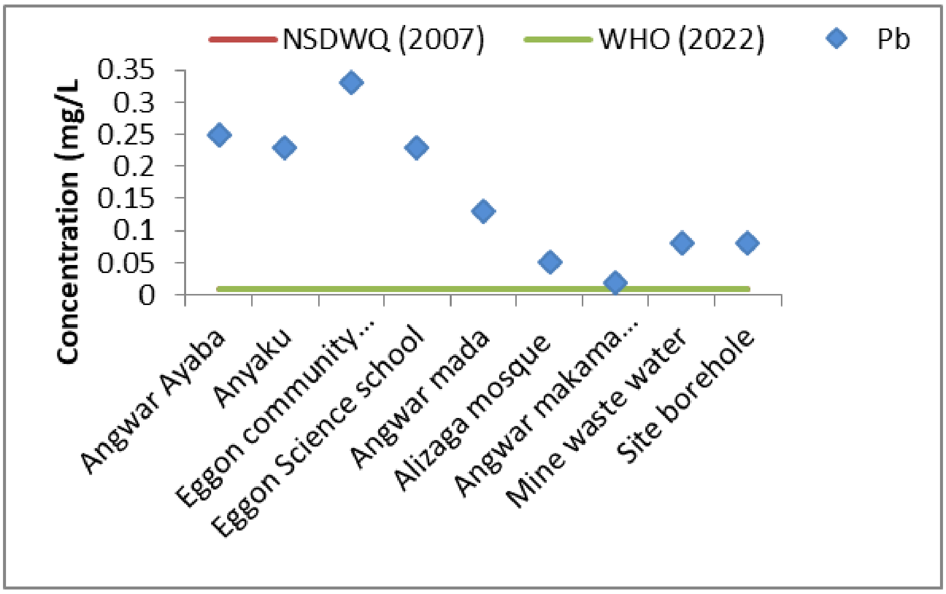

Figure 4.3a: Scatter plot of Pb concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards.

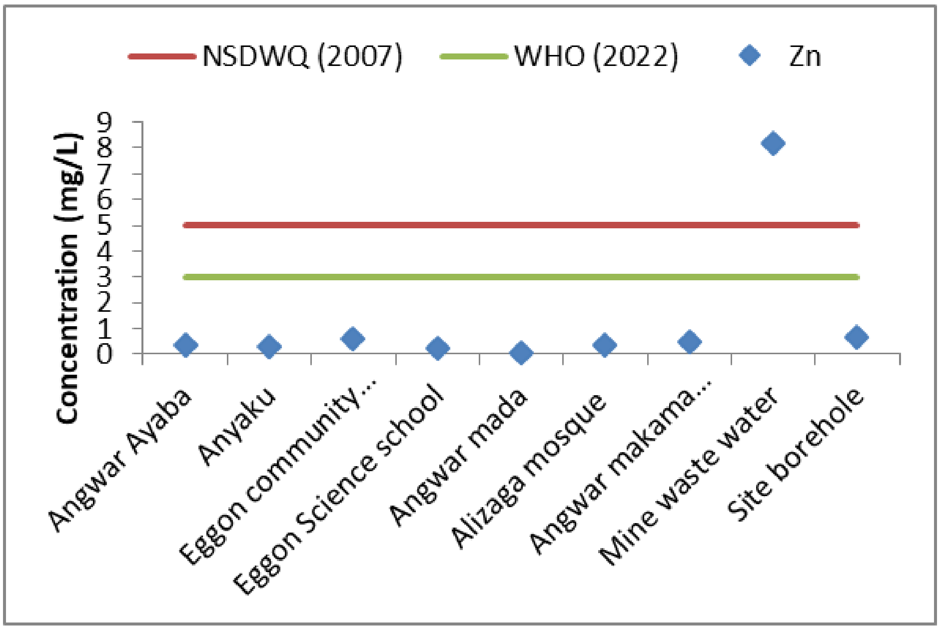

Figure 4.3b: Scatter plot of Zn concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards.

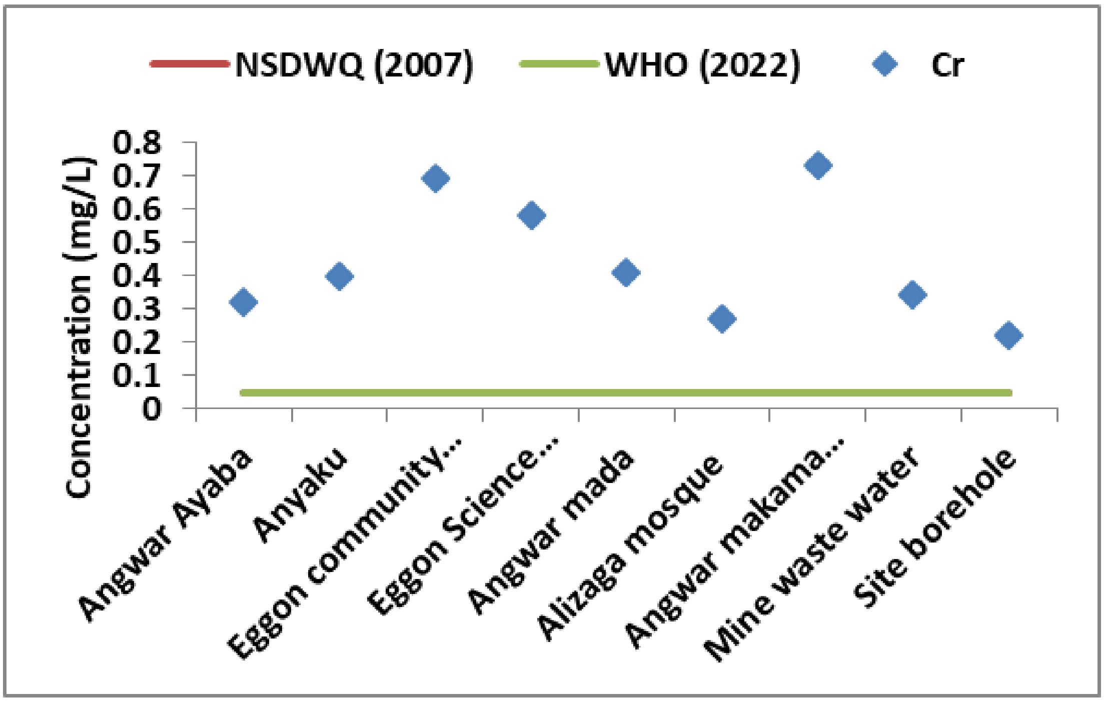

Figure 4.3c: Scatter plot of Cr concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards

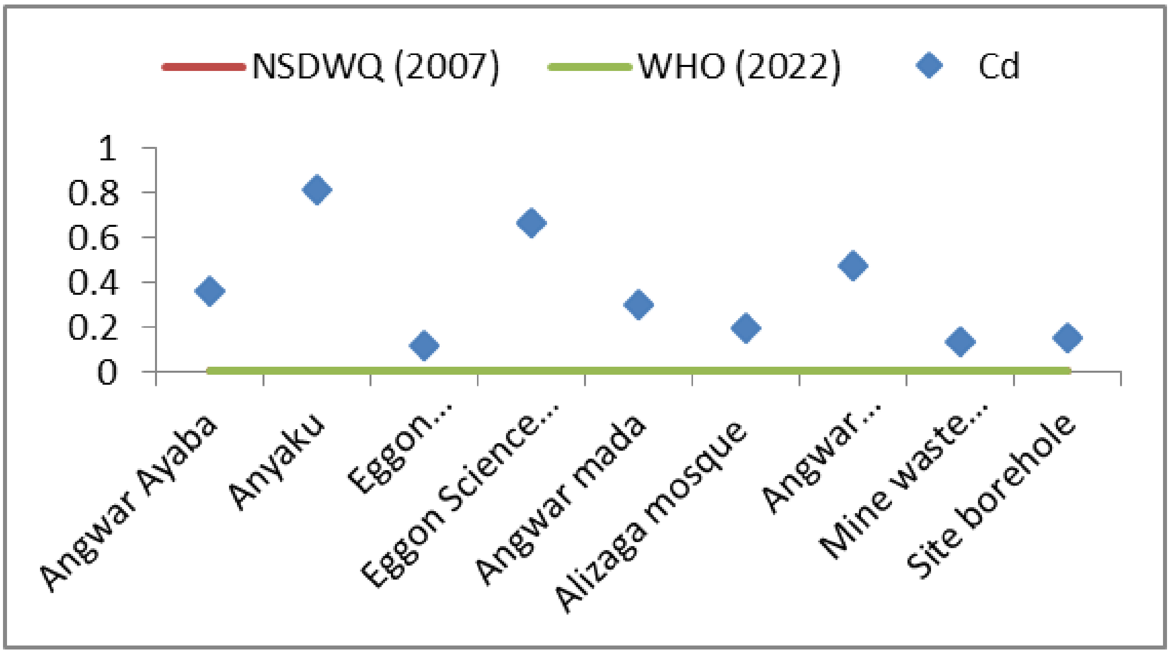

Figure 4.3d: Scatter plot of Cd concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards.

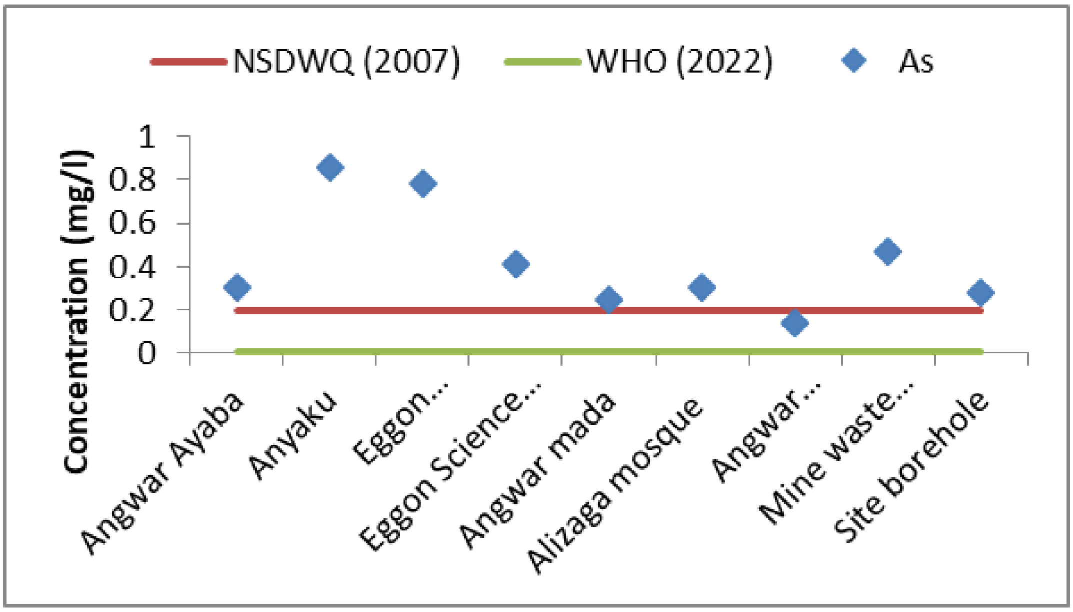

Figure 4.3e: Scatter plot of Cd concentration in groundwater of the study area compared to WHO (2022) and NSDWQ (2007) standards.

4.3 Assessment of Pollution Levels by PTEs in Soils and Stream Sediments of the Study Area.

Environmental pollution indices are Geo-accumulation Factor, Concentration Factor, Enrichment Factor and Modified Degree of Contamination and Pollution load.

4.3.1 Geo-accumulation factor

Soil within the mining area showed extreme pollution by Pb and Zn elements. This is indicated by the large size of the graduated circles and intensity in colour (Figures 4.4a(i) and 4.4a(ii) respectively). The pollution levels in surrounding cultivated lands are mostly strong to moderate for Pb and Zn.

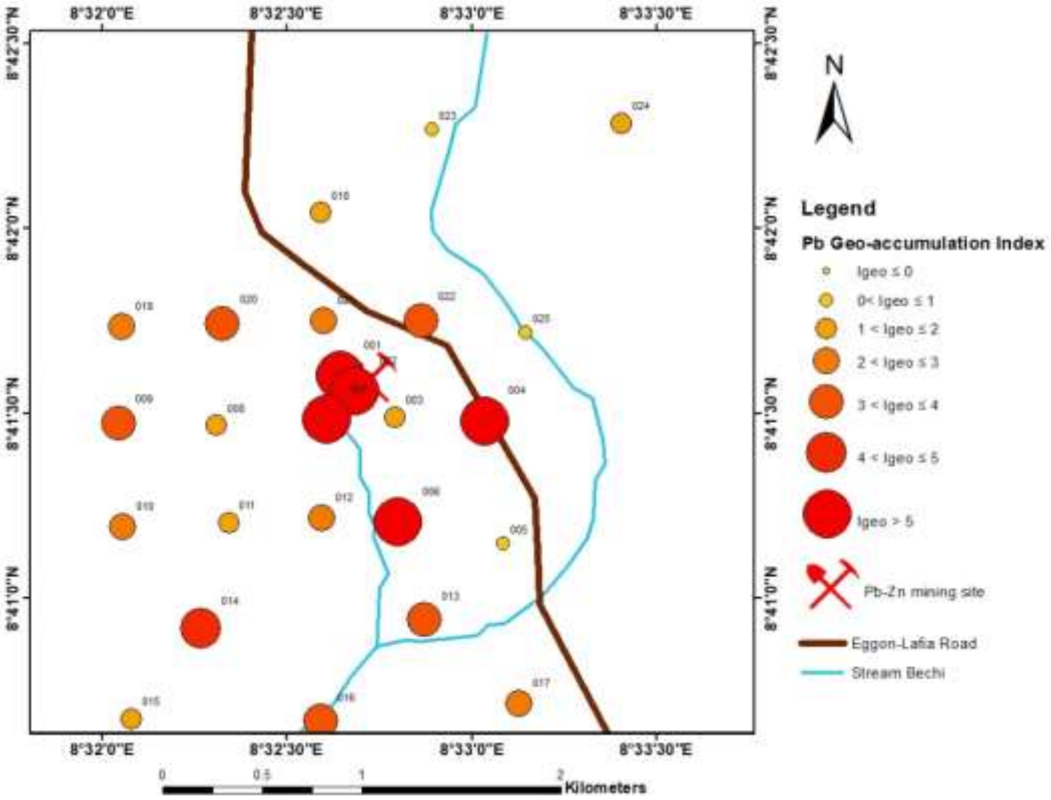

Figure 4.4a(i) Geo-accumulation of Pb in the soil of Alizaga

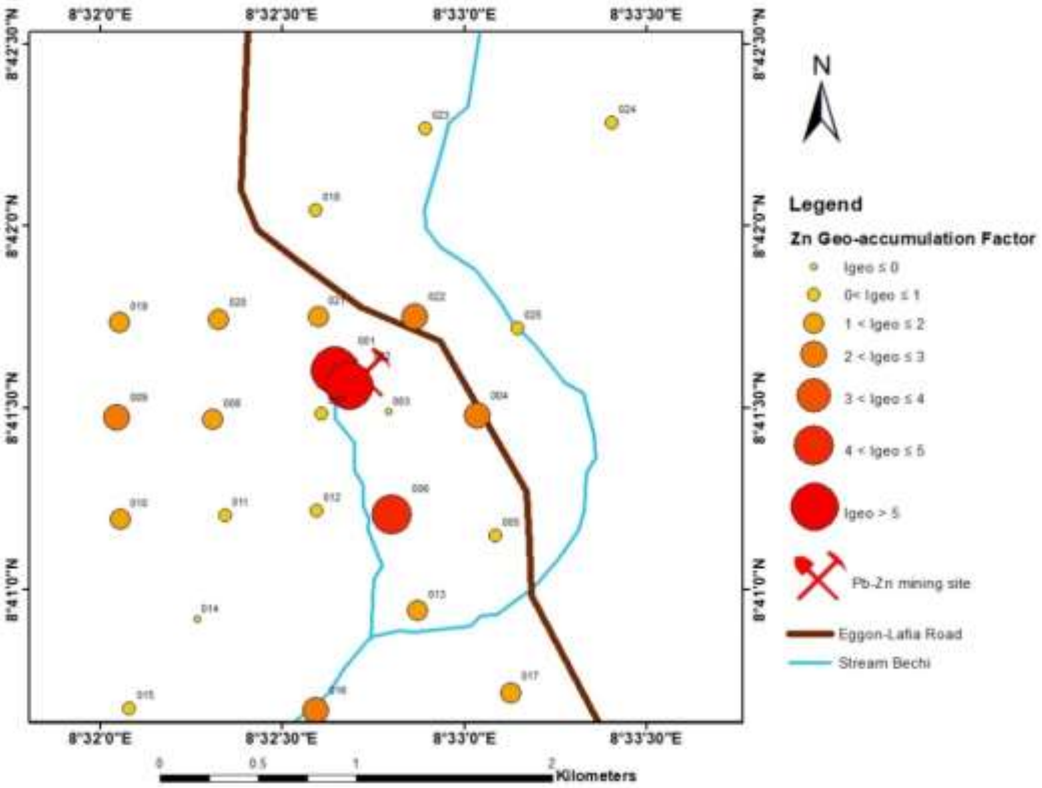

Figure 4.4a (ii) Geo-accumulation of Zn in the soil of Alizaga

Cu and Cd are extremely to strongly polluted only in the soil within the mining area while they are moderately to unpolluted in surrounding areas. This is indicated by the graduated circles having large size and high intensity only within the mines site (Figures 4.4a (iii) and 4.4a (iv) respectively). This corresponds to strongly polluted to extremely strongly polluted within the mining area but unpolluted to moderately polluted in the surrounding areas

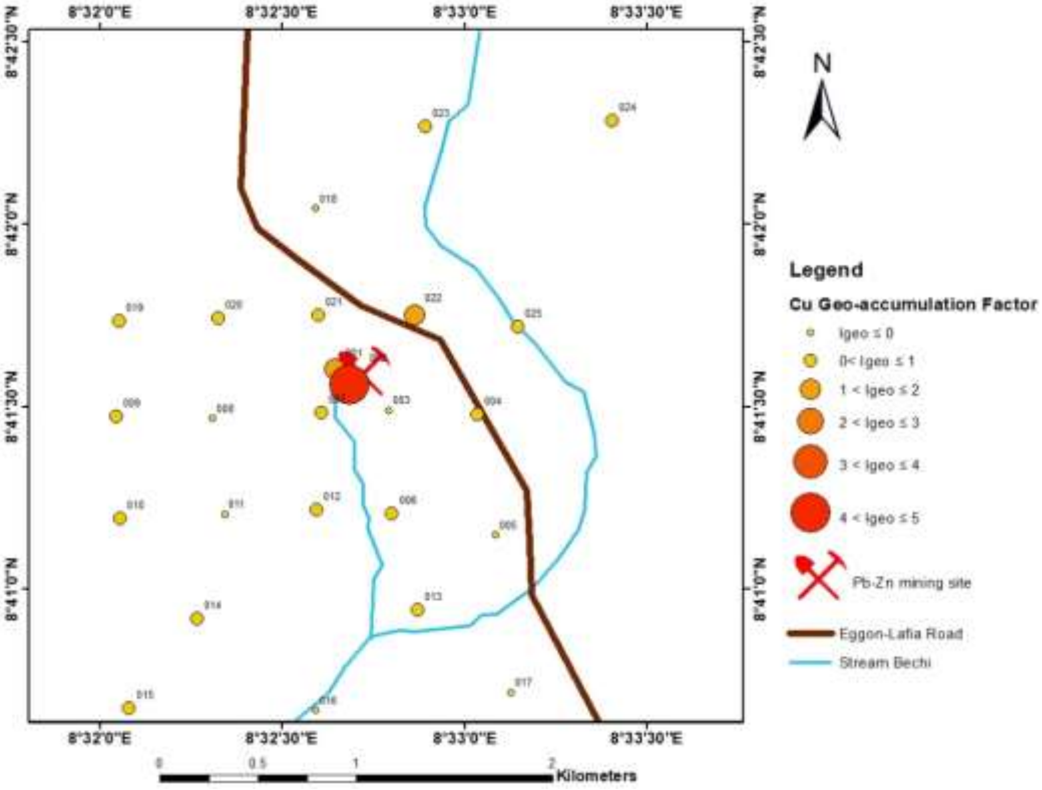

Figure 4.4a(iii) Geo-accumulation of Cu in the soil of Alizaga

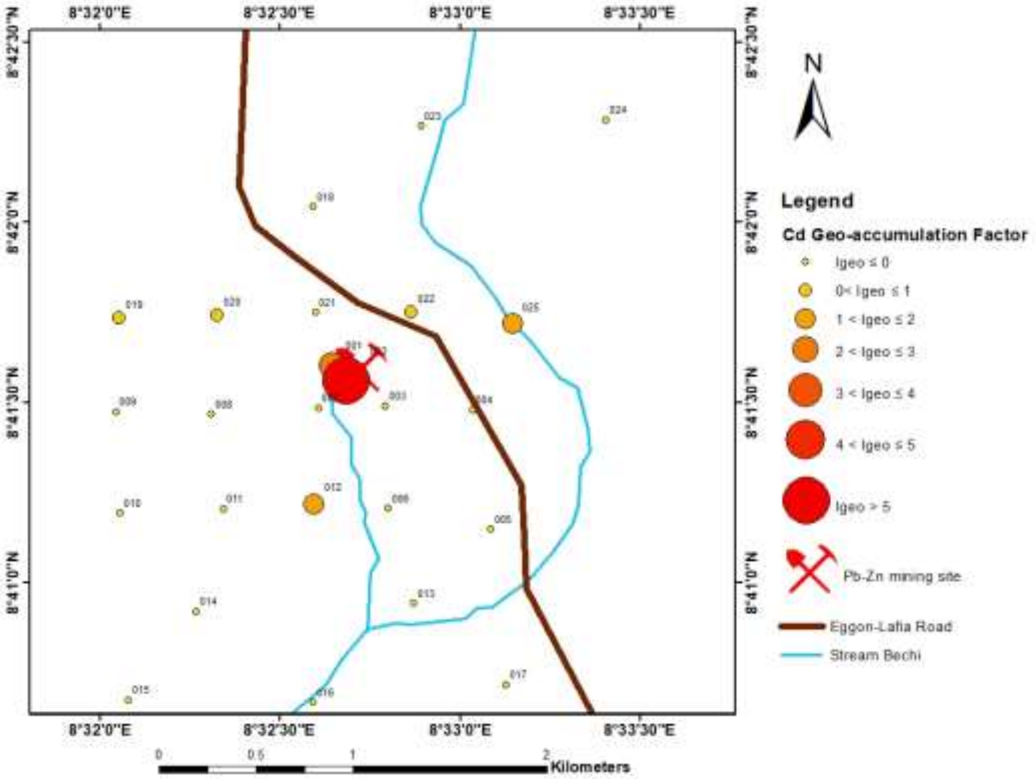

Figure 4.4a(iv) Geo-accumulation of Cd in the soil of Alizaga

However, Cr geoaccumulation factor in soil showed strong to extremely polluted only in few areas away from the mining site (Figure 4.4a(v)). The mining site is unpolluted by chromium in soil.

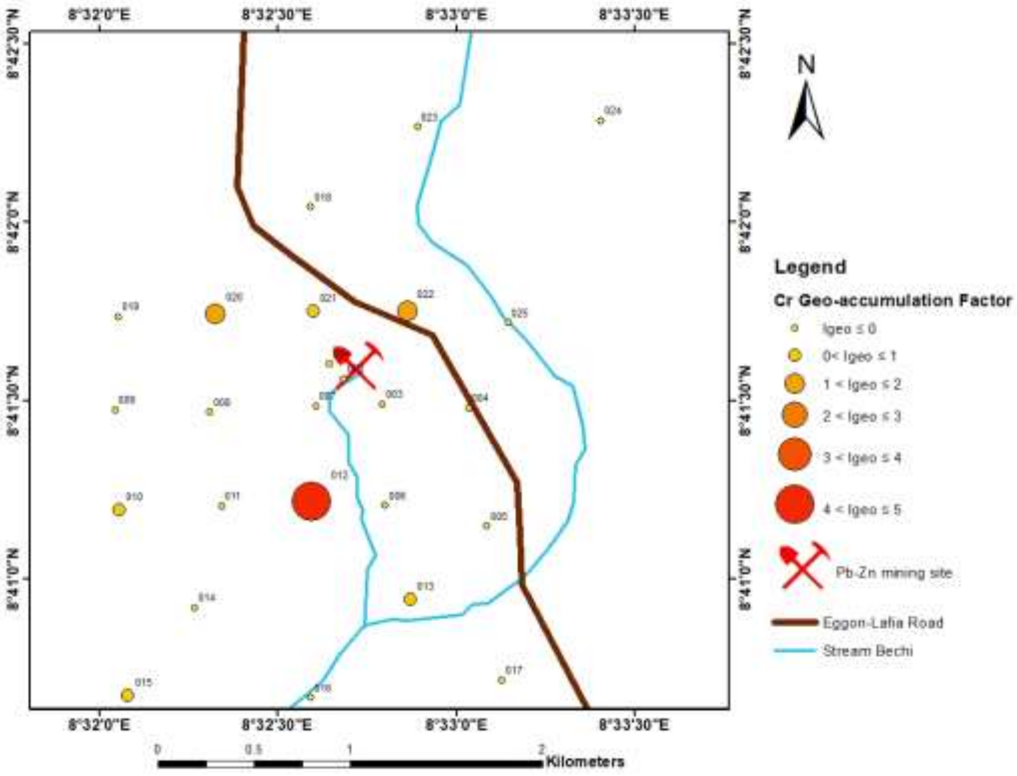

Figure 4.4a (v) Geo-accumulation of Cr in the soil of Alizaga

Apart from Cr, which is moderate to unpolluted in the stream sediments, the other PTEs studied are strongly to extremely polluted in the stream sediments close to the mining area. Assessment by Geo-accumulation Factor showed a decrease in pollution level away from their source due to dispersion. (Figures 4.4b(i-v)).

Geo-accumulation Factor in Pb and Zinc are especially pronounced in the stream sediments close to the immediate vicinity of the Pb-Zn mine site (Figures 4.4b(i) and 4.4b(ii) respectively. This can be directly related to mining and processing activities and disposal of mine waste and tailings into the stream channel.

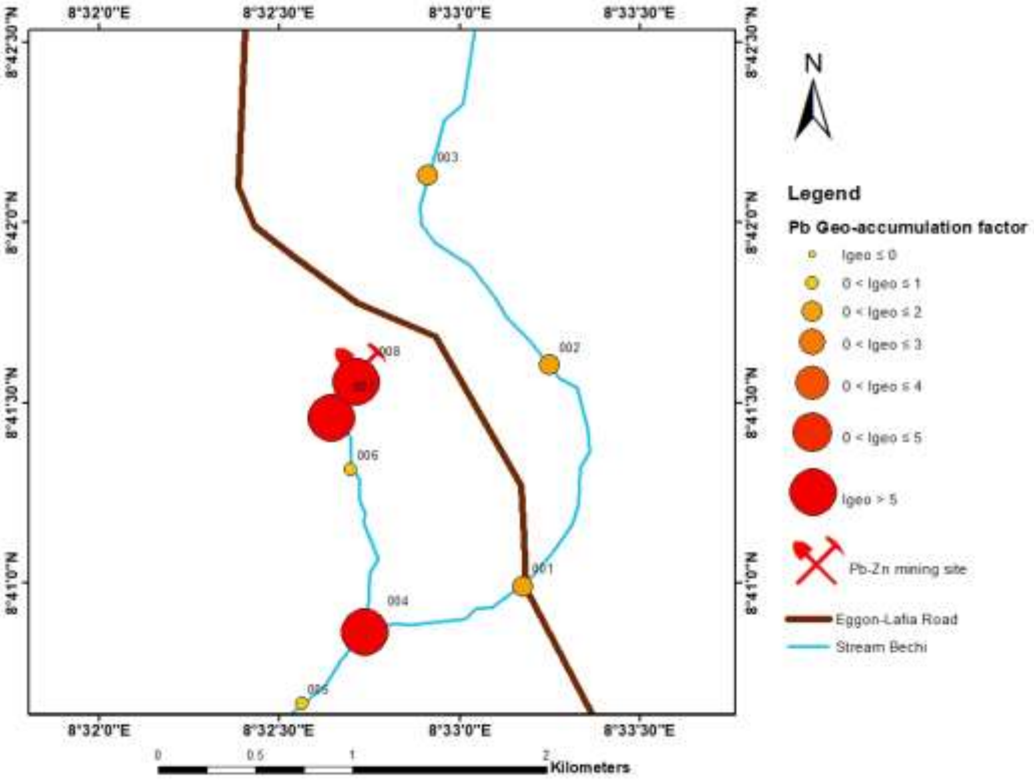

Figure 4.4b(i) Geo-accumulation of Pb in the stream sediment of Alizaga

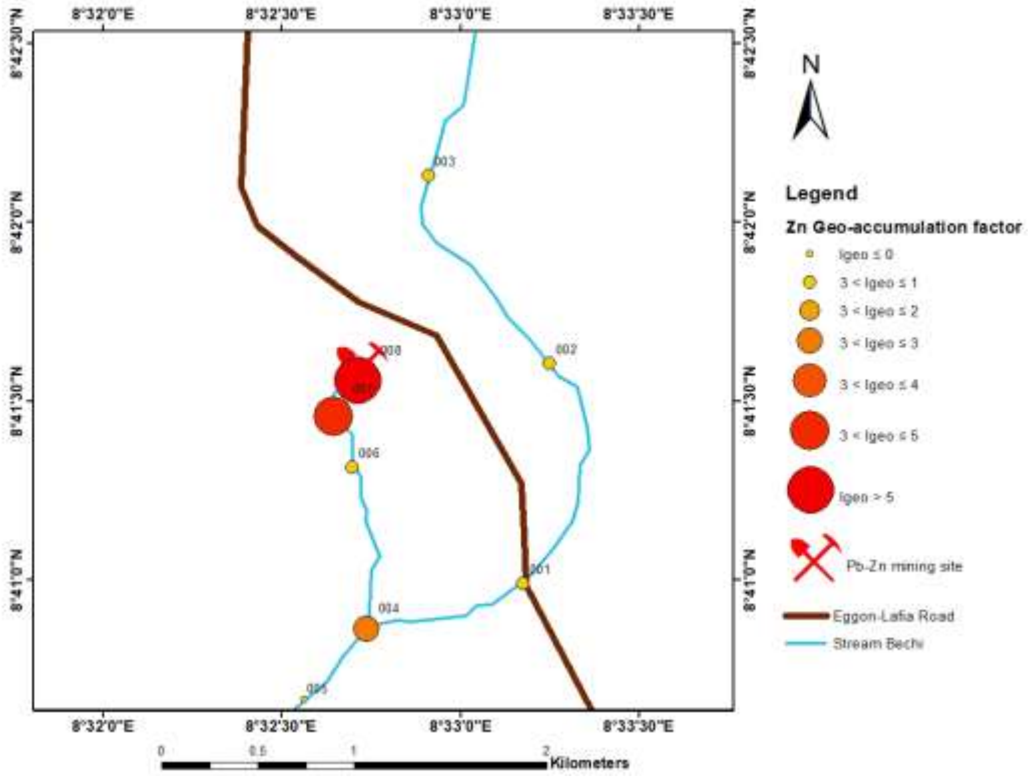

Figure 4.4b(ii) Geo-accumulation of Zn in stream sediments of Alizaga

Cu and Cd showed a high Geo-Accumulation Factor values in stream sediments closest to the mine site. That is indicated extreme and strong pollution in this part of the study area. However, there is a sharp and linear decrease from extreme pollution to unpolluted in other parts of the stream channel not within 200m radius of the mining site (Figures 4.4b(iii) and 4.4b(iv) respectively).

Again, Cr is unpolluted in the stream sediments of the study area (Figure 4.4b (v))

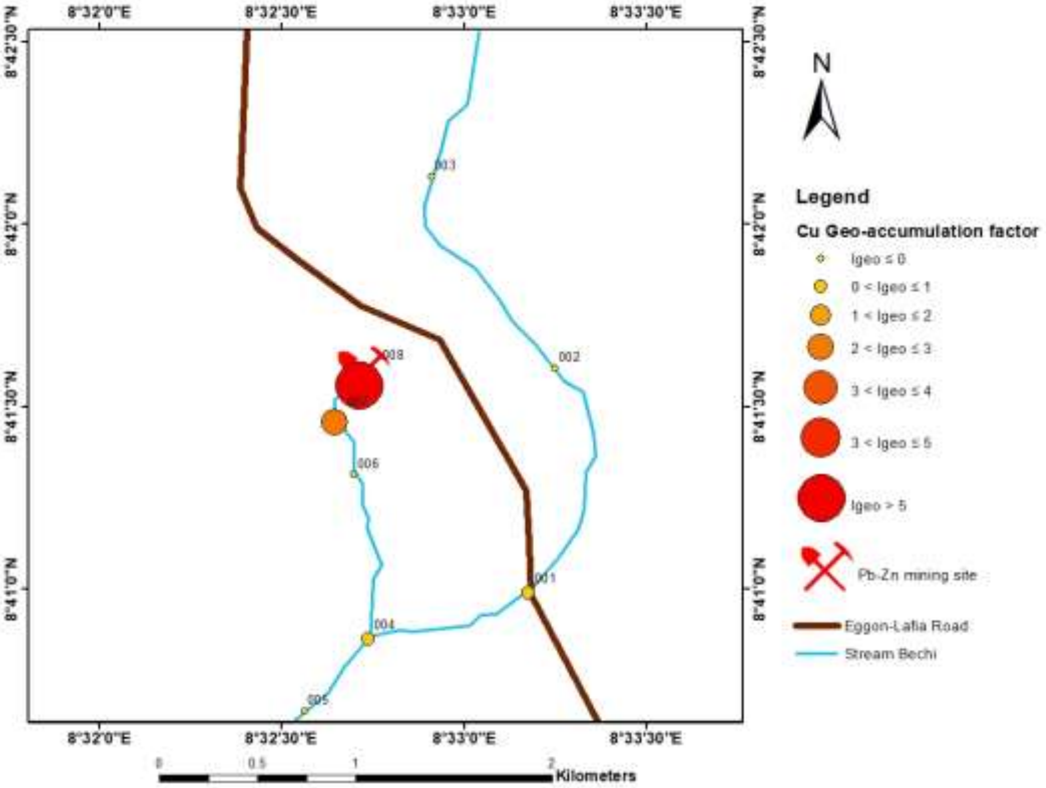

Figure 4.4b(iii) Geo-accumulation of Cu in stream sediments of Alizaga

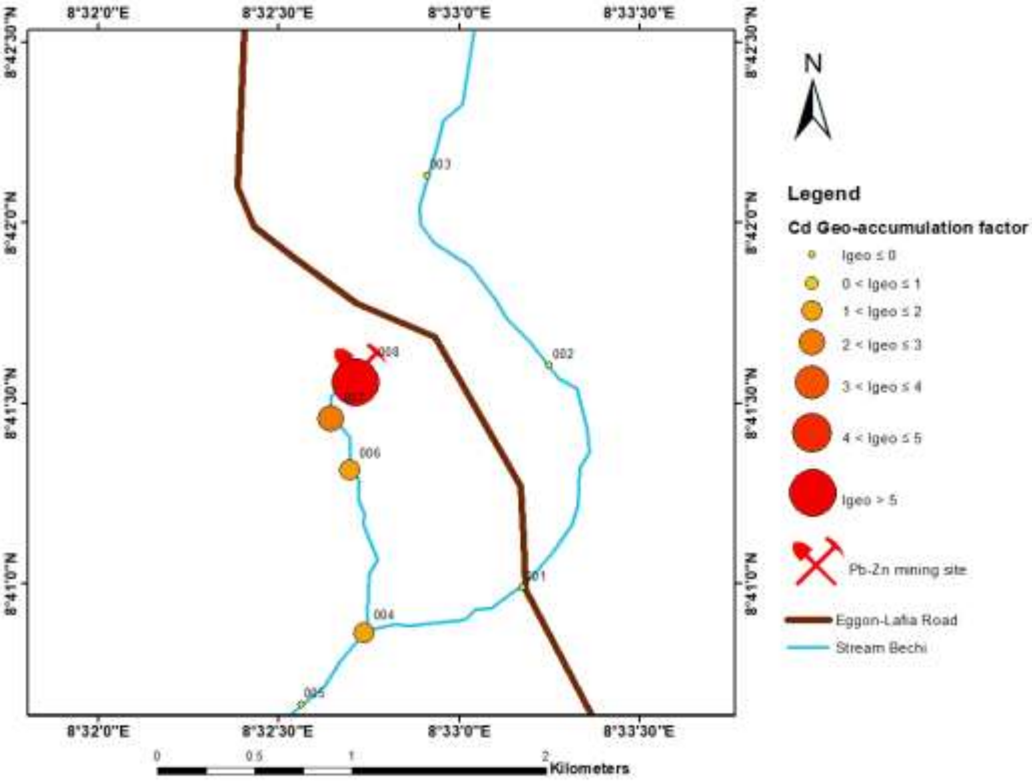

Figure 4.4b(iv) Geo-accumulation of Cd in stream sediments of Alizaga.

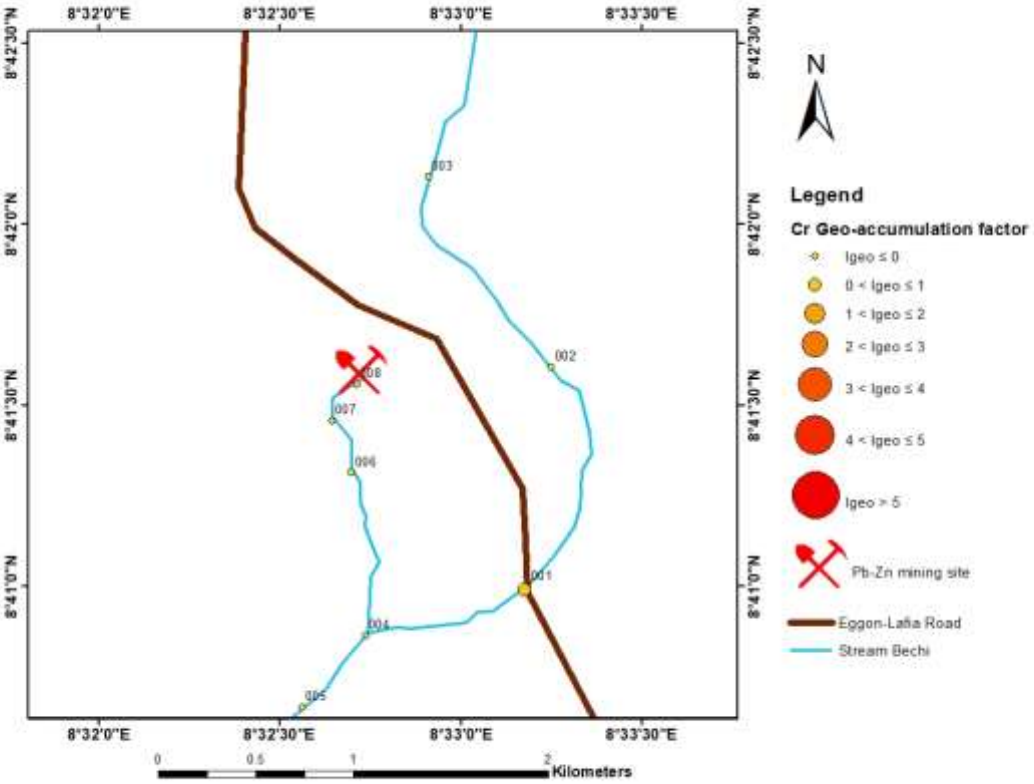

Figure 4.4b(v) Geo-accumulation of Cr in stream sediments of Alizaga

4.3.2 Contamination factor (CF)

Surface soil contamination for Pb and Zn is considerably high to moderate all over the study area (Figures 4.5a(i) and 4.5a(ii) respectively). The values for Contamination Factor, as indicated by the graduated circles and colour intensity, are high and well distributed in the area. That is, the study area mostly very high to considerable high contamination by Pb and Zn.

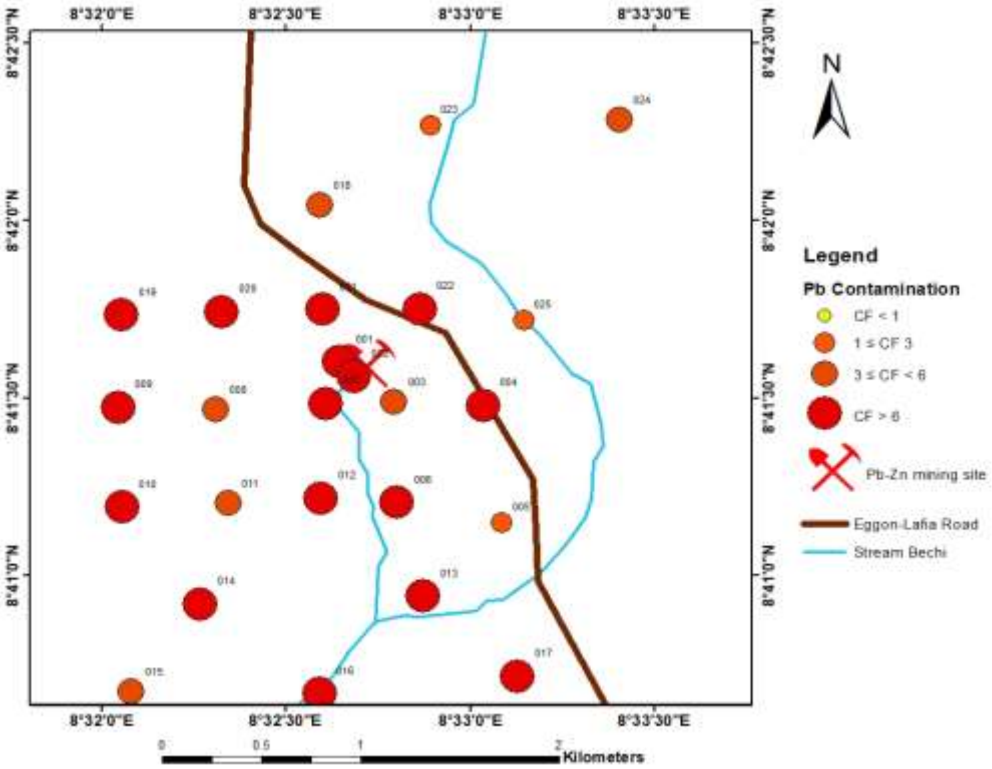

Figure 4.5a (i) Contamination by Pb in the soil of Alizaga

However, the intensity for Pb is more pronounced than Zn in the study area. Unlike, Pb, Zn has considerable to moderate contamination in surrounding areas away from the mining site (Figure 4.5a (ii)). Zinc is generally very mobile in the soil environment, especially in low pH. It is, therefore, assumed that they may have been leached and as a result depleted in the surface soil of surrounding areas.

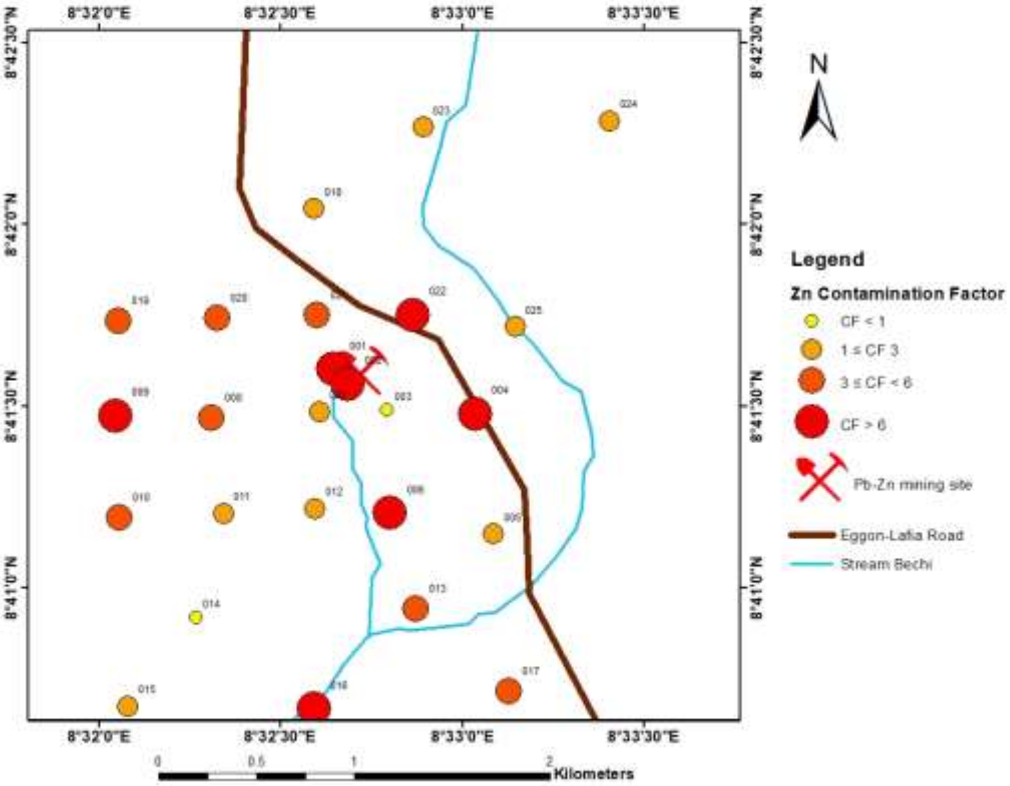

Figure 4.5a (ii) Contamination by Zn in the soil of Alizaga

Cu and Cd showed very high contamination within the vicinity of the mining site but moderate to low contamination in surrounding areas. Contamination seems to be distributed radially away from the mining site (Figure 4.5a(iii) and (iv) respectively). However, Cr showed high to moderate contamination in several areas away from the mines but low contamination within the mining area (Figure 4.5a(v)). This indicates that the source of Cr contamination may not be directly related to the mining site.

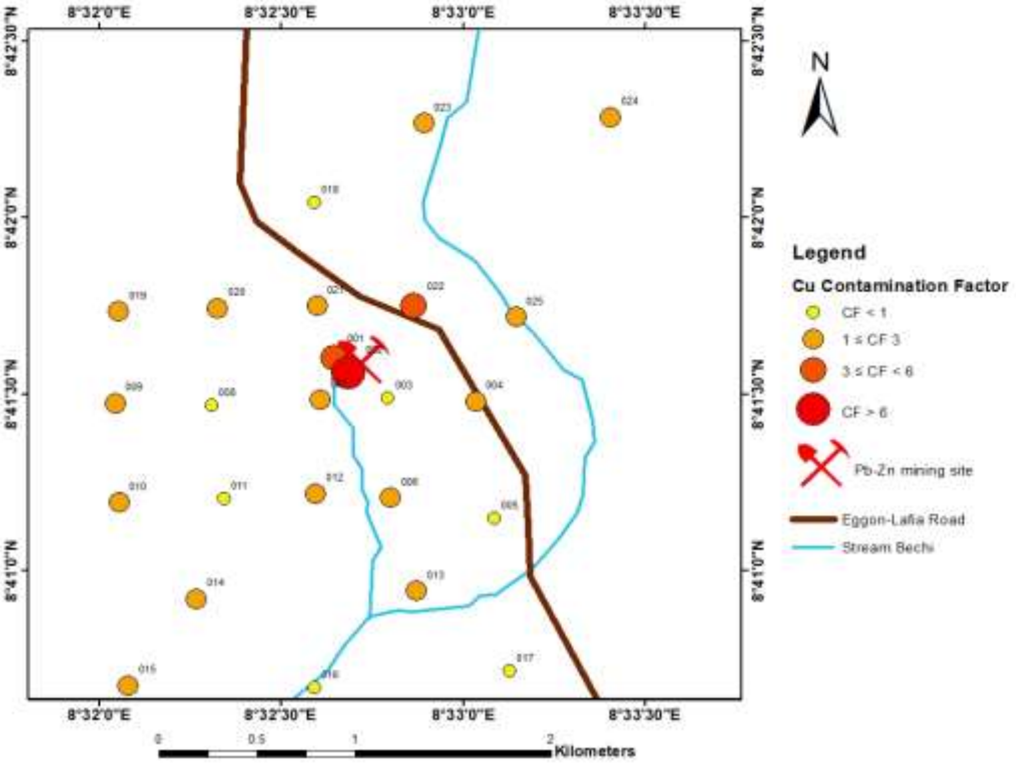

Figure 4.5a (iii) Contamination by Cu in the soil of Alizaga

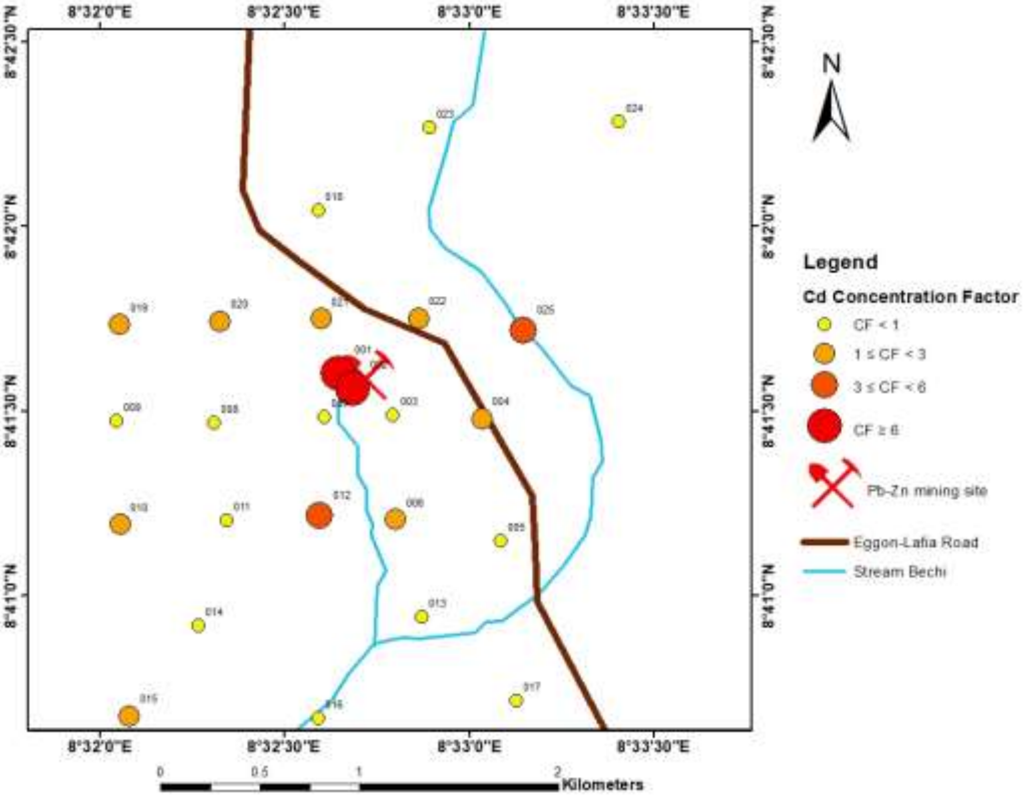

Figure 4.5a (iv) Contamination by Cd in the soil of Alizaga

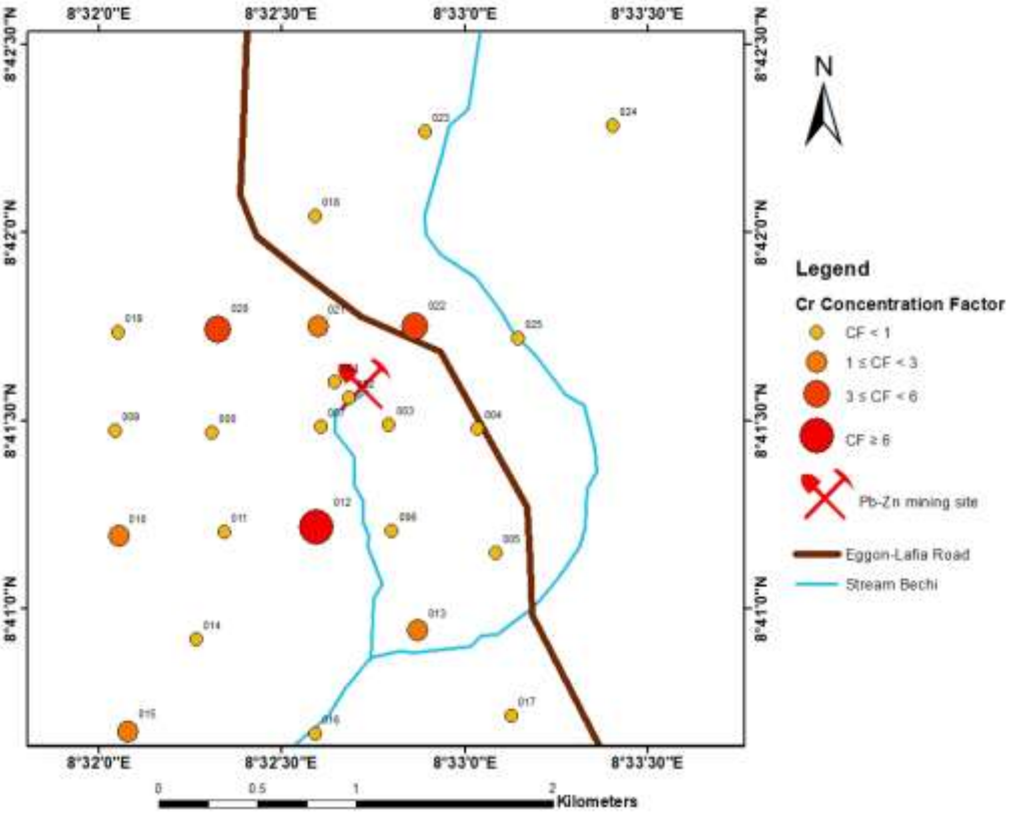

Figure 4.5a (v) Contamination by Cr in the soil of Alizaga

For the stream sediments, the values for Contamination Factor for Pb and Zn in samples very close to the mining and processing area (Figure 4.5b(i) and 4.5b(ii) respectively). Their Contamination Factor values are greater than six and this denotes very high contamination by Pb and Zn in the stream sediments where tailings from the processing area are directly discharged. The corresponding contamination is moderate to low in stream sediments away from the mining and processing area.

Again, the intensity of contamination by Pb is more than Zn. This can also be related to the high mobility of zinc, hence diluting the concentration in stream sediments.

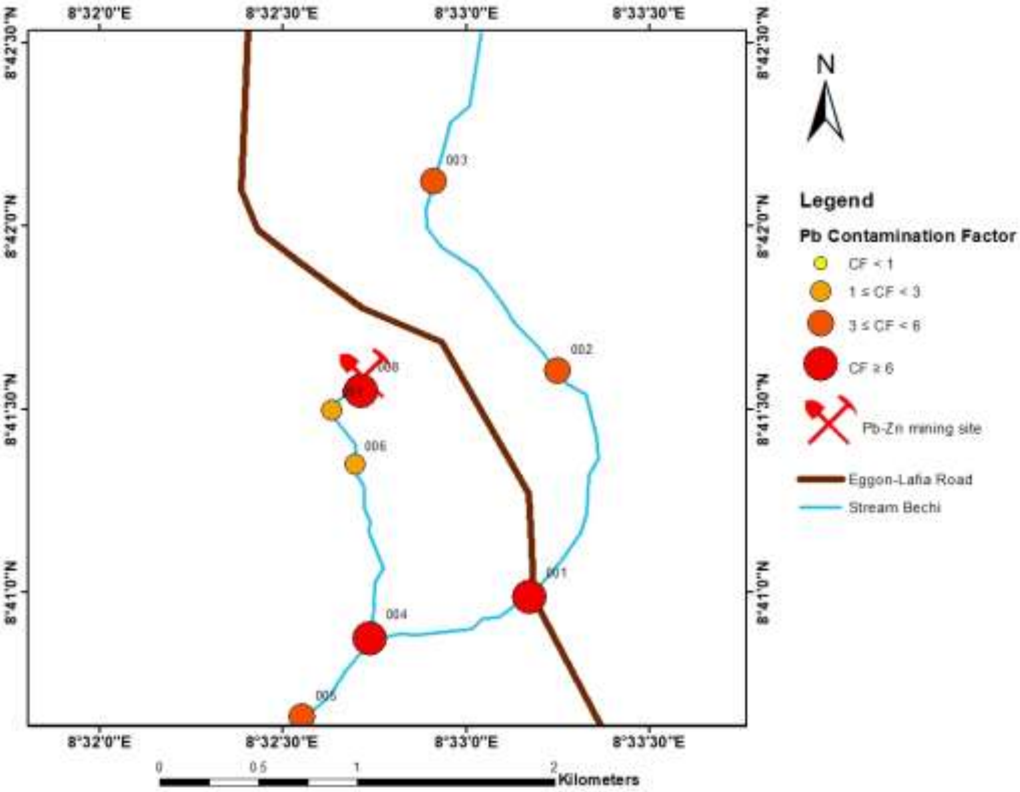

Figure 4.5b (i) Contamination by Pb in the stream sediments of Alizaga

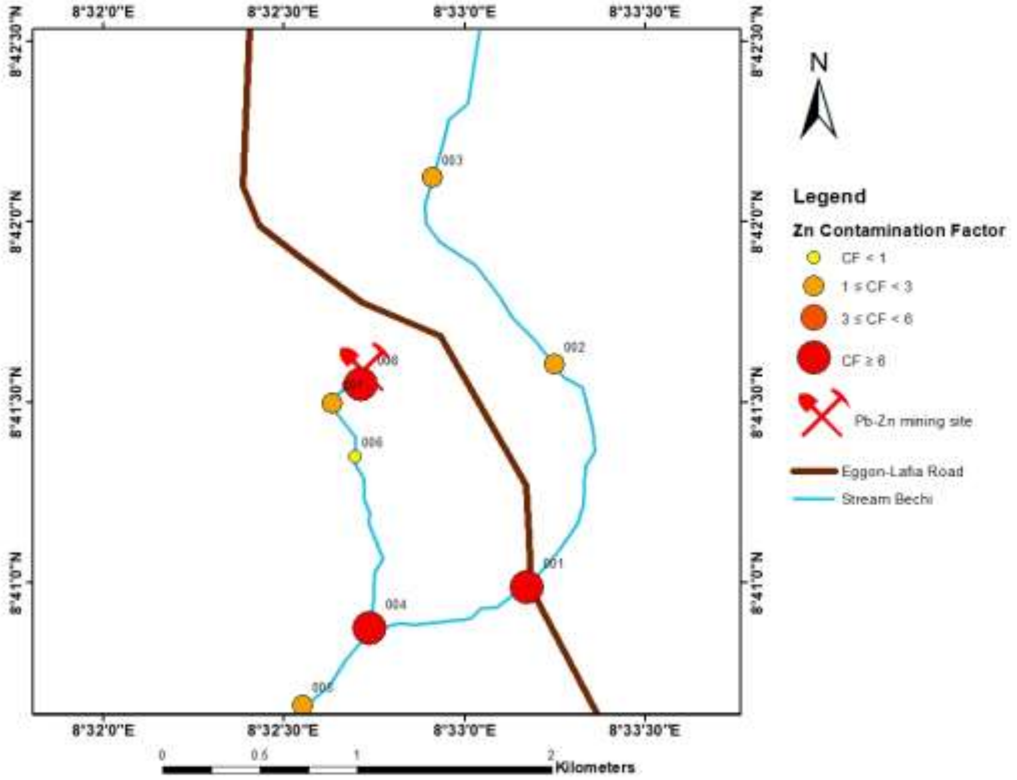

Figure 4.5b (ii) Contamination by Zn in the stream sediments of Alizaga

Cu and Cd contamination is considerably high to moderate in the stream sediments close to the mining site as well as where the road crosses the stream. (Figure 4.5b(iii) and 4.5b(iv) respectively). This can be related to both geogenic and anthropogenic factors contributing to their release on the study area. However, the stream on the north-eastern part of the study area, where it is not directly connected to the mining site showed low contamination by Cu and Cd.

However, Cr showed low contamination is in most of the streams of the study area. High contamination was detected in one stream sediment sample location away and directly not connected to the mining site (Figure 4.5b(v)). This can also be related to anthropogenic cause of contamination such as domestic waste disposal and possibly use of pesticides for farming in the area.

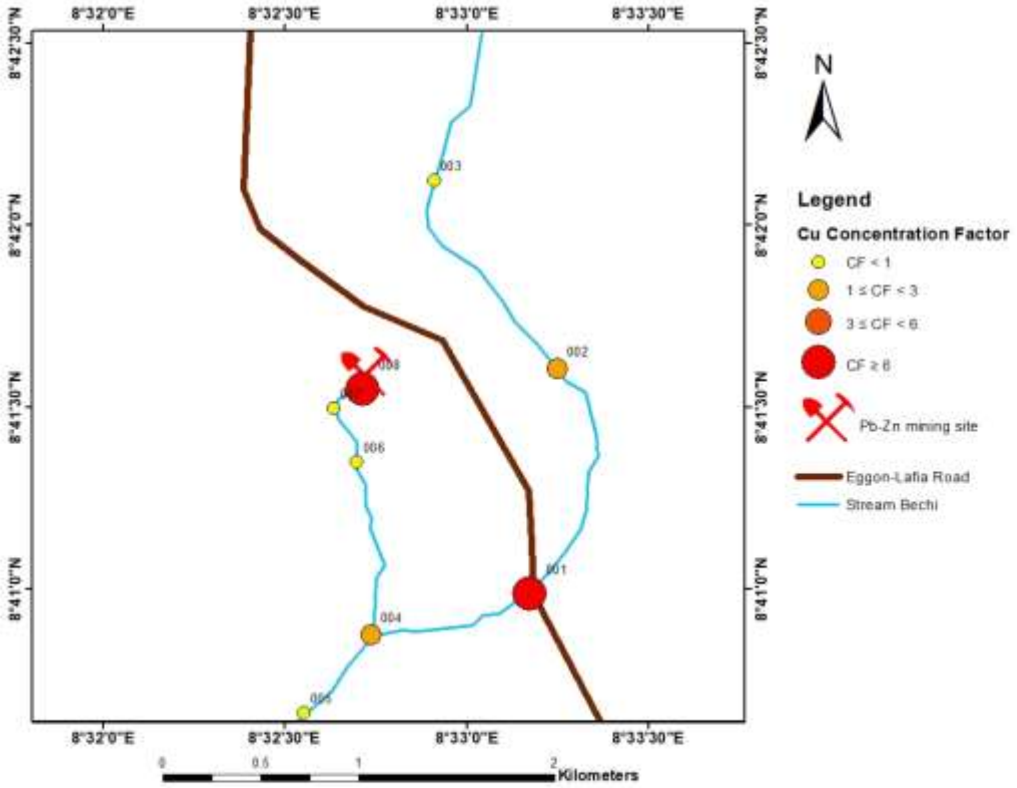

Figure 4.5b (iii) Contamination by Cu in the stream sediments of Alizaga.

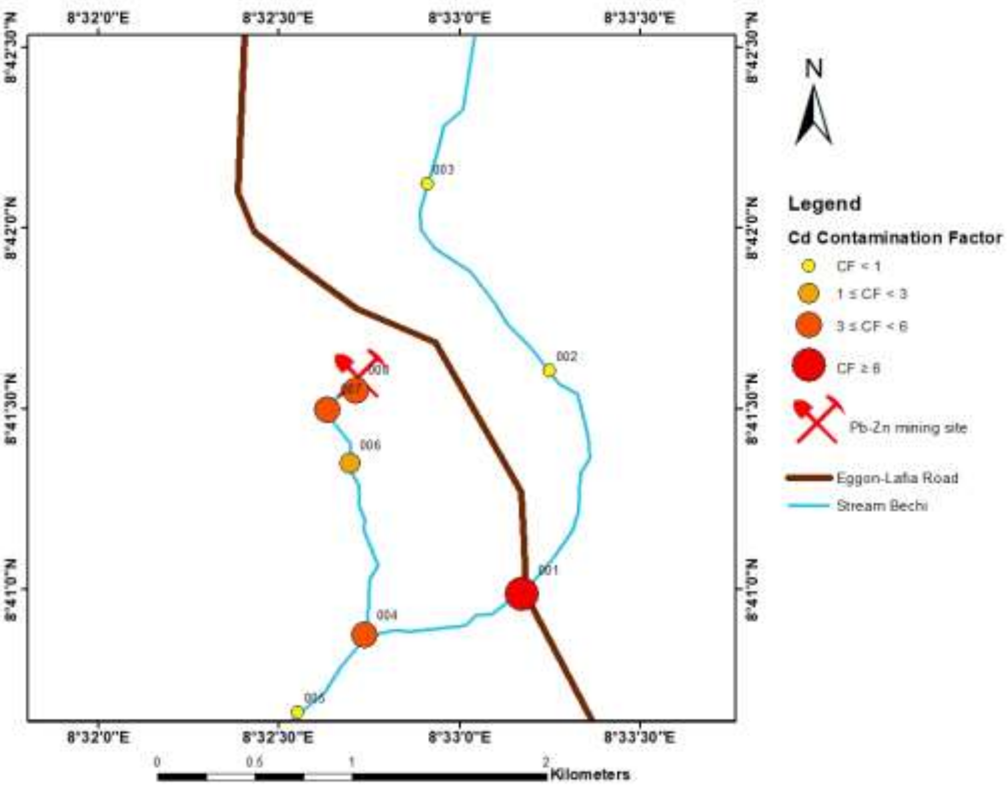

Figure 4.5b (iv) Contamination by Cd in the stream sediments of Alizaga

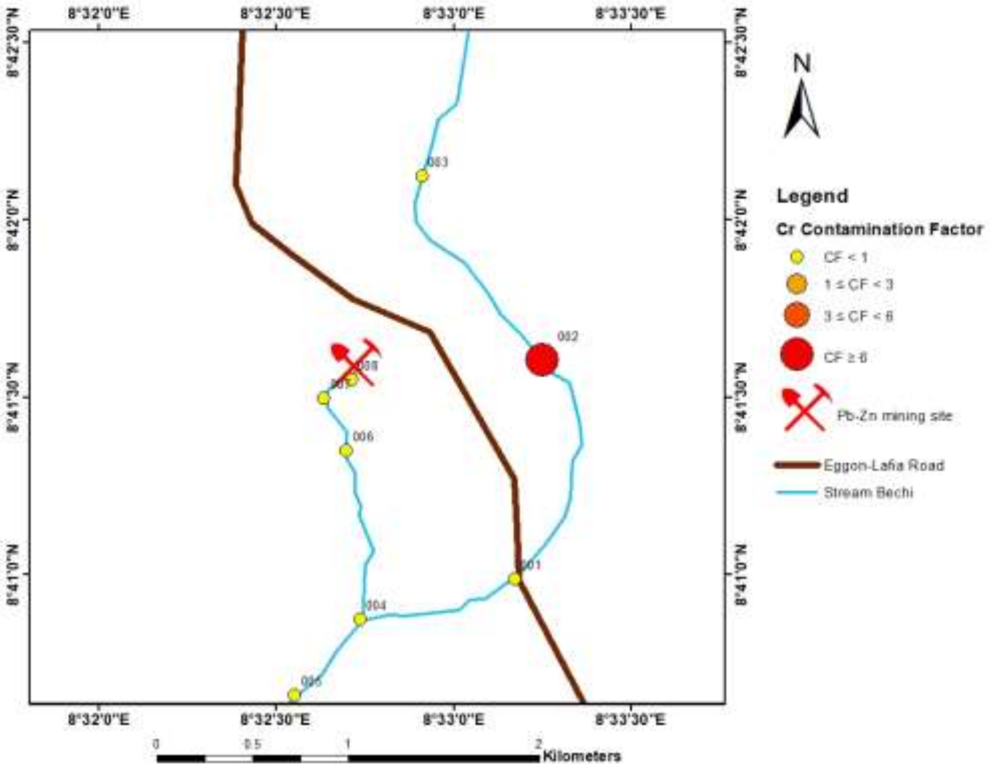

Figure 4.5b (v) Contamination by Cr in the stream sediments of Alizaga

4.3.3 Enrichment factor (EF)

The levels of enrichment by selected PTEs in the soils and stream sediments in the study area are presented in Figure 4.6a(i-v) and 4.6b(i-v). The soils show extremely high and significant enrichment by Pb and Zn within the vicinity of the mining site (Figure 4.6a(i) and 4.6b(ii) respectively). The presence of sulphides, galena (PbS) and zinc (ZnS) hosted in quartzites and biotite granites, can be related for this enrichment in soils. There is general deficiency in enrichment of Pb is surrounding areas outside 200m radius of the mining site. However, Zn enrichment gradually shifts from highly enriched in the soils within the mines to significant and minimal enrichment in surrounding areas (Figure 4.6a(ii)).

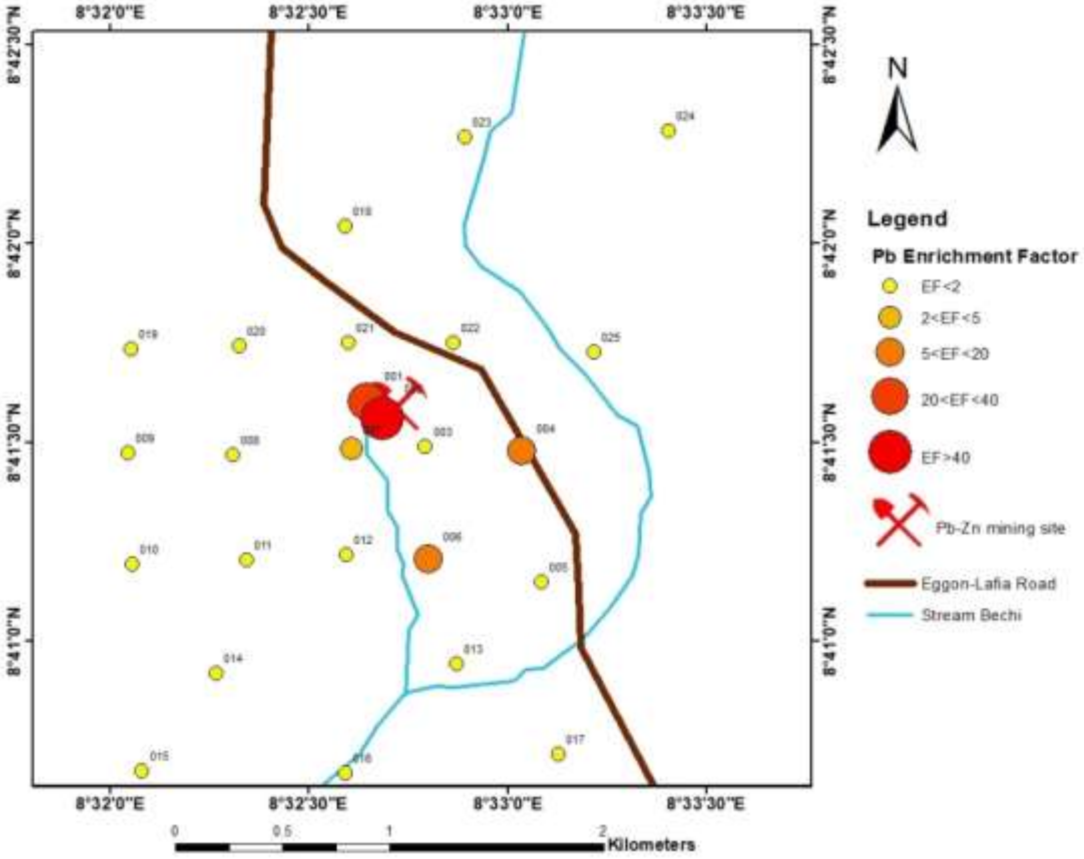

Figure 4.6a(i): Pb Enrichment in the soils of Alizaga

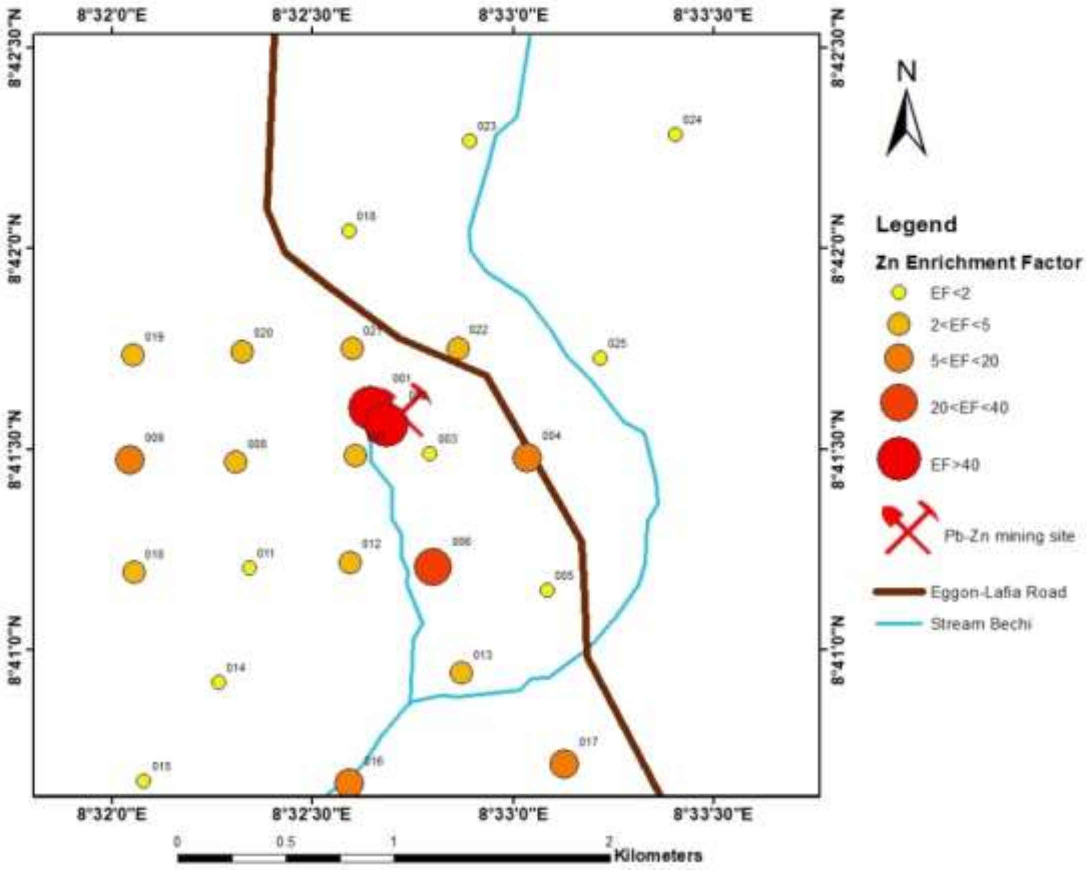

Figure 4.6a (ii): Zn Enrichment in the soils of Alizaga

Cu have very high enrichment to significant enrichment within 200m of the mining site. This quickly reduces to moderate and minimal enrichment in the surrounding areas (Figure 4.6a(iii)). However, Cd enrichment is very high within the immediate vicinity of the mining site and mostly minimal enrichment in surrounding areas (Figure 4.6a(iv)). This variation enrichment is generally radially in the study area but also visible along SSE from the mining site. This can be related to the mineralized quartzite ridge trending NW and SE in the area.

Furthermore, Cr shows a general deficiency to minimal enrichment within the mining area and surrounding areas. Although, there exist very few significant enrichment outside of the mining area (Figure 4.6a(v)). This suggests a different anthropogenic contamination that can be related to the use of phosphate fertilizers on cultivated lands.

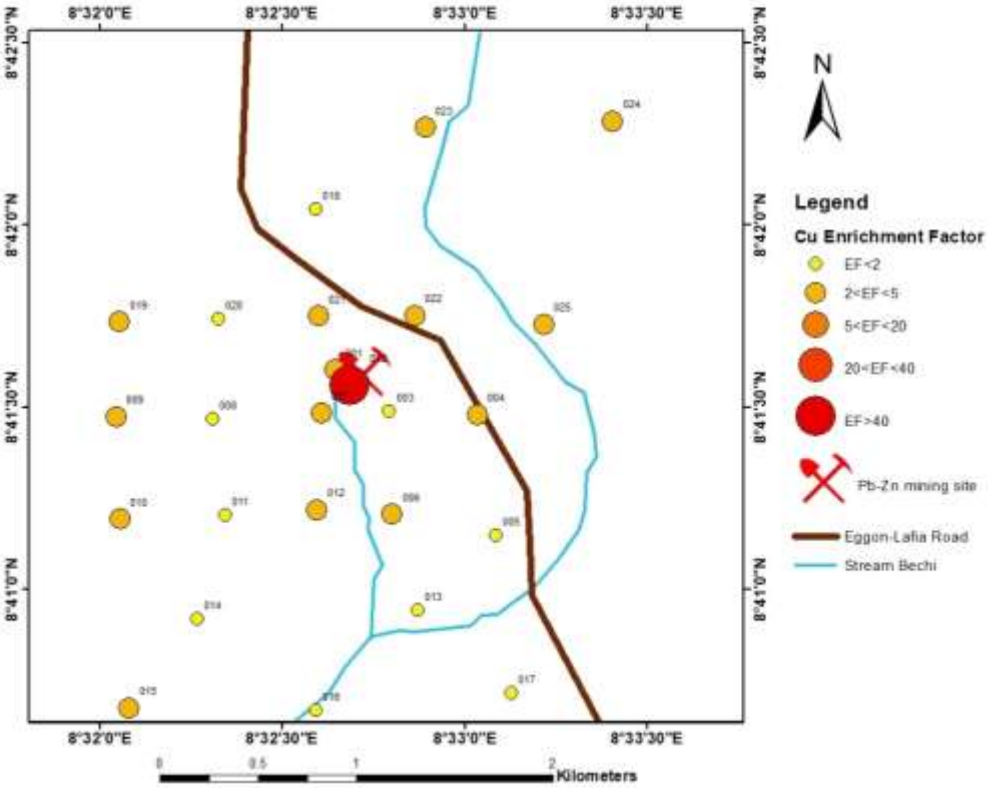

Figure 4.6a (iii): Cu Enrichment in the soils of Alizaga

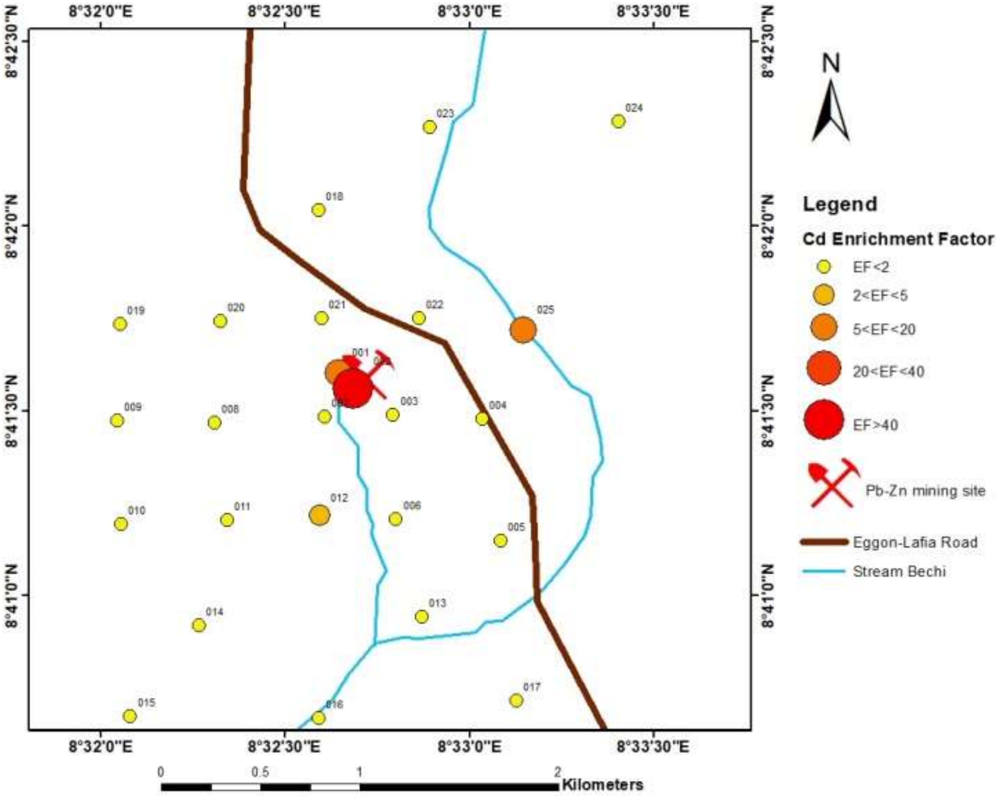

Figure 4.6a (iv): Cd Enrichment in the soils of Alizaga

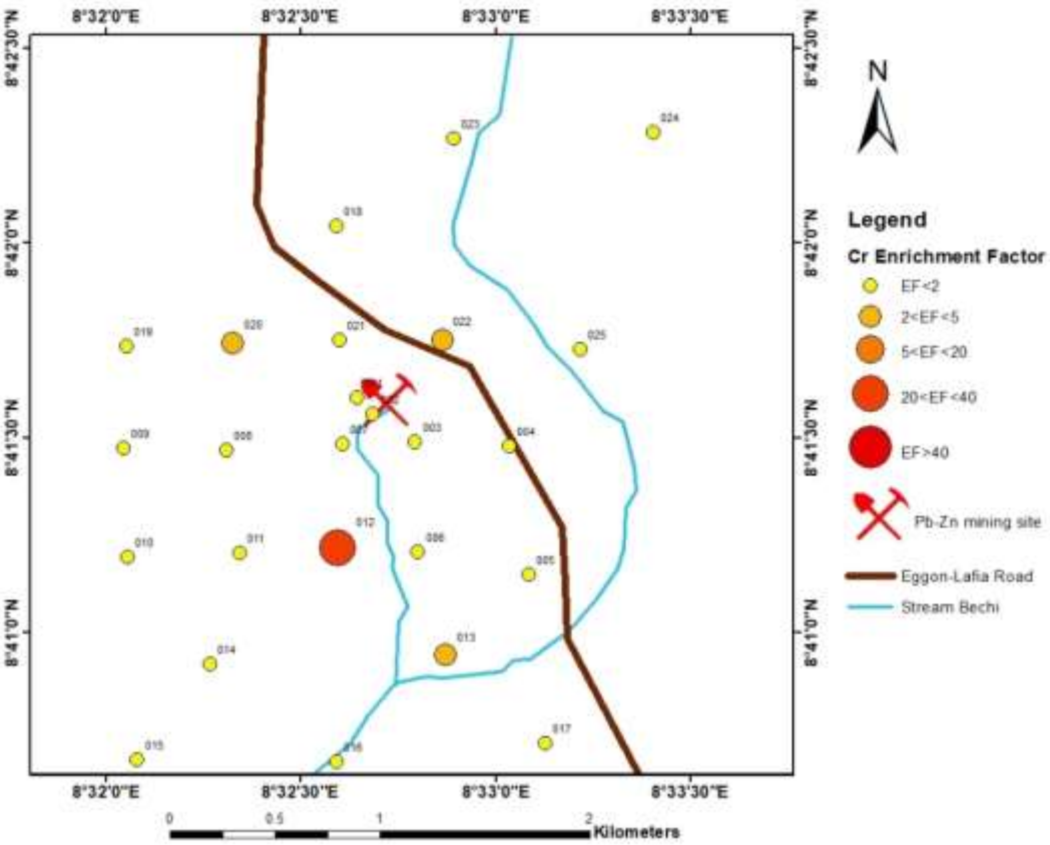

Figure 4.6a (v): Cr Enrichment in the soils of Alizaga

Apart from Cr which showed minimal enrichment in all the stream sediments samples, Pb, Zn, Cu and Cd have high enrichment to minimal enrichment in the stream sediments close to mines to those away from the mines respectively (Figures 4.6b(i-v).

The stream sediments show almost similar enrichment for both Pb and Zn. They are extremely high to very high enrichment in sediments within the mining and processing site. Although their enrichment is significant to moderate in stream sediments in surrounding areas, there is general decrease in enrichments of Pb and Zn away from the mines (Figures 4.6b(i) and 4.6b(ii) respectively).

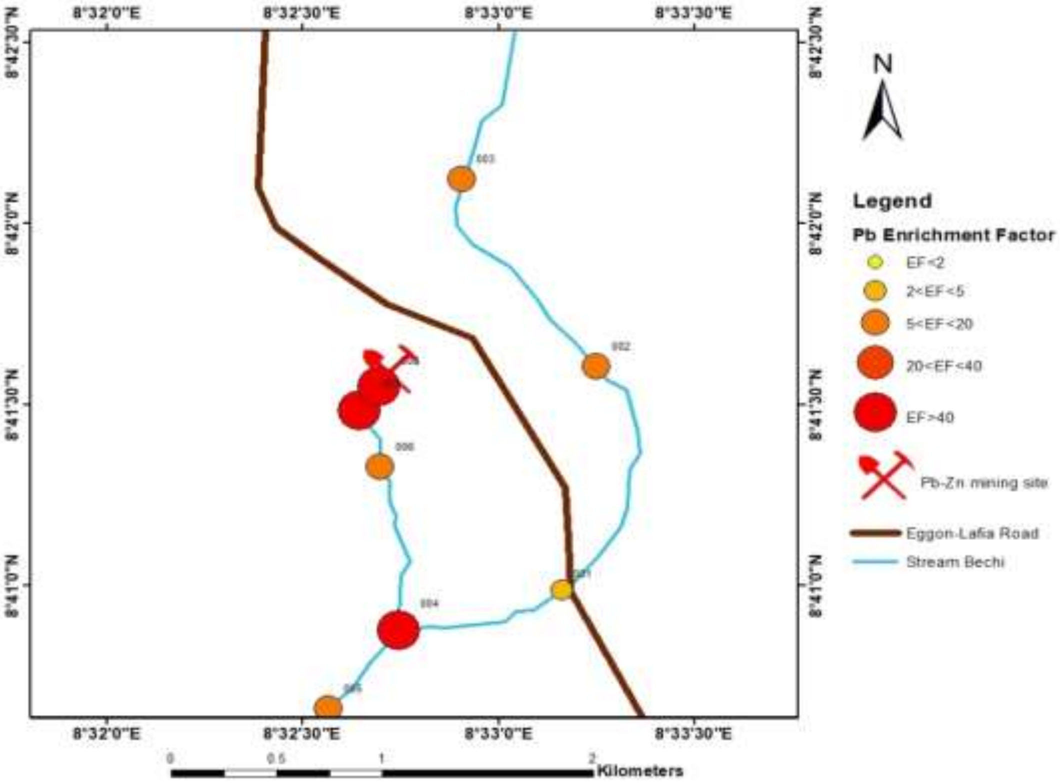

Figure 4.6b (i): Pb Enrichment in the stream sediments of Alizaga

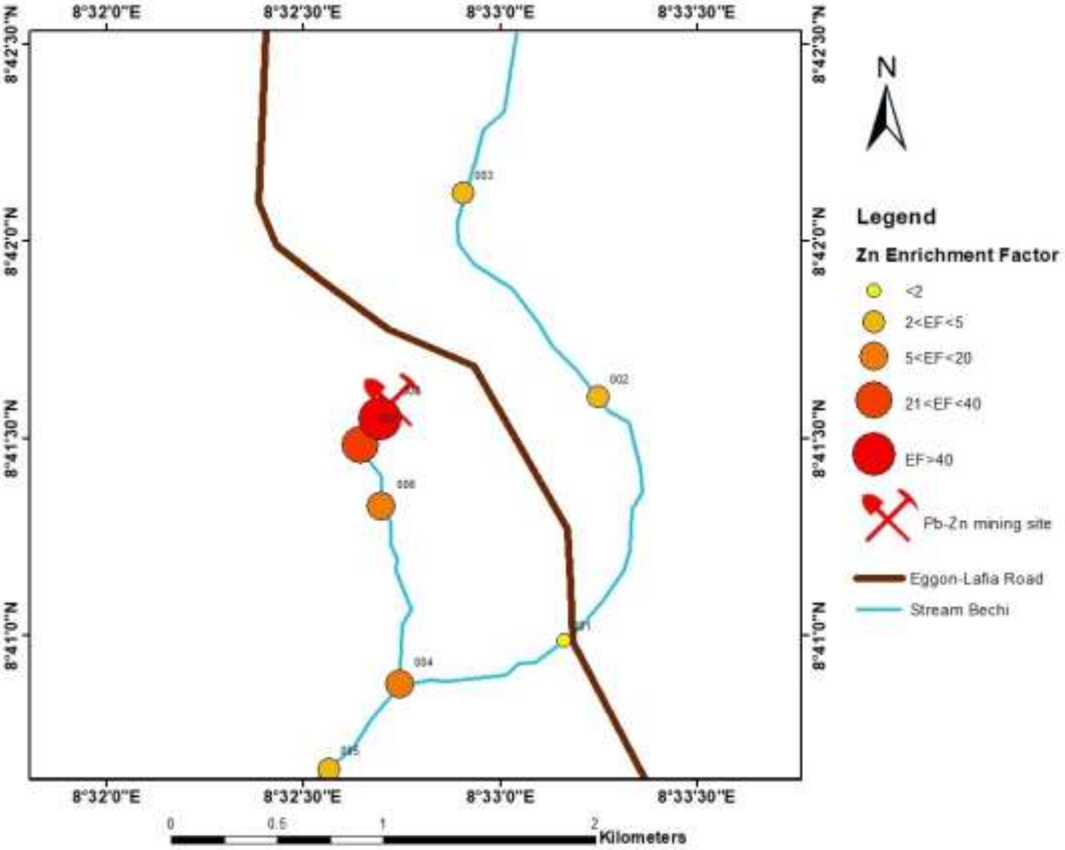

Figure 4.6b (ii): Zn Enrichment in the stream sediments of Alizaga

Cu and Cd enrichment in stream sediments of the study area are also similar. They are extremely high to significant enrichment at the stream channel closest to the mining and processing area (that is Enrichment Factor 5 and 40). This reduces to moderate to minimal enrichment away from the mining site (Figures 4.6b(iii) and 4.6(iv) respectively). Other part of the study area where the stream channel does not pass through the mining and processing site also have minimal enrichment (tha is, Enrichment Factor less than 2).

However, Cr have Enrichment Factor less than 2 in all stream sediments samples taken from the study area. This suggests a general deficiency or minimal enrichment of Cr in the area (Figure 4.6(v)).

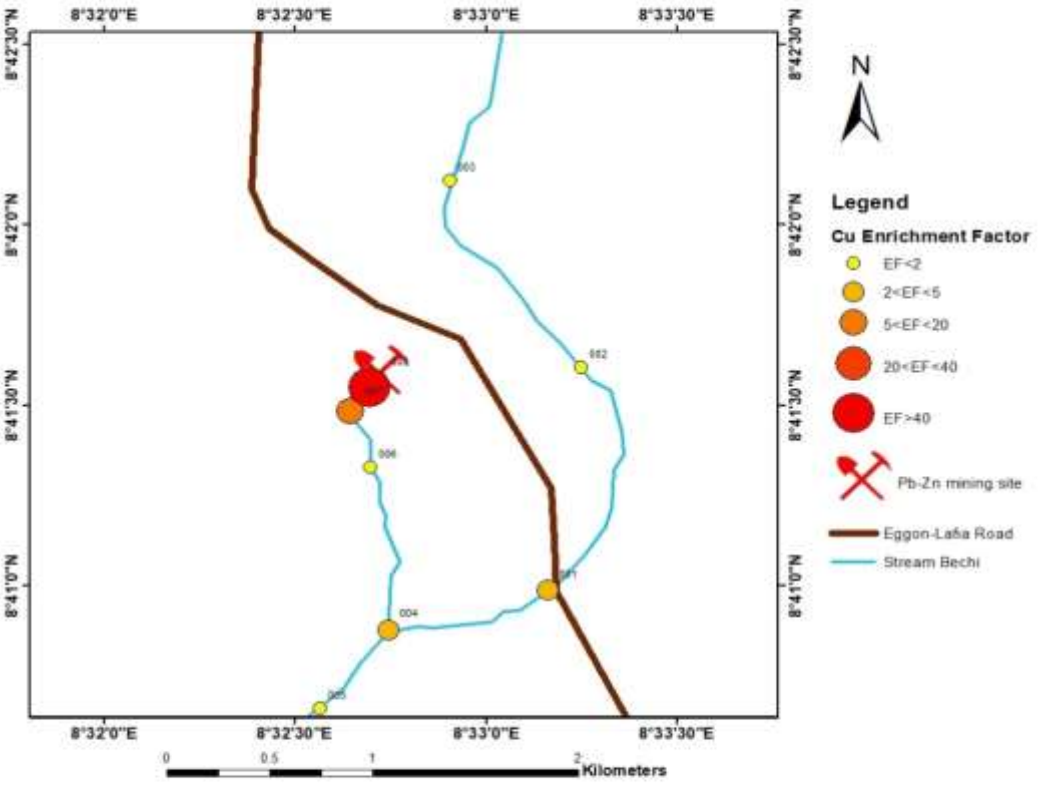

Figure 4.6b(iii): Cu Enrichment in the stream sediments of Alizaga

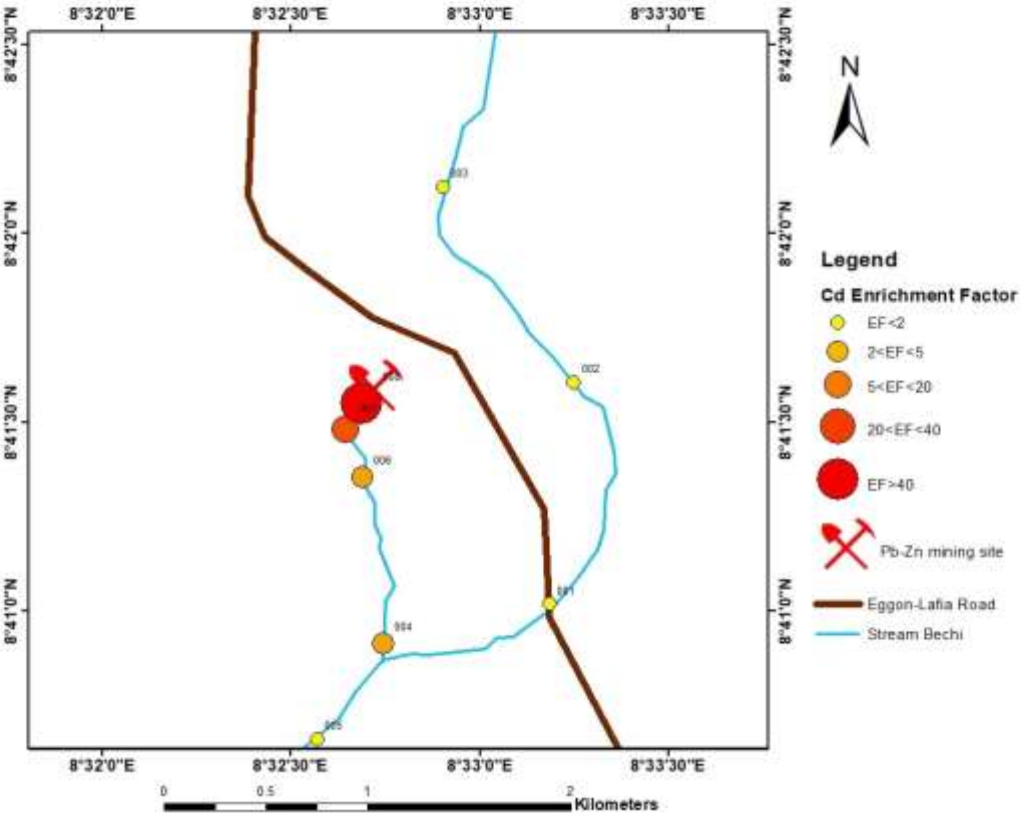

Figure 4.6b (iv): Cd Enrichment in the stream sediments of Alizaga

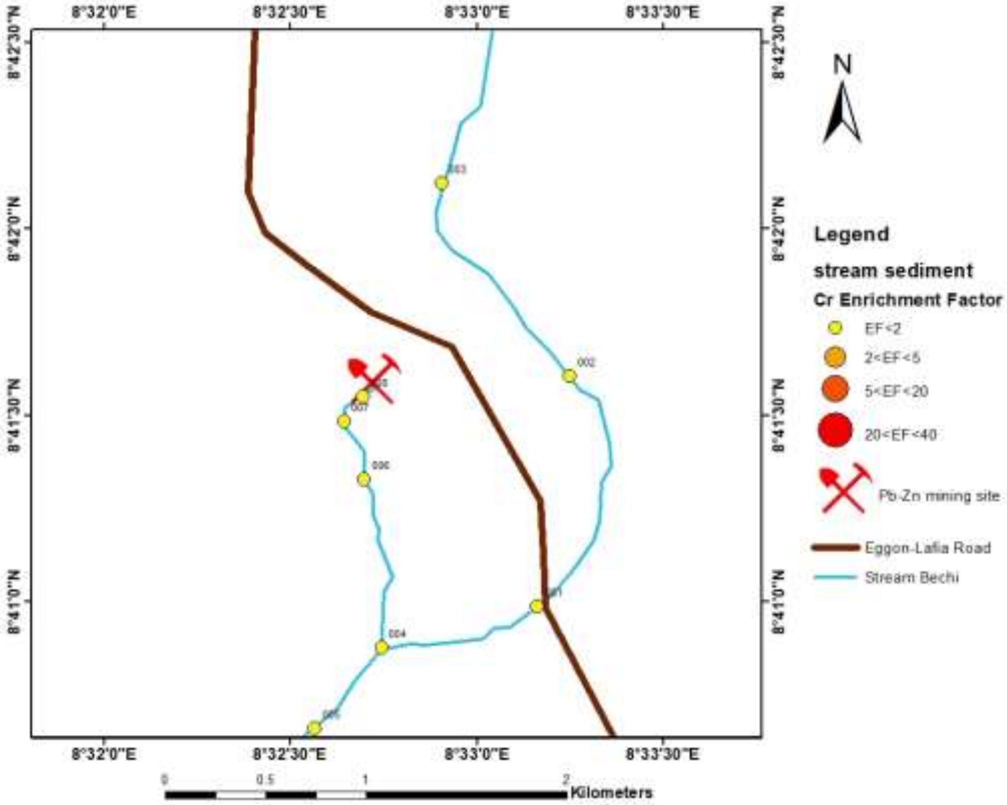

Figure 4.6b (v): Cr Enrichment in the stream sediments of Alizaga

4.3.4 Modified degree of contamination (mCd)

The modified degree of contamination helps in the assessment of overall metal contamination in the samples for better assessment of pollution level in the environment. In Figure 4.7a, the modified degree of contamination showed ultra-high to very high degree of contamination by the studied PTEs within the mining area and high to moderate degree of contamination in soils of surrounding areas.

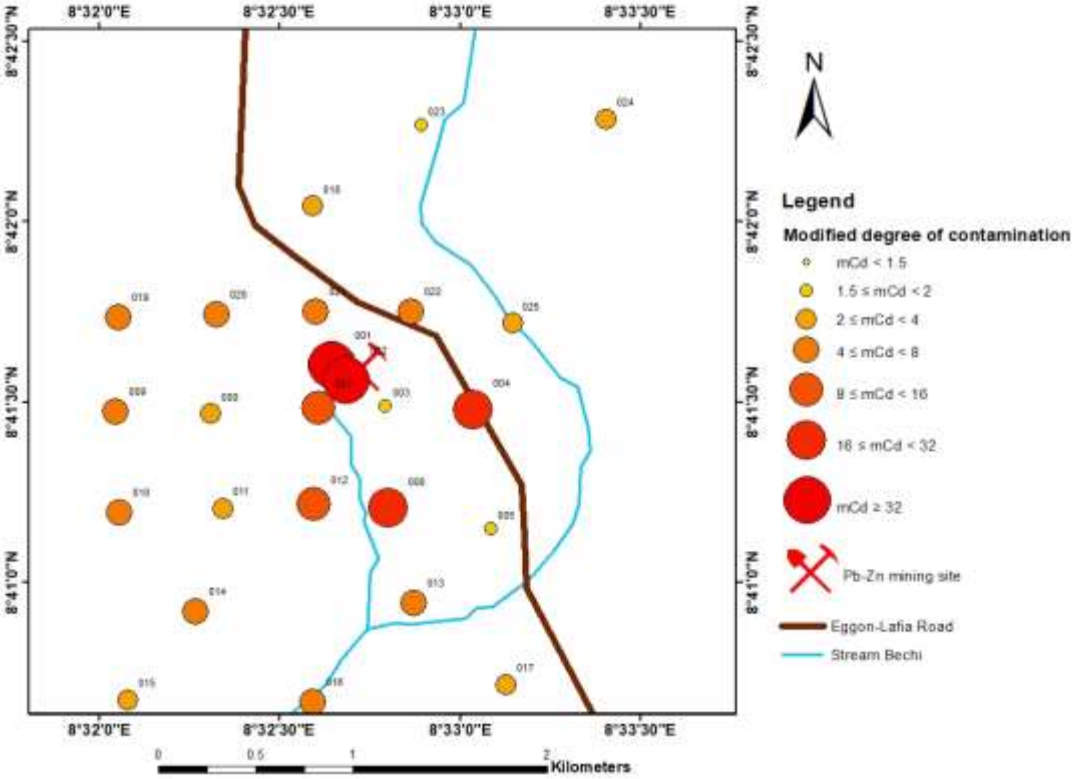

Figure 4.7a: Modified degree of contamination by Pb-Zn-Cu-Cr-Cd in Alizaga soil.

The stream sediments closest to the processing area also indicated ultra-high to very high degree of contamination and subsequently diluted downstream. This is presented by the graduated symbols and colours in the map in Figure 4.7b.

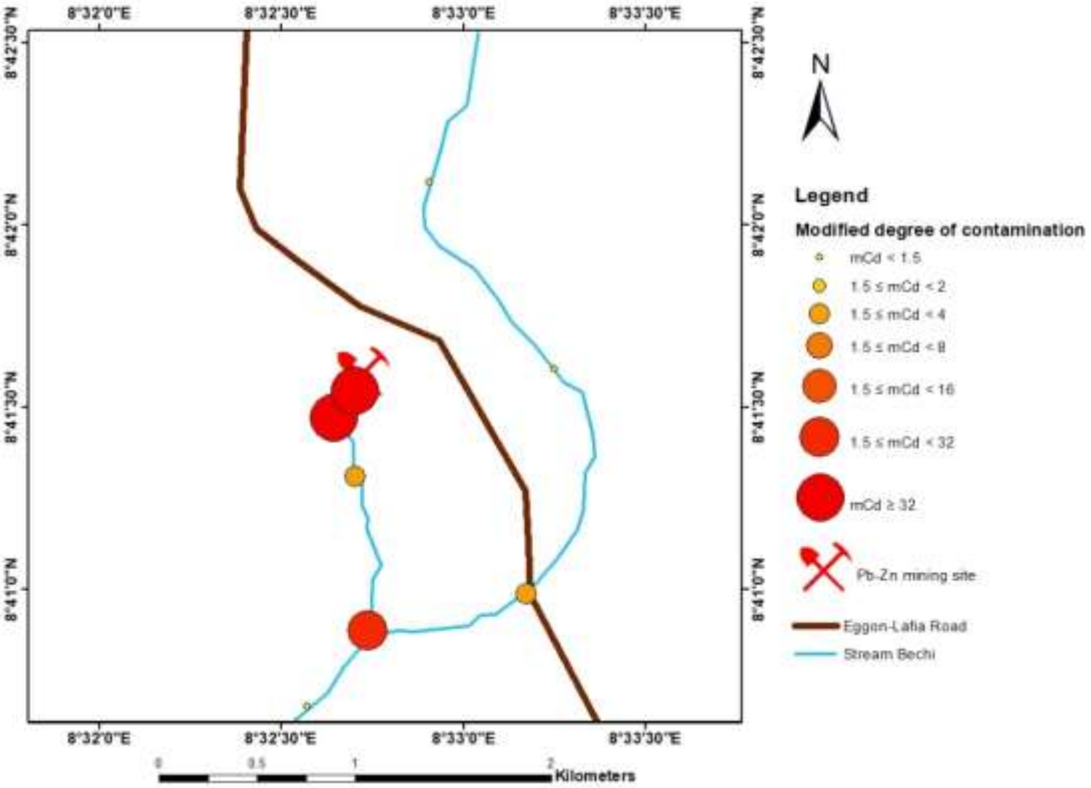

Figure 4.7b: Modified degree of contamination by Pb-Zn-Cu-Cr-Cd in Alizaga stream sediments.

4.3.5 Pollution load index (PLI)

This is used to determine the entire pollution levels in the studied environment. In Figure 4.8a, the graduated symbols in the map showed a uniform spread and this reveals that metal pollution exists in soils of the studied area. Figure 4.8b also showed that metal pollution exists in most of the stream sediments of the area. This can be related to geogenic sources such as weathering and soil erosion as well as anthropogenic activities such as Pb-Zn mining and processing, use of phosphate fertilizers on cultivated land and discharge of waste in the environment of the study area.

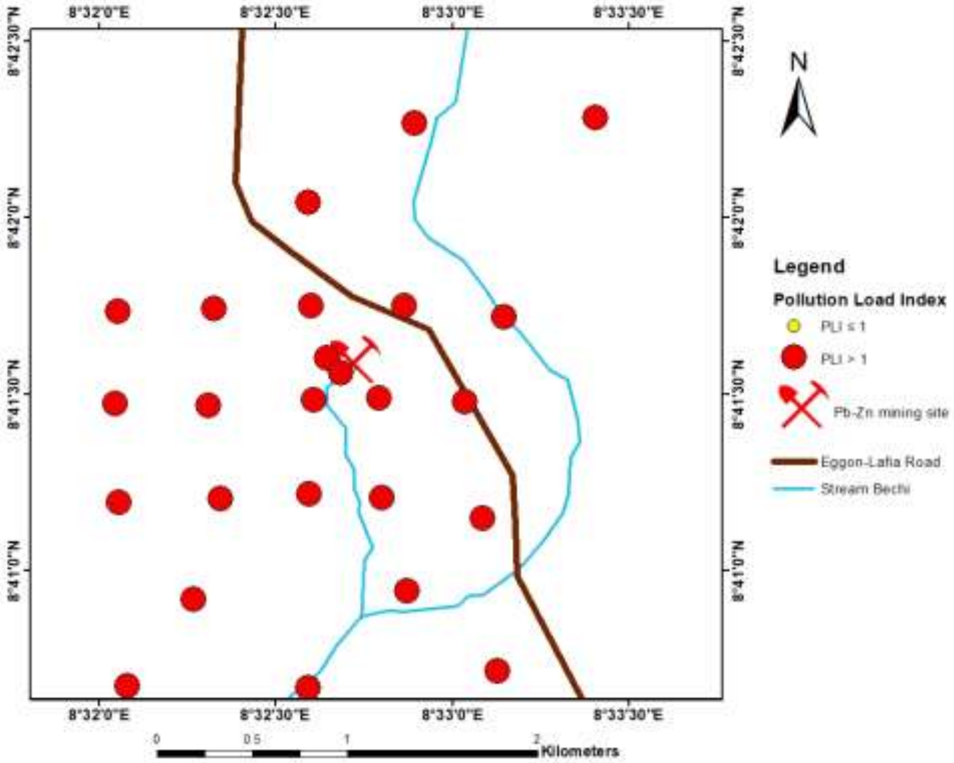

Figure 4.8a: Pollution Load Index by Pb-Zn-Cu-Cr-Cd in Alizaga soils.

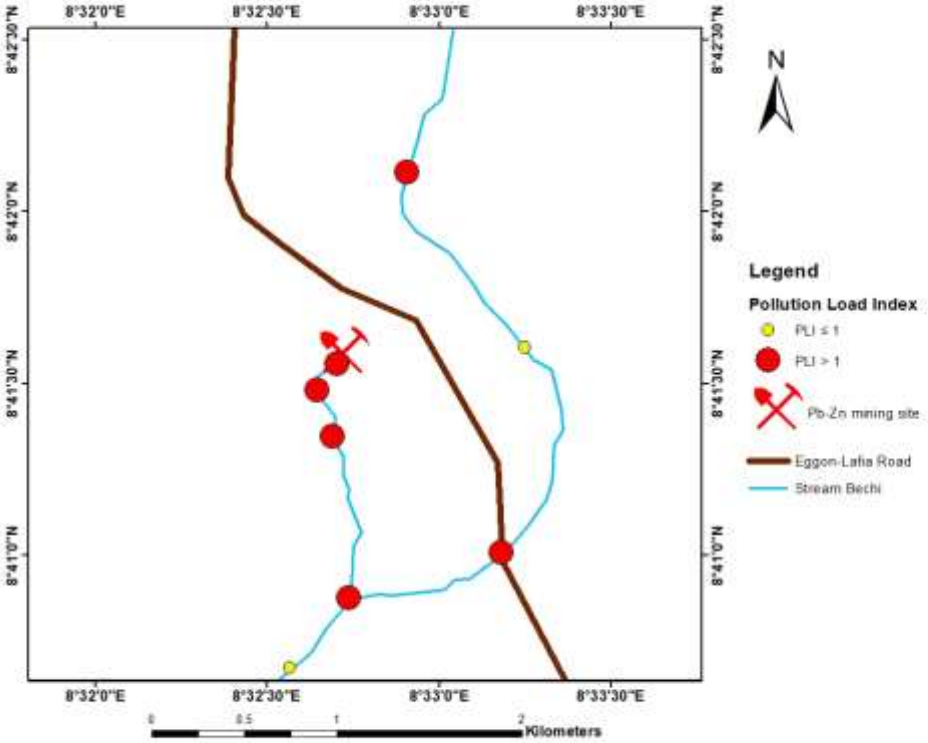

Figure 4.8b: Pollution Load Index by Pb-Zn-Cu-Cr-Cd in Alizaga stream sediments.

4.4 Ecological Risk Assessment

The ecological risk assessment of the PTEs in soils and stream sediments are presented in Figure 4.9a(i-v) and 4.9b(i-v) respectively. Pb showed very high ecological risk factor in the soils within the immediate vicinity of the mines, a radius of about 300 m (Figure 4.9a(i)). The risk factors reduced from considerable to low risk in surrounding settlements and farmlands. This risk reduces radially away from the mines, however, it is generally very low uphill at the northern part of the study area.

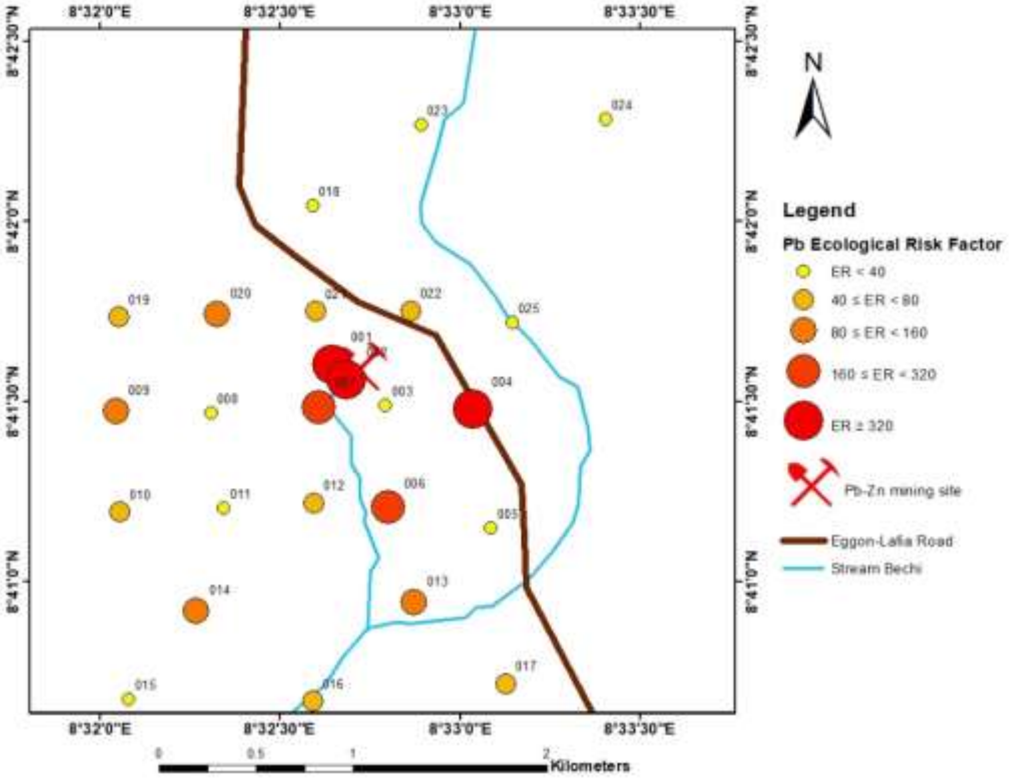

Figure 4.9a (i) Ecological risk by Pb in Alizaga soils

Zn and Cu showed high ecological risk only at the mines site but low in surrounding areas (Figures 4.9a(ii) and 4.9a(iii) respectively).

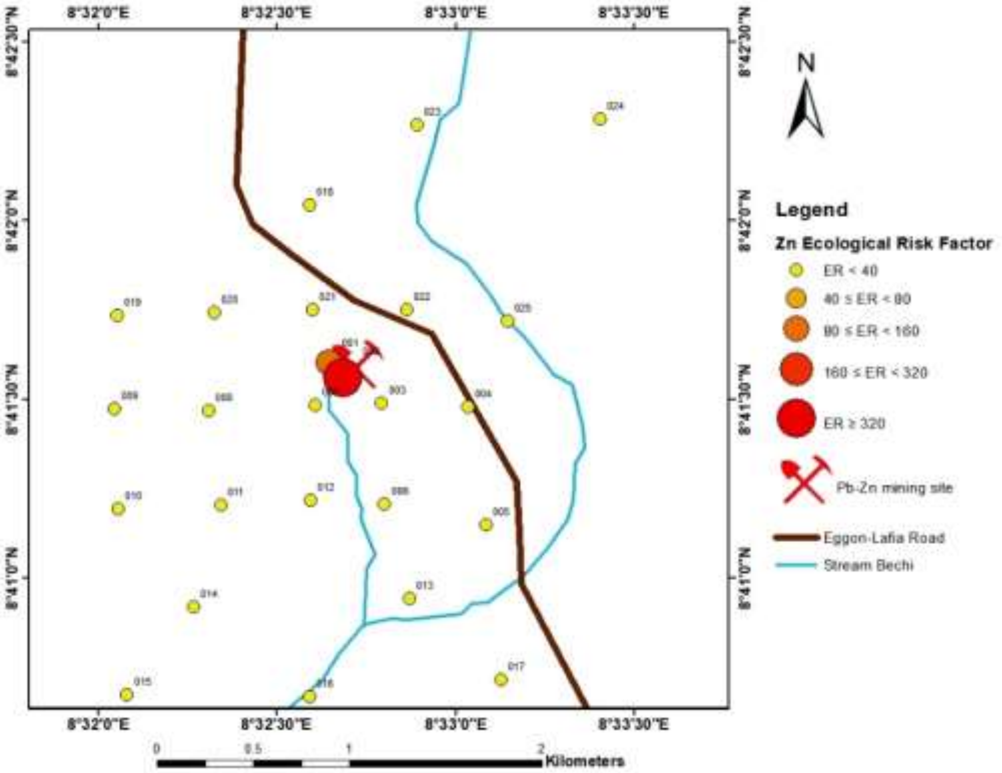

Figure 4.9a (ii) Ecological risk by Zn in Alizaga soils

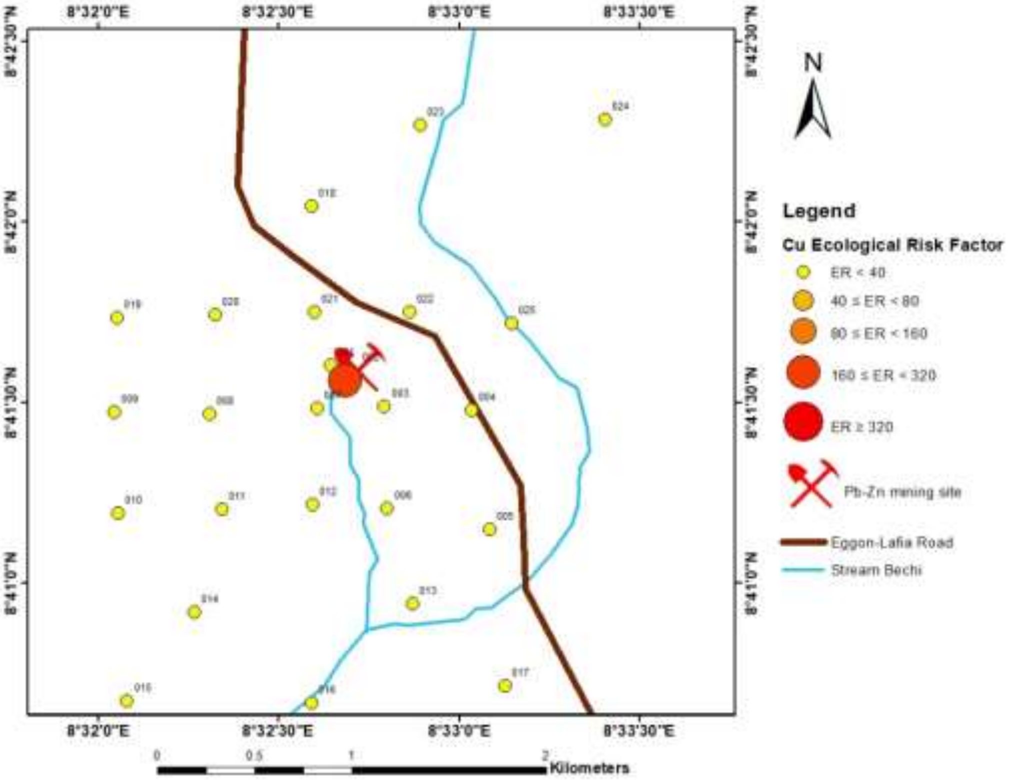

Figure 4.9a (iii) Ecological risk by Cu in Alizaga soils

Ecological risk posed by cadmium is very high within the mines, considerable to moderate in the surrounding farmlands but low in distant settlements especially north of the mines (Figure 4.9a(iv)).

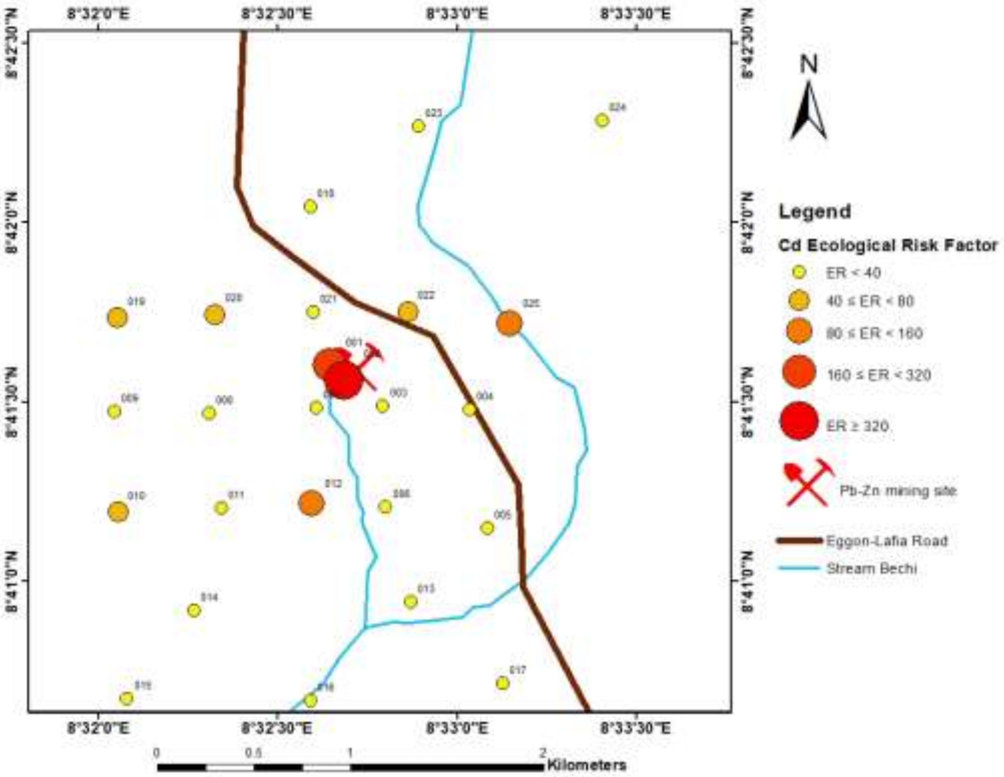

Figure 4.9a (iv) Ecological risk by Cd in Alizaga soils

Cr have ecological risk factor values to be less than 40. That is, they mostly showed low ecological risk in the soils of the study area (Figure 4.9a(v)).

Potential ecological risk posed by all the studied PTEs (Pb>Zn>Cu>Cd>Cr) in soils is very high within the mines, considerable to moderate risk in surrounding areas and low risk in those farthest from the mines. The risk tend to increase radially away from the mines (Figure 4.9a (vi)).

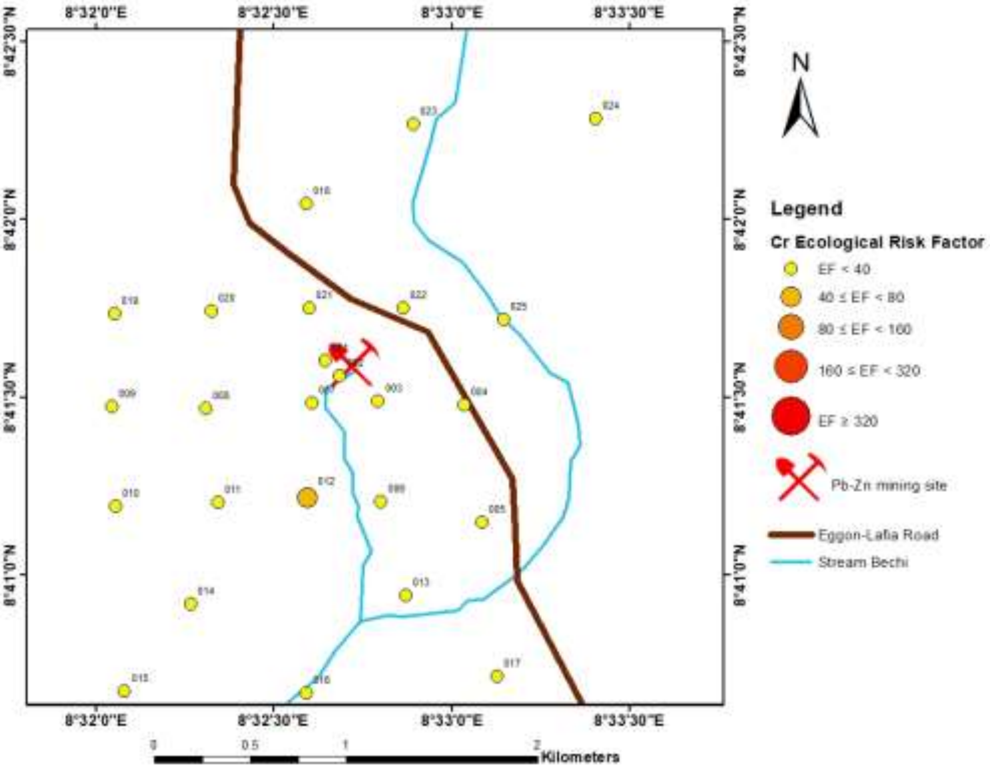

Figure 4.9a (v) Ecological risk by Cr in Alizaga soils

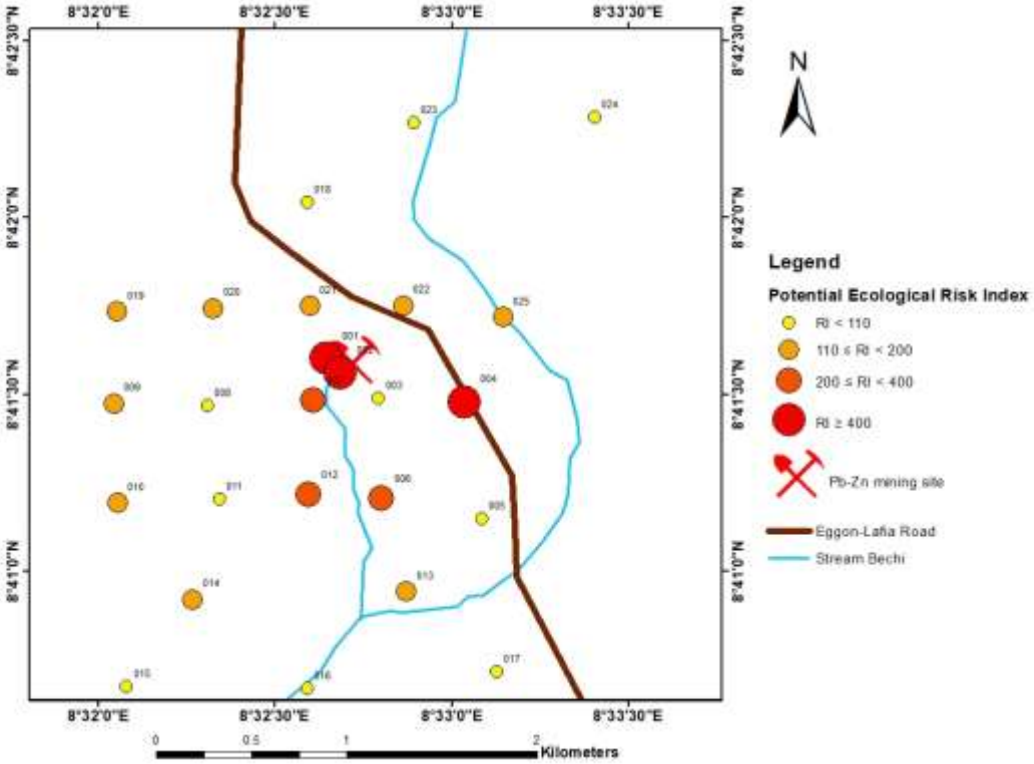

Figure 4.9a (vi) Potential ecological risk posed by PTEs (Pb, Zn, Cu, Cd and Cr) in Alizaga soils.

In Figure 4.9b (i-iii) ecological risks posed by the Pb, Zn and Cu on the stream sediments are very high risk to high risk. That is, RI values are greater than 320 and 160-320 respectively. This is where the waste water from Pb-Zn sorting and processing are discharged in to the stream, 300m away (Plate XIII).

In other areas away from the mining site, the risk levels mostly low. That is, RI values are less than 40. This means that the potential ecological risk is currently within the oart of the stream located on the immediate vicinity of the mining site (That is 300m radius).

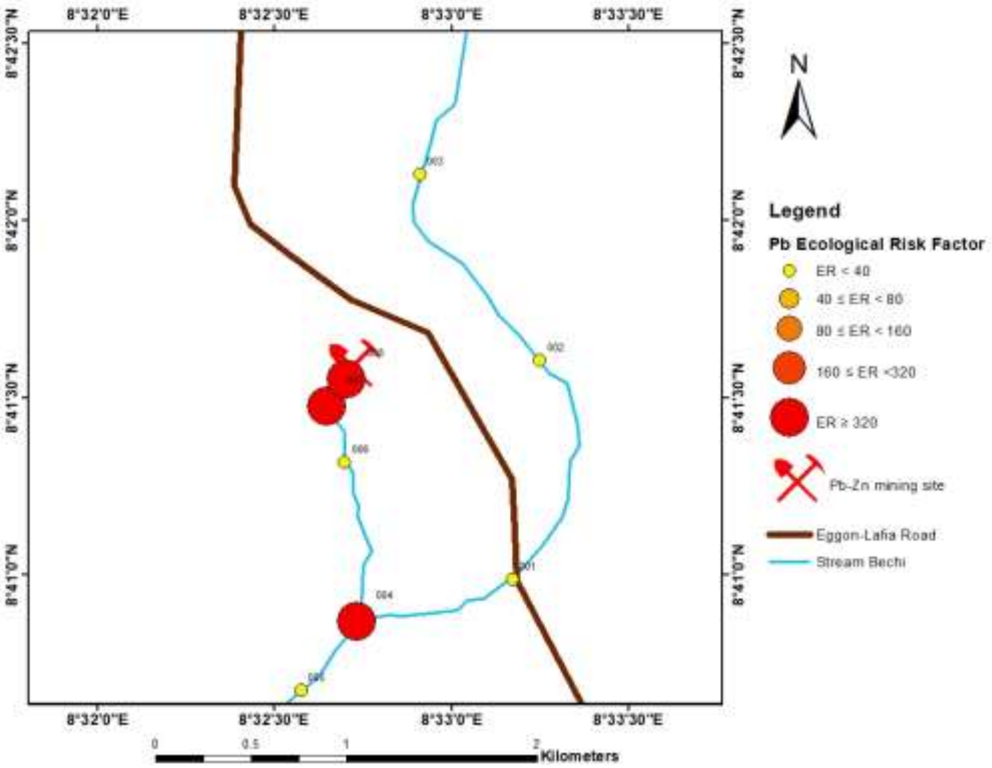

Figure 4.9b (i) Ecological risk by Pb in Alizaga stream sediments

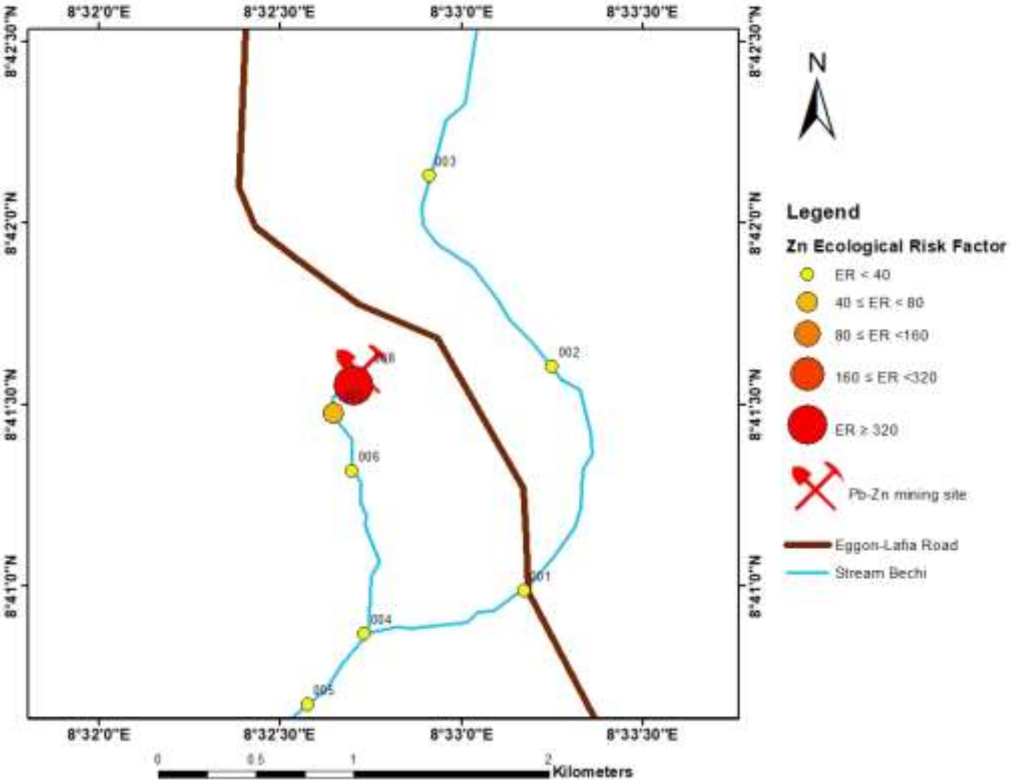

Figure 4.9b (ii) Ecological risk by Zn in Alizaga stream sediments.

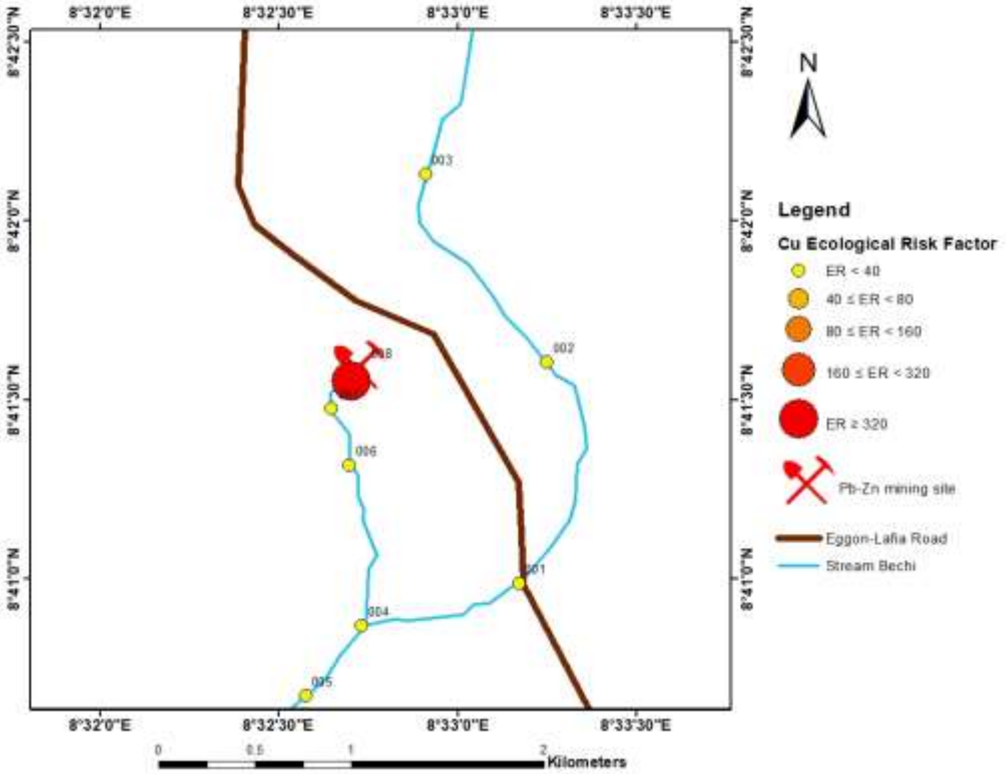

Figure 4.9b (iii) Ecological risk by Cu in Alizaga stream sediments

In Figure 4.9b (iv), RI value for Cd is greater than 320 in the stream sediment closest to the mining and processing area. This indicate very high risk potential ecological risk within this area. However, the RI values reduce gradually away from the mining area downstream and southwards. This indicate a transition from Very high potential risks to considerable and moderate risks and then low risks by Cd in stream sediments downstream.

Again, no potential ecological exist for Cr in the stream sediments of the study area (Figure 4.9b (v)).

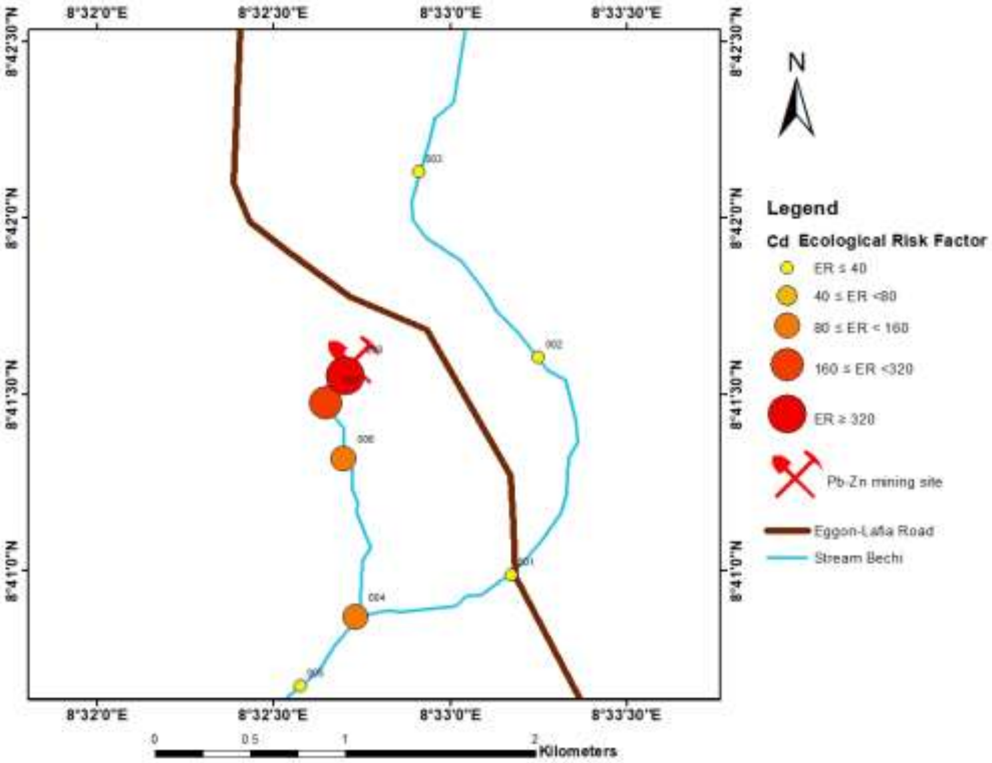

Figure 4.9b (iv) Ecological risk by Cd in Alizaga stream sediments

In Figure 4.9b (vi), potential ecological risk posed by all the studied PTEs (Pb, Zn, Cu, Cd and Cr) is generally high (RI > 400) at the mouth of the stream channel where waste water from Pb-Zn processing were directly discharged. It is low (RI < 110) in other parts of the stream within the study area except at the confluence due increased pollution load.

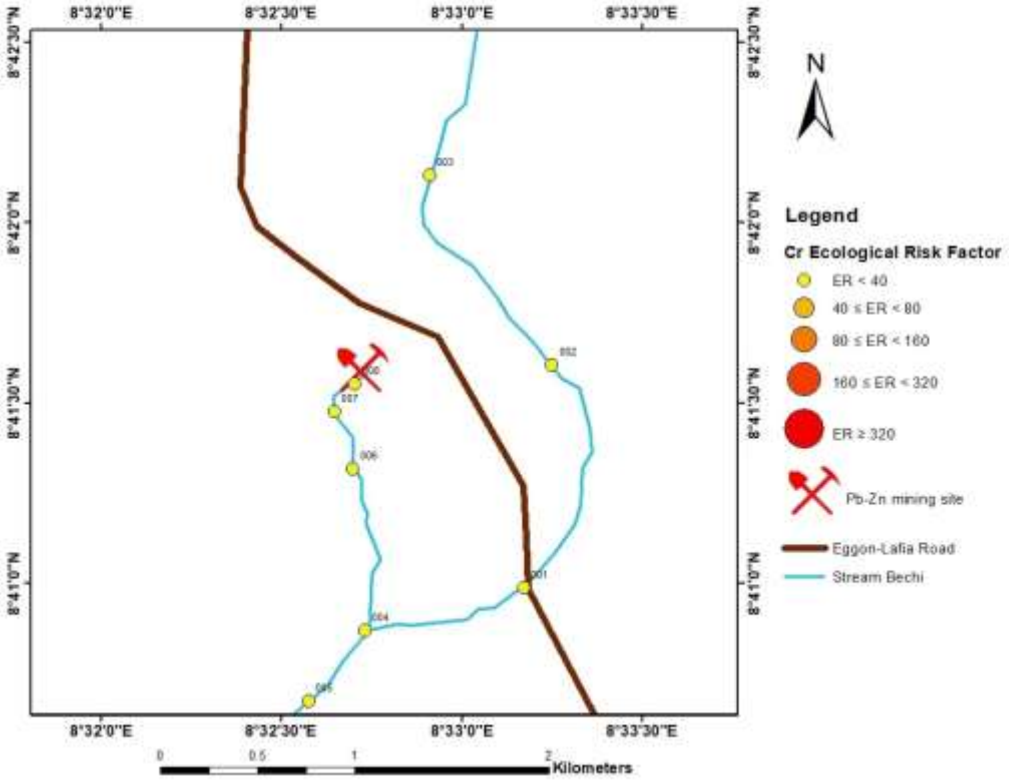

Figure 4.9b (v) Ecological risk by Cr in Alizaga stream sediments.

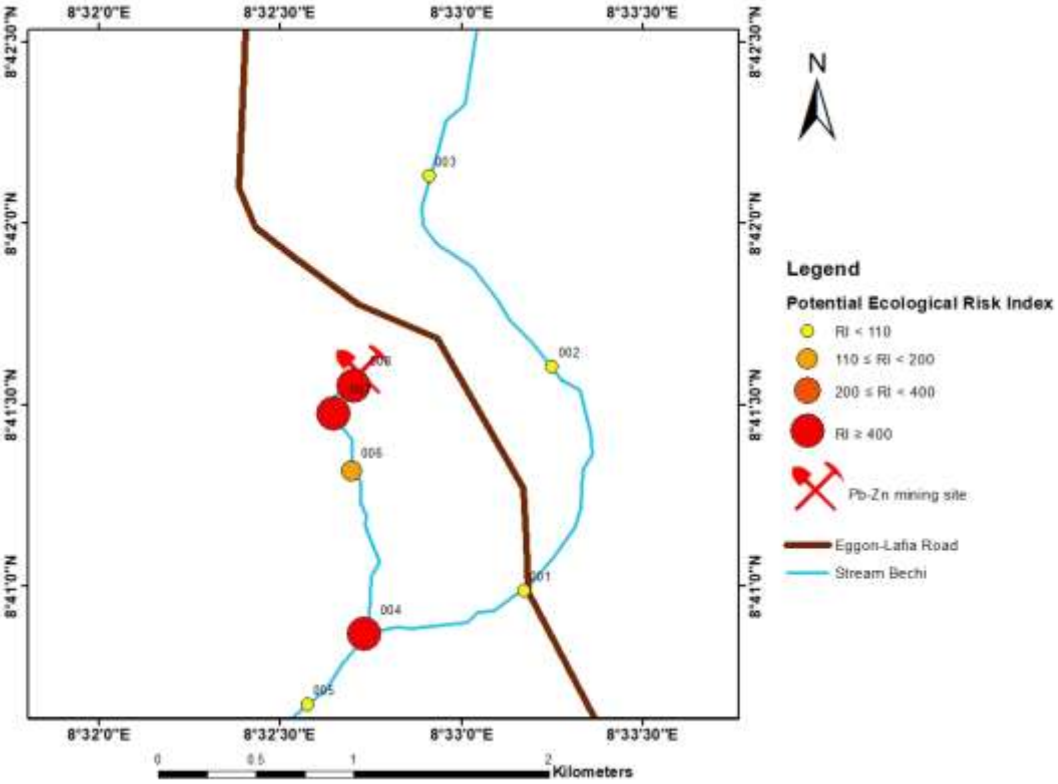

Figure 4.9b (vi) Potential ecological risk posed by PTEs (Pb, Zn, Cu, Cd and Cr) in Alizaga stream sediments.

4.5 Contribution of Mining and Processing Activities to the Release of PTEs in the Study Environment.

Lead-zinc mining and processing activities are actively taking place in the study area by both artisanal miners and a registered company as shown in Plate X. Both open cast and underground mining methods were used to win useful ore minerals in the area. The tailings produced in the process not only cover a large area but also release PTEs under the influence of surface runoff and water infiltration. The abandoned mines in Plate XI and XII have their mine dumps left on the surface and not backfilled. These were responsible for high concentration and contamination by PTEs in the soil within the mining area (an average of 47,975 ppm, 31291 ppm, 799 ppm, 68 ppm and 27 ppm for Pb, Zn, Cu, Cr and Cd respectively. The dispersion of PTEs in the soil is further enhanced when the overburden rocks are processed by the women and children in the area for some galena and sphalerite which are sold back to the company. The rock wastes (consisting majorly of quartzites and biotite granite with few disseminated Pb-Zn) are gathered and sold as rock aggregates.

Plate IX: Overview of Alizaga Pb-Zn mining and processing area.

Plate X: Abandoned surface Pb-Zn mines site.

The processing methods applied by the miners involve crushing, mineral sorting (Plate XI) and washing (Plate XII). The resulting tailings and processing water are discharged into the closest stream channel, a tributary of stream Bechi (Plates XIII and XIV). The settling pond for processing water constructed by the mining company is inadequate. There is absence of an impervious layer to restrict waste water infiltation into groundwater. It is also not wide enough, as a result it overflows and deposits mine waste water containing high concentration of PTEs into the closest stream channel.

Plate XI: Women involved quarrying overburden rocks into rock aggregates

Plate XII: Mines workers sorting and washing the Pb-Zn ore.

Plate XIII: Mines waste water and tailings from Pb-Zn processing into nearby stream channel.

Plate XIV: Women carrying out alluvial cassiterite mining on stream Bichi where domestic wastes are also discharged.

4.6 Human Health Risk Assessment

The exposure scenario considered in this study involves both children and adults having contact (average daily intake) with PTEs in soils (within the mines, schools, settlements and cultivated lands), stream sediments (close and away from mines) and groundwater (from shallow wells). The exposure pathways are through ingestion and dermal contact. In Plate XVI, children are more exposed because they can easily take up substances from the ground into their mouth in playgrounds. In Plate XVII, adults and mine workers were also exposed when adequate Personal Protective Equipment (PPE) are not used within the mines sites and through accidental contact with contaminated substances.

In Plate XV, panning of alluvial tin deposit were also carried out by women in several parts of the stream channel. This could also contributes to the dispersion of PTEs along the stream.

Plate XV: Pb-Zn ore handling by women at the sorting area without use of adequate Personal Protective Equipments (PPEs).

According to the USEPA (1989) classification of carcinogens and non-carcinogens, Pb, Zn, Cu and Cd were investigated for their non-carcinogenic risks while Cr and As were assessed for both carcinogenic and non-carcinogenic risks.

Plate XVI: Children play ground in a neighbouring village less than 1km from the mining site.

4.6.1 Non-carcinogenic risks

The non-carcinogenic risks posed by PTEs in the soils, stream sediments and groundwater have been calculated as Hazard Index (HI). Compared to adults, children have higher HI values for non-carcinogenic risk by ingestion (Table 4.7). This is because they are more susceptible to a given dose of toxin and have a higher likelihood to ingest significant quantities of soil since they easily pick objects from the soil when they play as well as their thumb-sucking behaviours. Among the PTEs studied, Pb appeared to cause greater non-carcinogenic risks in the soils than the others due to its higher concentration (Table 4.7).

The calculated average HI for PTEs due to ingestion of soil by adults at the mines sites, schools and settlements, and cultivated land were 1.28×10^{1}, 4.05×10^{-1} and 2.01×10^{-1} respectively. The calculated average HI for PTEs due to ingestion of soil by children at the mines sites, schools and settlements, and cultivated land were 8.94×10^{1}, 2.83×10^{0} and 1.40×10^{0} respectively.

Table 4.6: Calculated Average Daily Intake (ADI), Hazard Quotient (HQ) and Hazard Index (HI) by non-dietary ingestion of soil PTEs in Mines site, school, settlements and cultivated lands in the study area.

	PTEs	Mines Site		Schools and Settlements		Cultivated land	
		Adults	**Children**	**Adults**	**Children**	**Adults**	**Children**
ADI non-dietary	**Pb**	4.42×10^{-2}	3.10×10^{-1}	1.40×10^{-3}	9.80×10^{-3}	6.81×10^{-4}	4.77×10^{-3}
	Zn	2.86×10^{-2}	2.00×10^{-1}	5.23×10^{-4}	3.66×10^{-3}	6.66×10^{-4}	4.66×10^{-3}
	Cu	7.66×10^{-4}	5.36×10^{-3}	1.09×10^{-4}	7.66×10^{-4}	1.18×10^{-4}	8.25×10^{-4}
	Cr	4.02×10^{-5}	5.62×10^{-5}	8.03×10^{-5}	1.12×10^{-4}	1.68×10^{-4}	2.35×10^{-4}
	Cd	2.50×10^{-5}	1.75×10^{-4}	4.82×10^{-7}	3.38×10^{-6}	6.31×10^{-7}	4.42×10^{-6}
HQ non-dietary	**Pb**	1.26×10^{1}	8.84×10^{1}	4.00×10^{-1}	2.80×10^{0}	1.95×10^{-1}	1.36×10^{0}
	Zn	9.54×10^{-2}	6.68×10^{-1}	1.74×10^{-3}	1.22×10^{-2}	2.22×10^{-3}	1.56×10^{-2}
	Cu	1.92×10^{-2}	1.34×10^{-1}	2.74×10^{-3}	1.92×10^{-2}	2.95×10^{-3}	2.06×10^{-2}
	Cr	2.68×10^{-5}	3.75×10^{-5}	5.36×10^{-5}	7.50×10^{-5}	1.12×10^{-4}	1.57×10^{-4}
	Cd	2.50×10^{-2}	1.75×10^{-1}	1.61×10^{-4}	3.38×10^{-3}	6.31×10^{-4}	4.41×10^{-3}
	HI	1.28×10^{1}	8.94×10^{1}	4.05×10^{-1}	2.83×10^{0}	2.01×10^{-1}	1.40×10^{0}

The overall average HI due to soil ingestion (6.20×10^{-1} and 4.39×10^{0} for adults and children respectively) shows that children are more exposed to associated non-carcinogenic risks, since average HI for children is greater than 1 (Table 4.7). This exposure is usually when they play with the soils in schools, playground or when they accompany their parents to farmlands without adequate monitoring.

In Table 4.8, children have higher HI values greater than 1 for both sediments ingestion only close to the mines. The calculated average HI for PTEs due to stream sediments ingestion by adults and children close to the mines were 3.47×10^{-1} and 1.70×10^{0} close to the mines and 1.16×10^{-2} and 9.29×10^{-2} away from the mines respectively.

Table 4.7: Calculated Average Daily Intake (ADI), Hazard Quotient (HQ) and Hazard Index (HI) by non-dietary ingestion of stream sediments PTEs close and away from Alizaga mines site.

	PTEs	Close to Mines site		Away from Mines site	
		Adults	Children	Adults	Children
ADI non- dietary	Pb	1.76×10^{-4}	8.67×10^{-4}	5.59×10^{-6}	2.74×10^{-5}
	Zn	1.14×10^{-4}	5.61×10^{-4}	2.09×10^{-6}	1.02×10^{-5}
	Cu	3.06×10^{-6}	1.50×10^{-5}	4.37×10^{-7}	2.14×10^{-5}
	Cr	1.60×10^{-7}	1.57×10^{-7}	3.21×10^{-7}	3.15×10^{-7}
	Cd	9.96×10^{-8}	4.89×10^{-7}	1.92×10^{-9}	9.45×10^{-9}
HQ non-dietary	Pb	3.37×10^{-1}	1.65×10^{0}	1.07×10^{-2}	5.24×10^{-2}
	Zn	9.51×10^{-3}	4.67×10^{-2}	1.74×10^{-4}	8.54×10^{-4}
	Cu	5.66×10^{-4}	2.78×10^{-3}	8.09×10^{-4}	3.97×10^{-2}
	Cr	1.01×10^{-7}	1.05×10^{-7}	2.14×10^{-7}	2.10×10^{-7}
	Cd	3.32×10^{-5}	1.63×10^{-4}	6.41×10^{-7}	3.15×10^{-6}
HI		3.47×10^{-1}	1.70×10^{0}	1.16×10^{-2}	9.29×10^{-2}

However, the average HI values for stream sediments ingestion were less than 1 for both children and adults. This also suggests no non-carcinogenic risks by the studied PTEs in the stream sediments of Alizaga (Table 4.8).

Table 4.8: Calculated Average Daily Intake (ADI), Hazard Quotient (HQ) and Hazard Index (HI) of PTEs in Groundwater of the Study Area.

	PTEs	Adults	Children
ADI drinking	Pb	4.49×10^{-3}	7.86×10^{-3}
	Zn	1.04×10^{-2}	1.82×10^{-2}
	Cr	1.24×10^{-2}	2.17×10^{-2}
	Cd	1.06×10^{-2}	1.85×10^{-2}
	As	1.13×10^{-2}	1.34×10^{-2}
HQ drinking	Pb	1.28×10^{0}	2.24×10^{0}
	Zn	3.46×10^{-2}	6.06×10^{-2}
	Cr	8.27×10^{-3}	1.45×10^{-2}
	Cd	10.58×10^{0}	18.51×10^{0}
	As	37.81×10^{0}	66.16×10^{0}
HI		49.71×10^{0}	86.99×10^{0}

In Table 4.9, the average HI value for drinking groundwater contaminated by PTEs in the study area is far greater than 1 (that is, 4.97×10^{1} and 8.70×10^{1} for adults and children respectively). This further indicates the presence of non-carcinogenic risk posed by drinking contaminated groundwater in the area

Table 4.9: Calculated Average Incremental Lifetime Cancer Risk (ILCR) for Chromium and Arsenic in soils, stream sediments and groundwater of the study area.

		Soils					
		Mines		**Schools and Settlements**		**Cultivated lands**	
PTEs		**Ingestion**	**Dermal**	**Ingestion**	**Dermal**	**Ingestion**	**Dermal**
Cr	**Adults**	2.01×10^{-5}	NA	4.02×10^{-5}	NA	8.40×10^{-5}	NA
	Children	2.81×10^{-5}	NA	5.62×10^{-5}	NA	1.18×10^{-4}	NA
		Stream sediments					
		Close to Mines		**Away from Mines**			
		Ingestion	**Dermal**	**Ingestion**	**Dermal**		
Cr	**Adults**	4.70×10^{-5}	NA	3.13×10^{-5}	NA		
	Children	3.29×10^{-4}	NA	2.19×10^{-4}	NA		
		Ground water					
		Ingestion	**Dermal**				
Cr	**Adults**	6.20×10^{-3}	NA				
	Children	1.09×10^{-2}	NA				
As	**Adults**	1.70×10^{-2}	9.82×10^{-4}				
	Children	2.98×10^{-2}	2.27×10^{-3}				

‘NA’ means Data not available for calculation

4.6.2 Carcinogenic Risks

According to Fryer *et al*. (2006), carcinogenic risks greater than 1.0×10^{-4} are viewed as unacceptable, whereas risks below 1.0×10^{-6} are considered to pose considerable health effects. Risks in the range of 1.0×10^{-4} to 1.0×10^{-6} are generally considered tolerable. In Table 4.10, most of the carcinogenic risks by Cr contamination in soils (as it affects both adults and children in the mines, schools, settlements and cultivated lands) were between 1.0×10^{-6} and 1.0×10^{-4}, hence its cumulative effect is considered tolerable. Risks by Cr contamination through ingestion of stream sediments are also within tolerable limits for adults close and away from the mines. However, the risk level is unacceptable to children close (3.29×10^{-4}) and away (2.19×10^{-4}) from the mines.

Of great concern is the high calculated average Incremental Lifetime Cancer Risk (ILCR) level by chromium and Arsenic contamination in water from shallow wells in the study area. In table 4.10, ILCR values for ingestion of Chromium and Arsenic in water or dermal contact of Arsenic in water are all greater than 1.0×10^{-4} for both adults and children. Overall, the carcinogenic risk by chromium in soils, stream sediments and groundwater is 1.4 times, 7 times and 1.8 times greater in children than adults respectively. This further indicates that children are more exposed to cancerous risks than adults in the study area.

Although the risk assessment model used in this study are useful tools to distinguish the toxic chemicals and various exposure pathways in the environment, however, the risk assessment of PTEs here remained with some uncertainties, which are inherent in quantitative risk assessment. The bioavailable or bioaccessible concentration of PTEs is considered more reliable and accurate in ecological and human risk assessments which suggests that the human risk were assessed based on the total concentration of these elements (Cao *et al*., 2016). Hence, the potential health risks may have been overestimated.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study have assessed PTEs distribution, contamination and potential health risk in Alizaga. This is of great importance because it provides basic information on toxic element pollution levels so that prevention, protective and control measures can be taken by individuals, mining companies and government. Geologically, the study area is underlain by Basement Complex rocks of Nigeria. The dominant rock type is biotite granite (47%), followed by gneiss (31%), migmatite (11%), ryholite (10%), quartzite (0.9%) and dolerite dykes (0.1%).

PTEs concentration in the soil are in the sequence Pb>Zn>Cu>Cr>Cd within the mines and Pb>Zn>Cr>Cu>Cd away from the mines. Apart from cadmium concentration, the average concentration of studied PTEs in soils of the area is higher when compared to guidelines by Ministry of the Environment, Finland (MEF, 2007) and Background concentration in soils by Bowen (1979). PTEs concentration in stream sediments was generally highest close to the mines and lowest away from the mines with average sequence Pb>Zn>Cu>Cr>Cd. The average concentration of PTEs in shallow wells is such that Cr>As>Cd>Zn>Pb while it is Zn>As>Cr>Cd>Pb in site borehole (160m deep). The high concentration of arsenic and chromium is of serious concern in the study area, considering their high toxicity. Apart from zinc, other PTEs studied have their concentration in groundwater above permissible limits by World Health Organisation WHO (2022) and recommended guidelines by Nigerian Standard for Drinking Water Quality NSDWQ (2007).

Pollution levels for lead, zinc, copper and cadmium were highest for soils and sediments within the mines and moderate to unpolluted away from the mines. Their contaminations can be related to mining activities as well as use of fertilizers, pesticides and herbicides on cultivated lands. Lead and zinc were especially widely distributed due to their mineralization in the quartzites and adjoining biotite granites in the area. Whereas chromium contamination is low to unpolluted in the mines, it is polluted in some areas away from the mines. This could have been caused by other anthropogenic activities such as domestic and agricultural waste disposals which were observed on the stream channels and dump sites close to the main town. However, the high pollution load index in the soils and stream sediments furthers confirms the existence of metal(loids) pollution in the area.

The potential ecological risks posed by the studied PTEs is such that Pb>Zn>Cu>Cd>Cr. The highest risks is within the mines, considerable to moderate risks in surrounding areas and lowest risks in those areas farthest from the mines. Unplanned disposal of overburden rocks and tailings containing high concentration of some PTEs, uncontrolled use of fertilizers on cultivated lands and to some extent waste disposals at dump sites and stream channels have increased contamination by PTEs in Alizaga environment. Soil erosion and leaching have also aided their dispersion from the mines to surrounding areas.

This has also exposed the people of the area (both adults and children) to potential health risks through frequent and prolonged exposure to several dosage levels. Ingestion is the prevalent exposure pathway while dermal contact pose no serious health risks. Children are 1.4 to 7 times more exposed than adults and this is because they can easily pick up objects into their mouth when they play in schools, playgrounds or accompany parents to farms without adequate monitoring. Serious carcinogenic health risk by chromium and arsenic contamination in groundwater (from shallow wells) exist, it is a threat to both children and adults and this requires immediate attention. Non-carcinogenic health risk by soil ingestion exists to both children and adult within the mines while in surrounding areas, this risk is currently a threat to only children. Overall, there was no serious non-carcinogenic risk by studied PTEs in stream sediments of the area at this time.

5.2 Recommendations

Following the results and conclusion from this study, the recommendations are as follows:

Regular environmental audit should be enforced by National Environmental Standards and Regulations Enforcement Agency (NESREA), Federal and State Environmental Protection Agencies. This will ensure that Environment Management Plan as stated on the Environmental Impact Assessment are strictly adhered to. This will immediately arrest further deterioration of the environment by mining activities and waste disposal. For example, the settling pond for Pb-Zn processing must be wide and deep enough to prevent overflow. The walls and bottom should be covered with an impervious layer (or linings) such as clay to prevent or reduce leaching into the groundwater system. Overburden rocks and tailings can also be backfilled into the mining pits or stored where they cannot easily interact with the environment.

The consumption of groundwater from the shallow wells within 1km radius of the Pb-Zn mining area must be immediately discouraged. This is because of the high concentration of lead, copper, chromium and arsenic in groundwater. Since the concentration of these PTEs are not very high in deep borehole sampled, this may be considered as a better source of groundwater in the area. However, it is also important the government and mining companies working in the area develop pipe borne water supply with adequate treatment for use by the inhabitant of the area.

Personal Protective Equipment (PPE) such as protective clothing, hand gloves, nose mask or full face mask must be used by the mine workers to prevent dermal contact and inhalation of PTEs respectively. Regular hand washing or full body bath should be encouraged when workers leave the mining and processing site.

Several remediation practices can also be adopted to reduce the hazardous effects of PTEs and restore contaminated soil ecosystem especially within and around the mining area where pollution levels are high. Potential immobilization of PTEs in soils using various soil amendments to minimize the bioavailability and toxicity of these pollutants. Applying soil amendments is considered one of the easiest to adopt and most cost-effective in situ remediation techniques to improve soil quality through PTE immobilization (Palansooriya *et al*. 2020). A range of organic and inorganic soil amendments, such as animal wastes, biochar, biosolids, compost, clay minerals, coal fly ash, liming materials, metal oxides, and phosphates, are commonly used as PTE immobilizing agents. However, some important aspects such as soil characteristics and targets PTE behaviours must be considered when selecting a suitable immobilizing agent for any practical application.

In addition to regular monitoring of PTEs in aquifers and soils, there is also need for further research work on their uptake by plants and humans in the area. This is because PTEs can enter the human body through food chain. Consumption of food crops grown in cultivated lands that have been contaminated presents a health risk for local inhabitants. Therefore, prior to remediation of contaminated soils, cultivation of crops close to the mines should be discouraged.

In future work, sampled point-wise or location-by-location health risk approach instead of average values estimation that was used in this study can be applied to provide a more comprehensive health risk assessment of the area. Models that take care of several uncertainties leading to overestimation or underestimation of health risks, such as study by Di Bonito *et al*. (2018), should be developed. Also, Integrated Risk Information System (IRIS) by USEPA (1997) should be developed further to take care of variations in local environments.

5.3 Contribution to Knowledge

This work have updated the geological map of the study area. The dominant rock type is biotite granite (47%), followed by gneiss (31%), migmatite (11%), ryholite (10%), quartzite (0.9%) and dolerite dykes (0.1%). It also reveals a concentration range of 97-83299 mg/kg for lead, 80-55352 mg/kg for zinc, 80-1438 mg/kg for copper, 68-1916 mg/kg for chromium and 0.02-52 mg/kg for cadmium respectively in the top soils. In stream sediments of the study area, the concentration ranges are 97-58776 mg/kg for lead 80-107491 mg/kg for zinc, 80-2397 mg/kg for copper, 68-137 mg/kg for chromium and 2-93 mg/kg for cadmium respectively. Average Concentrations in groundwater are 0.18 mg/L for lead, 0.34 mg/L for zinc, 0.49 mg/L for chromium, 0.42 mg/L for cadmium and 0.43 mg/L for arsenic.

It also revealed that lead-zinc mining activities in the study area have contributed to the release of PTEs (Pb, Zn, Cu and Cd) into agricultural soils, stream sediments and groundwater in the study area, especially within immediate vicinity of the mine site. There exist contamination by chromium outside of the mine site which can be related to anthropogenic source such as use of fertilizers, pesticides and indiscriminate domestic waste disposal within settlements. This can form a basis for future research to understand the cause of chromium contamination in such areas.

REFERENCES

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

Adamo, P., Denaix, L., Terribile, F. and Zampella, M. (2003). Characterization of heavy metals in contaminated volcanic soils of the Solofrana river valley (southern Italy). *Geoderma,* 117 (3–4), 347–366.

Adamu, S., Ayuba, M., Murtala, A. and Lar, U.A. (2014). Assessment of Potentially Toxic Metals in Soil and Sediment of the Keana Brinefield in the Middle Benue Trough, Northcentral Nigeria. *American Journal of Environmental Protection,* 3(6-2), 77-88.

Ahmad, M., Lee, S.S., Yang, J.E., Ro, H.-M., Lee, Y.H. and Ok, Y.S. (2012). Effects of soil dilution and amendments (mussel shell, cow bone, and biochar) on Pb availability and phytotoxicity in military shooting range soil. *Ecotoxicology Environment Safety,* 79, 225–231.

Ahmad, M., Ok, Y.S., Rajapaksha, A.U., Lim, J.E., Kim, B.Y., Ahn, J.H., Lee, Y.H., Al-Wabel, M.I., Lee, S.E. and Lee, S.S. (2016). Lead and copper immobilization in a shooting range soil using soybean stover-and pine needle-derived biochars: chemical, microbial and spectroscopic assessments. *Journal Hazardous Materail,* 301, 179–186.

Akintunde, E. A., Ore, O. T., Durodola, S. S., Sharaibi, J. E. and Adegbite, O. B. (2020). Contamination Assessment of Potentially Toxic Metals in Road-Side Surface Soils Along Iwo-Ibadan Expressway, Nigeria. *Colloid and Surface Science,* 5(1), 1-5.

Alloway, B.J. (2013). Sources of Heavy Metals and Metalloids in Soils and their Bioavailability. In B. Alloway (Ed.), *Heavy Metals in Soils. Environmental Pollution* (pp. 11-50). Dordrecht, Springer.

Antoniadis, V., Golia, E.E., Shaheen, S.M. and Rinklebe, J. (2017). Bioavailability and health risk assessment of potentially toxic elements in Thriasio Plain, near Athens, Greece. *Environmental Geochemistry Health,* 39 (2), 319–330.

Ayiwulu, E. (2012). The Nature of Water Scarcity and Domestic Water Demand in Nassarawa-Eggon Town of Nasarawa State. Nigeria. Unpublished Ph.D. Thesis, University of Jos.

Barbieri, M. (2016). The importance of Enrichment Factor (EF) and geoaccumulation index (Igeo) to evaluate the soil contamination. *Geology Geochemistry,* 5, 1-4.

Bhatnagar, J. P. and Awasthi, S. K. (2000). Prevention of Food Alteration Act (Act No. 37 of 1954) along with Central and State Rules (as amended for 1999). Ashoka Law House.

Biasioli, M., Grcˇman H., Kralj, T., Madrid, F., Dı´az-Barrientos, E. and Ajmone-Marsan, F. (2007). Potentially Toxic Elements Contamination in Urban Soils. *Journal of Environmental Quality,* 3 (5), 230-238.

Bowen, H.J.M. (1979). *Environmental chemistry of the elements*. London, UK: Academic Press.

Buat-Menard, P. and Chesselet, R. (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth and Planetary Science Letters* 42 (3), 399-411.

Canadian Council of Ministers of Environment (2002). *Canadian Environmental Quality Guidelines* (2). Retrieved from http://ccme.ca/en/current-activities/canadian-environmental-quality-guidelines.

Cao, S.Z.; Duan, X.L.; Zhao, X.G.; Chen, Y.T.; Wang, B.B.; Sun, C.Y.; Zheng, B.H.; Wei, F.S. (2016). Health risks of children's cumulative and aggregative exposure to metals and metalloids in a typical urban environment in China. *Chemosphere,* 147, 404–411.

Cao, X., Ma, L.Q., Rhue, D.R. and Appel, C.S. (2004). Mechanisms of lead, copper, and zinc retention by phosphate rock. *Environmental Pollution*, 131 (3), 435–444.

Carla, C., Eduardo, F., Paula, F.Á and João, P.T. (2014). Identifying Sources and Assessing Potential Risk of Exposure to Heavy Metals and Hazardous Materials in Mining Areas: The Case Study of Panasqueira Mine (Central Portugal) as an Example. *Geosciences,* 4, 240-268.

Carlon, C., D'Alessandro, M., Swartjes, F. (2007). Derivation Methods of Soil Screening Values in Europe: A Review of National Procedures towards harmonisation. *Office for Official Publication of the European Communities EUR-OP. Scientific and Technical Research Series.*

Carter, M.R. and Gregorich, E.G. (2007) *Soil Sampling and Methods of Analysis. 2nd Edition*, Boca Raton: CRC Press

Chen, T., Liu, X., Zhu, M., Zhao, K., Wu, J., Xu, J. and Huang, P. (2008). Identification of Trace Element sources and associated risk assessment in vegetable soils of the urban-rural transitional area of Hangzhou, China. *Environmental Pollution.* 151 (1), 67–78.

Chen, Y.F. (2011). Review of the research on potentially toxic element contamination of China's city soil and its treatment methods. *China Population, Resources and Environment*, 21, 536-539.

Chui, S., Wong, Y.H., Chio, H.I., Fong, M.Y. and Chiu, Y.M. (2013). Study of heavy metals poisoning in frequent users of Chinese medicines in Hong Kong and Macau. *Phytotherapy Research*, 27, 859-863.

Cope, C.M., Mackenzie, A.M., Wilde, D. and Sinclair, L.A. (2009). Effects of level and form of dietary zinc on dairy cow performance and health. *Journal of Dairy Science*, 92, 2128-2135.

Das, R., Mohtar, A.T., Rakshit, D., Shome, D. and Wang, X. (2018). Sources of atmospheric lead (Pb) in and around an Indian megacity. *Atmosphere Environment,* 193, 57–65.

Davis, H.T., Aelion, C.M., McDermott, S. and Lawson, A.B. (2009). Identifying natural and anthropogenic sources of metals in urban and rural soils using GIS-based data, PCA and spatial interpolation. *Environmental Pollution,* 157 (8–9), 2378–2385.

Di Bonito, M., Lofts, S. and Groenenberg, J.E. (2018). Models of Geochemical Speciation: Structure and Applications. *Environmental Geochemistry,* 4(7), 237–305.

Edna, S.D., Renato, A.T., Hercilia, S.C., Fabio, J.O., Leonidas, C.A., Kelson, D.F. and Antonio, R.F. (2017). Assessment of Risks to Human Health from Simultaneous Exposire to Multiple Contaminants in an Artisanal Gold Mine in Serra Pelada, Brazil. *Science Total Environment,* 576, 683-695

Federal Surveys, Nigeria (1970). National Topographical Maps, Wamba Sheet 210 SW (1:50,000)

Ferreira, B.L. and Miguel, E.D. (2005). Geochemistry and risk assessment of street dust in Luanda, Angola: A tropical urban environment. *Atmosphere Environment,* 39, 4501–4512.

Ferreira, S. L., da Silva Junior, J. B., dos Santos, I. F., de Oliveira, O. M., Cerda, V., and Queiroz, A. F. (2022). Use of Pollution Indices and Ecological Risk in the Assessment of Contamination from Chemical Elements in Soils and Sediments–Practical Aspects. *Trends in Environmental Analytical Chemistry,* 35, 169.

Fryer, M; Collins, C.D.; ferrier, H; Colvile, R.N.; Nieuwenhuijsen, M.J. (2006). Human Exposure Modelling for chemical risks assessment: A review of current approaches and research and policy implications. *Environmental Science Policy,* 9, 261-274.

Gržetić, I. and Ghaariani, A.R.H. (2008). Potential health risk assessment for soil heavy metal contamination in the central zone of Belgrade (Serbia). *Journal of Serbian Chemistry Society,* 73, 923-934.

Guilarte, T. R. (2011). Manganese and Parkinson's disease: A critical review and new findings. *Ciência & Saúde Coletiva,* 16, 4549-4566.

Hakanson, L. (1980). Ecological risk index for aquatic pollution control, a sedimentological approach. *Water Resources,* 14, 975 -1001.

Hashimoto, Y., Matsufuru, H., Takaoka, M., Tanida, H. and Sato, T. (2009). Impacts of chemical amendment and plant growth on lead speciation and enzyme activities in a shooting range soil: an X-ray absorption fine structure investigation. *Journal of Environmental Quality,* 38 (4), 1420–1428.

Hatje, V., Pedreira, R.M.A., de Rezende, C.E., Schettini, C.A.F., de Souza, G.C., Marin, D.C. and Hackspacher, P.C. (2017). The environmental impacts of one of the largest tailing dam failures worldwide. *Scientific Reports,* 7 (1), 10706.

Hou, D and Li, F. (2017). Complexities surrounding China's soil action plan. *Land Degradation Development,* 28 (7), 2315–2320.

Keller, B., Faciano, A., Tsega, A. and Ehrlich, J. (2017). Epidemiologic characteristics of children with blood lead levels ≥45 μg/dL. *Journal of Pediatrics,* 180, 229–234.

Krishna A. K. and Dasaram B. (2021). Assessing Potentially Toxic Elements (PTEs) distribution and behaviour in soils around an agro-based industries (India): Ecological Risk, Environmental and Analytical Inferences. *Soil and Sediment Contamination,* 30 (5), 497-517.

Kuo, T. H., Chang, C.-F., Urba, A. and Kvietkus, K. (2006). Atmospheric gaseous mercury in Northern Taiwan. *Science Total Environment,* 368 (1), 10–18.

Ladan, M. T. (2012). Review of NESREA Act 2007 and Regulations 2009-2011: A New Dawn in Environmental Compliance and Enforcement in Nigeria. *Law, Environment and Development Journal. 8,* 116.

Laidlaw, M.A.S. and Filippelli G.M. (2008). Resuspension of Urban soils as a persistent source of lead poisoning of children: A Review and a new direction. *Applied Geochemistry* 23 (8), 2021-2039.

Lanphear, B.P, Winter N.L Apetz L., Elberly, S. and Weitzman M. (1996). A Random trial of the effects of dust control on Children's blood lead levels. *Pediatrics,* 98, 35-40.

Lar, U. A., Ngozi-Chika C. S. and Ashano E. C. (2013). Human exposure to lead and other potentially harmful elements associated with galena mining at New Zurak, Central Nigeria. *Journal of African Earth Sciences,* 84, 13–19.

Lee, C.S., Li, X., Shi, W., Cheung, S.C. and Thornton, I. (2006). Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. *Science Total Environment,* 356 (1–3), 45–61.

Lindemann, M.D., Cromwell, G.L., Monegue, H.J. and Purser, K.W. (2008). Effect of chromium source on tissue concentration of chromium in pigs. *Journal of Animal Science,* 86, 2971-2978.

Loska, K., Cebula, J., Pelczar, J., Wiechula, D. and Kwapulinski, J. (1997). Use of enrichment and contamination factors together with geoaccumulation indeices to evaluate the content of Cd, Cu and Ni in the Rybnik water reservoir in Poland. *Water, Air and Soil pollution,* 93(1), 347-365.

Luo, X.S., Yu, S., Zhu, Y.G. and Li, X.D. (2012). Trace metal contamination in urban soils of China. *Science of the Total Environment,* 421 (22), 17–30.

MacFarlane, G. R. and Burchett, M. D. (2002). Toxicity, growth and accumulation relationships of copper, lead and zinc in the grey mangrove Avicennia marina (Forsk.) Vierh. *Marine Environmental Research*, *54*(1), 65-84.

Mei, J., Li, Z., Sun, L., Gui, H. and Wang, X. (2011). Assessment of heavy metals in the urban river sediments in Suzhou City, northern Anhui Province, China. *Procedure of Environmental Science,* 10, 2547–2553.

Ministry of the Environment, Finland (2007). Government Decree on the Assessment of Soil Contamination and Remediation Needs. Retrieved from http://faolex.fao.org/docs/pdf/fin113198.pdf

Muller, G. (1979). Index of Geo accumulation in Sediments of the Rhine River. *Geology Journal,* 2, 109-118.

Murray, K., Bazzi, A., Carter, C., Ehlert, A., Ham's, A., Kopec, M., Richardson, J. and Sokol, H. (1997). Distribution and mobility of lead in soils at an outdoor shooting range in southeastern Michigan. *Journal of Soil Contamination,* 6 (1), 79–93.

Musa W. O., Wuana R. A., Itodo U. A. and Eneji I. S. (2021). Human Health Risks of Heavy Metal in Wells and Streams Water in the Vicinity of a Lead Mining in Nasarawa State, North Central, Nigeria. *Journal of Health and Environmental Research,* 7 (2), 82-93.

Nganje, T. N., Edeta, A., Cuthbert, S., Adamua, C. I. and Hursthouse, A.S. (2020). The concentration, distribution and health risk from potentially toxic elements in the soil - plant - water system developed on black shales in SE Nigeria. *Journal of African Earth Sciences*, 165 (2020) 103-806.

Nnabo, P. N. (2015). Assessment of heavy metal distribution in rocks from Enyigba Pb-Zn district, southeastern Nigeria. *International Journal of Innovation and Scientific Research,* 17 (1), 175-185.

NSDWQ (2007). Nigeria Standard for Drinking Water Quality. *Nigerian Industrial Standard,* 554, 13-14.

Obiora, S. C., Anthony C., and Davies T. C. (2016). Heavy metals and health risk assessment of arable soils and food crops around Pb–Zn mining localities in Enyigba, southeastern Nigeria. *Journal African Earth Science,* 116 (2016), 182-189.

O'Connor, D., Peng, T., Zhang, J., Tsang, D.C., Alessi, D.S., Shen, Z., Bolan, N.S. and Hou, D. (2018). Biochar application for the remediation of heavy metal polluted land: a review of in situ field trials. *Science Total Environment,* 619, 815–826.

Ombugus, M. A., Ahulle, W. R., Adams, I. U. and Shaibu, E. I. (2021). Human Health Risks of Heavy Metal in Wells and Streams Water in the Vicinity of a Lead Mining in Nasarawa State, North Central, Nigeria. *Journal of Health and Environmental Research,* 7(2), 76-87.

Palansooriyaa, K. N., Shaheen S. M., Chene S. S., Tsange D. C., Hashimoto Y., Houng D., Nanthi S., Rinklebe J. and Ok Y. S. (2020). Soil amendments for immobilization of potentially toxic elements in contaminated soils: A critical review. *Environment International,* 134 (2020), 40-50.

Pan, L., Fang, G., Wang, Y., Wang, L., Su, B., Li, D. and Xiang, B. (2018). Potentially Toxic Element Pollution Levels and Risk Assessment of Soils and Sediments in the Upstream River, Miyun Reservoir, China. *International Journal of Environmental Research,* 15, 23-64.

Pascual, M. T., Mehta, R. L., Soroko, S., Savage, B. R., Himmelfarb, J., Ikizler, T.A. (2004). Spectrum of acute renal failure in the intensive care unit: the PICARD experience. *Kidney International,* 66(4), 1613-1621

Pourret, O. and Hursthouse, A. (2019). It is Time to Replace the Term “Heavy Metals” with “Potentially Toxic Elements” when reporting Environmental Research. *International Journal of Environment, Research and Public Health,* 16(22), 4446

Rinklebe, J. and Shaheen, S.M. (2017). Assessing the mobilization of cadmium, lead, and nickel using a seven-step sequential extraction technique in contaminated floodplain soil profiles along the central Elbe River, Germany. *Water, Air, & Soil Pollution,* 225 (8), 20-39.

Sadik, N.A. (2008). Effects of diallyl sulfide and zinc on testicular steroidogenesis in cadmium-treated male rats. *Journal of Biochemical and Molecular Toxicology,* 22, 345-353

Salt, D.E., Prince, R.C., Pickeriong, I.J. and Raskin, I. (1997). Mechanisms of cadmium mobility and accumulation in Indian mustard. *Plant Physiology,* 109, 1427-1433

Shaheen, S.M., Shams, M.S., Khalifa, M.R., Mohamed, A. and Rinklebe, J. (2017). Various soil amendments and environmental wastes affect the (im) mobilization and phytoavailability of potentially toxic elements in a sewage effluent irrigated sandy soil. *Ecotoxicology Environmental Safety,* 142, 375–387.

Silas, A.S. (2019). The Geology, Petrography and Economic Potential of Parts of Nasarawa-Eggon and Environs, North Central Nigeria. *Environmental and Science Research Journal,* 6(1), 24-34.

Su, C., Jiang, L. and Zhang W. (2004). A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techniques. *Environmental Skeptics and Critics,* **3**, 24-38.

Sutherland, R.A. (2000). Bed sediments associated trace metals in urban stream, Oahu Hawaii. Bed sediments associated trace elements in an urban stream, Oahu, Hawaii. *Environmental Geology,* 39, 611-627.

Suzuki, K., Yabuki, T. and Ono Y. (2009). Roadside *Rhododendron pulchrum* leaves as bio indicator of heavy metal pollution in traffic areas of Okayama, Japan. *Environmental Monitoring and Assessment,* 149, 133-14.

Taylor, M.P., Mould, S.A., Kristensen, L.J. and Rouillon, M. (2014). Environmental arsenic, cadmium and lead dust emissions from metal mine operations: implications for environmental management, monitoring and human health. *Environmental Research,* 135, 296–303.

Tomlinson, D.C., Wilson, J.G., Harris, C.R. and Jeffrey, D.W. (1980). Problems in Assessment of Heavy Metals in the Estuaries and the Formation of Pollution Index. *Helgoland Marine Research,* 33, 566-575.

Toth, G., Hermann, T., Szatmari, G. and Pasztor, L. (2016). Maps of heavy metals in the soils of the European Union and proposed priority areas for detailed assessment. *Science Total Environment,* 565, 1054–1062.

United States Environmental Protection Agency (1989). *Risk Assessment Guidance for Superfund; Volume 1: Human Health Evaluation Manual (Part A)*; U.S. Environmental Protection Agency, Office of Emergency and Remedial Response: Washington, DC, USA.

United States Environmental Protection Agency (1997). *Exposure Factors Handbook. Volume 1: General Factors;* U.S. Environmental Protection Agency, Office of Research and Development: Washington, DC, USA.

United States Environmental Protection Agency (2002). *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites;* U.S. Environmental Protection Agency, Office of Emergency and Remedial Response: Washington, DC, USA.

United States Environmental Protection Agency (2011). *Risk Assessment Guidance for Superfund. Volume 1.* U.S. Environmental Protection Agency: Washington, DC, USA.

Van der Voet, E., Salminen, R., Eckelman M., Mudd, G., Norgate, T. and Hischier, R. (2013). UNEP (2013) Environment Risks and Challenges of Anthropogenic Metals Flow and Cycles. *A Report of the Working Group on the Global Metal Flows to the International Resource Panel.* Retrieved from https://orbit.dtu.dk/files/54666484/Environmental_Challenges_Metals_Full_Report

Varrica, D., Tamburo, E., Dongarra, G. and Sposito, F. (2014). Trace elements in scalp hair of children chronically exposed to volcanic activity (Mt. Etna, Italy). *Science Total Environment,* 4(4), 117–126.

Vineethkumar, V., Sayooj V. V., Shimod, K. P. and Prakash, V. (2020). Estimation of pollution indices and hazard evaluation from trace elements concentration in coastal sediments of Kerala, Southwest Coast of India. *Bulletin of the National Research Centre,* 4(2), 321-347.

Wang, L., Guo, Z., Xiao, X., Chen, T., Liao, X., Song, J. and Wu, B. (2008). Heavy Metal Pollution of Soils and Vegetables in the Midstream and Downstream of the Xiangjiang River, Hunan Province. *Journal of Geographic Science,* 18, 353-362.

Wong, C.S.C., Li, X. and Thornton, I. (2006). Urban environmental geochemistry of trace metals. *Environmental Pollution,* 142 (1), 1–16.

World Health Organization (2011). Guidelines for Drinking-water Quality. 4th Edition, Geneva Switzerland. *WHO Chronicle*, 38(4), 104-8.

World Health Organization (2016). News Release, Geneva. Retrieved from http://www.who.int/news-room/detail/15-03-2016-an-estimated-12-6-million-deaths-each-year-are-attributable-to-unhealthy-enviroments.

World Health Organization (2018). Lead Poisoning and Health. Retrieved from http://www.who.int/en/news-room/ fact-sheets/detail/lead-poisoning-and-health.

World Health Organization (2022). Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First and Second Addenda. Geneva