

Arsenic Contamination of Groundwater in South-Western Part of Ashanti Region of Ghana

A thesis approved by the Faculty of Environmental Sciences and Process Engineering at the Brandenburg University of Technology in Cottbus-Senftenberg in partial fulfillment of the requirement for the award of the academic degree of Doctor of Philosophy (Ph.D.) in Environmental Sciences.

by

Master of Philosophy

Crentsil Kofi Bempah

Born in Kumasi, Ashanti Region, Ghana

Supervisor: **Prof. Dr. rer. nat. habil. Hans-Jürgen Voigt**

Supervisor: **Prof. Dr. rer. nat. Rainer Herd**

Day of the oral examination: 04.11.2014

DECLARATION

This doctoral dissertation “Arsenic Contamination of Groundwater in South-Western Part of Ashanti Region of Ghana” was completed and written independently by me Crentsil Kofi Bempah. I hereby declare that:

1. This Ph.D. thesis was completed and written independently and that all used sources and tools are indicated in the thesis.
2. The publication of the thesis does not violate any copyright rules. All other work and/or words of others are appropriately cited or quoted.
3. I have never applied for a doctoral degree award in BTU or any institution before; or submitted any earlier applications to obtain permission for final examination or publication of my doctoral degree in part or in whole.
4. There has never been an instance where my application to get permission for final examination or publication of a doctoral degree has been cancelled, disqualified or unsuccessful due to my attempt to deceive.

The research is an accurate and original account of my work done under the framework of the Environmental and Resource Management doctoral program offered by the Brandenburg University of Technology, Cottbus-Senftenberg. It includes objectives, discussion of results, accurate representation of underlining data and detailed referencing of all sources and tools used.

Date: 04.11.2014

Crentsil Kofi Bempah

Lehrstuhl Umweltgeologie

Brandenburg University of Technology, Cottbus-Senftenberg

ACKNOWLEDGEMENT

The path that took me to this Doctoral Thesis has been paved with the support of several people to whom I owe my deepest gratitude. First of all, I would like to express my sincere thanks to my principal supervisor, Prof. Dr. Hans-Jürgen Voigt who has given inspirational guidance, willing support, scientific and motivating discussion throughout my study. Without his able guidance and tutelage, this research would never have been completed successfully.

My sincere gratitude goes to my second supervisor, Prof. Dr. Rainer Herd for his invaluable suggestions, constructive criticisms and corrections which proved indispensable in the preparation of this thesis. Dr. Christian Lorenz and Dr. Anthony Ewusi deserve special mention for their constructive comments and useful suggestions. Their engagement and help in proofreading this manuscript helped me much to complete this research.

Words could not express my sincere gratitude to Prof. E.H.K Akaho; former Director General of Ghana Atomic Energy Commission for his foresight, dedication and kindness for granting me study leave to study in Germany. I also wish to express my utmost gratitude to Katholischer Akademischer Ausländer-Dienst (KAAD) for granting me scholarship to successfully complete this PhD research. I must thank Ms. Simone Saure, officer of KAAD for her support and help for my daily life and travels in and out of Germany.

I really appreciated the contact to all the members of the Obuasi Municipal Assembly, Bekwai Municipal Assembly, Amansie West, Amansie Central and Adansi North District Assemblies for answering my questions and providing more than scientific information. A wealthy acknowledgment goes to Mrs. Ansah Asare for giving me a space in her home to conduct As removal technology.

Moreover, my special acknowledgments go to all-rounder Benjamin Agyei (Papa Attah) and my bachelor students from University of Ghana and University of Cape Coast for their enduring help. Without them, the fieldwork wouldn't have been done in this short time. Further, I appreciated the help of George Tetteh Ashiagbor, APERL GIS Center at the Faculty of Forest Resources Technology, KNUST, for his assistance during the processing of the GIS data.

Special thanks to Daniel Ayerebi Ansong, Agya Asabere and Solomon Obiri Yeboah for their permanent encouragement during the difficult periods of my work. Thanks to Francis Mensah, Dr-Ing. Roy, Emmanuel Ambe, Theodore, Ing. Kobla and John Kesita for their patience and help to get some distraction from my work if it was necessary...

Years seem very long to last, but I am grateful to my family, most especially to my darling mother and father as well as my revered in-laws for their support with words of encouragement and prayers as well as their reminder that they have been waiting for me and I should work hard, so that these long days need not to be wasted. I reckon it is impossible to have my research career without the massive support, love and encouragement from my dearest wife, Mrs. Juliana Bempah and my two wonderful children, Naana Abena Achiah Bempah and Oheneba Nana Yaw Kankam Bempah. This work could never have been completed without their encouragement and good will messages they sent across the miles. Through their unconditional love, they have been constant source of moral support that has helped make my dream come true.

DEDICATION

This thesis is dedicated to my beloved wife Mrs. Juliana Bempah, my treasured son Oheneba Nana Yaw Kankam Bempah and my dearest daughter Naana Abena Achiah Bempah.

TABLE OF CONTENTS

DECLARATION.....IV

ACKNOWLEDGEMENT.....IV

DEDICATION.....IV

TABLE OF CONTENTS.IV

LIST OF TABLES.....IX

LIST OF FIGURES.....XI

LIST OF ABBREVIATIONS.....XIV

UNITS OF MEASUREMENTS.....XV

ABSTRACT IN ENGLISH.....XVI

ABSTRACT IN DEUTSCH.....XVI

CHAPTER ONE 1

1.0 GENERAL INTRODUCTION..... 1

1.1 Background 1

1.2 Justification 4

1.3 Hypotheses 6

1.4 Objectives of the Research 7

CHAPTER TWO 9

1.0 HYDROGEOCHEMISTRY AND ARSENIC CONTAMINATION IN THE ENVIRONMENT – A LITERATURE REVIEW 9

2.1 Introduction..... 9

2.2 Arsenic in the Environment 10

2.3 Arsenic in Groundwater..... 11

2.4 Geochemistry of Arsenic Release to Groundwater..... 16

2.5 Arsenic Behavior and Speciation..... 19

2.6 Groundwater Flow and Transport..... 23

2.7 Arsenic Exposure and Human Health 24

2.8 Analytical Methods for Arsenic Determination in Drinking Water 28

2.9 Arsenic Removal Technologies 34

2.10 Mining Related Arsenic Problems in Ghana, an Overview 35

CHAPTER THREE	41
3.0 DESCRIPTION OF THE STUDY AREA	41
3.1 Location	41
3.2 Soils and Vegetation.....	43
3.3 Climate.....	45
3.4 Geology and Hydrogeology	46
3.5 Relief and Drainage	49
3.6 Land Use	51
CHAPTER FOUR.....	52
4.0 FIELD IDENTIFICATION AND SAMPLE COLLECTION – METHODOLOGY.....	52
4.1 Introduction.....	52
4.2 Fieldwork.....	52
4.3 Selection of Groundwater Sampling Sites	52
4.4 Selection of Tailings Dam Sampling Sites.....	55
4.5 Materials	57
4.6 Containers and Cleaning Processes.....	59
4.7 Groundwater Sample Collection	60
4.8 Mine Tailings Sample Collection.....	62
CHAPTER FIVE	64
5.0 ANALYSIS OF ARSENIC IN GROUNDWATERS – METHODOLOGY.....	64
5.1 Experimental Methods	64
5.2 Physicochemical Measurements	64
5.3 Ion Concentration Measurement Procedures	66
5.4 Metal Concentration Measurement Procedure.....	68
5.5 Evaluation of Arsenic Removal Technology.....	73
5.6 Quality Control Parameter for Groundwater Arsenic Determination.....	78
5.7 Data Analysis.....	80
CHAPTER SIX.....	82
6.0 TOTAL ARSENIC MEASUREMENTS – RESULTS AND DISCUSSION	82
6.1 Introduction.....	82
6.2 Hydrochemical Characteristics of Groundwaters	82
6.3 Incidence of Groundwater Arsenic (As) Contamination	93

6.4 Arsenic Speciation in Cases where Arsenic Concentrations in Groundwaters are Detected.....	101
6.5 Spatial Distribution of Arsenic and Well Depth	104
6.6 Distribution and Correlation of Arsenic with other Physicochemical Parameters and Trace Elements in Groundwater	112
6.7 The Effect of Season on Groundwater Quality	118
6.8 Natural versus Anthropogenic Source of Arsenic in Groundwater	124
6.9 Classification of Arsenic Contaminated Wells in Hypothesis I and II.....	125
6.10 Hydrogeochemical Factors Responsible for Arsenic Mobilization Processes in Groundwater	127
CHAPTER SEVEN	129
7.0 ARSENIC AND TRACE METALS CONTAMINATION FROM ACTIVE AND ABANDONED MINE TAILINGS - RESULTS AND DISCUSSION.....	129
7.1 Introduction.....	129
7.2 Particle Size Distribution and Texture of the Tailings Mud.....	129
7.3 Physicochemical Parameters of the Tailings Leachate.....	130
7.4 Relationship between As-Contaminated Tailings and Groundwater As Contamination	131
7.5 Incidence of Groundwater Arsenic (As) and Trace Metals Contamination	133
7.6 Tolerance Limit.....	134
7.7 Leachability of Arsenic from Mine Tailings.....	137
CHAPTER EIGHT	138
8.0 GROUNDWATER SUITABILITY FOR DOMESTIC AND AGRICULTURAL PURPOSES - RESULTS AND DISCUSSION.....	138
8.1 Introduction.....	138
8.2 Ionic and Heavy Metals Evaluation of Groundwater Quality for Domestic Use.....	138
8.3 Evaluation of the Suitability of Groundwater Quality for Domestic and Agricultural Purposes in the Study Area.....	143
CHAPTER NINE.....	159
9.0 EVALUATION OF TWO POINT-OF-USE ARSENIC REMOVAL TECHNOLOGY - RESULTS AND DISCUSSION.....	159
9.1 Introduction.....	159
9.2 The Three-Earthen Pot System	161
9.3 Household Coagulation and Filtration System/ Jerry Can System	163
Chair of Environmental Geology, BTU	VII

CHAPTER TEN.....	165
10. CONCLUSION AND RECOMMENDATION.....	165
10.1 Conclusion	165
10.2 Recommendation.....	169
REFERENCES	172
APPENDICES	

LIST OF TABLES

Table 2.1: Arsenic occurrence (after van Halem <i>et al.</i> , 2009).....	14
Table 2.2: The acid base reactions of arsenic species and their equilibrium constants	23
Table 2.3: Regions of the world with naturally elevated levels of arsenic in groundwater (IARC, 2004)	25
Table 4.1: Geographical location of sampling sites.....	53
Table 4.2: List of equipments used and their function.....	57
Table 5.1: Operating parameters employed for the determination of F ⁻ , Cl ⁻ , NO ₃ ⁻ , HCO ₃ ²⁻ , and SO ₄ ²⁻ by Ion chromatography with suppressed conductivity detection.....	67
Table 5.2: Operational conditions employed in the determination of As	70
Table 5.3: Electrothermal program.....	70
Table 5.4: Operating parameters of AAS used in the analysis of trace metals.....	71
Table 5.5: Accuracy of the analytical data with reference to the NIST standard	72
Table 5.6: Detection limit (DL) and Spikes recovery of the metals	72
Table 5.7: Calibration plots corresponding to the standard of arsenic and the standard addition method of different samples.....	78
Table 5.8: Analytical recoveries (%) ± standard deviation (SD) of As metal in water samples at 0.5, 1.0, 2.0 and 3.0 µg/L fortification levels (n=3).....	79
Table 5.9: Analytical recoveries (%) ± SD of As metal in mine tailings leachate samples at 10.0 µg/L fortification levels (n=3)	79
Table 5.10: Analytical characteristics for arsenic determination in groundwater samples by ETAAS.....	79
Table 5.11: Accuracy and precision of the proposed method for arsenic determination against standard reference materials.	80
Table 6.1: Summary of the main physico-chemical parameters, major cations and anions concentrations of the surveyed groundwater samples during the dry season in the south-western part of Ashanti Region of Ghana. Concentrations in mg/L except as noted.....	83
Table 6.2: Summary of the main physico-chemical parameters, major cations and anions concentrations of the surveyed groundwater samples during the wet (rainy) season in the south-western part of Ashanti Region of Ghana. Concentrations in mg/L except as noted.	85

Table 6.3: Concentration levels of As_{total} and other trace elemental characteristics of the surveyed groundwaters during the dry season in the south-western part of Ashanti Region of Ghana..... 95

Table 6.4: Concentration levels of As_{total} and other trace elemental characteristics of the surveyed groundwaters during the wet (rainy) season in the south-western part of Ashanti Region of Ghana. 96

Table 6.5: Total arsenic (As_{total}), arsenite (As-III) and arsenate (As-V) in groundwater samples from wells and boreholes of 26 communities for which arsenic speciation were measured..... 101

Table 6.6: Correlation matrix for groundwater quality during dry season 113

Table 6.7: Correlation matrix for groundwater quality during the wet season..... 115

Table 6.8: Physicochemical results of factor analysis scores 121

Table 6.9: Season-wise combined chemical composition of groundwater samples collected from the study area. 123

Table 6.10: Concentrations of water-quality constituents used to classify redox conditions of samples from south-western part of Ashanti Region of Ghana (Modified from Svensson, 2007) 125

Table 7.1: Particle size distribution and texture of the tailings..... 130

Table 7.2: Values of several chemical constituents in leachate of mine tailings (n=18)..... 130

Table 7.3: Concentrations of arsenic and metals in mine tailings, and arsenic leaching rates in rainwater (n=18) 134

Table 7.4: Soil quality standards of the EU 135

Table 8.1: Comparison of groundwater quality parameters with WHO Guideline values for drinking water during the dry and the wet seasons..... 138

Table 9.1: Arsenic and iron test results for the Three-Earthen Pot System..... 161

Table 9.2: Cost and Availability of the Three-Earthen Pot System..... 161

Table 9.3: Results of effluent from household coagulation and filtrations system 163

Table 9.4: Cost and availability of the household coagulation and filtration system..... 163

LIST OF FIGURES

Figure 2.1 Arsenic-affected countries (wine color) of the world with concentrations high above WHO guideline value of 10 $\mu\text{g/L}$ (Smedley and Kinniburgh, 2002; Appleyard <i>et al.</i> , 2006; Petrusovski <i>et al.</i> , 2007; Smedley <i>et al.</i> , 2007; van Halem <i>et al.</i> , 2009; Gunduz <i>et al.</i> , 2009). ...	14
Figure 2.2: Simplified transformation pathways of arsenic in the environment (Prohaska and Stingender, 2005).....	20
Figure 2.3: The Eh–pH diagram for arsenic at 25 °C and 1 atmosphere with total arsenic 10^{-5} mol/L and total sulfur 10^{-3} mol/L. Solid species are enclosed in parentheses in the cross-hatched area, which indicates a solubility in parentheses in the cross-hatched area, which indicates a solubility of less than $10^{-5.3}$ mol/L (Sharma and Sohn, 2009).....	22
Figure 3.1: Map of the study area and its boundaries	42
Figure 3.2: Land cover map of the study area	44
Figure 3.3: Mean monthly rainfall (mm) distribution at the study site (<i>Source: Meteorological Department, AngloGold Ashanti, Obuasi</i>).....	45
Figure 3.4: Total monthly rainy days at the study site (<i>Source: Meteorological Department, AngloGold Ashanti, Obuasi</i>).	46
3.5: Geological map of the study area (<i>Source: AngloGold Ashanti mines</i>)	48
Figure 3.6: Hydrological map of the study area.	50
Figure 3.7: Illegal mining operators.....	51
Figure 4.1: Well location map of the study area.....	55
Figure 4.2: Map of Obuasi Municipality showing the Sanso, Dokyiwa and Pompura tailing dams.	56
Figure 5.1 Schematic diagram of the Three Earthen Pot System	74
Figure 5.2: The actual three-earthen pot arsenic removal system used in this study.....	75
Figure 5.3: Schematic diagram of the household coagulation and filtration system/ Jerry can system.	77
Figure 6.1: Piper diagram showing major ionic constituents in groundwater during both the dry (a) and wet seasons (b).....	88
Figure 6.2: Durov diagram showing the status of chemical components along with TDS and pH in groundwater.	91
Figure 6.3: Spatial distribution of arsenic (As) in south-western part of Ashanti Region of Ghana during the dry and the wet seasons.	94

Figure 6.4: Total arsenic distribution ($\mu\text{g/L}$) in groundwaters from south-western part of Ashanti Region of Ghana during the dry and wet seasons..... 99

Figure 6.5: Field Eh-pH diagram for As (at $25\text{ }^{\circ}\text{C}$ and fixed As activities of 10^{-3}), dashed lines indicate stability limits of water at 1 bar pressure. 102

Figure 6.6: Distribution of As-III and As-V in groundwater samples collected from south-western part of Ashanti Region of Ghana..... 103

Figure 6.7: Concentration levels of As-III and As-V against dissolved oxygen (DO) for groundwater samples within the study area. 104

Figure 6.8a: Relationship between As contaminated locations and total-arsenic/well depth during the dry season..... 105

Figure 6.8b: Relationship between As contaminated locations and total-arsenic/well depth during the wet season. 106

Figure 6.9a: Relationship between well depths, total-As and dissolved oxygen (DO) during the dry season..... 107

Figure 6.9b: Relationship between well depths, total-As and dissolved oxygen (DO) during the wet season. 108

Figure 6.10a: Relationship between well depths, total-As and pH during the dry season 109

Figure 6.10b: Relationship between well depths, total-As and pH during the wet season..... 110

Figure 6.11a: Relationship between well depths, total-As and Eh (electrode potential) during the dry season..... 111

Figure 6.11b: Relationship between well depths, total-As and Eh (electrode potential) during the wet season 120

Figure 6.12: Dendrogram for 21 variables from cluster analysis in R-mode 119

Figure 13: Dendrogram for 63 sampled wells from cluster analysis in Q-mode..... 120

Figure 7.1: Model of tailings dam and affected subsurface (after Rösner and van Schalkwyk, 2000). 132

Figure 8.1: Spatial distribution of pH in the study area during the dry and the wet seasons..... 144

Figure 8.2: Spatial distribution of TDS in the study area during the dry and the wet seasons... 146

Figure 8.3: Spatial distribution of TH in the study area during the dry and the wet seasons. 148

Figure 8.4: Spatial distribution of EC in the study area during the dry and the wet seasons. 150

Figure 8.5: Spatial distribution of SAR in the study area during the dry and the wet seasons... 152

Figure 8.6: Spatial distribution of % Na in the study area during the dry and the wet seasons. 154

Figure 8.7: Spatial distribution of RSC in the study area during the dry and the wet seasons... 156

Figure 8.8: Wells with highest concentration levels of metals and water quality parameters than their permissible limit. 157

Figure 9.1: Wells with concentration levels of arsenic and iron higher than their permissible limit. 160

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ABA	Aminobenzenearesonate
AES	Atomic Emission Spectroscopy
AFS	Atomic Fluorescence Spectroscopy
AGA	AngloGold Ashanti
AGC	Ashanti Goldfields Corporation
AMD	Acid Mine Drainage
AMEP	Ashanti Mine Expansion Program
As	Arsenic
As-III	Arsenite
As-V	Arsenate
ASV	Anodic Stripping Voltammetry
BCMoe	British Columbia Ministry of Environment
BGS/DPHE	British Geological Survey/Department for International Development
BIOX	Bio-Oxidation
CE	Capillary Electrophoresis
CZE	Capillary Zone Electrophoresis
DFID	Department for International Development
DMA	Dimethylarsonite
EC	European Council
EC	Electrical Conductivity
ET-AAS	Electro-Thermal Atomic Absorption Spectroscopy
ETA-LEAFS	Electro-Thermal Atomization Laser-Excited Atomic Fluorescence Spectroscopy
F-AAS	Flame-Atomic Absorption Spectroscopy
GF-AAS	Graphite Furnace-Atomic Absorption Spectroscopy
HG	Hydride Generation
HPLC	High Pressure Liquid Chromatography
IARC	International Agency for Research on Cancer
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma-Mass Spectroscopy
LIBS	Laser Induced Breakdown Spectroscopy
MCL	Maximum Contaminant Level
MMA	Monomethylarsonate
MS	Mass Spectroscopy
NAA	Neutron Activation Analysis
NAS	National Academy of Sciences
NIST	National Institute of Standards and Technology
NRCD	National Revolution Council Decree
OSHA	Occupational Safety and Health Administration
PhAs	Phynylarsonate
QRP	Oxygen Reduction Potential
US-EPA	United States Environmental Protection Agency
WHO	World Health Organization
XRF	X-ray Fluorescence

UNITS OF MEASUREMENTS

µg:	microgram
µl:	micro litre
mg:	milligram
kg:	kilogram
L:	liter
mL:	milliliter
mm:	millimeter
µg/L:	micrograms per liter
mg/L:	milligrams per liter
cm:	centimeters
m:	meter
km:	kilometers
µS:	micro Siemens
nm:	nanometer
pH:	negative logarithm of hydrogen ion concentration
pKa:	first dissociation constant
ppb:	part per billion
ppm:	part per million
°C:	degree Celsius
mA:	milliamper
mV:	millivolt
meq/L:	milliequivalents per liter
NTU:	Nephelometric Turbidity Units

ABSTRACT

Groundwater samples were collected from 63 community wells and boreholes within southwestern part of Ashanti Region of Ghana to examine their hydrogeochemical characteristics and elemental features to better understand the sources and mobilization processes responsible for arsenic (As) enrichment as well as the suitability of the groundwater for domestic and agricultural purposes. In addition, gold mine tailings dams were also investigated to ascertain the potential source of As and other trace metals (Fe, Cu, Mn, and Zn) contamination and their dissolution into the adjoining environmental media. Further, two point-of-use As removal technologies were evaluated for their effectiveness and appropriateness. A transparent small volume flow-through cell coupled with a calibrated hand held YSI[®] Multi-Parameter Water Quality Meter (Model YSI 610-DM/600XL) was used simultaneously to measure indicator field parameters. Anions and cations were determined simultaneously in groundwater samples using Metrohm 761 Compact IC and Dionex 4500i IC system, respectively. Total As and trace metals analysis of the groundwater samples and gold mine tailings were performed on electrothermal and flame atomic absorption spectrometry. As speciation were performed using disposable cartridges. Spatial distribution maps were produced for hydrogen ion concentration (pH), total dissolved solids (TDS), total hardness (TH), electrical conductivity (EC), sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and percentage sodium (% Na) using the geographic information system (GIS). Results for the analysis of groundwater samples from 63 boreholes and wells (depth 1.5-100 m) within the study area demonstrate that the groundwater composition varies from Ca-Mg-HCO₃ to Na-K-HCO₃ and anoxic in nature. As concentrations ranged from <0.1-72 µg/L and <0.1-83 µg/L during the dry and the wet seasons, respectively. High As concentrations were generally present in the shallow to medium depth (20-70 m) of the aquifer along with high Fe ranging from <0.01-12.3 mg/L and <0.01-16.3 mg/L during the dry and the wet seasons, respectively and relatively low Mn (1.8-498.0 µg/L during the dry season and 2.3-583.8 µg/L during the wet season). The data demonstrated that 59 % of the groundwater samples contained no detectable level of As, 17 and 22 % of the samples gave results with levels of As above the World Health Organization (WHO) guideline value for drinking water standard of 10.0 µg/L, while 24 and 19 % of the samples showed results below the WHO drinking water guideline value during the dry and the wet seasons, respectively. Dissolved inorganic As species

predominate with arsenite (As-III) as the main form. It appears that high As concentrations in the study area result from the contribution of different mechanisms which can be grouped into two namely aquifers under oxidizing conditions (aided by sulphide alteration) and aquifers under reducing conditions resulting from the reduction dissolution of arseniferous iron oxyhydroxide that exist as a dispersed phase on the sedimentary grains of the aquifer. In addition, water residence time and different water use practices also influence As concentrations in the groundwater. The results of the gold mine tailings dam revealed elemental concentrations ranging up to 1752 mg/kg As, 75.16 wt.% Fe, 1848.12 mg/kg Mn, 92.17 mg/kg Cu and 177.56 mg/kg Zn. Sulphate was the dominant anion throughout the leachate, reaching a maximum dissolved concentration of 58.43 mg/L. The As concentration levels of the mine tailings were very much higher than the Netherlands soil protection guideline value of 55 mg/kg. A higher amount of the total As content in the mine tailings registered leaching levels in a range of 0.04–0.56 %. It was observed from the study that the groundwater was predominantly soft in nature and its pH in desirable range which is within safe limits for domestic use during the dry season while 82.8 % of the analyzed groundwater samples registered a non-desirable pH range (acidic) during the wet season. The results for the spatial distribution of pH, TDS, TH, EC, SAR, % Na and RSC of the groundwater samples analyzed generally appear to be within safe limits. The two point-of-use As removal technologies evaluated shown that the Three-earthen pot system is the most effective and appropriate technology. Moving forward, it is my anticipation that the findings of this study will serve as a master piece to advice policy makers, well and borehole owners about the dangers or potential risks associated with As and other trace metals in drinking water supplies sourced from groundwater and how these can be managed. In addition, this research has identified high-risk As-contaminated areas, potential health issues, methodology for assessing As in groundwater, and a broad outline of two point-of-use As treatment options which can target risk populations to protect public health and help shape the national, regional, municipal and districts water monitoring policies.

Keywords: Arsenic contamination, Groundwater, Gold mine tailings, Trace metals, Removal technologies.

ABSTRACT

Es wurden Grundwasserproben von 63 gemeinschaftlichen Brunnen und Bohrlöchern im Südwesten der Region von Ashanti in Ghana entnommen, um ihre hydrogeochemischen Eigenschaften und ihre elementare Beschaffenheit zu analysieren. In diesem Zusammenhang wurde das Ziel verfolgt, die Quellen und die Mobilisierungsprozesse, die für die Arsenanreicherung (As) verantwortlich sind, besser zu erfassen. Gleichzeitig ging es auch darum, die Eignung des Grundwassers im Bereich der Haushalte und der Landwirtschaft zu prüfen. Des Weiteren wurden auch Goldminenbetriebe erforscht, um sich über die potentielle Arsen-Quellen-Kontaminierung und die Kontaminierung durch andere Spurenmetalle (wie z.B. Fe, Cu, Mn und Zn) zu versichern und die Auflösung in den angrenzenden Bereichen der Umgebung festzustellen. Des Weiteren wurden die Entfernungstechnologien mit zwei Nutzungspunkten für As auf ihre Wirkungskraft und Eignung überprüft. Eine transparente Durchflusszelle mit einem geringen Volumen, gekoppelt mit einem kalibrierten, manuellen Multiparameter-Wasserqualitätsmesser des Typs YSI[®] (Modell YSI 6 10-DM/600XL) wurden gleichzeitig eingesetzt, um die Feldparameter des Indikators zu messen. Die Anionen und die Katoden wurden gleichzeitig in den Grundwasserproben ermittelt. In diesem Zusammenhang wurden jeweils das System Metrohm 761 Compact IC und das System Dionex 4500i IC eingesetzt. Die Gesamtanalyse der As- und Spurenmetallwerte innerhalb der Grundwasserproben und in den Goldminenbetrieben wurden mit Hilfe der elektrothermischen Flammen-Atomabsorptionsspektrometrie ermittelt. Die Speziation des As wurde mittels Einwegkartuschen bestimmt. Es wurden räumliche Verteilungskarten für die Konzentration der Wasserstoffionen (pH), die Gesamtmenge der aufgelösten Festkörper (TDS), die Gesamthärte (TH), die elektrische Leitkapazität (EC), das Absorptionsniveau von Natrium (SAR), die Menge des Restnatriumkarbonats (RSC) und den Prozentsatz von Natrium (% Na) erstellt. Dies erfolgte mittels des geographischen Informationssystems (GIS). Die Ergebnisse der Analyse der Grundwasserproben von 63 Bohrlöchern und Brunnen (von einer Tiefe von 1,5 bis 100 m) im Rahmen des Forschungsbereiches beweisen, dass die Grundwasserzusammensetzung unterschiedlich gestaltet ist und von der Beschaffenheit des Typs Ca–Mg–HCO₃ bis zur Beschaffenheit des Typs Na–K–HCO₃ und der anoxischen Beschaffenheit reicht. Die As-Konzentrationen waren in der Trocken- bzw. in der Regenzeit im Bereich zwischen <0,1-72 µg/L bzw. <0,1-83 µg/L g angesiedelt. Hohe As-Konzentrationen waren im Allgemeinen im seichten Bereich bis zu einer mittleren Tiefe (von 20 bis 70 m) des Aquifers vorhanden. Hier fanden sich auch entsprechend hohe Fe-Mengen zwischen <0,01-12,3 mg/L und <0,01-16,3 mg/L während der Trocken- bzw. Regenzeit. Der Mn-Wert war während der Trockenzeit ziemlich niedrig (zwischen 1,8 und 498,0 µg/L während der Trockenzeit und zwischen 2,3 und 583,8 µg/L während der Regenzeit). Die Daten bewiesen, dass 59 % der Grundwasserproben ein nicht erfassbares Niveau von As aufwies. 17 und 22 % der Proben ergaben As-Niveaus oberhalb des von Seiten der Weltgesundheitsorganisation (WHO) vorgeschriebenen Wertes für den Trinkwasserstandards in Höhe von 10,0 µg/L, während 24 und 19 % der Proben Werte während der Trocken- bzw. Regenzeit unterhalb des Wertes der WHO-Richtlinie für Trinkwasser ergab. Die aufgelösten unorganischen As-Typen herrschen mit dem Arsenittyp (As-III) als Hauptform vor. Es geht hervor, dass die hohen As-Konzentrationen innerhalb des Bereichs der Studie auf den Beitrag der verschiedenen Mechanismen zurückzuführen sind, die in zwei Aquifere aufgeteilt werden können: einerseits das Aquifer bei oxydierenden Bedingungen (die durch eine Sulphidalteration unterstützt werden) und andererseits das Aquifer bei reduzierenden

Bedingungen, die auf die reduzierende Auflösung des As-haltigen Eisenoxidhydroxids zurückzuführen sind, das in Form einer Dispersionsphase auf den Sedimentkörnern des Aquifers vorhanden ist. Des Weiteren beeinflussen auch die Aufenthaltszeit des Wassers und die verschiedenen Praxen der Nutzung des Wassers die As-Konzentrationen im Grundwasser. Aus den Ergebnissen des Stauwerks der Goldminen gehen Konzentrationen bis zu 1752 mg/kg As, 75.16 wt.% Fe, 1848.12 mg/kg Mn, 92.17 mg/kg Cu und 177.56 mg/kg Zn hervor. Sulfat war das Hauptanion im Sickerwasser und erreicht eine höchste Konzentration bei Auflösung in Höhe von 58,43 mg/L. Die Konzentrationsniveaus des Arsens der Goldminen lagen weit über der niederländischen Richtlinie für den Bodenschutz, die einen Wert in Höhe von 55 mg/kg vorschreibt. Eine höhere Gesamtmenge an As-Gehalt in den Goldminen ergab Sickerwasserniveaus im Bereich zwischen 0,04 und 0,56 %. Im Rahmen der Studie wurde beobachtet, dass das Grundwasser hauptsächlich weich war und sein pH-Wert im vorgeschriebenen Bereich lag, d.h. innerhalb der sicheren Grenzwerte für den häuslichen Gebrauch während der Trockenzeit, während 82,8 % der analysierten Grundwasserproben während der Regenzeit einen unerwünschten pH-Wert (als Säuren) aufwiesen. Die Ergebnisse hinsichtlich der räumlichen Verteilung von pH, TDS, TH, EC, SAR, % Na und RSC der analysierten Grundwasserproben befinden sich innerhalb der sicheren Grenzwerte. Die Entfernungstechnologien für As mit zwei Nutzungspunkten, die im Rahmen der vorliegenden Studie bewertet wurden, haben aufgezeigt, dass das System mit den drei Erdkolken die wirkungsvollste und angemessenste Technologie darstellt. Im weiteren Verlauf der Forschungsarbeit nehme ich vorweg, dass die Erkenntnisse dieser wissenschaftlichen Arbeit der Beratung von Politikern, Besitzern von Brunnen und Bohrlöchern dienen werden, um sie bezüglich der Gefahren und potentiellen Risiken in Verbindung mit diesen Phänomenen des As aufzuklären. Ich denke hier beispielsweise an andere As-Spurenelemente in der Trinkwasserversorgung, die aus Grundwasserquellen stammen. Die Studie behandelt auch die Modalitäten, nach denen diese Risiken und Probleme bezüglich des As gemanagt werden können. Des Weiteren wurden im Rahmen dieser Studie As-kontaminierte Bereiche mit hohem Risiko, potentielle gesundheitliche Probleme, eine Methode für die Bewertung des As im Grundwasser und ein allgemeines Konzept mit zwei Nutzungspunkten als Optionen zwecks As-Entfernung behandelt. Diese Behandlungsoptionen richten sich an die dem Risiko ausgesetzte Bevölkerung als Zielgruppe, um die öffentliche Gesundheit zu schützen und die nationalen, regionalen, Gemeinde- und Bezirksrichtlinien für die Überwachung der Gewässer auf politischer Ebene zu gestalten.

Keywords: Arsenverschmutzung, Grundwasser, Goldminenbetrieb, Spurenmetalle, Entfernungstechnologie.

CHAPTER ONE

1.0 GENERAL INTRODUCTION

1.1 Background

Arsenic (As) is a metal that occurs naturally in the environment in a wide variety of forms. It is a component of several minerals in the Earth's crust (Fraser Health Authority and BC-MoE, 2008). The therapeutic properties of inorganic As compounds have been recognized for centuries. Thus, despite Paul Ehrlich's pioneering use of the As-containing drug salvarsan to treat syphilis, As is now more known for its contamination of wells and borehole water supplies in some parts of the world, particularly, countries in southern and central Asia. It is worth noting that, in Asiatic countries, As contaminated groundwater is not just used for drinking, but also for irrigation of crops, particularly (for the staple food) paddy rice, which provides up to 73 % of calorific intake (Sivaraman, 2004). This constitutes an additional route of human exposure to As in these countries. Presently, the effect of As on human health has become an issue of global concern.

Today, the word, "arsenic" is synonymous with "poison". Through the years, the toxicology of As and its compounds have attracted increasing attention. In recent times the current awareness on As toxicity is on the increase. Accordingly, proposed regulatory changes in guidelines for drinking water in developed nations like US, Japan and EU have prompted considerable research efforts towards the development of new water treatment methods that target As and its compounds. This concern over levels of As in drinking water and its potential toxicity has been heightened by the latest findings by the US National Academy of Science, (2001).

In a bulletin of WHO report, Smith *et al.*, (2000) indicated studies in other countries where the population has had long-term exposure to arsenic in groundwater and further posited that 1 in 10 people who drink water containing 500 µg/L of arsenic may ultimately die from cancers and non-cancers (e.g. cardiovascular diseases, diabetes, anemia, reproductive, developmental, immunological, and neurological effects) caused by arsenic, including lung, bladder and skin cancers.

Meanwhile, stringent measures and studies to ensure better water quality with reference to “tighter” limit for As similar to the World Health Organization (WHO) provisional guideline of 10 µg/L (ppb) to protect public health have been initiated in developed states including USA, EU, etc. (US-EPA, 1985, 2001; Maity *et al.*, 2004; Melamed, 2005). In the case of third world nations, measures are poorly developed or non-existent. This may be due to (i) lack of financial support for scientific research; (ii) the limited number of environmental advocacy groups and non-governmental agencies that would raise concern about environmental quality; and (iii) the lack of environmental policy and regulations.

In countries where they exist, agencies responsible lack the required capacity to ensure compliance and enforcement of regulations (Bempah *et al.*, 2012). Regrettably, the reality is that the mining of gold is on the increase in gold-rich developing nations, and the lack of safe and environmentally sound production methods are leading to effects on human health and severe contamination of the environment. Many developing nations including Ghana who are groundwater dependent suffer from As poisoning because groundwater constitutes the only easily exploitable source of water for the large rural and suburban population, both for human consumption and for use in industrial, agricultural and livestock production (Smeldley, 1996).

As worldwide extraction of groundwater is accelerated to meet increasing demand, the significance of the chemical quality of groundwater also increases relative to its economic value and usefulness. Ghana is under the grip of extreme pressure to meet demand for its water resources due to urbanization, improvements in living standards, exploding population etc. The population of Ghana is 24,658,823 million (Ghana Statistical Services Census Report, 2010) and therefore requires 4,875 million liters of water a day (MLD) to meet its domestic need. However, what it gets stands closer to 1,595 MLD and the average water consumption in Ghana is estimated at being between 60 and 120 liters per capita per day (in the well served areas only) and 25 to 60 liters per capita per day when poor households buy water from vendors (Abraham *et al.*, 2007). Beside this, huge amount of water is needed for irrigation and other industrial uses.

In the semi urban areas, intensive agriculture and mining industry become the backbone of livelihood of the peoples residing in these areas and for this, they are extracting huge amount of groundwater resulting in depletion of groundwater table. Moreover, groundwater in hard-rock

aquifers is known to be particularly vulnerable to quality problems that may have an impact on human health (Smedley *et al.*, 1995).

The study area and its environs, have a geology known to be pyrite and arsenopyrite. Arsenic is released into the environment as a result of the mining and processing of the gold ore which is associated with sulphide mineralization, particularly arsenopyrite and pyrite (Griffis *et al.*, 2002) as well as carbonaceous materials (Asiam, 1996) in such a way that the gold cannot be sufficiently liberated even by fine grinding for cyanide leaching. The sulphide concentrations are, therefore, roasted (Asiam, 1996) to release the occluded gold. During roasting, however, arsenic and sulphidic sulphur are eliminated from the reaction zone as arsenic trioxide fume and sulphur dioxide gas respectively, while the gold is concentrated in calcite. Consequently, arsenic trioxide and sulphur dioxide have been discharged directly into the Obuasi countryside particularly for the past 50 years and this poor environmental practice has had some adverse impacts on the environment (Asiam, 1996).

Arsenic is mobilized in the environment as a result of oxidation of arsenopyrite. High arsenic concentrations has been reported in the soils (Amasa, 1975), and rivers (Smeldley *et al.*, 1996) close to the mining operations and ore processing plants. At the AngloGold Ashanti mine, the long period of mining and metallurgic activities have resulted in increased concentrations of the physico-chemical parameters in water bodies, as well as degradation of agricultural lands (Anon, 1992).

For example, from 1947 until 1992, effluents were discharge without precaution, thereby resulting in the degeneration of the environment (Carboo, 1997; Tufour, 1997; Tsidzi, 1993). Exploitation of hitherto low-grade ore as a result of the Ashanti Mine Expansion Programme (AMEP) caused increased mining activities, hence increased chemical contamination at the Obuasi mine and its satellite areas (Anon, 2002). AMEP was part of the several responses of the Ghanaian Mining Industry Policy Initiative to promote investment in the sector. Unfortunately, these initiatives were rather weak on the provision of guidelines for the management of the associated negative environmental impacts (Akabzaa, 2000).

Arsenic oxides cause a lot of dangers to human and it span from prenatal to adult stages. They cause damage to chromosomes, cause congenital malformations due to placental transfer of the elements, reduce birth weights, induce spontaneous abortions, contribute to lung cancer and disturb the functions of the liver and central nervous system.

Recent study in parts of the Amansie West District in Ashanti region showed Buruli ulcer prevalence in the settlements along arsenic-enriched drainage channels and farmlands (Duker *et al.*, 2005). However, very few studies have been conducted in Ashanti Region to assess the possible impacts of arsenic in groundwater within the communities surrounding the mine. Therefore, there is an urgent need for the planners and the decision makers to characterize the groundwater pollution and search for a useful and sound method for monitoring of groundwater resources and associated contamination.

The purpose of the study is to measure levels and distribution of arsenic in groundwater in gold mining areas within the south western part of Ashanti Region of Ghana. The primary source of drinking water in this area is groundwater.

1.2 Justification

Arsenic in drinking water is increasingly becoming recognized as a potential health hazard for rural communities in developing countries. High As concentrations have been found in groundwater sources, which provide drinking water for millions of people in parts of South America, Mexico, China, Taiwan, India and Bangladesh (Smeldley, 1996).

As remains permanent in the environment and cannot be transformed from the toxic to non-toxic form; however, it cycles through the environment (Frankenberger, 2002). In recognition of the potential health risks, WHO has reduced its recommended maximum value for As in drinking water from 50 $\mu\text{g/L}$ to a provisional value of 10 $\mu\text{g/L}$. In areas where chronic endemic arsenosis problems are occurring, concentrations of As in drinking water are significantly higher than this recommended limit, sometimes in excess of 1 mg/L (Smeldley, 1996).

Arsenic found in the environment generally results from a combination of natural processes (weathering, biological activity and volcanic emissions) and anthropogenically induced activities including mining, fuel combustions, wood preservation, the use of As-based pesticides in agriculture, etc. These actions are responsible for the emission of As into the atmosphere, from where it redistributes on the earth's surface by means of dry fallout and rain. Arsenic is also mobilized by dissolution in water, with aquatic and soil/sediment concentrations being controlled by variety of input and removal mechanisms (Cullen and Reimer, 1989).

In Africa, As has only been identified as a water quality problem in some localized areas closely associated with sulphide mining activity. Williams and Smith, (1994) found As concentrations up to 72 mg/L in acidic waters draining from gold (Au) mining areas in Zimbabwe. Earlier studies in Obuasi and other mining centers indicated high levels of As in soils, fruits, and surface waters (e.g. Amonoo-Neizer, 1980, 1996; Amasa, 1975; *Bowell et al.*, 1994; *Golow et al.*, 1996; *Smedley et al.*, 1995). *Smedley et al.* (1996) reported As concentrations of up to 350 µg/L in stream waters affected directly by mining pollution in the Obuasi area of south-western Ashanti Region of Ghana.

Ghana is Africa's second-largest gold producing country after South Africa. Most mining areas particularly in Ashanti Region (Obuasi) and Western Region (Tarkwa), until the introduction of the bio-oxidation (BIOX) technology of extracting gold, the processing of the ore for gold involved the crushing and grinding of ore to fine powder followed by dissolution and precipitation of free gold. During the ore preparation by roasting, sulphur dioxide and As trioxide were released into terrestrial and atmospheric environments. In addition, As rich tailings heaped and kept in dams were left at the mercy of the rain with subsequent leaching into rivers, streams and aquifers (*Gish et al.*, 1973). Groundwaters in the Au belt of Ashanti Region are therefore potentially vulnerable to the generation of high concentrations of dissolved As as a result of oxidation of the sulphide minerals.

Other mine wastes as particulates were/are transported far and near through the air. There is also continuous wet/dry deposition of particles unto land, water and plants. Humans and animals are exposed to As through drinking, diet and inhalation. In this regard, several scientific studies on As have been conducted in mining towns especially where the geology is known to be pyrite and

arsenopyrite in many parts of the world (e.g. USA, Welch *et al.*, 1988, 2000) unlike the third world gold mining nations. Thus, there is relatively little published information on As in groundwater in most gold mining areas in Ghana, including south-western part of Ashanti Region.

1.3 Hypotheses

Based on the literature study, two possible hypotheses are prevailing to describe the cause (mobilization) of arsenic into the groundwater of the south-western part of Ashanti Region of Ghana.

- I. The first hypothesis proposed the oxidation of sulphide minerals either through the roasting of arsenical ores or through acid mine drainage (AMD) resulting from the atmospheric exposure via the open shaft workings and weathering of sulphide-bearing rocks, such as the waste rock and mine tailings generated during mining and milling operations as the main source of arsenic. The oxidation results in arsenic anions that under the prevailing oxidizing environment form insoluble complexes with iron-oxyhydroxide. As a result of the generally high water table during the rainy season, the system is reduced and arsenic anion mobilizes and stays in the water phase and may enter the network of fractures within the crystalline rocks of the study area.

- II. This hypothesis suggests that As is released into the groundwater as a result of the reduction dissolution of arseniferous iron oxyhydroxide that exist as a dispersed phase on the sedimentary grains of the aquifer. Due to a wide variety of process such as groundwater pumping for domestic, agricultural and industrial purposes (mining activities); organic carbon is introduced into the aquifer. The mineralization of organic carbon caused anoxic condition in the aquifer, and lowered the redox potential. The reducing environment caused the breakdown of iron oxyhydroxide, and released the previously adsorbed arsenic into the groundwater.

In water typical for hypothesis I, common features of the groundwaters are high concentrations of dissolved oxygen and relatively high sulphate (with low iron and manganese). In hypothesis II a linear correlation between arsenic and iron concentrations would be expected. Other indicators include lack of dissolved oxygen, low sulphate concentration and often low redox potential.

1.4 Objectives of the Research

1.4.1 Main Objective

The main objective of this study is in two folds: (1) is to determine the possible source of arsenic contamination and (2) is to identify and characterize the distribution and concentration levels of arsenic in drinking water from groundwater sources in three major districts and two Municipalities in south-western part of Ashanti Region of Ghana.

1.4.2 Specific Objectives

The specific objectives comprise the following:

- To measure the levels and evaluate the seasonal trends of As and its distribution in groundwater.
- To determine spatial and well depth distribution of As within the wells of the study area.
- To assess the As concentrations in relation to physico-chemical and other trace metal composition of groundwater.
- To determine the distribution of As and trace metals in mine tailings as the possible source of these metals in mine drainage and groundwater in the area.
- To understand the spatial distribution of hydrogeochemical constituents of groundwater related to its suitability for domestic and agriculture use.
- Evaluate the effectiveness of treatment systems in reducing arsenic in drinking water to acceptable concentrations.

The two important keys to meet these objectives are:

Arsenic Contamination in Groundwater

- understanding the geochemical mechanisms governing arsenic in groundwater, and
- understanding the relationship between the geology/hydrogeology and arsenic concentration in groundwater.

CHAPTER TWO

1.0 HYDROGEOCHEMISTRY AND ARSENIC CONTAMINATION IN THE ENVIRONMENT – A LITERATURE REVIEW

2.1 Introduction

Arsenic is an element known throughout history as a classic poison. When, in his play *Under Milk Wood*, the Welsh poet and humorist Dylan Thomas created the henpecked husband character of Mr. Pugh, a man whose favorite reading was drawn from *Lives of the Great Poisoners*, it was clear that the poison of his fantasies was arsenic (...whispering as he took breakfast tea to his wife's room "Here's your arsenic, dear and your weed killer biscuit... Here's your... nice tea, dear"). So it is that, from ancient times until the present day, the word arsenic has been associated with the poisonous properties of this material (Vaughan, 2006).

Inorganic arsenic, largely arsenic trioxide (As_2O_3), is a well-known poison, greatly favored in earlier times as an efficient means of doing away with inconvenient spouses and the like (Frankenberger, 2002). Its once widespread use as homicidal agent was curtailed, however, from the 1830s when the forensic chemist Marsh, developed a sensitive and reliable analytical method that was suitable for determining traces of As in food, wine and biological tissues (Francesconi, 2005). Today problems still lie with inorganic As, but they are of a completely different nature. Several epidemiological studies have clearly identified inorganic arsenic as a human carcinogen, and its presence in drinking water in certain regions of the world threatens the health of millions of people.

Thus among the various sources of As in the environment, drinking water is inferably the one which threatens and affects human health. The combination of reported cases of high toxicity and widespread occurrence of arsenic in groundwater has necessitated urgent need for effective monitoring and measurement of As in groundwater. As a result of continuous increased in the evidence for acute and chronic toxicological effects of As in drinking water, the European Council (EC) and US-EPA have reduced As in drinking water from 50 to 10 $\mu\text{g/L}$. Yet, in developing nations, the most As affected operate presently at 50 $\mu\text{g/L}$ standard because of lack

of financial support for scientific research and/or lack of adequate testing facilities to measure such lower concentrations.

Accordingly, the need exists for As monitoring at sites supposedly contaminated because of the high toxicity and the widespread occurrence, such as landfills, facilities handling As containing wastes, and sites where As is found at toxic concentrations in groundwater. In cognizance of these, many studies have/are been carried out around the world, especially in most developed nations, not only in USA and Europe.

2.2 Arsenic in the Environment

Fluxes of As in the environment originate via natural and anthropogenic sources. The ratio of natural and anthropogenic inputs is 60:40 and there is a general agreement that most anthropogenic inputs are from mining, agriculture, smelting operations and fossil fuel combustion (Cullen and Reimer, 1989).

2.2.1 Arsenic Sources

Arsenic occurs naturally in the earth's crust and is a major constituent in more than 245 minerals, including elemental arsenic, arsenides, sulfides, oxides, arsenates, and arsenites (Christen, 2001; Ninno and Dorosh, 2001).

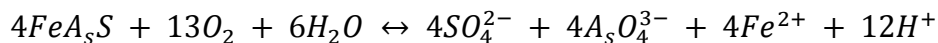
Arsenic can enter the environment through natural or anthropogenic processes. The most common anthropogenic sources are mining industry, agriculture, wood preservation activities and coal combustion (Bhattacharya *et al.*, 2002). One of the most important factors influencing the concentration of geogenic arsenic is the arsenic content in the bedrock or the parent materials from which the soil is derived. The geologic background of a particular soil determines its native As content. Most are ore minerals or their alteration products and are relatively rare in the natural environment.

The greatest concentrations of them occur in sulfide minerals of which pyrite (FeS_2) is the most abundant. Pyrite is formed in a low temperature sedimentary environment under reducing conditions. During formation some of the soluble arsenic will be incorporated in the crystal

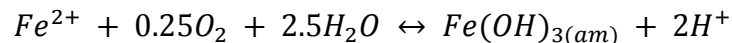
structure as a substitute for sulphur resulting in an arsenic-rich mineral such as arsenopyrite (FeAsS) (Smedley and Kinniburgh, 2002). Other major arsenic sulfides found in mineralized areas are realgar (As₂S₂), orpiment (As₂S₃) and arsenopyrite (FeAsS) (Nordstrom, 2000).

Under a wide range of geochemical conditions, arsenic has also been associated with minerals such as iron oxides (Fe₂O₃), iron hydroxides (Baldvins, 2011), other metal oxides and magnetite (Fe,Mg)Fe₂O₄ (Hem, 1985; Smedley and Kinniburgh, 2002; Korte, 1991; Sullivan and Aller, 1996; Yan *et al.*, 2000).

Arsenic is first mobilized from the soil environment due to chemical weathering of arsenopyrite or other arsenic-rich primary minerals. Weathering of the minerals depends on several different factors, i.e. pH, the presence of water, dissolved oxygen, temperature and the redox potential. In an oxidizing environment, oxidation of arsenopyrite results in the production of SO₄²⁻ and H⁺ ions resulting in decrease in pH as the following reaction shows:



In the reaction arsenic is oxidized from As⁰ to As(V) forming oxyanions. Depending on the level of dissolved O₂, Fe²⁺ can be oxidized to Fe³⁺ and precipitate as Fe³⁺-oxyhydroxides.



In groundwater where the source of aqueous arsenic is weathered sulphides, a correlation between sulphate and arsenic might be expected. This may however not be true as the formation of secondary minerals including sulphate (e.g. CaSO₄·2H₂O in the presence of high Ca²⁺) and/or adsorption of arsenic may occur thus disrupting the relationship (Svensson, 2007).

2.3 Arsenic in Groundwater

Arsenic is a metal that occurs naturally in the environment in a wide variety of forms. It is a component of several minerals in the Earth's crust, and often ends up in groundwater through the erosion and weathering of minerals and soils (Fraser Health Authority and BC-MoE, 2008). One

of the most important factors influencing the concentration of As in groundwater is the As content in the bedrock or the parent materials from which the soil is derived. Wang and Mulligan, (2006) published paper cited by Fraser Health Authority and BC-MoE, (2008) indicated that, As entering groundwater depends upon local geology, hydrogeology, geochemical characteristics of the aquifer, plus climate changes and human activity. They further posited that, arsenic is usually found in two oxidation states (As-III and As-V) in groundwater and binds with water to form H_3AsO_3 (arsenite) found in anoxic conditions or H_2AsO_4^- (arsenate) most commonly found in oxic environments.

Groundwater is important natural resources for many nations including Ghana. Ecology Global Network (2013) reports that, groundwater makes up 98 percent of the Earth's fresh water and it supply portable drinking water to over 1.5 billion people living in major urban centers, and low-cost water to the rural folks for both agricultural and domestic purposes. For instance in the USA, groundwater is the sole source of drinking water for many rural communities and some large cities; and in 1990, groundwater accounted for 39 % of the public water supply for cities and towns and 96 % for self-supply system for domestic use (Solley *et al.*, 1998; Navin *et al.*, 2006). Thus as a principal resource to many communities around the world, similar reliance on groundwater comparable to that of USA is experienced in other nations, for example Nigeria (Alagbe, 2006), Argentina (Paoloni *et al.*, 2005), and Australia (Appleyard *et al.*, 2006).

In Ghana, the increasing demand for this valuable resource has led to massive groundwater development in several communities. Many boreholes and dug wells are in operation to abstract groundwater (e.g. Pelig-Ba, 1998; Kortatsi, 2003; Kortatsi and Quansah, 2004). This elevated reliance on groundwater could lead to the impairment in its quality. In addition to the water-use demand, land use demand and improper disposal of human and animal waste may also contribute to the contamination of groundwater. Overall, even though groundwater resources appear to be ample, spatial availability of groundwater may vary at large.

2.3.1 Worldwide Occurrence of Arsenic in Groundwater

In many nations (e.g. USA and Australia), water from public supply systems or privately supplied is mostly drawn from unconsolidated and bedrock aquifers (groundwater) accounting for a larger proportion of all drinking water (Ayotte *et al.*, 2003; Appleyard *et al.*, 2006). The natural chemistry of groundwater relates to the geochemistry of the aquifer materials through which it flows and the residence time of the water in those aquifer materials (Ayotte *et al.*, 2003).

Although the occurrence of several high As-contaminated groundwater cases have been well documented in recent times and the concentration levels are usually low or very low. In addition to this, most groundwaters have concentrations below the WHO provisional guideline value for drinking water at 10 µg/L and many have concentrations below analytical detection limits (Smedley, 2008).

The most well-known and severe case of arsenic poisoning in the world is through drinking water. The WHO report in 2001 shows an estimation of about 130 million people who are exposed to drinking arsenic contaminated groundwater above 50 µg/L. South-east Asia are the most affected region including Bangladesh (>30 million exposed people), India (40 million), China (1.5 million) as well as United States of America (2.5 million). These countries are not the only affected regions as it has been illustrated by the map in Figure 2.1 (van Halem *et al.*, 2009).



Figure 2.1 Arsenic-affected countries (wine color) of the world with concentrations high above WHO guideline value of 10 µg/L (Smedley and Kinniburgh, 2002; Appleyard *et al.*, 2006; Petrusovski *et al.*, 2007; Smedley *et al.*, 2007; van Halem *et al.*, 2009; Gunduz *et al.*, 2009).

Geothermally influenced groundwater, desorption in the oxidizing environment, reductive desorption and mineral dissolution (e.g., pyrite oxidation) causes arsenic contamination of groundwater (van Halem *et al.*, 2009). Table 2.1 gives an overview of the arsenic concentrations worldwide

Table 2.1: Arsenic occurrence (after van Halem *et al.*, 2009)

Sources of arsenic	Arsenic concentration (µg/L)
Arsenic-rich sediments (e.g., Bangladesh, Vietnam, China)	10-5,000
Groundwater contaminated by mining activities (e.g., Ghana)	50-5,000
Geothermal influenced water (e.g., USA, Argentina)	<10-50,000

In the oxidizing environment arsenic predominantly occurs as arsenate (As-V), when reducing conditions prevail, the dominant species is generally arsenite (As-III) but in the case of slow oxidation process, both arsenite (As-III) and arsenate (As-V) may be found to co-exist (van Halem *et al.*, 2009).

Large scale arsenic contamination resulting in strongly reducing aquifers and subsurface areas in West Bengal Delta of Bangladesh and China are the cause of arsenic mobilization. In the northern province of China (Inner Mongolia), concentrations of arsenic as high as up to 1800 µg/L was measured. Vietnam and Cambodia, however, registered concentrations as high as 1340 µg/L resulting from dissolution of young sediments. Active and inactive volcanic areas of Italy and Mexico, respectively showed evidence of arsenic mobilization caused by mineral dissolution (van Halem *et al.*, 2009).

van Halem *et al.*, (2009) cited by the Daily Kos Action Media publication on March 03, 2010 indicated that, more countries in other parts of the world have detected concentration levels of As in their groundwaters mainly due to mining wastes in the past years, e.g., Poland, Korea and Brazil (Marszałek and Wasik, 2000; Woo and Choi, 2001; Borba *et al.*, 2003). Smedley and Kinniburgh (2002) also indicated that, mining activities have contributed to arsenic contamination in Latin American groundwaters mainly due to the oxidation of sulphide minerals.

Mining related arsenic-contaminated groundwater cases were further revealed by Smedley and Kinniburgh (2002) in countries such as Canada, Germany, Ghana, Greece, Mexico, South Africa, Thailand, UK, USA and Zimbabwe. In addition, groundwaters in Burkina Faso was measured by Smedley *et al.*, (2007) and was contaminated by arsenic, up to 1630 µg/L caused by mining activities. Again, Gunduz *et al.* (2009) cited by van Halem *et al.*, (2009), reported elevated arsenic levels (max. 561.5 µg/L) in groundwaters found in Turkey influenced by geothermal and mining activities.

The revised drinking water regulations and guidelines for As, has heightened awareness of the toxicity of As, and the recent discovery of As enrichment on large scale in Bangladesh have highlighted the need for fast reassessment of situation in many countries. As regards intensive investigation on As (occurrence, extent of exposure, distribution, the health effects, and methods

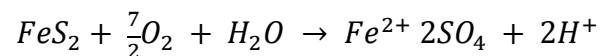
for removing As from drinking water) is performed in India (Patel *et al.*, 2005; Bhattacharjee *et al.*, 2005), United States (Welch *et al.*, 2000; Steinmaus *et al.*, 2005), Korea (Lee *et al.*, 2003), and other developed nations (Appleyard *et al.*, 2006). However, in Ghana, such studies are limited, as such As contamination of groundwater and its health implications have not been much investigated.

2.4 Geochemistry of Arsenic Release to Groundwater

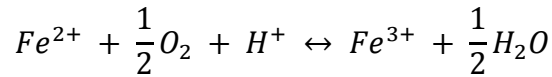
Although industrial, agricultural and mining wastes are potential sources of arsenic contamination to groundwater, the primary source of arsenic to groundwater is naturally-occurring arsenic (Welch *et al.*, 2000). Arsenic is rare in continental crustal materials, but is commonly concentrated in sulfide minerals and hydrous iron oxides (Nordstrom, 2002), which may be present in aquifer sediments. Arsenic in groundwater has been attributed to oxidation of sulphidic aquifer materials (Schreiber *et al.*, 2003), release of arsenic from iron oxides (Welch *et al.*, 1988), evaporative concentration in arid regions (Welch *et al.*, 2000), and desorption or reductive dissolution of arsenic from aquifer materials (Acharyya *et al.*, 2000; Appelo *et al.*, 2002; Kim *et al.*, 2002; McArthur *et al.*, 2001).

2.4.1 Oxidation of Sulfide Minerals

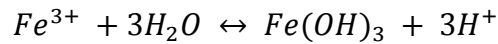
Many mining areas with an abundance of sulfide minerals demonstrate the environmental effects of sulfide mineral oxidation. Acid mine drainage is one notable consequence (World Bank/Water and Sanitation Program, 2005). In Blowes (1997) proceedings of exploration, edited by Gubins indicated that, the oxidation of pyrite by atmospheric oxygen can be described by the reaction:



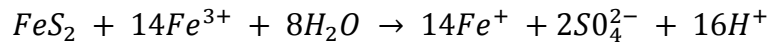
This reaction consumes pyrite, oxygen and water and generates low pH conditions, and releases Fe(II) and SO₄ to the water flowing through the mine waste. The Fe(II) released by sulfide oxidation may be oxidized to Fe(III) through the reaction:



The resulting Fe(III) may precipitate as a ferric oxyhydroxide phase, through a reaction of the form:



Alternatively, Fe(III) may oxidize additional pyrite or other sulfide minerals through reactions of the form:



Within mine wastes, sulfide oxidation proceeds rapidly, and is catalyzed by chemolithotrophic bacteria of the Thiobacillus group (Blowes, 1997). In addition to the iron-sulfide minerals, other metal-sulfide minerals are susceptible to oxidation, releasing elements such as As, Cd, Co, Cu, Ni, Pb and Zn to the water flowing through the mine waste.

2.4.2 Release from Iron Oxides

2.4.2.1 Release under reducing conditions

Iron-III oxides and other iron minerals are ubiquitous in aquifer sediments throughout the world (Zachara *et al.*, 2001). Iron oxides can be present as discrete grains or as a coating on other sediment grains. Iron minerals, iron oxides in particular, have a high surface area and are reactive (Schwertmann and Cornell, 2000). The adsorptive capacity of iron hydroxides has an influence on dissolved groundwater concentrations of many metals, such as phosphorus, arsenic, cobalt, and nickel (Houben, 2003; Pierce and Moore, 1982; Schwertmann and Cornell, 2000).

Iron oxide aging and dissolution mechanisms have been discussed extensively in the literature as potential mechanisms for mobilization of trace metals in aquifer systems (Bose and Sharma, 2002; Farquhar *et al.*, 2002; Lovley *et al.*, 1998). Natural trace metal mobilization has led to

areas of both local and widespread contamination of groundwater, particularly by arsenic (Mandal and Suzuki, 2002).

The source of As release due to the reduction of arsenic from its oxidized (As-V) form to its reduced (As-III) form often results from some critical reactions in the change to reducing conditions. As-III is less strongly adsorbed to iron oxides than As-V and reduction should therefore involve a net release from adsorption sites under many conditions. Factors such as dissolution of the iron oxides under reducing conditions and competition from other anionic solutes (for example phosphate) for adsorption are equally important processes for release of As in groundwater (World Bank/Water and Sanitation Program, 2005).

It is important to note, for example, that reducing aquifers such as those of Bangladesh, West Bengal, and China have relatively high concentrations of dissolved phosphate which reduces the sorption of both arsenic species as phosphate competes for sorption sites (Hiscock *et al.*, 2002), thus limiting the concentration of arsenic species. Accumulation of sediments in Bengal delta formed as a result of reducing conditions facilitates microbial activity, which plays an important role in the generation of the reducing conditions (World Bank/Water and Sanitation Program, 2005).

Microbes play a very important role in the reduction and mobilization process of arsenic in groundwater. In some sediment layers of Bangladesh for example microbial degradation of organic matter contributes to reductive dissolution of metal oxides and releases arsenic which is bound in both the oxides and organic phases. Moreover, dissolve organic carbon contains redox active functional groups and can thus act as an electron shuttle between microorganisms or H₂S and iron or organic pollutants (Bauer and Blodau, 2006).

The nature of the organic matter involved in the generation of reducing conditions in arsenic-affected aquifers has been disputed in recent years (World Bank/Water and Sanitation Program, 2005). A number of research studies however, have been performed to elucidate the interaction of organic matter strongly with As influencing its speciation and mobility in aquatic environments. Wang and Mulligan (2006) indicated that, in the As affected delta area of Taiwan, waters tapped from organic black sediments of the lagoons in the endemic area were full of As.

They also observed that, dissolved organic carbon (DOC) concentration correlated well with the As concentration in aqueous extracts from soil whiles sedimentary organic matter and peat soils were suggested to be important materials relating to the high concentration of As in sediments of the Bengal delta.

2.4.2.2 Release at high pH

Under aerobic and acidic to neutral conditions characteristic of many natural environments, adsorption of arsenic (as As-V) to iron oxides is normally strong and aqueous concentrations are therefore usually low (World Bank/Water and Sanitation Program, 2005) as seen in figure 2.3. However, As adsorption on ferric oxy-hydroxide indicate that higher pH solutions have a lower adsorption capacity relative to more acidic solutions resulting from the formation of negative surface charge on ferric oxy-hydroxide as a result of electrostatic between the sorbed and the arsenic anion (Welch *et al.*, 1988). There are other similar processes for the release of arsenic in oxidizing quaternary sedimentary aquifers because ferric oxyhydroxide is nearly always found in such aquifers by lowering the adsorption capacity at elevated pH.

2.4.3 Release from Other Metal Oxides

More research has been done on arsenic and its association with other iron oxides such as goethite and magnetite which affect the mineral adsorption capacity and arsenic mobility (Erickson, 2005). Aluminum and manganese oxides as an additional source of As which are less significant in controlling arsenic concentrations in groundwater than iron oxides have been cited as potential sources of arsenic in some aquifers in Bangladesh and Argentina (World Bank/Water and Sanitation Program, 2005).

2.5 Arsenic Behavior and Speciation

2.5.1 Cycling and Speciation of Arsenic in the Environment

Figure 2.2 shows the most important transformation pathways of arsenic species in the environment. Oxidation, reduction, adsorption, desorption, dissolution, precipitation and

volatilization may occur and seem to be of different importance (Inskeep *et al.*, 2002). Redox potential (Eh) and pH are the most important factors controlling As speciation. The stability of different arsenic compounds in the environment depends on the pH and the redox potential of the environment.

Although Eh-pH diagrams are often used to predict the speciation, the non-equilibrium behavior of the As-V/As-III couple relative to other common indicators of redox status (i.e. dissolved oxygen, Pt-electrode measurement) was documented by several studies. This non-equilibrium behavior indicates biological activity and/or slow kinetics (Inskeep *et al.*, 2002).

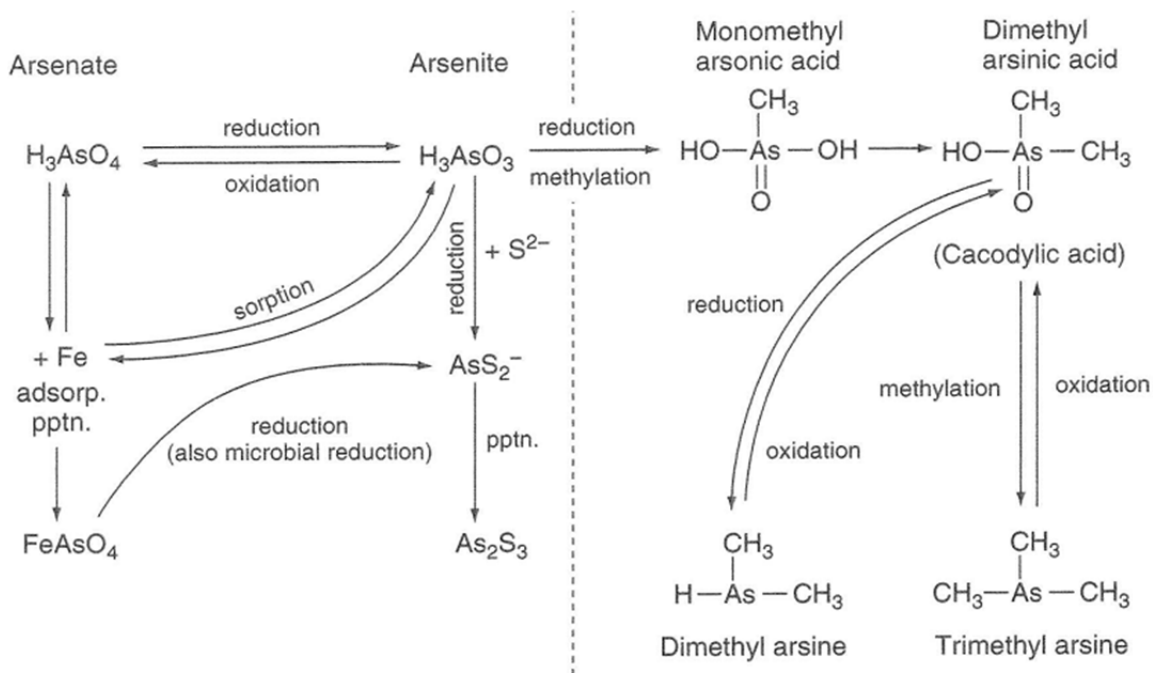


Figure 2.2: Simplified transformation pathways of arsenic in the environment (Prohaska and Stingender, 2005).

2.5.2 Arsenic Speciation in Natural Waters

First, arsenic is unique among the heavy metals and oxy-anion forming elements (As, Se, Sb, Mo, V, Cr, U, Re) in its sensitivity to pH values commonly found in natural waters. In natural waters, inorganic As is predominantly found in the oxidation states of +3 and +5. Organic forms

of As might also be produced by biological activity but they are rarely quantitatively important (Smedley and Kinniburgh, 2002).

The toxic metals occurring as cations in natural waters (e.g. Pb^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+}) become increasingly insoluble as the pH increases due to precipitation/co-precipitation/adsorption onto hydroxides, metal oxides or carbonates found in natural waters in that pH range of 7-8. Therefore, the mobility of the metal cations in this pH range is relatively low. In contrast, the oxy-anions (As, Se, Cr, and U) tend to sorb less as the pH increases. Under highly reducing conditions, most of the trace metals have very low mobility due to the formation of insoluble sulfides. This exemplifies As which is detectable in the mg/L range under highly reducing conditions (Smedley and Kinniburgh, 2002).

The speciation of inorganic arsenic in fresh waters is a function of pH and Eh. Thermodynamic predictions provide useful insight into its equilibrium chemistry and Figure 2.3 shows the stability of arsenic in water. In oxygenated waters, As-V is dominant, existing in anionic forms of H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} over the pH range of 5-12. Under mildly reducing (anoxic) conditions, As-III is the more stable oxidation state, forming the arsenious acid species H_3AsO_3 , H_2AsO_3^- and HAsO_3^{2-} .

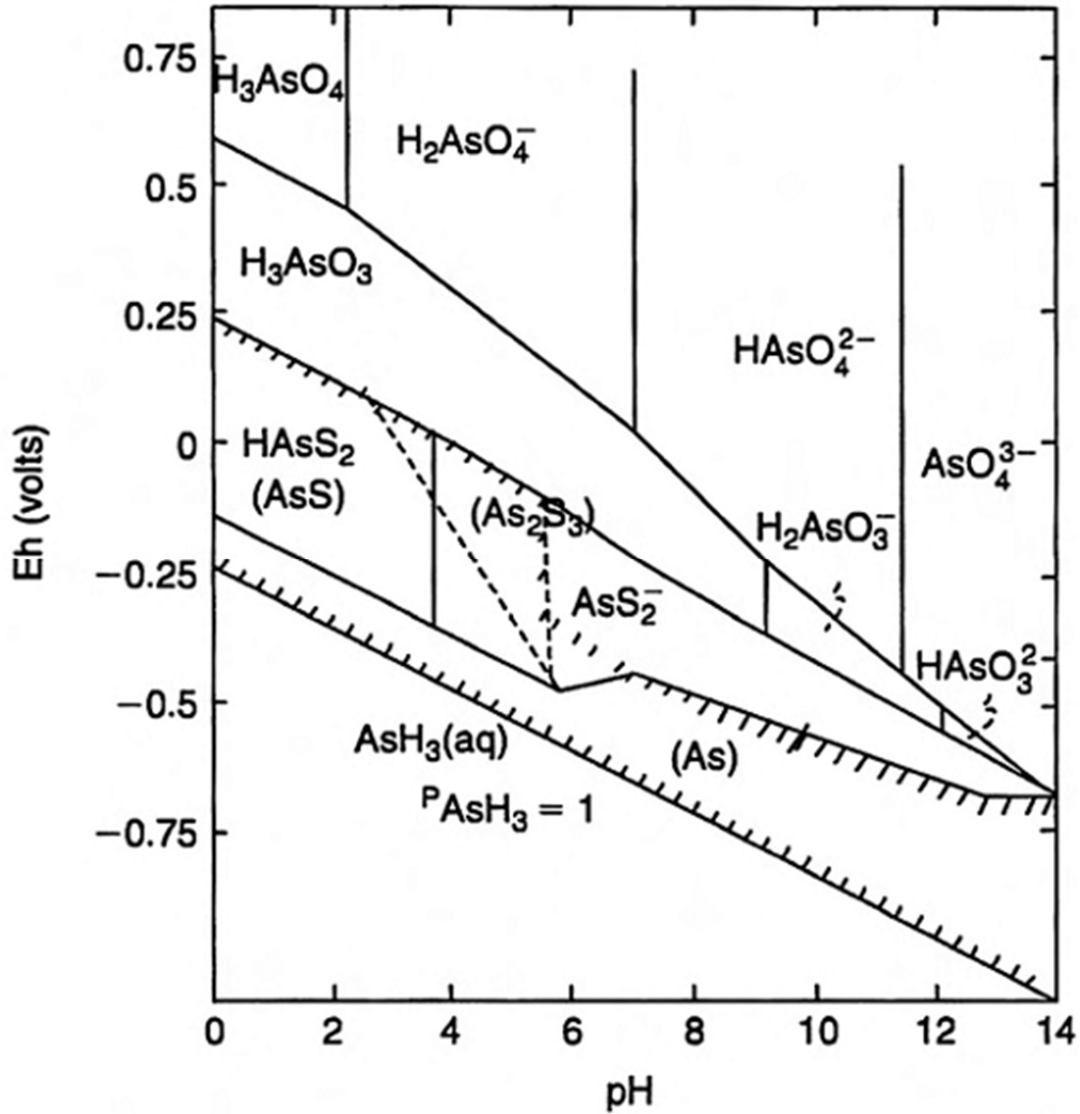


Figure 2.3: The Eh–pH diagram for arsenic at 25 °C and 1 atmosphere with total arsenic 10^{-5} mol/L and total sulfur 10^{-3} mol/L. Solid species are enclosed in parentheses in the cross-hatched area, which indicates a solubility of less than $10^{-5.3}$ mol/L (Sharma and Sohn, 2009).

The acid-base reactions of inorganic arsenic species (Hering and Wilkie, 1996) are given in Table 2.2.

The acid base reactions of arsenic species and their equilibrium constants

Reaction	LogK
$\text{AsO}_4^{3-} + \text{H}^+ = \text{HAsO}_4^{2-}$	11.6
$\text{AsO}_4^{3-} + 2\text{H}^+ = \text{H}_2\text{AsO}_4^-$	18.35
$\text{AsO}_4^{3-} + 3\text{H}^+ = \text{H}_3\text{AsO}_4$	20.6
$\text{AsO}_3^{3-} + \text{H}^+ = \text{HAsO}_3^{2-}$	13.41
$\text{AsO}_3^{3-} + 2\text{H}^+ = \text{H}_2\text{AsO}_3^-$	25.52
$\text{AsO}_3^{3-} + 3\text{H}^+ = \text{H}_3\text{AsO}_3$	34.74

Below pH 5.5, in the presence of sulfides and for an Eh value of approximately 0 Volts, precipitation of AsS (realgar) or As₂S₃ (orpiment) may remove soluble As-III and exert control over trace arsenic concentrations. HAsS₂ is predominant in the presence of sulfide and AsS₂⁻ predominates at pH greater than 3.7. At lower Eh elemental As is thermodynamically stable. At low Eh values, arsine (AsH₃) may also be formed (Ferguson and Gavis, 1972; Ferguson and Anderson, 1974).

Although thermodynamics provide a basis for predicting possible changes in a system subjected to non-equilibrium conditions, it gives no insight into the rate at which those changes can occur. In general, acid-base reactions can be assumed to occur instantaneously, whereas changes in oxidation state may require indeterminate periods in fresh waters. For instance, the conversion of As-III to As-V in oxygenated water is thermodynamically favored, yet the transformation may take days to months depending on specific conditions. Presence of other cations and complexes can enhance the oxidation (Ferguson and Anderson, 1974).

2.6 Groundwater Flow and Transport

Most groundwater moves relatively slowly through rock underground because it moves in based on their differences in water pressure and elevation. Groundwater within the upper portion of the saturated zone tends to move downward following the slope of the water table. Geochemical conditions suitable for arsenic release are important in generating groundwater arsenic problems

but the problems will only remain if the arsenic is not flushed away by moving groundwater over time (World Bank/Water and Sanitation Program, 2005).

Another feature of many of the high-arsenic groundwater provinces of Asia is slow groundwater movement as a result of the smaller nature of the rock pores and the slope of the water table. Arsenic accumulated through geochemical processes has not been flushed from the aquifer during its evolutionary history as a result of combination of factors such as young sediments (often <10,000 years old) and slow rates of aquifer flushing (for example low rates of recharge, poor sediment permeability, low hydraulic gradients). This phenomenon has been used in part to explain why the deep aquifers of Bangladesh and other near-coastal aquifers have low arsenic concentrations (World Bank/Water and Sanitation Program, 2005).

2.7 Arsenic Exposure and Human Health

2.7.1 Human Exposure via Drinking Water

The natural and anthropogenic occurrence of arsenic in drinking water has been recognized as a major public health treat in certain parts of the world, especially for developing countries over decades. Areas affected by arsenic span the globe, and significant exposures have been identified in Bangladesh, India, Taiwan, China, Mexico, Argentina, Chile and the USA. Table 2.3 summarizes the geological characteristics of the regions of the world with naturally elevated levels of arsenic in the drinking water. Recent reviews have outlined the worldwide problem of arsenic in drinking water (IARC, 2004).

Globally, many millions of people currently drink water containing unacceptably high arsenic levels, which are responsible for increases in a wide range of arsenic-related illnesses such as congenital malformations, ischemia, keratosis, hypertension, reduction in birth weight, neuropathies, different types of cancer and diseases of the vascular system. Other health problems, such as peripheral vascular disorders, severe arteriosclerosis and adverse reproductive outcomes have also been observed in certain locations, but the evidence is, however, not yet conclusive, although it keeps increasing.

Table 2.3: Regions of the world with naturally elevated levels of arsenic in groundwater (IARC, 2004)

Country/region	Affected area (km ²)	Potentially exposed Population	Arsenic concentration (µg/L)	Environmental conditions	Reference
Bangladesh	118 849	$\sim 3 \times 10^7$	< 0.5–2500	Holocene alluvial/deltaic sediments; abundance of organic matter; strongly reducing, neutral pH, high alkalinity, slow groundwater flow rates	Chakraborti <i>et al.</i> (2002); Smedley&Kinniburgh (2002)
India/West (Bengal)	38 865	6×10^6	< 10–3200	Same as Bangladesh	Chakraborti <i>et al.</i> (2002); Smedley&Kinniburgh (2002)
Vietnam				Pleistocene and Holocene sediments; strongly reducing conditions	Berg <i>et al.</i> (2001)
China/Taiwan	4 000	$\sim 10^5$	10–1820	Coastal zones, sediments, including black shales; strongly reducing, artesian conditions, some groundwaters contain humic acids	Smedley&Kinniburgh (2002)
China/Xinjiang, Shanxi	38 000	~ 500	40–750	Holocene alluvial plain; reducing	Smedley&Kinniburgh (2002), Cao (1996)
Thailand	100	1.5×10^4	1–< 5000	Dredge quaternary alluvium; oxidation of disseminated arsenopyrite due to mining	Smedley&Kinniburgh (2002)
Mongolia/Inner Mongolia	4 300	$\sim 10^5$	< 1–2400	Holocene alluvial and lacustrine sediments; strongly reducing, neutral pH, high alkalinity, some groundwaters contain humic acids	Cao (1996); Smedley&Kinniburgh (2002); Sun <i>et al.</i> (2001)
Argentina/Chaco-Pampean Plain	10 ⁶	2×10^6	< 1–7550	Holocene and earlier loess with rhyolitic volcanic ash; oxidizing, groundwaters often saline.	Nordstrom (2002); Smedley&Kinniburgh (2002)

Table 2.3 (cont'd)

Country/region	Affected area (km ²)	Potentially exposed Population	Arsenic concentration (µg/L)	Environmental conditions	Reference
Northern Chile/ Antofagasta	35 000	5×10^5	100–1000	Quaternary volcanogenic sediments; generally oxidizing, arid conditions, high salinity	Queirolo <i>et al.</i> (2000); Smedley&Kinniburgh (2002)
Bolivia		5×10^4		Same as Argentina and Northern Chile	Nordstrom (2002)
Mexico	32 000	4×10^5	8–620	Volcanic sediments; oxidizing, neutral to high pH	Smedley&Kinniburgh (2002)
Germany/Bavaria	2 500		< 10–150	Mineralized sandstone	Nordstrom (2002)
Hungary, Romania/ Danube Basin	110 000	4×10^5		Quaternary alluvial plain; reducing conditions, some high in humic acid	Smedley&Kinniburgh (2002)
Spain		$> 5 \times 10^4$	< 1–100	Mineralization; alluvial sediments	Nordstrom (2002)
Greece		1.5×10^5		Mineralization; thermal springs; Mining	Nordstrom (2002)
Ghana		$< 1 \times 10^5$	< 1–175	Sulfide mineralization, particularly arsenopyrite; gold mining	Nordstrom (2002)
Canada/Moira Lake, Ontario	100		50–3000	Mine tailing; ore mining	Smedley&Kinniburgh (2002)
Canada/British Columbia	50		0.5–580	Sulfide mineralization in volcanic rocks; neutral to high pH groundwater	Smedley&Kinniburgh (2002)
USA/Arizona	200 000		< 1300	Alluvial basins, some evaporites; oxidizing, high pH	Smedley&Kinniburgh (2002)
USA/ California	5 000		< 1–2600	Holocene and older basin-fill sediments; internally drained basin, mixed redox conditions, high salinity	Smedley&Kinniburgh (2002)
USA/Nevada	1 300		< 2600	Holocene mixed Aeolian, alluvial and lacustrine sediments; mainly reducing, some high pH, some with high salinity due to evaporation	Smedley&Kinniburgh (2002)

In many countries, water supplies are still not routinely tested for arsenic, although as testing becomes more widespread, more and more locations of arsenic contamination are being discovered (IARC, 2004).

Finally, in some high-risk areas, we are probably only seeing the “tip of the iceberg.” Several studies suggest that there is a long latency period between exposure to arsenic and the development of internal cancers, sometimes forty years or more. Since cancers and other diseases can take decades to appear, it is possible there will be a sharp increase in these diseases over the next few decades in arsenic prone areas like China, Bangladesh, and India. In Ghana, levels of arsenic exposures are relatively recent, and the effects of arsenic are only now being more closely monitored.

2.7.2 Toxicological Effects of Arsenic in Drinking Water

Recent epidemiological studies on carcinogenicity of arsenic have triggered increased concern about the concentration of arsenic in drinking water and have prompted re-evaluation of arsenic's current maximum contaminant level (MCL) of 50 µg/L. The range of arsenic MCL proposed by the US Environmental Protection Agency (US-EPA) is 2-20 µg/L. In 1993, the World Health Organization (WHO) decreased the guideline from 50 µg/L to a value of 10 µg/L (Swedlun *et al.*, 1996).

Humans are exposed to arsenic primarily from air, food and water. Majority of harmful As exposure comes from drinking water particularly from wells drilled through As bearing rocks (Mead, 2005). Drinking water primarily contains inorganic As in the forms, As-III and As-V. Arsenite tends to be more toxic in human than As-V. This is because it binds to sulfhydryl groups in enzyme systems essential for metabolism, which inhibit their action. It also affects respiration by binding to the vicinal thiols in pyruvate dehydrogenase and 2-oxo-glutarate dehydrogenase. In recent times, As is believed to interact with glucocorticoid receptor. Arsenate on the other hand is a molecular analog of phosphate and inhibits oxidative phosphorylation. This affects cellular energy production, thus short-circuiting man's life energy (Oremland and Stolz, 2003; Mandal, 2002).

Chronic As exposure via drinking water has adverse health effects on human, from skin and internal cancers of the bladder, kidney, liver, lung, colon, uterus, prostate and stomach. Other

examples are diabetes mellitus and vascular, reproductive, developmental and neurological effects (Mead, 2005).

The non-cancer effects also arise from both chronic and acute exposure. Symptoms resulting from acute exposure to As contaminated drinking water include abdominal pain, vomiting, diarrhea, muscular weakness and cramping, pain to the extremis, erythematous skin eruptions and swelling of eyelids, feet and hands. A progressive deterioration in the motor and sensory responses may also result, finally leading to shocks and death (Mead, 2005). The non-cancer effect of chronic As poisoning includes anemia, headache, confusion, hypertension, diabetes, atherosclerosis and a variety of skin lesion (Mead, 2005).

2.8 Analytical Methods for Arsenic Determination in Drinking Water

2.8.1 Arsenic Determination in the Laboratory

Studies of human exposure to arsenic and its consequences for human health are important for toxicological studies and remediation efforts (IARC, 2004). The biophysiochemical properties of arsenic species in particular require quantitation of individual species in addition to total arsenic concentration (Bednar *et al.*, 2004). Several methods have been developed and improved for the measurement of total arsenic, and have been widely used for the evaluation of drinking-water contamination and the resulting concentrations of arsenic in humans. On the other hand, analytical methods allowing arsenic speciation have gained increasing interest because individual arsenic species, particularly at low levels, can present problems. The environmental fate and behavior, bioavailability and toxicity of arsenic vary dramatically with the chemical form (species) in which it exists. The inorganic As-III and As-V being far more toxic than MMA and DMA therefore require more straight-forward methods for its determination in comparison to more laborious classical techniques.

Historically, colorimetric/spectrophotometric methods have been used to determine total arsenic concentration. Several commercial field kits have been based on these methods (IARC, 2004). However, recent advances in instrumentation offering more sensitivity and involving coupling multiple instruments into automated hyphenated techniques, such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), high-performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) and etc., have provided more accurate

methods for the determination of arsenic and its species in groundwater. The most commonly used methods for the analysis of arsenic and arsenic compounds in water are described below:

2.8.1.1 Inductively coupled plasma–atomic emission spectroscopy (ICP–AES)

The ICP-AES is a less used technique and normally applied for a comparison and more accurate analysis of a multi-element sample (Bose *et al.*, 2011). It provides for the multi-element determination of metals in solution using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectroscopy. It involves the introduction of aqueous samples into the instrument via a peristaltic pump or by pneumatic nebulization. The resulting aerosol is desolvated before being transported to the plasma torch. Radio-frequency inductively coupled plasma which is dispersed produces element-specific spectra by a grating spectrometer. The intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Quantitation of the target analyte(s) is performed by comparing the spectral intensity for each element to known calibration standards. Background correction is required to compensate for variable background contribution. For greater sensitivity, axial torch configuration and ultrasonic nebulization is used (US-EPA, 1999).

2.8.1.2 Inductively coupled plasma–mass spectrometry (ICP–MS)

Inductively coupled plasma–mass spectrometry (ICP-MS) is one of the most common techniques for elemental analysis. Its high specificity, multi-element capability and good detection limits result in the use of the technique in a large variety of applications. All kinds of dissolved samples can be analyzed, varying from solutions containing high salt concentrations to diluted acids. A plasma source is used to dissociate the sample into its constituent atoms or ions, exciting them to a higher energy level. They return to their ground state by emitting photons of a characteristic wavelength depending on the element present. This light is recorded by an optical spectrometer. When calibrated against standards the technique provides a quantitative analysis of the original sample (US-EPA, 1999). ICP–MS is classified among the US-EPA approved analytical methods for arsenic (US-EPA, 2002), with detection limit of 0.1 µg/L. The sensitivity can be further improved by the use of hydride generation (HG) techniques leading to a more efficient sample introduction and to matrix

removal. The use of a high-resolution mode with HG-ICP-MS allows a 10-fold decrease in the detection limit (0.01 µg/L) for arsenic in water samples (IARC, 2004).

2.8.1.3 High performance liquid chromatography (HPLC) and ICP-MS

High-performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICP-MS) is used for the analysis of nonvolatile compounds or ions in solution. It is this flexibility in the choice of both stationary and mobile phases, including gradient techniques where the mobile phase changes composition during the chromatographic run, which makes HPLC such a powerful separation technique for many applications (Agilent Technologies, 2007). As an HPLC detector ICP-MS is the only universal, element-specific detector available for liquid chromatography and its highly sensitive and robust detector system is been used recently for rapid analysis of arsenic speciation (B'Hymer and Caruso, 2004).

2.8.1.4 Liquid chromatography coupled with ionspray tandem mass spectroscopy

Ionspray mass spectroscopy, a well-established organic analysis technique, has been coupled to HPLC for speciation of organic arsenic compounds (Corr and Larsen, 1996; Bose *et al.*, 2011). The ionspray source and differentially pumped interface of the mass spectrometer were operated in dual modes for elemental and molecular analysis. Tandem mass spectrometry was employed to increase selectivity (Bose *et al.*, 2011).

2.8.1.5 Electro-thermal atomization laser-excited atomic fluorescence spectrometry (ETA-LEAFS)

ETA-LEAFS is a highly sensitive and selective method that has been developed by the combination of laser-excited atomic fluorescence spectrometry with electro-thermal atomization in graphite cup or tube furnaces (IARC, 2004). The best flame LEAFS detection limits are comparable to atomic absorption spectrometry (AAS) with an electrothermal atomizer (ETA AAS). LEAFS detection limits have been improved, by factors of 10 to 1000, by substituting an electrothermal atomizer for the flame (ETA LEAFS) (Preli *et al.*, 1997). The technique provides excellent analytical performance at ultra-trace levels, with a detection limit of 0.065 µg/L for arsenic in undiluted serum. This approach allows measurements to be

taken directly on the serum samples after a simple dilution step. It also minimizes the amounts of sample required and can provide multiple measurements when only limited amounts of sample are available (IARC, 2004).

2.8.1.6 Atomic absorption spectrometry (AAS)

AAS is one of the most common analytical procedures for measuring arsenic in both environmental and biological materials. The main methods are flame AAS (FAAS), electrothermal AAS (ET-AAS), also referred to as graphite furnace AAS (GF-AAS), and HG-AAS (IARC, 2004). The principal difference among the various AAS techniques is the means and form of presentation and atomization of the sample. In GF-AAS, a small aliquot, rather than a continuous flow of sample, is deposited in a graphite furnace in which it is completely dissolved and mineralized in situ (IARC, 2004). The atomic absorption spectroscopic methods operate on the following principal where by trivalent arsenic is converted to its volatile hydride (arsine) by reaction with zinc and hydrochloric acid or sodium borohydride (US-EPA, 1999).

The volatile hydrides are swept into an argon-hydrogen flame or into a heated quartz cell positioned in the optical path of an atomic absorption spectrophotometer. A light beam from a hollow cathode lamp or electrodeless discharge lamp (EDL) containing the element of interest is directed through the flame or quartz cell, into a monochromator, and into a detector that measures the amount of light absorbed by the arsine. For total or total recoverable arsenic, the sample is first acid digested or placed in a special reaction vessel to destroy organic arsenic compounds and oxidize the arsenic to As-V. The As-V is then reduced to As-III by reaction with potassium iodide or tin chloride and then converted to their volatile hydrides with zinc or borohydride. HG-AAS is probably the most widely used method and classified among the US-EPA-approved analytical methods for arsenic in water (IARC, 2004)

2.8.2 Science and Technology for Arsenic Analyses in the Field

Technologies for As detection in the field, including a survey of scientific and technological research are discussed below.

2.8.2.1 Colorimetric test kits

Colorimetric test kits can be used extensively to test for arsenic in groundwater. This kit may however be applied to solid waste and arsenic-contaminated soil testing by either the use of acidic oxidation digestion or acidic extraction of the sample (Environmental Monitoring and Control, 2010).

These test kits use the “Gutzeit’s” method, which generates highly toxic arsine gas above the threshold limiting value of 0.05 mg/L by volume recommended by the Occupational Safety and Health Administration (OSHA). In addition, these assays generate toxic mercuric solid waste since the test strips contain mercuric bromide (Melamed, 2005). Currently, a more sensitive and accurate method in use involves electrochemical reduction of the arsenite ion into arsine gas instead of NaBH_4 . The arsine gas reacts with silver compound to give a highly colored complex.

2.8.2.2 Portable X-ray fluorescence

Another effective technology for detecting As in the field is the use of X-ray fluorescence. An X-ray fluorescence analyzer can provide qualitative and quantitative analysis regarding the thickness and composition of the material being tested. This technology involves radiation of environmental samples with X-ray or gamma rays. For As detection, a sealed Cd^{109} radioisotope source is often used. After the sample irradiation, the atoms of the sample absorb energy from the X-rays which become temporarily excited and then emit secondary X-rays characteristic of each atom, termed X-ray fluorescence (US-EPA, 2004). This combination uses a specific energy photon for the photoelectric effect while precisely measuring the energy of the XRF photon emitted by the sample to allow for an accurate identification of the elements in the sample (US-EPA, 2004). Presently, there are portable XRF devices to measure As in groundwater down to 50 $\mu\text{g/L}$ (Melamed, 2005).

2.8.2.3 Anodic stripping voltammetry (ASV)

Electrochemical assays for the detection of As have demonstrated promise for detecting As in the field (US-EPA, 2004). These methods work best for liquid samples, for example groundwater; solid samples usually digested or extracted before testing (Melamed, 2005). ASV provides an alternative analytical technique for measuring dissolved As in drinking

water. The ASV method is equally sensitive for As-III and As-V and is suitable for measuring lower concentration of As. This method uses anodic stripping to quantify free dissolved As as As-III and As-V ions at a potential of +145 mV with respect to saturated calomel electrode from a conditioned gold-plated electrode (US-EPA, 2004).

Newly field ASV has been designed to detect As in liquid media in the range of 0.05-0.5 µg/L. This technology is highly sensitive and good for As speciation. However the durability of the electrode has been questioned and there is interference from copper, mercury and zinc. In spite of this, this technique is used to measure As in groundwater and surface water samples.

2.8.2.4 Electrophoresis Techniques

Kumaresan and Riyazuddin (2001), showed a modification of the high performance capillary electrophoresis (CE) and capillary zone electrophoresis (CZE), which used two different detection systems (photometric and conductimetric) presented by Schlegel *et al.*, (1996). After the analysis the CZE shows excellent suitability for As speciation and the separation of different species. As-III, As-V and DMA were determined by photometric detector while As-V, DMA, *p*-aminobenzenearsonate (ABA) and phenylarsonate (PhAs) were determined by photometric detector.

Capillary electrophoresis is only a technique that can extract and separate ions species from an environmental matrix. It has good separation capabilities, which allow for As speciation. When used with indirect measurement methods, As was detected in aqueous extracts from actual soil samples. This has a high sensitivity and can detect lower concentration of less than 1 µg/L.

2.8.2.5 Laser Techniques

Laser induced breakdown spectroscopy (LIBS) for As detection is one of the techniques for the As measurement but has not been widely applied to field application. It is fast and has remote sensing capabilities. Multiple types of metals, non-metals and metalloids are measured each time. It has a low sensitivity for As up to 400 mg/L (Melamed, 2005).

2.9 Arsenic Removal Technologies

Numerous technologies have been shown to be effective for arsenic removal, either on a large scale for public water system treatment or small scale for home use. Many of the treatment technologies involve ion exchange or adsorbing arsenic onto a metal oxide media (Amy *et al.*, 2000; Badruzzaman *et al.*, 2004; Chwirka *et al.*, 2000; Daus *et al.*, 2004; Goel *et al.*, 2004; Ladeira and Ciminelli, 2004; Wickramasinghe *et al.*, 2004).

These treatment technologies often target As-V, so these technologies often require a pre-process to oxidize As-III to As-V (Kim and Nriagu, 2000; Thirunavukkarasu *et al.*, 2005; Zhang *et al.*, 2003a; 2003b). Interference by site-specific geochemical conditions, such as elevated silicate, is being explored (Holm, 2002; Kundu *et al.*, 2004) and in most often the infrastructure costs can be high, even for small communities. New, innovative, and potentially less expensive technologies are in the process of being developed and tested (Ghimire *et al.*, 2003; Han *et al.*, 2003; Kim *et al.*, 2003; Kumar *et al.*, 2004; Loukidou *et al.*, 2003; Smith and Edwards, 2002; Vaishya and Gupta, 2003). However, in this research two most commonly used point-of use arsenic/iron removal systems by some well owners and many families within the south-western part of Ashanti Region were considered and the most common methods include adsorption, oxidation, precipitation, coagulation, sedimentation and filtration.

Adsorption is a natural process in which molecules of a liquid or gas are attracted and then held at the surface tension of a solid that causes molecules to be held at the surface of a solid either by chemical or physical adsorption. Excellent adsorption is achieved when the adsorbent has a large amount of surface area that is accessible for the adsorption process contain within the material (Nyer, 1992). Arsenic is adsorbed onto the surface of granular materials, clays and processed cellulosic materials such as activated carbon, oxides, clay minerals, and sawdust (Murcott, 2013).

Oxidation is a reaction involving the loss of an electron by an atom, which can come about with the addition of oxygen to a compound (Hemond, 2000). Supplying oxygen to, or aerating, water with arsenic oxidizes the arsenic and iron that co-occurs, resulting in the formation of precipitate. Therefore, passive precipitation occurs when naturally occurring iron is in solution with arsenic in the presence of oxygen (Hurd, 2001). In the process of precipitation, chemicals are normally used to transform dissolved contaminants into an

insoluble solid and filtration is then used to remove the insoluble solids from the liquid phase. Oxidation can be used prior to coagulation, filtration, adsorption or sedimentation to improve the removal of inorganics, particulates, taste or odor.

Coagulation is based on adhesion when small particles cling together, creating particles large enough to be filtered out. This is a chemical process that involves the addition of a chemical coagulant such as alum [$KAl(SO_4)_2 \cdot 12H_2O$] or ferric sulfate to the arsenic-water (US-EPA, 2013). The resulting aggregated precipitate or particle (also called *floc*) can be removed from the water column by sedimentation and/or filtration. Sedimentation is a step in water treatment where particles in water fall to the bottom of a tank and are removed.

Filtration is a process of running water through a filter to remove undissolved impurities. The groundwater may be filtered through layers of sand, gravel and/or coal. The raw water travels through the various filter materials and out into the treatment plant reservoir. Thus, the two arsenic removal technologies that were evaluated in south-western Ashanti used one or a combination of several of the above processes.

The Three-Earthen Pot system works by combining the processes of oxidation, precipitation, adsorption, and filtration; the household coagulation and filtration system popularly known by the local folks as jerry can or “Kufour” gallon system as its name stand uses the processes of precipitation, adsorption, coagulation, sedimentation and filtration.

2.10 Mining Related Arsenic Problems in Ghana, an Overview

Ghana, formerly known as the Gold Coast, is an important gold mining country located in the western part of sub-Saharan Africa (Bempah *et al.*, 2013). Gold mining in the Ashanti Region dates back to the 19th century. The mining is believed to have started 1890 by three Fante concessionaires: Joseph Edmund Biney, Joseph Eltruson Ellis and Joseph Peter Brown. Edwin Cade later bought the mine from them with government’s recognition of his agreement, to form the new company called Ashanti Goldfields Corporation (AGC) limited in June 1897. A lease period for 90 years was granted to AGC by the government. The mineral concession covered 259 km² (Kesse, 1985).

In January 1969, the Corporation was taken over by Lonhro Limited of Britain. The government of Ghana then extended the period of the lease by 50 years (ending 2018) with

20 % holding of Ashanti shares in the new agreement. However in October 1st, 1972, under the Mining Operations (Government Participation) Decree (N.R.C.D. 132), AGC became Ashanti Goldfields Corporation (Ghana) Limited (Kesse, 1985) with the government of Ghana having 55 % share. Until its merger in 2004 as AngloGold Ashanti, the corporation remained jointly owned by government of Ghana and Lonrho of Britain.

AngloGold Ashanti mine accounts for more than 50 % of the total annual gold production in the country. Gold brings about 45 % of the total export revenue to the nation (Borough, 1997; Akabzaa and Dramani, 2001). Nevertheless, mining and processing of the ore have contributed immensely to environmental degradation and pollution in the area.

The Ashanti and Western regions are the major gold mining locations. The gold (Au) is associated with sulphide mineralization, particularly arsenopyrite. The belief is that the Upper Birimian formation of the study area has over ten times the average crustal abundances of gold and arsenic (Bempah *et al.*, 2013).

The gold deposits at the study area most especially within Obuasi municipality and its satellite areas are part of a prominent gold belt of Proterozoic (Birimian), inter-layered sedimentary and igneous formations as well as volcano flow rocks metamorphosed to a low greenschist facies of the Barovlan type. The rocks normally extend for a distance of approximately 300 kilometers in a northeast southwest trend in southwestern Ghana. The area mineralization is shear zone-related, and there are three main structural trends hosting gold mineralization: the Binsere trend, the Gyabunsu trend and the Obuasi trend (AngloGold Ashanti Annual Report, 2006). Two main ore types are mined; namely quartz and sulfide:

- quartz veins, which consist mainly of epigenetic gold associated with disseminated sulfides and other lesser amounts of metals including copper, iron, lead and zinc. The fine-grained gold particles are occasionally visible to the naked eye; and
- sulfide ore, which is characterized by the inclusion of gold in the crystal structure of a sulfide material. The fine-grained gold particles are mostly locked up in the arsenopyrite. Finer-grained arsenopyrite crystals are commonly contained in the higher gold grades. Sericite, quartz and chlorite are the other prominent minerals found in the area mineralization (AngloGold Ashanti Annual Report, 2006).

Due to the nature of the gold ore and the previous method of mining and processing of the metal, environmental degradation and metal pollution are restricted to only mining areas especially Obuasi, Kenyasi, Prestea, and Tarkwa (Bempah *et al.*, 2013). Mining operations going on in the study area have been identified as one of the major driving forces causing rapid land-cover changes (the other is urbanization). This confirms a report that the upsurge of gold mining has resulted in the increase in gold production from an annual total of more than 1.2 million troy ounces, which established Ghana as Africa's second largest gold producer, next to South Africa (Regional Surveys of the World, 2004).

Moreover, the AngloGold Ashanti Company also confirms that mining in the area has grown over the time and is artisanal and small-scale miners who encroach illegally onto the company-owned land in their search for minerals. Thus the barren land is seen to have increased from 2002 to 2008, while farmland in this period is found to have lost 799 ha to barren land, because illegal miners, in their search for gold, leave the land surface bare after exploiting it. Nonetheless, an area of 12.10 km² has been maintained by AngloGold Ashanti for large tracts of teak plantation as green belt within its concession (Yeboah, 2008).

Environmental arsenic damage has also been documented in those areas, although there is currently little evidence of detrimental effects on human health. Hence arsenic mobilizes in the environment as a result of arsenopyrite oxidation induced by mining activities (especially dispersal of tailings). The degeneration of the Ghanaian mining environment by mine chemical wastes is principally the consequence of poor management of mine spoil facilities and the reckless manner in which alluvial and open pit activity are carried out (Bempah *et al.*, 2013).

Bempah *et al.*, (2013) further indicated that, around the town of Obuasi, Prestea and Tarkwa studies in these locations revealed high As concentration in water, soil, fruits, food crops, biological tissues, rivers, school compounds, farmlands and settlements close to the mine sites.

Heavy metals in stream water and sediments in south-western part of Ashanti Region abound in the literature. Akabzaa *et al.*, (2005) measured high concentrations of heavy metals in Jim River Basin located within the mining concession of AngloGold Ashanti mine that receives drainage and effluent from the mining, processing and waste containment facilities as well as from the activities of illegal small scale miners (galamseys) in the area. They indicated that

Fe, As and Mn concentration values particularly in stream water were generally high ranging from <0.002 to 17.100 mg/L, 0.001 to 6.318 mg/L and <0.001 to 2.584 mg/L, respectively. Again metal concentrations were highest in sediments with Fe values ranging from 2210-50180 mg/kg and averaged 28270 mg/kg while As values ranged between 0.24 to 7591.58 mg/kg and averaged 1746.51 mg/kg. Akabzaa *et al.*, (2005) also concluded that such high metal concentrations in sediments resulted from high tropical rainfall, which could lead to sporadic regimes of re-suspension of the stream and over-bank sediments when river flow increases.

Amonoo-Neizer *et al.*, (1996) also investigated As pollution on food and food crops in and around the mining town of Obuasi recording unimaginable levels of As including cocoyam (1.86 mg/kg dry mass), plantain (3.43 mg/kg dry mass), cooked food (3.81 mg/kg dry mass), goat meat (3.48 mg/kg dry mass) and fish (2.60 mg/kg dry mass). Similar studies by Amasa, (1975) and Amonoo-Neizer and Busari, (1980) gave large quantities of As in soils, crops and vegetation in locations far and near the mine centers. Amonoo-Neizer and Busari, (1980) revealed high levels of As-contaminated soils as a result of gold smelters from Obuasi mines with an average concentration of 71 mg/kg (range = 22-157 mg/kg). Soils derived from rocks known to contain anomalously high quantities of arsenic but which had not been contaminated also registered an average As levels of 9.8 mg/kg (range = 0.6-62.5 mg/kg).

Studies of Amasa (1975), recorded high As content (4700 mg/kg) in fern plants located close to Obuasi mine chimney. Bahama grass and the palm trees also registered As levels of 20 and 2875 mg/kg, respectively. Food items such as oranges and sugar cane had values of 2.29 and 14.75 mg/kg, respectively, while Kwabrafosso dam water and drinking water recorded As values of 2.25 and 1.40 mg/kg, respectively. These values were all above the WHO normal values.

Amonoo-Neizer and Amekor, (1993) had ascertained that As content of some environmental samples, particularly soil and water registering high As levels of 19.39 mg/kg (5.40-26.60 mg/kg) and 5.19 mg/kg (2.80-10.40 mg/kg), respectively, making it dangerous to aquatic life or for domestic use. Arsenic concentrations in river samples from Tarkwa ranged <1.0-73 ug/L (Ansong Asante *et al.*, 2005); whereas the determination of As in water bodies at Konongo and its surrounding communities showed significant levels of As (Boadu *et al.*, 2001).

Around the town of Obuasi, high arsenic concentrations have been found in soils close to the mines and treatment works as well as the mine tailings. Smedley (1996) revealed high concentrations of As in river waters close to the mining activity. Total As concentrations detected in the groundwaters (from dug wells and boreholes) range between $< 1 \mu\text{g/L}$ and $64 \mu\text{g/L}$. Many of the monitored wells and boreholes exceeded the revised WHO maximum guideline value for drinking water, but were much less than concentrations observed in regions (Bangladesh, India, Taiwan, Mongolia etc) where chronic health problems related to As have been detected. The high concentrations of As were found to be present in relatively reducing groundwaters. Oxidizing groundwaters, especially from shallow hand-dug wells within the area also recorded low As concentrations. This was taken to be due to strong adsorption onto hydrous ferric oxides under the prevailing acidic groundwater conditions (median pH 5.4 in dug wells; Smedley *et al.*, 1996).

Bowell *et al.*, (1994) reported that in mine-contaminated soils of Obuasi, As concentration decreases with increasing depth while in the uncontaminated soils overlying bedrock, As concentration increases down the soil profile with the highest values of about (1025 mg/kg) occurring directly over mineralized bedrock. However, in the soil overlying the unmineralised bedrock, As concentration shows very little variation.

Overall, Norman *et al.*, (2006) put 10 % of Ghana's rural boreholes water wells to have As levels greater than WHO guideline value of $10 \mu\text{g/L}$. This is due to the upper Birimian rock, gold-As mineralization, low pE and high total dissolve solids (TDS). Furthermore, there are reports on health studies (e.g. hyperkeratosis and hyperpigmentation) in some individuals living in Obuasi (Golow *et al.*, 1996). Duker *et al.*, (2004) noted Buruli ulcer (caused by *Mycobacterium ulcerans*) is very common in Amansie West District of Ghana and it is as a result of As enriched drainages and farmlands.

In cognizance of the above, it is apparent that, As research in the Ghanaian environment focused primarily on surface waters, sediments, soils, food crops, fruits and biological samples with limited studies on groundwater identified as the major source of As poisoning globally.

More so, the few studies performed in some parts of Ashanti Region were restricted only to few sites with most communities unattended. Unfortunately, gold mining is progressing steadily in the south-western Ashanti Region environment known to have geology rich in

arsenopyrite. Yet, the impact of this element in the Ghanaian environment has not received the fullest attention (Bempah *et al.*, 2013).

CHAPTER THREE

3.0 DESCRIPTION OF THE STUDY AREA

3.1 Location

The study area comprises of three districts and two Municipal Assemblies namely Amansie West District, Amansie Central District, Adansi North District, Obuasi Municipality and Bekwai Municipality formerly known as Amansie East District. These districts and municipalities form part of the 27 Metropolitan, Municipal and District Assemblies located at the Ashanti Region of Ghana (Figure 3.1) and is about 64 km south of Kumasi, the regional capital and 300 km north-west of Accra, the capital of Ghana (Bempah *et al.*, 2013). The study area (for instance Obuasi municipality) houses the administrative headquarters of the biggest gold mining industry (Ashanti Goldfields Company, now AngloGold Ashanti – Obuasi Mine) in West Africa sub-region with its headquarters in South Africa.

The study site is situated averagely at latitude $6^{\circ} 18' 47''$ North and longitude $1^{\circ} 44' 06''$ West. It is located in the tropical evergreen rain forest belt of Ashanti Region surrounded by hills, mountains made up of igneous and sedimentary rocks. The rocks are rich in gold ore. It covers an overall area of about 5154.7 square Kilometers and is bounded by Atwima-Mponua, Atwima-Nwabiagya, Atwima-Kwanwoma, Bosomtwe, Bosome-Freho, Adansi South, Upper Denkyira East, Upper Denkyira West and Bibiani/Anwiaso/Bekwai Districts.

The population of the area is about 618,828 using the 2010 Housing and Population Census as a base and applying a 4 % annual growth rate. There are approximately equal number of males and females (306,036 and 312,792 respectively), comprising of all the different ethnic groupings in Ghana with majority being Akans as the predominant ethnic group in Ghana (Mensah, 2012). There are few foreign nationals from various parts of the world also dwelling there, working in the mines or doing different businesses. The major industrial activity in the area is gold mining, whereas farming is the main occupation of the indigenous inhabitants. Others also engage in trading and illegal small-scale gold mining popularly known as “galamsey”.



Figure.3.1: Map of the study area and its boundaries

3.2 Soils and Vegetation

The study area is located within a moist, semi-deciduous forest zone undergoing degradation consequent on anthropogenic action (Figure 3.2). Human interaction with the forest has reduced most of the forest areas to savanna. Large portion of the forest has been destroyed for cocoa and food crop production (Smedley *et al.*, 1995) while vegetation around AngloGold Ashanti mine has virtually perished from aerial As pollution (Ahmad and Carboo, 2000).

The vegetation thrives well within forest ochrosols developed under forest vegetation with mean annual rainfall between 125 cm and 175 cm. The soil ochrosols are very rich in humus and conducive for both cash and food crop production (Yeboah, 2008). Further, because of the high rainfall, the soils are leached kaolinite-muscovite laterites with average thickness of 1-3 m. However, the thickness depends on the underlying saprolite lithology, topography and drainage (Bowell, 1993). The upper layer soil because of its richness in organic matter is known to associate with As, and As levels are known to be high in the mining areas, in particular.

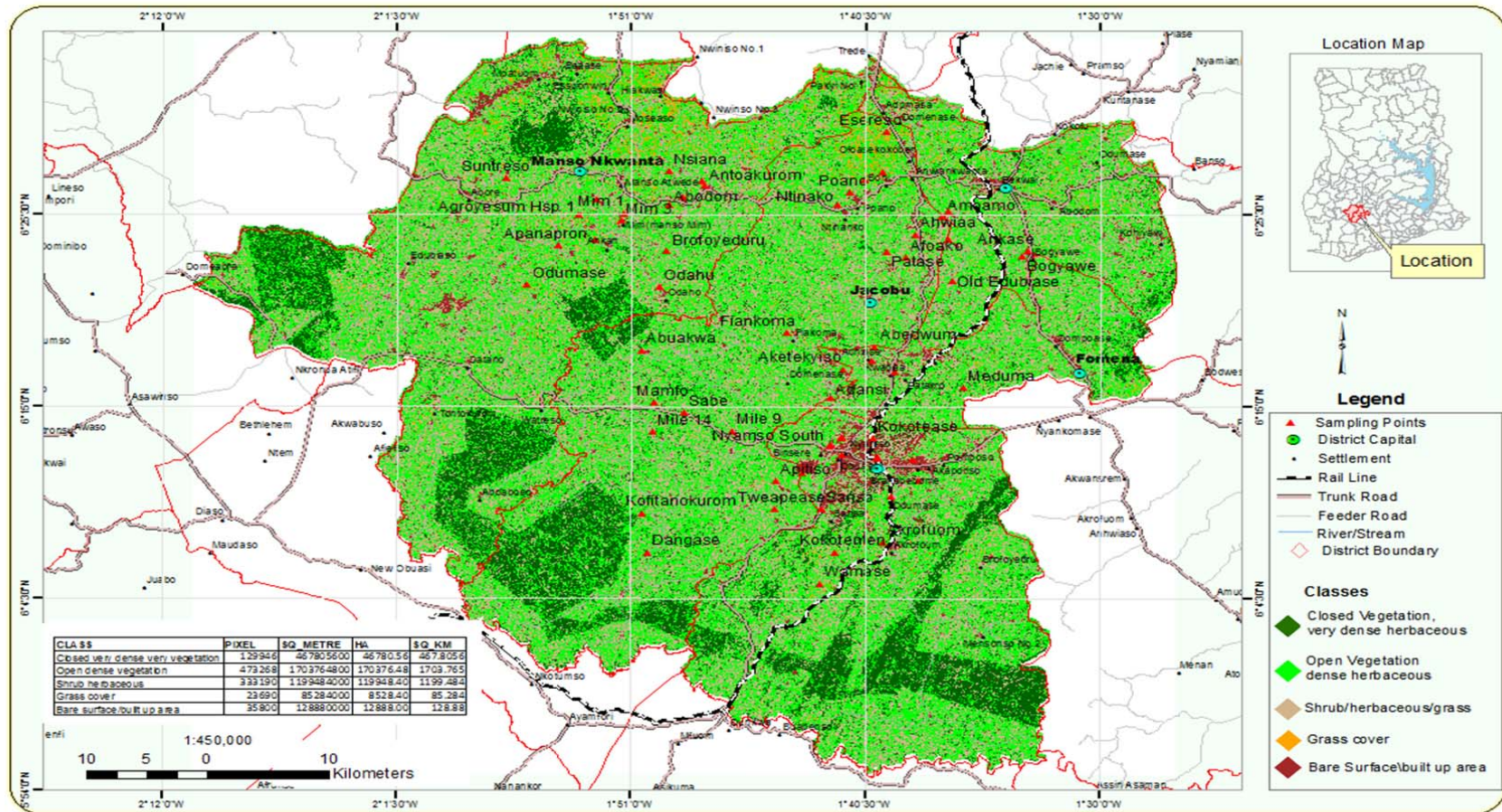


Figure 3.2: Land cover map of the study area

3.3 Climate

The climate within the study area is hot and humid and is influenced by the moist southwest monsoon winds and the dry dust-laden northeastern trade winds (Atta-Quayson, 1999). The area falls within the semi-equatorial type of climate and experiences double rainfall regime (Figure 3.3). The major rains begin in March and end in July with the month of June being the peak. The minor rains start in September and end in November (MoFA, 2011). This is separated by short cool dry month of August and a relatively long dry season from November to March. Mean annual rainfall value ranges between 1250-1750 mm (MoFA, 2011).

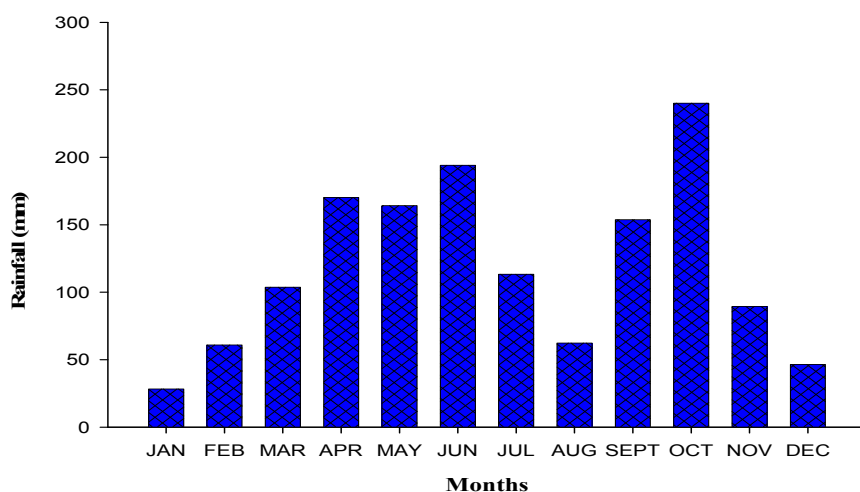


Figure 3.3: Mean monthly rainfall (mm) distribution at the study site (*Source: Meteorological Department, AngloGold Ashanti, Obuasi*).

Thus, the study area on the average has minimum of 10 continuous rainy months, with December-February as the driest months (Figure 3.4). Average temperatures are approximately 29.7 °C at mid-day and 21.10 °C at night with a mean temperature of 25.39 °C. February and March are the hottest months registering temperatures of 28.5 °C and 30.0 °C, respectively.

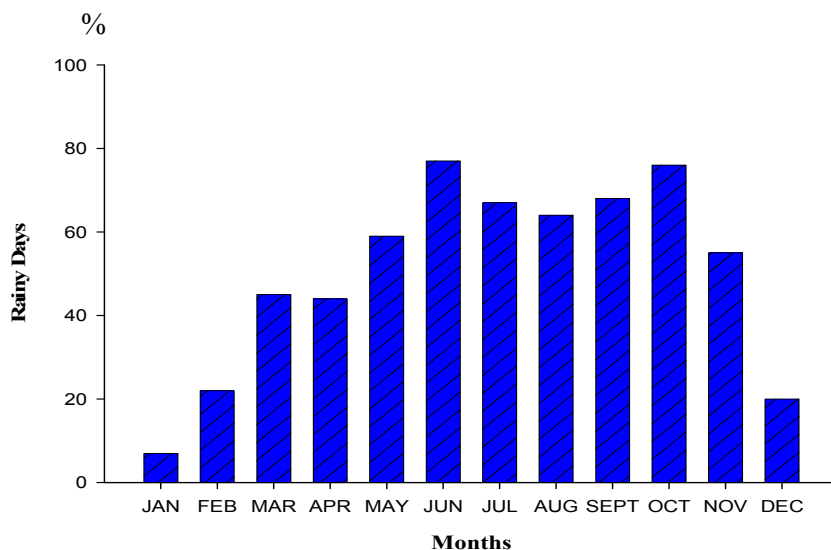


Figure 3.4: Total monthly rainy days at the study site (Source: Meteorological Department, AngloGold Ashanti, Obuasi).

During this period, maximum daily temperatures may at times rise above 30 °C and a minimum temperature of 18 °C. The coldest month is in August; and temperature increases as one move northwards. Wind directions are predominantly southwest/northwest throughout the year. The average wind speed is 3.4 km/h.

The area experiences low evaporation as compared to other parts of the region while humidity is usually high. Average evaporation is 3.3 mm/day over the year with a range of 2.4-7.7 mm/day. The relative humidity (RH) is 85 % at 0:900 hrs and 67 % at 15:00 hrs. The annual mean RH is about 76 % (Asamoah, 2004). Humidity is high (80 %) during the rainy season. The months of December to February, however, record very low humidity. It must be stressed however that, current trends in the climatic conditions of the area is becoming unpredictable as a result of climatic change (MoFA, 2011).

3.4 Geology and Hydrogeology

The geology of the study site (Figure 3.5) consists of Proterozoic rocks of the Birimian (upper and lower Birimian), Tarkwaian (pre Cambrian) and Intrusive systems noted for their mineral potentials (Kesse, 1985). The upper and lower Birimian units are found partially overlaid by rocks of the Tarkwaian sedimentary series (Osae *et al.*, 1995). The upper Birimian is predominantly made up of metavolcanic rocks with components of black slates,

sericite schist, tuffaceous sediments, pelites with subordinate grey, sandy phyllites and greywackes, whereas the lower Birimian rocks are characterized by argillaceous and fine to intermediate arenaceous rocks dominated by phyllite (containing variable amounts of carbonaceous matter), greywacke, schist, sandstone and horn-stone (Osae *et al.*, 1995). Metabasite and main 'Ashanti' shear zone also form part of the Birimian rocks.

The Tarkwaian system is mainly a thick series of white and grey quartzites (Abontenten and Dampaiyau quartzites) with a few intercalated bands of bluish and pink mudstone, Kawere group-grits, conglomerates, sandstones and chlorotoid phyllite containing chlorite, magnetite, etc. (Kesse, 1985). The Intrusive setting is made up of granitoid comprising of granite, dacite, granodiorite and rhyo-dacite. Olivine norite epidiorite, gabbro, amphibolite and unclassified 'late slage' basic dyke also form part of the intrusive system.

Groundwater is the major source of water supply for most of the communities. The occurrence of groundwater in this area depends on the geology, i.e. the Birimian super group system and particularly in areas where the rocks are highly weathered, fractured or inter-bedded with quartz veins. The groundwater flow is mostly restricted to joints, fractures or other openings within the crystalline rock formations.

Borehole yields are therefore often limited. In some areas, thick layer of weathered friable material called regolith overlies the crystalline basement and provides potential for increased groundwater storage (Kesse, 1985). The bedrock is not inherently permeable but has secondary permeability or porosity developed because of fracturing and weathering. In general, two types of aquifers are identified: weathered rock aquifers and fractured rock aquifers. These aquifers tend to act as confined or semi confined aquifers. The aquifers are perennial and may go dry in the dry season.

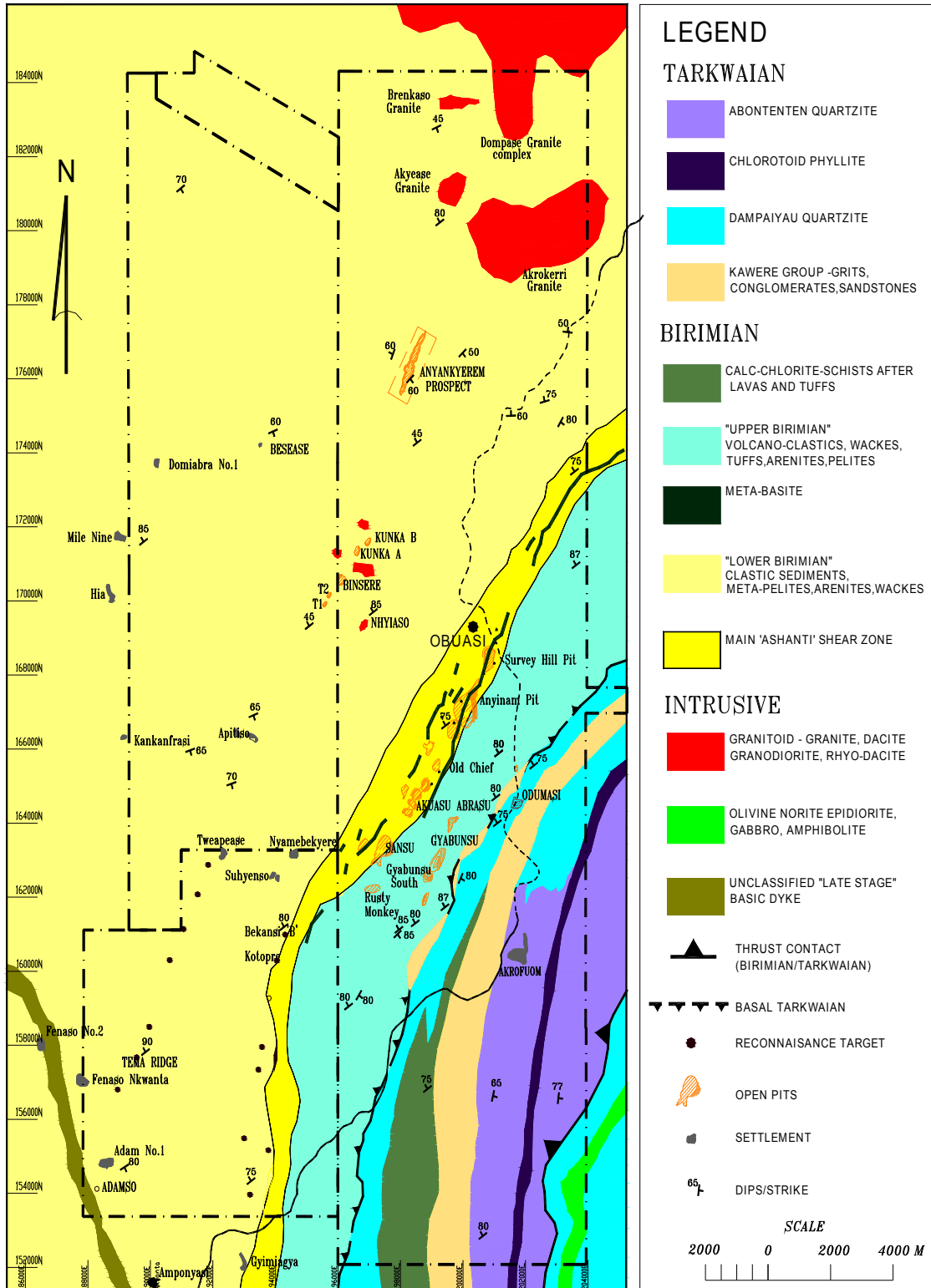


Figure 3.5: Geological map of the study area (Source: AngloGold Ashanti mines)

3.5 Relief and Drainage

The natural environment of the area originally is hilly in terms of relief and this is accompanied with rainforest vegetation. The hills can be seen throughout the area. In between the hills are valleys most of which contain streams. Low lying areas rise sharply from 152 m to 427 m (MoFA, 2011). The Moinsi and Daupaiyam mountains rise to about 500 m above sea level, over a plain of about 210 m above sea level (Foli, 2004). The highest point is located on the Pompo range at 634 m near Obuasi. Highland ranges include Dampaia (the most extensive) in the east, Kusa in the northeast, Pompo and Sanso near Obuasi. No area falls below 100 m above sea level.

Some of the rivers and streams that drain the area are Oda, JeniBonte, Pompo, Nyamso, Akapori, Kwabrafo, Nyam, Kwaw, Nyamso, Enewopeanom, Nkesu and Gyimi (Figure 3.6). Others include Wheaseamo, Konka, Nyame and Nyankuma streams all of which depict dendritic pattern of flow. The Kwabrafo receives effluent from the Pompora Treatment Plant (PTP) area, whereas the Nyankuma drains some open pit and the Sulphide Treatment Plant (STP) area. The rivers flow mainly from northeast to southwest. Most of these rivers and streams have been polluted by mining and other human activities (Yeboah, 2008). Again the area is endowed with springs which can be tapped as potable drinking water.

It is worthy to note that two confluences rivers of Offin and Pra as well as Birim and Pra within the study area which could be a huge tourism potential for revenue mobilization (MoFA, 2011).

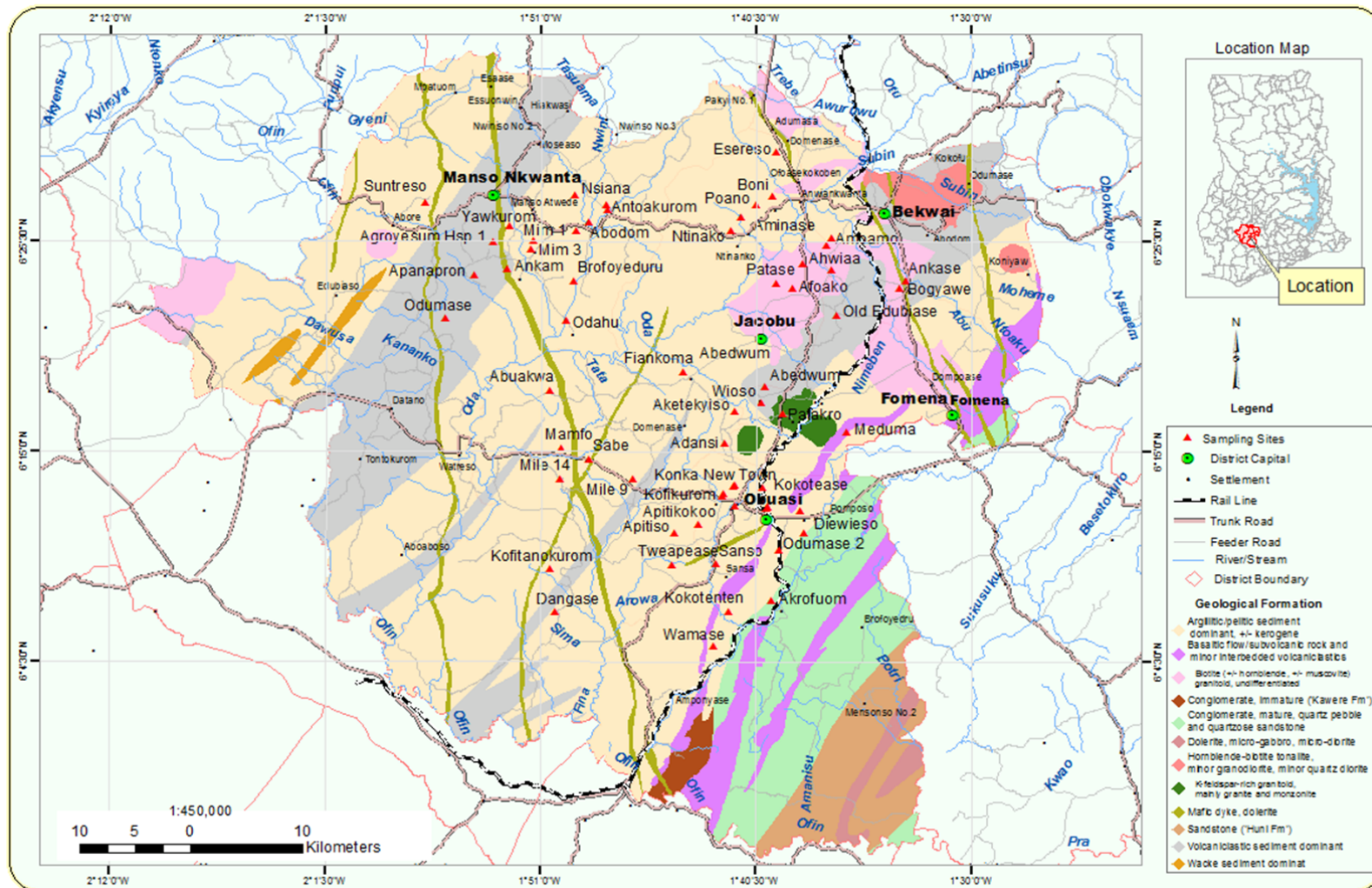


Figure 3.6: Hydrological map of the study area.

3.6 Land Use

The study area has large deposits of gold. This has led to proliferation of large and small scale mining activities. AngloGold Ashanti mine under leased hold status is the leading mining company in the area. Illegal mining activities such as “galamsey” operations are highly patronized by the youth (Figure 3.7).



Figure 3.7: Illegal mining operators

Geology varies in the study area as well as land use. Agriculture is the second major land use activity in the area since most of the inhabitants are farmers. Many of the inhabitants are engaged in crop farming whereas others solely depend on the livestock and poultry farming. Other land usages that affect nutrient loading include few large wastewater plants located at the outskirts of the study area. Due to the rapid increase in population, a great numbers of developmental projects are taking place exclusively housing which utilizes septic systems as their means of wastewater disposal.

CHAPTER FOUR

4.0 FIELD IDENTIFICATION AND SAMPLE COLLECTION – METHODOLOGY

4.1 Introduction

Gold mining in and around the study area dates back to the 19th century. Deep mining was the order, even unto this day. The extraction, purification and recovery of the pure gold led to different environmental insults, the release of As into fresh waters via surface and groundwaters. Water supplies in the study area are generally from rivers, streams and groundwater. These water bodies are characterized by their natural geographical distribution and accessibility as well as unsustainable water use. Water is life, livelihood and health. It is for this reason that this study was conducted to determine the levels and distribution of groundwater As contamination in the south-western part of Ashanti Region of Ghana which is the major gold mining area. Hence, this chapter describes the fieldwork, various procedures for sample collection, and preparation of samples for laboratory analysis.

4.2 Fieldwork

The procedures given by 2007 published edition of Environmental Geology Handbook of Field Methods and Case Studies (Knödel *et al.*, 2007) with modifications were followed during the fieldwork. This section describes the methods and procedures employed for the selection of sampling sites, sample collection and its preparation for laboratory analysis.

4.3 Selection of Groundwater Sampling Sites

Initially, to understand the general variation in groundwater chemistry and geographical information of the study area, a well inventory was carried out in July 2011. A Garmin III global positioning system (GPS) was used for location reading (Table 4.1). These data were used to select the 63 representative boreholes and wells for groundwater sampling in order to achieve the research objective by evaluating the arsenic (As) contamination status during the two major seasons (seasonal variations) in Ghana.

Table 4.1: Geographical location of sampling sites

Site No	Location	Site code	Well type	Latitude (6°N) Mins	Longitude (1°W) mins
1	Apitiso	AC-3	Bore hole	10.65	43.88
2	Ankase	BM-5	Bore hole	23.41	33.12
3	Mile 9	AC-3	Bore hole	13.49	46.28
4	Mile 14	AC-3	Bore hole	13.47	49.61
5	Bogyawe	BM-5	Bore hole	23.22	32.88
6	Dunkwa Nkwanta	AN-1	Bore hole	12.91	41.32
7	Wamase	OB-4	Shallow well	5.28	41.91
8	Kokotease	AN-1	Bore hole	12.85	40.9
9	Kofikurom	AN-1	Bore hole	11.89	40.92
10	Boni	AC-3	Bore hole	27.57	39.43
11	Huntado	AC-3	Bore hole	26.92	40.41
12	Poano	AC-3	Bore hole	26.52	40.73
13	Ntinako	AC-3	Bore hole	25.73	41.43
14	Dwondoso	BM-5	Shallow well	23.77	36.48
15	Aminase	BM-5	Shallow well	25.50	36.47
16	Amoamo	BM-5	Shallow well	25.30	37.4
17	Kofitanokurom	AC-3	Bore hole	9.20	49.91
18	Yawkurom	AW-2	Bore hole	26.28	52.31
19	Obuasi BH 3	OB-4	Bore hole	12.24	39.56
20	Odumto	AC-3	Bore hole	15.43	50.48
21	Abuakwa	AC-3	Bore hole	18.13	50.31
22	Fiankoma	AC-3	Bore hole	19.10	43.62
23	Mim 1	AW-2	Bore hole	25.42	51.20
24	Abodom	AW-2	Bore hole	25.73	48.76
25	Mim 2	AW-2	Bore hole	25.18	51.28
26	Antoakurom 1	AW-2	Bore hole	27.14	47.43
27	Manso Akropon	AW-2	Bore hole	26.38	48.39
28	Antoakurom 2	AW-2	Bore hole	27.28	47.49
29	Nsiana	AW-2	Bore hole	28.0	48.78
30	Dangase	AC-3	Shallow well	7.10	50.15
31	Obuasi BH 2	OB-4	Bore hole	12.24	39.56
32	Obuasi BH 1	OB-4	Bore hole	12.21	39.57
33	Tweapease	AC-3	Bore hole	8.92	44.33
34	Ankam	AW-2	Bore hole	24.17	51.97
35	Agroyesum Hsp	AW-2	Bore hole	24.98	52.79
36	Apanapron	AW-2	Bore hole	23.58	53.75
37	Odahu	AW-2	Bore hole	21.42	49.43
38	Dekyewa	AC-3	Bore hole	12.43	42.97
39	Odumase	AW-2	Bore hole	9.75	39.20
40	Manso Atwere	AW-2	Bore hole	27.58	51.40
41	Nhyiaso	OB-4	Bore hole	11.29	42.22
42	Sabe	AC-3	Bore hole	14.49	47.96
43	Mensakrom	OB-4	Shallow well	9.90	42.65
44	Mamfo	AC-3	Bore hole	15.22	49.58
45	Nyamekyere	OB-4	Bore hole	8.78	43.18
46	Akrofuom	OB-4	Shallow well	7.45	39.43
47	Old Edubiase	BM-5	Bore hole	22.0	35.94
48	Meduma	AN-1	Bore hole	16.11	35.64
49	Sanso	OB-4	Bore hole	9.33	41.86

Arsenic Contamination in Groundwater

50	Brahabebome	OB-4	Bore hole	12.15	37.80
51	Diewieso	OB-4	Bore hole	10.67	37.67
52	Nyamso North	OB-4	Bore hole	12.65	41.63
53	Nyamso South	OB-4	Bore hole	12.59	41.67
54	Konka New Town	OB-4	Bore hole	12.86	41.34
55	Apitikokoo	OB-4	Bore hole	10.93	42.78
56	Kokotenten	OB-4	Bore hole	6.71	41.50
57	Mile 18	AC-3	Bore hole	8.78	43.18
58	Patakro	AN-1	Bore hole	17.5	38.71
59	Wioso	AN-1	Bore hole	16.99	39.72
60	Afoako	AC-3	Bore hole	23.19	38.41
61	Abedwum	AN-1	Shallow well	18.26	39.63
62	Aketekyiso	AC-3	Shallow well	16.72	41.31
63	Patase	AC-3	Bore hole	22.96	39.31

The locations of the 63 observation boreholes and wells were also digitized to produce a well-location map of the study area (Figure 4.1). The wells and boreholes were selected to represent different geological formations, the locations of the AngloGold Ashanti mining site, illegal artisanal mining activities, active and decommissioned tailings dam as well as land-use pattern and different depths of the aquifer. Information on the well depth was acquired through personal communication with the well owners and community heads in locations where records on the well depth were lacking. The well depths ranged from 1.5 to 100 m (Appendix 5).

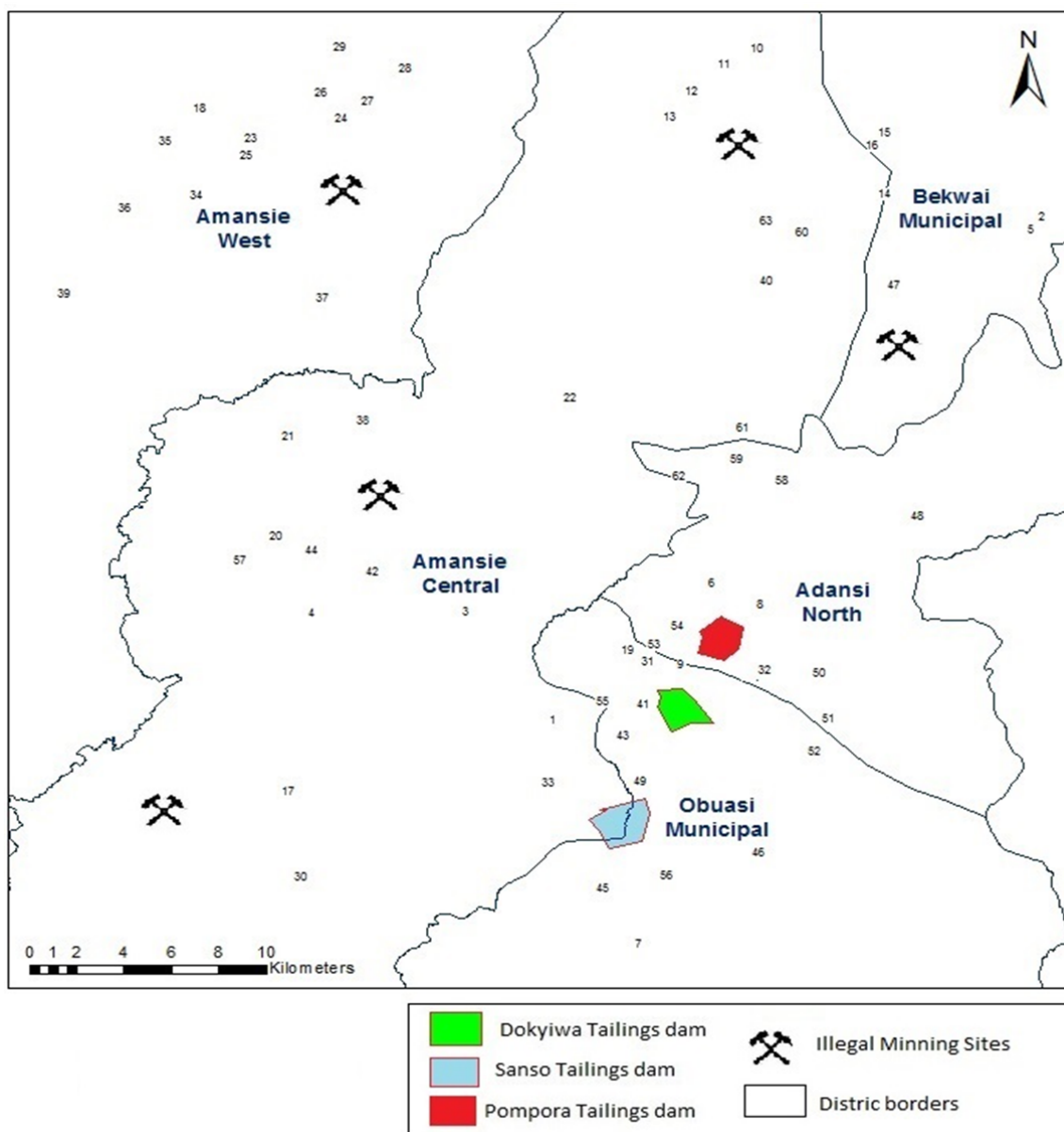


Figure 4.1: Well location map of the study area

4.4 Selection of Tailings Dam Sampling Sites

Active and abandoned gold mine tailings dams (Figure 4.2) were selected for the tailings sample collection and analysis in the present study to investigate the issue of gold mine tailings dams as a potential source of arsenic and other trace elements contamination and their dissolution into the adjoining environmental media in the study area. The tailings dams

include Sanso active tailings dam and two abandoned tailings dams at Pompora and Dokyiwa communities, respectively. The Sanso active tailings dam was built some two decades ago with the decommissioning of the old dam, which was used for several decades (Antwi-Agyei *et al.*, 2009). Six spots were selected randomly at each study site for sampling using soil auger and chisel hoe. Mini pits were dug at selected points, the soils were identified by the series name and sampled at a depth of 0-20 cm. Samples were however, not taken from locations that were difficult to access.

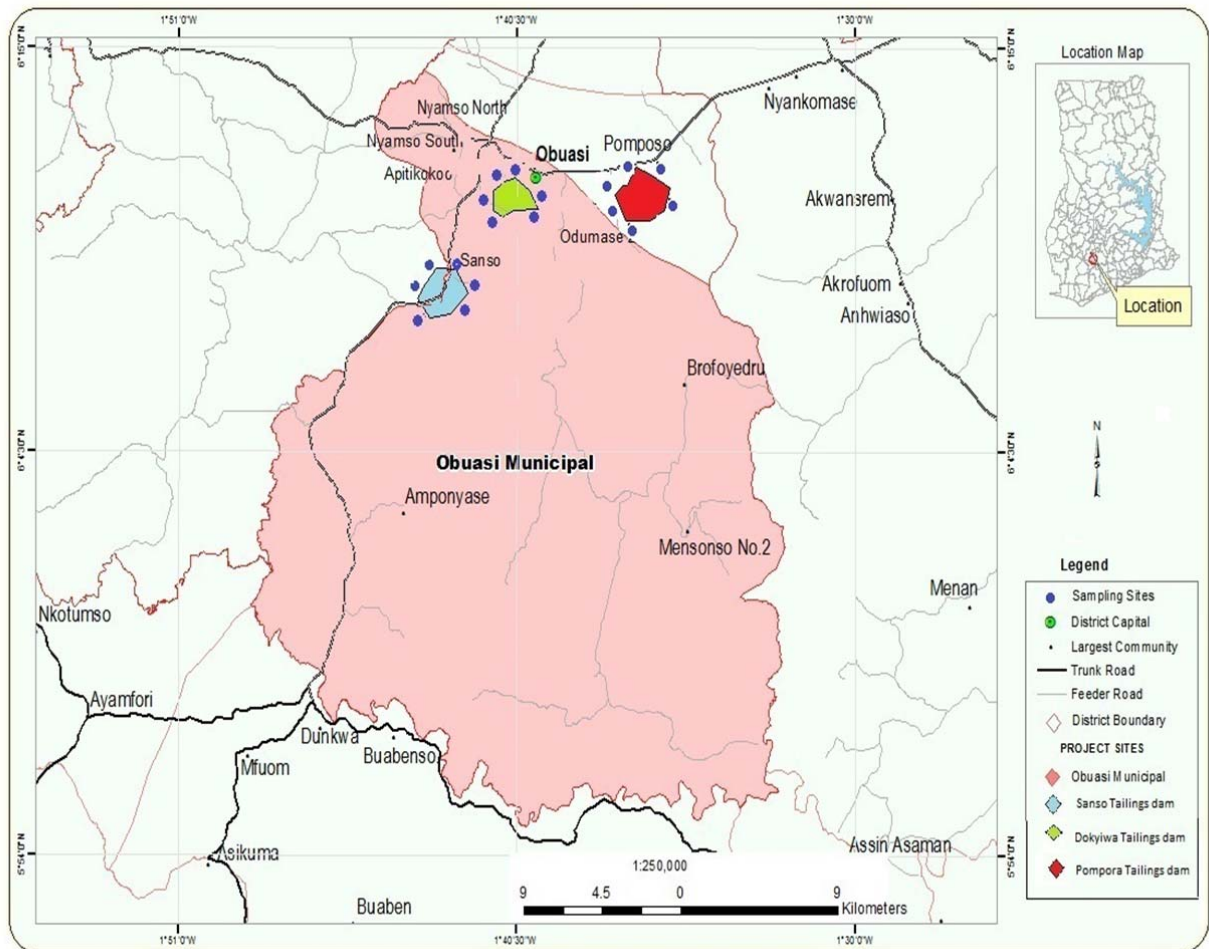


Figure 4.2: Map of Obuasi Municipality showing the Sanso, Dokyiwa and Pompora tailing dams.

4.5 Materials

4.5.1 Apparatus

Table 4.2: List of equipments used and their function

Equipment type	Function
Atomic Absorption Spectrometer- A Varian Model 240FS equipped with air-acetylene flame atomizer.	For analyzing of metals and some metalloids.
Hollow cathode lamp of As, Mn, Fe, Cu, Zn	To provide for the analytical light line for the element of interest and a constant yet intense beam of that analytical line.
Hydride generator- Varian GTA-3000, equipped with gas-liquid separator adapted to an FIA system.	Suck up (aspirate) liquid sample at a controlled rate; Mix liquid sample with sodium borohydride and HCl; Create a volatile hydride of the analyte metalloid from that reaction and flow that gaseous hydride into the optical cell.
Metrohm 761 Compact IC and Dionex 4500i IC system (<i>Metrohm</i> , Switzerland).	For determination of anions and cations of groundwater.
Hach 2100Q Portable turbidimeter	To provide accurate turbidity measurements.
Flow-through cell coupled with water quality meter (Model YSI 6 10-DM/600XL)	For measuring pH, electrical conductivity, dissolved oxygen, temperature and oxygen reduction potential.
Sample digester-digestion battery for Kjeldahl flasks coupled to temperature and time control module (<i>Selecta</i> , Barcelona, Spain).	For powering the sample digester.
Microwave sample digester-Model MDS-2000 (650 W; CEM Corp., Matthews, NC).	For digesting groundwater and tailings leachate samples.
Glassware and polyethylene bottles- Previously washed and decontaminated.	For collecting groundwater samples.
Micropipettes (<i>Gilson Pipetteman</i> TM).	For measuring and delivering of microliter volumes.
Bouyoucos hydrometer (<i>Canadawide Scientific</i> , Canada).	For quantitative determination of the distribution of particle sizes in soil.
The Stainless Steel Hand Auger (<i>Envco-</i>	For augering shallow holes in fine grained.

Environmental Equipment Inc, Australia).	
Chisel hoe (Envco-Environmental Equipment Inc, Australia).	For general sampling of most soil types and for gaining access to sampling points.
Polyethylene bags (Packen Solutions, Toronto)	For sealing soil samples and sampling bottles.
Sample Pro [®] groundwater sampling Pump (QED Environmental Systems) Dexter USA.	For groundwater sampling and purging.
Water level indicator (Type BFK- Audio and visual alert) Boode b.v. Netherlands.	For measuring water levels in wells and boreholes.
QuickFilter [®] groundwater sampling disposable filter (QED Environmental Systems) Dexter USA.	For filtering of the groundwater samples.
MP40C MicroPurge Engine/Compressor (QED Environmental Systems) Dexter USA.	To facilitate the purging and pumping of groundwater.
Course sand and fine sand	Acting as a filtration tool.
Earthen pots and jerry cans	Used as a storage media and was used for evaluating arsenic removal technology
90-PPI-White-Polyester	Acting as a filtration tool.

4.5.2 Reagents for Laboratory Analysis

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). All solutions were prepared with ultrapure water with a specific resistivity of 18 mohm cm⁻¹ obtained by passing distilled water through exchange resins in a Milli-Q[®] (Millipore) water purification system. This involved removal of organic, metal and anion impurities, by sequentially passing distilled water through a Super-C carbon cartridge, Ion-ex anion and cation exchange cartridges, an Organex-Q cartridge and finally a Millipak[®] 0.22 µm pore size filter. The Organex-Q cartridge removes organics by adsorption to activated carbon. All solutions prepared were stored in high density polypropylene bottles.

All solutions were prepared from analytical reagent grade reagents:

- a) HNO₃ (65 %), HCl (37 %), H₂SO₄ (96 %), KI, NaBH₄, V₂O₅ and acid mixture comprising nitric, sulfuric and perchloric acids (6+3+1, v/v).

- b) Argon (99.98%, Oksan, Ankara)
- c) Commercially available 1000 mg As L⁻¹ (prepared from As₂O₃ in 50 mL conc. HCL; Tritisol; Merck).
- d) Commercially available 1000 mg Mn L⁻¹ (prepared from MnCl₂.4H₂O in 50 mL conc. HCL; Tritisol; Merck)
- e) Commercially available 1000 mg Cu L⁻¹ (prepared from Cu(NO₃)₂.3H₂O in 250 mL of ultrapure water; Merck).
- f) Commercially available 1000 mg Fe L⁻¹ (prepared from FeCl₃.6H₂O in 250 mL of ultrapure water; Merck).
- g) Commercially available 1000 mg Zn L⁻¹ (prepared from ZnO in 5 mL of ultrapure water followed by 25 mL of 5M hydrochloric acid; Tritisol; Merck).
- h) 500 or 250 µg mL⁻¹ of Palladium modifier solutions (prepared from a commercially available stock solution of 10 000 µgmL⁻¹ Pd(NO₃)₂ (Merck) with 1% v/v HNO₃ solution).
- i) 50 gL⁻¹ of La (prepared by dissolving 5.86 g La₂O₃ (Merck) in 10 mL of HNO₃ + H₂O mixture (1:1) and diluting to 100 mL of ultrapure water.

4.6 Containers and Cleaning Processes

Cleaning of the laboratory equipment was necessary to reduce the chance that contamination could alter the trace metal measurements. New polypropylene containers were used. The polypropylene bottles were rinsed with ultrapure water and immersed in a warm liquid soap bath for two days, then rinsed with ultrapure water, immersed in 10 % HNO₃ at room temperature for three days.

Bottles were again rinsed three times with ultrapure water, and then immersed in 50 % HNO₃ bath at 90 °C for 24 hours. Bottles were further rinsed with ultrapure water and then filled with ultrapure water containing 1 % high purity HCl. They were capped loosely and placed overnight in a clean oven at 60 °C. The bottles were then removed from the oven and allowed to cool-down. The acidified water was discarded, and the oven step repeated once more. After bottles were rinsed three times with ultrapure water, they were filled with ultrapure water acidified with Optima-HCl, capped tightly, and double bagged in re-sealable new polyethylene bags and stored.

Again sand used in evaluating arsenic/iron removal technology was obtained from Elmina beach, Cape Coast and was sieved through a 0.2 mm sieve to obtain fine and coarse grades. The sand was sieved through the screen once to obtain fine sand and the coarse sand (2.0-0.6 mm diameter) was retained on the screen. Both the fine and coarse sand were thoroughly washed repeatedly with distilled water until the rinse water appeared clean. It was then boiled for fifteen minutes to remove any bacterial contamination.

4.7 Groundwater Sample Collection

The sixty three sampling sites were visited during the entire study period. The samples were collected using acid washed polypropylene bottles to avoid unpredictable changes in characteristic as per standard procedures (Knödel *et al.*, 2007). Sampling was designed to cover 12 months, covering the dry and wet periods of 2012 and 2013. Samples were collected at monthly intervals, beginning from August and November 2012 to February 2013 for dry season and from September to October 2012 and March to July 2013 samples for rainy season. Care was taken to collect subsequent samples from same location in both seasons.

Overall, 63 wells including shallow wells, boreholes and hand-dug wells were sampled. The samples were collected by wearing polyethylene gloves, employing the sampling protocol methods as described by Knödel *et al.*, (2007) with modifications. Once the acidified water was emptied, 1.0 L-capacity plastic bottles were rinsed with the groundwater samples before being filled completely and preserved airtight in order to avoid evaporation.

Wells were purged (pumped) prior to sampling because a fresh water sample is needed to accurately assess groundwater quality. Water standing in a well for a period of time undergoes changes that can affect and alter the water quality; it stagnates. Hence a peristaltic pump was used to purge groundwater from each well using the low flow purging techniques. A flow-through cell and a calibrated hand held YSI[®] Multi-Parameter Water Quality Meter (Model YSI 610-DM/600XL) was connected to a low-flow pump (peristaltic pump) at a flow rate of 500 mL/min. This instrument contains probes that simultaneously measure pH, conductivity, dissolve oxygen, oxygen reduction potential (ORP) and temperature, except turbidity. Turbidity samples were collected before the flow-through-cell. A "T" connector coupled with a valve was connected between the pumps tubing and flow-through-cell. When a turbidity measurement is required, the valve is opened to allow the groundwater to

flow into a container. The valve is closed and the container sample is then placed in the calibrated Hach 2100Q Portable turbidimeter to provide accurate turbidity measurements.

The depth to groundwater was measured and the tubing intake end was immersed approximately 0.2 feet beneath the water table surface. This method ensured that the entire stagnant water column was displaced by fresh formation water entering the screen. The wells were purged of approximately 3 to 5 casing volumes at an approximate rate of 500 mL/min. Indicator parameters, including pH, conductivity, dissolve oxygen, oxygen reduction potential (ORP) and temperature, were measured at 15 minutes intervals throughout the purge period. Indicator parameters were stabilized after removal of approximately 3 casing volumes. In fact, many of the wells and boreholes were been used by the local people when we (sampling crew) arrived at the respective sampling sites.

When the parameters stabilized to consistent readings, and without interrupting flow from the well, the tubing was immediately disconnected from the flow through cell to fill the sample containers. One person of the sampling crew was chosen to handle the sampling bottles. Unfiltered samples were collected for total (dissolved + particulate) As whiles filtered groundwater samples were collected for major anions and cations, arsenic species, other trace metals and nitrates analysis. The final readings for all the filed data including sampling date and time, well depth, sampling source and location etc were all recorded. At each designated sample collection interval, pump rates were reduced to between 100 and 300 mL/min to prevent turbulence as the water was directed into the sample containers. The sample bottles were filled to capacity (i.e., minimal headspace) to minimize air exposure.

The samples were immediately acidified to a pH of < 2 using nitric acid for total As and the trace metals. The nitric acid preserves the sample by lowering the sample pH to 2 which prevents the precipitation of iron and to prevent the oxidation of any Fe^{2+} in solution which might cause some arsenic to be sorbed as being described by Holm *et al.*, (2004). Iron precipitation would decrease measured aqueous arsenic concentrations because of arsenic adsorption onto precipitated iron oxides. The indicator parameters were again measured from a fresh sample of groundwater. Teflon-lined caps were applied to ensure a tight seal. For each monitoring well location, groundwater samples were collected using the low flow on the same day to reduce day-to-day variation in concentration of site contaminants that may exist at each sampling location.

The samples were then placed in coolers within iced-packed containers to ensure refrigeration at 4 °C to prevent changes due to chemical or biological activity as well as loss due to evaporation until arrival at the Environmental Research Laboratory under chain-of-custody (Appendix 1). After the sample collection, the sampling well locations, the well ID, notes on individual samples, date and time of sampling, and the type of analyses requested were recorded (Appendix 2).

A simple questionnaire, consisting of five questions in yes/no format, was used to investigate residence perceptions of taste and odor (Appendix 3). Randomly twenty people were interviewed on each location who are supposed to be regular consumers of that particular well or borehole. The questionnaire also included a provision for the research team's observations on the color of water, general state of water point and location as well as the amount of water consumed daily per household. An investigation on the variability of measurements taken for the same parameter but using different instruments was carried out and in all the cases, deviations in measurements using different instruments did not exceed 5 %, which was deemed negligible for practical purposes.

4.8 Mine Tailings Sample Collection

Two abandoned (Pompura and Dokyiwa) mine tailing dams and one active (Sanso) in Obuasi which had produced mainly gold were selected for the sample collection and analysis in the present study. Mining works had generated large quantities of waste materials, including mine tailings, waste rock and slag, which might be disposed to nearby valleys and cultivated lands without appropriate treatment.

At each demarcated selected point within every site, three 1 kg soil samples were collected at a depth of 20 cm from six different locations apart by about 15 m (Figure 4.2). The samples were placed into plastic bag, and then stored in a cooler in the field. The samples were transported to the Environmental Research Laboratory for the analysis.

The concentrations of As, Fe, Mn, Cu and Zn were determined using an atomic absorption spectrometer (AAS, Varian Models 240FS). Particle size distribution was determined using the modified Bouyoucos hydrometer (Day, 1965). Soil pH and Electrical Conductivity (EC) were also determined by glass electrode in a soil-water ratio of 1:2.5. Dissolved oxygen (DO,

YSI model 58) was measured. The values of several anions (Cl^- , F^- , NO_3^- , and SO_4^{2-}) were determined by an ion chromatography.

Apart from the collection and analysis of groundwater and mine tailings samples, information about study area were collected from the various Municipal and Districts Assemblies visited during the entire study.

CHAPTER FIVE

5.0 ANALYSIS OF ARSENIC IN GROUNDWATERS – METHODOLOGY

5.1 Experimental Methods

This section describes the methods and procedures employed for the determination of various groundwater quality parameters, arsenic (As) and other trace metals (Cu, Fe, Mn, Zn). The physicochemical parameters were analyzed both in the field using portable meters and in the laboratory. Arsenic and trace metals determination in mine tailings were also discussed in this section.

5.2 Physicochemical Measurements

The procedures given by Knödel *et al.*, (2007) with modifications were followed during the laboratory works. The physicochemical analyses of groundwater samples represented indicator field parameters (temperature, electrical conductivity, pH, dissolved oxygen, oxygen reduction potential and turbidity), total suspended solids (TSS), total dissolved solids (TDS), total hardness, alkalinity, sodium absorption ratio (SAR), residual sodium carbonate (RSC) and percentage sodium (% Na) in the water samples were determined.

5.2.1 Indicator Field Parameter Measurements

A transparent small volume flow-through cell (this allows observation of air bubbles and sediment buildup in the cell, which can interfere with the operation of the monitoring instrument probes, to be easily detected and its small volume cell nature facilitated rapid turnover of water in the cell between measurements of the indicator field parameters) coupled with a calibrated hand held YSI® Multi-Parameter Water Quality Meter (Model YSI 610-DM/600XL) was used simultaneously to measure indicator field parameters such as pH, electrical conductivity (EC), dissolve oxygen (DO), oxygen reduction potential (ORP) and temperature, except turbidity which was measured separately with a calibrated Hach 2100Q Portable turbidimeter.

5.2.2 Total Dissolved Solids (TDS)

Total dissolved solids (TDS) are the measure of total inorganic salts and other substances that are dissolved in water. TDS was determined using Electrical Conductivity (EDT-RE387T x Microprocessor Conductivity Meter). It was calibrated using standard solutions before each sampling.

5.2.3 Determination of Total Suspended Solids (TSS)

TSS was determined by gravimetry method. Water samples (1 L) were vacuum filtered through the pre weighed filter paper with 0.45µm pore size syringe filter (Sartorius Minisart, non-pyrogenic CE). The filter paper with the solids was dried in an electrical oven at a temperature of 103-105 °C and cooled. TSS was determined by using the following formula (Anon, 1992):

$$TSS \text{ mg/L} = \frac{(final \text{ wt} - initial \text{ wt})}{amount \text{ of samples taken}} \times 1000$$

5.2.4 Determination of Total Hardness (TH)

50 cm³ of the water sample was introduced into a conical flask and 2-3 cm³ buffer (pH 10) solution added. 0.03 g of the solid indicator was also added and the solution stirred properly to obtain a deep wine-red color. The mixture was titrated with 0.01 M EDTA (Ethylenediaminetetraacetic acid) solution until the color changed from the wine-red to dark blue with no tinge of wine-red color remaining. The total hardness of the water sample was calculated as mg/L.

5.2.5 Determination of Alkalinity

100 mL of the groundwater samples was pipetted into a 250 cm³ Erlenmeyer flask and two drops of Phenolphthalein indicator added and swirled. The solution was titrated with sulphuric acid till the color changes to colorless. Two drops of mixed indicator was also added and titrated with sulphuric acid till the color changes to red. The titre value was then recorded as the total alkalinity of the water samples.

5.2.6 Determination of Sodium Adsorption Ratio (SAR)

The SAR was computed using the formula (Hem, 1991):

$$SAR = \frac{Na^+}{\frac{\sqrt{Ca^{2+} + Mg^{2+}}}{2}}$$

5.2.7 Determination of Residual Sodium Carbonates (RSC)

RSC was calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water for agricultural purposes (Eaton 1950) and was determined by the formula:

$$RSC = (HCO_3 + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$$

Where all ionic concentrations are expressed in milliequivalents per liter.

5.2.8 Determination of Percentage Sodium (% Na)

Percentage of Na^+ is normally used to assess groundwater suitability for irrigation and agricultural purposes. % Na is calculated based on the relative proportion of cations present in groundwater. The content is expressed in terms of percentage sodium or soluble sodium percentage defined as:

$$\% Na = \frac{(Na^+ + K^+) \times 100}{Ca^{2+} + Mg^{2+} + Na^+ + K^+}$$

5.3 Ion Concentration Measurement Procedures

Groundwater samples were analyzed for anions [bicarbonates, fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-})] and cations [sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+})] using ion chromatography. These anions and cations were determined simultaneously in groundwater samples using Metrohm 761 Compact IC and Dionex 4500i IC system, respectively.

5.3.1 Analysis of F^- , Cl^- , NO_3^- , HCO_3^{2-} , and SO_4^{2-}

Ion chromatography (IC) with suppressed conductivity detection is used for the determination of fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), bicarbonate (HCO_3^{2-}) and sulfate (SO_4^{2-}) ions in groundwater samples. The eluent was 2.0 mM/L Na_2CO_3 and 1.3 mM/L $NaHCO_3$. The operating parameters of the IC are presented in Table 5.1.

A Metrohm 761 Compact IC with suppressed module, equipped with an anion-separator column (Dual 2) was used for the analysis. 2.0 mM/L Na_2CO_3 and 1.3 mM/L $NaHCO_3$ were prepared from analytical reagent grade anhydrous sodium carbonate and sodium hydrogen carbonate respectively.

The mobile phase and eluent were degassed and filtered using 0.45 μm filters before use. 20 mM sulphuric acid was used as a regeneration solution. Calibration standards of appropriate concentration were prepared on a daily basis by diluting IC Multi-element standard (Merck) containing 100 ppm F^- , 250 ppm Cl^- , 500 ppm NO_3^- , 500 ppm HCO_3^{2-} , 500 ppm SO_4^{2-} , and 1000 ppm PO_4^{2-} . The linear regression was used to calculate the calibration graphs and the fit was excellent ($r^2 = 0.999$). All solutions were prepared in HPLC grade deionized water and filtered before analysis.

Table 5.1: Operating parameters employed for the determination of F^- , Cl^- , NO_3^- , HCO_3^{2-} , and SO_4^{2-} by Ion chromatography with suppressed conductivity detection.

Parameters	Setting/value
Column	Anion-separator (Dual 2)
Detection mode for anions	Conductivity
Eluent composition	2.0 mmol/L Na_2CO_3 and 1.3 mmol/L $NaHCO_3$. Conductivity after chemical suppression approximately 14 $\mu S/cm$
Flow-rate of eluent	0.5 mL/min
Pressure	4 MPa
Analysis time	20 min
Loop	20 μL
Suppressor regenerant	20 mM H_2SO_4 , HPLC grade deionized water. Autostep with fill

5.3.2 Analysis of Na^+ , K^+ , Mg^{2+} and Ca^{2+}

All cations determination was performed using a Dionex 4500i IC system with Dionex columns, conductivity detector and computer interface. The entire system was operated using

the DionexAutoIons program (version 3.2). The cations were separated on a CSIO separation column after a CGIOguard column and the back-ground conductivity of the eluent was suppressed using a CMMSII membrane suppressor. The suppressor was continually regenerated using 100 mM tetramethylammonium hydroxide (FlukaBuchs, Switzerland).

The eluent and all standard solutions were prepared using 18-M&2 deionized water. Merck 1000 mg/L cation stock standard solutions were used to prepare all of the cation working standard solutions. All working standard solutions were prepared in clean polypropylene bottles and stored in a refrigerator. Fresh standard solutions were prepared prior to each set of pore water analyses.

The eluent was 40.0 mM HCl, 12 mM DL-2,3-diaminopropionic acid monochloride (DAP) (Fluka), which allows the separation and determination of Na^+ , K^+ , Mg^{2+} and Ca^{2+} . For the groundwater samples, a 250 μL injection loop was employed and the instrument was calibrated with 20, 50, 250, and 1000 ng/g (ppb) mixed cation standards (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) using linear regression. The linearity of the calibration graph for each of the cations over this concentration range was excellent ($r^2 = 0.999$). The accuracy of the chemical analysis was verified by calculating ion balance error (Vasanthavigar *et al.*, 2012) where the errors were generally around $\pm 7\%$.

5.4 Metal Concentration Measurement Procedure

Total arsenic and other trace metals (Fe, Cu, Mn, and Zn) analysis of the groundwater samples were performed on electrothermal and flame atomic absorption spectrometry which is one of the most extensively used techniques for determining various elements with significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and fairly low operational cost. However, in the case of arsenic determination, some interferences effects from anions and cations, high background signals and volatilization of analyte together with organic compounds may occur in the direct determinations. The influence of a complicated matrix greatly affects the analytical results. Therefore Palladium modifier solution was employed to reduce the background signals and chemical interferences.

5.4.1 Preparation of 1000 ppm Stock Arsenic Atomic Absorption Standards

Stock arsenic standard solutions were prepared from analytical reagent grade reagents: HNO₃ (65 %). Commercially available 1000 mg As/L, was prepared from As₂O₃ in 5M HNO₃ (Tritisol; Merck). All solutions were prepared with ultrapure water with a specific resistivity of 18mohm cm⁻¹ obtained by filtering double-distilled water through a Milli-Q purifier (Millipore, Bedford, MA, USA) immediately before use. These stock solutions were kept at 4 °C in darkness. All standard solutions used in this work were prepared daily by adequate dilution of the stock solution.

5.4.2 Preparation of Arsenic Working Standard Solutions

Dilutions of the 1000 ppm standard arsenic were prepared using nitric acid mixed with distilled water to make 0.5 % nitric acid solutions. The arsenic was diluted to concentrations of 10 mg/L. From this secondary standard solution, more dilute standards of 250 µg/L were prepared and stored in amber bottles. A blank was prepared similarly. When AAS analysis was performed for arsenic metal, serial dilution was prepared daily from the 250 µg/L standard solution to obtain concentrations used to make calibration curves of the target metal.

5.4.3 Groundwater Sample Digestion

To ensure the removal of organic impurities from the samples and thus prevent interference in analysis, the samples were digested with concentrated nitric acid. 10 mL of nitric acid was added to 50 mL of groundwater samples in a 250 mL conical flask. The samples were then digested following five-steps program: (i) 5 min at 150 °C and 50 % power; (ii) 5 min at 220 °C and 70 % power and (iii–iv) 5 min at 100 °C and 10 % power after which it was allowed to cool and then filtered. Finally, the filtrate was adjusted to pH 3.0–4.5 with dilute HNO₃ before it was made to volume in a 10-mL calibrated flask. A reagent blank was prepared in parallel. The dilute sample (10 mL) was analyzed immediately after preparation.

5.4.4 Groundwater Sample Analysis of Total Arsenic (*As_{total}*)

A Varian Model electrothermal atomic absorption spectrometer (ETAAS) equipped with GTA 3000 graphite furnace, with deuterium arc background corrector was used. Measurements were made at 193.7 nm, using a single-element hollow cathode lamp for arsenic that was operated at 20 mA and a bandwidth of 0.7 nm. Both peak height and peak

Chair of Environmental Geology, BTU

area absorbance values were measured. Varian pyrolytically coated graphite tubes with a preinstalled pyrolytic graphite L'vov platform were used. Argon (300 mL/min) was used as a carrier gas during all stages except for the atomization step (gas stop).

A sample volume of 20 μL was injected into a pyrolytical coated graphite furnace, immediately followed by the injection of 10 μL of 1000 $\mu\text{g mL}^{-1}$ Pd modifier solution. Then, the temperature program was run and integrated atomic absorbance was measured under the conditions shown in Table 5.2. The temperature programs used are listed in Table 5.3. Background-corrected integrated absorbance was used as the analytical signal.

Table 5.2: Operational conditions employed in the determination of As

Parameter	Set value
Wavelength (nm)	193.7
Source Lamp (mA)	20
Slit Width (nm)	0.7
Background Correction	Deuterium
Purge gas	Argon
Calibration Algorithm	Linear thru Zero
Integration Time	5.0
Sample Volume	20
Matrix Modifier Volume	5
Graphite furnace	Pyrolytical coated tube-type

Table 5.3: Electrothermal program

Step	Temperature ($^{\circ}\text{C}$)	Ramp Time (sec)	Hold Time (sec)	Gas flow (mL/min)
Injection	20	–	–	–
Drying	75	15	10	300
	110	15	10	300
	250	20	10	300
Pyrolysis	1300	15	15	300
	1300 ^a	0	1	0.0
Atomization	2500	0	2	0.0
Cleaning	2500	0.5	1	300
Cooling	40	25	5	300

^aWhen cool-down step to 100 $^{\circ}\text{C}$ was applied, a 6 sec. ramp and 0 sec. hold times were added before the atomization step.

5.4.5 Arsenic Speciation by Disposable Cartridges

Arsenic speciation was performed in cases where groundwater samples analyzed showed detectable levels of arsenic. In all, groundwater samples were sampled from 26 community wells which showed detectable levels of As within the study area and were analyzed in-situ for arsenic speciation (As-III and As-V).

With this aim, samples were filtered using 0.45 μm filter capsule (Gelman) and filtered samples were passed through disposable cartridges packed with 2.5 g of selective aluminosilicate adsorbent. A highly selective aluminosilicate adsorbent was packed in a 4×0.3 in. polypropylene column previously conditioned with 5 mL of deionized water for the separation of As-III and As-V.

Each disposable cartridge contained 3.0 g of adsorbent and attached to a 5-mL syringe (with luer slip tip) filled with the groundwater samples. Then, 5 mL of sample was passed and 15 mL of deionized water was used to elute As-III selectively from the cartridge at a flow rate of 60±20 mL per min or less than 1 min filtration time per sample. As-V was retained in the cartridge. The eluted solution was then acidified with suprapure HNO₃ (1:100 v/v) and stored at 4 °C until analysis (as described in section 5.4.4). The method was tested extensively prior to this analysis and was found to be reliable.

5.4.6 Groundwater Sample Analysis of Trace Metals (Fe, Cu, Mn, Zn)

For determining the amounts of Fe, Cu, Mn, and Zn in the rest of the samples, an atomic absorption flame emission spectrophotometer was used. The analysis was carried out using respective hollow cathode lamps under standard instrumental conditions (Table: 5.4).

Table 5.4: Operating parameters of AAS used in the analysis of trace metals

Condition	Fe	Cu	Mn	Zn
Wavelength (nm)	248.3	324.8	279.5	213.9
Slit (nm)	0.5	0.5	0.2	1.0
Lamp Current (mA)	4	4	5	5
Air flow (L/m)	13.5	13.5	13.5	13.5
Acetylene flow (L/m)	2	2	2	2

All the spectroscopic measurements of the standard metal solutions as well as the sample solutions were done at their respective wavelength of maximum absorptions λ_{max} (Assignment Point, 2013). The accuracy of the instrumental methods and analytical procedures were checked by duplications of the samples, as well as by using the independent reference standard solutions (Table 5.5).

Table 5.5: Accuracy of the analytical data with reference to the NIST standard

Name of the metal	Fe	Cu	Mn	Zn
Certified Value (ppm)	1	0.2	0.1	0.2
Measured Value (ppm) \pm SD	0.982 \pm 0.007	0.197 \pm 0.003	0.101 \pm 0.003	0.195 \pm 0.002

SD – Standard deviation

Moreover, the known concentration of an independent respective metal solution is measured periodically with the measurement of sample solution. Recalibration was done for the various respective metals when the measured value of the standard metal solution shown deviation more than ten percent (10 %) from its known concentration per standard procedures prescribed by Assignment Point (2013). Hence, the accuracy and precision of the analytical data were strictly followed throughout the present study.

The detection limit of the element for the instrument and the spike recovery rates of the elements analyzed under the experimental conditions were determined (Table 5.6).

Table 5.6: Detection limit (DL) and Spikes recovery of the metals

Metals	Fe	Cu	Mn	Zn
DL (ppm)	0.01	0.01	0.01	0.01
Recovery (%)	90-99	92-98	93-106	95-98

5.4.7 Mine Tailings Sample Digestion and Analysis

In order to determine the total concentrations of arsenic and other trace metals (Fe, Cu, Mn and Zn) in the mine tailings, the samples were dried using a freeze-drier for 3–4 days and homogenized by thorough mixing. The homogenized dried samples were sieved through a 0.2 mm sieve and were digested using EPA method 6010 (Roy-Keith, 1998). A total of 18 samples were digested separately in order to degrade the bonds within the sample matrix.

Replicated results for each sample were obtained by repeating the same process on two different days.

Chemical sequential extraction was carried out to extract arsenic bound to the solid-phase of the homogenized tailing samples. Two grams of the sample were accurately weighed into a 10 mL polypropylene centrifuge tubes in triplicate. 5 mL of de-ionized water and separate aliquots of increasing concentrations of HNO₃ (0.1, 0.5, 1 and 5 M) and 30 % H₂O₂ (0.25, 0.50, 0.75 and 1 mL) were added. The tubes were placed on a shaking apparatus and rotated overnight. After 24 hours, de-ionized water was added to the tubes to make a volume of approximately 10 mL and the supernatant separated via centrifugation at 3000 rotations per minute (RPM) for three and half hours. The supernatant was filtered through 0.45µm micropore membrane, acidified to pH of 2 and stored at 4 °C until analysis. The solutions obtained were analyzed for As and trace metals using AAS.

Lastly, leaching concentrations of arsenic from the mine tailings were evaluated. Leaching tests of the active (Sanso) and abandoned (Pompora and Dokyiwa) mine tailing samples were performed by the use of normal rain (approximately pH 5.8) to indirectly evaluate release and mobility of As to the surrounding environmental media. Rain water was used for the leaching test in order to preserve arsenic species without change of their oxidation states and to prevent added chemicals from affecting As dissolution process.

The homogenized tailing samples were packed in 200 mm diameter cylindrical cells having an open cell top and a drain fitting in the bottom of the cell. The samples were leached once a week with 1.0 L of rainwater for a period of 16 weeks (4 months). The apparatus was conducted in open laboratory for exposure to humidity conditions. The leachate was collected in a glass beaker, measured and leaching rate per every sample was recorded as well. The entire leaching experiments were carried out in triplicate for all samples from both the active and abandoned tailing dams.

5.5 Evaluation of Arsenic Removal Technology

Two point-of-use arsenic removal technologies were evaluated for their effectiveness and appropriateness under field conditions in south-western part of Ashanti Region of Ghana.

5.5.1 The Three-Earthen Pot Set-Up

The Three-Earthen Pot System was assembled at the Sabe community. This system consists of three earthen pots stacked on top of each other (Figure 5.1). For the purposes of this research, the size of the earthen pots used typically hold 18-20 liters of water and are made of ceramic material (clay). We feel 18-20 liter is sufficient for drinking and cooking for a family of four. The three-earthen pots were obtained locally from a potter at Obuasi town. It was thoroughly washed with soap and rinsed with boiled water followed by distilled water before use.

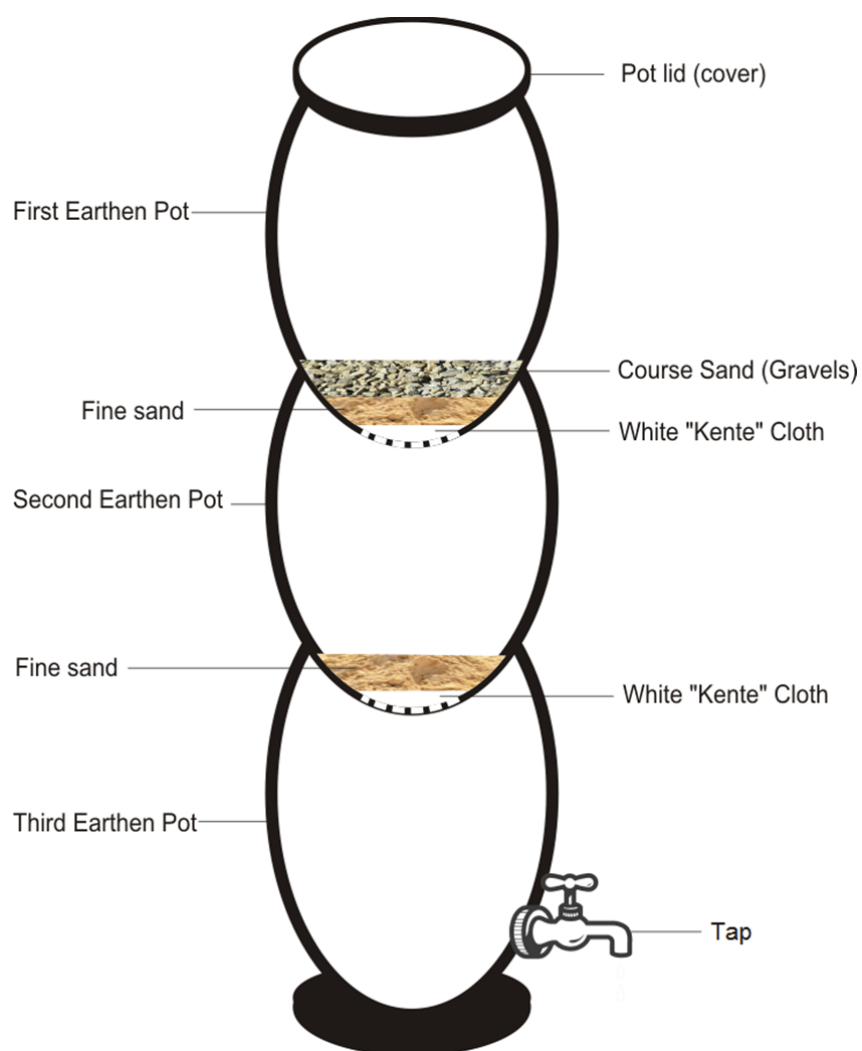


Figure 5.1 Schematic diagram of the Three Earthen Pot System

The top and the middle pots were having six 0.2 cm holes drilled apart in the bottom and was covered by a thoroughly cleaned coarsely weaved white “Kente” cloth so that water poured into the top pot will percolate and be filtered down to the bottom receiving pot. We made many experiments (twelve weeks period and five times daily) before using “Kente” cloth to know whether it is safe to use from toxicity point of view. The cloth was covered with 2 kg course sand in the top pot followed by another 2 kg of fine sand in the middle pot acting as a filtration system.



Figure 5.2: The actual three-earthen pot arsenic removal system used in this study.

Once assembled (Figure 5.2), arsenic-contaminated groundwater from Sabe community well which has already been analyzed for arsenic and heavy metals (see section 5.4) was first collected into a 20 L plastic bucket. 1:1 ratio by weight, of ferric chloride (coagulant/co-precipitant) and charcoal powder (adsorbent) and 8 % sodium hypochlorite solution (oxidant) was added to the 20 L well water and stirred several times intermittently (approximately every thirty minutes) for 2-hour duration. Sodium hypochlorite (NaOCl) was used as an oxidant to facilitate the oxidation of arsenite to arsenate as arsenate is more effectively removed than arsenite. In addition, hypochlorite significantly reduces the microbial contamination of treated water. The charcoal powder was used as an adsorbent to remove the residual chlorine resulting from the use of hypochlorite and helps reduce other contaminants in the water.

After allowing the solids to settle, the supernatant water was slowly poured into the top pot carefully not to disturb the media and the sludge was disposed into a manure pit (cow dung) or latrine to methylate the As and transform it into a volatile compound that is lost to the air. The treated water then trickles down through the first pot into the middle pot then to the bottom collection pot. The coarse sand, and later the fine sand, acted as a filter to prevent the precipitate from flowing through the middle pot, which allowed clean water to flow into the bottom pot. 1 L each of the clean water was collected via a plastic pipe located in the lower end of the pot into two of 1 L polyethylene bottles and was refrigerated at 4 °C prior to arsenic and iron analysis using AAS to check for the efficiency of the system.

5.5.2 Household Coagulation and Filtration System/ Jerry Can System Set-Up

The system uses a 20 L Jerry can or what is commonly known as “Kufuor” gallon and it comes in a variety of sizes, but for the purposes of this study, two 20 L plastic jerry cans were purchased from Obuasi market and were used for this analysis. It is one of the commonest jugs that are used for the collection and storage of water in Ghana.

In order to use the system, the 20 L arsenic-contaminated water from Sabe community well was collected first into 20-liter jerry can. About 4 mg of potassium permanganate acting as an oxidant was added to pre-oxidize arsenite (As-III) to arsenate (A-V), followed by coagulation and co-precipitation using the 40 mg coagulant, alum [$KAl(SO_4)_2 \cdot 12H_2O$]. The jug was

shaken for 15 minutes. For better mixing a wooden or plastic handle was used. It was left undisturbed for it to settle for 1 hour.

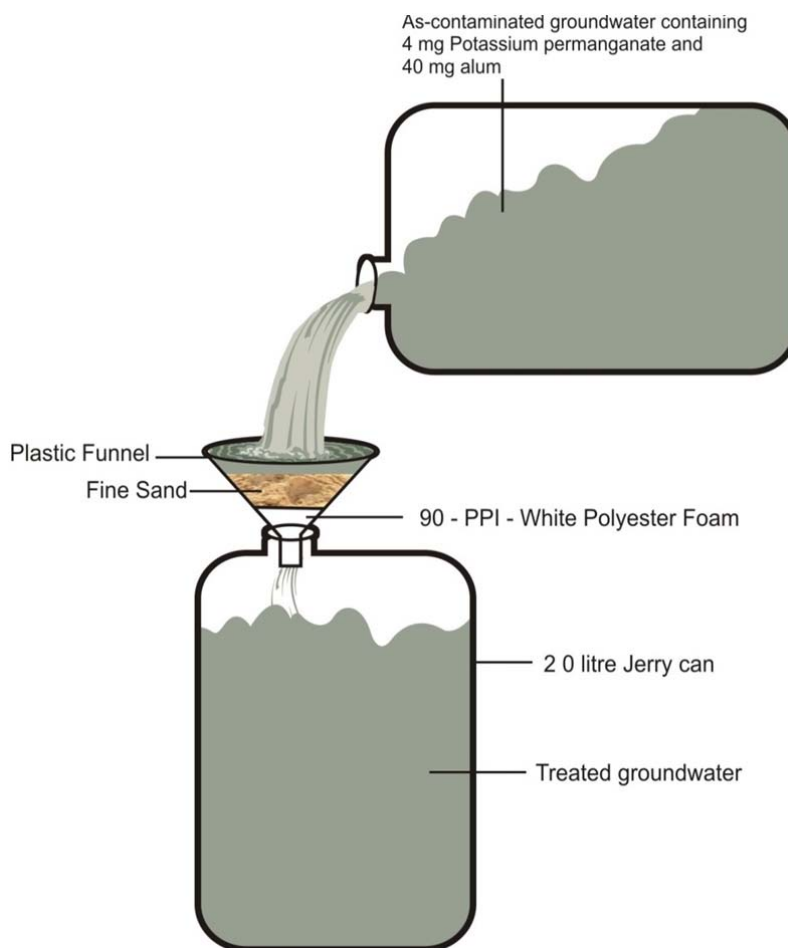


Figure 5.3: Schematic diagram of the household coagulation and filtration system/ Jerry can system.

The jug was then covered with a lid and precipitates were allowed to settle for 1 hour. Then, the water was poured into another 20-liter jug, by passing through a funnel overlaid with 90-PPI-White-Polyester foam covered with sand media serving as a filter (Figure 5.3). The treated water was then poured into 1 L of two polyethylene bottles and refrigerated at 4 °C prior to arsenic and iron analysis using AAS to check for the effectiveness of the system. The entire exercise was carried out for twelve weeks period and five times daily.

5.6 Quality Control Parameter for Groundwater Arsenic Determination

Quality control measures were incorporated into the analytical scheme. Instrumental calibration, replicates and field blanks were prepared according to Knödel *et al.*, (2007). A quality control (QC) standard was run routinely during the sample analysis to monitor instrument drift and overall quality of the analysis (Bempah *et al.*, 2013).

For instrument calibration, a 100 µg/L As standard was prepared from serial dilutions of a 1000 µg/L stock standard. A calibration curve of 0.1, 0.5, 1.0, 1.5 and 2.0 µg/L was prepared from that 100 µg/L arsenic standard. To detect possible interferences and matrix effects, which are considered important for arsenic determinations, the standard addition method was used with five arbitrarily chosen samples (Table 5.7).

The analytical characteristics for arsenic determination in both groundwater and mine tailings leachate samples were done by spiking five groundwater and three leachate samples from their respective tailings dam with 0.1, 0.5, 1.0 and 1.5 µg arsenic to five equal fractions of the groundwater samples, and 10 µg arsenic to three equal fractions of leachate samples, respectively. A matrix modifier of 5 µg of Pd and 3 µg of Mg(NO₃)₂, was used for each 20 mL of sample and was added into the blank, standard and samples. All samples and blanks (n=10) were digested and diluted using the same procedure (section 5.4.7). Reagent blank determinations were used to correct the instrument readings which were usually very low for this method (Bempah *et al.*, 2013).

Table 5.7: Calibration plots corresponding to the standard of arsenic and the standard addition method of different samples

Standard of As	<i>r</i> (correlation coefficient)	a (intercept)	b (slope)	Slope ratios of As standard/sample
Standard of As	0.9998	0.0001	0.049	1.000
BK1	0.9979	0.0390	0.045	1.365
OB2	0.9999	0.0026	0.040	1.333
AW3	0.9995	0.0135	0.041	1.304
AC4	0.9993	0.0860	0.014	4.305
AN5	0.9989	0.0018	0.026	2.000

Absorbance = a+b (As, ppb).

Table 5.8 shows the analytical characteristics for arsenic determination in groundwater samples by AAS. The percentage recovery and repeatability tests were performed following procedures already described in section 5.4.3.

Table 5.8: Analytical recoveries (%) ± standard deviation (SD) of As metal in water samples at 0.5, 1.0, 2.0 and 3.0 µg/L fortification levels (n=3)

Groundwater samples	Analytical recoveries (%) ± SD at different fortification levels (µg/L)			
	0.5	1.0	2.0	3.0
BK1	92.1±8.7	96.4±5.52	97.5±4.73	98.2±6.29
OB2	97.4±5.4	98.1±7.01	87.0±8.54	87.3±8.42
AW3	101.3±8.7	103.8±3.8	96.4±5.09	97.8±5.18
AC4	98.7±6.4	97.2±4.3	96.4±5.17	97.0±5.63
AN5	96.4±5.57	92.8±6.6	98.1±7.21	92.3±9.41
OB6	98.1±7.21	94.1±3.9	103.8±3.7	95.1±7.14

Table 5.9 shows the analytical characteristics for arsenic determination in mine tailings leachate samples by AAS.

Table 5.9: Analytical recoveries (%) ± SD of As metal in mine tailings leachate samples at 10.0 µg/L fortification levels (n=3)

Leachate samples	SpikedAs (mgL ⁻¹)	Recovered As (%)
Dokyiwa	10	98.4± 0.3 ^a
Pompora	10	94.9± 1.7
Sanso	10	88.3 ± 1.2

^a Average ± standard deviation.

Mean recovery for the several added samples considered was 97.21±2.83 % (n=6). Mean relative standard deviations were lower than 7.00 %.

Table 5.10: Analytical characteristics for arsenic determination in groundwater samples by ETAAS

Detection limit ^a (µg/L)	Characteristic mass ^b (µg)	Recovery ^c (%)		Precision, RSD (%)
		Mean	SD	
0.1	0.782	97.21	2.83	6.43 ^d 8.34 ^e

^aDetection limit is the analyte concentration corresponding to three times the standard deviation (SD) of the blank for a measured volume of 10 mL. The corresponding limit of quantification is 0.14 µg/L.

^bCharacteristic mass is µg corresponding to 0.0044 milliAbsorbance Units.

^cResults obtained from recovery assays of six samples.

^dRelative standard deviation (RSD) for three replicate determinations in each of six samples.

^eRelative standard deviation for three replicate determinations (interday) in each of six samples.

The arsenic concentrations determined in the certified reference material NIST CRM 1643d (National Institute of Standard and Technology) containing trace elements in water and total arsenic at a certified concentration of $56.02 \pm 0.73 \mu\text{g/L}$, was also analyzed ($n=10$) and was not significantly different from certified levels ($p > 0.05$) (table 5.11).

Table 5.11: Accuracy and precision of the proposed method for arsenic determination against standard reference materials.

Reference material	Mean total As \pm SD ($\mu\text{g/L}$)		Accuracy (%)	Precision RSD (%)
	Certified value ^a	Measured value ^a		
NIST CRM 1643d	56.02 ± 0.73	54.67 ± 0.89	96.41	5.33

5.7 Data Analysis

The analytical data obtained from the analysis of groundwater samples were processed for detailed geochemical and statistical analysis. AquaChem (Aqueous geochemical analysis) software package which features a fully customizable database of physical and chemical parameters and its comprehensive selection of analysis tools, calculations and graphs for interpreting groundwater quality data (Tabue *et al.*, 2012) was used to classify major ions and summarized major contrast in hydrogeochemical composition of the groundwater sources. When analyzing in AquaChem, half of the detection limit was used for values below the detection limit. This was made in order not to exclude important minerals when modeling.

Electro-neutrality of anions and cations were calculated to determine the accuracy of chemical analysis. If samples depart more than 5 % from electro-neutrality a comparison of sums of anions, cations and conductivity were also made to determine where the error is likely to be situated (Appello and Postma 1999). Basic parametric statistical parameters such as minimum, maximum, mean, median and standard deviation were computed using IBM SPSS statistics 19.

Spearman non-parametric correlation coefficient (Spearman R) was used to evaluate the seasonal variation of the groundwater quality parameters. To do this, a specific integer number was assigned to each season (dry = 1 and wet = 2). Then Spearman correlation was established between all of the water quality parameters and the ordinal variables (Garizi *et al.*, 2011). Spearman correlation was again used to evaluate the relationship between As and

well depth in order to assess the source of As release into the groundwater samples from the study area.

Again, multivariate statistical techniques such as factor and cluster analysis were then applied for the explanation and interpretation of the seasonal changes of groundwater quality data set. It was further used to identify the similarity and dissimilarity of the physicochemical variables and classifying the pollution sources.

In addition, student's *t*-test was used to evaluate seasonal variations of the water quality parameters. It was used for the interpretation of groundwater quality data set. A student's (*t*) test was carried out for testing significant difference between means of factors for dry and wet season periods against left sided alternative hypothesis, i.e., the mean of dry season is less than that of the other. The test statistic, which follows *t*-distribution with (n_1+n_1-2) degrees of freedom, is given by:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{S^2 (1/n_1 + 1/n_2)}}$$

where \bar{x}_1 is the mean of variable of dry season

\bar{x}_2 is the mean of variable of wet season

S^2 is the variance of combined sample,

n_1 is the number of observations on variable of dry season and

n_2 is the number of observations on variable of wet season.

If computed value is greater than critical value (left sided alternative), there is no difference between means. Otherwise, the difference is significant.

CHAPTER SIX

6.0 TOTAL ARSENIC MEASUREMENTS – RESULTS AND DISCUSSION

6.1 Introduction

The results of the total arsenic (As), arsenic species (As-III, As-V) and the main physico-chemical parameters including major cations and anions, trace metals concentrations, pH and the well depth of the groundwater samples collected at the south-western part of Ashanti Region of Ghana are presented in this chapter. Although the focus of this research is on As contamination, other water quality parameters such as physicochemical properties and heavy metals concentrations of the groundwater samples were also analyzed to assess their influence on the elevated As levels of the groundwater. The results are also compared with the World Health Organization (WHO) permissible levels in drinking water (WHO, 1996a, b, 2004) and concentrations falling above the guideline values were identified and discussed.

6.2 Hydrochemical Characteristics of Groundwaters

Results of the physico-chemical analysis of the water samples collected from the 63 community wells and boreholes during the dry and wet (rainy) seasons in the study area (south-western part of Ashanti Region of Ghana) and their statistical data are summarized in Table 6.1 and 6.2, respectively. Groundwater in south-western part of Ashanti Region was predominantly slightly acidic to alkaline (pH value 6.02–8.47) and more acidic to slightly alkaline (pH value 3.13–7.55) during the dry and wet seasons, respectively, as a result of the presence of fine aquifer sediments mixed with clay and mud, which are unable to flush off the salts during the rainy season and hence retained longer on other seasons (Laluraj *et al.*, 2005).

Arsenic Contamination in Groundwater

Table 6.1: Summary of the main physico-chemical parameters, major cations and anions concentrations of the surveyed groundwater samples during the dry season in the south-western part of Ashanti Region of Ghana. Concentrations in mg/L except as noted.

Study area	Location	Depth (m)	T (°C)	pH	EC (µS/cm)	Eh (mV)	DO	HCO ₃	F	CL	SO ₄	PO ₄	Na	K	Mg	Ca	NO ₃	DOC	TDS
Detection Limit							0.1	5	0.01	0.15	0.1	0.1				0.1	0.1	5	
Adansi North District	Meduma	53	27.2	7.78	109	422	0.9	58.71	0.01	2.09	1.36	0.16	19.04	3.86	4.26	6.12	0.8	1.81	73.9
	Abedwum	6	31.4	6.56	62	412	1.6	113.96	0.03	4.43	3.23	0.28	6.04	0.15	0.71	7.03	1.03	4.05	42.1
	Wioso	18	29.8	7.47	97	467	2.0	83.42	0.13	4.96	1.72	0.36	11.18	2.73	1.65	3.62	<0.1	2.07	65.8
	Patakro	36	28.3	7.21	303	252	1.6	212.10	0.41	7.34	1.92	0.19	21.12	4.02	8.63	42.07	<0.1	0.93	205.6
	Dunkwa Nkwanta	25.5	29.2	6.58	43	463	2.6	78.03	0.03	3.20	1.21	0.13	19.87	0.87	2.88	1.16	1.05	0.34	29.2
	Kokotease	35	27.4	7.78	71	402	3.8	82.34	0.03	4.32	1.34	0.18	17.12	0.32	3.02	3.35	1.7	1.86	48.2
	Kofikurom	38	26.2	6.55	109	414	1.9	36.63	0.04	3.45	0.23	0.24	11.14	0.24	12.34	6.57	1.25	3.56	73.9
Amansie West District	Odahu	60	25.9	8.14	159	257	0.5	93.67	0.17	6.3	1.82	0.10	18.97	0.04	8.25	5.21	0.42	0.77	107.9
	Agroyesum Hsp	52	27.7	6.12	391	242	<0.1	269.42	0.20	3.20	1.33	0.20	30.35	0.24	11.13	58.9	<0.1	0.36	265.3
	Apanapron	80	25.3	7.39	282	274	<0.1	163.40	0.18	7.40	1.07	0.31	13.9	0.32	4.01	38.99	1.03	3.70	191.4
	Ankam	38	31.5	6.54	157	241	1.2	98.83	0.31	6.12	5.09	0.17	14.3	0.05	5.02	16.33	1.33	1.02	106.5
	Mim 1	57	27.3	6.85	226	317	1.1	91.48	0.21	2.45	0.12	0.21	14.38	0.46	6.17	23.34	0.33	0.85	153.4
	Abodom	46	26.2	8.05	128	412	1.4	70.20	0.08	6.45	1.63	0.11	10.43	0.34	1.09	4.46	1.04	1.01	86.9
	Mim 2	49	27.6	6.94	201	402	1.0	68.32	0.19	7.87	0.16	0.13	17.45	0.37	6.33	11.17	1.47	3.95	136.4
	Antoakuum 1	70	25.7	8.42	293	233	0.5	182.42	0.09	17.07	1.30	0.19	14.47	0.91	5.15	38.09	0.42	0.30	198.8
	Manso Akropon	43	29.2	6.57	189	405	<0.1	52.0	0.17	7.45	0.87	0.14	17.23	0.01	3.19	7.49	1.08	1.45	128.3
	Antoakuum 2	32	25.3	7.34	132	252	1.9	79.43	0.04	12.15	1.43	0.11	19.42	0.36	4.17	4.02	1.86	1.37	89.6
	Nsiana	49	29.8	6.58	148	433	0.8	40.65	0.07	9.03	0.21	0.13	14.2	1.45	3.89	7.09	1.7	1.27	100.4
	Yawkurom	49	27.2	8.44	202	237	<0.1	132.91	0.19	7.89	0.27	0.27	10.45	0.43	7.18	21.85	0.26	1.36	137.1
	Manso Atwere	19	28.4	6.53	112	392	0.5	97.30	0.07	4.00	3.04	0.19	14.2	0.63	5.30	7.20	<0.1	2.73	76.0
	Odumase	43	29.2	6.18	402	282	1.3	48.0	0.09	5.30	0.72	0.11	15.4	0.67	13.04	41.3	<0.1	3.02	272.8
Amansie Central District	Mile 9	46	28.4	7.61	168	352	1.2	92.37	0.18	7.43	1.16	0.30	22.33	0.54	1.91	16.03	0.36	2.06	114.0
	Mile 14	64.5	26.9	8.47	221	239	0.4	221.33	0.04	8.98	0.23	0.37	14.26	0.32	24.9	24.12	0.23	1.32	149.9
	Boni	66	28.3	6.58	326	436	0.7	38.04	0.07	6.32	1.04	0.12	23.26	1.75	22.09	26.89	1.03	1.3	221.2
	Hunatado	54	26.9	7.86	122	459	2.3	21.13	0.05	3.90	0.23	0.15	19.17	1.36	3.43	4.98	1.32	1.05	82.8
	Poano	61	29.5	8.23	207	263	<0.1	126.18	0.09	3.56	1.43	0.21	9.18	0.43	14.32	15.9	0.62	0.82	140.5
	Ntinako	52	26.9	7.71	197	326	1.3	68.16	0.09	21.53	1.65	0.21	21.43	0.28	3.55	8.24	<0.1	0.33	133.7
	Kofitanokrom	8	31.2	6.64	143	412	1.7	109.18	0.05	5.46	1.23	0.11	24.29	1.48	0.93	6.73	0.77	1.95	97.0
	Patase	34	28.8	8.46	142	348	2.8	26.18	0.13	11.34	0.82	0.10	25.4	3.23	2.34	14.43	1.24	1.02	96.4
	Apitiso	43.5	25.7	8.36	304	397	1.1	103.42	0.07	23.25	1.03	0.21	23.54	0.32	16.34	26.21	<0.1	3.67	206.3
	Fiankoma	65	29.4	6.85	113	292	<0.1	42.43	0.08	4.43	0.53	0.14	22.70	0.24	9.39	6.34	<0.1	1.07	76.7
	Dangase	4	31.6	6.59	42	313	1.1	111.13	0.02	3.06	2.02	0.32	11.09	0.34	0.38	0.33	1.38	2.45	28.5
	Odumto	15	29.9	8.14	70	411	1.5	92.30	0.05	7.00	1.13	0.30	7.20	0.52	0.93	0.33	1.43	1.06	47.7
	Sabe	22	29.0	8.33	295	219	<0.1	183.65	0.39	9.35	0.11	0.31	16.47	1.25	20.98	21.48	0.14	1.06	200.2
	Mile 18	8	30.0	6.84	142	293	1.8	127.30	0.06	5.09	2.43	0.13	13.4	0.41	4.03	4.73	1.08	2.39	96.4
	Mamfo	28	28.5	8.18	302	341	<0.1	192.65	0.23	4.84	1.52	0.14	14.7	0.32	2.23	3.98	0.64	0.23	204.9
Dekyewa	24	29.4	6.62	134	267	0.5	91.43	0.05	7.28	2.52	0.21	13.8	0.68	3.13	1.75	1.90	1.95	90.9	

Arsenic Contamination in Groundwater

Table 6.1 (Cont'd)

Study area	Location	Depth (m)	T (°C)	pH	EC (µS/cm)	Eh (mV)	DO	HCO ₃	F	CL	SO ₄	PO ₄	Na	K	Mg	Ca	NO ₃	DOC	TDS
Detection Limit							0.1	5	0.01	0.15	0.1	0.1				0.1	0.1	5	
Amansie Central District	Afoako	42	27.3	7.45	56	458	3.7	26.13	0.07	3.21	1.73	0.15	8.17	4.38	0.92	3.34	<0.1	0.23	38.0
	Aketekyiso	3	29.7	7.27	59	319	1.1	108.14	0.05	7.09	3.38	0.15	9.04	0.49	0.33	0.38	1.20	3.27	40.0
	Tweapease	43	25.3	8.42	163	313	0.8	93.43	0.21	5.90	0.75	0.11	17.4	0.26	4.12	10.35	0.16	0.27	110.6
	Abuakwa	48	25.9	6.02	202	273	0.3	123.42	0.04	7.43	1.29	0.31	13.54	0.34	3.09	26.32	0.78	1.08	137.1
Obuasi Municipal Assembly	Nhyiaso	18	28.9	6.52	98	401	1.6	109.12	0.07	8.42	2.19	0.13	13.40	0.32	2.71	3.04	<0.1	2.09	66.5
	Akrofuom	32	31.3	7.73	638	233	1.1	63.16	0.15	41.09	2.03	0.28	24.17	1.18	4.04	8.23	1.47	2.04	432.9
	Sanso	42	29.8	6.52	167	452	3.1	116.13	0.06	5.48	5.61	0.14	27.74	0.49	7.13	10.34	0.93	1.07	113.3
	Brahabehome	19	31.6	7.32	98	474	1.3	52.18	0.03	1.97	3.85	0.27	9.07	1.23	0.66	14.39	0.11	1.71	66.5
	Diewieso	25	29.8	6.53	321	527	2.1	98.12	0.13	28.94	2.38	0.28	27.19	3.18	4.62	3.91	<0.1	2.89	217.8
	Nyamso North	48	27.4	7.54	112	384	0.6	54.36	0.28	4.92	1.04	0.13	11.14	0.15	4.82	3.73	0.67	1.05	76.0
	Nyamso South	32	25.8	7.05	67	352	<0.1	85.32	0.03	3.86	1.38	0.30	9.23	0.24	3.46	2.01	1.47	1.38	45.5
	Konka New Town	30	28.9	6.52	102	212	1.1	72.43	0.05	8.36	1.17	0.17	16.30	0.18	1.93	0.43	1.62	2.45	691.2
	Apitikokoo	40	31.4	6.63	111	254	1.3	17.11	0.03	6.93	0.13	0.13	11.12	2.91	4.12	1.83	0.80	1.92	75.3
	Kokotenten	34	30.5	8.46	274	494	3.6	162.42	0.19	2.18	4.12	0.12	19.30	2.31	5.14	27.09	1.08	0.33	185.9
	Nyamekyere	43	27.0	6.52	67	283	1.2	31.30	0.05	7.04	0.52	0.20	7.60	0.13	1.02	2.01	1.30	2.48	45.5
	Obuasi BH 3	100	25.2	8.31	984	651	0.5	217.42	0.13	16.89	9.55	0.11	31.50	2.43	41.06	82.56	1.71	2.39	442.4
	Mensakurom	9	26.2	6.92	98	413	1.5	13.0	0.05	4.60	5.86	0.10	7.30	0.83	0.69	0.93	0.32	0.73	66.5
	Obuasi BH 2	70	25.9	6.15	654	662	2.6	143.64	0.13	11.14	8.14	0.13	33.15	1.01	45.21	61.46	1.03	2.02	443.8
	Obuasi BH 1	70	26.0	8.19	652	586	2.1	122.43	0.39	10.53	8.97	0.12	28.67	0.98	85.12	82.32	0.80	2.55	667.7
Wamase	4	33.3	8.12	96	371	1.7	132.71	0.07	4.70	6.82	0.23	23.25	0.24	0.09	7.25	<0.1	1.82	65.1	
Bekwai Municipal Assembly	Old Edubiase	43	29.7	7.01	132	419	2.1	72.13	0.14	3.13	1.14	0.11	22.31	1.07	3.01	7.98	0.33	2.05	89.6
	Dwondoso	5.5	32.6	6.73	42	243	1.6	83.15	0.04	3.20	6.17	0.23	18.39	0.76	0.14	7.23	<0.1	1.74	28.5
	Aminase	4	33.9	6.65	88	299	3.0	125.19	0.09	5.87	7.01	0.31	26.44	0.86	0.32	4.45	0.62	0.41	59.71
	Amoamo	1.5	34.6	8.19	278	341	<0.1	31.40	0.19	29.42	1.82	0.28	13.19	0.19	2.45	19.02	0.31	0.82	188.6
	Ankase	48	27.2	6.84	152	413	0.9	14.14	0.12	4.28	0.13	0.30	12.13	2.71	11.09	8.79	0.43	1.97	103.1
	Bogyawe	58	26.8	6.14	164	215	1.2	113.18	0.31	2.54	1.32	0.23	21.43	3.43	9.34	10.16	0.93	0.86	111.2
Statistical Data	Minimum		25.2	6.02	42.0	212.0	<0.1	13.0	0.01	1.97	0.11	0.10	6.04	0.01	0.09	0.33	<0.1	0.23	28.5
	Maximum		34.6	8.47	984.0	662.0	3.8	269.42	0.41	41.09	9.55	0.37	33.15	4.38	85.12	82.56	1.9	4.05	691.2
	Mean		28.54	7.22	200.3	359.06	1.53	96.53	0.13	8.01	2.18	0.20	17.06	1.02	7.86	15.04	0.74	1.64	145.9
	Median		28.40	7.21	148.0	352.0	1.20	92.3	0.08	6.12	1.32	0.19	16.30	0.49	4.03	7.25	0.78	1.38	103.1
	Standard deviation		2.27	0.75	168.84	103.72	0.86	55.32	0.09	7.15	1.36	0.08	6.59	0.09	5.06	12.03	0.59	0.98	133.9

Arsenic Contamination in Groundwater

Table 6.2: Summary of the main physico-chemical parameters, major cations and anions concentrations of the surveyed groundwater samples during the wet (rainy) season in the south-western part of Ashanti Region of Ghana. Concentrations in mg/L except as noted.

Study area	Location	Depth (m)	T (°C)	pH	EC (µS/cm)	Eh (mV)	DO	HCO ₃	F	CL	SO ₄	PO ₄	Na	K	Mg	Ca	NO ₃	DOC	TDS
Detection Limit							0.1	5	0.01	0.15	0.1	0.1				0.1	0.1	5	
Adansi North District	Meduma	53	26.0	5.43	132	473	1.2	61.22	<0.01	3.43	1.48	0.19	22.45	4.32	5.43	9.19	0.7	2.63	88.50
	Abedwum	6	25.7	6.76	73	412	2.2	127.40	<0.01	7.18	3.56	0.34	8.22	2.33	2.33	11.23	1.42	3.23	43.66
	Wioso	18	23.4	5.53	105	472	2.4	100.75	0.10	6.12	1.88	0.27	13.25	3.54	4.36	5.32	0.82	2.36	78.45
	Patakro	36	26.0	7.55	338	268	1.9	235.58	0.34	7.56	2.20	0.17	19.32	6.12	11.34	44.25	0.55	1.08	215.73
	Dunkwa Nkwanta	25.5	25.5	4.23	73	472	3.2	98.37	0.42	8.33	1.34	0.19	22.31	1.54	4.35	5.32	1.15	0.78	46.70
	Kokotease	35	25.7	5.90	56	398	3.5	113.32	<0.01	41.17	1.46	0.23	19.43	2.43	5.38	7.33	1.62	2.53	53.85
	Kofikurom	38	24.3	5.05	112	423	2.7	77.32	0.02	5.17	0.98	0.16	15.32	1.32	14.87	6.32	1.05	4.73	98.35
Amansie West District	Odahu	60	26.8	5.33	185	267	0.8	125.50	0.13	2.05	2.05	0.15	21.22	3.45	11.87	9.34	0.43	1.43	135.40
	Agroyesum Hsp	52	25.7	6.25	432	258	0.6	320.45	0.17	30.62	1.45	0.28	38.56	2.35	15.33	65.11	0.86	0.78	288.56
	Apanapron	80	25.0	6.56	305	285	0.4	187.40	0.15	5.15	1.13	0.43	19.35	3.42	6.37	44.23	0.65	4.26	223.40
	Ankam	38	26.3	5.67	138	273	1.5	110.23	0.26	4.32	5.22	0.15	11.46	3.22	7.55	21.23	1.42	1.84	125.67
	Mim 1	57	25.2	6.04	233	298	1.7	100.25	0.27	8.86	1.33	0.12	17.36	3.45	9.63	28.43	0.55	1.64	183.80
	Abodom	46	26.7	6.17	153	422	1.9	110.36	0.06	7.21	1.83	0.18	21.26	1.22	3.22	8.33	1.04	1.78	123.20
	Mim 2	49	23.7	6.15	241	382	1.3	75.48	0.10	2.57	0.46	0.19	19.46	2.33	9.67	15.23	1.47	4.38	158.20
	Antoakurom 1	70	26.1	6.55	345	248	0.5	220.34	0.03	7.83	1.42	0.21	25.33	3.13	7.22	44.22	0.42	0.87	235.37
	Manso Akropon	43	26.7	5.23	222	442	0.7	77.84	0.15	19.15	1.22	0.13	21.34	3.22	5.87	8.30	1.23	1.95	156.89
	Antoakurom 2	32	24.2	5.88	337	268	2.2	98.46	<0.01	4.92	1.56	0.16	22.43	0.22	9.66	7.13	1.96	1.67	112.40
	Nsiana	49	23.6	5.84	128	452	1.3	67.54	0.03	13.20	0.25	0.19	17.54	2.33	5.87	9.32	1.22	1.85	152.95
	Yawkurom	49	24.9	6.58	278	252	0.2	784.56	0.12	11.24	0.33	0.23	22.34	0.56	9.15	25.63	0.58	1.74	154.38
	Manso Atwere	19	25.9	6.75	98	412	0.6	134.57	0.03	6.25	3.67	0.15	19.35	0.99	8.46	11.30	0.45	3.63	95.75
	Odumase	43	24.7	5.58	398	305	1.5	86.54	0.07	3.78	0.98	0.17	17.98	1.23	17.33	45.32	0.84	3.53	294.76
Amansie Central District	Mile 9	46	24.5	5.85	174	352	1.7	113.23	0.12	3.67	1.33	0.30	26.32	0.57	2.33	21.37	0.56	2.83	145.30
	Mile 14	64.5	24.6	6.56	288	248	0.5	265.43	<0.01	6.21	0.27	0.39	22.65	0.76	27.87	29.45	0.93	1.74	158.48
	Boni	66	23.7	5.75	353	457	1.2	76.83	0.03	32.43	1.14	0.17	27.58	0.67	28.45	31.58	1.78	1.38	222.50
	Hunatado	54	25.1	4.94	155	472	2.6	65.48	0.02	5.24	0.68	0.19	21.87	1.66	7.36	8.47	1.65	1.85	120.32
	Poano	61	24.7	5.46	225	283	0.7	158.49	0.07	3.72	1.47	0.24	12.48	0.94	16.33	19.46	0.90	1.34	145.30
	Ntinako	52	25.7	5.84	320	337	1.5	100.38	0.05	4.43	1.95	0.22	28.93	0.65	7.45	11.48	0.66	0.87	165.42
	Kofitanokrom	8	26.8	5.72	187	425	2.3	135.85	0.03	7.72	1.35	0.14	31.65	1.22	3.44	9.76	0.83	2.53	110.35
	Patase	34	25.3	5.51	164	358	3.1	87.39	0.10	6.30	1.28	0.18	33.68	3.66	5.35	17.85	1.54	1.78	113.84
	Apitiso	43.5	24.9	5.58	335	412	1.3	145.30	0.04	7.87	1.23	0.22	29.57	0.38	17.88	31.67	0.88	3.93	233.45
	Fiankoma	65	24.4	5.32	156	320	0.7	87.49	0.03	8.75	0.74	0.11	30.34	0.73	13.76	9.45	0.64	1.65	95.87
	Dangase	4	24.9	3.88	89	324	2.3	129.35	<0.01	44.64	2.43	0.37	17.48	0.66	3.26	5.37	1.67	2.96	43.56
	Odumto	15	24.4	5.40	112	438	2.6	112.65	0.03	6.05	1.05	0.34	11.36	1.23	2.55	4.16	1.62	1.58	72.12
	Sabe	22	23.6	6.55	387	229	0.8	268.50	0.24	2.87	0.15	0.39	16.94	1.76	26.46	27.45	0.55	1.26	223.74
	Mile 18	8	26.7	5.48	125	382	2.5	174.39	0.03	32.55	2.33	0.12	17.49	0.33	6.33	8.49	1.54	2.85	120.43
	Mamfo	28	25.6	6.28	333	363	1.1	220.45	0.17	5.85	1.64	0.17	65.35	0.47	5.38	5.55	0.75	0.76	258.47
Dekyewa	24	25.5	5.73	148	282	0.9	127.73	0.02	4.20	2.34	0.22	19.47	0.92	8.32	1.64	1.98	2.33	103.52	

Arsenic Contamination in Groundwater

Table 6.2 (Cont'd)

Study area	Location	Depth (m)	T (°C)	pH	EC (µS/cm)	Eh (mV)	DO	HCO ₃	F	CL	SO ₄	PO ₄	Na	K	Mg	Ca	NO ₃	DOC	TDS
Detection Limit							0.1	5	0.01	0.15	0.1	0.1							
Amansie Central District	Afoako	42	25.6	5.86	87	472	3.2	45.57	0.05	3.75	1.93	0.17	14.38	4.56	2.36	4.33	0.53	0.67	64.73
	Aketekyiso	3	26.8	5.20	95	338	1.4	118.95	0.03	7.68	3.45	0.15	17.49	0.75	3.46	3.85	1.38	3.84	88.60
	Tweapease	43	26.9	5.68	184	354	1.2	125.67	0.18	6.34	0.92	0.14	22.37	0.56	7.43	15.46	0.66	0.68	143.54
	Abuakwa	48	25.5	6.38	252	280	1.7	148.90	0.02	7.98	1.38	0.33	19.45	0.72	7.44	31.36	0.95	1.94	167.28
Obuasi Municipal Assembly	Nhyiaso	18	25.5	5.42	73	426	2.6	118.46	0.05	8.65	2.32	0.17	17.56	0.66	4.35	5.22	0.40	2.38	89.34
	Akrofuom	32	25.3	3.13	674	262	1.8	88.85	0.12	44.56	2.12	0.31	31.37	1.19	7.95	15.34	1.58	2.84	543.27
	Sanso	42	25.3	6.15	242	475	3.6	178.62	0.04	6.09	5.82	0.15	35.48	0.83	13.66	14.33	1.05	1.48	182.34
	Brahabebo	19	23.8	5.85	125	482	1.5	100.25	0.02	4.32	4.30	0.27	11.35	1.67	4.66	18.47	0.56	2.05	68.43
	Diewieso	25	23.5	4.32	290	513	2.2	138.90	0.10	33.34	2.56	0.31	30.37	3.87	7.55	5.63	0.85	3.26	246.32
	Nyamso North	48	25.3	5.54	132	372	1.4	100.45	0.24	6.33	1.35	0.28	13.45	0.59	6.48	7.33	1.22	1.38	110.20
	Nyamso South	32	25.4	5.05	167	313	1.7	128.90	0.05	5.65	1.67	0.30	16.73	0.38	8.64	4.85	1.58	1.85	76.34
	Konka New Town	30	26.2	5.25	137	242	1.5	98.37	0.03	10.23	1.22	0.21	21.36	0.37	5.88	2.34	1.87	2.95	732.45
	Apitikokoo	40	23.4	6.63	142	267	1.9	45.78	0.07	7.44	0.24	0.19	15.38	3.05	5.23	5.33	1.02	2.53	98.72
	Kokotenten	34	25.4	6.46	312	526	3.8	223.76	0.13	4.43	5.24	0.17	22.48	2.70	7.10	33.25	1.54	0.78	205.87
	Nyamekyere	43	26.4	5.72	88	288	1.4	74.68	0.03	9.32	1.33	0.21	13.28	0.63	4.87	5.37	1.53	2.84	75.39
	Obuasi BH 3	100	26.5	6.45	1230	727	0.5	285.40	0.09	21.68	10.5	0.13	38.47	2.98	44.88	95.67	1.82	2.69	512.15
	Mensakurom	9	26.2	4.20	128	554	1.7	63.20	0.04	8.32	6.35	0.11	16.74	1.04	5.46	4.38	0.45	1.26	88.46
	Obuasi BH 2	70	25.7	6.35	886	788	2.7	198.47	0.08	18.43	9.86	0.15	42.15	1.65	56.33	78.54	1.30	2.48	498.80
	Obuasi BH 1	70	25.0	5.19	898	734	2.5	155.90	0.34	20.12	9.13	0.12	33.90	1.44	93.67	96.55	0.95	2.96	720.47
Wamase	4	26.3	5.12	102	355	2.2	168.30	0.05	6.85	7.56	0.20	31.45	0.73	3.22	11.33	1.22	2.05	87.55	
Bekwai Municipal Assembly	Old Edubiase	43	24.7	5.31	98	512	2.5	115.45	0.11	4.05	1.72	0.13	28.75	1.56	6.44	10.26	0.38	2.67	123.46
	Dwondoso	5.5	24.4	5.93	56	284	1.9	120.36	0.02	3.86	6.89	0.25	22.18	1.37	8.33	9.65	1.04	1.88	56.43
	Aminase	4	26.8	5.75	120	332	3.4	186.34	0.07	6.35	7.56	0.34	31.22	1.45	2.37	7.54	0.76	0.75	98.34
	Amoamo	1.5	23.6	5.39	308	364	0.9	87.34	0.12	31.43	2.06	0.31	19.38	1.53	7.59	22.38	0.67	1.10	132.29
	Ankase	48	25.3	6.19	137	445	1.8	56.33	0.08	5.33	0.38	0.32	17.84	3.01	16.20	11.46	0.83	2.05	167.44
	Bogyawe	58	23.0	6.14	232	228	0.6	187.40	0.27	6.78	1.95	0.27	26.73	3.83	13.54	13.47	0.97	1.64	135.85
Statistical Data	Minimum		23.0	3.13	56.0	228.0	0.2	45.57	<0.01	2.05	0.15	0.11	8.22	0.22	2.33	1.64	0.4	0.67	43.6
	Maximum		26.9	7.55	1230.0	788.0	3.8	784.56	0.42	44.64	10.5	0.43	65.35	6.12	93.67	96.55	2.0	4.73	732.5
	Mean		25.24	5.70	240.13	382.49	1.92	141.95	0.10	10.92	2.49	0.22	22.85	1.78	11.31	19.19	1.05	2.12	173.2
	Median		25.30	5.73	167.0	363.0	1.70	118.46	0.07	6.7	1.56	0.19	21.26	1.37	7.43	11.23	0.95	1.88	132.2
	Standard deviation		1.03	0.74	207.74	119.78	0.84	102.1	0.09	10.72	2.47	0.08	9.21	1.30	6.13	14.17	0.45	0.98	143.3

Groundwater temperatures (T) was almost uniform in all samples, ranging from 25.2 to 34.6 °C (mean: 28.54 ± 2.27 °C) during the dry season and 23.0 to 26.9 °C (mean: 25.24 ± 1.03 °C) during the wet season, respectively. The mean temperature during the dry season was higher due to the prevalent atmospheric conditions. Higher number of sunshine hours would naturally implied lower relative humidity, temperature increase of water bodies due to conduction and convection processes by the earth crust.

Electrical conductivity (EC) varies from 42 to 984 $\mu\text{S}/\text{cm}$ and 56 to 1230 $\mu\text{S}/\text{cm}$ during the dry and wet seasons, respectively at different depths. The electrical conductivity in groundwater is higher in the wet season than in the dry season. This may be attributed to the solvent action of rainwater when in contact with soluble mineral content of soils and rocks (Idoko *et al.*, 2012). This result corroborates the findings of *Bowell et al.*, (1996) and *Efe et al.*, (2005). Traditionally, EC values should be lower in wet season due to dilution by increased volume of water. The highest EC value was observed in the deep aquifer (Obuasi BH 3).

The electrode potential (Eh) values ranged from 212 to 662 mV during the dry season and 228 to 788 mV during the wet season. The high Eh values during the wet season may be attributed to mixing of groundwater from several redox zones as a result of the intensity of the rainfall and during pumping which is mainly due to large screen intervals of the monitored wells.

In this work, a Piper diagram for all data coded by the geographical areas (Amansie Central District, Adansi North District, Amansie West District, Bekwai Municipal and Obuasi Municipal), were derived from all the data sets using the AquaChem 2012.1 computer software package (Schlumberger Water Services). Input parameters are simply four major cations (sodium, potassium, calcium and magnesium) and three major anions (chloride, sulphate and bicarbonate/carbonate).

Piper diagrams display relative concentrations of the selected major cations and anions for a given sample in two separate trilinear plots (Figure 6.1): cations (bottom left), and anions (bottom right). The two points for each sample are then projected to form a single point in the central diamond that represents the overall water type for a given sample in general terms (Waikato Regional Council, 2006).

Arsenic Contamination in Groundwater

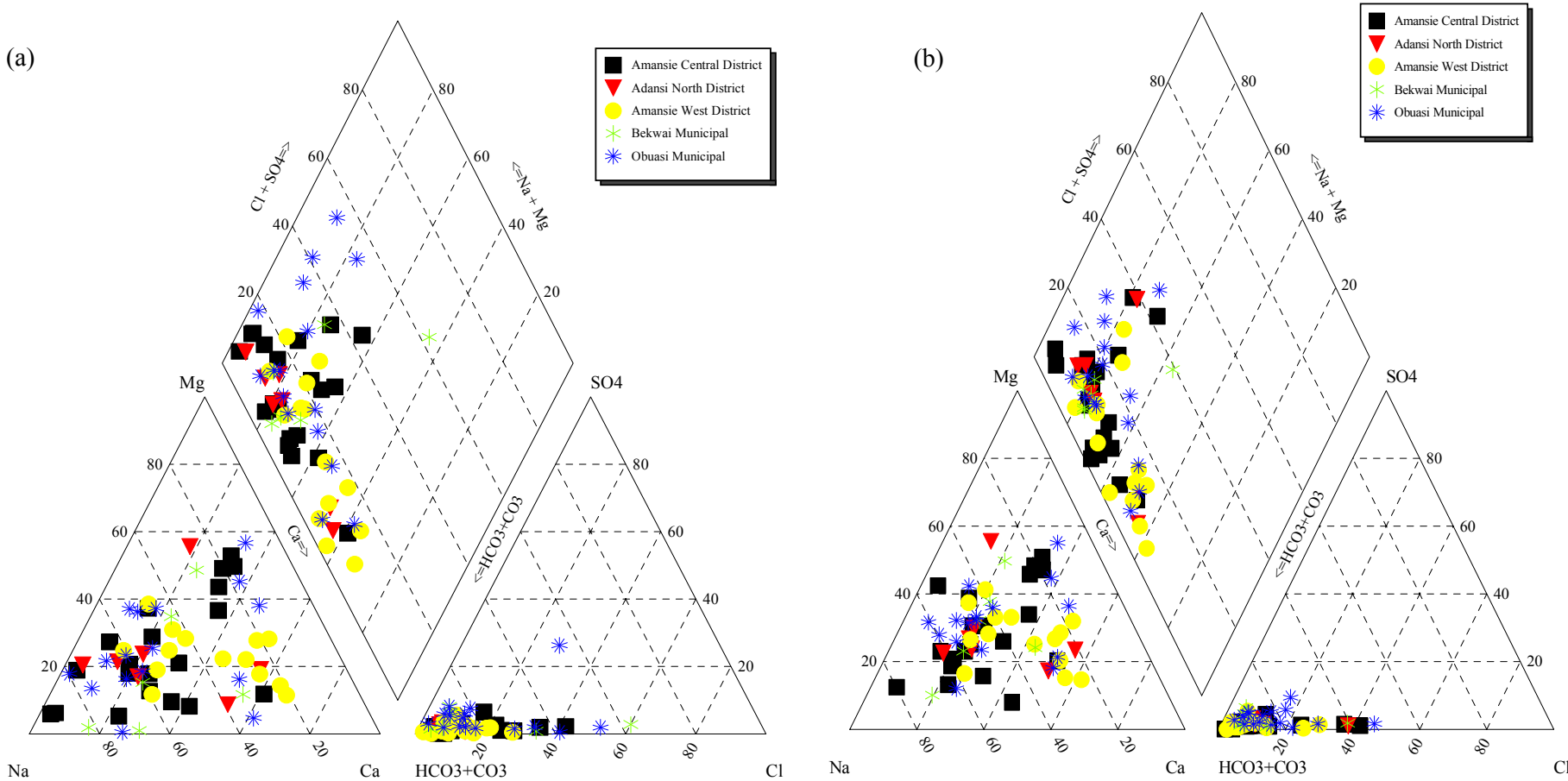


Figure 6.1: Piper diagram showing major ionic constituents in groundwater during both the dry (a) and wet seasons (b).

Plots of major ions on a Piper diagram (Figure 6.1) during both seasons (dry and wet) showed majority of samples from the south-western part of Ashanti Region grouped into a cluster that might be characterized as temporary hardness (marginally higher calcium+magnesium and bicarbonate) and alkali carbonate class (higher sodium+potassium and bicarbonate); although during the dry season, few samples from Obuasi Municipal are more toward the permanently hard category (higher calcium+magnesium, accompanied by higher sulphate+chloride) and a sample from Bekwai Municipal was quite central (denoting no one dominating ion) whilst in the wet season, a handful of samples from Obuasi Municipal and Amansie Central District are quite toward the permanently hard category.

According to the concentrations of major cations and anions, the groundwater composition varies from Ca–Mg–HCO₃ to Na–K–HCO₃ type, as a result of alumino-silicate weathering as well as dissolution of carbonate minerals, followed by Ca and/or Mg ion exchange with Na on clay minerals (Ujevic' *et al.*, 2010). This result corroborates the findings of Appelo and Postma, (2005).

There was a considerable increase in the concentration of ions during the wet season and this increase in the ionic concentration may be essentially due to the anthropogenic activities. During the wet season, the water table in the study area is nearer to the surface and active leaching and subsequent infiltration would have changed the chemical composition of groundwater.

During the dry season, the concentration of Ca, Mg, Na, K ions hovers between 0.33–82.56 mg/L; 0.09–85.12 mg/L; 6.04–33.15 mg/L and 0.01–4.38 mg/L with a mean of 15.04, 7.86, 17.06 and 1.02 mg/L, respectively. The order of abundance is Na > Ca > Mg > K. However, during the wet season the concentration of Ca, Mg, Na, K ions ranged from 1.64–96.55; 2.33–93.67; 8.22–65.35 and 0.22–6.12 mg/L with their corresponding means of 19.19, 11.31, 22.85 and 1.78 mg/L, respectively. The order of abundance is Na > Ca > Mg > K. The seasonal change has no effect on the order of abundance of major ions; however, there was a considerable change in the concentration of the ions as high cationic concentrations were observed in the wet season than the dry season.

Relatively high sodium concentrations in both seasons may be ascribed to the silicate weathering. Calcium (Ca²⁺) ion usually occurs in water as HCO₃, and CO₃ are not

uncommon. Calcium enters the water mainly through the dissolution of the carbonate minerals, which are abundant among sedimentary rocks in the study area. The level of magnesium ion in the groundwater samples has insignificant role to deteriorate groundwater quality. Potassium (K^+) concentration in most natural water rarely exceed 20 mg/L probably because most potassium bearing minerals are resistant to decomposition by weathering. Release of Ca^{2+} , Mg^{2+} , Na^+ and K^+ into groundwater from silicate and carbonate mineral weathering is normally enhanced by respired CO_2 from oxic and anoxic degradation of organic matter (Kar *et al.*, 2010).

Similarly in the case of anions during the dry season, HCO_3 , SO_4 , Cl, NO_3 , are in the order of 13–269.42; 011–9.55; 1.97–41.09 and <0.1–1.9 mg/L with a mean of 96.53, 2.24, 8.01 and 0.74 mg/L, respectively. The order of abundance is $HCO_3 > Cl > SO_4 > NO_3$. During the wet season HCO_3 , SO_4 , Cl, NO_3 ranged from 45.57–784.56; 0.15–10.5; 2.05–44.64 and 0.4–2.0 mg/L with a mean of 141.95, 2.53, 10.92 and 1.05 mg/L, respectively. The order of abundance is $HCO_3 > Cl > SO_4 > NO_3$.

The high concentration of bicarbonates (HCO_3) observed in both seasons would be expected for groundwaters having infiltrated to deeper levels in the aquifer and having had a longer residence time for chemical reaction (Smedley *et al.*, 1995). High HCO_3 concentrations are also typical features of both shallow and deep groundwaters. HCO_3 was observed to be relatively high in deeper wells >50 m. Most HCO_3 in groundwater is likely released during oxidation of organic matter and/or dissolution of carbonate minerals (Jeong, 2001; Kar *et al.*, 2010).

Sulfate (SO_4), nitrates (NO^-) and chloride (Cl^-) on the other hand may trace anthropogenic input to groundwater in agriculture areas within some of the areas where groundwaters were sampled. Indeed, higher concentrations of SO_4 , Cl and NO_3 detected in some groundwaters during the wet seasons might indicate leachate from the mining site (Christensen *et al.*, 1994) or could be due to agricultural fertilizers (Kim *et al.*, 2009) although some were in small concentrations.

Fluorides (F) and phosphates ions (PO_4) varied from 0.01–0.41 and 0.10–0.37 mg/L with a mean of 0.12 and 0.20 mg/L, respectively in the dry season and during the wet season they varied from <0.01–0.42 and 0.11–0.43 mg/L with a corresponding means of 0.10 and 0.22 mg/L, respectively. Phosphate recorded a marginal increase in concentration during the wet

season; however, for fluoride (F), lack of evaporation which is often exacerbated by the cold conditions (wet seasons) had no influence on its concentrations since there was no significant variation in their concentrations for both seasons, however, their concentrations were measured at below 1.0 mg/L.

Total dissolved solid (TDS) is also an important parameter that can be used to observe the influence of major components in groundwater quality. During the dry season, the concentration of TDS ranged from 28.5–691.2 mg/L with a mean of 145.9 mg/L and during the wet season, the TDS hovers between 43.6–732.5 mg/L with a mean of 173.2 mg/L, respectively. The concentration of TDS in groundwater are noted to be higher in wet season than in dry season and this is in variance with the findings of *Bowell et al.*, (1996) and *Efe et al.*, (2005). The high TDS contents during the wet season therefore suggest that the waters have had long contact times with the host rock materials and that rock dissolution has been high as a result of rainfall and the groundwaters having undergone the least amounts of reaction. In the Durovs diagram it was distinctly clear for the status of the major chemical components along with TDS (Figure 6.2).

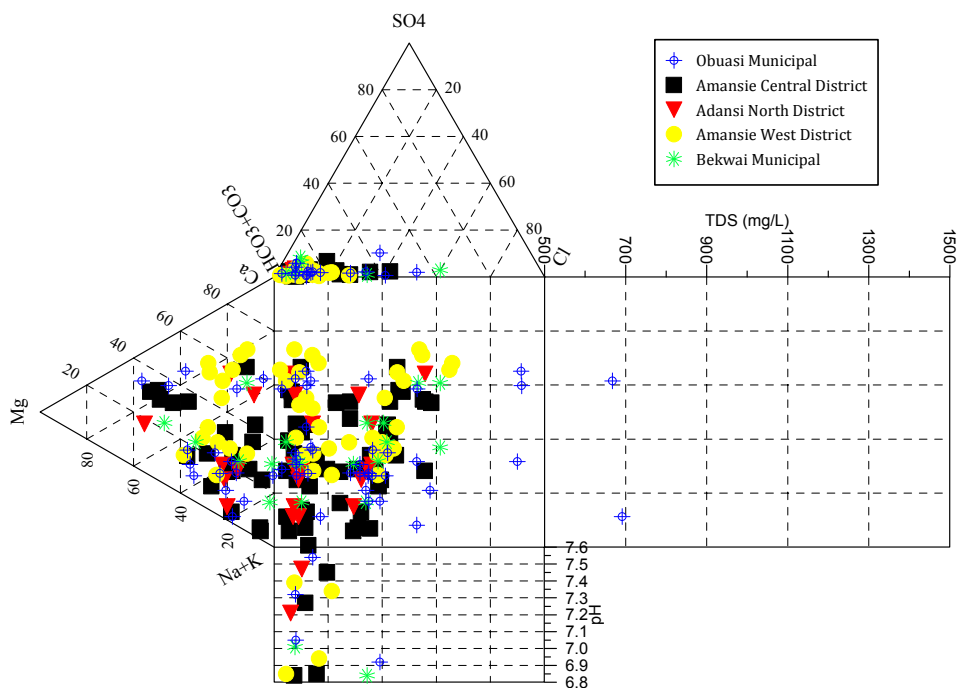


Figure 6.2: Durov diagram showing the status of chemical components along with TDS and pH in groundwater.

For the seasonal variation of the heavy metals contamination in groundwater, the results (Table 6.3 and 6.4) revealed iron (Fe) concentrations in groundwater ranging from <0.01–12.3 mg/L and <0.01–16.33 mg/L with their corresponding means of 1.51 and 2.12 mg/L for both dry and wet seasons, respectively. Per this data, Fe concentrations in the groundwater samples are higher in wet season than in the dry season. This may be due to the contact of rainwater with soil and rocks which releases ferrous iron into groundwater sources (Idoko *et al.*, 2012).

Manganese (Mn) in water sample analyzed ranged from 1.8–498 µg/L with a mean of 118.52 µg/L during the dry season as against 2.30–583.8 µg/L with a mean value of 150.51 µg/L in the wet season. The mean concentrations level of manganese was higher in the wet season, compared to the dry season.

Zinc (Zn) concentrations in the water samples for both dry and wet seasons ranged from 5.0–2301 µg/L with a mean of 109.15 µg/L and 7–2854 µg/L with a mean of 135.32 µg/L, respectively. From the analyses, Zn concentrations in the groundwater samples were lower in the dry season when compared to that of wet season. This is consistent with the findings of *Bowell et al.*, (1996). However, it was in variance with a study by *Okereke et al.*, (2007). The differences in the results of the above mentioned studies may be as a result of variation in the geology of the different study areas as well as dissimilar human activities and land use pattern occurring in the area.

Copper (Cu) concentrations in the analyzed groundwater samples ranged from <0.1–77 µg/L with a mean of 17.84 µg/L for the dry season as against <0.1–81 µg/L with a mean of 14.19 µg/L for the wet season. Copper concentrations are noted to be higher in the dry season than in the wet season. Sources of Cu commonly found in drinking water come from corrosion of household plumbing systems and erosion of natural deposits (Idoko *et al.*, 2012).

Metals like iron, manganese, and zinc recorded higher concentration in the wet season whiles copper registered high concentration in the dry season. This implies that as the climate becomes either wetter or drier concentration levels of heavy metals in groundwater are appropriately affected. High concentrations of the metals observed in the wet season samples could be an indication that the soluble forms of the metals are either present in the environment or produced after chemical reaction have occurred (Idoko *et al.*, 2012).

6.3 Incidence of Groundwater Arsenic (As) Contamination

Groundwater samples were analyzed for arsenic from 63 selected wells and boreholes in south-western part of Ashanti Region of Ghana to achieve our research objectives. The 63 monitored boreholes and wells were distributed among 63 communities in three district and two municipal assemblies including Amansie West District, Amansie Central District, Adansi North District, Bekwai Municipal and Obuasi Municipal Assemblies, respectively. The five study areas are in the same geological setting. The arsenic concentrations levels of the two seasons (dry and wet) were mapped to illustrate spatial distribution of As within the groundwater system at each community under the study (Figure 6.3). The spatial distribution of the total As concentrations occurred during the dry and wet seasons were not homogenous over the entire study area.

Arsenic was detected in groundwater samples from 26 community wells out of 63 wells and boreholes from the study area during the two seasons. The concentrations ranged between <0.1 (below detection limit) to 72.0 µg/L during the dry season and <0.1 to 83 µg/L during the wet season, respectively (Table 6.3 and 6.4).

Out of the total 63 monitored wells and boreholes, approximately 17 % (11) and 22 % (14) of the analyzed wells and boreholes had elevated arsenic concentrations greater than or equal to the World Health Organization (WHO) guideline value for drinking water standard of 10.0 µg/L during the dry and the wet seasons, respectively. The concentration levels of arsenic detected above the guideline value for drinking water were found in eleven (i.e. Mile 14, Yawkurom, Obuasi BH 3, Antoakurom 1, Obuasi BH 1, Tweapease, Agroyesum, Sabe, Mamfo, Sanso and Kokotenten) and fourteen (i.e. Mile 14, Yawkurom, Obuasi BH 3, Antoakurom 1, Obuasi BH 1, Tweapease, Agroyesum, Sabe, Mamfo, Sanso, Kokotenten, Apitiso, Apanapron, and Obuasi BH 2) community monitored wells during both the dry and wet seasons, respectively (Table 6.3 and 6.4).

Arsenic Contamination in Groundwater

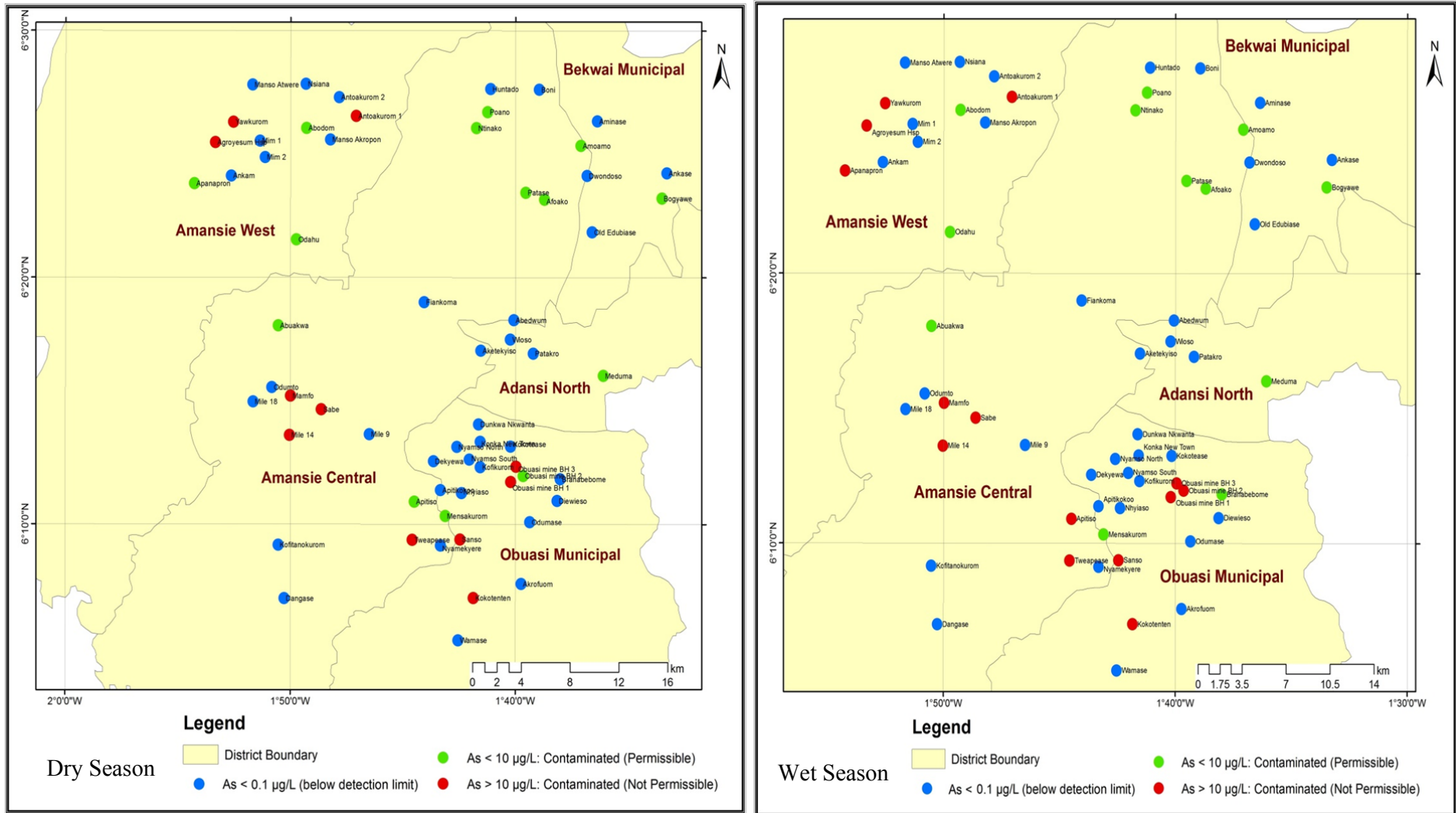


Figure 6.3: Spatial distribution of arsenic (As) in south-western part of Ashanti Region of Ghana during the dry and the wet seasons.

Table 6.3: Concentration levels of As_{total} and other trace elemental characteristics of the surveyed groundwaters during the dry season in the south-western part of Ashanti Region of Ghana.

Study Area	Location	Depth (m)	pH	Fe (mg/L)	Mn (µg/L)	As _{total} (µg/L)	Cu (µg/L)	Zn (µg/L)
DL				0.01	0.1	0.1	0.1	0.1
Adansi North District	Meduma	53	7.78	<0.01	1.8	5.0	9.0	7.0
	Abedwum	6	6.56	0.08	29.7	<0.1	<0.1	39.0
	Wioso	18	7.47	0.06	14.3	<0.1	44.0	31.0
	Patakro	36	7.21	2.89	175.0	<0.1	<0.1	11.0
	Dunkwa Nkwanta	25.5	6.58	0.35	22.4	<0.1	4.0	12.0
	Kokotease	35	7.78	<0.01	6.8	<0.1	5.0	13.0
	Kofikurom	38	6.55	0.06	32.1	<0.1	9.0	19.0
Amansie West District	Odahu	60	8.14	0.37	103.7	2.0	<0.1	33.0
	Agroyesum Hsp	52	6.12	6.65	319.0	43.0*	<0.1	9.0
	Apanapron	80	7.39	1.72	201.0	9.0	<0.1	19.0
	Ankam	38	6.54	0.61	58.7	<0.1	7.0	21.0
	Mim 1	57	6.85	1.03	82.1	<0.1	<0.1	6.0
	Abodom	46	8.05	<0.01	11.9	4.0	17.0	14.0
	Mim 3	49	6.94	0.01	11.7	<0.1	11.0	17.0
	Antoakurom 1	70	8.42	0.73	327.0	48.0*	<0.1	9.0
	Manso Akropon	43	6.57	0.42	347.0	<0.1	21.0	42.0
	Antoakurom 2	32	7.34	<0.01	91.3	<0.1	27.0	15.0
	Nsiana	49	6.58	<0.01	27.3	<0.1	13.0	11.0
	Yawkurom	49	8.54	0.13	257.0	56.0*	7.0	17.0
	Manso Atwere	19	6.53	0.23	93.2	<0.1	8.0	17.0
	Odumase	43	6.18	1.73	130.0	<0.1	<0.1	172.0
Amansie Central District	Mile 9	46	7.61	0.17	88.2	<0.1	13.0	19.0
	Mile 14	64.5	8.47	0.16	212.0	58.4*	8.0	5.0
	Boni	66	6.58	0.03	92.3	<0.1	34.0	31.0
	Hunatado	54	7.86	0.02	41.9	<0.1	11.0	14.0
	Poano	61	8.23	3.72	251.0	5.0	5.0	11.0
	Ntinako	52	7.71	0.01	16.8	4.0	19.0	39.0
	Kofitanokrom	8	6.64	0.02	17.6	<0.1	<0.1	55.0
	Patase	34	8.46	0.04	34.0	1.03	9.0	14.0
	Apitiso	43.5	8.36	0.02	33.6	9.0	17.0	41.0
	Fiankoma	65	6.85	5.12	203.0	<0.1	<0.1	39.0
	Dangase	4	6.59	<0.01	17.3	<0.1	<0.1	13.0
	Odumto	15	8.14	5.63	52.8	<0.1	8.0	23.0
	Sabe	22	8.33	0.24	192.4	72.0*	<0.1	253.0
	Mile 18	8	6.84	0.04	211.0	<0.1	<0.1	9.0
	Mamfo	28	8.78	0.72	173.7	22.0*	<0.1	38.0
	Dekyewa	24	6.62	11.13	102.3	<0.1	<0.1	1206.0
	Afoako	42	7.45	0.04	11.6	3.0	24.0	21.0
	Aketekyiso	3	7.27	0.42	17.3	<0.1	13.0	35.0
	Tweapease	43	8.52	0.64	71.3	13.0*	<0.1	15.0
Abuakwa	48	6.02	0.73	319.0	5.0	<0.1	9.0	
Obuasi Municipal Assembly	Nhyiaso	18	6.52	<0.01	21.9	<0.1	<0.1	13.0
	Akrofuom	32	7.73	0.19	194.6	<0.1	27.0	64.0
	Sanso	42	6.52	6.49	122.0	19.0*	<0.1	11.0
	Brahabebome	19	7.32	0.04	7.6	2.0	77.0	508.0
	Diewieso	25	6.53	0.02	273.0	<0.1	48.0	72.0
	Nyamso North	48	7.54	0.38	103.5	<0.1	<0.1	15.0
	Nyamso South	32	7.05	0.16	48.5	<0.1	<0.1	27.0
	Konka New Town	30	6.52	0.01	49.7	<0.1	<0.1	13.0
	Apitikokoo	40	6.63	0.03	49.7	<0.1	35.0	31.0
	Kokotenten	34	8.46	0.93	206.0	13.0*	<0.1	7.0
	Nyamekyere	43	6.52	0.50	52.3	<0.1	9.0	28.0
	Obuasi BH 3	100	8.31	12.03	472.0	21.0*	<0.1	231.0
	Mensakurom	9	6.92	0.04	21.3	2.0	<0.1	13.0
	Obuasi BH 2	70	6.15	5.13	498.0	7.0	43.0	2301.0
	Obuasi BH 1	70	8.19	9.06	424.0	10.0*	9.0	892.0
Wamase	4	8.12	0.31	50.7	<0.1	11.0	33.0	
Bekwai	Old Edubiase	43	7.01	<0.01	4.8	<0.1	17.0	14.0

Arsenic Contamination in Groundwater

Municipal Assembly	Dwondoso	5.5	6.73	0.04	7.3	<0.1	<0.1	93.0
	Aminase	4	6.55	0.04	38.9	<0.1	<0.1	33.0
	Amoamo	1.5	8.19	0.17	196.0	2.0	5.0	29.0
	Ankase	48	6.84	0.01	7.2	<0.1	13.0	14.0
	Bogyawe	58	6.18	1.86	116.0	5.2	5.0	9.0
Statistical Data	Minimum		6.02	<0.01	1.8	<0.1	<0.1	5.0
	Maximum		8.47	12.3	498.0	72.0	77.0	2301
	Mean		7.22	1.51	118.52	17.98	17.84	109.15
	Median		7.21	0.24	71.30	8.0	12.00	19.0
	SD		0.75	0.84	82.12	10.26	15.58	73.48

DL=Limit of detection; SD= Standard deviation

*Values designated by asterisks are higher than the WHO permissible limit (10 µg/L) for the arsenic in drinking water. Each value is the mean of three samples with three determinations.

Among the wells that exceeded the recommended levels, the highest concentration was achieved in Sabe community borehole during both the dry and wet seasons registering a mean concentration levels of 72.0 and 83.0 µg/L, respectively and the least observed in Obuasi BH 1 in the dry season and Obuasi BH 2 in the wet seasons with mean concentration levels of 10 and 11 µg/L, respectively. These results are however, much less than concentrations observed in regions where chronic arsenic health problems have been detected (Smedley *et al.*, 1995).

Table 6.4: Concentration levels of As_{total} and other trace elemental characteristics of the surveyed groundwaters during the wet (rainy) season in the south-western part of Ashanti Region of Ghana.

Study Area	Location	Depth (m)	pH	Fe (mg/L)	Mn (µg/L)	As _{total} (µg/L)	Cu (µg/L)	Zn (µg/L)
DL				0.01	0.1	0.1	0.1	0.1
Adansi North District	Meduma	53	5.43	0.05	2.3	3.0	8.0	10.0
	Abedwum	6	6.76	0.15	31.4	<0.1	3.0	27.0
	Wioso	18	5.53	0.13	17.8	<0.1	40.0	36.0
	Patakro	36	7.55	3.02	186.4	<0.1	<0.0	17.0
	Dunkwa Nkwanta	25.5	4.23	0.73	28.4	<0.1	<0.0	28.0
	Kokotease	35	5.90	<0.01	10.5	<0.1	4.0	9.0
	Kofikurom	38	5.05	0.09	36.7	<0.1	11.0	7.0
Amansie West District	Odahu	60	5.33	0.57	132.5	8.6	2.0	42.0
	Agroyesum Hsp	52	6.25	7.05	386.5	48.5*	3.0	16.0
	Apanapron	80	6.56	2.32	224.3	16.0*	<0.1	21.0
	Ankam	38	5.67	0.33	73.2	<0.1	6.0	29.0
	Mim 1	57	6.04	1.53	100.6	<0.1	3.0	13.0
	Abodom	46	6.17	0.05	24.5	7.0	19.0	19.0
	Mim 3	49	6.15	<0.01	19.7	<0.1	15.0	22.0
	Antoakurom 1	70	6.55	0.95	385.8	53.8*	2.0	15.0
	Manso Akropon	43	5.23	<0.01	423.4	<0.1	19.0	48.0
	Antoakurom 2	32	5.88	0.07	176.5	<0.1	23.0	23.0
	Nsiana	49	5.84	<0.01	46.4	<0.1	17.0	14.0
	Yawkurom	49	6.58	0.15	335.4	62.5*	9.0	26.0
	Manso Atwere	19	6.75	<0.01	120.8	<0.1	12.0	29.0
	Odumase	43	5.58	2.03	167.4	<0.1	<0.1	225.0
Amansie Central District	Mile 9	46	5.85	0.19	125.5	<0.1	11.0	27.0
	Mile 14	64.5	6.56	0.13	286.43	65.6*	14.0	17.0
	Boni	66	5.75	0.07	127.4	<0.1	30.0	35.0
	Hunatado	54	4.94	0.05	87.4	<0.1	8.0	19.0

Arsenic Contamination in Groundwater

	Poano	61	5.46	4.02	287.5	9.0	11.0	21.0
	Ntinako	52	5.84	0.07	89.4	7.0	21.0	43.0
	Kofitanokrom	8	5.72	0.07	45.2	<0.1	2.0	62.0
	Patase	34	5.51	0.08	67.8	4.5	13.0	17.0
	Apitiso	43.5	5.58	0.05	84.3	13.0*	21.0	48.0
	Fiankoma	65	5.32	6.13	287.5	<0.1	3.0	44.0
	Dangase	4	3.88	0.05	23.4	<0.1	<0.1	19.0
	Odumto	15	5.40	5.01	65.8	<0.1	5.0	31.0
	Sabe	22	6.55	0.30	205.8	83.0*	<0.1	365.0
	Mile 18	8	5.48	0.07	184.6	<0.1	<0.1	18.0
	Mamfo	28	6.28	0.83	234.6	28.0*	<0.1	46.0
	Dekyewa	24	5.73	15.14	264.9	<0.1	<0.1	1475.0
	Afoako	42	5.86	0.09	23.5	5.0	29.0	33.0
	Aketekyiso	3	5.20	0.56	26.4	<0.1	7.0	47.0
	Tweapease	43	5.68	0.72	97.3	17.0*	5.0	21.0
	Abuakwa	48	6.38	0.83	368.5	8.0	3.0	18.0
Obuasi	Nhyiaso	18	5.42	<0.01	48.3	<0.1	5.0	21.0
Municipal	Akrofuom	32	3.13	<0.01	225.4	<0.1	24.0	72.0
Assembly	Sanso	42	6.15	7.56	164.5	24.0*	9.0	17.0
	Brahabebome	19	5.85	0.08	22.5	9.0	81.0	633.0
	Diewieso	25	4.32	<0.01	239.5	<0.1	52.0	85.0
	Nyamso North	48	5.54	0.25	77.5	<0.1	<0.1	24.0
	Nyamso South	32	5.05	0.33	64.3	<0.1	5.0	37.0
	Konka New Town	30	5.25	<0.01	67.2	<0.1	<0.1	19.0
	Apitikokoo	40	6.63	0.07	87.6	<0.1	37.0	39.0
	Kokotenten	34	6.46	1.05	287.5	19.0*	11.0	11.0
	Nyamekyere	43	5.72	0.78	45.8	<0.1	4.0	32.0
	Obuasi BH 3	100	6.45	16.33	583.8	28.0*	9.0	275.0
	Mensakurum	9	4.20	3.06	43.7	5.0	6.0	21.0
	Obuasi BH 2	70	6.35	10.14	520.7	11.0*	47.0	2854.0
	Obuasi BH 1	70	5.19	13.66	557.3	17.0*	17.0	1055.0
	Wamase	4	5.12	1.32	34.7	<0.1	8.0	47.0
Bekwai	Old Edubiase	43	5.31	0.04	13.5	<0.1	14.0	23.0
Municipal	Dwondoso	5.5	5.93	<0.01	18.9	<0.1	3.0	85.0
Assembly	Aminase	4	5.75	0.06	67.5	<0.1	<0.1	38.0
	Amoamo	1.5	5.39	0.23	212.8	1.5	7.0	27.0
	Ankase	48	6.19	<0.01	17.8	<0.1	11.0	17.0
	Bogyawe	58	6.14	2.08	167.5	2.2	9.0	11.0
Statistical	Minimum		6.02	<0.01	2.30	<0.1	<0.1	7.0
Data	Maximum		8.47	16.33	583.80	83.0	81.0	2854
	Mean		5.70	2.12	150.51	21.39	14.19	135.32
	Median		7.05	0.33	89.40	12.00	9.00	27.0
	SD		0.74	1.73	96.07	11.63	9.69	86.93

DL=Limit of detection; SD= Standard deviation

*Values designated by asterisks are higher than the WHO permissible limit (10 µg/L) for the arsenic in drinking water. Each value is the mean of three samples with three determinations.

Various degrees of As contamination lower than the WHO guideline value of 10 µg/L was recorded in most wells within the study area during both the dry and the wet seasons. During the dry season for instance, 24 % (15 wells) of the 63 monitored wells registered lower levels of arsenic contamination with two boreholes (located in Apitiso and Apanapron) registering As concentration of 9.0 µg/L each with Patase borehole having the least value of 1.03 µg/L. Similarly 19 % (12 wells) observed lower levels of arsenic that were less than the WHO intervention value of 10 µg/L with two wells (Brahabebome and Poano community wells)

registering a mean concentration level of 9.0 µg/L each and the least mean level of 1.5 µg/L found in Amoamo community well during the wet season. Nevertheless, 59 % (37) boreholes and wells located within the study area were having a non-detectable value of < 0.1 µg/L during both seasons.

In general, the variation in the mean concentration values of arsenic from dry (17.98 µg/L) to wet (21.39 µg/L) seasons is more prominent by virtue of the fact that, the soluble forms of the arsenic metals are either present in the environment or produced after chemical reaction have occurred. One of the possible reasons of high arsenic concentrations in the wet season (Figure 6.4) is that arsenic in groundwater of study area may be controlled by the aquifer itself, because its concentrations in the aquifer will be diluted in wet season more easily compared with that in dry season due to the higher groundwater recharge in wet season (Guanxing *et al.*, 2014).

The peak values in the wet (rainy) period may likely due to inputs of As contaminated particles from run-offs (particularly from the arsenic-contaminated tailings dams from the AngloGold mines and the illegal artisanal mining activities), top surface soil and frequent flooding seeping through the semi-permeable rock layer. Another reason pointed out by Leung and Jiao (2006) is that, some metals could also be leached out from vadose zone into groundwater as a result of the generally higher water table during the wet season (Guanxing *et al.*, 2014).

Further the total As levels when compared with safe guideline value for groundwater consumption on one hand and in similar groundwater systems elsewhere impacted by the geology or gold mining activities on the other hand, the following trends are observed:

First the recorded numbers in the study area except wells and boreholes in Mile 14, Yawkurom, Obuasi BH 3, Antoakurom 1, Obuasi BH 1, Tweapease, Agroyesum, Sabe, Mamfo, Sanso, and Kokotenten communities wells during the dry season (Table 6.3) and wells and boreholes from Mile 14, Yawkurom, Obuasi BH 3, Antoakurom 1, Obuasi BH 1, Tweapease, Agroyesum, Sabe, Mamfo, Sanso, Kokotenten, Apitiso, Apanapron, and Obuasi BH 2 communities during the wet season (Table 6.4), do not exceed the WHO recommended guideline maximum value of 10.0 µg/L for drinking water (WHO, 1996a, b, 2004).

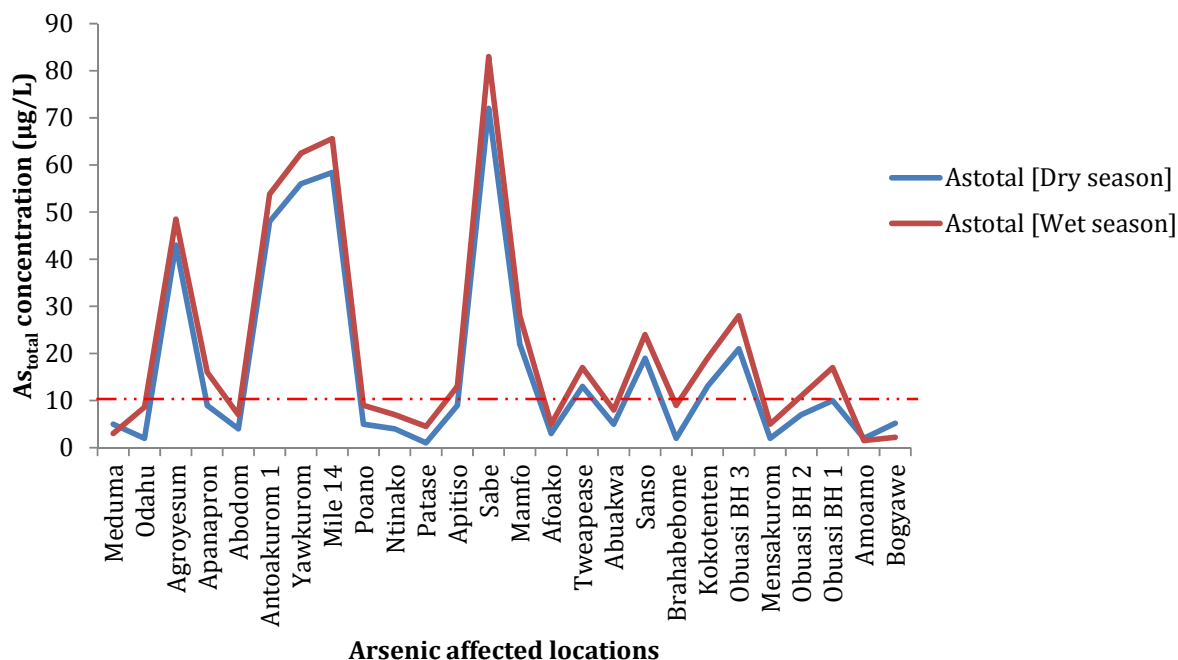


Figure 6.4: Total arsenic distribution ($\mu\text{g/L}$) in groundwaters from south-western part of Ashanti Region of Ghana during the dry and wet seasons.

Secondly the total mean concentration levels of As in south-western part of Ashanti Region of Ghana recorded during the two seasons are far less than values reported for As contamination from mining activities in a number of areas in the USA (Welch *et al.*, 1988; 1999); for example up to 48,000 $\mu\text{g/L}$ has been reported for Fairbanks gold mining district of Alaska (Welch *et al.*, 1988), California (Webster *et al.*, 1994) and Nevada (Grimes *et al.*, 1995).

In Wisconsin, up to 12,000 $\mu\text{g/L}$ have been documented as a result of the oxidation of sulphide minerals present in the aquifer (Schreiber *et al.*, 2000). In Thailand, total As values up to 5000 $\mu\text{g/L}$ have been found in past tin and gold mining operations sites at Ron Phibun district (Williams *et al.*, 1996; Williams, 1997) several orders of magnitude higher than numbers obtained from this study area. Accordingly, the mobilization of As in the aforementioned locations is believed to be the caused by oxidation of primary sulfide As-bearing sulfide minerals exacerbated by the mining activities and re-mobilization of As from iron hydroxides or other secondary As-bearing phases.

A comparison of this data, with that obtained by Smedley *et al.*, (1995) in a previous study revealed interesting results. Smedley *et al.*, (1995) measured total As with ICP-AES and ICP-MS to obtain two set of data. Values of total As from this study were generally higher in magnitude than what has been reported by Smedley *et al.*, (1995) applying ICP-AES instrument. This difference in results can be attributed to factors such as differences in sampling seasons and/or sample collection/handling procedures/analytical tools and methods employed.

Additionally other studies conducted by Smedley *et al.*, (1996) at other different locations noted that many of the groundwaters in some areas of south-western part of Ashanti Region were low which was in agreement with the findings of this work. Besides, those workers also noted that, areas where elevated As concentrations existed, for instance in Amansie West and Central Districts did not necessary relate to large-scale mining activity but findings of this study also considered illegal artisanal mining (Galamsey) activities which were located sparsely within the entire study area, and this might have contributed to elevated As concentration within those wells and boreholes in the study area.

Despite the high arsenic concentrations in the contaminated soils and tailings dams located within the vicinity of the study area (Kumi-Boateng, 2007; Antwi-Agyei *et al.*, 2009; Boateng *et al.*, 2012, Bempah *et al.*, 2013) and bedrocks close to both AngloGold Ashanti mines and some illegal artisanal mining activities within the study area, many of the groundwaters of the area and its satellite communities had low concentrations of arsenic with a mean value in wells and boreholes of 17.98 $\mu\text{g/L}$ and 21.39 $\mu\text{g/L}$ during the dry and the wet seasons, respectively. Some higher concentrations were observed (up to 72 $\mu\text{g/L}$ in the dry season and 83 $\mu\text{g/L}$ in the wet season), were not generally within the vicinity of the AngloGold Ashanti mines area (Obuasi Municipality) but were closer to illegal artisanal mining activities occurring within the Amansie Central District. Similarly, elevated concentrations of As were also recorded in five communities (Obuasi BH1, Obuasi BH2, Obuasi BH3, Sanso and Kokotenten) close/within the AngloGold mines which might be related to the large scale mining activity.

Nonetheless, the study revealed the presence of several illegal artisanal mining activities which might have accounted for the high As concentrations in relatively reducing groundwaters in areas of high As levels. Again, dissolved As from the geology as well as

sulphide materials generated by anthropogenically disturbance as a consequence of the mining might also have contributed to the high As levels.

6.4 Arsenic Speciation in Cases where Arsenic Concentrations in Groundwaters are Detected

Arsenic speciation is very important in assessing the geochemistry, transport and fate of arsenic, since the geochemical behavior depends on its species (Wongyai *et al.*, 2013). It is equally very important in determining the toxicity of the arsenic species.

As noted in Chapter five (Section 5.4.5), groundwater samples within 26 community wells which detected arsenic concentration levels were collected for As speciation analysis. Results are presented in Table 6.5. Total arsenic and As-III were measured directly as described in Chapter five (Section 5.4.5), and As-V was estimated as the difference between the two.

Table 6.5: Total arsenic (As_{total}), arsenite (As-III) and arsenate (As-V) in groundwater samples from wells and boreholes of 26 communities for which arsenic speciation were measured.

Study Area	Location	As_{total} ($\mu\text{g/L}$)	As-III ($\mu\text{g/L}$)	As-V ($\mu\text{g/L}$)	Percentage As-III (%) ^a
Detection limit		0.1	0.1	0.1	
Adansi North District (N=1)	Meduma	4.0	2.8	1.2	76
Amansie West District (N=6)	Odahu	5.3	4.7	0.7	89
	Agroyesum	45.8*	27.0*	18.8*	59
	Apanapron	12.5*	9.0	3.5	72
	Abodom	5.5	4.9	0.6	89
	Antoakurom 1	51.0*	44.0*	7.0	86
	Yawkurom	59.3*	41.2*	18.1*	69
Amansie Central District (N=10)	Mile 14	62.0*	58.0*	4	94
	Poano	7.0	7.0	nd	100
	Ntinako	5.5	3.2	2.3	58
	Patase	2.8	2.8	nd	100
	Apitiso	11.0*	11.0*	nd	100
	Sabe	77.5*	67.0*	10.5*	86
	Mamfo	25.0*	8.0	17.0*	32
	Afoako	4.0	4.0	nd	100
	Tweapease	15.0*	6.0	9.0	40
	Abuakwa	6.5	6.5	nd	100
Obuasi Municipal Assembly (N=7)	Sanso	21.5*	17.0*	4.5	79
	Brahabebome	5.5	5.5	nd	100
	Kokotenten	16.0*	7.0	9.0	44
	Obuasi BH 3	24.5*	21.3*	3.2	87
	Mensakurom	3.5	3.5	nd	100
	Obuasi BH 2	9.0	6.0	3.0	67
	Obuasi BH 1	13.5*	8.2	5.3	61

Bekwai Municipal Assembly (N=2)	Amoamo	1.8	1.8	nd	100
	Bogyawe	3.7	1.6	2.1	43
Statistical data	Minimum	1.8	1.6	0.6	
	Maximum	77.5	67.0	18.8	
	Mean	19.18	14.57	6.65	
	Median	10.0	6.76	4.25	
	Standard deviation	9.07	5.38	1.95	

^aCalculated as the ratio As-III/As-III+As-V, multiplied by 100.

nd= not detectable (below detection limit of 0.1 µg/L)

*Values designated by asterisks are higher than the WHO permissible limit (10 µg/L) for the arsenic in drinking water. Each value is the mean of three samples with three determinations.

Generally in As-contaminated groundwater, two important As species are available as oxyacids arsenite (H_3AsO_3 , uncharged at neutral pH) and arsenate (H_3AsO_4 , anionic at neutral pH). Under reducing conditions, the predominant form of arsenic is arsenite (As-III), which is particularly mobile form of arsenic. In contrast, a less mobile form called arsenate (As-V) predominates under oxidizing conditions (USGS, 1999).

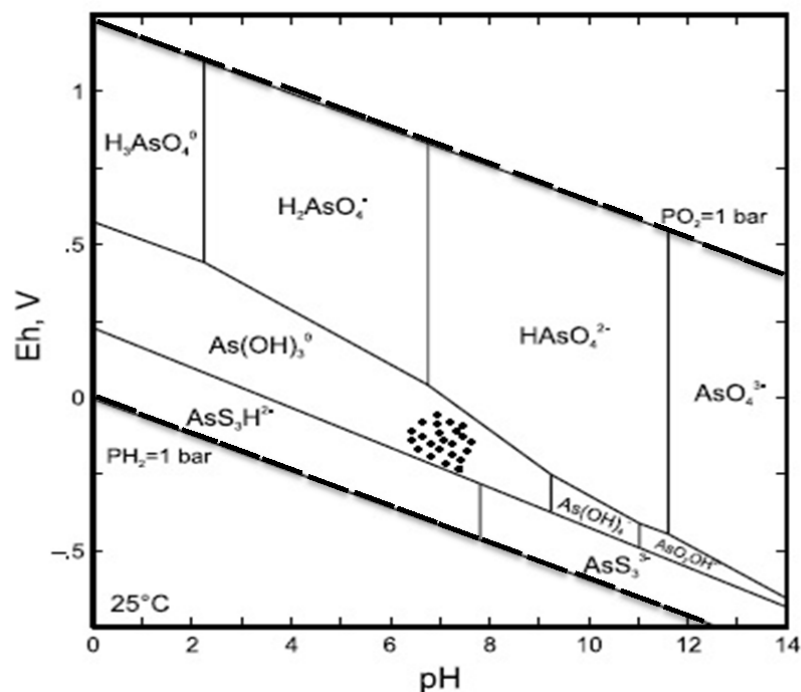


Figure 6.5: Field Eh-pH diagram for As (at 25 °C and fixed As activities of 10^{-3}), dashed lines indicate stability limits of water at 1 bar pressure.

Arsenic speciation studies revealed a large range in the relative proportions of dissolve As-III and As-V in the groundwaters. However, it is evident that the concentration of As-III was found to be higher than As-V in 85 % of the total arsenic detected in the groundwater

samples analyzed within the study area, indicating that the reducing conditions were present in the groundwaters within the vicinity of the wells and boreholes. In strongly reducing aquifers, typified by Fe-III and sulfate reduction, As-III typically dominates, as expected from the redox sequence. Generally, additional indicators of reducing conditions in the arsenic-affected aquifers include low concentrations of nitrate, dissolved oxygen (DO), low to very low concentrations of sulfate and reduction of Fe-oxyhydroxides as observed in the study area.

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation in aqueous systems. The field Eh-pH diagram (Figure 6.5) shows H_3AsO_3 (As-III) is the dominant As species in the groundwater of south-western part of Ashanti Region of Ghana in agreement with the present speciation study (Figure 6.6).

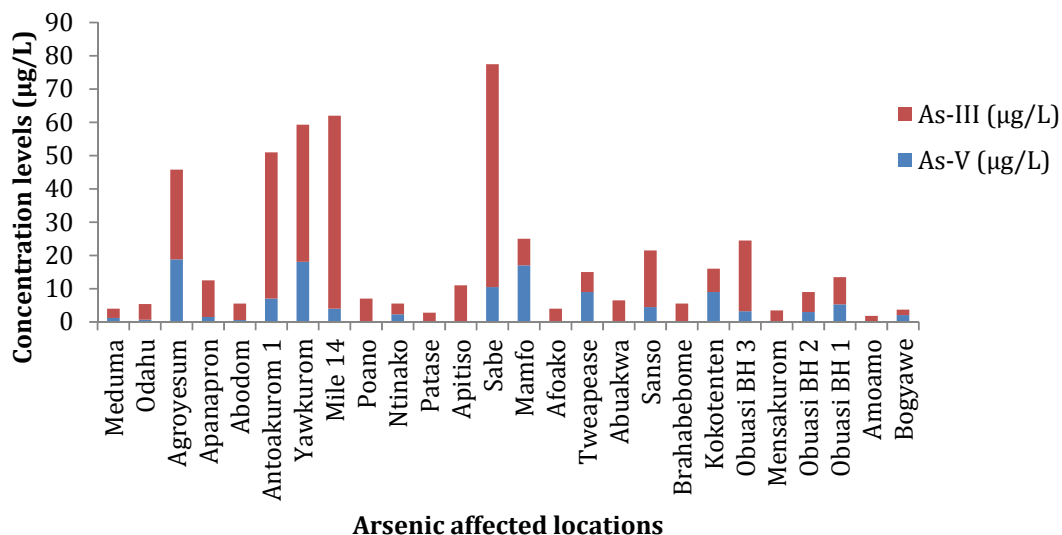


Figure 6.6: Distribution of As-III and As-V in groundwater samples collected from south-western part of Ashanti Region of Ghana.

In groundwater, arsenic and iron will normally undergo chemical degradation and change oxidation states as redox conditions change (Allen *et al.*, 1993). For example, as the subsurface environment reaches reducing conditions (i.e., DO decreases), iron and arsenic will reduce to ferrous iron (Fe^{+2}) and arsenite (As-III), respectively (Figure 6.7). Since conversion of arsenate (As-V or AsO_4^{3-}) to arsenite (As-III or AsO_2^-) is significant in terms of potential exposure and risk to people drinking such groundwater, because the latter is usually more mobile in the subsurface than the former and due to differing adsorption characteristics (Waikato Regional Council, 2006).

The toxicity of arsenite is also estimated to be between 25-50 times greater than that of arsenate (Waikato Regional Council, 2006). Thus both deeper and shallower groundwaters observing high concentrations of As-III are more a cause for concern with respect to As.

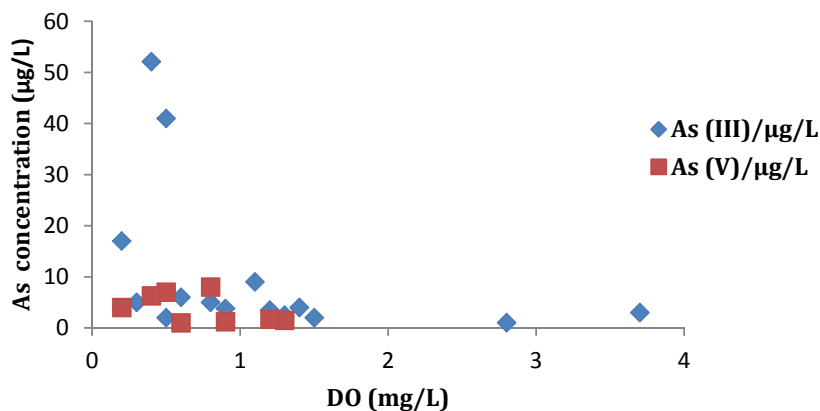


Figure 6.7: Concentration levels of As-III and As-V against dissolved oxygen (DO) for groundwater samples within the study area.

6.5 Spatial Distribution of Arsenic and Well Depth

Depth data were available for all the 63 wells and boreholes monitored sites during the dry and the wet seasons. The relation of arsenic concentration to depth is discussed in section 6.5.1. There was obvious relation of arsenic concentration to well depth within the study area. On a local scale, well depths appear to be a useful parameter for predicting arsenic concentrations. The patterns of As to depth distribution during the dry and wet seasons were apparent.

6.5.1 Relationship between Well Depth and Total Arsenic Concentration

The relationship between well depth and total arsenic concentrations observed within the seasons were evaluated to assess if the possible source of arsenic is natural or potentially associated with land use or mining activities. Deep wells are generally less sensitive to contamination from land use activities. If the high arsenic levels are predominantly in deep wells and confined aquifers it is hypothesized that the source of the high arsenic concentrations is from natural sources contained in the surficial materials in the region from which the groundwater is extracted (Fraser Health Authority and BC MoE, 2008).

For the dataset as a whole (dry and wet seasons), the results provided in Figure 6.8a, 6.8b and Table 6.6 as well as 6.7 showed a weak correlations (Spearman’s rho=0.43 and 0.41 during dry and wet seasons, respectively) between well depth and arsenic concentrations with deeper wells (70 to 100 m) having significantly lower arsenic concentrations compared to the shallow wells having intermediate depths between 20–70 m.

Though the depth of 22 m at Sabe community well is characterized by a peak of dissolved As concentrations of 72 and 83 µg/L during the dry and the wet seasons which signifies the presence of As source in the aquifer which might be induced by anthropogenic activities unlike the deepest depth (100 m) of Obuasi BH 3 registering As concentrations levels of 21 and 28 µg/L during the dry and the wet seasons, respectively, indicating dissolution of As from sediments.

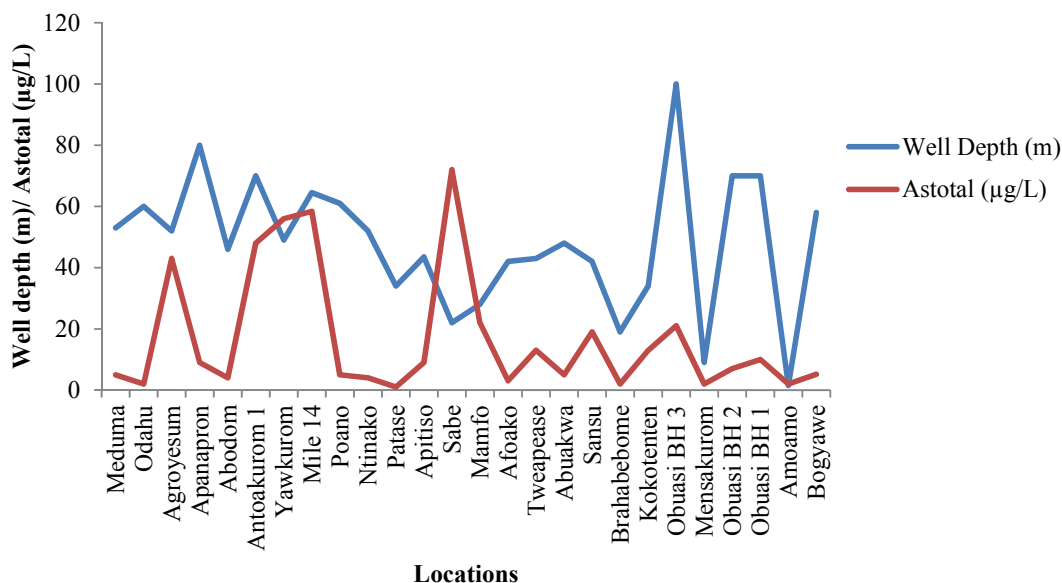


Figure 6.8a: Relationship between As contaminated locations and total-arsenic/well depth during the dry season.

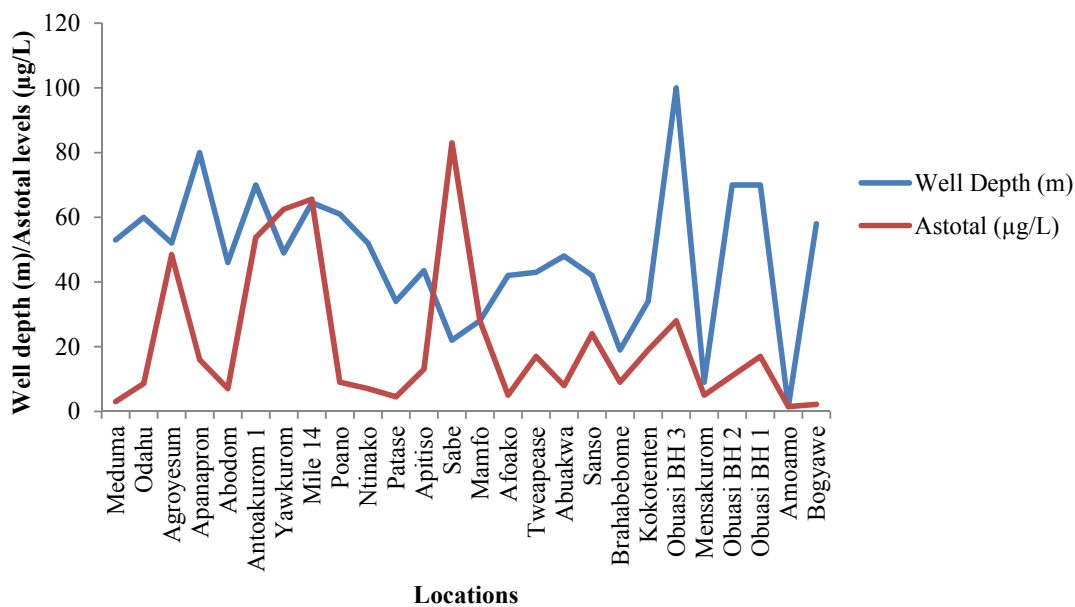


Figure 6.8b: Relationship between As contaminated locations and total-arsenic/well depth during the wet season.

Comparatively low As concentrations were also found in groundwater at a depth of >70 m. Earlier studies by Smedley *et al.*, (1996) reflected similar patterns of As in the groundwater samples from the same region (particularly, Obuasi and its satellite areas) and reported low arsenic concentrations (median value < 2 µg/L and 5–17 µg/L, respectively) in deeper (70–100 m) groundwater and higher values (up to 64 µg/L) in intermediate depth (40–70 m).

According to the reports of Nickson *et al.*, (1998; 2000), arsenic concentrations increased with depth in wells at several places in India and Bangladesh. However, other researchers elsewhere reported opposite trend in the same area that is the decrease of arsenic concentration with well depth (Acharyya *et al.*, 1999; Chowdhury *et al.*, 1999).

The results confirm the findings of weak correlations found between well depth and total arsenic concentrations (Spearman’s rho, $r=0.43$ and 0.42 for dry and wet seasons, $p>0.05$) (Table 6.6 and 6.7). The high arsenic levels are predominantly in the shallower wells and confined aquifers as compared to the deeper wells. Thus the source of high arsenic concentrations in the various wells and boreholes are as a result of anthropogenic induced activities such as large scale mining from AngloGold Ashanti mines and illegal artisanal

mining activities spread across the study area. Hence the potential anthropogenic source of arsenic in the study area may be attributed to mining.

Gold reserves have long been mined in south-western part of Ashanti Region of Ghana. The gold there is also associated with sulfide mineralization, particularly arsenopyrite. Arsenic mobilizes in the local environment as a result of arsenopyrite oxidation, and is induced or aided by the mining activity. The minerals pyrite and arsenopyrite in the rocks tend to release arsenic which is sufficient to cause the local distribution of arsenic, and this would primarily affect shallow wells. Nonetheless, the presence of high As concentration levels in some of the deeper wells are partly associated with natural sources contained in the surficial materials in the bedrock from which the groundwater is extracted.

6.5.2 Association of As with Well Depth and Three Chemical Constituents

For the current study, concentration levels of As in both seasons were assessed based on its association with well depth and three chemical constituents namely – dissolved oxygen (DO), hydrogen ion concentrations (pH) and electrode potential (Eh).

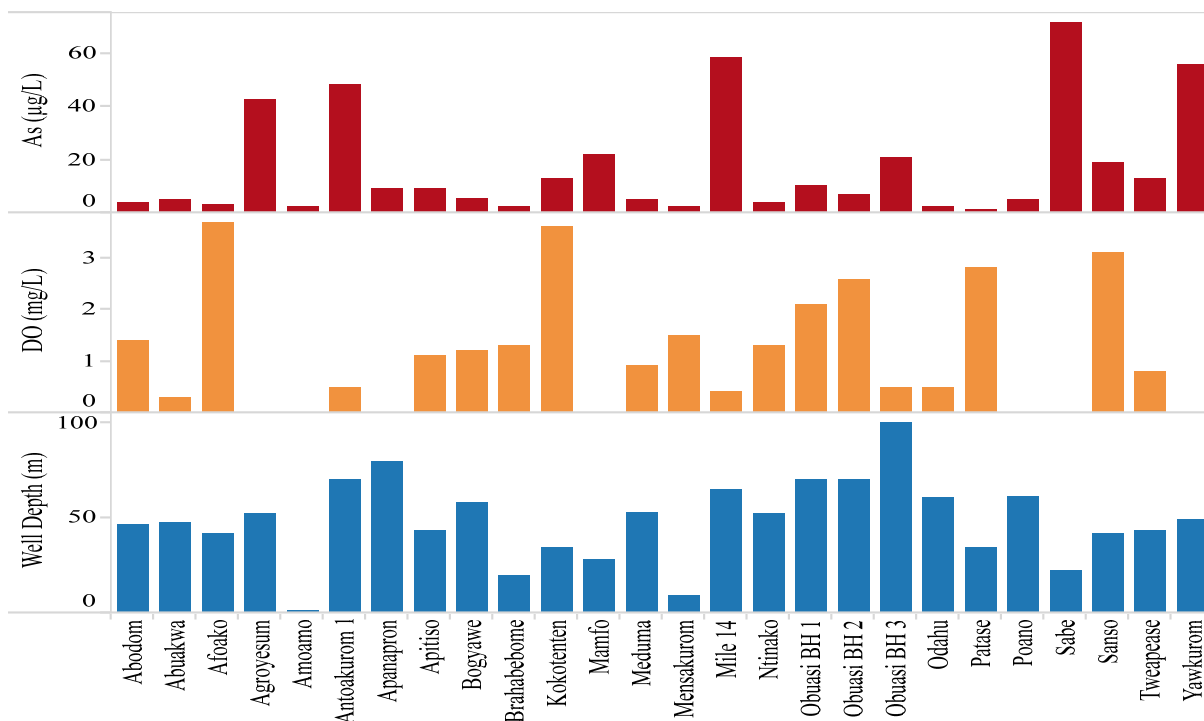


Figure 6.9a: Relationship between well depths, total-Arsenic and dissolved oxygen (DO) during the dry season.

With increasing depth and residence time, dissolved O₂ was gradually consumed by the oxidation of sulphide minerals and mildly reducing conditions became prevalent and it is likely this explains why higher As concentrations were observed in low-oxygen; more reducing groundwaters during both the dry and wet seasons, respectively in the study area (Figure 6.9a and b).

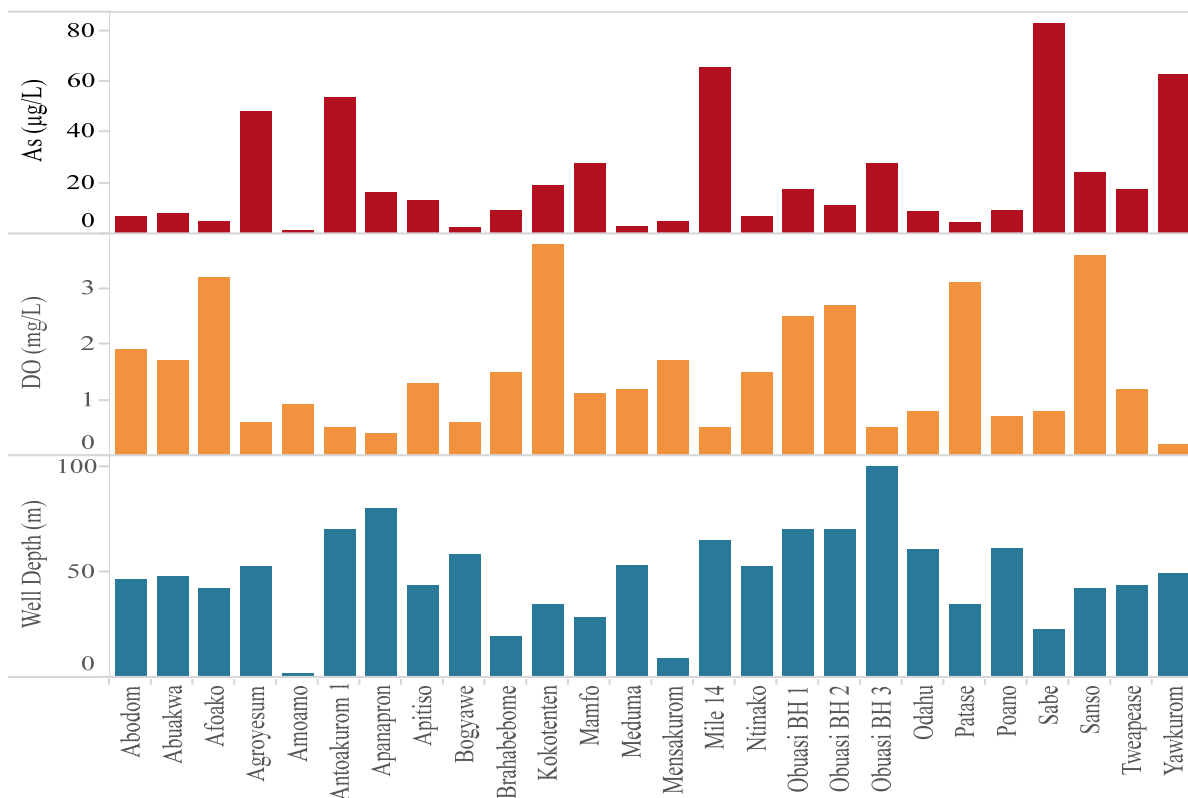


Figure 6.9b: Relationship between well depths, total-As and dissolved oxygen (DO) during the wet season.

The oxidation process normally releases Fe and SO₄ (and arsenopyrite releases As) into solution. Under such conditions, As in sulphide minerals is not readily oxidized to As-V and As-III constitutes an important proportion of the total As present. The lower sorption affinity of arsenite for ferric hydroxide, coupled with the higher solubility of the latter under more reducing conditions, allows As to remain as a stable soluble oxyanion species in the deeper, more reducing groundwater environment.

In the deepest parts of the aquifer (>60 m) as observed in the study area, the groundwater is more reducing with negligible dissolved O₂ concentrations with the exception of Obuasi BH 1 and 2 which recorded a relatively high levels of DO during the dry seasons (2.1 and 2.6

mg/L) and wet seasons (2.5 and 2.7 mg/L), respectively. Sulphide minerals may be present, but few electron acceptors are available in the aquifer to allow oxidation to proceed significantly.

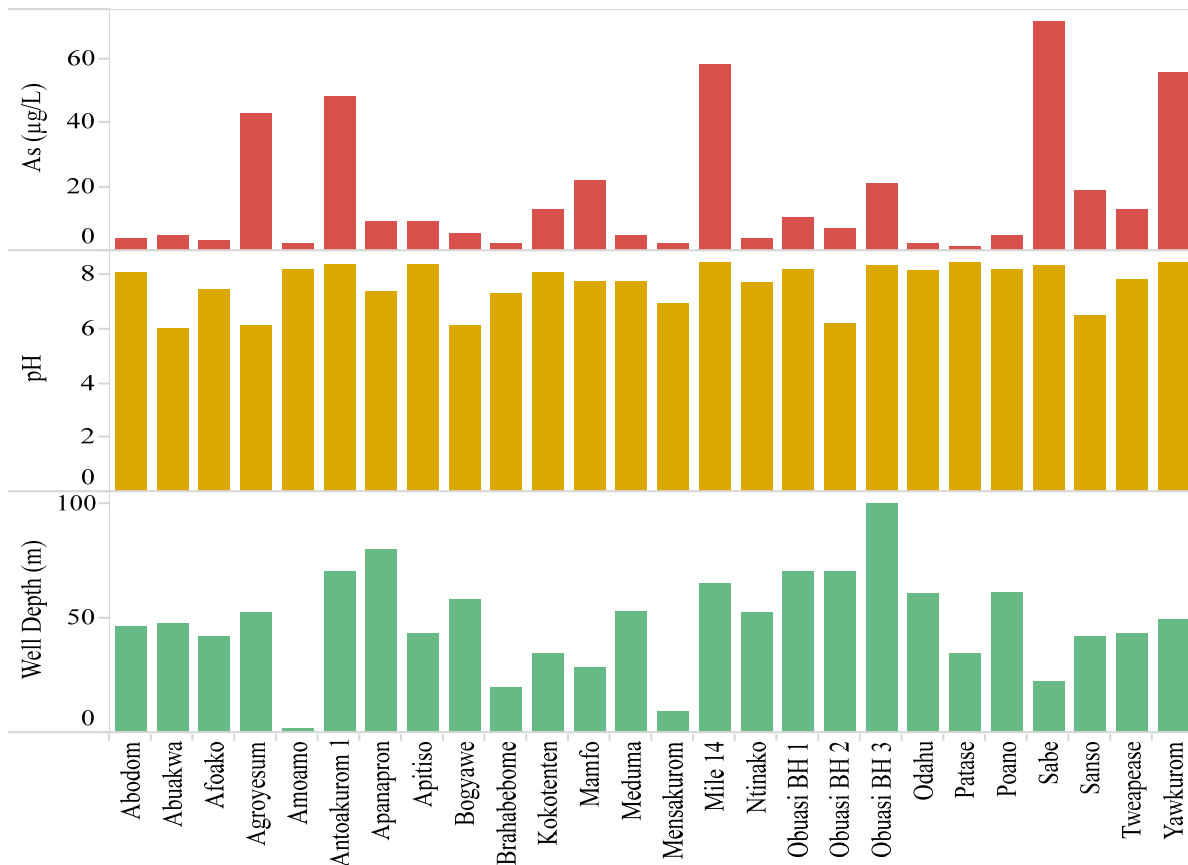


Figure 6.10a: Relationship between well depths, total-As and pH during the dry season

Interestingly, total As concentrations are high at higher groundwater pH ($pH > 6.7$) (Figure 6.10a and b) and under more reducing to less oxidizing conditions, generated by silicate (and carbonate) reaction and consumption of dissolved O_2 with increasing residence time or might be long contact times between groundwater and the aquifer. In these parts of the aquifers, bedrock weathering (lateritization) is less well-advanced and some fresh and partly fresh sulphide minerals remain (Smedley, 1996). Partial oxidation of these leads to the release of As into solution.

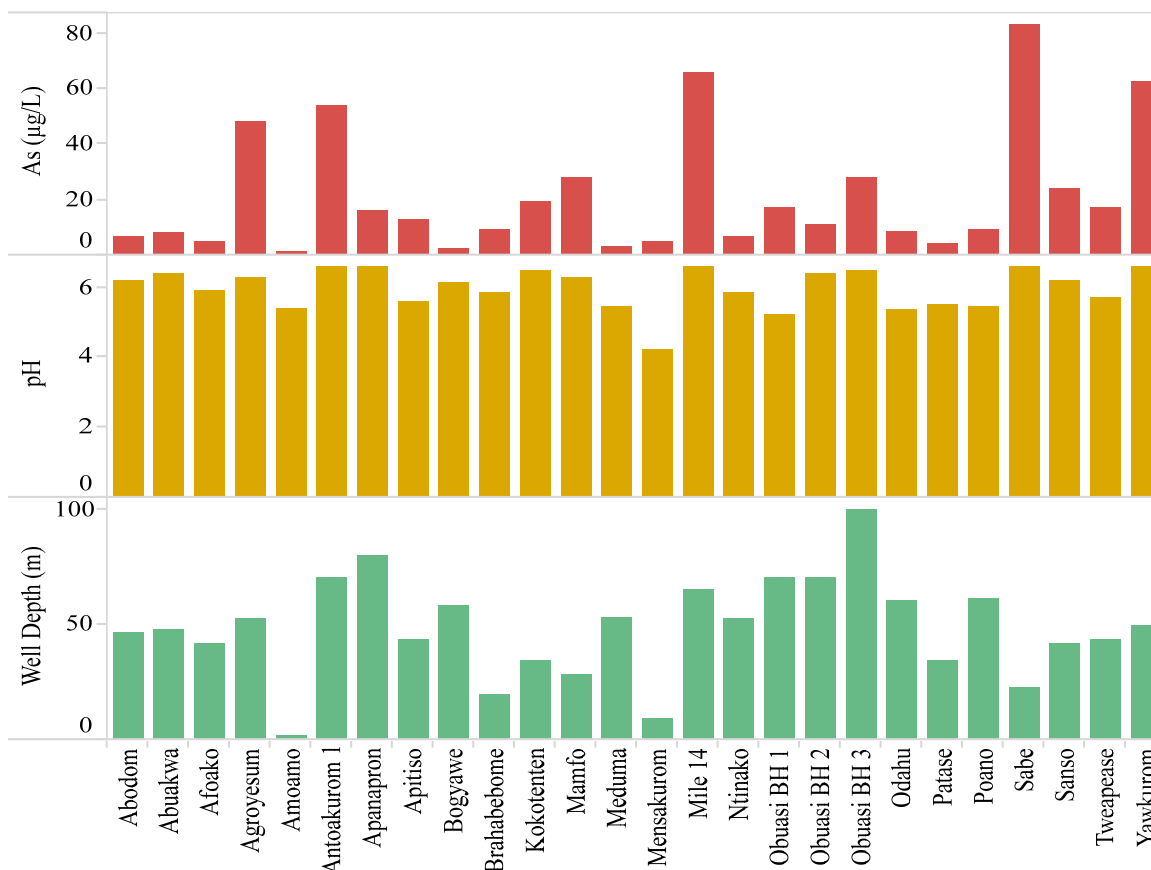


Figure 6.10b: Relationship between well depths, total-As and pH during the wet season

Under the mildly reducing conditions, As is stabilized in soluble form largely as the As-III oxyanion. More reducing groundwaters ($Eh \leq 250$ mV); thus groundwater with low Eh values do not only have higher As-total contents (Figures 6.11a and b) but also largely have higher As-III/As_{total} ratios. This explains why As in sulphide minerals is not readily oxidized to As-V and As-III constitutes an important proportion of the total As present under more reducing conditions during both seasons.

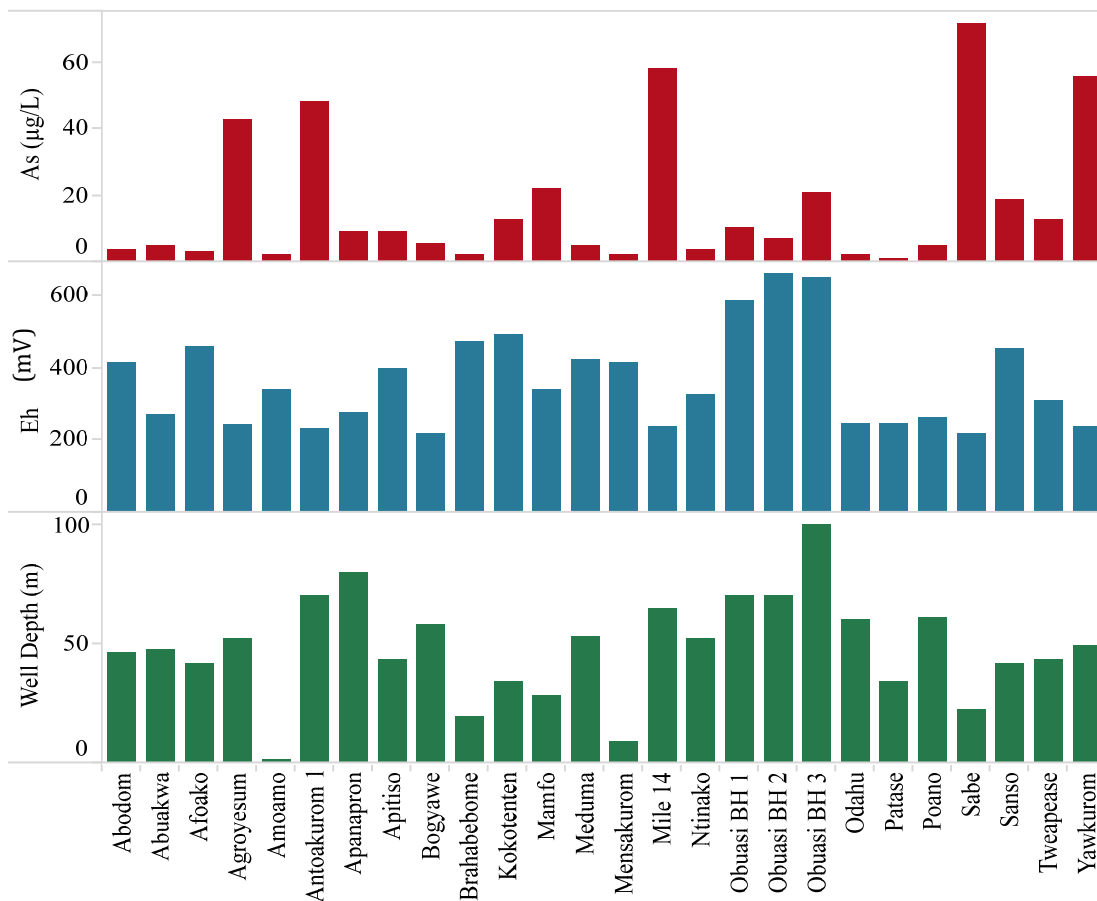


Figure 6.11a: Relationship between well depths, total-As and Eh (electrode potential) during the dry season.

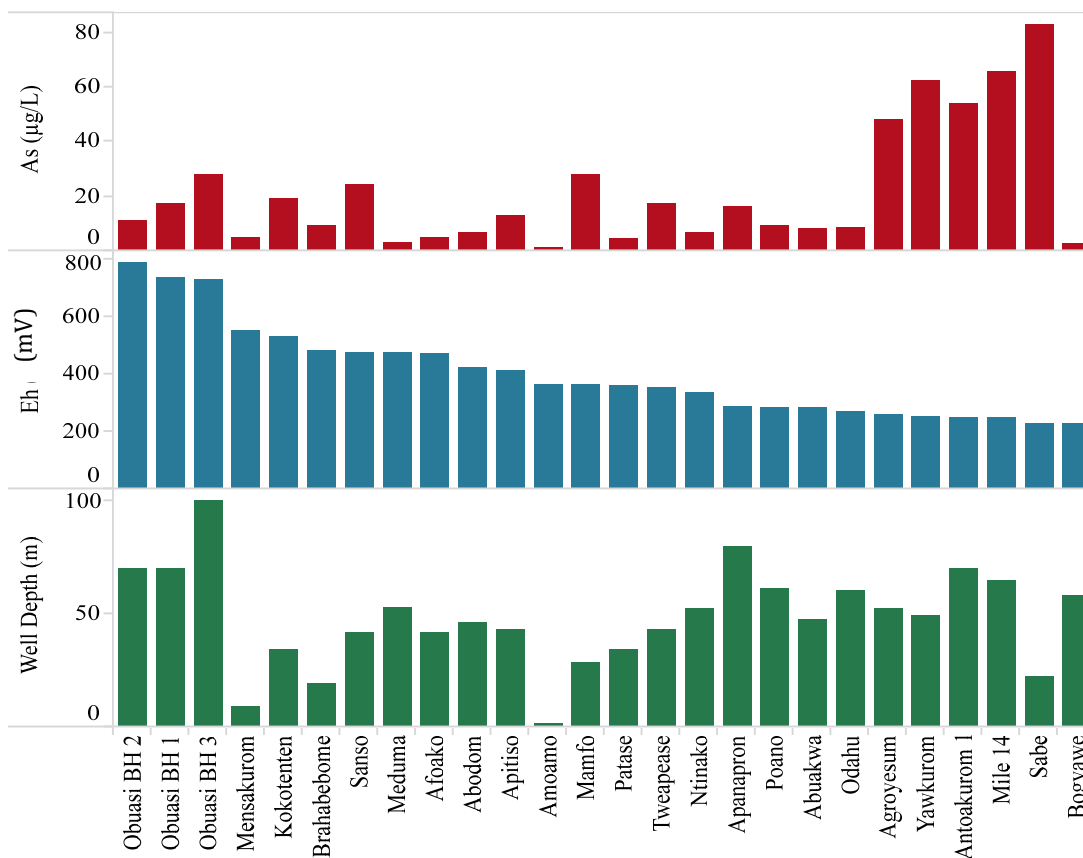


Figure 6.11b: Relationship between well depths, total-As and Eh (electrode potential) during the wet season.

6.6 Distribution and Correlation of Arsenic with other Physicochemical Parameters and Trace Elements in Groundwater

6.6.1 Correlation Studies between Groundwater Geochemical Parameters

A correlation analysis employed was a bivariate method, which simply exhibits how well one variable predicts the other. In this study, the relationship between various elements has been studied using the Spearman rank coefficient which is based on the ranking of the data and not their absolute values. The analytical results of groundwater geochemical parameters was statistically correlated and the correlation coefficient >0.5 are considered to be strongly correlated with other variables. The correlation matrix (Tables 6.6 and 6.7) shows high values of positive and negative correlations among various elements. During the dry season, good correlation was observed between TDS and EC with Ca, Mg and F^- (Table 6.6).

Table 6.6: Correlation matrix for groundwater quality during dry season

Variables	Well Depth	pH	EC	Eh	DO	Na	K	Mg	Ca	Cl	HCO ₃	SO ₄	NO ₃	PO ₄	F	DOC	TDS	Cu	Fe	Mn	Zn	As	
Well Depth	1.000																						
pH	0.162	1.000																					
EC	<i>0.550</i>	0.176	1.000																				
Eh	-0.003	-0.039	-0.097	1.000																			
DO	-0.311	-0.144	-0.322	0.440	1.000																		
Na	0.280	-0.025	<i>0.503</i>	0.077	0.217	1.000																	
K	0.041	0.062	0.133	0.297	0.367	0.240	1.000																
Mg	<i>0.690</i>	0.082	<i>0.716</i>	-0.071	-0.294	0.360	0.089	1.000															
Ca	<i>0.552</i>	0.181	<i>0.796</i>	-0.079	-0.220	0.443	0.123	<i>0.625</i>	1.000														
Cl	0.127	0.235	0.478	-0.194	-0.160	0.235	-0.067	0.191	0.232	1.000													
HCO ₃	0.054	0.112	0.374	-0.221	-0.152	0.247	-0.069	0.237	0.398	0.118	1.000												
SO ₄	-0.370	-0.095	-0.093	0.222	0.326	0.145	0.059	-0.260	-0.048	-0.033	0.350	1.000											
NO ₃	0.024	-0.050	-0.132	0.042	0.053	-0.079	-0.070	-0.066	-0.249	0.105	-0.122	-0.043	1.000										
PO ₄	-0.188	-0.017	-0.098	-0.234	-0.239	-0.255	-0.095	-0.135	0.006	-0.019	0.228	-0.047	-0.147	1.000									
F	0.323	0.193	<i>0.644</i>	-0.163	-0.220	0.333	0.026	0.406	<i>0.537</i>	0.242	0.285	-0.054	-0.250	-0.099	1.000								
DOC	-0.125	-0.238	-0.067	0.167	0.069	-0.050	-0.052	0.020	-0.061	0.174	-0.032	0.010	0.185	0.150	-0.263	1.000							
TDS	<i>0.511</i>	0.122	<i>0.948</i>	-0.162	-0.320	0.493	0.074	<i>0.664</i>	<i>0.719</i>	<i>0.506</i>	0.350	-0.103	-0.076	-0.095	<i>0.602</i>	-0.021	1.000						
Cu	0.096	0.091	0.004	0.352	0.251	0.048	0.282	-0.018	-0.040	0.205	-0.427	-0.098	0.021	0.024	-0.080	0.217	-0.037	1.000					
Fe	0.230	-0.036	0.375	-0.139	-0.263	0.125	-0.118	0.342	0.379	-0.013	0.427	0.178	-0.037	0.054	0.412	-0.168	0.322	-0.361	1.000				
Mn	0.371	0.054	<i>0.701</i>	-0.258	-0.384	0.282	-0.116	<i>0.556</i>	<i>0.523</i>	0.389	<i>0.524</i>	0.069	-0.023	0.029	0.459	-0.115	<i>0.676</i>	-0.242	<i>0.673</i>	1.000			
Zn	-0.183	0.020	0.092	0.151	-0.016	0.150	-0.016	-0.068	0.000	0.307	-0.088	0.240	-0.086	0.032	0.065	0.333	0.061	0.245	0.157	0.052	1.000		
As	0.428	0.430	<i>0.508</i>	-0.091	-0.279	0.150	0.055	0.385	<i>0.529</i>	0.166	0.484	0.066	-0.223	-0.012	0.312	-0.378	0.467	-0.166	0.307	0.420	-0.121	1.000	

The italics are significant values because those values are exceeding >0.5 and it is considered to be strongly correlated with other variables

It reveals that high concentration of calcium, magnesium and fluoride levels can be resulted from dissolution of the carbonate minerals, such as calcite and dolomite which are abundant among sedimentary rocks in the study area as well as dissolution of fluoride minerals. There was also a strong correlation observed between EC and Na as well as TDS and Cl⁻. This high concentration of sodium and chloride levels can be resulted from weathering of plagioclase feldspar, road salts, and also due to heavy exploitation of groundwater (Hem, 1985) and chloride derived from anthropogenic input in groundwater (Sunil Kumar and Ramanathan, 2008) as no regular sources from lithology is noted. It can also result from salts in the soils which have been accumulated by evaporation.

During the wet seasons (Table 6.7), TDS and EC shows good correlation with Ca²⁺, Mg²⁺ and Na⁺ indicating, Ca and Mg²⁺ derived from carbonate weathering as well as Na⁺ deriving from silicate weathering and/or dissolution of soil salts (Na₂SO₄).

EC and TDS were found to be higher in wet seasons than the dry seasons, due to availability of higher surface areas of rock matrix for dissolution (Srinivasamoorthy *et al.*, 2007). Besides the positive correlation exhibited between the above-mentioned parameters, PO₄, SO₄, NO₃ and DOC did not show any significant relation with any parameter during the study.

Among the heavy metals, Mn–Fe exhibited good correlation followed by the pairs such as Mn–Zn, Fe–Zn, Cu–Zn and Mn–As showed relatively moderate correlation whereas Mn–Cu, Fe–Cu, Fe–As, Cu–Zn, Cu–As and Zn–As showed relatively lower correlations due to dilution effect.

Table 6.7: Correlation matrix for groundwater quality during the wet season

Variables	Well Depth	pH	EC	Eh	DO	Na	K	Mg	Ca	Cl	HCO ₃	SO ₄	NO ₃	PO ₄	F	DOC	TDS	Cu	Fe	Mn	Zn	As	
Well Depth	1.000																						
pH	0.274	1.000																					
EC	<i>0.518</i>	0.282	1.000																				
Eh	-0.057	-0.239	-0.186	1.000																			
DO	-0.419	-0.263	-0.377	0.467	1.000																		
Na	0.277	0.039	<i>0.510</i>	0.083	-0.025	1.000																	
K	0.189	0.195	0.032	0.161	0.061	-0.078	1.000																
Mg	<i>0.546</i>	0.181	<i>0.663</i>	-0.164	-0.384	0.263	0.005	1.000															
Ca	<i>0.532</i>	0.463	<i>0.700</i>	-0.101	-0.309	0.365	0.190	<i>0.575</i>	1.000														
Cl	-0.041	-0.158	0.098	0.087	0.028	0.218	-0.127	-0.006	0.030	1.000													
HCO ₃	0.044	0.403	0.374	-0.238	-0.185	0.362	-0.098	0.246	0.429	0.100	1.000												
SO ₄	-0.351	-0.096	-0.099	0.288	0.291	0.153	0.058	-0.112	-0.010	0.103	0.329	1.000											
NO ₃	-0.108	-0.194	-0.038	0.035	0.230	0.013	-0.205	0.002	-0.207	0.240	-0.112	0.038	1.000										
PO ₄	-0.142	0.153	-0.040	-0.346	-0.109	-0.185	0.004	-0.142	0.000	-0.083	0.159	-0.176	0.081	1.000									
F	0.211	0.050	0.389	-0.066	-0.130	0.168	0.302	0.190	0.336	-0.004	0.210	-0.005	-0.302	-0.113	1.000								
DOC	-0.079	-0.162	-0.166	0.141	0.049	-0.106	-0.065	-0.016	-0.057	0.114	-0.127	0.015	0.248	0.005	-0.312	1.000							
TDS	<i>0.529</i>	0.261	<i>0.861</i>	-0.140	-0.331	0.497	0.049	<i>0.611</i>	<i>0.645</i>	0.154	0.340	-0.140	-0.066	-0.077	0.442	-0.018	1.000						
Cu	0.211	-0.004	0.139	0.405	0.110	0.128	0.152	0.123	0.101	0.000	-0.280	0.032	0.041	-0.102	-0.048	0.153	0.092	1.000					
Fe	0.260	0.147	0.357	-0.100	-0.177	0.078	0.026	0.270	0.323	-0.051	0.413	0.194	-0.057	-0.152	0.295	-0.318	0.186	-0.299	1.000				
Mn	0.424	0.252	<i>0.771</i>	-0.266	-0.416	0.406	-0.060	<i>0.542</i>	<i>0.531</i>	0.249	<i>0.521</i>	0.013	-0.016	-0.080	0.323	-0.208	<i>0.680</i>	-0.038	<i>0.510</i>	1.000			
Zn	-0.196	-0.165	0.153	0.099	-0.087	0.133	-0.147	0.062	-0.031	-0.032	0.055	0.264	0.012	-0.049	0.099	0.171	0.041	0.130	0.096	0.156	1.000		
As	0.414	0.402	<i>0.538</i>	-0.052	-0.354	0.330	0.054	0.334	<i>0.527</i>	-0.089	<i>0.525</i>	0.038	-0.310	0.044	0.218	-0.367	0.446	0.078	0.423	0.478	-0.051	1.000	

The italics are significant values because those values are exceeding >0.5 and it is considered to be strongly correlated with other variables

6.6.2 Correlation Studies of Arsenic with other Physico-chemical Parameters

The correlations between As concentrations in groundwater with NO_3^- , SO_4^{2-} , DOC, PO_4^{3-} and HCO_3^- during both the dry and wet seasons are shown in Table 6.6 and 6.7. As concentration increases with decreasing NO_3^- and SO_4^{2-} concentrations in most of the groundwater samples analyzed during both seasons. This suggests that high As concentrations are associated with reducing conditions in the aquifer system. This corroborates the findings of Kar *et al.*, (2010).

However, relatively, high SO_4^{2-} concentrations were evident in the present study during both seasons at wells from Brahabebome, Sanso, Kokotenten, Mensakurom, Obuasi BH1, BH2 and BH3 all found within Obuasi municipality compared to the generally low SO_4^{2-} concentrations in other As-affected wells (Table 6.1 and 6.2).

Total As concentrations weakly correlated with the concentrations of SO_4^{2-} in both season. DOC and NO_3^- , however, negatively correlated with As during both dry and wet seasons, respectively (Table 6.6 and 6.7).

Phosphate concentration shows negative and weak correlation with As in groundwater during dry and wet seasons, respectively which could point to a possible competition of As with PO_4^{3-} ion (Su and Pulse, 2001) or a similar mobilization process (Rowland *et al.*, 2008).

Strong correlation was observed between As and HCO_3^- (Table 6.6 and 6.7) in the study area during dry and wet seasons. High HCO_3^- concentrations achieved may generate either from the oxidation of organic matter by microorganisms during reduction of Fe oxyhydroxides and release of As (Nickson *et al.*, 1998, 2000; McArthur *et al.*, 2004; Kar *et al.*, 2010), or due to the desorption of As oxyanions under the competitive sorption effect of elevated HCO_3^- (Stollenwerk *et al.*, 2007).

NO_3^- and DOC concentrations are relatively low and there is a weak statistical correlation between these two parameters during both seasons (Table 6.6 and 6.7); this does not support the suggestions that reducing conditions in the groundwater are being driven by the microbial degradation of natural organic matter (Ujevic' *et al.*, 2010).

6.6.3 Correlation Studies of Arsenic with Trace Elements in Groundwater

The distribution of As, Fe and Mn in groundwaters from the study area are also depth-dependent with significantly higher concentrations in the intermediate wells (20–70 m depth), characterized by lower Eh and higher pH conditions, generated as a result of rock reaction, oxidation reactions and residence time during the entire seasons (dry and wet seasons). However, the deepest well (Obuasi BH 3) with a depth of 100 m is also enriched with As and Fe having mean concentration levels of 21.0 µg/L and 12.03 mg/L, during the dry season and 28.0 µg/L and 16.33 mg/L during the wet seasons, respectively (Table 6.1 and 6.2). Groundwaters abstracted from the deepest level in the study area are more reducing with negligible dissolved O₂ concentrations. Hence, sulphide oxidation should be slow under such conditions.

Among the elements, Fe and Mn in groundwater may be associated with the presence of arsenic. Fe concentrations vary over a wide range, from below detection limit (<0.01 mg/L) up to 12.3 mg/L and from <0.01 mg/L to 16.33 mg/L during the dry and the wet seasons, where as Mn varied from 1.8 to 498 µg/L and 2.3 to 583.8 µg/L in the dry and wet seasons, respectively. As correlated moderately with Mn, likewise Fe (Table 6.6 and 6.7) during both seasons. As correlating moderately with Fe is in variance to what is generally expected in case of As release as a result of reductive dissolution of Fe oxides in such reducing environments, which implies additional mechanisms. However, the results corroborates the findings of Ujevic' *et al.*, (2010) who did a similar study in Eastern Croatia relating their observation to an increase of the net Fe precipitation rate, when pH increases to the circumneutral range, resulting in lower Fe concentrations in solution.

Additionally, lack of strong correlation between As and Fe concentrations highlights the occurrence of superimposed mechanisms. This lack of strong correlation has been observed elsewhere (e.g. Bangladesh, Inner Mongolia, Taiwan and West Bengal district of India) and attributed it to the precipitation of secondary Fe, once Fe oxides have been reduced and solubilized (Ujevic' *et al.*, 2010).

Nonetheless, Mukherjee-Goswami *et al.*, (2008) cited other processes that may result in poor As–Fe correlations: (i) arsenic and iron may be sequestered differentially into diagenetic pyrite or secondary iron oxide phases; (ii) dissolved iron may be derived from weathering of

biotite and/or (iii) arsenic, originally sorbed to Mn-oxides but released during reduction, may be resorbed to FeOOH (or residual Mn oxides) rather than being released to groundwater.

The variability of As, Fe and Mn in the shallow aquifer is probably the result of complex precipitation-dissolution processes combined with biodegradation of organic matter (Bhattacharya *et al.*, 2006; McArthur *et al.*, 2001; Hasan *et al.*, 2007). There is however, a strong correlation between Fe and Mn concentrations in groundwater samples from the study area as a result of their similarity in terms of geochemical behavior.

Of the other elements, Zn and Cu showed significant presence at various depths during both seasons (Table 6.3 and 6.4). High concentrations of Zn may be derived from the new metallic pumps and decrease with age. Addition of Zn fertilizer to soil in some of the farming areas closer to monitoring wells and boreholes within the study area may also increase Zn availability in groundwater. Some other potentially harmful metals like Cu also showed their heterogeneity in groundwater at different depths.

6.7 The Effect of Season on Groundwater Quality

6.7.1 Cluster Analysis

In this study, R-mode and Q-mode cluster analysis were used such that R-mode depicts relationships between variables, while Q-mode identified relationships between samples. So the hydrochemical results of all samples were statistically analyzed. Generally, prior to cluster analysis data were normalized, the weight per group method was applied in Euclidean distance (Sharaf and Subyani, 2011).

The analytical results of multivariate analysis were performed for the set of groundwater samples from 63 monitored wells and 21 variables. Figure 6.13 shows the R-mode cluster analysis dendrogram of the 21 descriptors. The variables cluster into two major groups. From this dendrogram one can find the relationship between different variables. With this hierarchical cluster analysis, the chemical species were grouped based on their concentrations. PO₄, F, NO₃, Fe, DO, K, DOC, SO₄, pH, Cl, Mg, Na, Ca, Cu and As were grouped together (Figure 6.12). EC, TDS, HCO₃, Mn, Zn and Eh formed cluster two. Although Zn and Eh had a relatively higher linkage, they were closely related based on the fact that they did not correlate with any other variables analyzed.

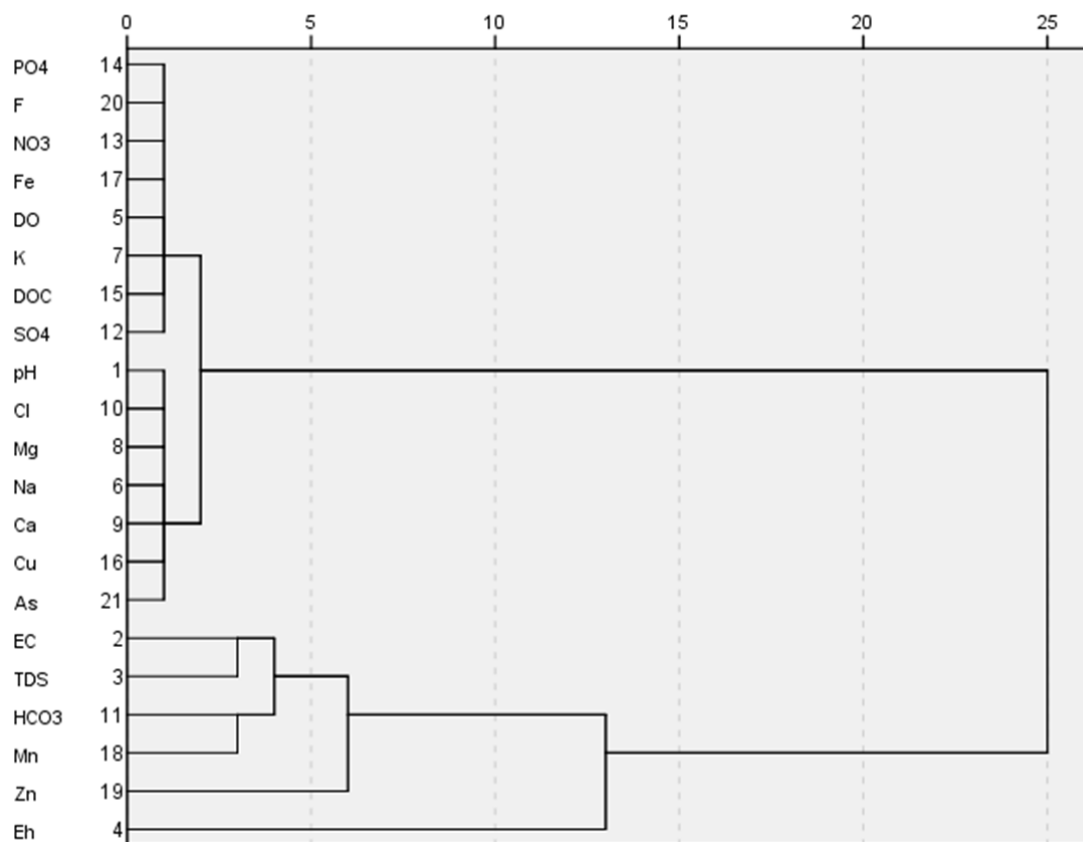


Figure 6.12: Dendrogram for 21 variables from cluster analysis in R-mode

Figure 6.13 shows the clustering of the wells in Q-mode according to the similarity. Sixty three sampled sites were categorized into three (3) clusters using the Q-mode hierarchical cluster analyses. With this analysis, 28 sampled locations comprised the first cluster, 32 sampled locations formed the second cluster and 3 locations including Obuasi BH3, BH1 and BH2 the third cluster, (Figure 6.13). The third cluster had their distance of linkage greater than that of the other clusters. This linkage could be attributed to the fact that, those wells were situated within the same vicinity. There is a distinct relationship between the clusters and well locations. The first cluster is made up of community wells (Sabe, Mile 14, Yawkurom, Antoakurom1, Agroyesum, Mamfo, Twepease, Apanapron and Apitiso) that contain the highest concentration levels of arsenic in all the wells monitored during the dry and the wet seasons. However, Sanso community well which also registered high As concentration levels was found situated in cluster 2 while Obuasi BH1, Obuasi BH2 and Obuasi BH3 observing high As concentrations made up of the third cluster.

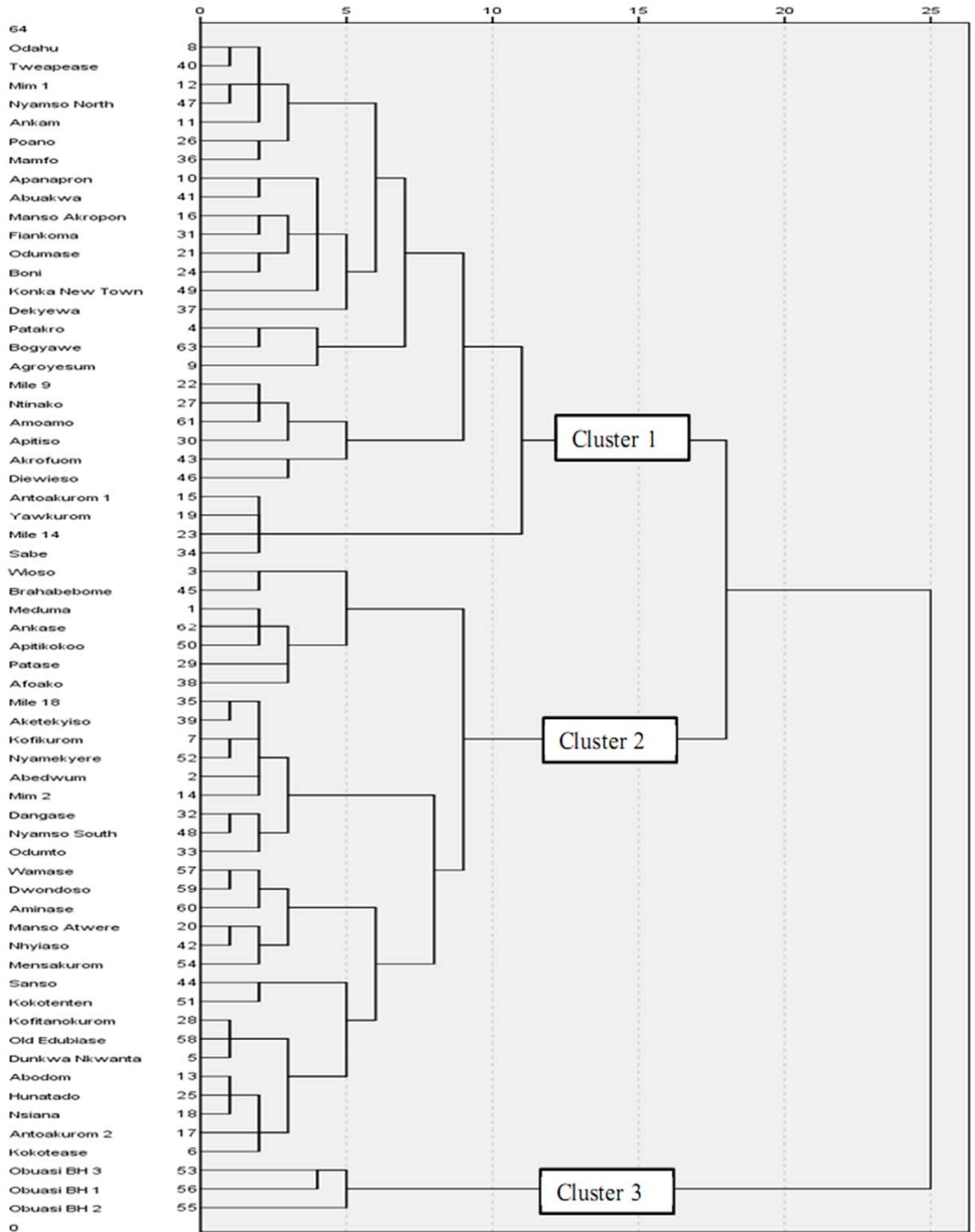


Figure 13: Dendrogram for 63 sampled wells from cluster analysis in Q-mode

6.7.2 Factor Analysis

To identify the similarity and dissimilarity of the physicochemical variables and classifying the pollution sources, factor analysis (FA) was carried out using SPSS. In order to determine the number of factors, the variances and co-variances of the variables were computed. Then, the Eigen values and Eigen vectors were evaluated for the covariance matrix and the data was transformed into factors. Table 6.8 presents the Eigen value and percentages of variance associated with each factor. These values were also summed to express as cumulative Eigen value and percentage of variance. A total of four factors were identified in both seasons. It is observed in terms of total variance, loading matrix and Eigen value exhibited by the same factor.

Table 6.8: Physicochemical results of factor analysis scores

Parameters	Dry season				Wet season			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.132	-0.101	0.139	0.364	0.164	-0.258	-0.599	-0.080
EC	<i>0.912</i>	-0.026	0.301	0.012	<i>0.941</i>	-0.041	0.058	-0.004
Eh	0.292	<i>0.577</i>	0.139	-0.186	<i>0.467</i>	<i>0.627</i>	-0.023	0.231
DO	-0.160	<i>0.761</i>	-0.019	0.052	-0.226	<i>0.738</i>	0.151	-0.045
HCO ₃ ⁻	<i>0.537</i>	-0.219	-0.307	0.314	0.342	-0.372	-0.038	-0.544
F ⁻	0.404	-0.064	-0.036	0.371	0.196	0.143	-0.392	-0.305
Cl ⁻	0.256	-0.190	<i>0.618</i>	0.006	0.298	-0.068	<i>0.612</i>	0.021
SO ₄ ⁻	<i>0.485</i>	0.387	-0.138	-0.143	<i>0.499</i>	<i>0.570</i>	0.095	-0.130
PO ₄ ⁻	-0.116	-0.320	0.151	0.076	-0.108	-0.539	0.185	0.015
Na ⁺	<i>0.555</i>	0.308	0.068	0.120	<i>0.476</i>	0.195	0.146	-0.436
K ⁺	-0.011	<i>0.465</i>	0.199	0.338	0.029	0.089	-0.660	0.244
Mg ²⁺	<i>0.829</i>	0.125	0.035	-0.058	<i>0.872</i>	0.083	-0.019	0.086
Ca ²⁺	<i>0.902</i>	0.021	-0.033	0.118	<i>0.895</i>	-0.078	-0.170	-0.008
NO ₃ ⁻	0.065	-0.025	-0.054	-0.434	0.137	0.036	<i>0.617</i>	0.184
DOC	0.064	-0.114	0.222	-0.491	0.133	-0.220	0.254	<i>0.681</i>
TDS	<i>0.747</i>	-0.083	0.237	-0.109	<i>0.788</i>	-0.069	0.187	0.049
Eigen values	6.110	2.447	1.135	1.035	6.457	3.115	1.831	1.437
% of variance	27.772	11.122	5.159	4.706	29.352	14.158	8.322	6.532
Cumulative %	27.772	38.893	44.052	48.758	29.352	43.509	51.831	58.363

The italics are significant values because those values are exceeding >0.5 and it is considered to be strongly correlated with other variables

During dry season, Factor I represents 27.77 % of total data variance (TDV), with high positive factor loadings of EC, HCO₃⁻, Na⁺, Mg²⁺, Ca²⁺, SO₄⁻ and TDS indicating high concentration of ions, influenced by a similar source. The higher loading in HCO₃⁻, Ca²⁺, Mg²⁺ and Na⁺ ions might be due to weathering of minerals along the flow-paths. Factor II

was represented by high positive loadings of Eh, DO and K^+ with 11.12 % of TDV. Factor III represented with 5.16 with high positive loading of Cl^- . The variability caused by Cl^- was insignificant, and this could be attributed to variable redox processes and biotic activities within and surrounding well screens (Gbolo and Gerla, 2013). Factor IV was not considered because they had factor loadings less than 0.50 and it does not have important role in determining the whole water chemistry of the groundwater during the dry season.

During wet season, Factor I represents 29.35 % of TDV with high positive loadings of EC, Eh, SO_4^- , Na^+ , Mg^{2+} , Ca^{2+} and TDS. Ca^{2+} and Mg^{2+} from ion exchange processes derived from carbonate dissolution as an indication of a similar source. Factor II (14.16 TDV), represented by high positive loadings of Eh, DO and SO_4^- indicate carbonate dissolution. Factors III indicates high positive loadings of Cl^- and NO_3^- with 8.32 indicating the influence of agricultural activities from leaching of plant nutrient and nitrate fertilizers (Freeze and Cherry 1979; Madison and Brunett 1984; Vasanthavigar *et al.*, 2012). Factor IV with 6.53 of TDV represent anthropogenic impact (decomposition of organic material) indicating positive loading of DOC. Generally, in many cases, the factor loading patterns of minor factors tend to compensate for the gap between the actual water chemistry and that composed by the combination of the major factors. The variations in factors for both seasons could also be due to the relationship between the chemical species and water level within individual wells.

6.7.3 Student's test (t-tests) for difference of means

To examine the effect of season on groundwater quality, *t*-tests was carried out for the combined data of dry and wet seasons. Results of the calculated *t*-tests are shown in Table 6.9. The table value (critical value) at 232 degrees of freedom is -1.65 for left-sided alternative hypothesis (after Subba Rao, 2006; Chattopadhyayi *et al.*, 2010). Since the computed values of *t* are less than the critical value of -1.65 for all the variables precluding Cu, the difference of means between dry and wet seasons is significant at 5 % level. Hence, the results clearly indicate that there is evidence of seasonal effect on the mean values of groundwater quality.

Table 6.9: Season-wise combined chemical composition of groundwater samples collected from the study area.

Chemical constituents	Dry season			Wet season			<i>t</i>	Remark
	Mean	σ	CV	Mean	σ	CV		
pH (units)	7.22	0.75	10.39	5.70	0.74	12.98	-11.73	significant
EC ($\mu\text{S}/\text{cm}$)	200.30	168.84	84.29	240.13	209.74	87.34	-5.37	significant
Eh (mV)	357.32	104.54	29.26	382.49	119.78	31.32	-5.62	significant
DO (mg/L)	1.53	0.86	56.10	1.92	0.84	43.75	-7.87	significant
HCO ₃ ⁻ (mg/L)	96.53	55.32	57.31	141.95	102.08	71.91	-4.54	significant
F ⁻ (mg/L)	0.13	0.09	72.31	0.10	0.09	93.00	-3.07	significant
Cl ⁻ (mg/L)	8.01	7.15	89.26	10.92	10.72	98.17	-2.33	significant
SO ₄ ⁻ (mg/L)	2.24	1.36	60.71	2.53	2.47	97.63	-7.26	significant
PO ₄ ⁻ (mg/L)	0.20	0.08	40.00	0.22	0.08	36.36	-4.58	significant
Na ⁺ (mg/L)	17.06	6.59	38.63	22.85	9.21	40.31	-7.19	significant
K ⁺ (mg/L)	1.02	0.09	88.24	1.78	1.30	73.03	-6.48	significant
Mg ²⁺ (mg/L)	7.85	5.06	64.46	11.32	6.13	54.15	-14.57	significant
Ca ²⁺ (mg/L)	15.04	12.03	79.99	19.19	14.17	73.84	-11.61	significant
NO ₃ ⁻ (mg/L)	0.94	0.50	53.19	1.13	0.46	40.71	-5.79	significant
DOC (mg/L)	1.64	0.99	60.37	2.12	0.98	46.23	-14.01	significant
TDS (mg/L)	145.79	133.89	91.84	173.22	143.30	82.73	-10.22	significant
Fe (mg/L)	1.75	0.84	48.00	2.35	1.73	73.62	-3.21	significant
Mn ($\mu\text{g}/\text{L}$)	118.53	82.12	69.28	150.51	96.07	63.83	-7.05	significant
Zn ($\mu\text{g}/\text{L}$)	109.15	73.48	67.32	135.32	86.93	64.24	-2.59	significant
Cu ($\mu\text{g}/\text{L}$)	18.24	15.63	85.69	18.97	16.12	84.98	-1.16	insignificant
As ($\mu\text{g}/\text{L}$)	17.98	10.28	57.17	22.51	11.63	51.67	-7.03	Significant

Seasonal variation in the concentrations of chemical constituents (Table 6.9) might be as a result of reaction of the chemical constituents with rain water and/or leaching of soil salts by recharge waters during raining season. For example, variation in the concentrations of Na⁺ (17.06–22.85 mg/L) and Cl⁻ (8.01–10.92 mg/L) from dry to wet seasons is more prominent by virtue of their higher solubility. The concentration of Ca²⁺ as well as that of Mg²⁺ varies from 15.05 to 19.19 mg/L and 7.86 to 11.31 mg/L, respectively and dominant in the wet season. This is caused by ion exchange between Na⁺ and Ca²⁺ and/or precipitation of CaCO₃ (Subba Rao, 2006), suggesting an enrichment of Na⁺ relative to Ca²⁺ and attaining higher concentration of Mg²⁺ than Ca²⁺ in the groundwater.

The content of K⁺ is also more in the wet season (1.78 mg/L) than in the dry season (1.02 mg/L), as a result of lack of absorption of K⁺ onto the clay horizons. In the case of HCO₃⁻ and SO₄²⁻ ions, their variations are also significant in the wet season (141.95 and 2.55 mg/L) compared to that in dry season (96.53 and 2.24 mg/L) indicates the role of leaching activity (Subba Rao, 2003). Again, there is a considerable variation of NO₃⁻ from dry season (0.74

mg/L) to wet season (1.05 mg/L), reflecting the involvement of anthropogenic sources. Thus, the groundwaters with concentrations in both seasons are characterized by $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$; $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^{2-}$ facies (Appendix 4).

These variations are also reflected clearly in the concentrations of DOC and TDS. For instance, the concentration of DOC in the wet season is more (2.12 mg/L) than in the dry season (1.64 mg/L) in the groundwaters. Similarly, the TDS shows higher concentration in wet season (173.2 mg/L) than in dry season (145.9 mg/L), because of leaching of various salts into the groundwaters as a result of the rain water by infiltrating recharge waters. Per the results for the statistical analysis data (Table 6.9), the seasonal effect of the concentrations of TDS, DOC, Na^+ , Ca^{2+} , Mg^{2+} , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^{2-} and F^- were observed to be significant in the groundwater quality of the study area.

6.8 Natural versus Anthropogenic Source of Arsenic in Groundwater

South-western part of Ashanti Region of Ghana is one of the major mining centers in Ghana. The area (for instance Obuasi municipality) houses the administrative headquarters of one of the largest gold mining firm in Africa; Ashanti Goldfields Company, now AngloGold Ashanti mine with some other illegal artisanal mining activities sparsely located within the area, which leads to much discussion about whether or not As within the groundwater sources is derived from anthropogenic or natural sources.

The investigation by Akabzaa *et al.*, (2005) of Obuasi Municipality showed the highest As concentrations in sediments and stream water. A recent study of arsenic concentrations in tailings dams and soils around mining site show highest As concentrations in some areas of south-western Ashanti (Antwi-Agyei *et al.*, 2009; Bempah *et al.*, 2013). These elevated As concentrations in the top soil can leached into the sub-soil and ultimately the aquifers.

However, the areas with higher As concentrations in soils, sediments and the tailings dams related positively with areas where high As concentrations have been observed in the groundwater in this study particularly in wells close to the AngloGold Ashanti mine (Obuasi BH 1, 2 and 3), Amansie West and Central districts where there is intensive illegal artisanal mining activities (“Galamsey”). Further, most of the wells showing the highest As values, possibly originating from anthropogenic inputs, exhibited low SO_4^{2-} , NO_3^- and Cl^-

concentrations. This may suggest increased As concentrations in the groundwaters are related to As release from the soil.

6.9 Classification of Arsenic Contaminated Wells in Hypothesis I and II

Due to large scale mining and illegal artisanal mining activities in south-western part of Ashanti Region of Ghana, it is generally agreed that anthropogenic activities, are the dominant source of arsenic contamination in the study area. However, natural processes also contributed to the release of As into the groundwater resources in the study area. Several hypotheses have been put forward as to the source and release mechanisms of arsenic in groundwater. The results of the total mean of the water quality constituents observed from the monitored wells and boreholes during both seasons (dry and wet) in the study area were used to classify the wells and boreholes into redox conditions (Table 6.10) relating to the two main hypotheses (section 1.3 of Chapter one) prevailing to describe the cause (mobilization) of arsenic into the groundwater of the south-western part of Ashanti Region of Ghana.

Table 6.10: Concentrations of water-quality constituents used to classify redox conditions of samples from south-western part of Ashanti Region of Ghana (Modified from Svensson, 2007)

Class	Redox Classification	Fe (mg/L)	SO ₄ (mg/L)	Mn (mg/L)
1	High redox potential/aerobic water	<0.1	>5	<0.05
2	Moderately to high Redox potential/aerobic water	<0.1	>5	>0.05
3	Low redox potential anaerobic water	>0.1	>5	>0.05
4	Very low redox potential/anaerobic water	>0.1	<5	>0.05
5	Mixed water			
	Type 1	<0.1	<5	All values
	Type 2	>0.1	All values	<0.05

6.9.1 Hypothesis I Wells

Wells from Mensakurom had one of the least arsenic concentrations of 3.5 µg/L. The sulphate concentration of 6.11 mg/L was among the highest of the wells sampled. Unlike sulphate, iron concentration was 1.55 mg/L. The redox classification put the well in redox class 1. The data indicate that the water is aerobic with a long contact time between water and bedrock which means that the well is a hypothesis I well.

The wells from Sanso, Obuasi BH 1, Obuasi BH 2 and Obuasi BH 3 had arsenic concentrations of 21.5, 13.5, 9.0 and 24.5 $\mu\text{g/L}$, respectively. Iron, sulphate and manganese concentrations for the respective wells in those areas were high which put the wells into redox class 3. Again, the wells were having a relatively high dissolved O_2 and redox potential which points to redox class 3. Nonetheless, their redox classification was again confirmed by the arsenic speciation which showed As-III as predominant As species. From these results the conclusion can be drawn that the processes leading to high arsenic concentrations in the above-mentioned wells work accordingly with hypothesis I.

6.9.2 Hypothesis II Wells

Sabe, Mile 14, Antoakurom 1 and Yawkurom wells recorded the highest As concentrations in all the wells analyzed in this study. Sabe well had the highest As concentration of 77.5 $\mu\text{g/L}$, followed by Mile 14 (62 $\mu\text{g/L}$), Yawkurom (59.3 $\mu\text{g/L}$) and to Antoakurom 1 (51 $\mu\text{g/L}$), respectively. These wells had a relatively high iron and very low sulphate concentrations of all the analyzed wells. Unlike the high As levels in the above-mentioned wells, Odahu, Abuakwa, Apanapron, Amoamo and Poano community wells registered lower levels. Again wells from these communities registered a relatively high iron, low dissolved O_2 and very low sulphate concentrations. The redox classification according to the redox table (Table 6.10) put the wells in redox class 4. Arsenic speciation also indicated a reducing water as arsenic present was predominantly As-III. The low sulphate concentration, low redox potential and relatively high iron concentration as well as the results from redox classification make these wells a probable hypothesis II well.

6.9.3. Mixed Water Wells

The groundwaters from Meduma, Abodom, Ntinako, Afoako, Apitiso, Patase and Brahabehome community wells contained As concentrations of $<10 \mu\text{g/L}$ with the exception of Apitiso which obtained a concentration of 11 $\mu\text{g/L}$. Iron, manganese and sulphate concentrations observed from those wells were generally low which in the redox classification indicated a mixed water. Based on the observation of relatively high dissolved O_2 and redox potential as well as the redox classification the conclusion is drawn that the arsenic in wells from the communities originates from processes connected to hypothesis I.

The wells from Mamfo, Twepease, Kokotenten and Bogyawe had arsenic concentrations of 25, 15, 16 and 3.7 $\mu\text{g/L}$, respectively. These wells had a relatively high iron and very low sulphate concentrations of all the analyzed wells which put the wells into redox class 4; however, the wells were having a relatively high dissolved O_2 and redox potential (> 250 mV) which is in contrast with redox classification 4. Nonetheless, their redox classification was again confirmed by the arsenic speciation which showed As-V as predominant As species present in the samples indicating an oxidizing environment. Even though, the wells had relatively high manganese and iron concentrations. The wells are probably connected to more than one aquifer which makes the results hard to interpret, but based on the arsenic speciation the most probable hypothesis for these wells is hypothesis I.

6.10 Hydrogeochemical Factors Responsible for Arsenic Mobilization Processes in Groundwater

Arsenic in water supply is highly undesirable because of its toxicity, even in small amounts. At least 618,828 inhabitants of south-western part of the Ashanti Region of Ghana (study area) are at a risk of arsenic poisoning as a result of groundwater arsenic contamination. Arsenic contamination in groundwater is of global concern. Therefore, there is an urgent need to provide the communities or rural households in south-western part of Ashanti Region of Ghana with As-free portable drinking water.

Given the local distribution of As-bearing minerals, geochemical composition of groundwater, especially As and its major species (As-III and As-V) and the relationships between As and other parameters in south-western part of Ashanti Region of Ghana, the most likely source of As is oxidation of sulphide minerals model which releases As either through the roasting of arsenical ores or through acid mine drainage (AMD) resulting from the atmospheric exposure via the open shaft workings and weathering of sulphide-bearing rocks, such as the waste rock and mine tailings generated during mining and milling operations as the main source of arsenic.

The next source of As in most groundwater samples from the study area are the sulphide minerals, of which pyrite and arsenopyrite are the most common, particularly in the sediments. Oxidation of sulphide minerals is mostly seen as the dominant control on mobilization of As and other trace metals analyzed in the study. Oxidation of sulphide minerals corroborates the findings of this study having the available electron acceptors in the

system such as O₂, nitrate, ferric iron and one of the key products of the reaction (SO₄) to allow sulphide oxidation reactions to proceed and As to be released into solution.

The fact that high As concentrations in most groundwaters of south-western part of Ashanti Region of Ghana having relatively moderate levels of SO₄ and indeed having weak linear correlation with arsenic might suggest sulphide oxidation responsible for the release of As into the groundwaters of some aquifers. Documented evidence from groundwaters from arsenic-affected aquifers in Mexico, Argentina, Chile and parts of the USA (e.g., San Joaquin Valley, California; Fujii and Swain, 1995; Smedley *et al.*, 2001) demonstrates some notable similarities with the investigated study areas.

The introduction of O₂ into the aquifer sediments via the open shaft workings as a consequence of large scale mining, groundwater development and during pumping as part of our sampling procedure may have caused changes in the water chemistry; thus, As concentration in the aquifer can significantly increase if As-rich sulfide minerals are oxidized as it has occurred elsewhere (Schreiber *et al.*, 2000; Habuda-Stanic' *et al.*, 2007). Oxygenation of the aquifer around those wells may have led to Fe oxidation and subsequent precipitation which corroborates the findings of Romić' and Subotić', (1997). Such Fe precipitation that occurs did not decrease As concentrations, contrary to what could have been expected due to adsorption mechanisms (Pierce and Moore, 1982; Ujević' *et al.*, 2010).

In contrast, groundwaters from other arsenic-affected aquifers (Oahu, Abuakwa, Sabe, Mile 14, Antoakurom 1, Yawkurom, Poano, Apanapron, Agroyesum, Patase and Bogyawe) are typically reducing involving sulphate reduction. As-III is found to compose a substantial proportion of the total dissolved arsenic concentration. The findings show notable similarities in arsenic-bearing groundwaters from Taiwan, India, Bangladesh, Hungary, Romania, Vietnam and some parts of USA typically also occur under strongly reducing conditions (e.g., Tseng *et al.*, 1968; Welch *et al.*, 1998, 2000; Varsányi *et al.*, 1991; Berg *et al.*, 2001, Smedley *et al.*, 2001). Lastly, the location of the monitored wells and boreholes either in recharge or discharge areas may also have a strong influence on As concentrations, as observed for As affected aquifers in Eastern Croatia and Hungary (Ujević' *et al.*, 2010; Varsányi and Kovacs, 2006).

CHAPTER SEVEN

7.0 ARSENIC AND TRACE METALS CONTAMINATION FROM ACTIVE AND ABANDONED MINE TAILINGS - RESULTS AND DISCUSSION

7.1 Introduction

Mining operations in AngloGold Ashanti mines located in the south-western part of Ashanti Region generally produce many types of mine wastes. Mine waste is often a waste rock which is normally removed for the ore to be extracted and processed to separate the target mineral from the valueless portion. Once the minerals are processed and recovered, the remaining rock becomes another form of mining waste called tailings (BC Wild and Environmental Mining Council of BC, 2001). “These tailings contain large amounts (between 10 and 30 kg/ton) of sulphide minerals, such as pyrite, which are prone to generate acid mine drainage (AMD). AMD is a global pollution problem and is generally reflected by high salt loads and acidification of the affected environment” (Rösner and van Schalkwyk, 2000).

Mine tailings generally act as a sink for arsenic and heavy metals and if improperly secured, contaminants in mine waste can leach out into surface and groundwater causing serious pollution as a result of their mobile and soluble nature and this can last for many generations (BC Wild and Environmental Mining Council of BC, 2001). Most of the mine tailings within the study area are situated either close to some communities with streams and rivers or valuable agricultural land. Hence this study presents results of As and other heavy metals from active mine tailing (Sanso) and abandoned (Pompura and Dokyiwa tailings dam) mine tailings dams from AngloGold Ashanti mine site as a potential source of environmental contamination to the adjoining soils, nearby rivers and streams and subsequently to the groundwater.

7.2 Particle Size Distribution and Texture of the Tailings Mud

Data on particle size distribution are presented in Table 7.1. Generally mine tailings from Sanso, Pompura and Dokyiwa tailings dams were reddish-brown to dark-grey coloration and sticky. The moisture content of the samples were in a range of wet to moderately dry state containing 9.6 %, 3.2 % and 2.4 % water from the mine tailings from Sanso, Pompura and Dokyiwa tailings dam, respectively. The texture of the mine tailings at Sanso is silty clay loam whereas those of Pompura and Dokyiwa are sandy clay. The silty clay loamy texture of

Sanso tailings increases the adsorption of adsorbate as a result of higher surface area available for adsorption, leading to low As and trace metals concentrations in leach solutions.

Furthermore the diffusive path length into the interior of the adsorbent particles are reduced due to the finer particles sizes resulting in the Sanso active tailings dam having a lesser concentration of As and trace metals compared to the coarser particle sizes of the abandoned tailings dam of Pompora and Dokyiwa (Table 7.3).

Table 7.1: Particle size distribution and texture of the tailings

Sampling location	Depth (cm)	Particle size distribution (%)				Texture	Moisture content
		Sand	Silt	Clay			
Sanso	0-20	12	56	32	Silty clay loam	9.6	
Pompora	0-20	37	12	28	Sandy clay	3.2	
Dokyiwa	0-20	35	17	26	Sandy clay	2.4	

Data represent means of 6 samples per site

7.3 Physicochemical Parameters of the Tailings Leachate

Table 7.2 shows pH, DO and the concentrations of fluoride, chloride, nitrate and sulfate in the leachate of mine tailings. The pHs of leachate in the analyzed samples were strongly acidic to acidic conditions. In many cases, the mine leachate where acid mine drainage occurs would show very low pH values such as 2-4 (Bempah *et al.*, 2013). The leachates from the tailings are also characterized by high concentration of sulfate. This indicates the production of sulfate as a result of the oxidation of sulfide minerals that has occurred in the mine tailings (Lim *et al.*, 2009).

Table 7.2: Values of several chemical constituents in leachate of mine tailings

Sampling location	pH	EC ($\mu\text{S}/\text{cm}$)	Chemical constituent (mg/L)				
			DO	F ⁻	Cl ⁻	NO ₃	SO ₄ ⁻²
Sanso 1	4.13±1.23 ^a	686±48.36	3.32±1.12	0.04±0.02	1.42±0.96	0.35±0.09	53.17±7.74
Sanso 2	4.53±0.98	690±52.68	3.76±1.42	0.06±0.03	0.39±0.13	0.57±0.36	58.43±9.64
Pompora 1	6.12±2.34	798±79.22	3.83±1.08	0.28±0.14	0.19±0.07	0.48±0.84	32.73±6.46
Pompora 2	5.85±2.02	773±0.74.64	3.67±1.03	0.15±0.09	0.23±0.17	0.76±0.62	40.13±7.15
Dokyiwa 1	5.17±1.42	665±35.46	4.95±1.72	0.78±0.16	4.44±1.24	0.13±0.07	39.64±5.33
Dokyiwa 2	6.14±1.06	732±42.83	5.03±2.08	1.26±0.84	3.97±1.03	0.17±0.03	56.87±9.14

^aMean ±standard deviation.

The EC values of the tailings ranged from 665 to 798 $\mu\text{S}/\text{cm}$, which were considered quite similar values compared with those in other abandoned metal mines in Korea (Kim *et al.*, 2005). The highest EC values were measured at mine tailings (Pompora 1=798 and Pompora 2=773 $\mu\text{S}/\text{cm}$). The concentrations of other anions in the leachate were very low (<1.5 mg/L, with an exceptional value of 4.4 mg/L for Cl⁻). The values of DO were relatively low (3.32–5.03 mg/L at 25 °C).

7.4 Relationship between As-Contaminated Tailings and Groundwater As Contamination

The vadose (unsaturated) zone is considered to be a geochemical and physical barrier between the primary source of contamination (i.e. tailings dam) and the recipient groundwater system. Moisture movement and attenuation processes such as adsorption in the vadose zone have the potential to mitigate the contamination of the groundwater (Rösner and van Schalkwyk, 2000). However, once this barrier has become contaminated, there might be the likelihood of groundwater contamination as this barrier continuous to act as a source of pollution. A conceptual model of the various pathways of contamination released from a tailings dam in the subsurface is shown in Figure 7.1 (after Rösner and van Schalkwyk, 2000).

The low pH in the leachate (pH 4.13–6.14) may result from the oxidation of sulphide minerals and the generation of AMD from the tailings. When the leachate becomes highly acidic (pH around 4.5), the acidity starts to migrate into the aquifer. This condition results in permanent degradation of the land and contamination of groundwater causing serious problems for future land use and water for both domestic and agricultural purposes.

Leachate acidity constitutes an increase in mobility of trace elements in solution or as a result of seepage. However, groundwater samples from the study area revealed a pH of 6.02-8.47 during the dry season and a pH of 3.13-7.55 during the wet season, respectively (Table 6.3 and 6.4). The pH registered during the dry season invariably has a fairly neutral pH compared to the slightly acidic nature registered in the wet season as a result of a fluctuating groundwater table that may cause a mixing and dilution effect.

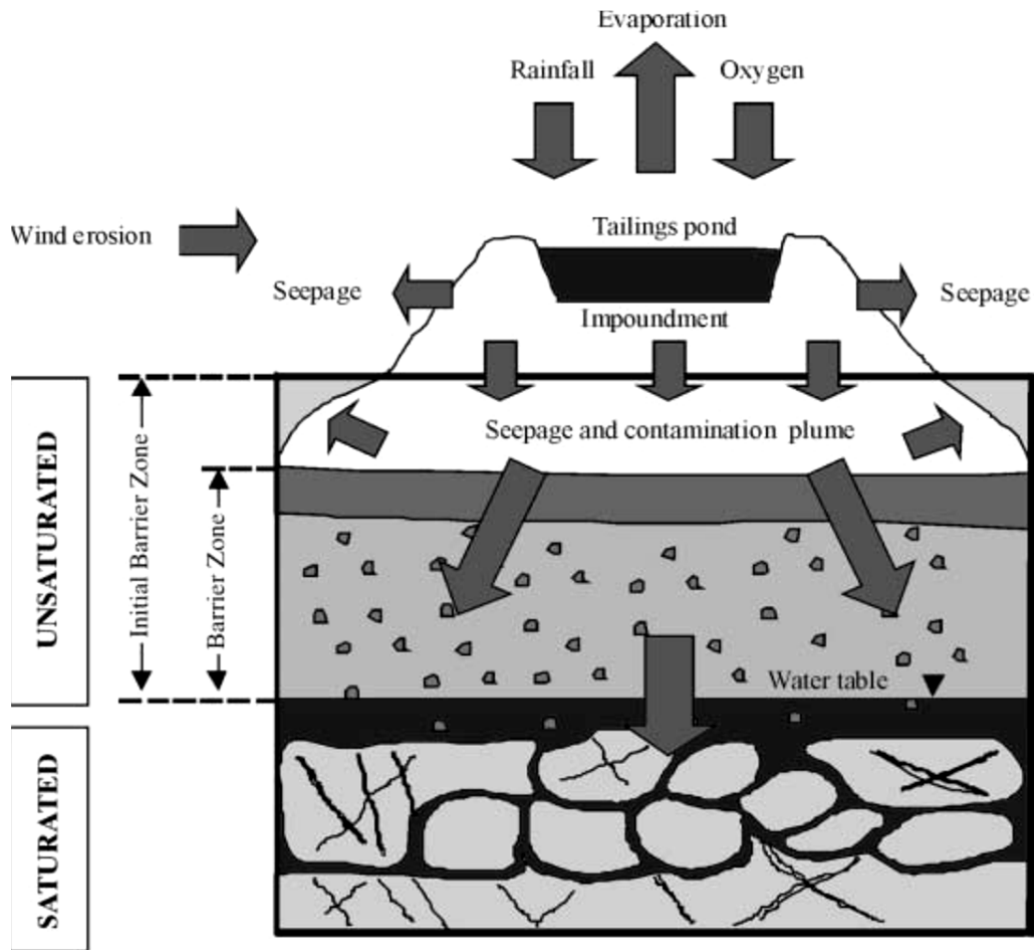
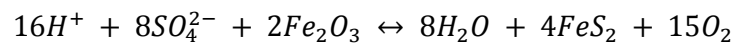


Figure 7.1: Model of tailings dam and affected subsurface (after Rösner and van Schalkwyk, 2000).

The results from the gold mine tailings shown high sulphate concentrations resulting from sulphide mineral weathering (oxidation) process which led to the generation of AMD. This process can be expressed in the overall reaction (Canfield, 2005):



Furthermore, wells from the AngloGold Ashanti mine site (Obuasi mine BH 1, Obuasi mine BH 2, Obuasi mine BH 3 and Sanso) investigated in this study shown elevated concentrations of As and trace metals which correspond to the high levels of As and trace metals within the tailings that are exposed to the weather resulting in the mobilization of these metals and other chemical compounds (Kumi-Boateng, 2007). In a related development, Akabzaa *et al.*,

(2005) measured high concentrations of heavy metals in the environment and indicated that heavy metals such as iron (Fe) and As had ranges of 2210-50180 mg/kg and 0.24-7592 mg/kg in sediments and 0.26-17.19 mg/L and <0.01-6.32 mg/L in water respectively. Amonoo-Neizer *et al.*, (1996) also investigated mercury (Hg) and As pollution on soils, food crops and fish in and around the mining town of Obuasi recording unimaginable levels of As.

Similar studies by Amasa, (1975) and Amonoo-Neizer, (1980) gave large quantities of As in soils, crops and vegetation in localities far and near the mine centers. Amonoo-Neizer and Amekor, (1993) had ascertained that As content of some environmental samples, particularly surface waters (rivers and streams closer to the mining site) was too high making it dangerous to aquatic life, or for domestic use. Akabzaa *et al.*, (2005) assessed the impact of mining activities on water resources in the vicinity of the AngloGold Obuasi mine site. The groundwater samples analyzed shown iron and arsenic concentrations ranging from 0.025 mg/L to 17.19 mg/L and < 0.001 mg/L to 18.91 mg/L, respectively.

This might suggest leaching or seepage of acid mine drainage and associated contaminants from the tailings dam into the vadose zone and possibly the groundwater system. Again the effect of wind is also a contributing factor in the case of abandoned tailings dam because they were dried and uncapped thus prone to the effect of wind. However, the comparison of contaminant concentrations (e.g. As and the trace metals) in groundwater and tailings shown an exponential decrease in concentration with groundwater.

7.5 Incidence of Groundwater Arsenic (As) and Trace Metals Contamination

Table 7.3 shows the total concentrations of arsenic and other trace metals (As, Fe, Mn, Cu and Zn) in the mine tailings and arsenic leaching rates in rainwater. The results showed that concentrations of arsenic in the tailings are in much higher magnitude than the EU target and intervention values (Table 7.4). Concentrations in the tailings pile and tailings-contaminated soils up to several thousands of mg/kg have been reported elsewhere (Smedley and Kinniburgh, 2002). The values reflect not only increased abundance of primary arsenic-rich sulfide minerals, but also secondary iron arsenates and iron oxides formed as a reaction product of the original ore minerals (Smedley and Kinniburgh, 2002).

The mine tailings were heavily polluted with other heavy metals, and total concentrations of each element were diverse. The total elemental concentrations in the mine tailings were up to

1752 mg/kg As, 75.16 wt.% Fe, 1848.12 mg/kg Mn, 92.17 mg/kg Cu and 177.56 mg/kg Zn. The order of abundance of the trace elements was Fe>As>Mn>Zn>Cu in the analyzed mine tailings (Table 7.3).

Table 7.3: Concentrations of arsenic and metals in mine tailings, and arsenic leaching rates in rainwater (n=18)

Sampling location	Concentrations of arsenic and metals in mine tailings					Leaching rate in rainwater
	As (mg/kg)	Fe (wt. %)	Mn (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	As (%)
Sanso 1	542±21.34 ^a	7.87±4.34	154.63±21.35	33.42±6.32	88.67±33.58	0.04
Sanso 2	622±35.46	4.14±0.53	129.56±34.57	24.16±7.32	79.47±17.94	0.06
Pompورا 1	1634±124.53	33.26±14.32	846.13±77.34	82.44±13.57	185.13±24.87	0.43
Pompورا 2	1752±154.34	46.41±16.46	1204.63±127.46	79.12±18.3	204.56±43.65	0.36
Dokyiwa 1	1412±112.78	57.23±21.02	1848.12±168.96	92.17±11.35	165.48±54.86	0.56
Dokyiwa 2	1292±175.49	75.16±31.21	1653.43±143.62	88.64±7.34	177.56±33.42	0.55

^aMean ±standard deviation.

7.6 Tolerance Limit

The concentrations of arsenic and heavy metals in the tailings samples were compared with soil quality standards using the “Dutch List” (Netherlands Ministry of Housing, Physical Planning and Environment 2000). The Dutch List provides “target” and “intervention values” (Table 7.4) for soils and is accepted within the European Union (EU). All limits are valid for a “standard soil” (with 25 % clay and 10 % humus). The “target value” is the maximum permissible concentration with no risk for humans, plants, animals and ecological systems. The “intervention value” implies a significant risk and if exceeded, would require remedial measures. The extent of remediation is dependent not only on the toxic properties of the contaminant itself, but also on the proposed land use and potential groundwater vulnerability. As a consequence, only the findings of an overall site assessment would identify an appropriate remediation strategy (Rösner and van Schalkwyk, 2000). It is important to emphasize that currently there is no published soil quality standards available in Ghana.

Table 7.4: Soil quality standards of the EU

Soil quality standards	Elements				
	As	Fe	Mn	Cu	Zn
Target value (mg/kg)	29	-	-	36	140
Intervention value (mg/kg)	55	-	-	190	720

Arsenic concentrations in the tailing from the abandoned tailings dam site (Pompora and Dokyiwa tailings dam) far exceeded that from the active tailings dam (Sanso tailings dam). In relation to Dutch List, As levels in soil beyond 55 mg/kg dry weight requires remediation (Antwi-Agyei *et al.*, 2009). At this threshold, all the tailings tested, especially tailings from abandoned and active tailings dams sites, showed poor quality with respect to As and may pose environmental health concern. Potential intrusions of As from the abandoned tailings dam was approximately three fold that from the active tailings dams (Bempah *et al.*, 2013).

At the moment there is no Netherlands intervention value for Fe in contaminated soils, however, the analysed samples registered high levels of Fe which meant that the presence of the tailings dams, both active and abandoned might impact the surrounding soils with significant amount of Fe. Soils within the study area are rich in iron, associated with gold ore deposits principally characterized by sulphide minerals in arsenopyrite form (Antwi-Agyei *et al.*, 2009; Bempah *et al.*, 2013).

Mn contamination from the active tailings dams is marginal compared to the abandoned tailings dam. The marginal differences in Mn concentration between tailings from both the active and abandoned tailings might be poor mobility of Mn in tailings sample. Mn contamination from the dams via movement through the tailings might take considerably long time to manifest, probably, a reason why the Mn contamination was more pronounced in the abandoned dam compared to the active dam. Another possible reason might be the susceptibility of old dried tailings of the abandoned dam to transport via air, in view of the fact that it was not capped (Bempah *et al.*, 2013); however, there is currently no Netherlands intervention value for Mn in contaminated soil.

The mean concentration levels of Cu from abandoned tailings dams exceeded the recommended limit of 36 mg/kg for a typical uncontaminated soil whilst the levels in active tailings dam fall below its recommended limit. Although all the values registered in both the

active and abandoned tailing dams were still within Cu intervention limit of 190 mg/kg for contaminated sites.

Zn contamination from the active tailings dams is also marginal, as in the case of Cu levels from the active tailings dam. The mean levels of Zn from the active tailing dam were within the recommended limit of 140 mg/kg for a typical uncontaminated soil. However, Zn levels of soil samples from the abandoned tailings dam site fell short of recommended background level of 140 mg/kg, but were still within intervention limit of 720 mg/kg.

The following observations were made concerning the tailings dam sites with the highest levels of As and trace metals: abandoned tailings dam site (Dokyiwa) > abandoned tailings dam site (Pompora) > active tailings dam site (Sanso).

The high level of trace elements contamination potentially associated with the abandoned tailings dam in this study could be a function of dust, since the tailings were dried and uncapped, and easily prone to long-term effects of windblown (Bempah *et al.*, 2013; Antwi-Agyei *et al.*, 2009). Hence the tailings dam will release a considerable amount of these contaminants into the surrounding or adjoining soils.

The low levels of As and trace metals observed in the active tailings dam may be as a result of the active tailings dams being relatively recent, because it was built in 1991 and might have benefited from substantial technological improvement over the abandoned one, which was one of the earliest to be operated at the AngloGold Ashanti mines (Antwi-Agyei *et al.*, 2009). Coupled with recent implementation of an environmental management system that is ISO 14001 compliant (since December 2006), there has been great institutional commitment to keep contamination from mining operations very low at the AngloGold Ashanti mines (Bempah *et al.*, 2013; Antwi-Agyei *et al.*, 2009).

In addition the presence of security around tailings facilities has prevented vandalization of these facilities, perhaps, constituted a network of management activities that altogether might have worked to ensure the reduced level of contamination around the active tailings dams. Indeed, provision of improved security to protect tailings facilities has substantially reduced deliberate damages to tailings transmitting lines by illegal small-scale artisanal miners, who often seek to obtain and reprocess these tailings (Bempah *et al.*, 2013; Antwi-Agyei *et al.*, 2009).

Thus far, such damages to tailings lines resulted in spillage problems that affected land, vegetation and nearby rivers (AngloGold Ashanti, 2006). The active tailings dams are also presently equipped with facility for draining and re-treatment of effluent, which did not exist during operation of the old abandoned dams (Bempah *et al.*, 2013).

7.7 Leachability of Arsenic from Mine Tailings

Leaching tests of the active (Sanso) and abandoned (Pompora and Dokyiwa) mine tailings were performed by the use of normal rain (approximately pH 5.8) to indirectly evaluate release and mobility of As to the surrounding environmental media. Table 7.3 shows leaching concentrations of As from the active and abandoned mine tailings. The Sanso active mine tailings registered As leaching levels of 0.04-0.06 %, Pompora abandoned tailings dam registered 0.36-0.43 % As leaching levels while 0.55-0.56 % As leaching levels was recorded for Dokyiwa mine tailings dam.

The leaching concentration levels of As from Pompora and Dokyiwa abandoned mine tailings were higher compared to that of the Sanso active mine tailings. This may be as a result of the texture and finer nature of the particles (silty clay loam) creating a diffusion layer on the surface of the particles reducing the leaching effect on the active tailings compared to the coarser particulate size (sandy clay) of the abandoned tailings. Again, infiltration rate was generally low because of the small particle size and low permeability of the Sanso active tailings pile. In addition to this, the low leaching concentration in the active mine tailings indicates that easily soluble fraction of As might be already released by the oxidation of sulfide minerals with water and air for a long period at the As-contaminated tailings deposition site (Lim *et al.*, 2009).

CHAPTER EIGHT

8.0 GROUNDWATER SUITABILITY FOR DOMESTIC AND AGRICULTURAL PURPOSES - RESULTS AND DISCUSSION

8.1 Introduction

Groundwater is a major resource for meeting huge domestic and agricultural requirements of not only south-western part of the Ashanti Region of Ghana but the world at large. Therefore, evaluation of its quality in terms of suitability for domestic and agricultural purposes is necessary for sustainable management of the resource (Goyal *et al.*, 2010). The present study has determined trace metals and physicochemical parameters of groundwater samples from boreholes and shallow wells spread over the entire study area. Spatial distribution maps were generated to assess the groundwater quality for hydrogen ion concentration (pH), total dissolved solids (TDS), total hardness (TH), electrical conductivity (EC), sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and percent sodium (% Na) using geographic information system (GIS) which is an effective and efficient tool in handling problems pertaining to various quality parameters in their spatial extent (Goyal *et al.*, 2010).

8.2 Ionic and Heavy Metals Evaluation of Groundwater Quality for Domestic Use

The results of chemical analysis of groundwater were compared with the domestic water standards of WHO guideline value for drinking water (WHO, 1996a, b, 2004) to arrive at conclusions (Tables 8.1).

Table 8.1: Comparison of groundwater quality parameters with WHO Guideline values for drinking water during the dry and the wet seasons.

Chemical constituents	Dry Season			Wet Season			WHO
	Min.	Max.	Mean	Min.	Max.	Mean	
pH	6.02	8.47	7.23	3.13	7.55	5.70	6.5-8.5
Temp ($^{\circ}$ C)	23.0	26.9	25.24	23.0	26.9	25.24	-
Eh (mV)	212	527	349.54	228.0	788.0	382.49	-
EC (μ s/cm)	42	984	200.30	56.0	1230.0	240.13	1500
DO (mg/L)	0.2	3.8	1.4	0.2	3.8	1.92	5
TDS (mg/L)	28.5	667.71*	135.92	43.6	732.5*	173.2	500
Ca (mg/L)	0.33	82.56	15.04	1.64	96.55	19.19	200
Mg (mg/L)	0.09	85.12	7.86	2.33	93.67	11.31	150
Na (mg/L)	6.04	33.15	17.06	8.22	65.35	22.85	200

K (mg/L)	0.01	4.38	1.02	0.22	6.12	1.78	-
HCO ₃ ⁻ (mg/L)	13	269.42	96.53	45.57	784.56*	141.95	384
SO ₄ (mg/L)	0.11	7.01	1.61	0.15	10.5	2.49	400
Cl (mg/L)	1.97	41.09	8.01	2.05	44.64	10.92	600
NO ₃ (mg/L)	<0.2	1.9	0.94	0.4	2.0	1.05	45
F (mg/L)	0.01	0.41	0.12	<0.01	0.42	0.10	1.5
PO ₄ (mg/L)	0.16	4.05	2.01	0.11	0.43	0.22	-
As (µg/L)	<0.1	72.0*	17.98*	<0.1	83.0*	21.39*	10
DOC (mg/L)	0.23	4.05	1.64	0.67	4.73	2.12	-
Fe (mg/L)	<0.01	12.3*	1.51*	<0.01	16.33*	2.12*	0.3
Mn (µg/L)	1.8	498	118.52	2.30	583.80*	150.51	500
Cu (µg/L)	<0.1	77	17.84	<0.1	81.0	14.19	500
Zn (µg/L)	5	2301	109.15	7.0	2854	135.32	5000

*Values designated by asterisks are higher than the WHO guideline values for drinking water.

8.2.1 Ionic Evaluation of Groundwater Quality for Domestic Purposes

Bicarbonate (HCO₃⁻) value varied from 13 to 269.42 mg/L and 45.57 to 784.56 mg/L with corresponding mean values of 96.53 and 141.95 mg/L during both the dry and the wet seasons, respectively. The acceptable drinking water limit for HCO₃⁻ is 384 mg/L. Above this limit, taste becomes unpleasant. The analytical data show that HCO₃⁻ analyzed in all the groundwater samples from the study area were below the safe limits in all the analyzed groundwater samples precluding Yawkurom which registered a mean value of 784.56 mg/L during the wet season.

Most chloride (Cl⁻) in inland groundwaters originates indirectly from evaporated seawater that enters aquifers as rainfall recharge. Rainfall contains high levels of Cl⁻ near the coast and as a consequence it is found at higher concentrations in groundwaters that originate nearer to the coast. This effect does not apply to the study area wells which are recharged from waters that originate inland. The Cl⁻ concentration varied between 1.97 to 41.09 mg/L (mean = 8.01 mg/L) during the dry season and 2.05 to 44.64 mg/L (mean = 10.92 mg/L) during the wet season. The permissible limit of Cl⁻ in potable water is 250 mg/L, and none of the samples exceeded the Cl⁻ limit. Based on the WHO guidelines for potable water, the groundwaters could generally be said to be fresh and suitable for domestic use.

The nitrate (NO₃⁻) concentration in groundwater samples range from <0.2 to 1.9 mg/L with a mean value of 0.94 mg/L during the dry season and 0.4 to 2.0 mg/L with a mean value of

1.05 mg/L during the wet season, respectively. All the analyzed samples were below the desirable limit of 45 mg/L as per WHO norms. In confined aquifers with oxygen deficient or anaerobic conditions as observed in the study area, NO_3^- is naturally reduced to ammoniacal nitrogen and further to nitrogen gas. This process is called denitrification and it actually improves groundwater quality from a human health and eutrophication perspective by reducing NO_3^- levels. However this process can also produce small amounts of the greenhouse gas nitrous oxide if the process does not proceed through to nitrogen, which is the main component of air.

According to Chapman (1992), sulphate (SO_4^{2-}) concentrations in natural waters are usually between 2 and 80 mg/L, although they may exceed 1,000 mg/L near industrial discharges and in sandstones with sulphate cement. High concentrations greater than 400 mg/L may make water unpleasant to drink. SO_4^{2-} is a naturally occurring ion in all waters and plays an important role in total hardness of water. Concentrations of SO_4^{2-} above 400 mg/L are objectionable for domestic water uses. SO_4^{2-} values recorded in this study varied from 0.11 to 7.01 mg/L with a mean value of 1.61 mg/L and 0.15 to 10.5 mg/L with a mean value of 2.49 mg/L during the dry and the wet seasons, respectively and thus, SO_4^{2-} ions are in compliance with WHO limits.

Fluoride (F^-) generally occurs naturally and is one of the main trace elements in groundwater. High concentration of fluoride in groundwater is as a result of bedrocks containing this ion (Ramesh and Thirumangai, 2014). Fluorides are also present in tectorial active areas for example, the Great African Rift Valley. F^- values varied from 0.01 to 0.41 mg/L with an average value 0.12 mg/L and <0.01 to 0.42 mg/L with a corresponding mean value of 0.10 mg/L during the dry and the wet seasons, respectively. All samples examined exhibit suitable for drinking (maximum allowable limit is 1.5 mg/L according to WHO).

Calcium (Ca^{2+}) values varied from 0.33 to 82.56 mg/L with a mean value of 15.04 mg/L during the dry season and 1.64 to 95.55 mg/L with a mean value of 19.19 mg/L during the wet season. Ca is most often the dominating cation in most fresh waters in the world. The desirable limit of Ca^{2+} for drinking water is specified by WHO as 200 mg/L. It is observed that all the samples were below this limit during both the dry and the wet seasons.

Magnesium (Mg^{2+}) concentrations varied from 0.09 to 85.12 mg/L with a mean value of 7.86 mg/L during the dry season and 2.33 to 93.67 mg/L with a mean value of 11.31 mg/L during

the wet season. Out of the total samples analyzed, none of the samples exceeded the WHO desirable value of Mg^{2+} which is 150 mg/L. Magnesium concentration in the groundwaters is exceptionally low. Exceptionally low values are usually attributable to natural softening by cation exchange where sodium-rich clay displaces Ca^{2+} and Mg^{2+} from solution.

The recommended WHO limit for sodium (Na^+) concentration in drinking water is 200 mg/L. Na concentration ranges from 6.04 to 33.15 mg/L with a mean value of 17.06 mg/L during the dry season and 8.22 to 65.35 mg/L with a mean value of 22.85 mg/L during the wet seasons, respectively. Concentrations of Na are within the prescribed limit of 200 mg/L in all the analyzed samples although Na is more common by-product in groundwater as a result of the breakdown of clay minerals and rock salt occurrences.

Potassium (K^+) varies from 0.01 to 4.38 mg/L with a mean concentration of 1.02 mg/L during the dry season and 0.22 to 6.12 mg/L with a mean value of 1.78 mg/L during the wet season in all the groundwater samples analyzed. Concentrations of potassium are generally low in the surveyed aquifers because of natural exchange processes that might have removed it from groundwater, and this is in conformity of the groundwaters in south-western part of Ashanti Region. Chapman (1992) reported that concentrations of K in natural waters are usually less than 10 mg/L, whereas concentrations of 100 and 25,000 mg/L can occur in brines. K in the study area is generally low which might suggest that orthoclase, which occurs to a smaller extent in the rocks of the study area, is resistant to attack by water.

Thus the mean concentration of major ions in groundwater during both seasons is in the following order: Anions: - Bicarbonate > Chloride > Sulphate > Nitrate whiles Cations: - Sodium > Calcium > Magnesium > Potassium.

8.2.2 Arsenic and Trace Metals Evaluation of Groundwater Quality for Domestic Purposes

Arsenic (As) enters into the environment from natural processes, industrial activities, mining, pesticides, and industrial waste, smelting of copper, lead, and zinc ore (Reddy *et al.*, 2012). The concentration of the As in our study area ranged from <0.1–72.0 $\mu g/L$ with a mean concentration level of 17.98 $\mu g/L$ and <0.1–83.0 $\mu g/L$ with a mean concentration level of 21.39 $\mu g/L$ during the dry and the wet seasons, respectively. The groundwater quality standard of As desirable and maximum permissible limit (WHO) is 10.0 $\mu g/L$. 41.0 % of the sampling areas recorded several variations of As with 17.0 % and 22.0 % having exceeded

the WHO desirable and maximum permissible limit of Arsenic during the dry and the wet seasons, respectively.

Iron (Fe) in rural groundwater supplies is a common problem, its concentration levels from the study area ranges from <0.01–12.3 mg/L with a mean value of 1.51 mg/L and <0.01–16.33 mg/L with a concentration mean value of 2.12 mg/L during the dry and the wet seasons. The WHO recommended level is 0.3 mg/L. Approximately 43.0 % and 44.0 % of the analyzed groundwater samples contained Fe with concentrations high above the WHO recommended guideline value during the dry and the wet seasons respectively. Fe occurs naturally in the aquifer but their high levels in groundwater may be increased by dissolution of ferrous borehole and hand pump components. Iron-bearing groundwater is often noticeably orange in color, causing discoloration of laundry, and has an unpleasant taste, which is apparent in drinking and food preparation. The common denominators for the presence of high Fe levels are either chemically reduced conditions linked to a lack of oxygen, or long contact times between groundwater and the aquifer forming gravels. Both factors cause groundwater to naturally become more mineralized.

Manganese (Mn) occurs naturally as mineral from sediment and rocks or from mining and industrial waste (Reddy *et al.*, 2012). The concentration of Mn in our study area ranged from 1.8–498.0 µg/L with a mean concentration value of 118.52 µg/L during the dry season and 2.30–583.80 µg/L with a corresponding mean value of 150.51 µg/L during the wet season. The WHO groundwater quality standard of Mn is 500 µg/L. In our study area all sampling locations were having Mn concentrations less than WHO permissible limit during the dry season with 5 % of the analyzed samples having exceeded the quality standard of Mn during the wet season. Excess concentrations of Mn make water distasteful to drinking with no specific toxic effects (Reddy *et al.*, 2012).

Copper (Cu) enters into water bodies mostly through anthropogenic activities such as metal plating, industrial and domestic waste, mining, and mineral leaching (Reddy *et al.*, 2012). The concentration of Cu in our study area ranged from <0.1–77.0 µg/L with a mean concentration value of 17.84 µg/L during the dry season while the wet season registered Cu concentration ranging from <0.1–81.0 µg/L with a mean value of 14.19 µg/L. The groundwater quality standard of Cu desirable limit (WHO) is 500 µg/L and maximum permissible limit is 1500 µg/L. All the sampling locations have Cu concentrations below WHO desirable limit and less than maximum permissible level of Cu during both seasons.

Zinc (Zn) occurs naturally in water and can also be introduced into water bodies through anthropogenic activities most frequently in areas where it is mined and from industrial waste, metal plating, and plumbing, and is a major component of sludge (Reddy *et al.*, 2012). The source of Zn in groundwater might also come from weathering of the minerals and rocks which contain Zn (Ramesh and Thirumangai, 2014). The concentration of Zn in our study area ranged from 5.0–2301 $\mu\text{g/L}$ with a mean value of 109.15 $\mu\text{g/L}$ during the dry season and during the wet season, the concentration ranged from 7.0–2,854 $\mu\text{g/L}$ with a mean value of 27.0 $\mu\text{g/L}$. All the analyzed groundwater samples in the study area were below the WHO groundwater quality standard of Zn desirable limit and maximum permissible limit of 5,000 and 10,000 $\mu\text{g/L}$, respectively.

8.3 Evaluation of the Suitability of Groundwater Quality for Domestic and Agricultural Purposes in the Study Area

Geographic information system (GIS) based spatial distribution maps were produced for hydrogen ion concentration (pH), total dissolved solids (TDS), total hardness (TH), electrical conductivity (EC), sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and percentage sodium (% Na) during the dry and wet seasons to ascertain the quality and the suitability of groundwater for both domestic and agricultural purposes.

8.3.1 Evaluation of Groundwater Quality for Domestic Use

Spatial distribution maps for hydrogen ion concentration (pH), total dissolved solids (TDS) and total hardness (TH) was developed to ascertain the quality and the suitability of groundwater sources within the study area for domestic purposes during the dry and the wet seasons.

The WHO standards revealed that for domestic use the pH values of the groundwater should range between 6.5 and 8.5. The pH values for different observation wells during the entire study period (dry and the wet seasons) in the study area were found to be between 6.02–8.47 and 3.13–7.55 during the dry and the wet seasons, respectively. The pH distribution maps of the study area demonstrated that 92 % and 17.5 % area of the south-western part of Ashanti Region had hydrogen ion concentration in desirable range during the dry and the wet seasons, respectively (Figure 8.1).

Arsenic Contamination in Groundwater

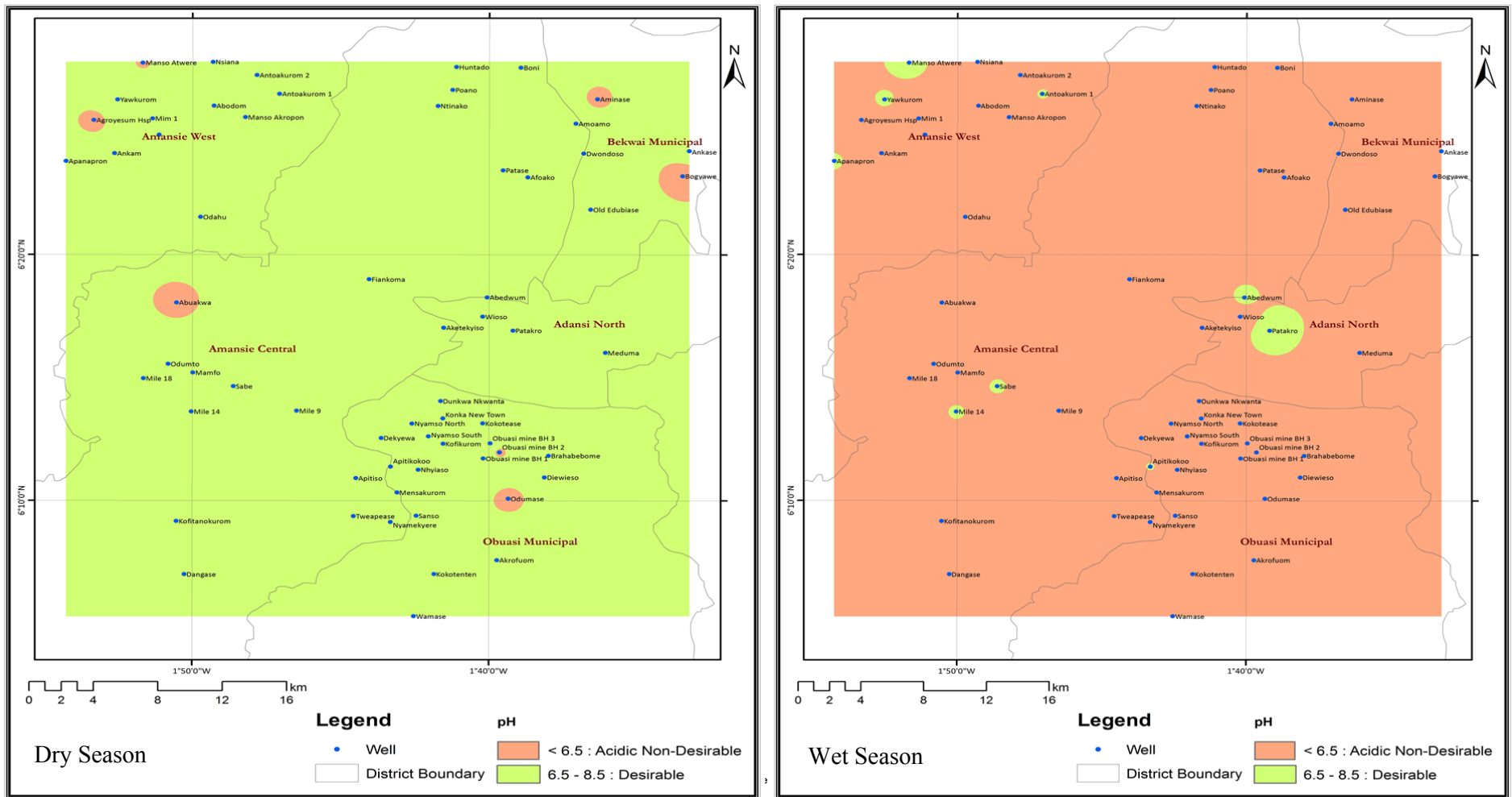


Figure 8.1: Spatial distribution of pH in the study area during the dry and the wet seasons.

However, an area of 8 % and 82.5 % were in non-desirable range with pH below 6.5 (acidic) during the dry and the wet seasons, respectively. The pH registered during the dry season invariably has a fairly neutral pH. The slightly acidic nature of the groundwater during the wet seasons may have resulted from fluctuating groundwater table that might have caused mixing and dilution effect unlike the fairly neutral nature of the dry season groundwater.

The observed minimum, maximum and average total dissolved solids (TDS) were 28.5, 667.71 and 135.92 mg/L during the dry seasons whilst 43.6, 732.5 and 173.2 mg/L were registered during the wet seasons, respectively, in the study. Spatial distribution maps of TDS demonstrated that 96.8 and 93.7 % area had groundwater in desirable class during the dry and the wet seasons, respectively in the study area (Figure 8.2). However, 3.2 and 6.3 % of the total study area was observed to have a little higher concentration, although in the range of permissible class (500-2000 mg/L).

TDS was generally higher during the wet season compared to dry season this may be due to heavy rainfall leading to increase surface runoff which might carry a lot of suspended materials into the nearby rivers and streams and ultimately to the aquifer leading to high TDS values. Generally during wet season, suspended particles in the groundwater are always in motion due to water high rate of circulation whereas in the dry season, the particles tend to settle on submerged logs as there is little turbulence.

Arsenic Contamination in Groundwater

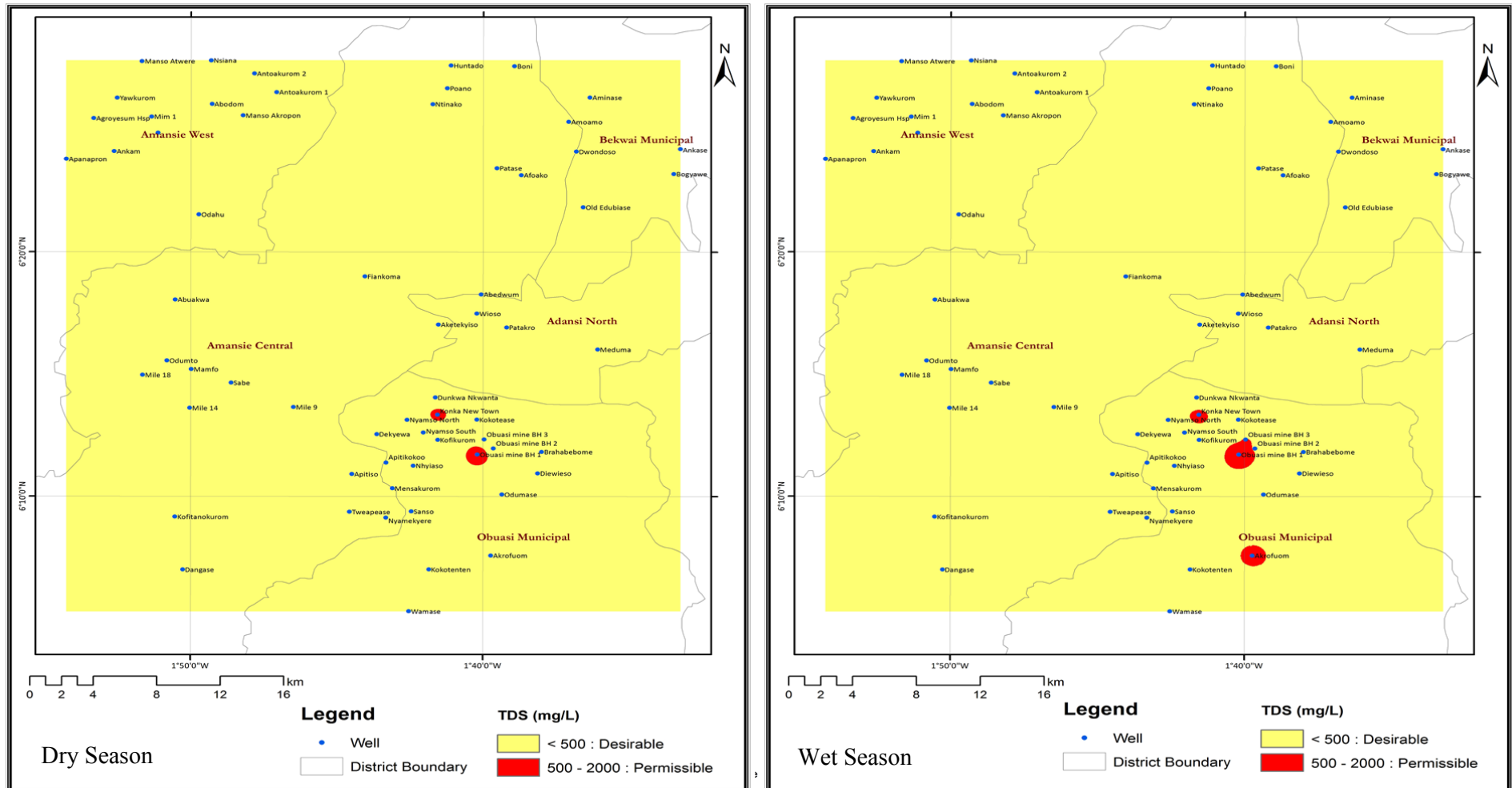


Figure 8.2: Spatial distribution of TDS in the study area during the dry and the wet seasons.

The mean total hardness (TH) was found to be 69.84 mg/L with a variation ranging from 2.31 to 555.6 mg/L during the dry season and during the wet season, the mean concentration value was 103.47 mg/L with a variation ranging from 20.5 to 626.5 mg/L. From the mean concentration of total hardness, concentrations in groundwater are higher in wet season than in the dry season. This is obvious because of the solvent action of rainwater coming in contact with soil and rocks which are capable of dissolving calcium and magnesium that promote water hardness.

Generally, the groundwater in the study area was soft, representing 73 and 59 % during the dry and the wet seasons which are well within the desirable range for domestic use (Figure 8.3). However, percentage (%) values of 16, 6 and 5 of the monitored groundwater samples were moderate, hard and very hard during the dry seasons whilst 25, 11 and 5 of the groundwater samples were moderate, hard and very hard during the wet seasons, respectively. The lower TDS and TH observed during the entire study may be attributed to groundwater recharge (Goyal *et al.*, 2010).

Arsenic Contamination in Groundwater

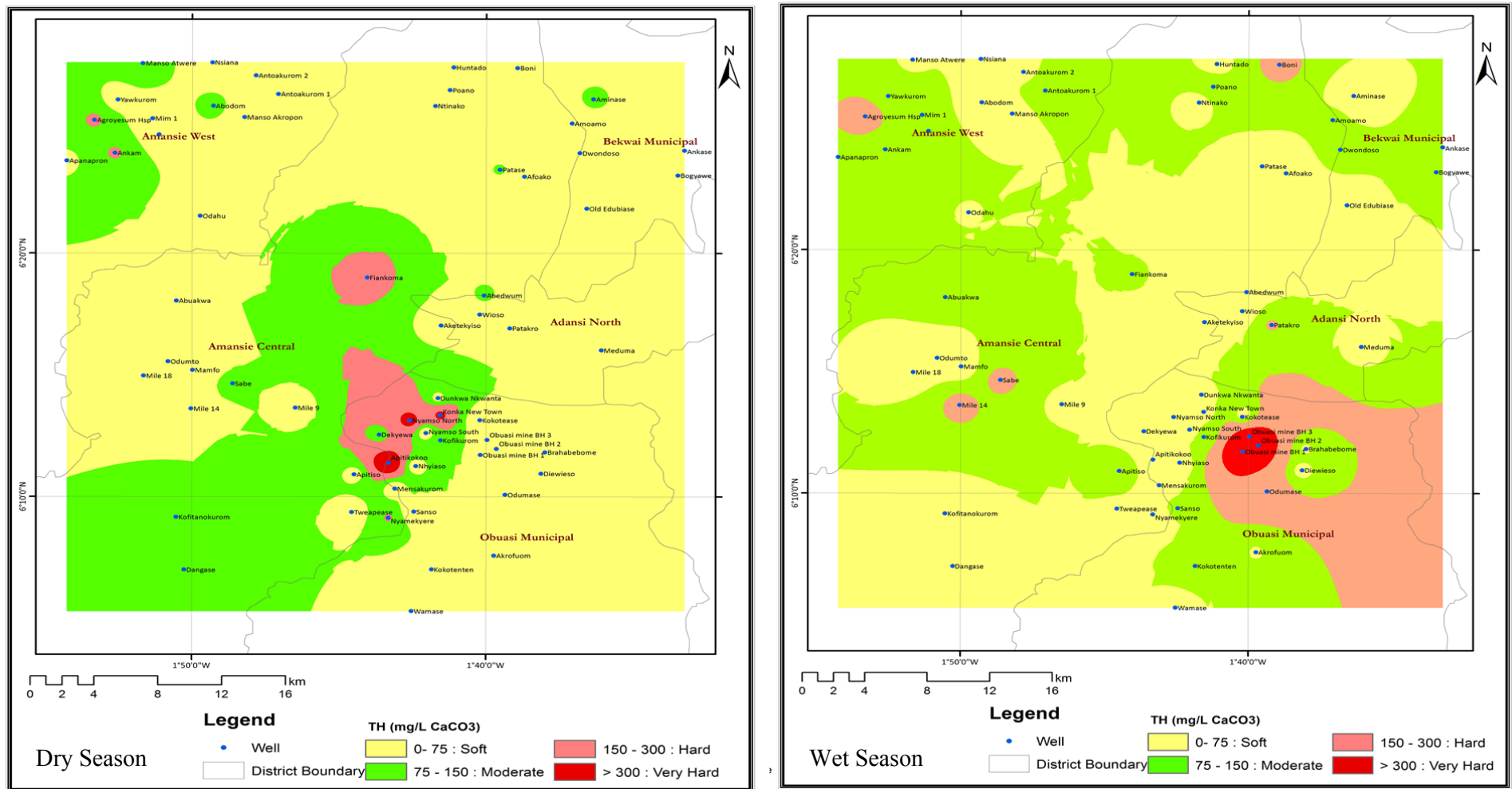


Figure 8.3: Spatial distribution of TH in the study area during the dry and the wet seasons.

8.3.2 Evaluation of Groundwater Quality for Agricultural and Irrigational Purposes

When assessing groundwater quality it is important to know what the water is intended to be used for, as some groundwaters will be suitable for crop irrigation, but not for human consumption. For instance the presence of waterborne microbes can make a drinking water supply unpotable, but it may be satisfactory for irrigation or agricultural purposes.

The suitability of groundwater in the south-western part of Ashanti Region of Ghana for agricultural use was ascertained by comparing their physicochemical parameters like electrical conductivity (EC), sodium adsorption ratio (SAR), percentage sodium (% Na) and residual sodium carbonate (RSC) with USSL standards (1954).

EC of groundwater ranged from 42 to 984 $\mu\text{S}/\text{cm}$ with a mean value of 200.3 $\mu\text{S}/\text{cm}$ during the dry season and 56 to 1230 $\mu\text{S}/\text{cm}$ with a mean concentration value of 240.1 $\mu\text{S}/\text{cm}$ observation period of the wet season (Figure 8.4). The water quality based on EC for agricultural use was observed to be of excellent, good and moderate categories. According to the USSL standards (1954) classification adopted, 74 and 67 % area had excellent water quality during the dry and the wet seasons, respectively whereas 24 % and 2 % had good to moderate levels during the dry seasons as well as 29 and 6 % of the analyzed groundwater samples had good to moderate levels of salinity during the wet season.

Results of the study indicate decrease in EC concentration during the dry season compared to the wet season. Reasons for the trend may be due to increase in concentration of rock salts, organic and inorganic materials as a result of discharges by the mine tailings dams and other effluents from the mining sites and illegal artisanal mining activities as well as runoff from domestic and other human activities during wet season.

Arsenic Contamination in Groundwater

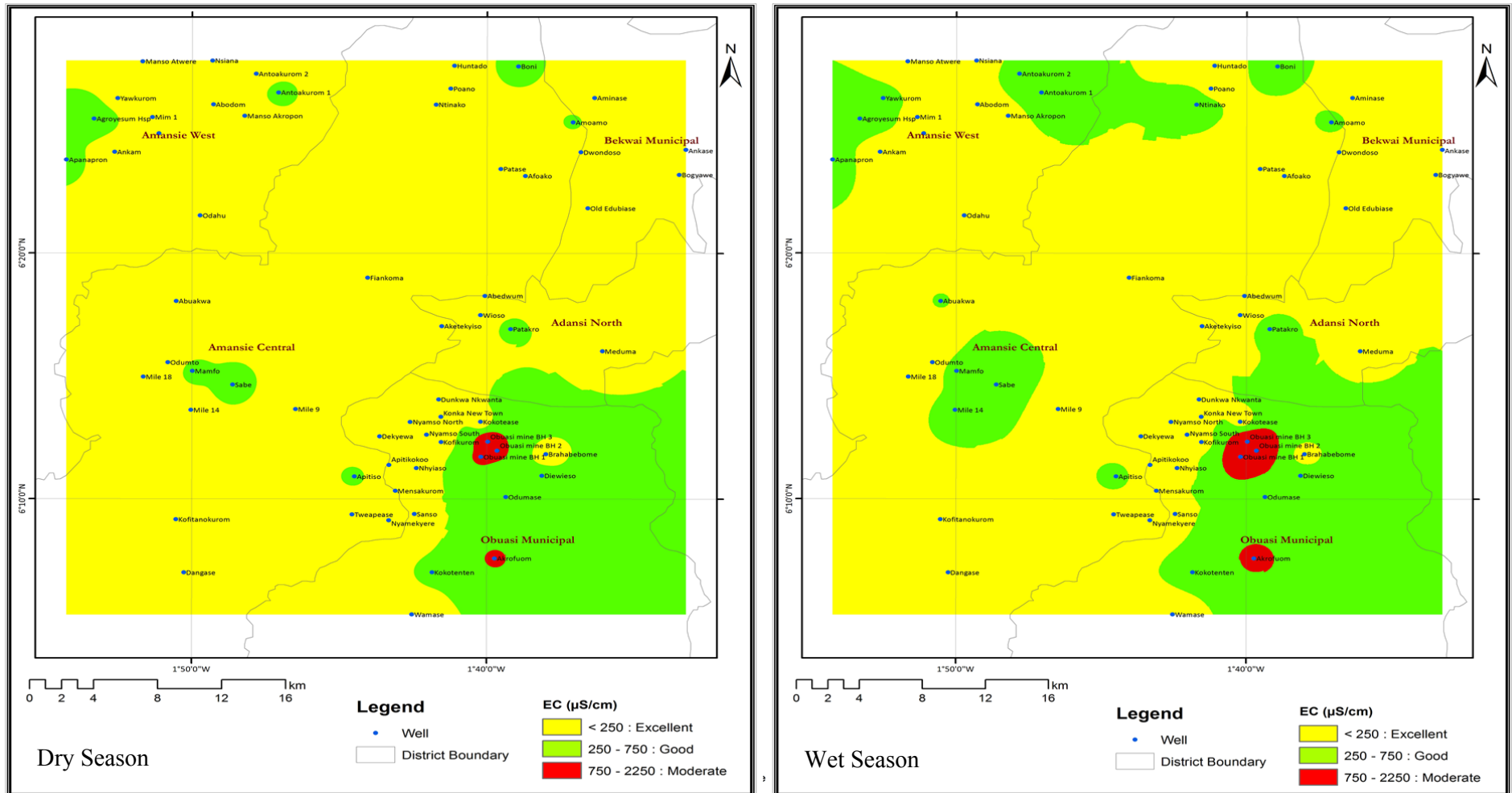


Figure 8.4: Spatial distribution of EC in the study area during the dry and the wet seasons.

The sodium or alkaline hazard for irrigation water is classified in terms of sodium absorption ratio (SAR) and it is important for agriculture and human pathology. However, in most cases, it varies considerably due to physiography, geology, hydrology and anthropogenic activities (Goyal *et al.*, 2010). In contrast to this study, SAR values attained were uniform throughout the entire study area (Figure 8.5). From the analysis of SAR, it was observed that groundwater in study area had excellent water quality and therefore will be suitable for irrigation and better crop cultivation in the study area.

Arsenic Contamination in Groundwater

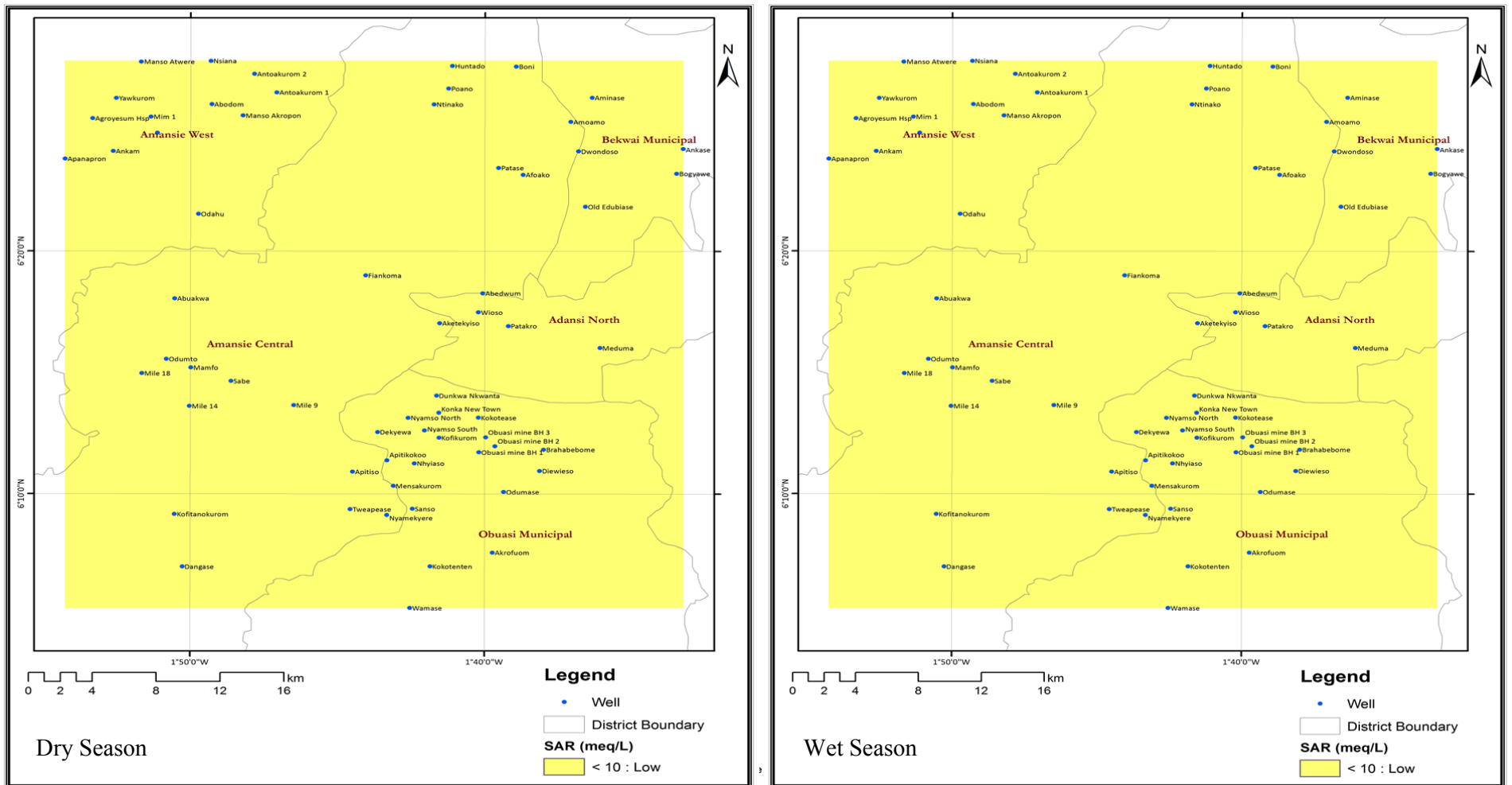


Figure 8.5: Spatial distribution of SAR in the study area during the dry and the wet seasons.

It is widely agreed that the high percentage of sodium (% Na) in irrigation water produces undesirable effects on soil structure, permeability and aeration which are needed for the growth of plants. In the study area, % Na for groundwater in the study area varied in the range of 14.04–94.15 % with a mean value of 56.04 % during the dry season. For the wet season, the % Na registered a range of 3.62–127.9 % with a mean concentration value of 54.16 %. It was revealed from the analysis that the groundwater in the study area was of 3 % excellent, 24 % of good and permissible, 36 % doubtful and 8 % of bad quality during the dry season whilst that for the wet season were of 10 % excellent, 27 % and 30 % of good and permissible, 16 % doubtful and 18 % of bad quality (Figure 8.6). Irrigation water with high % Na may cause sodium accumulation and calcium deficiency in the soil leading to a breakdown of its physical properties. Therefore, good drainage, high leaching and use of organic matter are required for its management in the area.

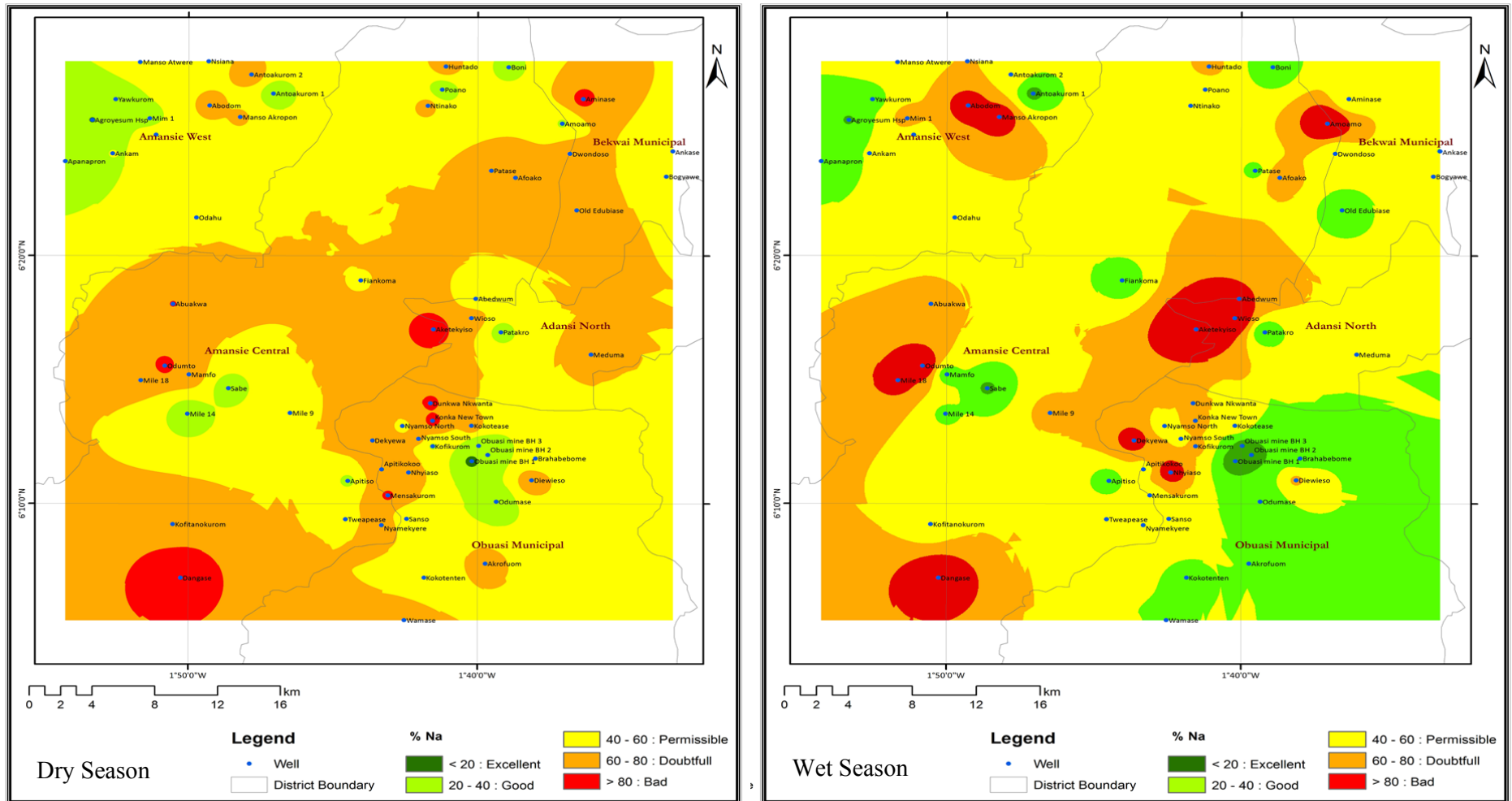


Figure 8.6: Spatial distribution of % Na in the study area during the dry and the wet seasons.

The sodium hazard also increases if the water contains a high concentration of bicarbonate ions. Bicarbonate hazard is usually represented in terms of residual sodium carbonate (RSC), which shows the tendency for calcium and magnesium to participate as the water in the soil becomes more concentrated (Alaya *et al.*, 2014; Carmelita Nishanthiny *et al.*, 2010). When the soil solution has a high concentration of carbonates as it has been observed in this study, the formation of calcium and magnesium carbonate precipitates increases the relative proportion of sodium in water (Eaton, 1950).

The RSC in the study area ranged from -9.1 to 2.45 meq/L with a mean concentration value of -0.15 meq/L during the dry season whilst the wet season registered a concentration level ranging from -9.97 to 10.83 meq/L with a mean value of 0.59 meq/L. Moreover, an observation of RSC revealed that in about 98 % of the study area, groundwater was suitable, whereas 2 % area was marginally suitable during the dry season. The wet season registered 78 % suitability of the groundwater samples, 19 % marginal, and 2 % of not suitable and bad quality (Figure 8.7).

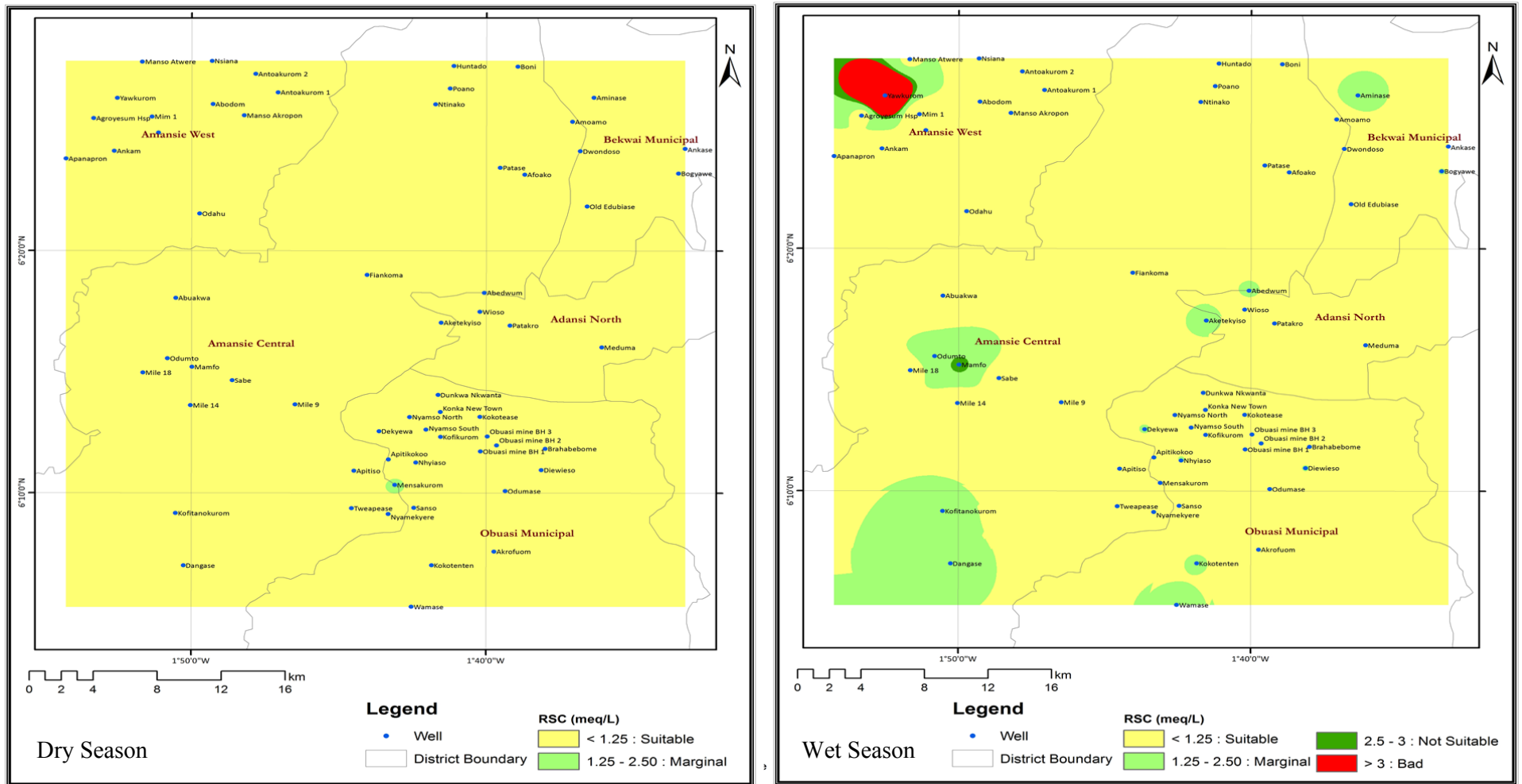


Figure 8.7: Spatial distribution of RSC in the study area during the dry and the wet seasons.

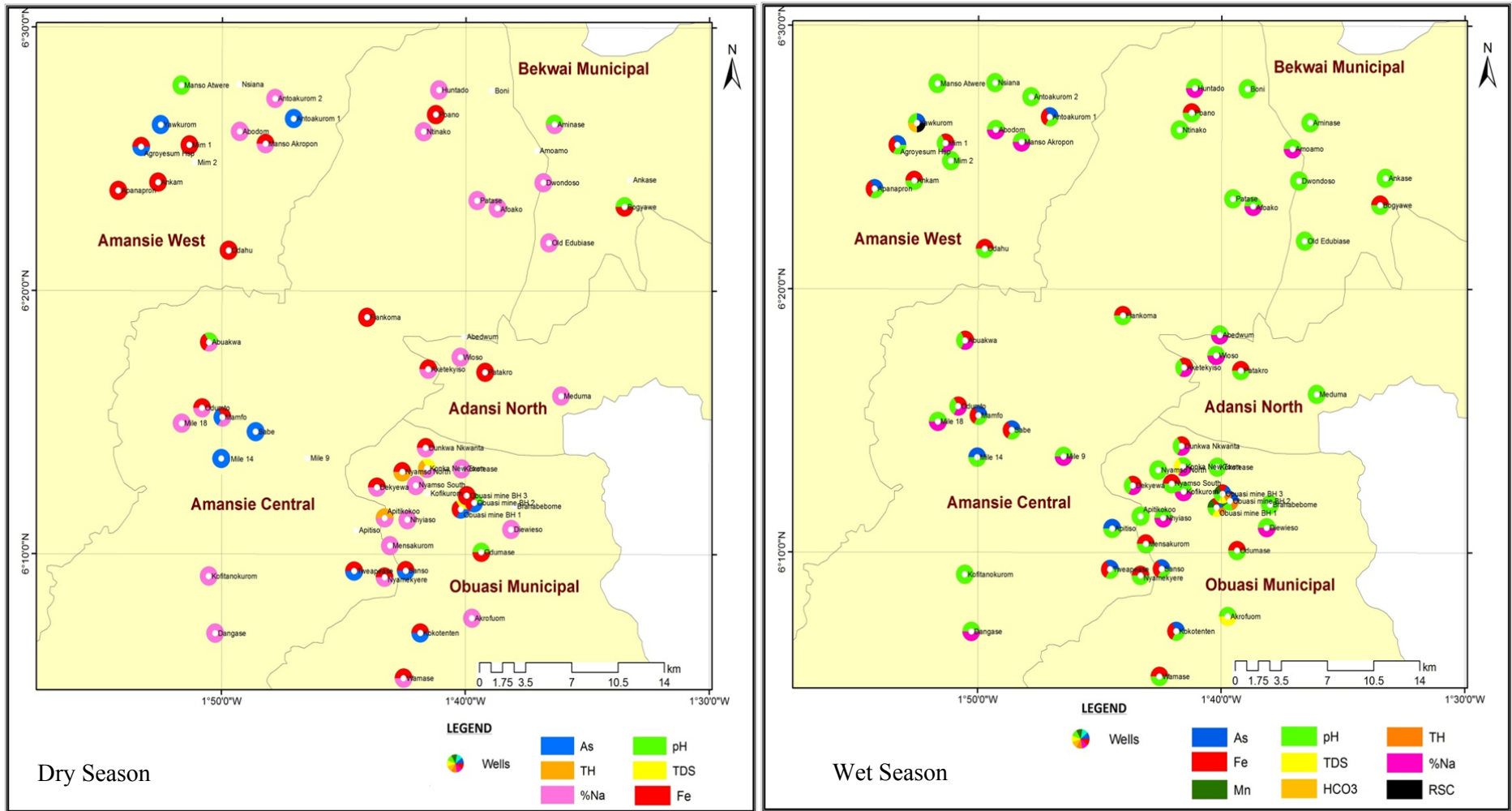


Figure 8.8: Wells with highest concentration levels of metals and water quality parameters than their permissible limit.

Overall, spatial distribution maps were generated for the various monitored wells and boreholes exhibiting concentration levels of As, trace metals (Fe and Mn) and other physicochemical parameters (pH, TDS, HCO_3 , TH, % Na, RSC) higher than their respective permissible levels during both the dry and the wet seasons (Figure 8.8). These maps were helpful in suggesting remedial measures in a holistic way for sustainable water management within the study area.

CHAPTER NINE**9.0 EVALUATION OF TWO POINT-OF-USE ARSENIC REMOVAL TECHNOLOGY - RESULTS AND DISCUSSION****9.1 Introduction**

Arsenic impacts to natural and process waters have become an increasingly global problem with no economic boundaries, being prominent in many countries (Hutton-Ashkenny *et al.*, 2011). According to the WHO, arsenic is considered to be “of significant concern in several geographic areas”. Despite this, there are limited proven industrial methods for efficient low cost removal technology (Bempah *et al.*, 2013).

During our field survey we noticed that many families due to high iron and suspected heavy metals in their wells and boreholes waters, they cannot drink the groundwater after withdraw directly, and to make it portable for drinking they keep the water after withdraw for some time for the brown precipitate to settle at the bottom of their barrels and/or water cans. After the said time, they either decant the upper water which is clear or use a common filter to arrest the aggregated precipitate or the floc. GIS-based spatial distribution mapping was developed to map out community wells and boreholes that registered concentration levels of arsenic and iron higher than their respective WHO drinking water guideline values of 10 µg/L for As and 0.3 mg/L for Fe (Figure 9.1).

It was against this backdrop that necessitated out effort to evaluate two different point-of-use groundwater treatment systems which are mostly in use by some well owners and many families for their effectiveness and appropriateness/applicability. These water treatment systems were not only used to treat arsenic but other heavy metals, particularly iron. There are a number of different technologies for the removal of arsenic from natural waters and for the purposes of this study two different arsenic removal technologies mostly used by the local folks were chosen to test for their effectiveness and appropriateness/applicability.

The two removal technologies chosen were the Three-Earthern Pot System, and the Household Coagulation and Filtration System popularly known as Jerry Can or “Kufour” Gallon System based on the technology being of simple design and easily produced; low cost (economically viable); made of local, easily accessible materials and it is of rural focus (socially acceptable). The effectiveness of these technologies was evaluated by testing the

Arsenic Contamination in Groundwater

arsenic concentration of influent and effluent water, i.e. before and after being treated. If the technologies remove or reduce arsenic below 10 ug/L, it was deemed effective.

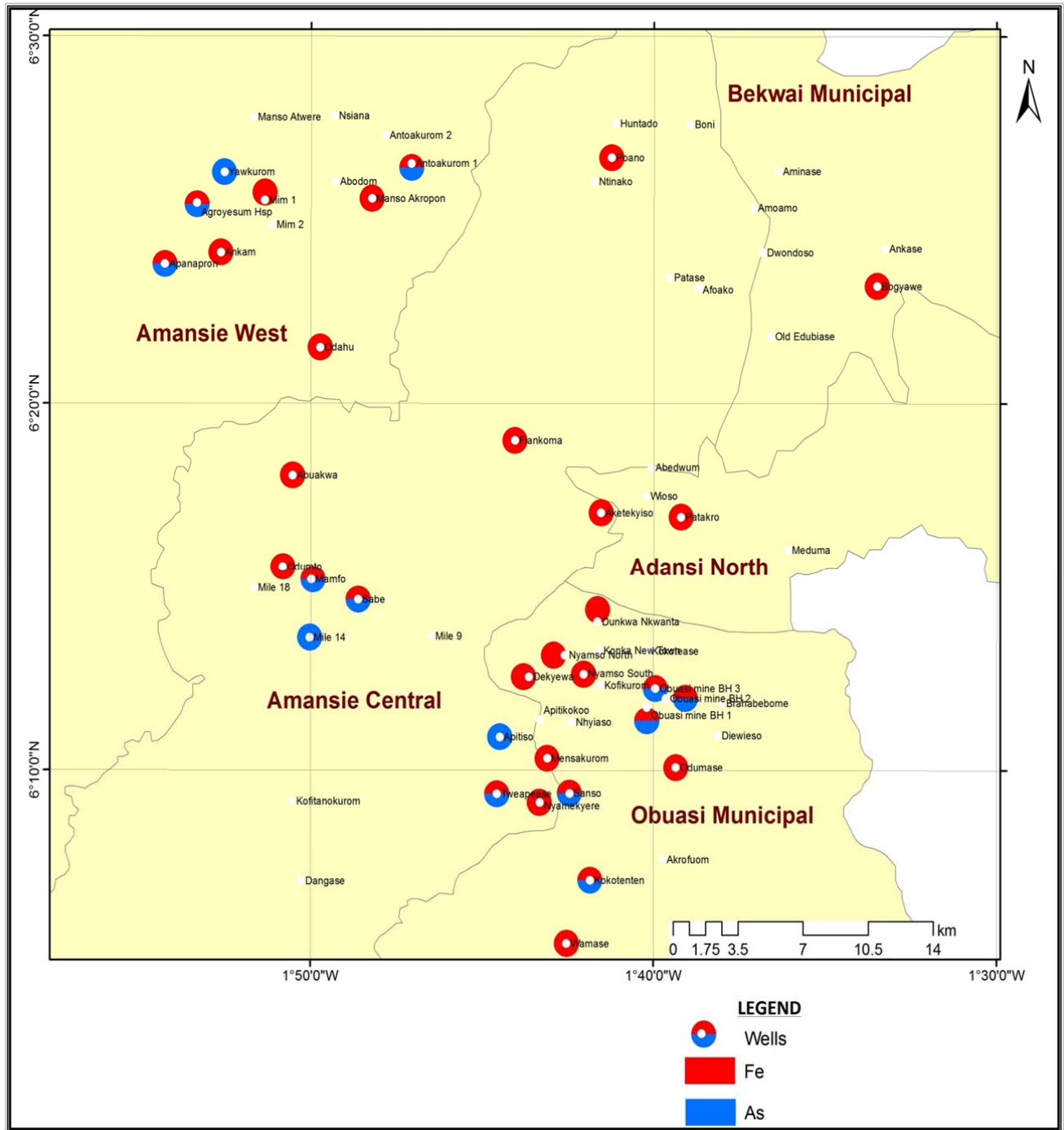


Figure 9.1: Wells with concentration levels of arsenic and iron higher than their permissible limit.

9.2 The Three-Earthen Pot System

The Three-Earthen Pot arsenic/iron removal system yielded reasonably removal efficiency results. Table 9.1 shows arsenic and iron concentrations of samples taken before and after the treatment.

Table 9.1: Arsenic and iron test results for the Three-Earthen Pot System

Test water ID	Concentration levels		Concentration levels		Percentages Removed (%)	
	Untreated water		Treated water		As	Fe
	As ($\mu\text{g/L}$)	Fe (mg/L)	As ($\mu\text{g/L}$)	Fe (mg/L)		
ACS 3-1	73	0.25	8	0.08	89	68
ACS 3-2	71	0.19	7	<0.01	90	100
ACS 3-3	72	0.27	9	0.04	88	85
ACS 3-4	70	0.26	11	<0.01	84	100
ACS 3-5	74	0.24	7	0.07	91	71

On average, the treatment yielded 87 % reduction in arsenic concentrations, and the range of arsenic concentrations in the treated samples was 7 to 11 $\mu\text{g/L}$ (mean: 8.4 $\mu\text{g/L}$). The mean concentration levels of arsenic in treated water were well below the WHO guideline value for arsenic in drinking water of 10 $\mu\text{g/L}$. Similarly, iron was substantially reduced in the treated water upon treatment through the Three-Earthen Pot arsenic/iron removal system. On average 85 % of iron removal was observed and the range of iron concentrations in the treated samples was <0.01 (below detection limit) to 0.08 mg/L (mean: 0.06 mg/L). The Three-Earthen Pot System was a success. Except for the fourth run which removed arsenic contamination of 11 $\mu\text{g/L}$ which was slightly above the WHO guideline value of 10 $\mu\text{g/L}$.

9.2.1 Cost and Availability of the Three-Earthen Pot System

Table 9.2 gives the cost component associated with the materials and reagents in the make-up of the Three-Earthen Pot unit.

Table 9.2: Cost and Availability of the Three-Earthen Pot System

Materials/reagents	Cost in Ghana (GHC)	Cost in Europe (€)
Three-Earthen Pots (25 L)	21	6.8
20 L capacity plastic bucket	3	1.0
Ferric chloride (1.0 Kg)	4.1	1.3
Charcoal powder (1.0 Kg)	13	4.2
Sodium hypochlorite solution (1.0 L)	4.6	1.5
Total Cost (First Year/Subsequent Years)	45.7/21.7	14.8/7.0

(Currency conversion uses exchange rate as of July 2013 updated in December 2013).

As shown in Table 9.1 and 9.2, the Three-Earthen Pot System was effective in removing arsenic from drinking water to below the 10 ug/L in four out of five runs. The results gave an average removal rate of over 87 %. Besides being effective, it is also an appropriate technology. The system has a simple design and was easily constructed. It has a relatively low cost of about GH¢ 45.7 for the first year and GH¢ 21.7 for the subsequent years. The materials necessary to assemble the system were obtained locally, with the exception of the chemicals which were purchased from MES Equipment Chemicals Limited in Accra, Ghana and are mostly available in other pharmaceutical and chemical companies/shops in Ghana.

The drawback to this system is that it has been known to become easily clogged. Clogging encourages the water to take a longer period of time for clean water to trickle down to the bottom receiving pot. If the system becomes too clogged, it will not be able to provide an adequate supply of water to its users. However, the problems of clogging was easily solved by removing the “Kente” cloth overlaid with fine and course sand and rinse it with boiled water. The “Kente” cloth can be reused up to twenty times before replacement. Since each batch treats twenty liters, this would mean that at least 400 liters of water could be treated before replacing the “Kente” cloth. Once 400 liters have been treated, the piece of “Kente” cloth must be replaced.

The results of this study is comparable to a similar work conducted by Alauddin, *et al.*, (2000) in Bangladesh using the Three-Kalshi System but there were some differences. The Three-Earthen Pot System proved to be more effective at removing arsenic than the results from the Three-Kalshi. While the Three-Earthen Pot System removed arsenic to an average concentration of 8.4 ug/L (with an average influent concentration of 72 ug/L) in Sabe community well in south-western Ashanti, the Three-Kalshi System had an average removal of 17 ug/L (with an average influent concentration of 90 ug/L). Since the testing for the Three-Kalshi System was done in Bangladesh, where the drinking water standard for arsenic in drinking water is set at 50 ug/L, the results for that system were satisfactory. Ghana, on the other hand, uses the WHO guideline value of 10 µg/L. Nonetheless, the Three-Earthen Pot Systems proved to be success in this regard.

9.3 Household Coagulation and Filtration System/ Jerry Can System

The result for the evaluation of the household coagulation and filtrations system popularly referred to as jerry can/"Kufuor gallon" are presented in Table 9.3 and 9.4, respectively.

Table 9.3: Results of effluent from household coagulation and filtrations system

Test water ID	Concentration levels Untreated water		Concentration levels Treated water		Percentages Removed (%)	
	As ($\mu\text{g/L}$)	Fe (mg/L)	As ($\mu\text{g/L}$)	Fe (mg/L)	As	Fe
ACS 3-1	73	0.25	11	0.17	85	32
ACS 3-2	71	0.19	9	0.06	87	68
ACS 3-3	72	0.27	14	0.14	81	85
ACS 3-4	70	0.26	8	0.13	86	48
ACS 3-5	74	0.24	10	0.09	86	63

With reference to the results obtained from the household coagulation and filtration system/ Jerry can system, 85 % reduction in arsenic concentrations was achieved on average and the concentrations ranges from 8 to 14 $\mu\text{g/L}$ with a mean value of 10.4 $\mu\text{g/L}$ which was slightly above the WHO recommended guideline value for drinking water. In a related development, iron exhibited a reduction in concentration. On average 59 % of iron removal was observed and the range of iron concentrations in the treated samples was 0.06 to 0.17 mg/L (mean: 0.12 mg/L).

9.3.1 Cost and Availability of the Household Coagulation and Filtration System

Cost of materials and reagents used in setting up the household coagulation and filtration system/ Jerry can system are presented in Table 9.4.

Table 9.4: Cost and availability of the household coagulation and filtration system

Materials/reagents	Cost in Ghana (C)	Cost in Europe (€)
20 L Jerry cans (2)	10	3.3
potassium permanganate (1.0 Kg)	6.3	2.0
alum, $\text{Al}_2(\text{SO}_4)_3$ (1.0 Kg)	2.1	0.7
90-PPI-White-Polyester foam (20 pieces)	10	3.3
Total Cost (First Year/Subsequent Years)	28.4/8.4	9.3/3.3

(Currency conversion uses exchange rate as of July 2012 updated in December 2013).

The household coagulation and filtration system/Jerry can system was not as effective at removing arsenic to an appreciable level as compared to the Three-Earthen Pot removal Chair of Environmental Geology, BTU

system as the former only gave appreciable results in two runs out of five runs as shown in Table 9.3. The results for the former gave an average removal rate of over 85 % for arsenic and 59 % of iron. Unfortunately, even if this system was effective, it is not appropriate. Although it is inexpensive (cost of construction was GHC 28.4 for the first year and GHC 8.4 for the subsequent years) and simple as compared to the Three-Earthen Pot system, that notwithstanding, household coagulation and filtration system requires much mechanical energy for better mixing.

CHAPTER TEN**10. CONCLUSION AND RECOMMENDATION****10.1 Conclusion**

Hydrogeochemical characteristics and elemental features of groundwater from monitored wells and boreholes have been studied to better understand the origin, sources, and mobilization process responsible for As-enrichment as well as to identify and characterize the distribution and concentration levels of arsenic in drinking water in parts of south-western Ashanti Region of Ghana. The main conclusions derived from this study are summarized as follows:

- Hydrogeochemical analysis of groundwater samples from 63 monitored wells and boreholes (depth 1.5–100 m) demonstrate that the groundwater composition varies from Ca–Mg–HCO₃ to Na–K–HCO₃ and anoxic in nature (mean Eh = 200.3 mV).
- The results for arsenic contamination revealed that, arsenic concentrations ranged from <0.1–72 µg/L and <0.1–83 µg/L during the dry and the wet seasons respectively. The data demonstrated that 59 % of the groundwater samples contained no detectable levels of As, 17 and 22 % of the samples gave results with levels of As above the World Health Organization (WHO) guideline value for drinking water standard of 10.0 µg/L, while 24 and 19 % of the samples showed results below the WHO drinking water guideline value during the dry and the wet seasons, respectively. Dissolved inorganic As species predominate with arsenite as the main form. Nonetheless, the continuous consumption of such groundwater with modest concentration levels of arsenic and its species can accumulate and result in acute and/or deadly chronic effects.
- The relationship between well depth and total arsenic concentrations revealed weak correlation (Spearman's rho, $r=0.43$ and 0.41 during the dry and the wet seasons, respectively, with $p>0.05$). The high arsenic levels were predominantly in the shallow wells (medium depth) of around 20 to 70 m as compared to the deeper wells (70 to

100 m). Thus the source of high arsenic concentrations in the various wells and boreholes may largely result from anthropogenic activities such as large scale mining from AngloGold Ashanti mines and illegal artisanal mining activities spread across the study area.

- Arsenic speciation studies demonstrated a large range in the relative proportions of dissolve As-III and As-V in the groundwaters. However, it is evident that the concentration of As-III was found to be higher than As-V in 85 % of the total arsenic detected in the groundwater samples analyzed within the study area, indicating that the reducing conditions were present in the groundwaters within the vicinities of the wells and boreholes.
- Distribution and correlation of As with the various physico-chemical parameters results show relatively lower concentrations of NO_3 and SO_4 along with higher values of HCO_3 . This observation suggested that arsenic was released when arsenic-rich iron oxyhydroxide was reduced in the anoxic condition, a process that mobilized iron and its absorbed load. Negative and much weaker correlation of As with NO_3^- and SO_4^{2-} was also observed, meaning that arsenic concentrations are high when nitrate and sulfate concentrations are low. Surprisingly, As concentrations did not correlate well with Fe, this contrasts with what is generally expected in case of As release from reductive dissolution of Fe oxides in such reducing environments
- During both the dry and the wet seasons, there was a strong correlation between TDS and EC, Mg, Ca and Mn. A strong correlation existed between EC and Na, Mg, Ca, Mn and As. Mg also correlated positively with Ca and Mn. Ca showed an impact as they exhibited positive correlation with Mn and As. Besides the positive correlation exhibited between the above-mentioned parameters, Eh, DO, SO_4 , NO_3 , PO_4 , pH, K and DOC did not show any significant relation with any parameter during the study.
- Among the heavy metals, Mn-Fe exhibited good correlation followed by the pairs such as Mn-Zn, Fe-Zn, Cu-Zn and Mn-As showed relatively moderate correlation whereas Mn-Cu, Fe-Cu, Fe-As, Cu-Zn, Cu-As and Zn-As showed relatively lower correlations during both seasons. The lower correlations may be due to dilution effect.

- It appears that high As concentrations in south-western part of Ashanti Region result from the contribution of different mechanisms which can be grouped into two namely aquifers under oxidizing conditions (aided by sulphide mineralization) and aquifers under reducing conditions as a result of reduction dissolution of arseniferous iron oxyhydroxide that exist as a dispersed phase on the sedimentary grains of the aquifer. In addition, water residence time and different water use practices also influences As concentrations in the groundwater.
- With reference to the distribution of arsenic and other heavy metals (Fe, Cu, Mn and Zn) contamination from the mine tailings dams, considerable amount of these contaminants were associated with gold mine tailings dams, irrespective of whether the dam was active or abandoned. The potential impact for the abandoned tailings dam was however greater compared to the active one and the serious threat is AMD from the tailings which can be either oxidized acidic or neutral leaching considerable amount of As and trace metals into groundwater and sediments that may be transported hundreds of kilometers downstream from their source. Arsenic contents of both tailings (active and abandoned) far exceeded the recommended Netherlands intervention value of 55 mg/kg, hence, constituted significant environmental health threat.
- Cu and Zn levels in abandoned tailings dam site fell short of recommended background level of 36 mg/kg and 140 mg/kg respectively, but all the tailings dam sites were still within the intervention limit of 190 mg/kg for Cu and 720 mg/kg for Zn, however, Fe and Mn contents of the mine tailings registered high levels, though they lack intervention values for contaminated soils which might not present direct environmental threat, although potentially, they could remobilize (with rainfall) and affect aquatic systems.
- With reference to the suitability of groundwater for domestic and agricultural purposes, almost all the parameters including pH, sodium, potassium, carbonate, bicarbonate, chloride were within the permissible limits prescribed by WHO during both the dry and the wet seasons; however, 82.8 % of the analyzed groundwater

samples registered a pH which were in non desirable range (acidic) during the wet season. This may come about as a result of fluctuating groundwater table that may cause mixing and dilution effect during the wet season. As far as cations and anions are concerned, all the analyzed shallow wells and boreholes within the study area are almost safe during both seasons.

- The groundwater in south-western part of Ashanti Region of Ghana is generally soft and has a high public acceptability for domestic and agricultural use. Further, there were no health-based concerns perceived in groundwater use for drinking and other domestic purposes in the study area. Thus, groundwater samples analyzed in the study area can deemed fit for drinking purposes but further exploitation may increase trace metals contamination and deteriorate the water quality in the near future.
- The results for the spatial distribution of pH, TDS, TH, EC, SAR, PS and RSC of the groundwater samples analyzed generally appear to be within safe limits. However, high % Na values observed within 44 and 34 % of the groundwater samples analyzed during the dry and the wet seasons of the study area might suggest erosion of sodium bearing rock minerals. Nonetheless, groundwater within the study area are generally of permissible to good quality and was found to be suitable for domestic and agricultural purposes.
- The evaluation of arsenic removal systems in south-western Ashanti Region of Ghana showed that the Three-Earthen Pot arsenic removal system could adequately achieved arsenic removal from the arsenic contaminated drinking well water. Additional evaluation using the household coagulation and filtration system/Jerry can system also showed reasonably good arsenic/iron removal rate assuming a correct application of adequate coagulant dose. However, the Three-Earthen Pot removal technology showed an impressive result which is not comparable to the household coagulation and filtration system/Jerry can system.
- In general, the two removal technologies, particularly the Three-Earthen Pot arsenic removal system were able to reliably reduce arsenic concentration below the WHO guideline value of 10 µg/L in the arsenic-concentration source water range tested (70-

74 $\mu\text{g/L}$). However, the Three-Earthen Pot and household coagulation and filtration removal technology were able to remove the arsenic to 7-11 and 8-14 $\mu\text{g/L}$, respectively.

- Considering the cost and the availability in building up a removal unit, it was observed that, the cost was fairly reasonable and the rural folks were not ready to compromise their health and many of the families we visited has resulted to one of these treatment mechanism.
- This study found that the two different point-of-use arsenic/iron removal systems can be used to achieve effective arsenic/iron removal, capable of reducing arsenic and iron concentration below the WHO guideline value for drinking water. However, the Three-Earthen Pot system was found to be more effective than the household coagulation and filtration system. Hence, the Three-Earthen Pot arsenic removal system is a viable option that can be immediately implemented in order to address a growing arsenic contamination problem not only in south-western Ashanti but also arsenic and iron affected areas in Ghana.

10.2 Recommendation

The potential for elevated arsenic and other trace metals in groundwater is not an issue with which many groundwater users are aware, but this work has now delineated areas that are susceptible to this problem and has enhanced better overall understanding of the characteristics, source and release mechanism of arsenic in groundwater resources in the south-western part of Ashanti Region of Ghana. The following recommendations give an outline of a list of suggested future work and regulatory implications as appropriate means of mitigating risks associated with elevated arsenic concentrations in groundwater:

- Despite the fact that some groundwaters in the study area have As concentrations higher than the revised WHO recommended limit, it is convincingly clear that groundwater from even potentially vulnerable areas such as gold-mining towns, can

still provide a much healthier source of potable water than the unsafe surface waters which may have high concentrations of toxic trace metals derived from both mining activity and natural sulphide-bearing aquifers. Hence, As-contaminated groundwater should be investigated as a potential health risk, but the groundwaters occurring within the study area should not necessarily be demised as unsuitable for rural-water supply.

- Drinking As-contaminated groundwater has been associated to cancer occurrence in highly exposed populations in some other parts of the world. Hence it would be very helpful if a comprehensive health and epidemiological studies are carried out in south-western part of Ashanti Region and other unstudied mining regions in Ghana because, it is possible the more people than considered today are affected by arsenic contaminated groundwater sources.
- Regular monitoring of As contamination in groundwater within the nation is to identify the existence of any long term trends that might be linked to human activities, such as irrigation of farm and mining effluents on to land, or draw-down of groundwater.
- Additionally, public health education must be focused on As-contaminated areas and new guidelines should be developed to routinely test groundwaters by well drillers after drilling to prevent and/or reduce a significant number of families from being exposed to arsenic from their drinking water.
- The construction of a containment facility on the tailings dam by the mining companies is important to prevent future spillage of waste materials over the site and into the nearby rivers and streams. Further, soil management measures such as liming are crucial to prevent the migration of As and its associated contaminants from the topsoil into the subsoil and groundwater.
- Further research is needed to understand the capacity of the vadose zone to retain and attenuate arsenic and other trace elements in the long-term as well as the mobility and bioavailability of pollutants as the vadose zone underneath gold mine tailings dams is

expected to be contaminated for an extended period of time. Again studies to understand the mechanisms of As transport from the tailings dams, the distance profile of the As from the tailings dams and As remobilization potential, especially during rainy seasons have also been identified for further reserach.

- To reduce the level of risk posed by exposure to arsenic contaminated drinking water, recommended preventative measures including simple cost effective point-of-use removal technology was developed to mitigate risks associated with elevated arsenic concentrations in groundwater. It is therefore recommended that grants be sought in order to implement this system on a large scale.
- In addition targeted monitoring is crucial in all satellites areas closed to mining centers in reducing the cost of testing for arsenic and other heavy metals in every monitored wells/boreholes and the methods developed here can also be applied in determining arsenic and other heavy metals in other unstudied mining regions and areas of public health concern.
- GIS based spatial distribution maps generated through this investigation for various groundwater quality parameters will be helpful for planners and policy makers in suggesting remedial measures in a holistic way for sustainable groundwater management in the study area.
- Moving forward, it is my anticipation that the findings of this study will serve as a master piece to advise policy makers, well and borehole owners about the dangers or potential risks associated with arsenic and other trace metals in drinking water supplies sourced from groundwater and how these can be managed. In addition, this research has identified high-risk As-contaminated areas, potential health issues, methodology for assessing arsenic in groundwater, and a broad outline of two point-of-use arsenic treatment options which can target populations at risk to protect public health and help shape the national, regional, municipal and districts water monitoring policies.

REFERENCES

- Abraham, E.M., van Rooijen, D., Cofie, O. and Raschid-Sally L. (2007): Planning urban water dependent livelihood opportunities for the poor in Accra, Ghana. SWITCH Scientific Meeting. University of Birmingham, UK. 9-10 January, 2007.
- Acharyya, S.K., Chakraborty, P., Lahiri, S., Raymahashay, B.C., Guha, S. and Bhowmik, A. (1999): As poisoning in the Ganges delta. *Nature*, 401, 545–546.
- Acharyya, S.K., Lahiri, S., Raymahashay, B.C. and Bhowmik, A. (2000): Arsenic toxicity of groundwater in parts of the Nengal Basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. *Environmental Geology*, 39(10): 1127-1137. *Environmental Health Perspectives*, 12, 131–135.
- Agilent Technologies (2007): Handbook of Hyphenated ICP-MS Applications. <http://www.chem.agilent.com/Library/applications/5989-6160EN.pdf> [Accessed on April 3, 2014].
- Ahmad, K. and Carboo, D. (2000): Speciation of As (III) and As (V) in some Ghanaian gold tailings by a simple distillation method. *Water, Air Soil Pollution*, 122, 317–326.
- Akabzaa, T.M. (2000): Boom and Dislocation. *Third World Network-Africa*, pp. 131.
- Akabzaa, T. and Darimani, A. (2001): Impact of mining sector investment in Ghana: a study of the Tarkwa Mining Region. Report to SAPRI.
- Akabzaa, T M., Banoeng-Yakubu, B.K. and Seyire, J.S. (2005): Heavy metal contamination in some mining communities within Jimi river basin in Ashanti Region. *Journal of the Ghana Science Association*, 7 no.1.
- Alagbe, S.A. (2006): Preliminary evaluation of hydrochemistry of the Kalambiana Formation, Sokoto Basin, Nigeria. *Environmental Geology*, 51, 39–45.
- Alauddin, M., Hussam, A., Khan, A.H., Habibuddowala, M., Rasul, S.B. and Munir, K.M. (2000). Critical evaluation of a simple arsenic removal method for groundwater of Bangladesh: Proceeding of Fourth International Conference on Arsenic Exposure and Health Hazards. San Deigo, CA. June, 2000.
- Alaya, M.B., Saidi, S., Zemni, T. and Zargouni, F. (2014): Suitability assessment of deep groundwater for drinking and irrigation use in the Djeffara aquifers (Northern Gabes, south-eastern Tunisia). *Environmental Earth Sciences*, 71, 3387–3421.
- Allen, H.E., Perdue, E.M. and Brown, D.S. (1993): *Metals in groundwater*. Michigan: Lewis publishers.
- Amasa, S.K. (1975): Arsenic pollution at Obuasi goldmine, town, and surrounding countryside. *Environmental Health and Perspective*, 12, 131–135.

- Amonoo-Neizer, E.H. (1980): Arsenate adsorption by some Ghana soils. *Bulletin of Science Association, Nigeria*, 6 (1), 2.
- Amonoo-Neizer, E.H. and Busari, G.L. (1980): Arsenic status of Ghana soils–Contamination of soils near gold smelters. *Ghana Journal of Science*, 20 (1,2), 57–62.
- Amonoo-Neizer, E.H. and Amekor, E.M.K. (1993): Determination of total arsenic in environmental samples from Kumasi and Obuasi, Ghana. *Environmental Health and Perspective*, 101(1), 44–49.
- Amonoo-Neizer, E.H., Nyamah, D. and Bakiamoh, S.B. (1996): Mercury and arsenic pollution in soil and biological samples around the mining town of Obuasi, Ghana. *Water, Air, and Soil Pollution*, 91, 363–373.
- Amy, G., Edwards, M., Brandhuber, P., McNeill, L., Benjamin, M., Vagliasindi, F., Carlson, K. and Chwirka, J. (2000): Arsenic treatability options and evaluations of residuals management issues. *American Water Works Association (AWWA). Research Foundation, Denver*, 259.
- AngloGold Ashanti. (2006): AngloGold Ashanti Annual Report 2006 – Annual Financial Statements.
- Anon, (1992): Ashanti mine expansion project; Environmental Impact Assessment, Jay minerals Service Limited, Obuasi.
- Anon, (2002): Ashanti Goldfields Company Limited long range planning department (unpublished).
- Ansong Asante, O., Agusa, T., Kubota, R., Subramania, A., Ansa-Asare, O. D. and Tanbe, S. (2005): 14th symposium on Environmental chemistry, Osaka.
- Antwi-Agyei, P., Hogarth, J.N. and Foli, G. (2009): Trace elements contamination of soils around gold mine tailings dams at Obuasi, Ghana. *African Journal of Environmental Science and Technology*, 3(11), 353–359.
- Appelo, C.A.J. and Postma, D. (1999): *Geochemistry, groundwater and pollution*. A.A. Balkema, Rotterdam. p. 536.
- Appelo, C.A.J. and Postma, D. (2005): *Geochemistry, groundwater and pollution*, second ed. A.A Balkema, Leiden, The Netherlands.
- Appelo, C.A.J., Van der Weiden, M.J.J., Tournassat, C. and Charlet, L. (2002); Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environmental Science and Technology*, 36, 3096–3103.
- Appleyard, S.J., Angeloni, J. and Watkins, R. (2006): Arsenic-rich groundwater in an urban area experiencing drought and increasing population density, Perth, Australia. *Applied Geochemistry*, 21, 83-97.

- Asamoah, K. (2004): AngloGold Ashanti Limited Obuasi mine (Arsenic disposal project) Environmental Impact Statement. AngloGold Ashanti, Obuasi – Ghana.
- Asiam, E.K. (1996): Environmental assessment of gold beneficiation: Arsenic audit and impact on Obuasi environs. *Ghana Mining Journal*, 2 (1), 17–20.
- Assignment Point (2013): Atomic absorption spectroscopy. <http://www.assignmentpoint.com/science/chemistry/atomic-absorption-spectroscopy.html> [Accessed on March 8, 2014].
- Atta – Quason, (1999). Atlas, Macmillan Education Limited.
- Ayotte, J.D., Montgomery, D.L., Flanagan, S.M. and Robinson, K.W. (2003): Arsenic in groundwater in Eastern New England: Occurrence, controls, and human health implications. *Environmental Science and Technology*, 37, 2075–2083.
- BC Wild and Environmental Mining Council of BC. (2001): Acid mine drainage. Mining and water pollution issues. Environmental Mining Council of BC.
- B’Hymer, C. and Caruso, J.A. (2004): Arsenic and its speciation analysis using high performance liquid chromatography and inductively coupled plasma mass spectrometry. *Journal of Chromatography A*, 1045, 1–13.
- Badruzzaman, M., Westerhoff, P. and Knappe, D.R.U. (2004): Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH). *Water Research*, 38(18), 4002–4012.
- Baldvins, S. (2011): Analytical Problem: Geochemical Mobilization of Arsenic to Ground Water. Chem 4101 Course Material http://blog.lib.umn.edu/arriaga/chem4101/2011/09/sara_baldvins_analytical_pro.html [Accessed on December 13, 2011].
- Bauer, M. and Blodau, C. (2006): Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Science of the Total Environment*, 354, 179–190.
- Bednar, A.J., Garbarino, J.R., Burkhardt, M.R., Ranville, J.F. and Wildeman, T.R. (2004): Field and laboratory arsenic speciation methods and their application to natural water analysis. *Water Research*, 38, 355–364.
- Bempah, C.K., Asomaning, J., Ansong, D.A., Boateng, J. and Asabere, S.B. (2012): Contamination levels of selected organochlorine and organophosphorous pesticides in Ghanaian fruits and vegetables. *Emirates Journal of Food and Agriculture*, 24 (4), 293–301.
- Bempah, C.K., Ewusi, A., Obiri-Yeboah, S., Asabere, S.A., Mensah, F., Boateng, J. and Voigt, H-J. (2013): Distribution of arsenic and heavy metals from mine tailings dams at Obuasi Municipality of Ghana. *American Journal of Engineering Research*, 2 (5), 61–70.

- Berg, M., Tran, H.C., Nguyen, T.C., Pham, H.V., Schertenleib, R. and Giger, W. (2001): Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. *Environmental Science and Technology*, 35, 2621–2626.
- Bhattacharjee, S., Chakravarty, S., Maity, S., Dureja, V. and Gupta, K.K. (2005): Metal contents in the groundwater of Sahebgunj district, Tharkhand, India, with special reference to Arsenic. *Chemosphere*, 58, 1203–1217.
- Bhattacharya, P., Jacks, G., Ahmed, K.M., Khan, A.A. and Routh, J. (2002): Arsenic in groundwater of the Bengal Delta Plain aquifers in Bangladesh. *Bulletin of Environmental Contaminants and Toxicology*, 69, 538–545.
- Bhattacharya, P., Claesson, M., Bundschuh, J., Sracek, O., Fagerberg, J., Jacks, G., Martin, R.A., Storniolo, A.R. and Thir, J.M. (2006): Distribution and mobility of arsenic in the Rio Dulce alluvial aquifers in Santiago del Estero Province, Argentina. *Science of the Total Environment*, 358, 97–120.
- Blowes, D.W. (1997): The environmental effects of mine wastes. In “Proceedings of Exploration 97: Fourth Decennial International Conference on Mineral Exploration” edited by A.G. Gubins, 1997, p. 887–892.
- Boadu, M., Osa, E.K., Gollow, A.A., Serfor-Armah, Y. and Nyarko, B.J.B. (2001): Determination of arsenic in some water bodies, untreated ore and tailing samples at Konongo in the Ashanti region of Ghana and its surrounding towns and villages by instrumental neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 249 (3), 581–585.
- Boateng, E., Dowuona, G.N.N., Nude, P.M., Foli, G., Gyekye, P. and Jafaru, H.M. (2012): Geochemical assessment of the impact of mine tailings reclamation on the quality of soils at AngloGold concession, Obuasi, Ghana. *Research Journal of Environmental and Earth Sciences*, 4(4), 466–474.
- Borba, R.P., Figueiredo, B.R. and Matschullat, J. (2003): Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil. *Environmental Geology*, 44(1), 39–52.
- Boroughs, D.L. (1997): Africa’s untapped billions: the new gold rush. *US News and World Report* 22:48.
- Bose, P. and Sharma, A., (2002): Role of iron in controlling speciation and mobilization of arsenic in subsurface environment. *Water Research*, 36, 4916–4926.
- Bose, U., Rahman, M. and Alamgir, M. (2011): Arsenic toxicity and speciation analysis in groundwater samples: A Review of Some Techniques. *International Journal of Chemical Technology*, 3, 14–25.
- Bowell, R.J. (1993): Mineralogy and geochemistry of tropical rain forest soils: Ashanti, Ghana. *Chemical Geology*, 106, 345–358.

- Bowell, R.J., Morley, N.H. and Din, V.K. (1994): Arsenic speciation in the pore waters from the Ashanti Mine, Ghana. *Applied Geochemistry*, 9, 15–22.
- Bowell, R.J., Fuge, R., Connelly, R.J. and Sadler, P.K.J. (1996): Controls on ochre chemistry and precipitation in coal and metal mine drainage. In: *Minerals, Metals and the Environment II*, Prague, September 1996. I.M.M., London, pp. 291–323.
- Cao, S. (1996): Current status of inorganic arsenic contamination in mainland China. *Chinese Journal of Public Health*, 15 (3), S6–S10 (in Chinese).
- Canfield, D.E. (2005): The early history of atmospheric oxygen: Homage to Robert M. Garrels. *Annual Reviews of Earth Planet and Science*, 33, 1–36.
- Carbo, D. and Sarfor-Armah, Y. (1997): Arsenic pollution in streams and sediments in the Obuasi Area, Proc. of UST-IDRC'97 National Symposium, Kumasi, Ghana. pp. 114.
- Carmelita Nishanthiny, S., Thushyanthy, M., Barathithasan, T. and Saravanan, T. (2010): Irrigation water quality based on hydro-chemical analysis, Jaffna, Sri Lanka. *American-Eurasian Journal of Agriculture and Environmental Sciences*, 7 (1), 100–102.
- Chakravarty, S., Dureja, V., Bhattacharyya, G., Maity, S. and Bhattacharjee, S. (2002): Removal of arsenic from groundwater using low cost ferruginous manganese ore. *Water research*, 36, 625–632.
- Chapman, D. (1992): *Water Quality Assessments. A guide to the use of biota, sediments and water in environmental monitoring.* University Press. Cambridge. UK.
- Chattopadhyayi, S., Gupta, S. and Saha, R.N. (2010): Spatial and temporal variation of urban air quality: A GIS approach. *Journal of Environmental Protection*, 1, 264–277.
- Chowdhury, T.R., Basu, G.K., Mandal, B.K., Biswas, B.K., Samanta, G., Chowdhury, U.K., Chanda, C.R., Lodh, D., Roy, S.L., Saha, K.C., Roy, S., Kabir, S., Quamruzzaman, Q. and Chakraborty, D. (1999): Arsenic poisoning in the Ganga delta. *Nature*, 401, 545–546.
- Christen, K. (2001): In Vietnam and other developing countries, arsenic contamination of groundwater is becoming the key environmental health problem of the 21st century. *Environmental Science and Technology*, 35 (13), 2621–2626.
- Christensen, T.H., Kjeldsen, P., Albrechtsen, H.J., Heron, G., Nielsen, P.H., Holm, P.L. and Bjerg, P.E. (1994): Attenuation of landfill leachate pollutants in aquifers. *Critical Review: Environmental Science and Technology*, 24, 119–202.
- Chwirka, J.D., Thomson, B.M. and Stomp, J.M.I. (2000): Removing arsenic from groundwater. *Journal / American Water Works Association*, 92, 79–88.
- Corr, J.J. and Larsen, E.H. (1996): Arsenic speciation by liquid chromatography coupled with ionspray tandem mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 11 (12), 1215–1224.

- Cullen, W.R. and Reimer, J.K. (1989): Arsenic speciation in the environment. *Chemical Reviews*, 89, 713–716.
- Daily Kos Action Media Network (2010): Look away Dixieland-coal ash and arsenic in South Carolina. <http://www.dailykos.com/story/2010/03/03/840142>. [Accessed on March 28, 2010].
- Daus, B., Wennrich, R. and Weiss, H. (2004): Sorption materials for arsenic removal from water: A comparative study. *Water Research*, 38, 2948–2954.
- Day, P.R. (1965): Particle fractionation and particle size analysis. In: *methods of soil analysis*, No. 9 Part 2. Black, C.A., (Ed.), American Society of Agronomy, Madison, Wisconsin, pp: 545–567.
- Duker, A.A., Carranza, E.I.M. and Hale, M. (2004): Spatial dependency of Buruli ulcer prevalence on arsenic-enriched domains in Amansei West District, Ghana: implications for arsenic meditation in mycobacterium ulcerans infection. *International Journal of Health and Geographics*, 3, 19.
- Duker, A.A., Carranza, E.J.M. and Hale, M. (2005): Arsenic geochemistry and health. *Environment International*, 31(5), 631–641.
- Eaton, F.M. (1950): Significance of carbonate in irrigation water. *Soil Sciences*, 69.
- Ecology Global Network. (2013): New way to protect groundwater. *Water Pollution*. <http://www.ecology.com/2013/04/25>. [Accessed on March 13, 2014].
- Efe, S.I., Ogban, F.E., Horsfall, M. and Akporhonor, E.E. (2005): Seasonal variation of physico-chemical characteristics of water resources quality in western Niger Delta region, Nigeria. *Journal of Applied Science and Environmental Management*, 191–195.
- Environmental monitoring and Control (2010): <http://wondersofebt.blogspot.de>. [Accessed on December 3, 2010].
- Erickson, M.L. (2005): Arsenic in Upper Midwest groundwater: Occurrence and geochemical mobilization mechanisms. P.hD. Dissertation, University of Minnesota, Minneapolis, Minnesota.
- Farquhar, J. Wing, B.A., McKeegan, K.D., Harris, J.W., Cartigny, P. and Thiemens, M.H. (2002): *Science* 298 (5602), 2369–2372.
- Ferguson J.F and Anderson, M.A. (1974): Chemical forms of arsenic and their removal. In: A.J Robin, ed., *Chemistry of Water Supply Treatment and Distribution*. Ann Arbor Science Publishers, Ann Arbor, Michigan. p.p. 293–319.
- Ferguson, J.F. and Gavis, J. (1972): A review of the arsenic cycle in natural waters. *Water Research*, 6, 1259–1274.

- Foli, G. (2004): Physico-chemical evaluation of some mining impacted water bodies within the Obuasi environment (MPil. Thesis, University of Ghana, Legon) p. 16.
- Francesconi, K.A. (2005): Current perspectives in arsenic environmental and biological research. *Environmental Chemistry*, 2, 141–145.
- Frankenberger Jnr, W.T. (2002): *Environmental chemistry of arsenic*. Marcel Dekker, Inc. New York.
- Fraser Health Authority and BC Ministry of Environment (2008): *Arsenic in Groundwater in the Surrey-Langley Area*. Institute for Resources & Environment. The University of British Columbia. <http://www.fraserhealth.ca/media/ArsenicReportSurreyLangley.pdf> [Accessed on July 3, 2013].
- Freeze, R. A. and Cherry, J. A. (1979): Groundwater. New Jersey: Prentice-Hall geochemical parameter distribution in a ground water system contaminated with petroleum hydrocarbons. *Journal of Environmental Quality*, 30, 1548–1563.
- Fujii, R. and Swain, W.C. (1995): Aerial distribution of selected trace elements, salinity, and major ions in shallow groundwater, Tulare Basin, Southern San Joaquin Valley. USGS water Resources Investigation Report 95–4048.
- Garizi, A.Z., Sheikh, V. and Sadoddin, A. (2011): Assessment of seasonal variations of chemical characteristics in surface water using multivariate statistical methods. *International Journal of Environment Science and Technology*, 8 (3), 581–592.
- Ghana Statistical Service. (2010): 2010 population and housing census. Ghana.
- Ghimire, K.N., Inoue, K., Yamaguchi, H., Makino, K. and Miyajima, T. (2003): Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste. *Water Research*, 37, 4945–4953.
- Gish, C.D. and Christinson, R.E. (1973): Cadmium, nickel, lead and zinc in earthworms from roadside soil. *Environmental Science and Technology*, 7, 71060–71062.
- Goel, R., Kapoor, S.K., Misra, K. and Sharma, R.K. (2004): Removal of arsenic from water by different adsorbents. *Indian Journal of Chemical Technology*, 11, 518–525.
- Golow, A.A., Schlueter, A., Amihere-Mensah, S., Granson, H.L.K. and Tetteh, M.S. (1996): Distribution of arsenic and sulphate in the vicinity of Ashanti goldmine at Obuasi, Ghana. *Bulletin of Environmental Contamination and Toxicology*, 56, 703–710.
- Goyal, S.K., Sethi, G.K. and Chaudhary, B.S. (2006): Integrated groundwater studies in Kaithal district of Haryana, using remote sensing and GIS. *Proceedings of National Conference on Environmental Conservation*. Sept 1–3, Pilani, India, pp 745–751.
- Griffis, R.J., Barning, K., Agezo, F.L. and Akosah, F.K. (2002): *Gold deposits of Ghana*. Minerals Commission of Ghana, Accra.

- Grimes, D.J., Ficklin, W.H., Meier, A.L. and McHugh, J. B. (1995): Anomalous gold, antimony, arsenic, and tungsten in groundwater and alluvium around disseminated gold deposits along the Getchell Trend, Humboldt County, Nevada. *Journal of Geochemistry and Exploration*, 52, 351–371.
- Guanxing, H., Zongyu, C. and Jichao, S. (2014): Water quality assessment and hydrochemical characteristics of groundwater on the aspect of metals in an old town, Foshan, south China. *Journal of Earth System Science*, 123 (1), 91–100.
- Gunduz, O., Simsek, C. and Hasozbek, A. (2009): Arsenic pollution in the groundwater of Simav Plain, Turkey: its impact on water quality and human health, *Water Air Soil Pollution*, doi:10.1007/s11270-009-0055-3.
- Habuda-Stanic', M., Kuleš, M., Kalajdz'ic', B. and Romić, Z'. (2007): Quality of groundwater in eastern Croatia. The problem of arsenic pollution. *Desalination*, 210, 157–162.
- Han, B., Zimbron, J., Runnells, T.R., Shen, Z. and Wickramasinghe, S.R. (2003): New arsenic standard spurs search for cost-effective removal techniques. *Journal of American Water Works Association*, 95, 109–118.
- Hasan, M.A., Ahmed, K.M., Sracek, O., Bhattacharya, P., von Bromssen, M., Broms, S., Fogelstrom, J., Mazumder, M.L. and Jacks, G. (2007): Arsenic in shallow groundwater of Bangladesh: investigations from three different physiographic settings. *Hydrogeology Journal*, 15, 1507–1522.
- Hem, J. D. (1985): Study and interpretation of the chemical characteristics of natural water. U. S. Geological Survey Water-Supply. Paper 2254.
- Hemond, H.F. and Fechner-Levy, E.J. (2000): Chemical fate and transport in the environment. San Diego: Academic Press, 2000.
- Hering J.G. and Wilkie J.A. (1996): Adsorption of arsenic onto ferric hydroxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloidal Surface A*, 107, 97–110.
- Hiscock, K.M., Rivet, M.O. and Davison, R.M. (2002): Sustainable groundwater development. Geological Society, London, Special Publication, 193, 165–179.
- Holm, T.R. (2002): Effects of Carbonate/bicarbonate, Si, and Phosphate on arsenic sorption to HFO. *Journal / American Water Works Association*, 94, 174–181.
- Holm, T. R., Kelly, W.R., Wilson, S.D., Roadcap, G.S., Talbott, J.L. and Scott, J.W. (2004): Arsenic geochemistry and distribution in the Mahomet aquifer, Illinois. Illinois Waste Management and Research Center (A Division of the Illinois Department of Natural Resources) Research Report Series. One Hazelwood Dr. Champaign, IL 61820.
- Houben, G.J. (2003): Iron oxide incrustations in wells. Part 1: genesis, mineralogy and geochemistry. *Applied Geochemistry*, 18, 927–939.

- Hurd, J.J. (2001): Evaluation of three arsenic removal technologies in Nepal. A master thesis submitted to the Department of Civil and Environmental Engineering in Partial Fulfillment of the requirements for the degree of Master of Engineering in Civil and Environmental Engineering at the Massachusetts Institute of Technology.
- Hutton-Ashkenny, M., Bowell, R.J. and Dey, M. (2011): Mine Water – Managing the Challenges: Engineering solutions for the removal of arsenic from aqueous solution: A Review. IMWA. SRK Consulting (UK) Ltd., Churchill House, Churchill Way, Cardiff CF10 2HH. p 353–358.
- Idoko, M.O., Ologunorisa, T.E. and Okoya, A.A. (2012): Temporal variability of heavy metals concentration in rural groundwater of Benue State, Middle Belt, Nigeria. *Journal of Sustainable Development*, Vol. 5, No. 2; Doi:10.5539.
- Inskeep, W.P., McDermott, T.R. and Fendorf, S. (2002): Arsenic (V)/(III)cycling in soils and natural waters: Chemical and microbiological processes. In *Environmental Chemistry of Arsenic*, pages 183–215. Marcel Dekker, Inc, New York, Basel, 2002.
- IARC (2004): IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans: Some drinking-water disinfectants and contaminants, including arsenic, Lyon, IARC Press, Vol. 84.
- Jeong, C.H. (2001): Effect of land use and urbanization on hydrochemistry and contamination of groundwater from Taejon area, Korea. *Journal of Hydrology*, 253, 194–210.
- Kar, S., Maity, J.P., Jean, J.S., Liu, C.C., Nath, B., Yang, H.J. and Bundschuh, J. (2010): Arsenic-enriched aquifers: Occurrences and mobilization of arsenic in groundwater of Ganges Delta Plain, Barasat, West Bengal, India. *Applied Geochemistry*, 25, 1805–1814.
- Kesse, G. O. (1985): The mineral and rock resources of Ghana. A.A. Balkema, Rotterdam.
- Kim, M., Ahn, K. and Jung, Y. (2002): Distribution of inorganic species in mine tailings of abandoned mines from Korea. *Chemosphere*, 49, 307–312.
- Kim, M.J. and Nriagu, J. (2000): Oxidation of arsenite in groundwater using ozone and oxygen. *Science of the Total Environment*, 247, 71–79.
- Kim, J.Y., Kim, K.W., Ahn, J.S., Ko, I. and Lee, C.H. (2005): Investigation and risk assessment modeling of As and other heavy metals contamination around five abandoned metal mines in Korea. *Environmental Geochemistry and Health* 27, 193–203.
- Kim, K., Moon, J.-T., Kim, S.-H. and Ko, K.-S. (2009): Importance of surface geologic condition in regulating As concentration of groundwater in the alluvial plain. *Chemosphere*, 77, 478–484.
- Kortatsi, B.K. (2003): Acidification of groundwater and its implication on rural water supply in the Ankobra Basin, Ghana. *West Africa Journal of Applied Ecology*, 4, 35–47.

- Kortatsi, B.K. and Quansah, J. (2004): Assessment of groundwater potential in the Sunyani and Techiman areas of Ghana for urban water supply. *West Africa Journal of Applied Ecology*, 5, 75–92.
- Korte, N.E. and Fernando, Q. (1991): A review of arsenic(III) in groundwater. *Critical Review of Environmental Control*, 21, 1–39.
- Knödel, K., Lange, G. and Voigt, H-J. (2007): *Environmental Geology, Handbook of field methods and case studies*. Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover Federal Institute for Geosciences and Natural Resources. Springer Berlin Heidelberg New York. pp 759–768.
- Kumar, P.R., Chaudhari, S., Khilar, K.C. and Mahajan, S.P. (2004): Removal of arsenic from water by electrocoagulation. *Chemosphere*, 55, 1245–1252.
- Kumaresan, M. and Riyazuddin, P. (2001): Overview of speciation chemistry of arsenic. *Current Science*, Vol. 80, No. 7.
- Kumi-Boateng, B. (2007): Assessing the spatial distribution of arsenic concentration from goldmine for environmental management at Obuasi, Ghana. MSc. Thesis. International Institute for Geo-Infomatics. Science and Earth Observation, Enschede, The Netherlands.
- Kundu, S., Kavalakatt, S.S., Pal, A., Ghosh, S.K., Mandal, M. and Pal, T. (2004): Removal of arsenic using hardened paste of Portland cement: batch adsorption and column study. *Water Research*, 38, 3780–3790.
- Ladeira, A.C.Q. and Ciminelli, V.S.T. (2004): Adsorption and desorption of arsenic on an oxisol and its constituents. *Water Research*, 38, 2087–2094.
- Laluraj, C.M., Gopinath, C.M. and Dineshkumar, P.K. (2004): Groundwater chemistry of shallow aquifers in the coastal zones of Cochin, India. *Applied Ecology and Environmental Research*, 3(1), 133–139.
- Lee, J.S., Yi, J.M. and Chon, H.T. (2003): Environmental contamination and chemical speciation of arsenic in water system in water system from some abandoned Au-Ag mines in Korea. *Journal de phique IV*. 107.
- Leung, C.M. and Jiao, J.J. (2006): Heavy metal and trace element distributions in groundwater in natural slopes and highly urbanized spaces in Mid-Levels area, Hong Kong; *Water Research*, 40, 753–767.
- Lim, M., Han, G.C., Ahn, J.W., You K.S. and Kim, H.S. (2009): Leachability of Arsenic and Heavy Metals from Mine Tailings of Abandoned Metal Mines. *International Journal of Environmental Research and Public Health*, 6, 2865–2879; doi:10.3390/ijerph6112865.
- Loukidou, M.X., Matis, K.A., Zouboulis, A.I. and Liakopoulou-Kyriakidou, M. (2003): Removal of As(V) from wastewaters by chemically modified fungal biomass. *Water Research*, 37, 4544–4552.

- Lovley, D.R., Fraga, J.L., Blunt-Harris, E.L., Hayes, L.A., Phillips, E.J.P. and Coates, J.D. (1998): Humic substances as a mediator for microbially catalyzed metal reduction. *Acta Hydrochimica et Hydrobiologica*, 26, 152–157.
- Madison, R. J. and Brunett, J. O. (1984): Overview of the occurrence of nitrate in ground water of the United States. In *National Water Summary 1984*. U.S. Geological Survey, Water Supply Paper, 2275.
- Maity, S., Chakravarty, S., Tharkur, P., Gupta, K.K., Bhattacharjee, S. and Roy, B.C. (2004): Evaluation and standardisation of a simple HG-AAS method for rapid speciation of As III and As V in some contaminated groundwater samples of West Bengal, India. *Chemosphere*, 54, 1199–1206.
- Mandal, B.K. and Suzuki, K.T. (2002): Arsenic round the world: A review. *Talanta*, 58, 201–235.
- Marszalek, H. and Wasik, M. (2000): Influenced of arsenic-bearing gold deposits on water quality in Zloty Stok mining area (SW Poland). *Environmental Geology*, 39(8), 888–892.
- McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S. and Chadha, D.K. (2004): Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Applied Geochemistry*, 19, 1255–1293.
- McArthur, J.M., Ravenscroft, P., Safiulla, S. and Thirlwall, M.F. (2001): Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resource and Research*, 37, 109–117.
- Mead, M.N. (2005): Arsenic: In Search of an Antidote to a Global Poison. *Environmental Health Perspectives*, 113(6): A378–A386.
- Melamed, D. (2005): Monitoring arsenic in the environment: a review of science and technologies with the potential for field measurements. *Analytical Chimica Acta*, 532, 1–13.
- Mensah, A. (2012): Municipal Planning Officer, Obuasi Municipal Assembly [oral reference: 18.11.2012].
- Ministry of Food and Agriculture (2011): Ashanti region districts performance. <http://mofa.gov.gh/site/> [Accessed on July 3, 2011].
- Mukherjee-Goswami, A., Nath, B., Jana, J., Sahu, S.J., Sarkar, M.J., Jacks, G., Bhattacharya, P., Mukherjee, A., Polya, D.A., Jean, J.S. and Chatterjee, D. (2008): Hydrogeochemical behavior of arsenic-enriched groundwater in the deltaic environment: Comparison between two study sites in West Bengal, India. *Journal of Contaminant Hydrology*, 99, 22–30.

- Murcott, S. (2013). Arsenic remediation. <http://web.mit.edu/civeng/html/people/faculty/html>. [Accessed on September 13, 2013].
- Navin, K.C.T. and Jagath, J.K. (2006): Sustainability of groundwater quality considering land use changes and public health risks. *Journal of Environmental Management*, 81, 405–419.
- Netherlands Ministry of Housing, Physical Planning and Environment. (2000): Environmental quality standards for soil and water. Netherlands Ministry of Housing, Physical Planning and Environment, Leidschendam.
- Nickson, R., McArthur, J., Burgess, W., Ahmad, K.M., Ravenscroft, P. and Rahman, M. (1998): Arsenic poisoning of Bangladesh groundwater. *Nature*, 395, 338.
- Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G. and Ahmed, K.M. (2000): Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Applied Geochemistry*, 15, 403–413.
- Ninno, C. and Dorosh, P.A. (2001): Averting a food crisis: private imports and public targeted distribution in Bangladesh after the 1998 flood. *Agricultural Economics*, 25 (2-3), 337–346.
- Nordstrom, D.K. (2002): Worldwide occurrences of arsenic in ground water. *Science*, 296, 2143–2145.
- Nordstrom, D.K., Alpers, C.N., Ptacek, C.J. and Blowes, D.W. (2000): Negative pH and extremely acidic mine waters from Iron Mountain California. *Environmental Science and Technology*, 34, 254–258.
- Norman, D. I., Miller, G. P., Branvold, L., Thomas, T., Appiah, H., Ayamsegna, J. and Nartey, R. (2006): Arsenic in Ghana, West Africa, Ground waters. USGS Workshop on Arsenic in the environment (Abstract) [online]. Available at <http://wwwbrr.cr.usgs/Arsenic/index.htm> [Accessed on September 7, 2012].
- Nyer, E.K. (1992): *Groundwater Treatment Technology*. 2nd Edition. A division of International Thomson Publishing Inc. USA. ISBN 0-442-00562-8.
- Okereke, S.C., Eze, C.O., Iloegbunam, R.O. and Nwachukwu, N.C. (2007): Seasonal variation of toxic/heavy metals of bilante rock mining pit water, Ishagu, Ebonyi State. *International Journal of Biotechnology and Allied Sciences*, 2 (3), 297–299.
- Oremland, R.S. and Stolz, J.F. (2003): The ecology of arsenic. *Science*, 300 (5621), 349–1036.
- Osaе, S., Kase, K. and Yamamoto, M. (1995): A geochemical study of the Ashanti gold deposit at Obuasi, Ghana. *Okayama University Earth Science Reports*, 2 (1), 81–90.
- Paoloni, J.D., Sequeira, M.E. and Florentino, C.E. (2005): Mapping of arsenic content and distribution in groundwater in the southeast Pampa, Argentina. *Journal of Environmental Health*, 67, p. 8.

- Patel, S.K., Brandt, R., Jakubowski, N., Corns, W. and Hoffman, P. (2005): Arsenic contamination in water, soil, sediment and rice of central India. *Environmental Geochemistry and Health*, 27, 131–145.
- Pelig-Ba, K.B. (1998): Trace elements in groundwater from some crystalline rocks in the Upper Regions of Ghana. *Water, Air, and Soil Pollution*, 103, 71–89.
- Petrusevski, B., van der Meer, W., Baker, J., Kruis, F., Sharma, S.K. and Schippers, J. C. (2007): Innovative approach for treatment of arsenic contaminated groundwater in Central Europe, *Water and Science Technology*. *Water Supply*, 7(3), 131–138.
- Pierce, M.L. and Moore, C.B. (1982): Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Resource*, 16, 1247–1253.
- Preli, F.R. Jr., Dougherty, J.P. and Michel, R.G. (1997): Laser-excited atomic fluorescence spectrometry with a laboratory-constructed tube electrothermal atomizer. *Analytical Chemistry*, 59, 1784–1789.
- Prohaska, T. and Stingender, G. (2005): Speciation of arsenic. In *Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine, and Occupational Health*, pages 69–85. John Wiley and Sons, Ltd.
- Queirolo, F., Stegen, S., Mondaca, J., Cortés, R., Rojas, R., Contreras, C., Munoz, L., Schwuger, M.J. and Ostapczuk, P. (2000): Total arsenic, lead, cadmium, copper, and zinc in some salt rivers in the Northern Andes of Antofagasta, Chile. *Science of the Total Environment*, 255, 85–95.
- Ramesh, K. and Thirumangai, V. (2014): Trace metals contamination of groundwater in and around tannery industrial area of Pallavaram, Chennai city, India. *International Journal of Research in Engineering and Technology*, 3 (5), 163–169.
- Reddy, T.B., Ramana, Ch.V., Bhaskar, Ch. and Jagadeesh chandrababu, P. (2012): Assessment of heavy metal study on ground water in and around Kapuluppada MSW site, Visakhapatnam, AP. *International Journal of Science and Nature*, 3(2), 468–471.
- Regional Surveys of the World (2004): *Africa South of the Sahara 2004*. 3rd edition. Europa Publications Ltd (Verlag) 978-1-85743-195-7 (ISBN), 97–112.
- Romic', Z'. and Subotic', I. (1997): Monitoring of the chemical and microbiological parameters as indicators of revitalization effect of the wells on the well field of the water supply company in Osijek. In: Gojo, M., Trajkov, N., Smolec, S. (Eds.), *Proceedings of the 15th Croatian Meeting of Chemists and Chemical Engineers*, vol. 2. Croatian Society of Chemical Engineers, Zagreb, pp. 347–348 (poster, abstract, in Croatian).
- Rösner, T. and van Schalkwyk, A. (2000): The environmental impact of gold mine tailings footprints in the Johannesburg region, South Africa. *Bulletin of Engineering and Geological Environment*, 59, 137–148.

- Rowland, H.A.L., Gault, A.G., Lythgoe, P. and Polya, D.A. (2008): Geochemistry of aquifer sediments and arsenic-rich groundwaters from Kandal Province, Cambodia. *Applied Geochemistry*, 23, 3029–3046.
- Roy-Keith, S. (1998): Guide to environmental analytical methods. 5th Edition. Genium Publishing Corporation. River Front Center, Amsterdam, NY 12010 (518), 842–4111.
- Schlegel, V., Mattusch, J. and Wennrich, V. (1996): Speciation analysis of arsenic and selenium compounds by capillary electrophoresis. *French Journal of Analytical Chemistry*, 354, 535.
- Schreiber, M.E., Simo, J.A. and Freiberg, P.G. (2000). Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, Eastern Wisconsin, USA. *Hydrogeology Journal*, 8, 161–176.
- Schreiber, M.E., Gotkowitz, M.B., Simo, J.A. and Freiberg, P.G. (2003): Mechanisms of Arsenic release to groundwater from naturally occurring sources, Eastern Wisconsin in Welch, A. and Stollenwerk K. eds., *Arsenic in groundwater*, Boston: Kluwer Academic Publishers: pp. 488.
- Schwertmann, U. and Cornell R.M. (2000): *Iron oxides in the laboratory*. Wiley-VCH, New York, 2nd ed. P 188.
- Sharma, V.K. and Sohn, M. (2009): Aquatic arsenic: Toxicity, speciation, transformations, and remediation. *Environment International*, 35, 743–759.
- Sharaf, M.A.M. Subyani, A.M. (2011): and Assessing of Groundwater Contamination by Toxic Elements through Multivariate Statistics and Spatial Interpolation, Wadi Fatimah, Western Arabian Shield, Saudi Arabia. *International Journal of Scientific and Engineering Research*, 2, 9.
- Sivaraman, D. (2004): Synthesis and characterization of thiol-functionalized chitosan based adsorbents for arsenic removal from water. A thesis presented to the graduate school of the University of Florida in partial fulfillment of the requirements for the degree of master of engineering. University of Florida.
- Smedley, P.L., Edmunds, W.M., West, J.M., Gardner, S.J. and Pelig-Ba, K.B. (1995): Vulnerability of shallow groundwater quality due to natural geochemical environment: Health problems related to groundwater in Obuasi and Bolgatanga areas, Ghana. A report prepared for the Overseas Development Administration under the ODA/BGS Technology Development and Research Programme, Project 92/5.
- Smedley, P.L. (1996): Arsenic in rural groundwater in Ghana. *Journal of African Earth Sciences*, 22, 459–470.
- Smedley, P.L. (2008): Sources and distribution of arsenic in groundwater and aquifers. <http://nora.nerc.ac.uk/10226/1/Chapter42.pdf> [Accessed on July 11, 2012].
- Smedley, P.L., Edmunds, W.M. and Pelig-Ba, K.B. (1996): Mobility of arsenic in groundwater in the Obuasi area of Ghana. In: Appleton, J.D., Fuge, R., McCall,

G.J.H. (Eds.), *Environmental Geochemistry and Health*, Geological Society Special Publication.113. Geological Society, London, pp. 163–181.

- Smedley, P.L., Zhang, M., Zhang, G. and Luo, Z., (2001): Arsenic and other redox-sensitive elements in groundwater from the Huhhot Basin, Inner Mongolia. In: Cidu, R. (Ed.), *Water-Rock Interaction 2001*, Vol. 1. Swets & Zeitlinger, Lisse, pp. 581–584.
- Smedley, P.L., Kinniburgh, D.G., Huq, I., Luo, Z. and Nicolli, H.B. (2001): International perspective on naturally occurring arsenic problems in groundwater. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), *Arsenic Exposure and Health Effects IV*. Elsevier, Amsterdam, pp. 9–25.
- Smedley, P.L. and Kinniburgh, D.G. (2002): A review of the source, behavior and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517–568.
- Smedley, P. L., Knudsen, J. and Maiga, D. (2007): Arsenic in groundwater from mineralised Proterozoic basement rocks of Burkina Faso, *Applied Geochemistry*, 22(5), 1074–1092.
- Smith, A.H., Lingas, E.O. and Rahman, M. (2000): Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. *Bulletin of WHO*, 78, 1093–1103.
- Smith, S.D. and Edwards, M. (2002): Bench-scale evaluation of innovative arsenic-removal processes. *Journal / American Water Works Association*, 94, 78–87.
- Solley, W. B., Pierce, R. R. and Perlman, H. A. (1998): Estimated use of water in the United States in 1995. U. S. Geological Survey Circular 1200, p. 71.
- Srinivasamoorthy, K., Chidambaram, S., Prasanna, M.V., Vasanthavihar, M., Peter, J. and Anandhan, P. (2007): Identification of major sources controlling groundwater chemistry from a hard rock terrain - a case study from Mettur Taluk, Salem District, Tamil Nadu, India. *Journal of Earth System Sciences*, 117, 49–58.
- Steinmaus, C.M., Yuan, Y. and Smith, A.H. (2005): The temporal stability of arsenic concentration in well water in Western Nevada. *Environmental Research*, 99, 164–168.
- Stollenwerk, K.G., Breit, G.N., Welch, A.H., Yount, J.C., Whitney, J.W., Foster, A.L., Uddin, M.N., Majumder, R.K. and Ahmed, N. (2007). Arsenic attenuation by oxidized aquifer sediments in Bangladesh. *Science of the Total Environment*, 379, 133–150.
- Su, C. and Pulse, R.W. (2001): Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulphate, chromate, molybdate and nitrate, relative to chloride. *Environmental Science and Technology*, 35, 4562–4568.
- Subba Rao, N. (2003): Groundwater quality - focus on fluoride concentration in rural parts of Guntur district, Andhra Pradesh, India. *Hydrological Science Journal*, 48, 835–847.

- Subba Rao, N. (2006): Seasonal variation of groundwater quality in a part of Guntur District, Andhra Pradesh India. *Environmental Geology*, 49, 413–429.
- Sullivan, K.A. and Aller, R.C. (1996): Diagenetic cycling of arsenic in Amazon shelf sediments. *Geochem. Cosmochim. Acta*, 60, 1465–1477.
- Sun, G., Pi, J., Li, B., Guo, X., Yamauchi, H. and Yoshida, T. (2001): Progresses on researches of endemic arsenism in China: Population at risk, intervention actions, and related scientific issues. In: Chappell, W.R., Abernathy, C.O. & Calderon, R.L., eds, *Arsenic Exposure and Health Effects IV*, Amsterdam, Elsevier, pp. 79–85.
- Sunil Kumar, S. and Ramanathan, A. L. (2008): Geochemical assessment of groundwater quality in vicinity of Bhalswa landfill, Delhi, India, using graphical and multivariate statistical methods. *Environmental Geology*, 53, 1509–1528.
- Svensson, M. (2007): Mobilization of geogenic arsenic into groundwater in Västerbotten County, Sweden. Department of Earth Sciences. Uppsala University, Villavägen 16, 75236 Uppsala. P 20.
- Swedlund, P.L., Webster, L.G. and Miskelly, G.M. (1996): Proceedings 18th New Zealand Geothermal Workshop, Rotorua, New Zealand. pp. 89-93. systems. *American Water Works Association Newsletter*, 13.
- Tabue, Y.J.G., Feumba, R., Wethe, J., Ekodeck G.E. and De Marsily, G. (2012): Evaluation of groundwater suitability for domestic and irrigational purposes: A case study from Mingoa River Basin, Yaounde, Cameroon. *Journal of Water Resource and Protection*, 4, 285–293.
- Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., Chaalal, O. and Islam, M.R. (2005): Arsenic removal in drinking water - Impacts and novel removal technologies. *Energy Sources*, 27, 209–219.
- Tseng, W.P., Chu, H.M., How, S.W., Fong, J.M., Lin, C.S. and Yeh, S. (1968): Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan, *Journal of National Cancer Institute*, 40, 453–463.
- Tsidzi, K.E.N.R.A. (1993): Some environmental aspects of mining and related activities in Ghana: seminar on current developments in the minerals industry of Ghana, IMME KNUST Kumasi, Ghana.
- Tufour, K. (1997): Mining degradation of forest land resources and rehabilitation: symposium on the mining industry and the environment, KNUST/IDRC.
- Ujevic', M., Duic', Z., Casiot, C., Sipos, L., Santo, V., Dacic', Z. and Halamic', J. (2010): Occurrence and geochemistry of arsenic in the groundwater of Eastern Croatia. *Applied Geochemistry*, 25, 1017–1029.
- United States Environmental Protection Agency (1985): United States Environmental Protection Agency, November 13. *Federal Register*, 50:219:46936.

- United States Environmental Protection Agency, (1999): Analytical methods support document for arsenic in drinking water. Office of Ground Water and Drinking Water Standards and Risk Management Division Targeting and Analysis Branch. EPA, December 1999, EPA-815-R-00-010.
- United States Environmental Protection Agency (2001): 40 CFR parts 9, 141, and 142 national primary drinking water regulations; Arsenic and clarifications to compliance and new source contaminants monitoring; Final rule. Federal Register, 66, No. 14; January 22. 6976–7066.
- United States Environmental Protection Agency (2002): Public Drinking Water System Programs. <http://www.epa.gov/safewater/pws/pwss.html> [Accessed on April 20, 2012].
- United States Environmental Protection Agency (2004): Monitoring arsenic in the environment: A review of science and technologies for field measurements and sensors. EPA 542/R-04/002. <http://www.epa.gov/tio> <http://clu.in.org> [Accessed on April 13, 2012].
- United States Environmental Protection Agency (2013). Arsenic in drinking water. Office of Water. <http://www.epa.gov/ogwdw000/ars/treat.html> [Accessed on September 13, 2013]
- United States Geological Survey (1999): Arsenic in groundwater of the Willamette Basin, Oregon. http://Oregon.usgs.gov/pubs_dir/online/Html/WRIR98-4205/. [Accessed on May 6, 2013].
- United States National Academy Sciences (2001): Arsenic. In medical and biological effects of environmental pollutants. Washington D.C.
- United States Salinity Laboratory (1954): Diagnosis and Improvement of Saline and Alkaline Soils, U.S. Dept. of Agriculture, Hand Book, 60, 147–160.
- Vaishya, R.C. and Gupta, S.K. (2003): Coated sand filtration: an emerging technology for water treatment. *Journal of Water Supply Research and Technology-Aqua*, 52, 299–306.
- van Halem, D., Bakker, S.A., Amy, G.L. and van Dijk, J.C. (2009): Arsenic in drinking water: a worldwide water quality concern for water supply companies. *Drinking Water Engineering and Science*, 2, 29–34.
- Varsányi, I., Fodre, Z. and Bartha, A. (1991): Arsenic in drinking water and mortality in the Southern Great Plain, Hungary. *Environmental Geochemistry and Health*, 13, 14–22.
- Varsanyi, I. and Kovacs, L.O. (2006): Arsenic, iron and organic matter in sediments and groundwater in the Pannonian Basin, Hungary. *Applied Geochemistry*, 21, 949–963.
- Vasanthavigar, M., Srinivasamoorthy, K. and Prasanna, M.V. (2012): Evaluation of groundwater suitability for domestic, irrigational, and industrial purposes: a case

study from Thirumanimuttar river basin, Tamilnadu, India, *Environmental Monitoring and Assessment*, 184, 405–42.

Vaughan D.J. (2006): *Arsenic. Elements*, Vol. 2, No.2.

Waikato Regional Council, (2006): *Arsenic in groundwater of the Waikato Region. Environment Waikato Technical Report 2006/14. Environment Waikato, Hamilton East. Document No.: 1002191. ISSN: 1172–4005.*

Wang, S. and Mulligan, C. (2006): Occurrence of arsenic contamination in Canada: sources, behavior and distribution. *Science of the Total Environment*, 366, 701–721.

Webster, J.G., Nordstrom, D.K. and Smith, K.S. (1994): Transport and natural attenuation of Cu, Zn, As, and Fe in the acid mine drainage of Leviathan and Bryant Creeks. In: Alpers, C.N., Blowes, D.W. (Eds.), *Environmental Geochemistry of Washington DC*, pp. 244-260.

Welch, A.H., Lico, M.S. and Hughes, J.L. (1988): Arsenic in ground-water of the Western United States. *Groundwater*, 26, 333–347.

Welch, A.H., Helsel, D.R., Focazio, M.J. and Watkins, S.A. (1999): Arsenic in ground water supplies of the United States. In: Chappell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), *Arsenic Exposure and Health Effects*. Elsevier, Amsterdam, pp. 9–17.

Welch, A.H., Westjohn, D.B., Helsel, D.R. and Wanty, R.B. (2000): Arsenic in ground water of the United States: occurrence and geochemistry. *Ground Water* 38, 589–604.

World Bank/Water and Sanitation Program (2005): *Towards a more effective operational response to arsenic contamination of groundwater in South and East Asian countries. Technical Report No. 31303 Vol. II. (Washington DC, USA).*

WHO (1993): *Arsenic in Drinking water. World Health Organization Factsheet 210. World Health Organization, Geneva.*

WHO (1996a): *Guidelines for drinking-water quality. 2nd ed., Health Criteria and Other Supporting Information, WHO, Geneva, Switzerland.*

WHO (1996b): *Water quality monitoring: a practical guide to the design and implementation of freshwater quality studies and monitoring programmes. E and FN Spon, London, UK.*


WHO (2004): *Guidelines for drinking-water quality: training pack. WHO, Geneva, Switzerland.*

Wickramasinghe, S.R., Han, B.B., Zimbron, J., Shen, Z. and Karim, M.N. (2004) Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh. *Desalination*, 169, 231–244.


Williams, M. (1997): *Mining-related arsenic hazards: Thailand case-study. Summary Report. British Geological Survey. Technical Report, WC/97/49.*

- Williams, M., Fordyce, F., Pajitprapong, A. and Charoenchaisri, P. (1996): Arsenic contamination in surface drainage and groundwater in part of the Southeastern Asian tin belt, Nakhon Si Thammarat Province, southern Thailand. *Environmental Geology*, 27, 16–33.
- Williams, M. W. and Smith, B. (1994): Empirical and modeled hydrochemistry of acid mine drainage, Iron Duke mine, Mazowe, Zimbabwe. British Geological Survey Technical Report WC/94/78/R.
- Wongyai, K., Garivait, S., Donald, O. (2013): A geochemistry study of arsenic speciation in overburden from Mae Moh Lignite Mine, Lampang, Thailand. *Environmental Earth Sciences*, DOI 10.1007/s12665-009-0423-8.
- Woo, N.C. and Choi, M.C. (2001): Arsenic and metal contamination of water resources from mining wastes in Korea. *Environmental Geology*, 40(3), 305–311.
- Yan, X.P., Kerrich, R. and Hendry, M.J. (2000): Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochim. Cosmochim. Acta*, 64, 2637–2648.
- Yeboah, J.Y. (2008): Environmental and health impact of mining on surrounding communities: a case study of AngloGold Ashanti in Obuasi. MSc. Thesis, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana.
- Zachara, B.A., Pawluk, H., Korenkiewicz, J. and Skok, Z. (2001): Selenium levels in kidney, liver and heart of newborns and infants. *Early Human Development*, 63, 103–111.
- Zhang, Y., Yang, M., Gao, Y.X., Wang, F. and Huang, X. (2003a): Preparation and adsorption mechanism of rare earth-doped adsorbent for arsenic(V) removal from groundwater. *Science in China Series B-Chemistry*, 46, 252–258.
- Zhang, Y., Yang, M. and Huang, X. (2003b): Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent. *Chemosphere*, 51, 945–952.

Appendix 1

 Brandenburgische Technische Universität Cottbus - Senftenberg <i>Chair of Environmental Geology</i>			CHAIN-OF-CUSTODY RECORD							No.:		Date:		Page of	
<i>Project No.:</i>			<i>ANALYSES</i>							<i>REMARKS</i>					
<i>Samplers (signature):</i>															
<i>Date</i>	<i>Time</i>	<i>Sample No.</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>cooled</i>	<i>water</i>	<i>acidified</i>	<i>No. of containers</i>	<i>Additional Comments</i>	
			<i>Turnaround time:</i>				<i>Results to:</i>			<i>Total No. of containers:</i>					
<i>Relinquished by (Signature):</i>		<i>Date:</i>		<i>Relinquished by (Signature):</i>			<i>Date:</i>		<i>Method of Shipment:</i>						
<i>Printed Name:</i>				<i>Printed Name:</i>											
<i>Company:</i>		<i>Time:</i>		<i>Company:</i>			<i>Time:</i>								
<i>Received by (signature):</i>		<i>Date:</i>		<i>Received by (signature):</i>			<i>Date:</i>		<i>Laboratory Comments and Log No.:</i>						
<i>Printed name:</i>				<i>Printed name:</i>											
<i>Company:</i>		<i>Time:</i>		<i>Company:</i>			<i>Time:</i>								

Appendix 2

 Brandenburgische Technische Universität Cottbus - Senftenberg <i>Chair of Environmental Geology</i>			WELL SAMPLING/DEVELOPMENT RECORD				
Well ID:				Initial depth to water:			
Sample ID:		Duplicate ID:		Depth to water after sampling:			
Sample Depth:				Total depth to well:			
Project No.:				Well diameter:			
Project Name				1. Casing (borehole vol.):			
Date:				2. Casing (borehole vol.):			
Sampled By:				3. Casing (Borehole vol.):			
Method of purging:				4. Casing (borehole vol.):			
Method of sampling				Total casing/borehole volume removed:			
Time	Intake depth (m)	Rate (gpm)	Cum. Vol. (gal.)	Temp. (°C)	pH	SEC (µS/cm)	Remarks (color, turbidity, and sediment)
pH Calibration (choose two)						Unit No.:	
Buffer solution	4.0	7.0	10.0				
Field temperature (°C)							
Instrument reading							
Specific Electrical Conductance Calibration (SEC)						UNIT No.:	
KCL Solution (µS/cm=µmhos/cm)	1500 at 25 °C	2300 at 45 °C					
Field Temperature (°C)							
Instrument Reading							
NOTES:							

Appendix 3



BRANDENBURG TECHNISCHE UNIVERSITÄT
 Faculty of Environmental Sciences and Process Engineering, Chair of
 Environmental Geology, Erich-Weinert-Straße 1, 03046
 Cottbus-Senftenberg, Germany

Questionnaire to find out the consumer's perceptions of the quality of groundwater for drinking purposes

(Please either fill in the blank space provided, or tick where applicable)

	Yes	No
Is this groundwater (well/borehole) your source of drinking water?	<input type="checkbox"/>	<input type="checkbox"/>
Do you experience any color of the groundwater other than colorless?	<input type="checkbox"/>	<input type="checkbox"/>
Do you experience any taste upon drinking of the groundwater?	<input type="checkbox"/>	<input type="checkbox"/>
Does the groundwater smell?	<input type="checkbox"/>	<input type="checkbox"/>
Is there any color change upon storing the water?	<input type="checkbox"/>	<input type="checkbox"/>
What might have caused the change in color of the water?	Storage tank <input type="checkbox"/>	well <input type="checkbox"/>
Do you have any health-based concerns regarding the use of the groundwater for drinking or for domestic purposes?	Yes <input type="checkbox"/>	No <input type="checkbox"/>

If so what are the concerns: _____

Overall water quality	Unacceptable	Poor	Fair	Good	Excellent
	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Do you think the water is safe to drink?	Yes	No
	<input type="checkbox"/>	<input type="checkbox"/>

If no why not? _____

How many gallons of water do you use per day? _____

Please leave any comment you have:

Appendix 4

Table 1 Hydrochemical facies of south-western part of Ashanti Region groundwaters.

Dry season		Wet season	
Well location	Hydrochemical facies	Well location	Hydrochemical facies
Meduma	Na-Mg-Ca-HCO ₃	Meduma	Na-Ca-Mg-HCO ₃
Abedwum	Ca-HCO ₃	Abedwum	Ca-Na-HCO ₃
Wioso	Na-HCO ₃	Wioso	Na-Mg-HCO ₃
Patakro	Ca-Na-HCO ₃	Patakro	Ca-Mg-Na-HCO ₃
Dunkwa Nkwanta	Na-HCO ₃	Dunkwa Nkwanta	Na-Mg-HCO ₃
Kokotease	Na-HCO ₃	Kokotease	Na-HCO ₃ -Cl
Kofikurom	Mg-Na-Ca-HCO ₃	Kofikurom	Mg-Na-HCO ₃
Odahu	Na-Mg-HCO ₃	Odahu	Mg-Na-Ca-HCO ₃
Agroyesum	Ca-Na-HCO ₃	Agroyesum	Ca-Na-Mg-HCO ₃
Apanapron	Ca-Na-HCO ₃	Apanapron	Ca-Na-HCO ₃
Ankam	Ca-Na-Mg-HCO ₃	Ankam	Ca-Mg-Na-HCO ₃
Mim 1	Ca-Na-Mg-HCO ₃	Mim 1	Ca-Mg-Na-HCO ₃
Abodom	Na-Ca-HCO ₃	Abodom	Na-Ca-HCO ₃
Mim 2	Na-Ca-Mg-HCO ₃	Mim 2	Na-Mg-HCO ₃
Antoakurom 1	Ca-HCO ₃	Antoakurom 1	Ca-Na-HCO ₃
Manso Akropon	Na-Ca-Mg-HCO ₃	Manso Akropon	Na-Mg-Ca-HCO ₃ -Cl
Antoakurom 2	Na-Mg-HCO ₃ -Cl	Antoakurom 2	Na-Mg-HCO ₃
Nsiana	Na-Ca-Mg-HCO ₃ -Cl	Nsiana	Na-Mg-Ca-HCO ₃ -Cl
Yawkurom	Ca-Mg-HCO ₃	Yawkurom	HCO ₃
Manso Atwere	Na-Mg-Ca-HCO ₃	Manso Atwere	Na-Mg-Ca-HCO ₃
Odumase	Ca-Mg-Na-HCO ₃	Odumase	Ca-Mg-Na-HCO ₃
Mile 9	Na-Ca-HCO ₃	Mile 9	Na-Ca-HCO ₃
Mile 14	Mg-Ca-HCO ₃	Mile 14	Mg-Ca-Na-HCO ₃
Boni	Mg-Ca-Na-HCO ₃	Boni	Mg-Ca-Na-HCO ₃ -Cl
Hunatado	Na-Mg-Ca-HCO ₃	Hunatado	Na-Mg-Ca-HCO ₃
Poano	Mg-Ca-HCO ₃	Poano	Mg-Ca-HCO ₃
Ntinako	Na-Ca-HCO ₃ -Cl	Ntinako	Na-Mg-Ca-HCO ₃
Kofitanokurom	Na-HCO ₃	Kofitanokurom	Na-Ca-HCO ₃
Patase	Na-Ca-HCO ₃ -Cl	Patase	Na-Ca-HCO ₃
Apitiso	Mg-Ca-Na-HCO ₃ -Cl	Apitiso	Ca-Mg-Na-HCO ₃
Fiankoma	Na-Mg-Ca-HCO ₃	Fiankoma	Na-Mg-Ca-HCO ₃
Dangase	Na-HCO ₃	Dangase	Na-HCO ₃ -Cl
Odumto	Na-HCO ₃	Odumto	Na-HCO ₃
Sabe	Mg-Ca-Na-HCO ₃	Sabe	Mg-Ca-HCO ₃
Mile 18	Na-HCO ₃	Mile 18	Na-HCO ₃ -Cl
Mamfo	Na-HCO ₃	Mamfo	Na-HCO ₃
Dekyewa	Na-HCO ₃	Dekyewa	Na-Mg-HCO ₃
Afoako	Na-Ca-HCO ₃	Afoako	Na-Ca-HCO ₃
Aketekyiso	Na-HCO ₃	Aketekyiso	Na-HCO ₃
Tweapease	Na-Ca-Mg-HCO ₃	Tweapease	Na-Ca-Mg-HCO ₃
Abuakwa	Ca-Na-HCO ₃	Abuakwa	Ca-Na-Mg-HCO ₃
Nhyiaso	Na-HCO ₃	Nhyiaso	Na-HCO ₃
Akrofuom	Na-Ca-Cl-HCO ₃	Akrofuom	Na-Ca-Mg-HCO ₃ -Cl
Sanso	Na-Mg-Ca-HCO ₃	Sanso	Na-Mg-Ca-HCO ₃
Brahabebome	Ca-Na-HCO ₃	Brahabebome	Ca-Na-Mg-HCO ₃
Diewieso	Na-HCO ₃ -Cl	Diewieso	Na-Mg-HCO ₃ -Cl
Nyamso North	Na-Mg-HCO ₃	Nyamso North	Na-Mg-Ca-HCO ₃
Nyamso South	Na-Mg-HCO ₃	Nyamso South	Na-Mg-HCO ₃

Arsenic Contamination in Groundwater

Konka New Town	Na-HCO ₃	Konka New Town	Na-Mg-HCO ₃
Apitikokoo	Na-Mg-HCO ₃ -Cl	Apitikokoo	Na-Mg-Ca-HCO ₃
Kokotenten	Ca-Na-HCO ₃	Kokotenten	Ca-Na-HCO ₃
Nyamekyere	Na-HCO ₃ -Cl	Nyamekyere	Na-Mg-HCO ₃
Obuasi BH 3	Ca-Mg-Na-HCO ₃	Obuasi BH 3	Ca-Mg-Na-HCO ₃
Mensakurom	Na-HCO ₃ -Cl-SO ₄	Mensakurom	Na-Mg-HCO ₃
Obuasi BH 2	Mg-Ca-Na-HCO ₃	Obuasi BH 2	Mg-Ca-Na-HCO ₃
Obuasi BH 1	Mg-Ca-HCO ₃	Obuasi BH 1	Mg-Ca-HCO ₃
Wamase	Na-HCO ₃	Wamase	Na-Ca-HCO ₃
Old Edubiase	Na-Ca-HCO ₃	Old Edubiase	Na-Mg-Ca-HCO ₃
Dwondoso	Na-Ca-HCO ₃	Dwondoso	Na-Mg-Ca-HCO ₃
Aminase	Na-HCO ₃	Aminase	Na-HCO ₃
Amoamo	Ca-Na-Cl-HCO ₃	Amoamo	Ca-Na-Mg-HCO ₃ -Cl
Ankase	Mg-Na-Ca-HCO ₃	Ankase	Mg-Na-Ca-HCO ₃
Bogyawe	Na-Mg-Ca-HCO ₃	Bogyawe	Na-Mg-Ca-HCO ₃

Appendix 5

Site details for groundwater samples from south-western part of Ashanti Region.

Sampling Location	Well No.	Sample ID	Sampling Source	Latitude (6°N) mins	Longitude (1°W) mins	Well Depth (m)
Meduma	48	ANS-1-01	bore hole	16.11	35.64	53
Abedwum	61	ANS-1-02	shallow well	18.26	39.63	6
Wioso	59	ANS-1-03	bore hole	16.99	39.72	18
Patakro	58	ANS-1-04	bore hole	17.5	38.71	36
Dunkwa Nkwanta	6	ANS-1-05	bore hole	12.91	41.32	25.5
Kokotease	8	ANS-1-06	bore hole	12.85	40.90	35
Kofikurom	9	ANS-1-07	bore hole	11.89	40.92	38
Odahu	37	AWS-2-01	bore hole	21.42	49.43	60
Agroyesum	35	AWS-2-02	bore hole	24.98	52.79	52
Apanapron	36	AWS-2-03	bore hole	23.58	53.75	80
Ankam	34	AWS-2-04	bore hole	24.17	51.97	38
Mim 1	23	AWS-2-05	bore hole	25.42	51.20	57
Abodom	24	AWS-2-06	bore hole	25.73	48.76	46
Mim 2	25	AWS-2-07	bore hole	25.18	51.28	49
Antoakurom 1	26	AWS-2-08	bore hole	27.14	47.43	70
Manso Akropon	27	AWS-2-09	bore hole	26.38	48.39	43
Antoakurom 2	28	AWS-2-10	bore hole	27.28	47.49	32
Nsiana	29	AWS-2-11	bore hole	28.00	47.78	49
Yawkurom	18	AWS-2-12	bore hole	26.28	52.31	49
Manso Atwere	40	AWS-2-13	bore hole	27.58	51.40	19
Odumase	39	AWS-2-14	bore hole	11.29	42.22	43
Mile 9	3	ACS-3-01	bore hole	13.49	46.28	46
Mile 14	4	ACS-3-02	bore hole	13.47	49.61	64.5
Boni	10	ACS-3-03	bore hole	27.57	39.43	66
Hunatado	11	ACS-3-04	bore hole	26.92	40.41	54
Poano	12	ACS-3-05	bore hole	26.52	40.73	61
Ntinako	13	ACS-3-06	bore hole	25.73	41.43	52
Kofitanokurom	17	ACS-3-07	bore hole	9.20	49.91	8
Patase	63	ACS-3-08	bore hole	22.96	39.31	34
Apitiso	1	ACS-3-09	bore hole	10.65	43.88	43.5
Fiankoma	22	ACS-3-10	bore hole	19.10	43.62	65
Dangase	30	ACS-3-11	shallow well	7.10	50.15	4
Odumto	20	ACS-3-12	bore hole	15.43	50.48	15
Sabe	42	ACS-3-13	bore hole	14.49	47.96	22
Mile 18	57	ACS-3-14	bore hole	8.78	43.18	8
Mamfo	44	ACS-3-15	bore hole	15.22	49.58	28
Dekeyewa	38	ACS-3-16	bore hole	12.43	42.97	24
Afoako	60	ACS-3-17	bore hole	23.19	38.41	42
Aketekyiso	62	ACS-3-18	shallow well	16.72	41.31	3
Tweapease	33	ACS-3-19	bore hole	8.92	44.33	43
Abuakwa	21	ACS-3-20	bore hole	18.13	50.31	48
Nhyiaso	41	OBS-4-01	bore hole	11.29	42.22	18
Akrofuom	46	OBS-4-02	shallow well	7.45	39.43	32
Sanso	49	OBS-4-03	bore hole	9.33	41.86	42
Brahabebome	50	OBS-4-04	bore hole	12.15	37.80	19
Diewieso	51	OBS-4-05	bore hole	10.67	37.67	25
Nyamso North	52	OBS-4-06	bore hole	12.65	41.63	48
Nyamso South	53	OBS-4-07	bore hole	12.59	41.67	32

Arsenic Contamination in Groundwater

Konka New Town	54	OBS-4-08	bore hole	12.86	41.34	30
Apitikokoo	55	OBS-4-09	bore hole	10.93	42.78	40
Kokotenten	56	OBS-4-10	bore hole	6.71	41.50	34
Nyamekyere	45	OBS-4-11	bore hole	8.78	53.18	43
Obuasi BH 3	19	OBS-4-12	bore hole	12.24	39.56	100
Mensakurom	43	OBS-4-13	shallow well	9.90	42.65	9
Obuasi BH 2	31	OBS-4-14	bore hole	12.24	39.56	70
Obuasi BH 1	32	OBS-4-15	bore hole	12.21	39.57	70
Wamase	7	OBS-4-16	shallow well	5.28	41.91	4
Old Edubiase	47	BMS-5-01	bore hole	22.0	35.94	43
Dwondoso	14	BMS-5-02	shallow well	23.77	36.48	5.5
Aminase	15	BMS-5-03	shallow well	25.50	36.47	4
Amoamo	16	BMS-5-04	shallow well	25.30	37.4	1.5
Ankase	2	BMS-5-05	bore hole	23.41	33.12	48
Bogyawe	5	BMS-5-06	bore hole	23.22	32.88	58