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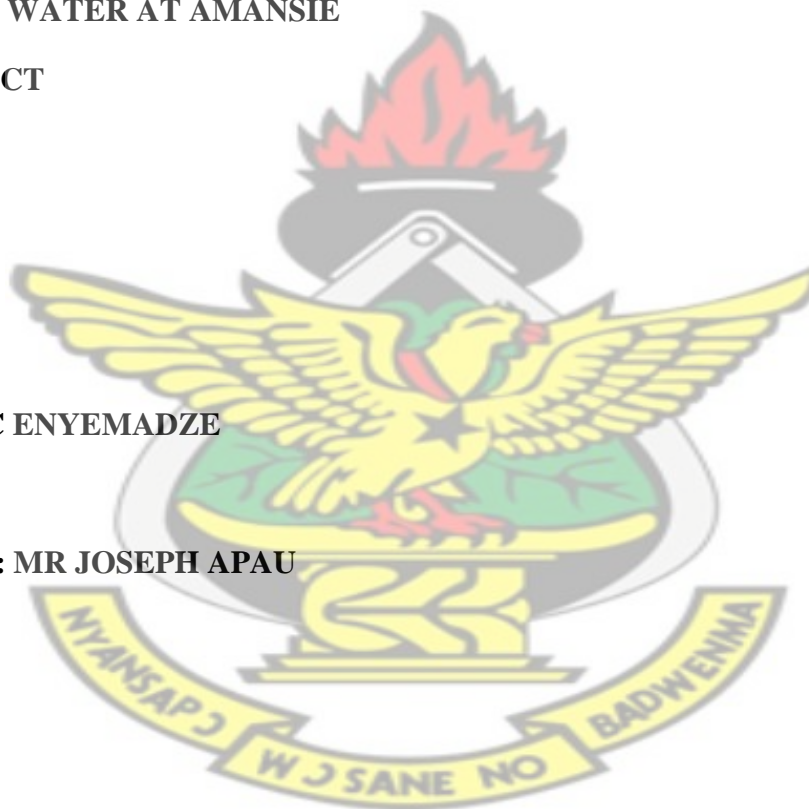
TOPIC:

**SPECIATION OF ARSENIC AND DETERMINATION OF HEAVY METAL LEVELS
IN DRINKING WATER AT AMANSIE**

WEST DISTRICT

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DECLARATION

I hereby declare that this submission is my own research work and that, to the best of my knowledge, it contains no materials previously published by another person or material which have been accepted for the award of any degree of the University, except where due acknowledgement have been made in the text.

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Date

Certified by
Mr Joseph Apau
(Supervisor)



.....
Date

Dr Bright Voegborlo
(Head Of Department)

.....
Date

DEDICATION

This is dedicated to my dear Baaba who has supported me in every way in my academic pursuit and also to all those who have suffered from arsenic poisoning as a result of environmental activities in Amansie West.

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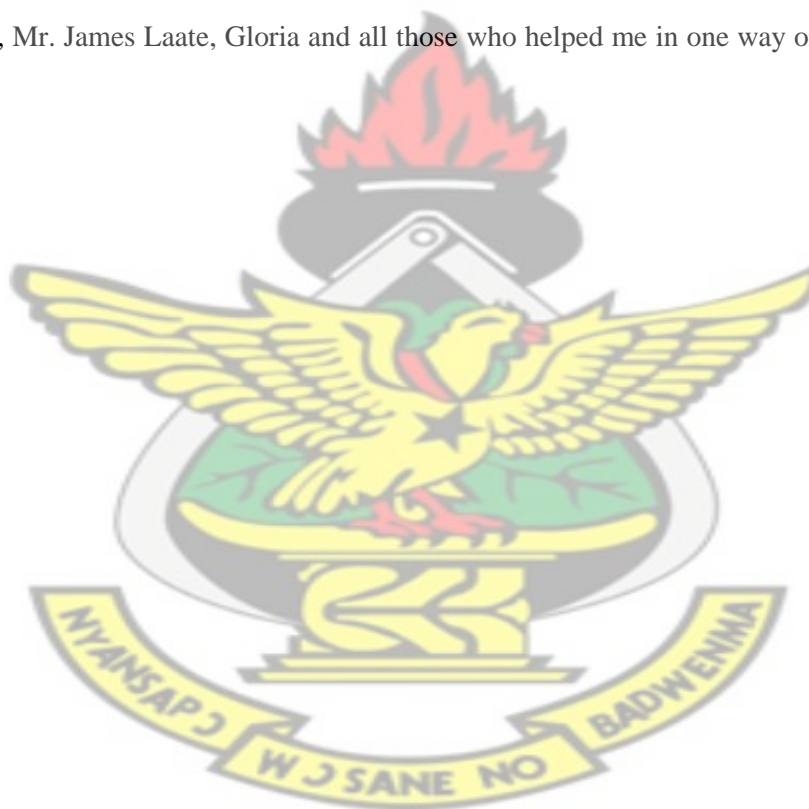
ACKNOWLEDGMENTS

Who is a faithful Lord like our God? You have helped me greatly oh Lord throughout this work and I am so grateful. Blessed be Jehovah forever and ever.

My special thanks go to Mr Joseph Apau, my supervisor for his support and excellent supervision.

My sincerest appreciations also go to Mr. Bentil for providing me with all equipment and chemicals I needed for this work and Dr S.K. Twumasi, Mr Osei Akoto and Dr Darko for their helping hand.

I would also like to thank Nana Acheampong and Uncle George, for taking us through Amansie West. Mr. David Adeda, Mr. James Laate, Gloria and all those who helped me in one way or the other to finish this work.



ABSTRACT

A study of arsenic speciation and heavy metals (Zn, Pb, Cd, Hg and Fe) content in drinking water of Amansie West District was conducted. Drinking water samples from boreholes, hand dug wells and streams were taken from 23 communities in the district. Amansie West is a gold mining community with surface mining being the main method used. Anthropogenic activities such as mining, agricultural and urbanization have led to the contamination by arsenic in streams and rivers. As (III) and As (V) in the water samples were separated using hydride generation and detected by flame AAS. Determination of Hg was also made by HG-AAS. Analysis of the other heavy metals were done using flame AAS.

The results obtained showed that the concentration of arsenic in streams, boreholes and hand dug wells fell between 0.24-37.22 $\mu\text{g/L}$, 13.49-26.41 $\mu\text{g/L}$, and 24.11-39.43 $\mu\text{g/L}$ respectively. Test of correlation between arsenic concentration and some physical parameters (pH, DO, conductivity and redox potential) was done to ascertain any relationship. For speciation study, results showed that arsenic (III) is the dominant inorganic arsenic species. On average, 64% of all inorganic arsenic species was in the more toxic (+3) oxidation state, the rest is in the (+5) oxidation state. There was a strong negative correlation between arsenic speciation and the redox potential.

91 % concentration of Zn, Pb, Cd, and Hg measured was below detection limits. The 9 % that was measured were below WHO acceptable limit for drinking water. However, the concentrations of Fe (0.141 – 1.082 $\mu\text{g/L}$) in the water samples were high.

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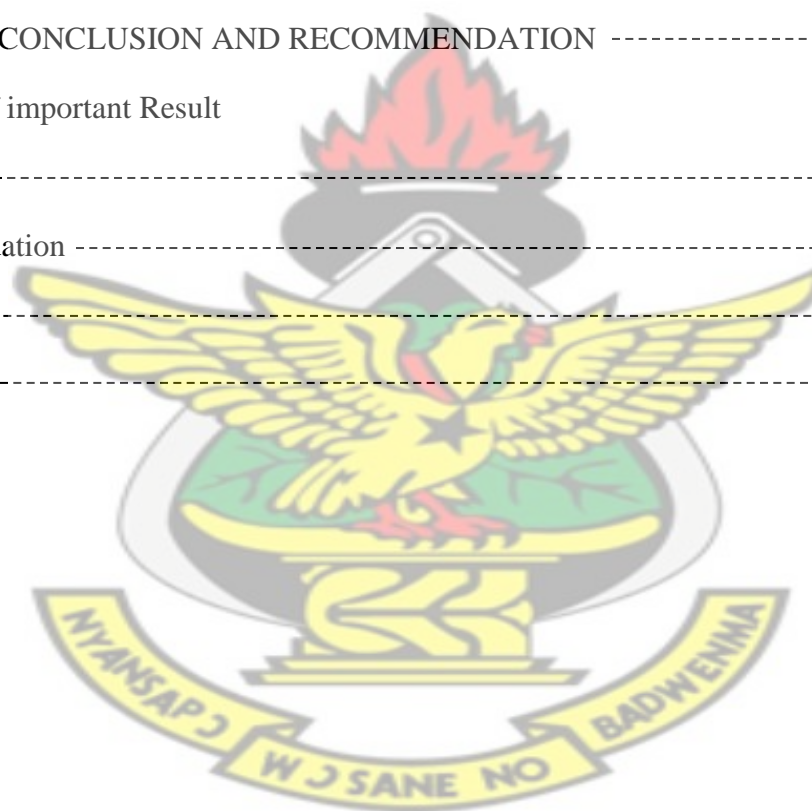
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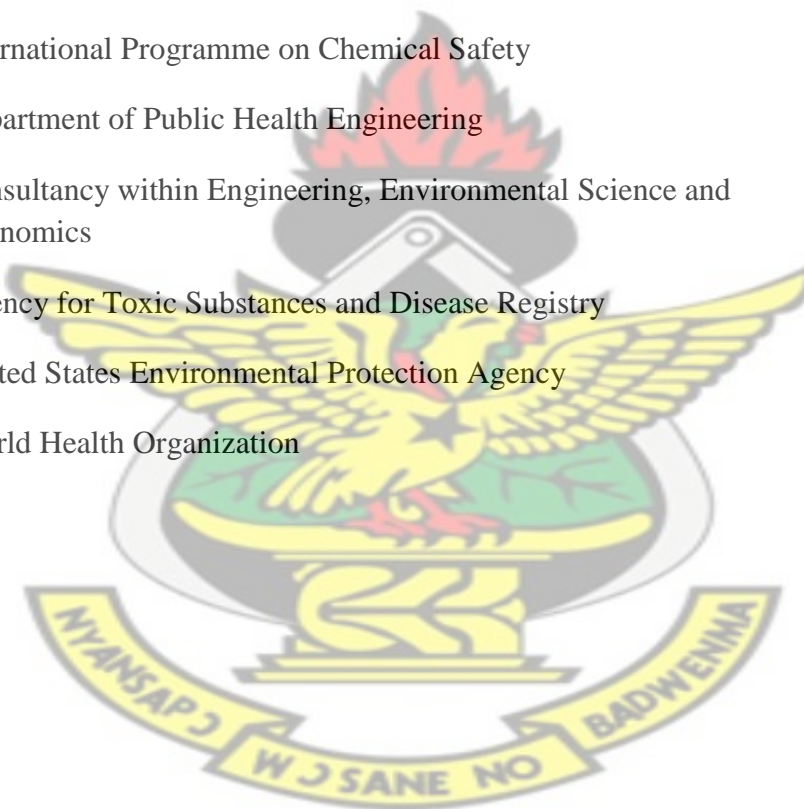
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LIST OF ABBREVIATIONS

A.A.S	Atomic Absorption Spectroscopy
G.W.C	Ghana Water Company
G.S.B	Ghana Standards Board
C.A.S No.	Chemical Abstracts Service Number
M.M.A	Monomethylatedarsonic Acid
D.M.A	Dimethylatedarsenic Acid
B.G.S	British Geological Survey
I.P.C.S	International Programme on Chemical Safety
D.P.H.E	Department of Public Health Engineering
C.O.W.I	Consultancy within Engineering, Environmental Science and Economics
A.T.S.D.R	Agency for Toxic Substances and Disease Registry
U.S.E.P.A	United States Environmental Protection Agency
W.H.O	World Health Organization



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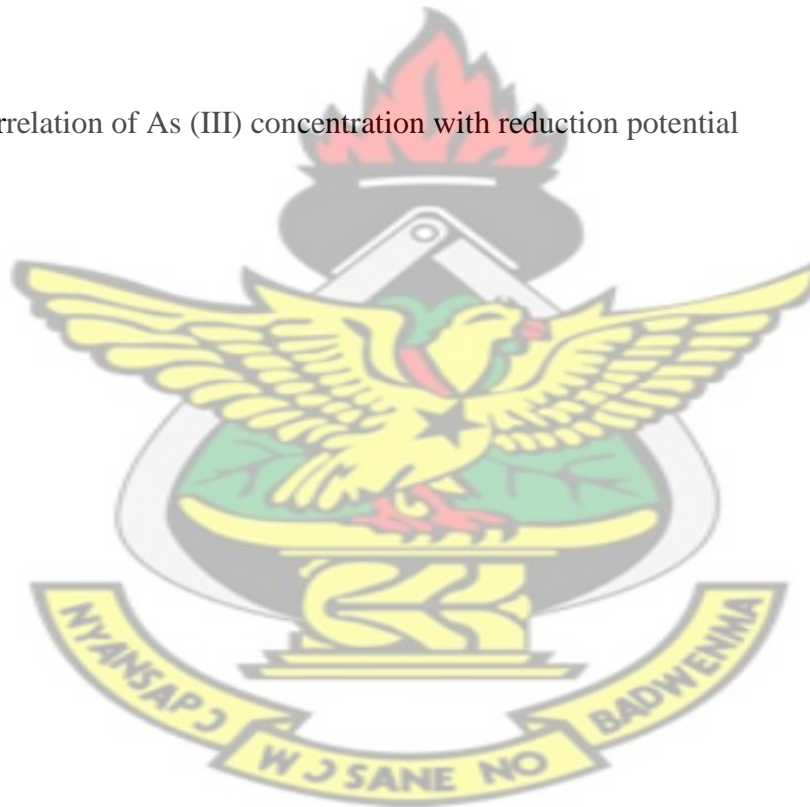
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CHAPTER ONE

1 Introduction

To understand toxicity, metabolism, and transport properties of elements it is important to know the chemical species of elements in environmental samples. Therefore, speciation analysis, since it has become an increasingly important tool in active-research in recent years. Many problems related with the arsenic speciation remain unresolved such as species instability during sample storage and sample treatment, incomplete recovery of all species, matrix interferences, and the lack of appropriate certified reference method, protocols and guidelines (Kumaresan and Riyazuddin, 2001).

In general arsenic speciation is transformation of arsenic species into variety of other forms and derivatives under different environmental condition such as physical, chemical and biological conditions when different arsenic species are formed. The toxicity of these forms and species varies from virtually nontoxic (e.g. biological derivatives of arsenic such as – arsenobetaine (AB) and arsenocholine (AC) to extremely toxic (e.g. arsenite) compounds of environmental interest (Ng, J.C., 2005)

Most studies reporting arsenic in the environment, in Ghana, involve only the total concentrations of arsenic and not speciation measurement, and studies were chiefly concerned with documenting the extent of elevated arsenic concentrations. (e.g. Golow et al 1996; Duker et al 2004; Amonoo Neizer et al 1993). However, in order to quantitatively understand arsenic behaviour and cycling in ground water flow systems, it is not enough to only measure total dissolved concentrations, but speciation data becomes critical. Knowledge of the speciation of

arsenic in natural water is important because the bioavailability, physiological and toxicological effects of arsenic depends on its chemical form. (Bose et al, 2010).

In oxidizing environment As^{5+} (arsenate) species are more stable and predominant, whereas in reducing conditions As^{3+} (arsenite) species becomes predominant (Ferguson and Gavis, 1972; Cherry et al, 1979; Cullen and Reamer, 1989). Flooding induces (anaerobic) reducing conditions in soils (McGreegan and Naylor, 1994; Reynolds et al, 1999). Swamps, alluvial and deltaic environments are mostly characterized by reducing conditions, which cause high arsenic concentrations in ground water (Smedly and Kinniburgh, 2002). In these environments, aquifer sediments contain organic matter (which uses available oxygen), resulting in the development of reducing conditions (Smedly & Kinniburgh 2002). In such conditions, As^{5+} is reduced to As^{3+} and adsorbed As^{5+} is released as As^{3+} (Reynolds et al, 1999).

Since its isolation in 1250A.D. arsenic has been used in various fields such as medicine, electronics, agriculture and metallurgy (Nriagu and Azcue, 1990). More than 245 minerals contain arsenic and although the ultimate source of arsenic is geological, human activities such as mining, the burning of fossil fuels, and pesticide application, also cause arsenic pollution (Bissen and Frimmel, 2003).

Speciation study has shown an increasing interest in the analytical and environmental circles during the last decade. Speciation of an element in a sample, (Ge, 2002), means determination of the concentration of different physicochemical forms of the element that together make up its total concentration in the sample. Interest in chemical and element speciation is expected to rapidly expand as more scientists asserts to the fact that mobility, risk assessment and

metabolism of an element must be done on the specific chemical rather than on the total concentration.

Some elements can be highly toxic to various life forms while others are considered essential at very small amounts, but become toxic at higher dose. For an example, while Cr (III) is an essential element, Cr (IV) is highly toxic (Kartiz and Salem, 1994). Inorganic arsenic in the form of As (III) is considered about 10 times more soluble and mobile and more toxic than As (V).

Elemental speciation is a discipline, which is of a great relevance to groups that include Chemist, Biologist, Toxicologist, Engineers, etc. In fact this area of Analytical Chemistry has become one of the most crucial, pertinent and challenging issues because of its impact on the environment, Eco – clinical toxicology, Medical and Nutrition science, Food and Energy industries.

1.1 Problem Statement

Arsenic in streams, wells and boreholes may contaminate both drinking water and agricultural soils in which food crops are cultivated. Arsenic occurs naturally in the earth's crust and can be released into the aquatic environment by redox processes and also leaching from mine tailings.

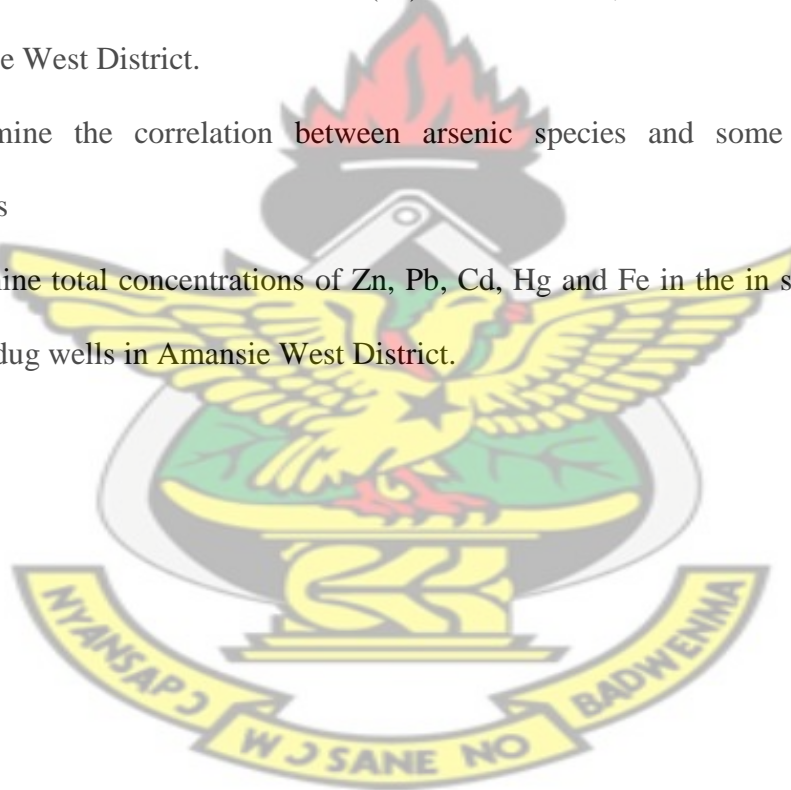
Amansie West is a gold mining district and a study (Duker, 2004) has reported high concentrations of total arsenic in rivers and streams. Buruli ulcer, which has been closely linked with arsenic poisoning, has also been found to be to be high in the district. Since local inhabitants largely depend on water sources from streams, boreholes and hand dug wells; ingestion of toxic arsenic is most likely and may pose a risk to the health of inhabitants of Amansie West District. Determination of species of arsenic is essential to understand behaviour

of arsenic in ground waters, and also to provide a basis for arsenic removal technology for the District.

1.2 Research Objectives

The research objectives can be outlined as follows:

1. To estimate total dissolved arsenic concentration in streams, boreholes and hand dug wells in Amansie West District.
2. To determine the concentration of As (III) in the streams, boreholes and hand dug wells in Amansie West District.
3. To determine the correlation between arsenic species and some physicochemical parameters
4. To determine total concentrations of Zn, Pb, Cd, Hg and Fe in the in streams, boreholes and hand dug wells in Amansie West District.



CHAPTER TWO

2 Literature Review

This literature review gives the chemistry and chemical processes of arsenic, its occurrence in water, its uses, health, environmental effects and methods of analysis of arsenic and other heavy metals.

2.1 Arsenic

The element arsenic is a member of group 15 of the periodic table that includes nitrogen, phosphorus, antimony, and bismuth. It has atomic number of 33 and a mass number of 74.91. Arsenic can exist in four oxidation states; viz -3 (arsine), 0 (arsenic), +3 (arsenite), and +5 (arsenate). It ranks 20th in natural abundance, 14th in seawater, and 12th in the human body (Mandal and Suzuki, 2002).

In addition to arsenite, arsenate, and their methylated derivatives, there are “fish arsenic” (arsenobetaine, AB and arsenocholine, AC) and arsenosugar (9-22 of table 2.1) compounds of environmental interest (Ng, 2005). The molecular formulae of inorganic and organic arsenic compounds are given in Table 2.1 and their structures provided in Figure 2.1. Both inorganic and organic forms of arsenic have been determined in water (IPCS, 2001). The organic arsenic compounds are generally less toxic and low in ground water compared to the inorganic species. (Amjad, 2001; Haque and Johanneson, 2005; Kim et al, 2009).

Table 2.1: Names of some arsenic compounds

NAME	STURCTURE
Arsenate	1
Arsenite	2
Methylarsonic acid, MMA	3
Dimethylarsinic acid, DMA	4
Trimethylarsine oxide	5
Tetramethylarsonium ion	6
Arsenobetaine, AB	7
Arsenocholine, AC	8
Dimethylarsinoylribosides	9-19
Trialkylarsonioribosides	20-21
Dimethylarsinoylribitol sulfate	22

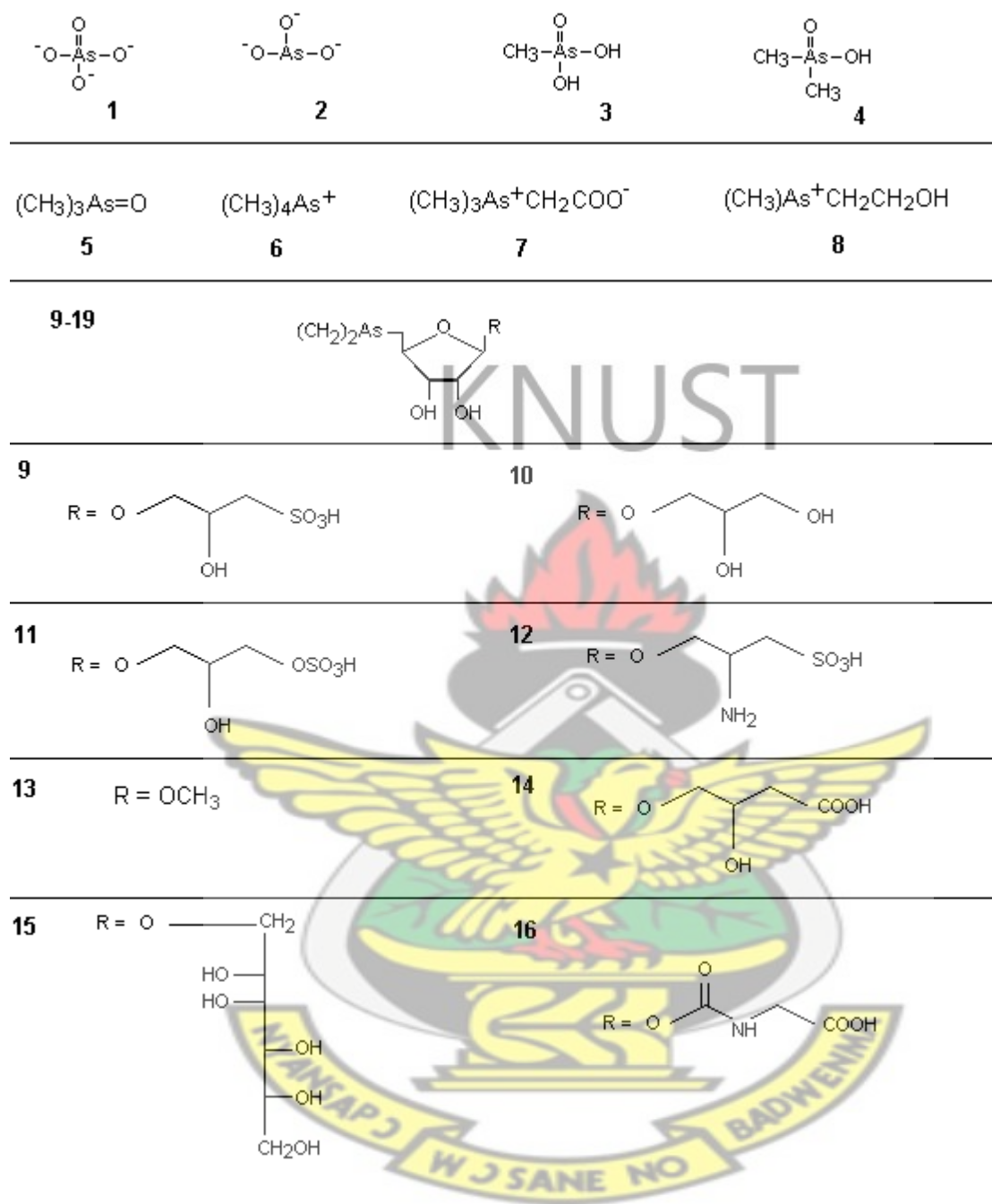
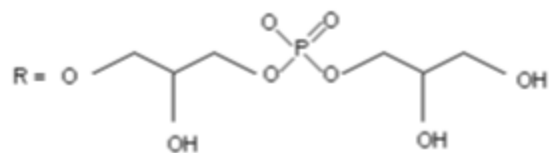
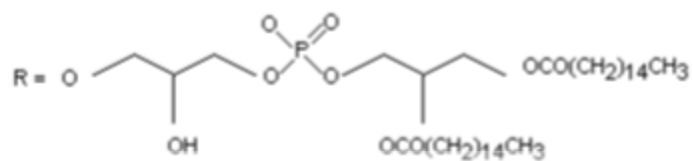


Figure 2.1: Structures of naturally occurring inorganic and organic arsenic species (WHO, 2001)

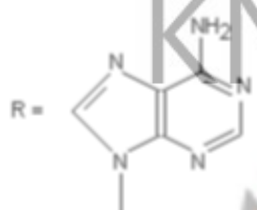
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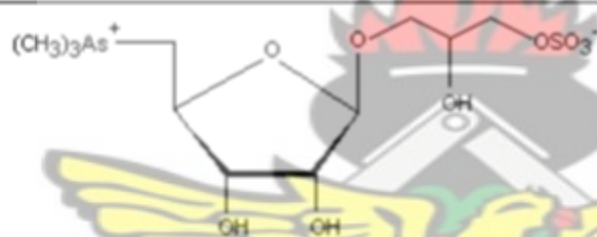
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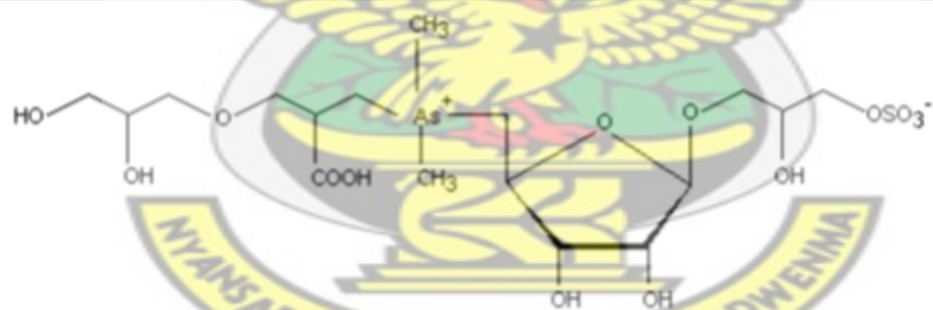
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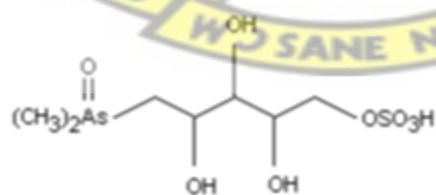


Figure 1.1: Structures of naturally occurring inorganic and organic arsenic species (WHO, 2001)

2.2 Heavy Metals

The term heavy metal refers to any metallic element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), chromium (Cr), thallium (Tl), zinc (Zn) and lead (Pb). Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking contaminated water (e.g. from lead pipes), high ambient air concentrations near emission sources, or intake through the food chain.

Among the inorganic contaminants of river water, heavy metals are becoming important for their non-degradable nature and they often accumulate through tropic levels causing serious biological effects. Compounds accumulate in living things any time they are taken up and stored faster than they are metabolized or excreted.

Heavy metals can enter a water supply through industrial activities such as mining, or even from acid rain breaking down soil aggregates and releasing heavy metals into streams, lakes, rivers, and groundwater (Khan, *et al.*, 1998). Also, indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture can cause the release of heavy metals into water bodies. Though some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and animals, many other metals like Cd, Hg and Pb have no known physiological activities, but they have proven detrimental beyond a certain limit. Deadlier diseases like edema of eyelids, tumor, congestion of nasal mucous membranes and pharynx,

stiffness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by some of these heavy metals have been documented (Johnson, 1998; Tsuji and Karagatzides, 2001; Abbasi, et al., 1998). Therefore, monitoring these metals is important for safety assessment of the environment and human health in particular.

2.3 Sources and Occurrence of Arsenic

2.3.1 Natural Sources

Arsenic is the main constituent of more than 200 mineral species, of which about 60 % are arsenate, 20 % sulfide and sulfosalts and the remaining 20 % include arsenides, arsenites, oxides and elemental arsenic (Onishi, 1969). The most common of the arsenic minerals is arsenopyrite, FeAsS. Arsenic is also found associated with many types of mineral deposits, especially those including sulfide mineralization (Boyle & Jonasson, 1973). It is generally accepted that arsenopyrite, together with the other dominant arsenic-sulphide minerals realgar and orpiment, are only formed under high temperature conditions in the earth's crust (Rittle et al, 1995).

Though not a major component, arsenic is also often present in varying concentrations in other common rock-forming minerals. Concentrations of various types of igneous rocks range from < 1 to 15 mg/kg, with a mean value of 2 mg/kg. Similar concentrations (< 1–20 mg/kg) are found in sandstone and limestone. Significantly higher concentrations of up to 900 mg/kg are found in argillaceous sedimentary rocks including shales, mudstone and slates. Up to 200 mg/kg can be present in phosphate rocks (O'Neill, 1990). Volcanic action is the next most important natural source of arsenic after low-temperature volatilization, and on a local scale it will be the dominant atmospheric source (WHO, 2001).

2.3.2 Anthropogenic sources

It has long been recognized that the smelting of non-ferrous metals and the production of energy from fossil fuel are the two major industrial processes that lead to anthropogenic arsenic contamination of air, water and soil. Other sources of contamination are the manufacture and use of arsenical pesticides and wood preservatives. Smelting activities generate the largest single anthropogenic input into the atmosphere (Chilvers & Peterson, 1987).

Tailings from metal-mining operations are a significant source of contamination, and can lead to contamination of the surrounding top soils, and, because of leaching, sometimes the groundwater too. It has been estimated that several billion tons of tailings waste exist in the USA alone (Wewerka et al, 1978).

In 1983, arsenical pesticides were one of the largest classes of biocontrol agent in the USA (Woolson, 1983). From the 1960s there was a shift, in herbicide use, from inorganic compounds (including lead and calcium arsenate and copper acetoarsenite) to organic compounds (arsenic acid, sodium arsenate, MMA and DMA). Use of total arsenical pesticides, excluding wood preservatives was estimated at $7-11 \times 10^3$ tonnes/year (WHO, 2001)

A list of some of the most common arsenic minerals is given in Table 2.2 Most are ore minerals or their alteration products. However, these minerals are relatively rare in the natural environment.

Table 2.2: Major arsenic minerals occurring in nature

Mineral	Composition	Occurrence
Niccolite	NiAs	Vein deposits and norites
Realgar	AsS	Vein deposits, often associated with orpiment, clays and limestones, also deposits from hot springs
Orpiment	As ₂ S ₃	Hydrothermal veins, hot springs, volcanic sublimation product
Cobaltite	CoAsS	High-temperature deposits, metamorphic rocks
Arsenopyrite	FeAsS	The most abundant As mineral, dominantly mineral veins
Tennantite	(Cu,Fe) ₁₂ As ₄ S ₁₃	Hydrothermal veins
Enargite	Cu ₃ AsS ₄	Hydrothermal veins
Arsenolite	As ₂ O ₃	Secondary mineral formed by oxidation of arsenopyrite, native arsenic and other As minerals
Claudetite	As ₂ O ₃	Secondary mineral formed by oxidation of realgar, arsenopyrite and other As minerals
Scorodite	FeAsO ₄ .2H ₂ O	Secondary mineral
Hoernesite	Mg ₃ (AsO ₄) ₂ .8H ₂ O	Secondary mineral, smelter wastes
Pharmacosiderite	Fe ₃ (AsO ₄) ₂ (OH) ₃ .5H ₂ O	Oxidation product of arsenopyrite and other As minerals
Conichalcite	CaCu(AsO ₄)(OH)	Secondary mineral
Pharmacosiderite	Fe ₃ (AsO ₄) ₂ (OH) ₃ .5H ₂ O	Oxidation product of arsenopyrite and other As minerals

2.4 Arsenic in Mining Environments

Arsenic occurs as a major constituent of more than 200 minerals, most of them are minerals or their weathering products (Mining Journal, 2000). Arsenic is most commonly found in sulphide minerals including arsenopyrite (FeAsS), orpiment (As_2S_3), and realgar (AsS). The principal gold bearing ore is arsenopyrite (Smedly and Kinniburgh 2002). When this host rock is crushed and treated to release gold, arsenic may also be released into the waste residues (tailings). This can cause high concentrations of arsenic in ground water (Del Razo et al, 1990; Smedley et al, 1996; Norman and Nartey 2000).

The extensive Achaean West African craton, stretching from Ghana to Sierra Leone, is underlain by Birimian formation which consists of folded and metamorphosed sediments and volcanic intruded by suites of granites, associated with gold – bearing sulphide mineralization. The upper Birimian rock formation has over 10 times the average crustal abundance of gold and arsenic (Mining Journal, 2000).

Ghana is richly mineralized with gold that is accompanied by arsenic mineralization. Ashanti region in Ghana has been a center of major gold – mining activities since the late 19th century. The entire Amansie West District has been found to be rich in gold deposits; with mining emerging as the most important economic activity in the District. The District has also been found to contain arsenic enriched drainages (A Duker et al, 2004).

2.5 Uses of Arsenic

Arsenic is produced commercially by reduction of As_2O_3 with charcoal. As_2O_3 is produced as a by-product of metal-smelting operations. It is present in flue dust from the roasting of ores, especially those produced in copper smelting. In the 1960s, the pattern of use for As_2O_3 in the USA is believed to have been 77 % as pesticides, 18 % as glass, 4 % as industrial chemicals and 1 % as medicine. However, the pattern has changed over the years as the use of arsenic compounds for timber treatment has been increasingly popular since the late 1980s (WHO, 2001). Worldwide usage in the early 1980s was estimated to be 16 000 tonnes/year as a herbicide, 12 000 tonnes/year as a cotton desiccant/defoliant and 16 000 tonnes/year in wood preservative (Chilvers & Peterson, 1987). By 1990, the estimated end-use of arsenic in the USA was 70 % in wood preservatives, 22 % in agricultural chemicals, 4 % in glass, 2 % in non-ferrous alloys and 2 % in other uses including semiconductors (US DOI, 1991). Arsenic pentoxide and As_2O_3 are used as additives in alloys, particularly with lead and copper; arsenic and As_2O_3 are used in the manufacturing of low-melting glasses. High-purity arsenic metal and gallium arsenide are used in semiconductor products. Fowler's solution (1 % potassium arsenite solution) was used as a medication (Cuzick et al., 1992). As_2O_3 has been used for the treatment of acute promyelocytic leukaemia (Soignet et al., 1998).

2.6 Toxic Effect of Arsenic

Arsenic is a common environmental agent whose toxic properties have been known for centuries. Since ancient time, arsenicals have been used as agents of suicide and murder. Arsenic as a poisonous and a killing agent was closely associated to the death of France's famous ruler, Napoleon Bonaparte, (Abdullah Salim, 2009). Arsenic is toxic to both plants and animals and inorganic arsenicals are proven carcinogens in humans (Ng, 2005). The toxicity of arsenic to human health ranges from skin lesions to cancer of the brain, liver, kidney, and stomach (Smith et al, 1992). A wide range of arsenic toxicity has been determined that depends on arsenic speciation, generally inorganic arsenic species are more toxic than organic forms to living organisms, including humans and other animals (Goessler and Kuehneltm 2002; Meharg and Shore, 2002; Ng, 2005).

The chemical forms and oxidation states of arsenic are important with regards to their toxicity which is directly related to their mobility in water and body fluids. The toxicity of arsenic compounds decreases in the following order; arsines > inorganic arsenates (As^{3+}) > arsenoxides > inorganic arsenates (As^{5+}) > organic pentavalent compounds > arsonium compounds > elemental arsenic (Mandal and Susuki, 2002; Prohaska and Stinger, 2005).

Arsenite is more toxic than arsenate due to the difference in their metabolic pathways. As^{3+} quenches the tricarboxylic acid (TCA) cycle by binding to thiols in pyruvate dehydrogenase. Arsenite binding to sulfhydryl groups also impairs the function of many proteins (US National Research Council, 1999). As^{5+} competes with phosphate, inhibiting the production of adenosine triphosphate (ATP) which transports energy within cells (Oremland and Stolz, 2003).

A recent study on arsenic toxicity has shown that exposure to arsenic through drinking water has direct effect on the early stages of life when the brain is usually most vulnerable (Hamadani et al, 2010). Another study by Tofailet et al (2009) has shown that exposure to contaminated drinking water during pregnancy is associated with low birth weight and fetal loss and there is concern that the infant's growth may be affected.

Long-term exposure to arsenic results in chronic arsenic poisoning (arsenicosis). This has been reported to occur in people who live in endemic areas with high arsenic concentrations in drinking water or in burning coal (Hopenhayn-Rich et al., 2000; Pi et al., 2000; Berg et al., 2001; Liu et al., 2002). Arsenicosis has also been reported in people due to occupational exposure to arsenic (Ng et al., 1998). Occupational exposure to arsenic can result in reduction of methylation capacity as indicated by elevation of unmetabolised inorganic arsenic in the urine (Ng et al., 1998). Skin lesions, which include change of pigmentation (e.g. melanosis) and keratosis of the hands and feet are characteristics of chronic arsenic poisoning and usually appear after 5–15 years after exposure (Tseng, 1977). Chronic arsenic poisoning may also lead to damages of internal organs the respiratory, digestive, circulatory, neural, and renal systems (ATSDR, 2000; IPCS, 2001). The most significant consequence of chronic exposure to arsenic is the occurrence of cancers in various organs especially the skin, lung, and bladder (ATSDR, 2000; IPCS, 2001). Examples of arsenicosis are shown in figure 2.2. In Taiwan, where residents were chronically exposed to high levels of arsenic in their drinking water, Black Foot Disease (BFD) has been the most severe manifestation associated with this type of exposure (Chen et al., 1985; Tseng, 1977). Peripheral neuropathy has also been reported to occur but after long-term exposure to inorganic arsenic in drinking water (Hindmarsh et al., 1977). Moreover, people occupationally exposed to

arsenic and through contaminated water are reported to have an increased risk of diabetes (Rahman and Axelson, 1995; Tseng et al., 2002).

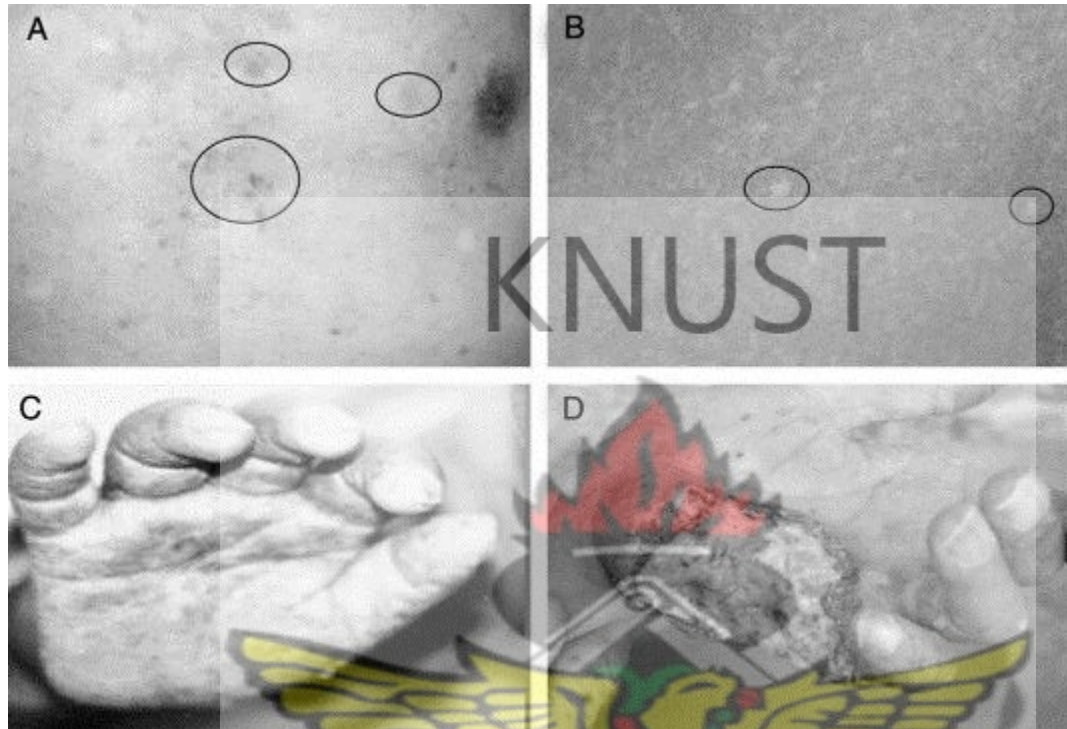


Figure 2.2: Typical skin lesions and skin cancer found in patients who have been chronically exposed to arsenic: (A) hyperpigmentation, (B) hypopigmentation, (C) keratosis, and (D) skin cancer.

The main loss pathway for arsenic in the body is excretion through urine (IARC, 2004). Humans and other animals are known to methylate inorganic arsenic, causing it to be less toxic and more readily excreted.

2.7 Geochemical Processes Controlling Arsenic Mobility

The mobility and toxicity of arsenic in the environment are dependent on the chemical form or species in which it exists. Some categories of processes which largely control arsenic mobility in aquifers are:

- pH, adsorption and desorption reactions
- Precipitation and dissolution reactions
- pH and Redox potential

2.7.1 pH, Adsorption and Desorption Process

Arsenic adsorption and desorption reactions are influenced by changes in pH, occurrence of redox reactions, presence of competing anions. Arsenic is a redox sensitive element. This means that arsenic may gain or lose electrons in redox reactions. As result, arsenic may be present in a variety of redox states. Arsenate and arsenite are the two forms of arsenic commonly found in ground water. (Mascheleyn et al, 1991).

Arsenate is present as the negatively charged oxyanions H_2AsO_4^- or HAsO_4^{2-} , whereas arsenite is present as the uncharged species H_3AsO_3 . The strength of adsorption and desorption reactions between these different arsenic species and solid – phase surfaces in aquifers varies, in part, because of these differences in charge. Differences in charge affect the character of electrostatic interactions between species and surfaces. Arsenate and arsenite adsorb to surface of a variety of aquifer materials, including iron oxides, aluminum oxides, and clay minerals. Adsorption-desorption reactions between arsenate and iron-oxide surfaces are particularly important

controlling reactions because iron oxides are widespread in the hydro geologic environment as coatings on other solids, and because arsenate adsorbs strongly to iron-surfaces in acidic and near neutral pH water (Dzombak and Morel, 1990; Waychunas et al, 1993). However, desorption of arsenate from iron – oxide surfaces become favored as pH values become alkaline (Fuller and Davis, 1989; Dzombak and Morel, 1990). The pH- dependence of arsenate adsorption to iron – oxide surfaces appears to be related to the change in charge iron oxide net surface from positive to negative as pH increases above the zero point of charge (pH at which the net surface charge is equal to zero) of about 7.7-8.0 (Dzombak and Morel, 1990; Stumm and Morgan, 1996).

Iron oxide surfaces also adsorb arsenite, and both arsenate and arsenite adsorb to aluminum oxides and clay mineral surfaces. However, these adsorption reactions appear generally to be weaker than is the case for arsenate adsorption to iron oxide surfaces under typical environmental pH conditions (Manning and Goldberg, 1997). Nevertheless, pH-dependent adsorption and desorption reactions other than those between arsenate and iron oxide surfaces may be important controls over arsenic mobility in some settings. As is the case for adsorption of arsenate to iron – oxide surfaces, adsorption of arsenite to iron oxide surfaces tends to decrease as pH increases, at least between the range from pH 6 to pH 9 (Dzombak and Morel, 1990). Unfortunately, arsenate and arsenite adsorption and desorption reactions with other common surfaces are less well characterized, and apparently more complex than is the case for adsorption and desorption reactions with iron –oxide surfaces (Manning and Goldberg, 1997).

2.7.2 Precipitation and Dissolution process

The various solid phases (minerals, amorphous oxides, organic carbon) of which aquifers are composed exist in a variety of thermodynamic states. At any given time, some aquifer solid phases will be undergoing dissolution, whereas others will be precipitating from solution. Arsenic contained within solid phases, either as a primary structural component or as an impurity in any of a variety of solid phases is released to ground water when those solid phases dissolve. Similarly, arsenic is removed from ground water when solid phases containing arsenic oxide (Waychunas et al, 1993), iron oxide may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for ground water.

2.7.3 Effect of pH and Redox Potential (E_h)

Both redox potential (E_h) and pH impose important controls on arsenic speciation in the natural environment (Ferguson and Gavis, 1972). Under oxidizing conditions (high E_h values), inorganic arsenic occurs primarily as H_3AsO_4 (As^{5+}). At low E_h values, H_3AsO_3 is the predominant inorganic arsenic species (As^{3+}) under reducing conditions. If E_h value below -250 mV exist in the environment, arsenic compounds such as As_2S_3 in the presence of sulphur or hydrogen sulphide can be formed but these conditions are not environmentally relevant.

2.8 Arsenic in Ground Waters

2.8.1 Aqueous Speciation

In aqueous systems, arsenic exhibits anionic behavior. Trivalent arsenic can exist as arsenious acids (H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} , AsO_3^{3-}) ions. Pentavalent arsenic commonly occurs as the arsenic acids (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-}) (Goa and Burau, 1997).

Arsenious acid (H_3AsO_3) appears at low pH and under mildly reduced conditions, but it is replaced by H_2AsO_3^- as the pH increases. Only when the pH exceeds 12 does HAsO_3^{2-} appear. In aerobic waters, arsenic acid predominates only at extremely low pH (< 2); with a pH range of 2 to 11, it is replaced by H_2AsO_4^- and HAsO_4^{2-} (Scow et al, 1981).

Most toxic trace metals occur in solution as cations. Which generally become increasingly insoluble as the pH increase (Smedly et al 2002). The solubility of most of these trace metals in water is limited by precipitation as oxides, hydroxides, carbonates, most oxy anions including arsenate tend to become less strongly sorbed as the pH increase (Dzombak and Morel, 1990). Therefore, the ox anion forming elements such as Cr, As, and Se are some of the most common trace contaminants in ground waters.

Arsenic in aquatic environment is distributed in both the aqueous solution and sediments. Elevated concentrations of arsenic in natural waters are usually associated with arsenic – rich sedimentary rocks of marine origin, weathered volcanic rocks, fossil fuels, geothermal areas.

In surface waters (lakes, streams and rivers) As (V) is generally the dominant species (Seyler and Martin, 1990; Pettine et al, 1992), though significant seasonal variations in speciation have been determined. Concentrations and relative proportions of As (V) and As (III) vary according to change in input sources, redox conditions and biological activity. The presence of As (III) may be maintained in oxic waters by biological reduction of As (V). Higher relative proportions of As (III) have been found in river stretches close to inputs of As (III) - dominated industrial effluent (Andreae and Andreae, 1989) and in waters as component of geothermal water.

In wells and boreholes (ground waters), the ratio of As (III) to As (V) can vary greatly as a result of variations in the abundance of redox – active solids, especially organic matter, the activity of microorganisms and the extent of convection and diffusion of O₂ from the atmosphere.

In strongly reducing aquifers (Fe (III) and SO₄²⁻ reducing aquifers), As (III) typically dominates. Reducing As – rich ground waters from Bangladesh have As (III) : As ratios varying between 0.1-0.9 but are typically around 0.5-0.6 (DPHE/BGS/MML, 1999; Smedley et al., 2001b). Ratios in reducing ground waters from inner Mongolia are typically 0.6 - 0.9 (Smeley et al., 2001a). Concentrations of organic forms are generally low or negligible in ground waters (e.g. Chen et al, 1995).

2.8.2 Atmospheric Precipitation

Arsenic is emitted into the atmosphere by high-temperature processes such as coal-fired power generation plants, burning vegetation and volcanism. Natural low-temperature biomethylation and reduction to arsines also release arsenic into the atmosphere. Arsenic is released into the atmosphere primarily as As_2O_3 and exists mainly adsorbed on particulate matter. These particles are dispersed by the wind and are returned to the earth by wet or dry deposition. (WHO, 2001)

The most important anthropogenic inputs are from smelter operations, mining and fossil fuel combustion. The arsenic appears to consist of mainly As_2O_3 dust particles (Cullen and Reimer, 1989). Nriagu and Pacyna, 1988 estimated that anthropogenic sources of atmospheric arsenic (around 18,800 tonnes/ annum) amounted to around 70 % of the global atmospheric arsenic pollution. While it is accepted that these anthropogenic sources have an important impact on airborne arsenic compositions, their influence on the overall arsenic cycle is not well established. Concentration of arsenic in rainfall is invariably low at typically less than 0.03 mg/L (WHO 2001).

Concentrations in areas affected by smelter operations, coal burning and volcanic emissions are generally higher. Andreae (1980) found rainfall potentially affected by smelting and coal burning to have As concentrations of around 0.5 mg/L, although higher concentrations (average 16 mg/L) have been found in rainfall collected in Seattle some 35 downwind of a Cu smelter (Creclius, 1975).

2.9 How arsenic is released into Water

Several hypotheses have been put forward as to the release mechanism of arsenic in groundwater. The two most popular hypotheses are pyrite oxidation and iron oxyhydroxide reduction. These two hypotheses were proposed to explain the high arsenic levels in Bangladesh.

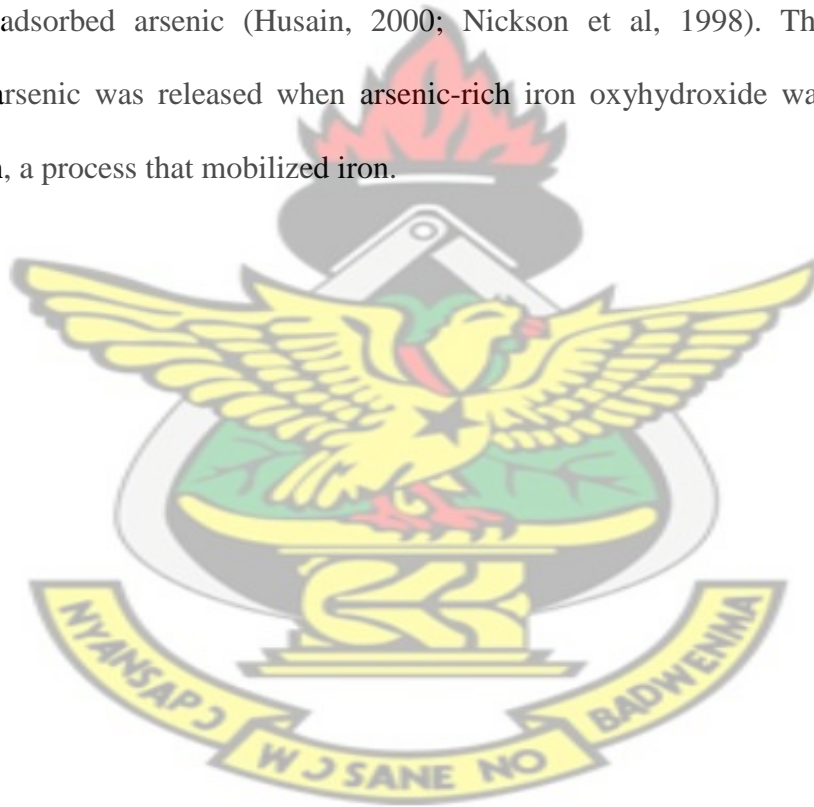
2.9.1 Pyrite oxidation

The pyrite oxidation hypothesis was proposed by Dr. Dipankar Chakraborti and his group (Ahmed, 2002). After tubewells were installed, the water table was lowered due to increased pumping. As a result, atmospheric oxygen invaded the aquifer by diffusing into the pore spaces of the soil and into the groundwater. The oxygen interacts with the arsenopyrite, turns the mineral into water-soluble form, thus releasing arsenic into the groundwater (Harvard University, 2002; Bridge, 2000; Dainichi Consultants, 2001).

However, this hypothesis was not consistent with the observation that shallow, oxygenated wells generally contained much lower level of arsenic than deeper, less oxygenated wells (Nickson et al 1998). In addition, if pyrite was oxidized, the aquifer should be rich in sulphate, but it was not the case (Chowdhury et al, 1998). Recent works by Harvey et al found sulphate levels were lower at locations with higher arsenic concentration (Harvey, 2002). In the conference on arsenic mitigation in Dhaka on January 14th -16th 2002, there was a widespread feeling that the oxidation theory was not reasonable (Harvard University, 2002).

2.9.2 Iron Oxyhydroxide Reduction Hypothesis

According to the iron oxyhydroxide reduction hypothesis, arsenic-rich sulphide minerals are weathered and adsorbed onto iron oxyhydroxides (FeOOH). The arsenic-iron oxyhydroxide is deposited in tube wells and aquifers. Due to a wide variety of processes, such as agriculture or groundwater pumping, organic carbon was introduced into the aquifer. The mineralization of organic carbon caused a decrease in dissolved oxygen in the aquifer, and lowered the redox potential. The reducing environment caused the breakdown of iron oxyhydroxide, and released the previously adsorbed arsenic (Husain, 2000; Nickson et al, 1998). These observations suggested that arsenic was released when arsenic-rich iron oxyhydroxide was reduced in the anoxic condition, a process that mobilized iron.



2.10 Guidelines and Regulation of Arsenic

The World Health Organization (WHO) develops Guidelines for Drinking Water Quality (GDWQ) in order to protect public health for drinking water contaminants. The 2011 4th edition of WHO GDWQ established the arsenic drinking water guideline to be 10 µg/L (0.01 mg/L). The United States Environmental Protection Agency (EPA) set the maximum contaminant level (MCL) for arsenic at 19 µg/L in January 2001.

Ghana Water Company and Ghana Standard Board set the maximum contaminant level for arsenic at 10 µg/L.

2.11 Arsenic Pollution in the world

Most high levels of arsenic in groundwater are the result of natural occurrences of arsenic and cases of arsenic pollution caused by anthropogenic means are numerous but tend to be localized.

Background concentrations of arsenic in groundwater in most countries are less than 10 µg/L and sometimes substantially lower. However, values quoted in literature show a very wide range, from < 0.5 to 5000 µg/L. In an extensive groundwater survey in the USA, it was reported that approximately half of the 30 000 samples analysed had naturally occurring arsenic levels ≤ 1 µg/L, with about 10 % exceeding 10 µg/L (Smedley and Kinniburgh, 2002). Geothermal water and high evaporation rates are associated with arsenic concentrations ≥ 10 µg/L in ground and surface waters. Welch et al. (2000) suggested three major types of natural geological condition giving rise to high level of arsenic in ground waters:

- i. aquifers composed of rocks or sediments enriched with arsenic – containing minerals of geogenic origin, such as sulfide mineralization;
- ii. aquifers containing sediments coated with iron oxyhydroxide (FeOOH) phases enriched in arsenic through hydrological action, where arsenic is mobilized into pore water under reducing conditions;
- iii. aquifers enriched in arsenic through high rates of evaporation in arid area, leading to increased mineral concentration in ground waters; the arsenic is mobile in such aquifers because of the high pH (> 8.5) caused by concentration of alkali and alkali earth metals in solution.

Similarly, from some 1200 groundwater analysed from various aquifers in England and Wales showed that, 68 % had concentrations of 1 ppb and 6 % had concentrations exceeding 10 ppb while 1 % had concentrations of 50 ppb and above (Smedley, 2006).

Arsenic levels above drinking water limits can and do occur in ground water from many aquifer of varying lithology (Smedley, 2006). It is increased testing of ground and surface waters for arsenic in recent years that has resulted in the recognition of many examples. However, occurrences of very high aqueous arsenic concentrations tend to be associated with a small number of specific of geological environments.



Figure 2.3: Arsenic distribution in the world above 50 µg/L by Smedley and Kinniburgh.

Areas of mineralization and mining can be seen to be associated with arsenic pollution in the world. Some high arsenic areas are also associated with occurrence of geothermal fluids. In some cases areas that are recognized as high arsenic ground waters, are not associated with mineralization or geothermal activity. These occur in extensive aquifers, which can be a major source of drinking water for large populations. High arsenic concentrations have been discovered through the identification of health problems.

Table 2.3: Chemical Speciation of Arsenic in Various Media

Environment	Speciation technique	Fraction/ concentration	Reference
Acid mine drainage	LC – ICP – MS	As (III) = 13, 000 µg/ L As(v) = 3700 µg/L	Bednar et al. (2002)
Coal fly ash	IC- ICP – MS	As (V) >> As (III)	Jackson and Miller (1998)
Drinking water (Natural water)	IC – ICP – MS	Particulate and soluble arsenic contributed 11.4 and 88.6 % of the total arsenic respectively. In the case of soluble As, As (III) and As V) were 47.3 and 52.7%, respectively.	Thirunavukkarasu et al. (2001)
Geothermal waters	HPLC/ GFAS and HPLC/HGAAS	Na ₂ HAsO ₄ was predominant (1997)	Buyuktuncel et al. (1997)

Environment	Speciation technique	Fraction/ concentration	Reference
Groundwater	LC – ICP – MS	As (III) = 720 µg/L As (III) = 1080 µg /L	Bednar et al. (2002)
Ground water	FI – HG – AAS	As (III) and As (V) were present in 1:1 ratio	Samanta et al.(1999)
Groundwater close to cattle tick dipsites	ICP – AES	As (V) was dominant	Kimber et al. (2002)
Human urine (Bangladesh)	IC – FI- HG- AAS	As (III) was the major species	Alauddin et al. (2003)
Mine tailings	AAS	Total As = 62350mg /kg	Kim et al (2002).
Polluted Water course	IC – ICP –MS	Dissolved As mostly as As(V) 130 µg/L	Gault et al. (2003)
River waters	HG – AAS using Na – tetrahydro Borate (III) reductant	As (V) was the principal species	Quinaia and Rollember (2001)

Environment	Speciation technique	Fraction/ concentration	Reference
Sewage sludge	HG – CT – AAS	At pH5.0 inorganic As > Organic As At pH 6.5 organic As > Inorganic As	Carbonell Barrachina et al.(2000)
Well waters	AAS	670 µg/L total dissolved Arsenic; As (III) was dominant	Chen et al. (1994).
Wetlands	XANES	As (III) > As (V)	La Force et al. (2000)

The most serious groundwater arsenic pollution in the world occurs in Bangladesh. The region has been under intensive water testing, treatment and mitigation efforts since arsenic problem was first reported in 1993. The high arsenic concentrations in the waters are from aquifers of Holocene age which comprise unconsolidated grey sands, alluvial and deltaic sediments (Smedley, 2007). Many studies have observed that the highest concentrations of arsenic in the aquifers occur at depth typically around 15-50 m, with high concentrations associated with greater depth (BGS and DPHE, 2001; Harvey et al, 2002; Klump et al, 2006). Arsenic concentrations have been determined in the range of < 0.5-1460 µg/L. The relative abundance of deposited organic matter leads to strongly reducing conditions in many parts of the aquifers. Speciation studies suggest strong dominance of As (III) (> 70 %) (Zheng et al 2005). Studies have revealed the presence of high groundwater arsenic concentrations in northern Burkina Faso, in the Yatenga and Zondoma province (COWI, 2004; Smedley et al, 2007).

These provinces are underlain with lower Birimian sedimentary rocks which have gold and associated with sulphide mineralization. Artisanal gold mining has expanded in these two provinces. Smedley (2007) reported from a study of 45 groundwater samples from the area that most had arsenic concentrations less than the WHO guideline (10 µg/L). A wide range of arsenic concentration 0.5-1630 µg/L was observed with most of the high arsenic concentrations were found in borehole waters. Available data suggests the presence of dissolved oxygen in most of the samples (1.4 – 4.5 mg/L in hand dug well and 0.1-5.8 mg/L in boreholes) (Smedley, 2007). Ron Phibun (2007) speciation studies in groundwater suggest dissolved arsenic occurs as As (V).

2.12 Arsenic Contamination in ground water in Ghana

Ghana is an important gold mining country and mining has been active since the late 19th century. Today, Ghana produces about one third of the world's gold. The most important mining area is the Ashanti Region of Ghana. Gold is associated with sulphide mineralization, particularly arsenopyrite. Arsenic is mobilized in the local environment as a result of arsenopyrite oxidation, or exacerbated by the mining activity.

Previous studies have reported that mining activities have resulted in arsenic contamination of surface water, soil, plant, food items, and humans in Obuasi, which is the most important mining area in Ghana (Amasa, 1975; Amonoo – Neizer and Amekor, 1993; Golow et al., 1996; Smedley, 1996; Smedley and Kinniburgh, 2002). Extremely high concentrations of arsenic were observed in dam water (2250 µg/ L) and drinking water (1400µg/ L) (Amasa, 1975). Smedley et al. (1996) reported concentrations of 175 µg/L in stream water affected by mining pollution. These levels were over the WHO drinking water guideline (10 µg/L) for arsenic (WHO, 2011).

At least 10 % of Ghana's rural borehole wells have arsenic concentrations exceeding 10µg/L (Mead, 2005). Because inorganic arsenic has carcinogenicity (WHO, 2001) human exposure of arsenic through the consumption of contaminated drinking water and food in these areas may cause serious health problems.

Despite the presence of high arsenic concentration in the contaminated soils and in bedrocks close to the mines, Smedley et al. (1996) found that many of the ground waters of the Obuasi area had low arsenic concentrations, with a median concentration in well waters of just 2 mg/L. Some higher concentrations were observed (up to 64 mg/L) but these were not generally near the mines or related directly to mining activity. Rather, the higher concentrations were found to be present in relatively reducing ground waters (Eh 220 – 250 mV). Oxidizing ground waters, especially from shallow hand – dug wells, had low arsenic concentrations. This was taken to be due to the retardation of arsenic by adsorption onto hydrous ferric oxides under the low pH condition of the ground waters (median pH 5.4 in dug wells; 5.8 in tube wells; Smedley, 1996; Smedley et al., 1996).

Very high levels of arsenic (19,000 µg/L and 14,000 µg/L) have been obtained from 120 m and 12 km respectively below the Weija dam in Accra. (Armah et al, 1998). Interestingly, buruli ulcer cases occurred in settlements both upstream and downstream of the Weija dam.

A reconnaissance survey of arsenic concentrations in 150 boreholes in southeast Ghana (Accra, Eastern and Volta regions) was conducted by Kortatsi et al (2004) using a field test kit which gives direct readout of arsenic concentration in the range 2 – 100 µg/ L. The study revealed low to medium concentrations of arsenic from 2-39 µg/L. Out of the 150 samples analysed, 147 had arsenic concentrations below detection limit (< 2 µg/L). Three boreholes in the Volta region had

arsenic concentrations of 19 µg/L, 28 µg/L, and 32 µg/L. These boreholes occurred in recent sand formations. The origin of the high arsenic concentration is not known but probably comes from anthropogenic sources (fertilizer and pesticide application in the area).

In 2006, Appiah et al analysed rural hand – dug wells and boreholes in a 6500 sq km area of southwest Ghana for arsenic. In addition, they measured arsenic in several wells near gold mining activities. Arsenic was detected in 52 of 207 wells studied. Concentration range was up to 2000 µg/L and 25 wells had arsenic greater than 5 µg/L. High arsenic waters were associated with upper birimian rock, gold mining area and low Eh. Speciation showed significant concentration of As (III) and a strong correlation was found between skin lesions and arsenic concentration in well waters. Evidence for arsenic related skin problems is explained by ingestion of arsenic bearing soils together with high consumption of water in the tropics.

Smedley in 1996 determined total arsenic concentrations in some ground water samples in two areas (Obuasi and Bolgatanga) which are characterized by sulphide mineralization. The arsenic concentrations in Obuasi and Bolgatanga varied from < 1-64 µg/L and <1-141 µg/L respectively. The wide range of arsenic concentrations was attributed to the depth of the water samples collected. The concentrations were low in shallowest waters, but increased at greater depths.

In the Amansie West district, irrigation of vegetable crops, especially in the dry season is by surface water, which contains 252 µg/L to 535 µg/L (Duker, 2004). In this study, buruli ulcer was related to arsenic levels in water samples (streams and boreholes). The results showed that buruli ulcer prevalence has a significant positive relationship with arsenic levels in surface water ($R^2 = 0.82$, $p < 0.0.5$) but not with arsenic level in groundwater ($R^2 = 0.10$, $p = 0.60$).



Figure 2.4: Pictures of some streams at Amansie West district

In an earlier study by Amofa et al (1999) on buruli ulcer cases in Ghana, approximately 6000 cases of buruli ulcer were recorded in the national survey. Of the 110 districts in Ghana, at least 90 of them were found to have buruli ulcer cases of which Amansie West district had the highest prevalence rate of 150.8 per 100 000 persons. The crude national prevalence rate according to the study was 20.7 per 100 000 persons.

2.13 Biotransformation of Arsenic

Arsenic compounds are methylated by bacteria and fungi to yield dimethyl and trimethylarsines by a mechanism that involves the replacement of substituent oxygen atoms by methyl groups (Chanllenger, 1997). Methylation is thought to be a detoxification mechanism for the microorganisms (Braman, 1974) and is important in the transfer of arsenic from the sediment to the water and atmosphere.

Mc Bride et al (1971) reported that arsenate could be reductively methylated to dimethylarsine by *Methanbacterium* under anaerobic conditions. The reaction (Figure 2.3) given by Saxena and Howard (1987), involves the initial reaction of arsenate to arsenite. Methylarsonic acid, formed by the methylation of arsenite, is reductively methylated to dimethylarsinic acid, which is reduced to dimethylarsine. Methylcobalamin is the methyl – donor in the reaction.

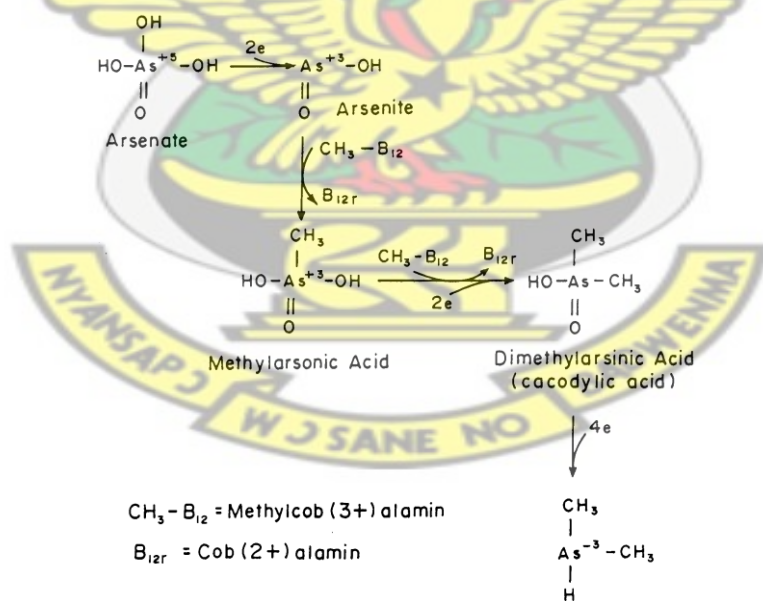


Figure 2.5: Reductive methylation of arsenite to dimethylarsine. (Current Science, Vol. 80, No. 7, April 10, 2001).

Under acidic conditions, the sewage fungi *Candida humicola* transform arsenate to trimethylarsine. Lesser amounts of trimethylarsine are also formed by the incubation of the fungi with arsenite, methylarsonate and dimethylarsinate. These may be intermediates in the reduction and alkylation of arsenate to trimethylarsine (Cox et al, 2003). Fungi capable of generating trimethylarsine from the pesticides monomethylarsonate and dimethylarsine include *Candida humicola*, *Glicaninum roseum* and a strain of *Penicillium* (Alexander, 1974). The rate of formation of trimethylarsine by *C. humicola* and other molds decrease as the mold reaches its resting stage (Thayer et al, 1982).

The toxic alkylarsines are volatile, with distinct garlic – like odour and are rapidly oxidized to less toxic products in the atmosphere. One such product dimethylarsenic acid has been shown to be an intermediate in the synthesis of dimethylarsine from arsenic salts (Wood, 1998). The methylation of arsenic is important because of the extremely toxic products that result. In addition, this process transfers arsenic from sediments back to the water column in aquatic systems, increasing arsenic mobility in the environment. Biotransformation of arsenic can produce highly volatile compounds such as arsine (AsH_3), dimethylarsine ($\text{As}(\text{CH}_3)_2$) and trimethylarsine ($\text{As}(\text{CH}_3)_3$).

Many aquatic organisms are capable of accumulating arsenic and may catalyse the oxidation of arsenite to arsenate while also promoting the formation of methylarsines through biomethylation reaction (Wood et al, 1998). Certain diatoms are known to reduce arsenate to arsenite and dimethylarsinic acid (Braman, 1974). The production of methylarsines by methogenic bacteria under aerobic conditions has been demonstrated by McBride and Wolfe (1989) which showed that dimethylarsinic acid and methylarsonic acid ($\text{CH}_3\text{As}(\text{OH})_2$) are intermediates in the reductive methylation of inorganic arsenic to dimethylarsine.

Organic arsenic compounds are also known to be present in marine animals, and recently the composition and structure of one such compound, arsenobetaine, isolated from the tail muscle of a western rock lobster was described (Edmonds et al, 1977). It is possible that such compounds could also find their way into natural waters.

2.14 Excretion

In humans, the major route of excretion of most arsenic compounds is via the urine. The biological half-time of inorganic arsenic is about 4 days, but is slightly shorter following exposure to arsenate than to arsenite (Crecelius, 1977; Yamauchi and Yamamura, 1979; Tam et al., 1979; Pomroy et al., 1980; Buchet et al., 1981). In six human subjects who ingested radiolabelled [^{74}As] arsenate, 38 % of the dose was excreted in the urine within 48 hours and 58 % within 5 days (Tam et al., 1979). The results of another study indicate that the data were best fit to a three-compartment exponential model, with 66 % excreted with a half-time of 2.1 days, 30.4 % with a half-time of 9.5 days and 3.7 % with a half-time of 38.4 days (Pomroy et al., 1980). In three subjects who ingested 500 μg arsenic in the form of arsenite in water, about 33 % of the dose was excreted in the urine within 48 hours and 45 % within 4 days (Buchet et al., 1981).

2.15 Degradation of arsenic

2.15.1 Abiotic degradation

The rates of photochemical decomposition of arsenite, DMA, MMA and arsenobetaine have been studied in both distilled water and seawater. All species were found to degrade rapidly in aerated distilled water. In deaerated solutions the rate of oxidation of arsenite was almost two orders of magnitude slower. Half-lives for the degradation of DMA, MMA and arsenite were 9.2, 11.5 and 0.9 min respectively for aerated distilled water and 25, 19 and 8 min for deaerated distilled water (WHO, 2001). In seawater, the rates of photochemical decomposition were slower. For example, in seawater only 20 % of DMA was converted to MMA after 300 min with no other products detected, whereas in distilled water DMA was completely degraded within 100 min (Brockbank et al., 1988). The implications for photochemical decomposition of arsenic species in natural waters is not clear, because sunlight is deficient in the lower-wavelength bands generated by the mercury lamp used in this study.

Von Endt et al. (1968) concluded that degradation of MSMA in soil was primarily due to soil microorganisms rather than abiotic factors. In 60 day tests in non-sterile soil 1.7–10% of the ¹⁴C-MSMA was degraded, whereas under steam-sterilized conditions only 0.7 % was degraded.

2.16.2 Biodegradation

The predominant form of arsenic in water is usually arsenate (Callahan et al., 1979; Wakao et al., 1988), but aquatic microorganisms may reduce the arsenate to arsenite and a variety of methylated arsenicals.

Marine organisms tend to contain much higher levels of arsenic than terrestrial organisms; this is because of the high arsenate/phosphate ratio in oceans, which is a consequence of the very low phosphate concentration (WHO, 2001). Most of the arsenic accumulated in marine organisms is in a water-soluble form of arsenic, namely arsenobetaine. Hanaoka et al. (1990) incubated marine sediments in the presence of arsenobetaine and demonstrated microbial degradation, with arsenate, arsenite, MMA, DMA and arsenobetaine being identified. Further experiments revealed the formation of trimethylarsine oxide during aerobic incubation of bottom sediments with arsenobetaine as the carbon source (Kaise et al., 1987). Under aerobic conditions, arsenobetaine is converted to its metabolites to a much greater extent than other methylarsenicals. Under anaerobic conditions little or no degradation of arsenobetaine occurred, whereas trimethylarsine oxide and DMA were converted to less methylated compounds (Hanaoka et al., 1990). Degradation of arsenobetaine has also been demonstrated in the water column in the presence of suspended substances (Hanaoka et al., 1992).

Organoarsenical pesticides (e.g. MMA and DMA) applied to soil are metabolized by soil bacteria to alkylarsines, MMA, and arsenate (ATSDR, 1993). The half-time of DMA in soil is about 20 days (ATSDR, 1993).

Cheng and Focht (1979) added arsenate, arsenite, methylarsonate and DMA to three different soil types. Arsine was produced in all three soils from all substrates but methylarsine and

dimethylarsine were only produced from methylarsonate and DMA respectively. Both *Pseudomonas* sp. and *Aliccaligenes* sp. produced arsine as the sole product when incubated anaerobically in the presence of arsenate or arsenite. The authors concluded that reduction to arsine, not methylation to trimethylarsine, was the primary mechanism for gaseous loss of arsenicals from soil.

Degradation of MSMA by soil microorganisms was studied by Von Endt et al. (1968). In 60-day tests they found that 1.7–10 % of the ^{14}C -MSMA was degraded; four soil microorganisms isolated in pure cultures degraded 3–20 % of ^{14}C -MSMA to $^{14}\text{CO}_2$ when grown in liquid culture at 10 mg MSMA/litre. Woolson and Kearney (1973) showed that sodium DMA was degraded to arsenate in soil under aerobic conditions but not under anaerobic conditions. Degradation of MSMA has been shown to be associated with soil organic matter oxidation. In a loamy soil, degradation increased with increasing organic matter content (Dickens and Hiltbold, 1967). Akkari et al. (1986) studied the degradation of MSMA in soils at concentrations up to 5 mg/kg. It was found that degradation followed first-order kinetics. The rate constant was temperature dependent only at soil water contents less than field capacity and the temperature effect was less under flooded conditions. The differences in degradation rate under aerobic conditions and 20 % water content were related to differences in the texture of the three soils. Half-lives for the clay and silty loam soils were 144 and 88 days respectively. Under anaerobic (flooded) soil conditions MSMA degradation occurs by reductive methylation to form arsenite and alkylarsine gases. The half-life values for the two soils indicate significantly faster degradation at 25 and 41 days respectively. The third soil, a sandy loam, produced the slowest degradation rate ($t_{1/2} = 178$ days) probably because of its low organic matter content which may have supported fewer microorganisms ((Tam et al., 1979).

The overall percentage of DMA (sodium salt) and MMA mineralized in a silty clay soil after 70 days ranged from 3 % to 87 % – values much higher than arsenic loss as volatile arsines (0.001–0.4 %). Arsenate was the main metabolite from the degradation of both sodium DMA and MMA. The amount of sodium DMA mineralized was linearly related to the concentration of sodium DMA in the soil, indicating that the rate is first order. Mineralization of sodium DMA increased with increasing soil moisture and temperature. It was concluded that the loss of arsenic from some soils to the atmosphere may not be a major pathway.

2.17 Processes That Changes Arsenic Species

Three major factors causes' arsenic – speciation changes during sampling and storage. They include:

1. Precipitation of HFOs and adsorption of arsenic species;
2. Photochemical reactions between Fe (III)/Fe (II) and As (III)/As (V); and,
3. Microbial activity.

In arsenic – contaminated waters, Iron is a common element present. Mobilization of arsenic in groundwater involves desorption of arsenic from ferric oxide precipitates of aquifer sediments and/or oxidation of arsenopyrites (FeAsS), so arsenic and Iron occur together in most groundwater (Smedley, Kinniburgh, 2002). Mine waters contain high concentrations of Fe and other metals besides arsenic. (Bender et al, 2005). Once groundwater is pumped to surface, the dissolved Fe (II) reacts with atmospheric oxygen, resulting in the precipitation of Fe as HFOs

and provides sorption sites for dissolved arsenic species. Since As (V) exists as anionic species, it is co-precipitated preferentially (Hug et al, 2001).

Co-precipitation of arsenic also occurs onto MnO_2 by a similar mechanism. In addition, MnO_2 could oxidize As (III) (B. Daus et al, 2000). Rapid oxidation of As (III) to As (V) in the presence of Fe (III) was observed in synthetic solutions preserved with HCl and light exposure (Emett and Khoe, 2001).

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In the presence of dissolved oxygen, the oxidation is further facilitated as:



2.18 General procedures for preservation of arsenic species

2.18.1 Filtration

Filtration through an uncreative 0.45 μm membrane filter is standard practice in trace-elemental analysis of water to differentiate particulate bound and dissolved fraction of an element. In arsenic-speciation analysis, filtration suppresses speciation changes partly through the removal of hydrated ferric oxides, and partly through the removal of microorganisms. Many bacteria have dimensions $< 0.45 \mu\text{m}$, hence filtration using 0.2 – 0.45 μm filters has been reported to improve species stability (Scudlark and Johnson, 1982).

However, the dissolved arsenic concentration determined after 0.2 μm filtration was significantly lower than that of 0.45 μm filtered samples due to the arsenic being sorbed onto colloidal particles sized in the range 0.2 – 45 μm (Kim et al, 2007). Filtration should be done on site and delays in filtration as small as a few hours could influence the aqueous versus particulate-bound arsenic proportion.

2.18.2 Acidification

Acidification of aqueous samples is an important practiced procedure aimed at suppressing the precipitation of Fe and Mn by increasing their solubility. Acidification also helps in reducing microbial activity. HCL is commonly used to preserve arsenic species (McCleskey et al, 2004). HNO_3 is an oxidizing agent and does not preserve arsenic species due to photo reduction of HNO_3 , which oxidizes As (III) to As (V). Some authors have used H_2SO_4 but it is not desirable because it is difficult to purify (V. Cheam, 1980). Further, it is not generally used for trace- metal preservation, because of the possibility of BaSO_4 precipitation. H_2PO_4 has been known to preserve arsenic speciation by complexing Fe and lowering pH (Daus et al, 2002).

Groundwater samples having Fe and Mn up to 15 mg/L and total arsenic concentration of 1 – 2 mg/L were successfully preserved up to 6 days using H_3PO_4 (0.01 mol/L). Increasing acid concentration to 10.00 mol/L sequestered up to 100 mg/L Fe and Mn for 3 months, but higher acid concentrations may damage ion – chromatographic columns (Daus al, 2006).

An important drawback of the addition of H_2SO_4 , and H_3PO_4 is that they may increase the solution Eh, particularly in oxic water samples ($\text{Eh} > 400 \text{ mV}$), resulting in the oxidation of As (III) (Daus et al, 2006)

2.18.3 Type of container

Generally, glass and various kinds of plastic (polyethylene, polypropylene, polycarbonate) containers are used for sample storage. The container material should not contribute towards adsorption loss and should not leach any constituent from it. Glass containers prewashed with HNO_3 are shown to leach out arsenic (Hunag 2004). The loss of arsenic in samples stored in plastic containers was attributed to the volatility and escape through the pores of plastics containers (Pandey et al, 2004). However, such an assumption was not supported by the literature. (Feldman, 1979; Cheam et al, 1980). It can be inferred that most of these losses could be due to photochemical reactions. Plastics containers are generally translucent, so some authors preferred opaque glass containers (Sandchez-Rodas et al, 2006). The results of a BCR study showed that both types of container are equally good for storage of samples for arsenic speciation analysis. Based on these observations, it appears that both glass and plastics container materials do not influence the As (III) As (V) interconversions, so both types of container can be used.

2.18.4 Refrigeration and Storage

Refrigeration of samples is recommended that in order to reduce biological processes that changes arsenic-species interconversion. Many authors recommend sample storage at 4°C for arsenic species stabilization (Rassler et al, 1998; Quevauviller, 1995; Aggette, Kriegman, 1978).

Biotic and abiotic oxidation rates of As (III) increase with temperature, so the stabilization period would be less if samples are stored at room temperature (Anderson, 1986; Gault et al, 2005). Precipitation of Fe and Mn was noticed in interstitial water samples of sediment due to freezing, which was not reversible upon gradual heating (Aggett and kriegman, 1987).

2.19 Analytical Technique for Elemental Analysis

Reliable and sensitive analytical methods have an important role in determining and evaluating the environmental impact of elemental pollution. It is realized that no single analytical technique can be used for all analysis. Several requirements for an analytical method to be acceptable are

1. Sensitivity, specificity and accuracy
2. Rapidity and ease of operation
3. The possibility of automation
4. Low cost of the equipment and reliability of result (Forstner and Wittman, 1983).

Instrumentation of analytical technique can be divided into nuclear and non-nuclear techniques. Activation analysis and X- ray fluorescence spectrometry are methods of analysis that are generally known for the nuclear analytical techniques. (Abdullah Salim, 2009)

The non nuclear techniques can be found in most analytical laboratory such as atomic absorption spectroscopy, inductively couple plasma mass spectrometry and chromatography techniques.

Speciation of arsenic in environmental samples usually involves several steps including derivitization, separation, and detection; hydride generation (HG), initially developed by Braman and Foreback in 1973, coupled to one of several separation and detection systems has been found to be one of the most common techniques used for speciation of arsenic. A number of detection systems have been used in arsenic analysis, of which the most popular and preferred one in terms of simplicity, sensitivity, precision, speed, and cost is AAS.

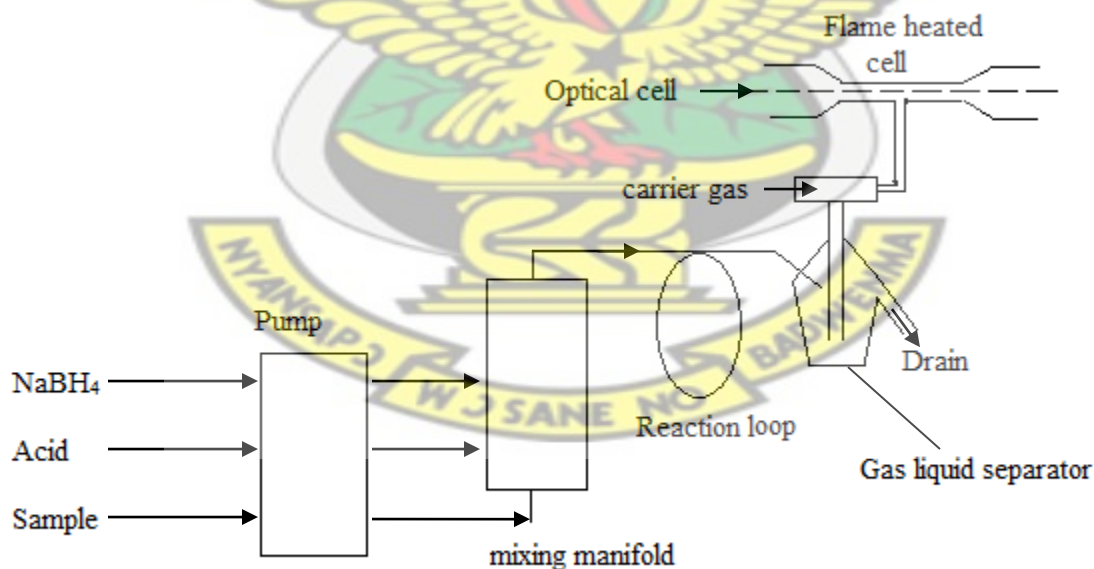


Figure 2.6: Schematic diagram of hydride generator

The HG-AAS technique is based on the production of volatile arsines (by the addition of sodium borohydrate/acid mixture) which are transported by an inert gas to the detection system. HG-AAS is probably the most widely used method to determine total arsenic in water (Rahman et al; 2001; Chekrabari et al, 2002) and various matrices (Wyatt et al, 1998; Das et al, 1995)

It is a single element specific technique with the advantage of being relatively inexpensive in terms of equipment. HG-AAS has been successfully used for the determination of arsenic in water, urine and plant samples (Guo et al 1997; Krachler et al, 2000; Sun et al, 2002).

Speciation of arsenic (As^{3+} , As^{5+}) was carried out in two stages, estimation of total arsenic followed by selective determination As (III). As (V) was determined by subtraction [(As (V) = As (T) – As (III)].

Different concentrations of acid/borohydride mixture have been used to determine total arsenic in water. However, 6M HCl has been shown to give the best peak for inorganic arsenic (As^{5+} and As^{3+}) in water. As (III) is almost generated exclusively in a weak acid/borohydride mixture. At 0.6M citric acid medium hydride of As (III) is exclusively generated.

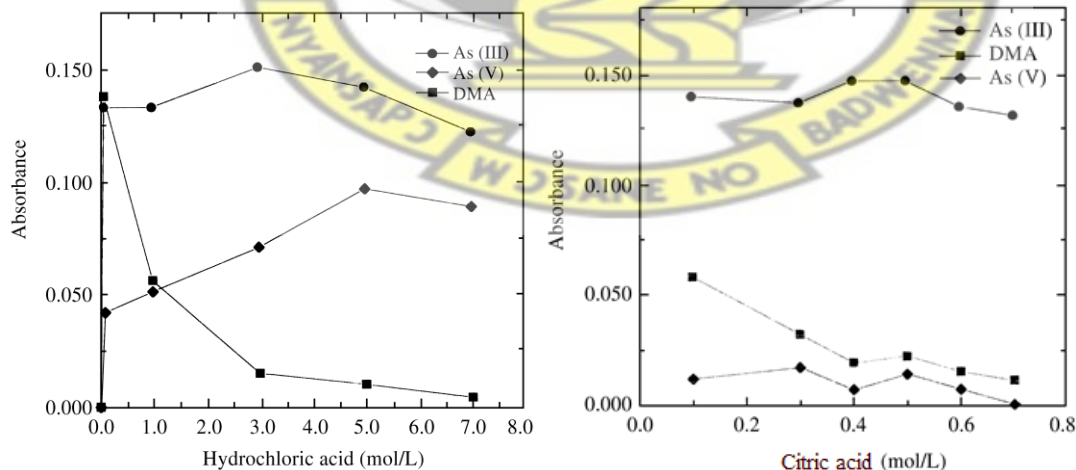


Figure 2.7: Effect of acid concentration on the response of As (III), As (V) and DMA (Sueli et al, 1998)

CHAPTER THREE

3 Methodology

This chapter describes the materials and the methodologies used for the determination of total arsenic and inorganic arsenic species (As^{+3} and As^{+5}) in water from boreholes, hand dug wells, and streams from Amansie West. The measured parameters, method of analysis and statistical analysis are also explained.

3.1 Water Characteristics

All water samples collected from boreholes were clear. The same characteristics cannot be said of in the well and stream water. Some of the water samples from the open shallow wells had fine grains settling after sometime. All the water samples from the streams were cloudy with fine grain particles.

All water samples collected were observed for living biota. Dark brown sediments were obtained from well (Nyankomase) and a stream from Kumpese. The dark brown colour might be associated with organic matter in the water.

3.2 Sampling Methodology

500 mL of water samples was taken from 15 boreholes at 15 different locations in Amansie West for the determination of total dissolved arsenic, As (III), and some heavy metals. Three water samples of 500 mL each were also taken from three hand-dug wells for the determination of total dissolved arsenic, As (III), and some heavy metals. Other 500 mL of water samples were taken from five streams for the determination of total dissolved arsenic, As (III), and some heavy metals. 500 mL water samples were collected from boreholes and hand-dug wells at Konongo as control sample. Konongo was chosen because; it has the same geological formations as that of the study area and artisanal mining activities is not as prevalent as compared to that in Amansie West. The water samples were collected using 250 ml opaque plastic containers. The containers were filled to the brim and acidified immediately with 4 % HCl. The sample identification was noted on the container using a permanent marker pen. The samples were transported in ice loaded container on the same day and stored in a refrigerator.

The samples were labelled BW, HW and SW corresponding to borehole water, hand-dug well water and stream water respectively. Refer to appendix A for sample locations in the study area.

3.3 Laboratory Apparatus

In the determination of trace metals, contamination and loss are of prime consideration. The typical potential contamination sources include improperly cleaned lab ware and dust from within the laboratory environment. All reusable apparatus (glass, Teflon, polyethylene) including sample containers were cleaned prior to use. Apparatus were washed with detergent, rinsed with

water and soaked in 4 % HCl for 24 hours. They were later rinsed with distilled water and oven dried.

3.4 Chemicals and Reagents

All chemicals used were of analytical grade. The chemicals used are

- Arsenic trioxide (As_2O_3) (Fluka, Switzerland),
- Sodium arsenate ($\text{AsHNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$) (Fluka, Switzerland),
- Sodium borohydride (BDH, England)
- Hydrogen peroxide (BDH, England)
- Sodium hydroxide (BDH, England)
- Potassium Iodide (BDH, England)
- Citric acid (BDH, England)
- Hydrochloric acid (BDH, England)

3.5 Study Area

This study was focused to three types of drinking water sources including boreholes, hand dug wells and streams which are in the Amansie West District. The sampling sites were based on the following:

1. Accessibility

2. Location to mining areas

The Amansie West District is one of the 112 districts in the country. It was carved out of the Amansie East District in Ashanti Region in 1989, as part of the Government's Decentralization policy. Manso Nkwanta is the district capital. The district is located in the south-western part of the Ashanti Region. It shares common boundary on its western part with the Atwima District.

On the northern part can be found the Bosomtwe District, while a regional boundary separates it from Central Region on its southern part. The entire district is rich in gold deposits; mining is therefore emerging as the most important economic activity in the district. Almost all the land area of the district has been acquired by mining companies for either prospecting or actual mining. The district is underlain by Lower Proterozoic Biriman and, to a lesser extent, Tarkwaian rocks. Throughout Ghana, Biriman rocks of West Africa are mainly volcanic greenstones with intervening sedimentary rocks and granitic intrusions, in places containing deposits composed of pyrite, arsenopyrite, minor chalcopyrite, sphalerite, galena, native gold and secondary hematite. (Amofah, Bonsu et al, 2001; Duker et al 2004)

There are clay deposits at Yawkrom, Abore and Essuowin, which have been identified as a potential resource for the District.

The major sources of water supply in the District are:

- River and Streams
- Hand dug wells
- Boreholes
- Pipe borne water

However, the pipe borne water in the District serves only two communities namely, Manso Atwere and Esaase. About 65 % of the communities in the District rely on streams and ponds as their major sources of water supply (Ghana districts site). Vegetation in the district is composed mainly of secondary forests, thicket, forb regrowth (i.e. stemmed leafy herbs, mostly the weeds, which appear on farms and have to be cut regularly) and swamp vegetation.

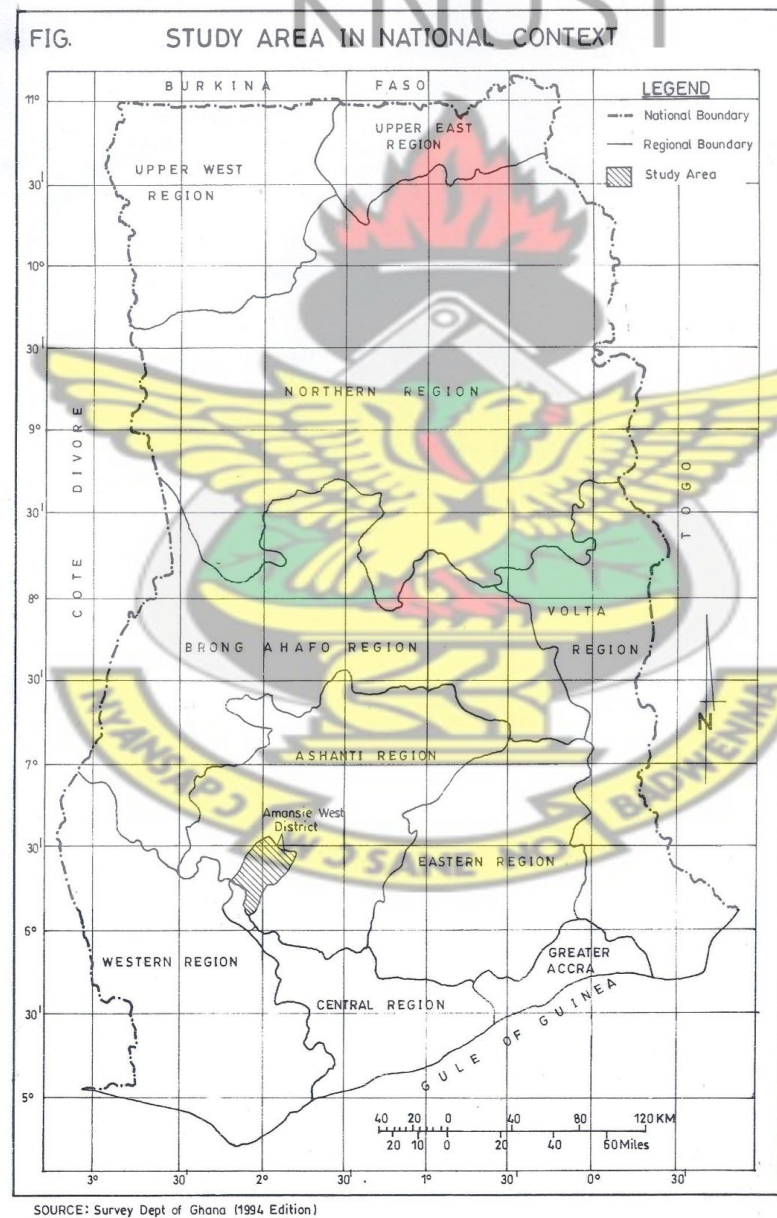


Figure 3.1: Map of Ghana showing Amansie West District

FIG.

MAP OF AMANSIE WEST DISTRICT SHOWING THE STUDY COMMUNITIES

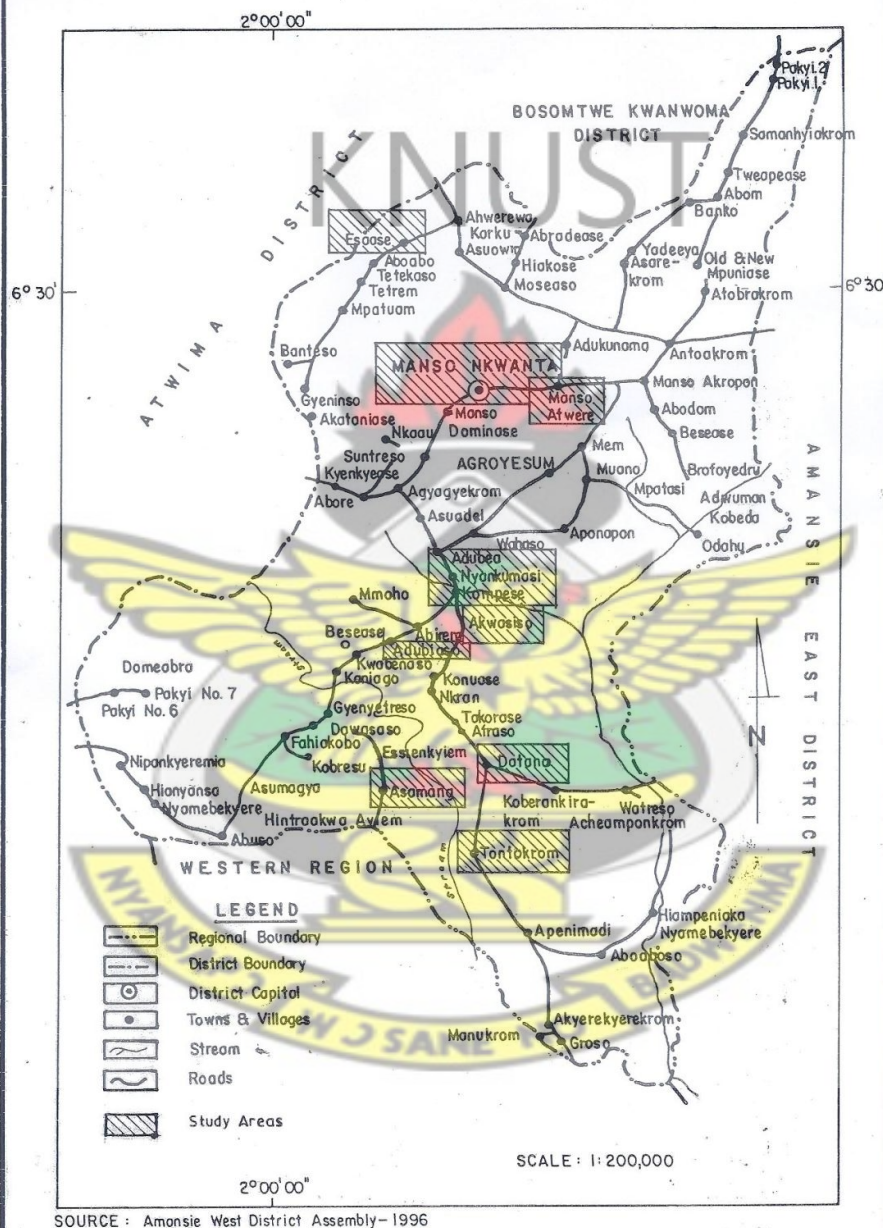


Figure 3.2: Map of Amansie West district showing towns and study areas

3.6 Determination of Physicochemical Parameters

The measurement of pH, dissolved oxygen (DO), and conductivity were done with a multiprobe meter which measures simultaneously pH, DO, and conductivity on site.

3.6.1 pH

Buffer solutions of pH 4, 7 and 10 were prepared for the calibration of the pH meter. The pH meter was calibrated by immersing the probe in 100 ml of the buffer solutions and then adjusting the pH meter to read the pH values. The pH of each water sample was determined by immersing the probe in a clean beaker containing water from either the borehole or hand-dug well or stream. For each sample, the pH reading was performed thrice and the mean value taken to represent the pH of the sample.

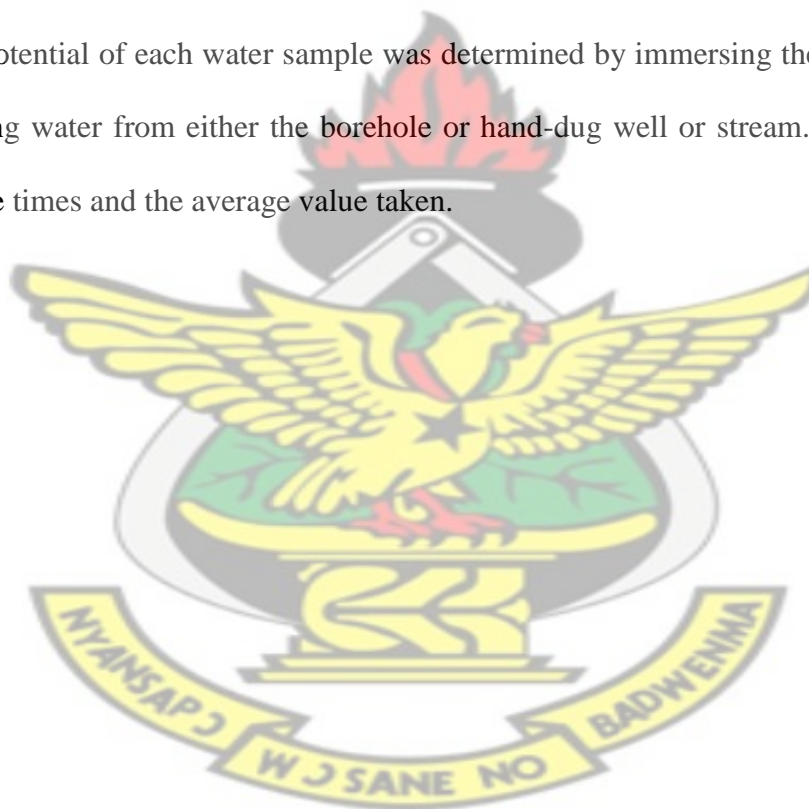
3.6.2 Conductivity

The conductivity meter was calibrated by immersing its electrode into 25 ml 0.01 N KCl solution. The meter was adjusted to read 1413 $\mu\text{S}/\text{cm}$. The electrode was removed and washed with distilled water (APHA, 1998). The conductivity of each water sample was determined by immersing the probe into a clean beaker containing the water sample. The values were made in triplicate and the average value taken to represent the conductivity of the sample.

3.6.3 Reduction Potential

Eutech make CyberScan pH 1100 Bench pH/mV RS232 meter, manufactured in Singapore, was used to measure the redox potential. In this instrument, measurement was made using the millivolt (mV) mode of a pH meter. Its mV range is $-1,850$ to $+1,850$ mV and resolution and accuracy is 0.1 mV and ± 0.2 mV. The potential of redox meter was adjusted to $+226$ mV at 25°C (Nordstrom 1977) and checked after every five observations, during the investigation period.

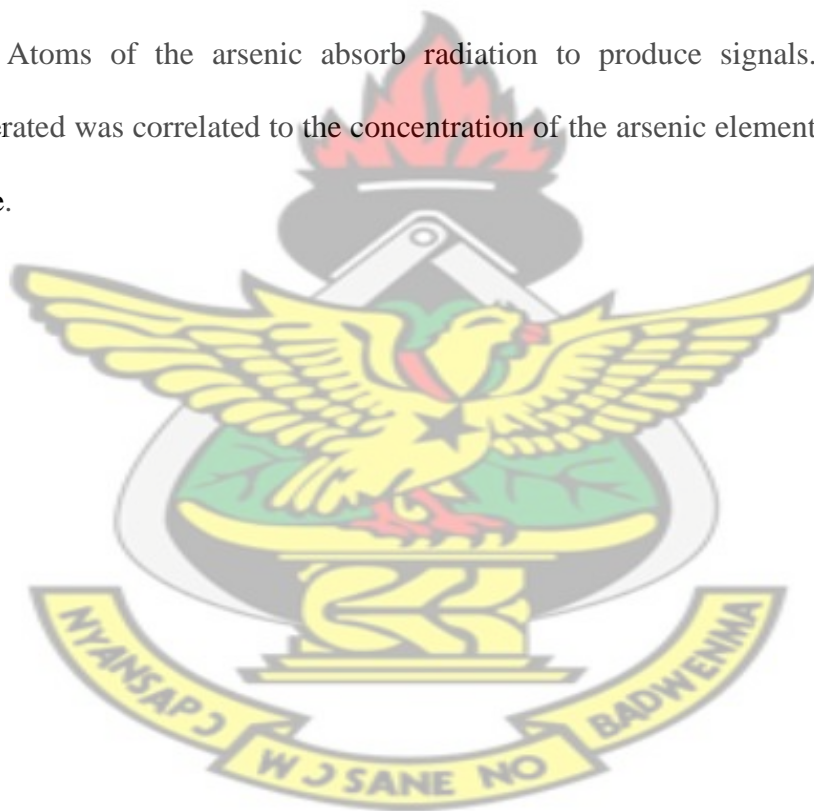
The reduction potential of each water sample was determined by immersing the probe in a clean beaker containing water from either the borehole or hand-dug well or stream. The values were determined three times and the average value taken.



3.7 Determination of total dissolved arsenic

The dissolved inorganic arsenic was measured with varian spectra AA 240 FS set to 193.7 nm and equipped with H₂ hollow cathode lamp as background corrector. Hydride generation was performed on a VGA-77 apparatus with a thermally heated cuvette and argon as the inert carrier gas. By the addition of 10 % KI (1 mL) to the sample, all arsenic species were reduced to As (V).

20 mL sample, 0.6 % NaBH₄, and 6M HCl is taken into the mixing chamber where reduction takes place. Hydrides of the arsenic are then aspirated to the burner head where atomization of arsenic occurs. Atoms of the arsenic absorb radiation to produce signals. The signals or absorbance generated was correlated to the concentration of the arsenic element within the linear calibration curve.



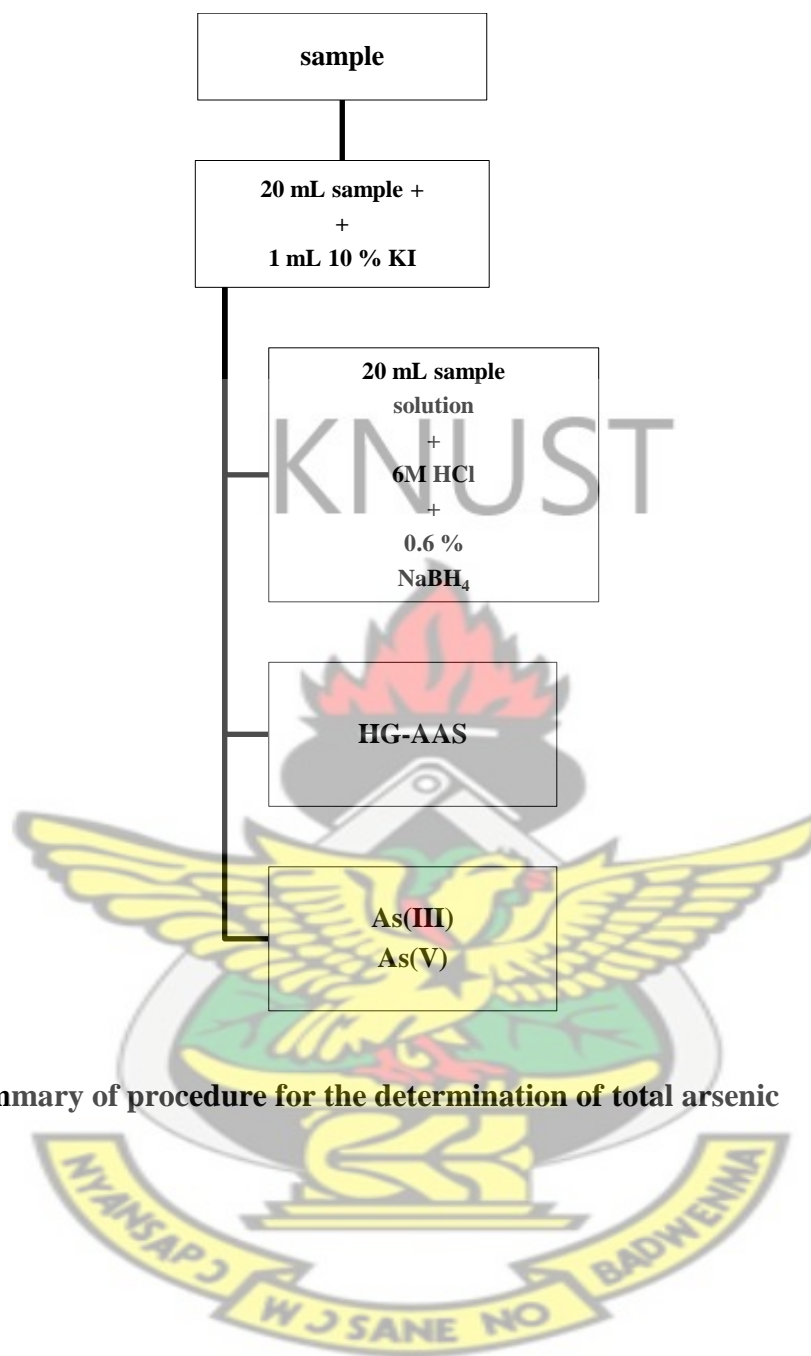


Figure 3.3: Summary of procedure for the determination of total arsenic

Recovery

The reliability of the instrument was obtained by performing the recovery of 0.02, 0.04, 0.06, and 0.10 mg/L standard arsenic solution. 20 ml of each standard was taken through the process described above. The concentration of arsenic were then measured

Table 3.1: Recovery of arsenic concentration

Reaction medium	Arsenic added (mg/L)	Arsenic recovered (mg/L)	% Recovery
Hydrochloric acid 6 mol/L	0.02	0.019	95
	0.04	0.038	95
	0.06	0.06	100
	0.10	0.097	97

Average % recovery = 97

3.9 Determination of Arsenic speciation

For arsenic in a weak organic acid, hydrides are generated almost exclusively for the As (III) species. As (V) species however, do not react or undergo any reaction.

The same setting of the varian spectra AA 240 FS was used but the 6M HCl was replaced with 0.4M citric acid. As (III) is exclusively reduced in the mixing chamber and its hydrides aspirated to the burner head for atomization. The absorbance produced is correlated to the concentration of the arsenic within the linear calibration curve.

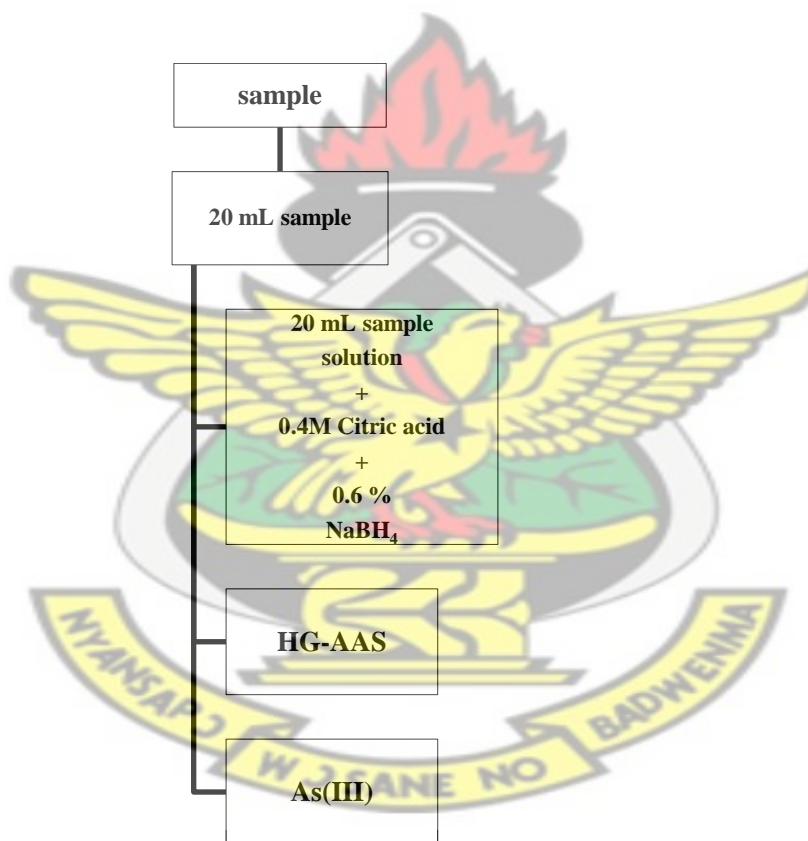


Figure 3.4: summary of procedure for the determination of As (III)

As (V) is obtained by subtracting As (III) from the total arsenic.

$$\text{As (V)} = \text{As (total)} - \text{As (III)}$$

Recovery

The reliability was obtained by performing the recovery of 0.02, 0.04, 0.06, and 0.10 mg/L standard arsenic solution. 20 mL of each standard was taken through the process described above. The concentration of As (III) were then measured

Table 3.2: Recovery of arsenic (III) concentration

Reaction medium	Arsenic added (mg/L)	Arsenic recovered (mg/L)	% Recovery
Citric acid 0.4 mol/L	0.02	0.018	90
	0.04	0.038	95
	0.06	0.057	95
	0.10	0.099	99

Average % recovery = 95

3.9 Determination of heavy metals

3.9.1 Determination of Zinc, Cadmium, Lead and Iron

Total metals were measured with varian spectra AA 240 FS equipped with multi element hollow cathode lamp and also H₂ hollow cathode lamp as background corrector. The wave length of Zn, Pb, Cd, and Fe were set at 213.9 nm, 217.0 nm, 228.8 nm and 248.3 nm respectively. The fuel gas used was acetylen-air mixture and argon as the inert carrier gas.

20 mL of the sample was aspirated onto the burner head where atoms of the elements to be determined are formed. By setting the wavelength of each element, their absorbance was measured.

Recovery

The reliability was obtained by performing the recovery of standard Zn, Cd, Pb, and Fe solution. 20 mL of each standard was taken through the process described above and their concentration was then measured.

Table 3.3: Recovery of Zinc, Lead, Cadmium and Iron

	Zn	Pb	Cd	Fe
Amount added/(mg/L)	0.5	5.0	0.5	5.0
Amount recovered/(mg/L)	0.48	4.99	0.49	4.99
% recovery	96	99	99	99

3.9.2 Determination of mercury

Mercury was determined using HG-AAS. Hydride generation was performed on a VGA-77 apparatus with a thermally heated cuvette and argon as the inert carrier gas. Detection was made with varian spectra AA 240 FS set to 253.7 nm and equipped with H₂ hollow cathode lamp as background corrector.

20 mL sample, 0.6 % NaBH₄ is taken into the mixing chamber where reduction takes place. Hydrides of the mercury are then aspirated to the burner head where atomization of mercury occurs. Atoms of the mercury absorb radiation to produce signals and the signals correlated to measure the concentration.

Recovery

The reliability of the instrument was obtained by performing the recovery of 0.02, 0.04, 0.06, and 0.10 mg/L standard mercury solution. 20 ml of each standard was taken through the process described above. The concentration of were then measured

Table 3.4: Recovery of mercury concentration

Mercury added (mg/L)	Mercury recovered (mg/L)	% Recovery
0.02	0.019	95
0.04	0.038	95
0.06	0.058	97

Average % recovery = 96

CHAPTER FOUR

4 Results and Discussion

This chapter explains and discusses the results of the experiments for the analysis of arsenic (As), cadmium (Cd), lead (Pb), iron (Fe), mercury (Hg), and zinc (Zn) including the analysis of inorganic As species (As^{+3} and As^{+5}) in the three drinking water systems of borehole, hand-dug well and stream.

The discussion includes an overview of the water quality based on five parameters which are temperature, pH, dissolved oxygen (DO), conductivity, and reduction potential (Eh). These physical parameters were applied for the correlation study to the concentration of total arsenic and arsenic species in the water samples.

4.1 Water Quality Parameters

The parameters of the water quality such as pH, DO, conductivity and reduction potential have a significant effect on the water quality. They also influence physiology of organisms in water and may contribute to metal forms in water (Forster and Wittmann, 1983). pH, DO, and conductivity were taken on site with a multimeter probe while the Eh was measured in the laboratory.

Table 4.1: Results obtained for pH, conductivity, dissolved oxygen and redox potential of water samples

Water Sample	pH	Conductivity $\mu\text{S/cm}$	DO mg/L	Eh mV
BW1	7.57	313.00	2.50	-8
BW2	7.69	312.50	2.50	-8
BW3	6.61	112.00	2.90	-20
BW4	7.60	234.20	3.30	23
BW5	7.10	360.00	4.10	-35
BW6	6.79	74.50	2.10	21
BW7	6.94	143.00	2.10	13
BW8	6.76	309.40	4.50	-10
BW9	7.04	212.00	2.90	-36
BW10	7.78	143.30	3.70	16
BW11	7.10	112.80	2.90	13
BW12	7.76	202.40	2.50	7
BW13	7.48	91.00	1.70	-6
BW14	6.57	124.10	3.70	1
BW15	7.06	263.40	1.70	-36
HW1	6.10	108.90	1.30	-7
HW2	7.62	210.70	1.70	15
HW3	6.88	82.03	2.90	-15
SW1	7.49	292.20	3.00	-7
SW2	7.34	152.60	1.70	14
SW3	8.27	563.40	1.30	0
SW4	7.10	188.00	0.29	-17
SW5	7.48	241.50	1.22	-37

BW = Borehole, HW = Hand-dug well, SW = stream

4.1.1. pH

pH is a measure of the acidity or alkalinity of a solution and it plays a critical role in the chemistry of freshwater systems. Ghana Water Company (GWC) and Ghana Standards Board (GSB) have set the drinking water guideline for pH at 6.5 – 8.5.

The pH values recorded from the borehole water samples ranges from 6.57 – 7.78 with an average value of 7.19. The pH values measured from hand-dug wells ranges from 6.10 – 7.62 with a mean value of 6.87. The pH measured from the stream ranges from 6.48 - 8.27 with an average value of 7.48.

As shown in table 4.8, the pH of both ground water (borehole and well) and surface water (streams) were from near neutral and to basic conditions and their mean values is within allowable limits (6.5 – 8.5) by GWC and GSB for drinking water. In terms of pH level, stream from Nkensere (8.27) may not be suitable for the support of aquatic life. The high pH level at Nkensere was a result of direct discharge from several artisanal mining activities in the area. Also, in terms of pH water from boreholes and wells are suitable for drinking and cooking purposes.

4.1.2 Dissolved Oxygen (DO)

The oxygen content of water is an important indicator of the level of pollution of a water body. Oxygen is a major requirement for the metabolic activities of aerobic organisms. DO is dependent on temperature, amount of rainfall, pollution and salinity (US EPA, 2010).

In a water body, the warmer the water the less DO can be measured in it. WHO criteria for human consumption and aquatic life require that the DO range from 3 – 7 mg/L (WHO, 2011).

The average level of DO measured from the boreholes is 2.87 mg/L and ranged from 1.70 – 4.50 mg/L. The mean value falls out of the range set by WHO for drinking water. The mean DO value from the streams was the lowest (1.50 mg/L) indicating some amount of pollution in the stream water. This is due to the effluent from activities of small scale mining activities into the streams. In general, the DO values are small which is indicative of slight reducing conditions in the water samples.

4.1.3 Conductivity

It is a measure of the ability of water to allow current to pass through (US EPA, 2012). Conductivity of water is affected by dissolved solids in their ionic state (Na^+ , Fe^{3+} , As^{5+} , Cl^- , NO_3^- , PO_4^{3-} , etc) (US EPA, 2012). The greater the concentration of the dissolved ions, the higher the measured conductivity.

The conductivity measured from the borehole ranges from 74.50 – 313.50 $\mu\text{S}/\text{cm}$ has an average value of 200.51 $\mu\text{S}/\text{cm}$ while that obtained from the hand-dug well ranges from 82.03 – 210.70 $\mu\text{S}/\text{cm}$ has an average value of 133.88 $\mu\text{S}/\text{cm}$. The conductivity measured from the streams ranges from 152.60-563.4 $\mu\text{S}/\text{cm}$ with an average of 287.54 $\mu\text{S}/\text{cm}$.

4.2 Concentration Arsenic

74 % of surface and ground water samples had arsenic concentrations above 10 µg/L.

Concentrations of arsenic ranged from 0.18-39.4 µg/L in boreholes, hand-dug well and streams.

Table 4.2: Results obtained for pH, conductivity, dissolved oxygen, redox potential and total dissolved arsenic concentration.

Water Sample	pH	Conductivity µS/cm	DO mg/L	Eh mV	As Total µg/L
BW1	7.57	313.00	2.50	-8	33.30
BW2	7.69	312.50	2.50	-8	33.21
BW3	6.61	112.00	2.90	-20	20.77
BW4	7.60	234.20	3.30	23	0.24
BW5	7.10	360.00	4.10	-35	37.22
BW6	6.79	74.50	2.10	21	0.77
BW7	6.94	143.00	2.10	13	34.35
BW8	6.76	309.40	4.50	-10	6.22
BW9	7.04	212.00	2.90	-36	9.86
BW10	7.78	143.30	3.70	16	0.96
BW11	7.10	112.80	2.90	13	21.63
BW12	7.76	202.40	2.50	7	23.83
BW13	7.48	91.00	1.70	-6	8.23
BW14	6.57	124.10	3.70	1	18.37
BW15	7.06	263.40	1.70	-36	15.31
HW1	6.10	108.90	1.30	-7	13.49
HW2	7.62	210.70	1.70	15	20.19
HW3	6.88	82.03	2.90	-15	26.41
SW1	7.49	292.20	3.00	-7	35.31
SW2	7.34	152.60	1.70	14	28.23
SW3	8.27	563.40	1.30	0	37.22
SW4	7.10	188.00	0.29	-17	24.11
SW5	7.48	241.50	1.22	-37	39.43

BW = Borehole, HW = Hand-dug well, SW = stream

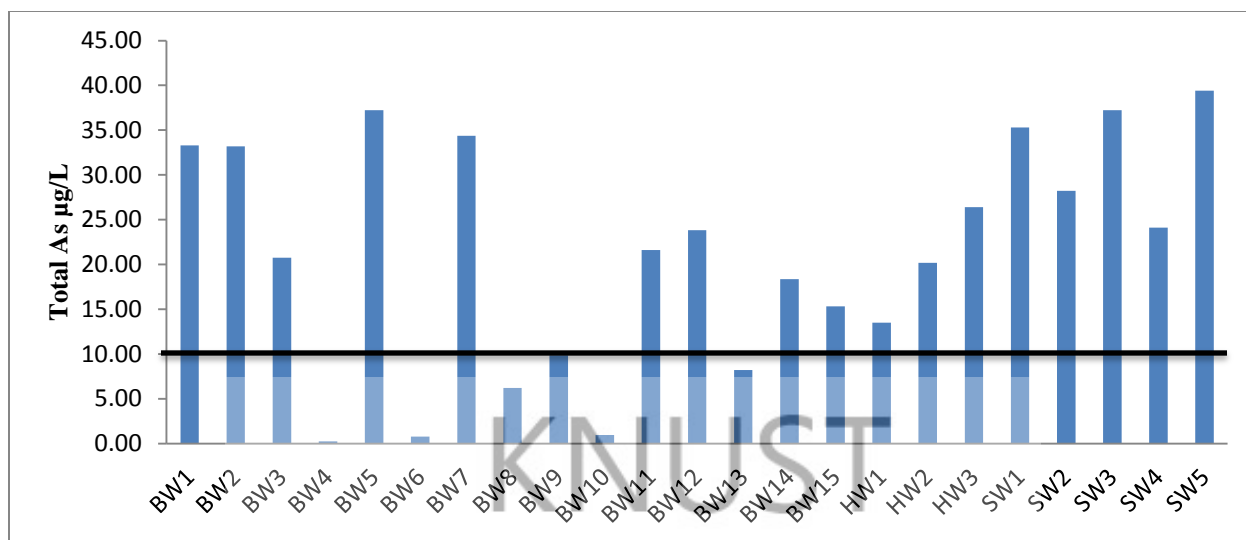


Figure 4.2: A graph of arsenic concentrations from boreholes, hand-dug wells and streams

Boreholes had arsenic concentrations ranging from below detection limit of 0.24 – 37.22 µg/L with an average value of 17.62 µg/L. In the 15 boreholes sampled, arsenic concentration in 6 boreholes (representing 40%) had arsenic concentration below WHO, and GWC/GSB maximum contaminant level (MCL) guideline for drinking water of 10 µg/L.

Hand-dug wells had relatively higher arsenic concentration ranging from 13.49 – 26.41 µg/L with a mean concentration of 20.03 µg/L. All the well water sampled had arsenic concentration above the GWC/GSB maximum contaminant level (MCL) guideline for drinking water.

Arsenic concentration measured from the streams ranged from 24.11 – 39.43 µg/L with an average concentration of 32.86 µg/L. The values are far above the WHO, and GWC/GSB maximum contaminant level (MCL) guideline for drinking water.

The highest arsenic concentration (39.43 µg/L) was measured from a stream at Yawkrom while the lowest arsenic concentration (0.24 µg/L) was measured from a borehole at Dadieso.

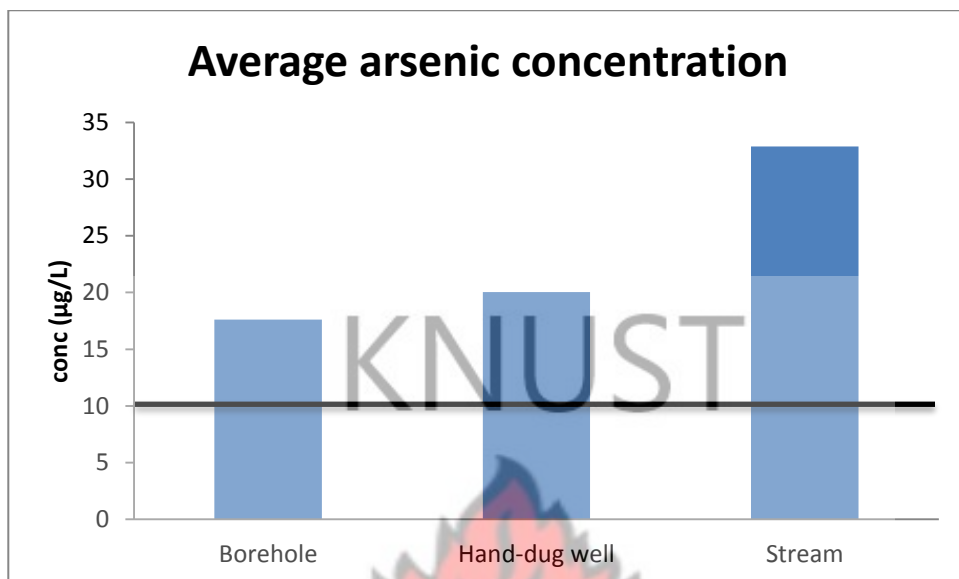


Figure 4.3: A graph showing average arsenic concentration from borehole, hand-dug well and stream

Smedley (1999) determined dissolved arsenic concentration in ground water samples in Bolgatanga and Obuasi. These towns are gold mining towns with sulphide minerals such as arsenopyrite and pyrite present in the Birimian basement rocks of both areas which is similar to that found in Amansie West district. The concentration of dissolved arsenic was relatively low with ranges from $< 1 - 64 \mu\text{g/L}$ (mean = $18.41 \mu\text{g/L}$) and $< 1 - 141 \mu\text{g/L}$ (mean = $31.20 \mu\text{g/L}$) in Bolgatanga and Obuasi respectively. High arsenic concentrations were found in water samples with reducing conditions and at high pH.

4.2.1 Relationship between Arsenic Concentration and Hydrogeochemical Parameters

In order to understand arsenic mobilization in ground and surface water, it is important to look into the relationship between the various parameters that influence arsenic concentration.

Correlation between arsenic levels and pH is positive in boreholes, hand-dug wells, and streams with the coefficient of correlation values of (0.0272, 0.531, and 0.657) respectively. The strong correlation between arsenic levels and pH in hand-dug wells and streams show that greater percentage of water samples with high arsenic concentration also has high pH values. 75 % of water samples with arsenic concentration greater than 10 $\mu\text{g/L}$ had pH values greater than 7 in hand-dug wells and streams. At high pH (6 -9) desorption of arsenic from clay minerals, iron and manganese oxides is promoted (Manning and Goldberg, 1997) which can result in excess concentration of arsenic to be released into water bodies.

There was a slight negative correlation between arsenic concentration and reduction potential. The coefficient of correlation obtained were -0.31, -0.23 and -0.35 for boreholes, hand-dug wells and streams respectively. Stream waters had the lowest magnitude of redox potential, which can be a reason for the high arsenic level in the stream, followed by water from boreholes and hand-dug wells. The lower redox potential means reduced conditions which is also the reason for the high arsenic content. In an oxidizing environment, solid iron and manganese oxides serve as sorption sites and eventually reduce the concentration of arsenic in natural water (Hundal et al, 2007). Under reduced environments, solid Fe (III) and Mn (IV) oxides also reduce to soluble Fe (II) and Mn (II) and thus release arsenic from the sorption sites and thereby enhances its concentration in water.

There is a strong positive correlation between arsenic levels and conductivity in the boreholes, wells and streams with coefficient of correlation as 0.416, 0.735, and 0.573 respectively. This result is indicative of high total dissolved ions found in the water.

4.2.2 Arsenic Speciation

Table 4.5: Results obtained for the concentration of dissolved arsenic (III), arsenic (V), and total arsenic.

Water Sample	As (III) mg/L	As (V) mg/L	As Total mg/L	As (III) as % of As total
BW1	0.012	0.021	0.033	36.364
BW2	0.012	0.020	0.033	36.364
BW3	0.012	0.009	0.021	57.143
BW4	0.007	0.004	0.010	63.636
BW5	0.017	0.020	0.037	45.946
BW6	0.000	0.001	0.001	0.000
BW7	0.023	0.011	0.034	67.647
BW8	0.005	0.002	0.006	83.333
BW9	0.007	0.003	0.010	70.000
BW10	0.001	0.000	0.001	100.000
BW11	0.014	0.007	0.022	63.636
BW12	0.021	0.002	0.024	87.500
BW13	0.006	0.002	0.008	75.000
BW14	0.013	0.005	0.018	72.222
BW15	0.012	0.003	0.015	80.000
HW1	0.012	0.002	0.013	92.308
HW2	0.015	0.005	0.020	75.000
HW3	0.009	0.017	0.026	34.615
SW1	0.031	0.004	0.035	91.429
SW2	0.018	0.011	0.028	64.286
SW3	0.018	0.019	0.037	48.649
SW4	0.014	0.011	0.024	58.333
SW5	0.026	0.014	0.039	66.667

Arsenic (III) concentration ranges from 0 – 0.023 mg/L in boreholes with an average concentration of 0.011 mg/L (10.89 µg/L). The average percentage of As (III) in total arsenic in borehole is 62 %. As (III) was dominant in 11 boreholes out of the 15 borehole water samples. Concentration of As (III) in the hand dug wells ranged from 0.009 – 0.015 mg/L with a mean concentration of 0.012 mg/L (12.73 µg/L). The average percentage of As (III) in total arsenic in wells was 67 %. Arsenic (III) in streams ranged from 0.014 – 0.032 mg/L with a mean concentration of 0.022 mg/L (22.53 µg/L). All stream samples showed dominant arsenic (III) concentration. Percentage of As (III) in total arsenic in stream water samples ranges from 48.6 % to 91.4 % of As (III) in arsenic total with an average of 65 %. It can be seen that greater percentage of arsenic total occurs in the form of As (III). This is due to the fact that under moderately reduced conditions trivalent arsenite (As^{3+}) is stable and its adsorption is lower compared to pentavalent arsenate (As^{5+}). The high percentage of As (III) as a percentage of total arsenic in the drinking water is a health concern because As (III) is the more toxic form of arsenic compared to arsenic (V). Average percentage of arsenic (V) in total arsenic obtained in boreholes, hand-dug wells, and streams was 38.2 %, 35.2 %, and 36.7 % respectively.

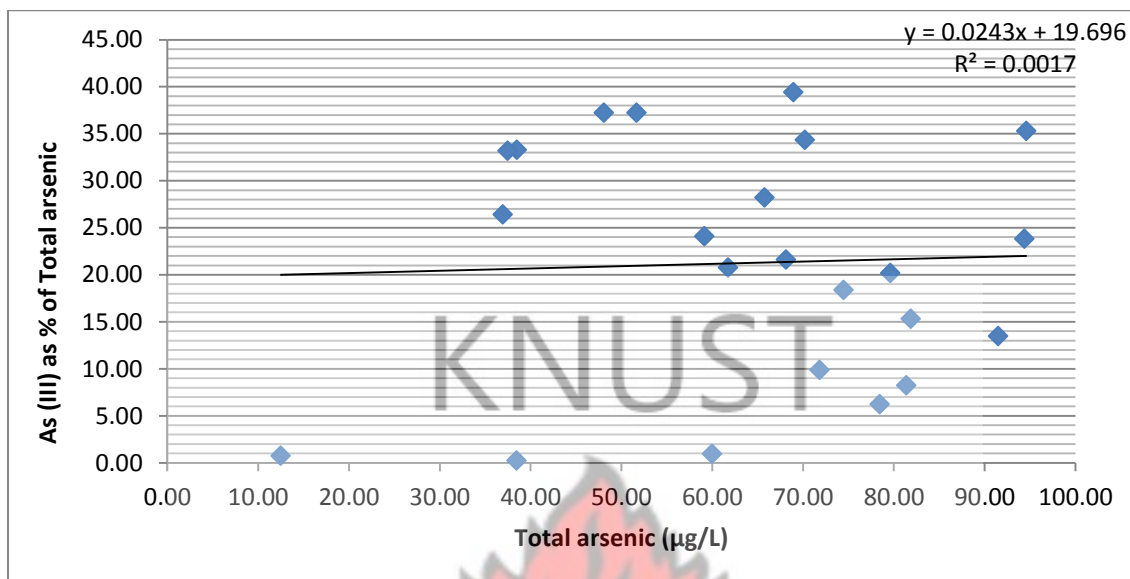


Figure 4.4 Correlation of As (III) concentration with As total

The comparison between total arsenic and arsenic speciation showed no correlation. The coefficient of correlation was 0.04. This implies that arsenic speciation could not be predicted by total arsenic concentration. In other words, it was impossible to derive any information on speciation using arsenic test methods that measured total arsenic only. An additional technique that separates arsenic (III) from arsenic (V) is necessary to determine speciation.

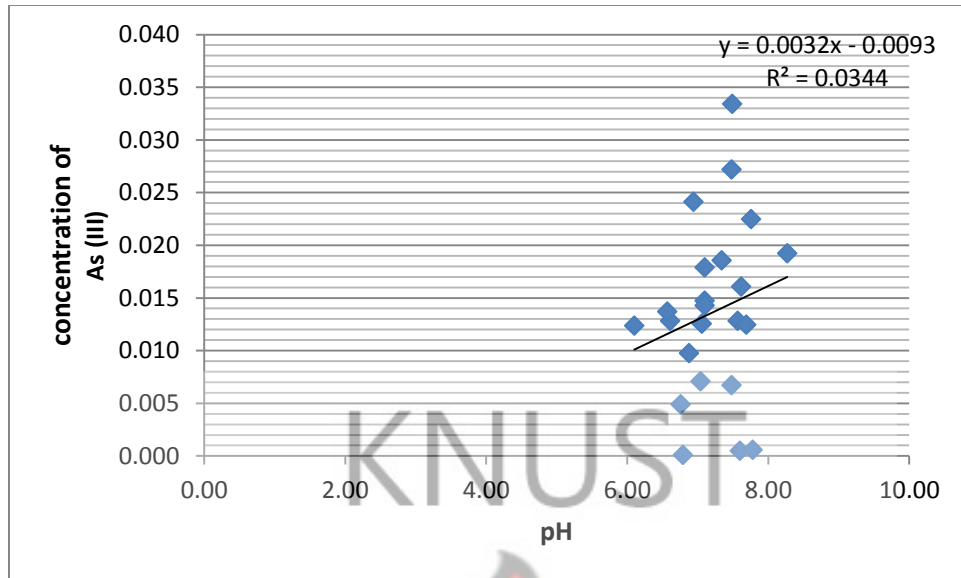
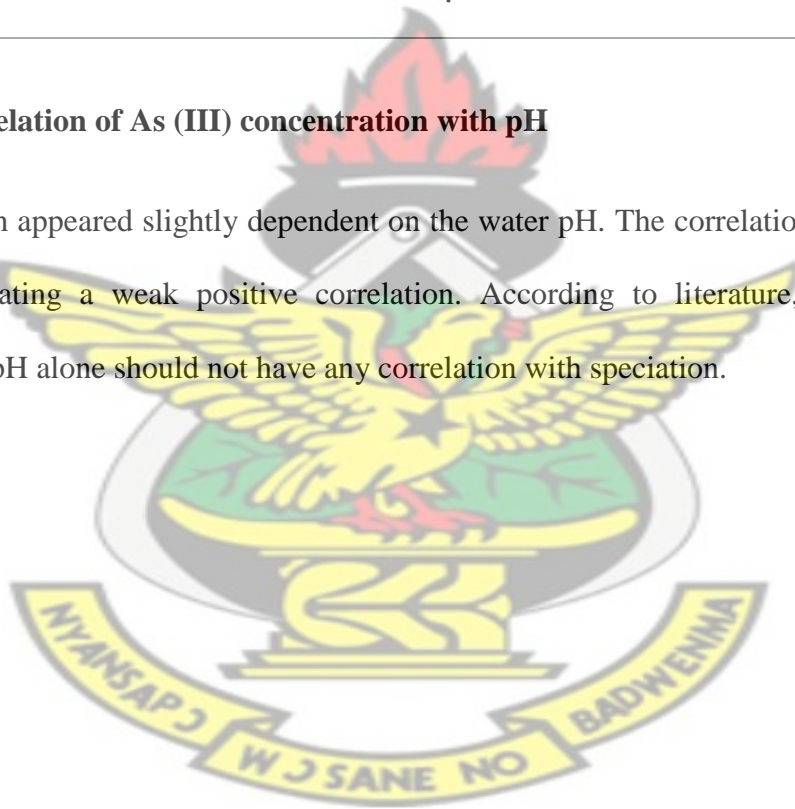


Figure 4.5: Correlation of As (III) concentration with pH

Arsenic speciation appeared slightly dependent on the water pH. The correlation coefficient was only 0.102 indicating a weak positive correlation. According to literature, ((Manning and Goldberg, 1997) pH alone should not have any correlation with speciation.



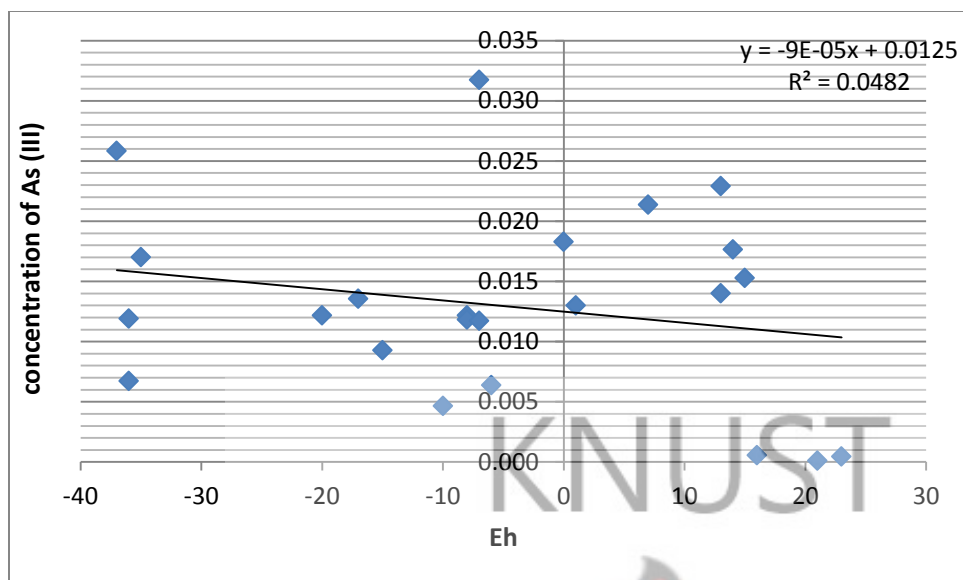


Figure 4.6: Correlation of As (III) concentration with reduction potential

The observed trend of arsenic (III) concentration decreasing with increasing Eh matched with theoretical prediction (Ngai, 2001). Correlation coefficient between As (III) concentration and reduction potential in boreholes hand-dug wells and stream water are -0.3111, -0.2367, -0.3576 respectively. The lower the Eh, the more reduced the water was. Thus, more arsenic would appear in its reduced form as As (III) than the in its oxidized form of As (V).

4.3 Determination of other heavy metals

Table 4.4: Results obtained for the concentration of Zinc, Lead, Cadmium, Mercury, Iron, and Arsenic.

	Conc. of Zn mg/L	Conc. of Pb mg/L	Conc. of Cd mg/L	Conc. of Hg mg/L	Conc. of Fe mg/L	As Total mg/L
BW1	bdl	bdl	Bdl	bdl	0.221	0.032
BW2	bdl	bdl	Bdl	bdl	0.224	0.032
BW3	bdl	bdl	0.064	bdl	0.613	0.020
BW4	bdl	bdl	Bdl	bdl	0.320	0.001
BW5	0.036	bdl	Bdl	bdl	0.255	0.035
BW6	bdl	bdl	Bdl	bdl	0.296	0.001
BW7	bdl	bdl	Bdl	bdl	0.281	0.033
BW8	bdl	bdl	Bdl	bdl	0.357	0.006
BW9	bdl	bdl	Bdl	bdl	0.312	0.009
BW10	bdl	bdl	Bdl	bdl	0.714	0.001
BW11	bdl	bdl	Bdl	bdl	0.140	0.021
BW12	bdl	bdl	Bdl	bdl	0.291	0.023
BW13	bdl	bdl	Bdl	bdl	0.329	0.008
BW14	bdl	bdl	Bdl	bdl	0.328	0.017
BW15	bdl	0.088	Bdl	bdl	0.232	0.015
HW1	bdl	bdl	Bdl	bdl	0.450	0.013
HW2	0.016	bdl	Bdl	bdl	0.151	0.019
HW3	bdl	bdl	Bdl	bdl	0.436	0.025
SW1	bdl	bdl	Bdl	bdl	0.201	0.034
SW2	bdl	bdl	Bdl	bdl	0.521	0.027
SW3	bdl	bdl	Bdl	bdl	0.218	0.035
SW4	0.052	bdl	Bdl	bdl	0.331	0.023
SW5	0.04	bdl	0.028	0.012	0.682	0.037

BW = Borehole, HW = Hand-dug well, SW = stream, bdl = below detection limit

Table 4.5: Guidelines for drinking water quality of Zn, Cd, Pb, Hg, and Fe

	WHO (mg/L)	GWC/GSB (mg/L)
Zinc	3.00	3.00
Lead	0.01	0.01
Cadmium	0.003	0.003
Mercury	0.001	0.001
Iron	0.30	0.30

4.3.1 Zinc

AAS analysis for dissolved metals revealed that Zn was found in the water samples at four sampled sites. One from a borehole at Bonsaaso (0.036 mg/L), another from a well at Kumpese (0.016 mg/L), and two from streams at Tontokrom and Yawkrom with values 0.052 mg/L and 0.04 mg/L respectively. These values are far below the WHO and GWC/GSB acceptable limit (3.0 mg/L) for drinking water. The low level of zinc in the water is probably because of the reduced conditions of the water. This is because the concentration of dissolved zinc in water increases with increasing acidity of the water (Kusima and Kusima, 2011). Zinc can also enter the environment as a result of natural processes such as dissolution of zinc pipes.

4.3.2 Lead

Lead was detected in only one water sample which was measured in a borehole at Yawkrom (0.088 mg/L). The concentration was higher than the WHO acceptable limit for drinking water (0.01 mg/L). Lead occurs naturally in small amounts in the earth's crust in ores such as sulphide galena (PbS), anglesite (PbSO₄), sulfenite (PbMoO₄). Anthropogenic sources of lead into the environment which include gasoline additives, batteries, etc. are non-existent in the study area. Like zinc, lead binds with the soil particles and does not migrate to ground water unless the water is acidic. This probably explains the low toxicity levels of lead in the ground and surface water since the pH of samples analysed were relatively reduced.

4.3.3 Cadmium

Cadmium was found in two of the water samples, one from a borehole at Assamang (0.016 mg/L) and at a stream at Yawkrom (0.028 mg/L). The WHO and GWC/GSB MCL for drinking water is 0.003 mg/L. These values obtained are far above the maximum contaminant level for drinking water. The amount found in the stream can probably be due to fertilizer application to crops that has leached into the stream. The amount of cadmium detected occurs naturally in the earth and is found in ores of zinc and lead. As a result, they can enter the environment through weathering. Cadmium is used as pigments, coating, electronic compounds and present as impurity in phosphate fertilizers, detergents and refined petroleum. In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer.

4.3.4 Mercury

Mercury was detected in only one water sampled. It was detected in a stream at Yawkrom (0.012 mg/L). This value is above the WHO and GWC/GSB MCL for drinking (0.001mg/L). Mercury rarely exist in nature although it can be found in the form of cinnabar (HgS) near recent volcanic rocks (Kortatsi, 2004) which was absent in the geology of the study area. Mercury amalgam technique is used by artisanal miners during gold processing, thus, its use pollute the water bodies. The mercury detected in the stream is due to activities of artisanal miners. Even though the concentration is quite low, it is still of health concern because of bioconcentration in fish and other aquatic biota which the locals depend on could have a long term effect.

4.3.5 Iron

Iron was detected in all the water samples measured. The WHO and GWC/GSB maximum contaminant level for drinking water is 0.30 mg/L. Excess levels of iron was measured in 52 % of the ground and surface water sampled. 47 % of borehole water samples had level above WHO MCL. The concentration measured in bore holes ranges from 0.141 – 0.714 mg/L with an average value of 0.328 mg/L. Concentration of iron in hand-dug well ranges from 0.151 – 0.450 mg/L with a mean value of 0.346 mg/L. 67 % of the water sampled from the wells had iron concentration above MCL with concentration ranging from 0.201 – 1.082 mg/L with an average concentration of 0.471 mg/L.

The presence of iron in the ground and surface water is probably due to the dissolution of iron bearing rocks (FeAsS) which is present the study area.

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CHAPTER FIVE

5 Summary, Conclusions and Recommendations

5.1 Summary of Important Result

On the average, 61 %, 69 % and 68 % of the total arsenic was in the more toxic arsenic (III) form in boreholes, hand-dug wells, and streams respectively. The removal of arsenic is therefore highly necessary. There was a strong correlation between reduction potential and arsenic speciation. The lower the reduction potential, the more arsenic are present in the more toxic arsenic (III) form. There was no clear correlation between the total arsenic and pH on arsenic speciation. The practical implication of this finding is that one should be able to use the relatively undemanding redox measurement as an acceptable surrogate for determining the fraction of the arsenic present as As (III), i.e. arsenic speciation. Redox potential however, was a relatively poor predictor of total arsenic levels. However, reduction potential is a better predictor for arsenic species.

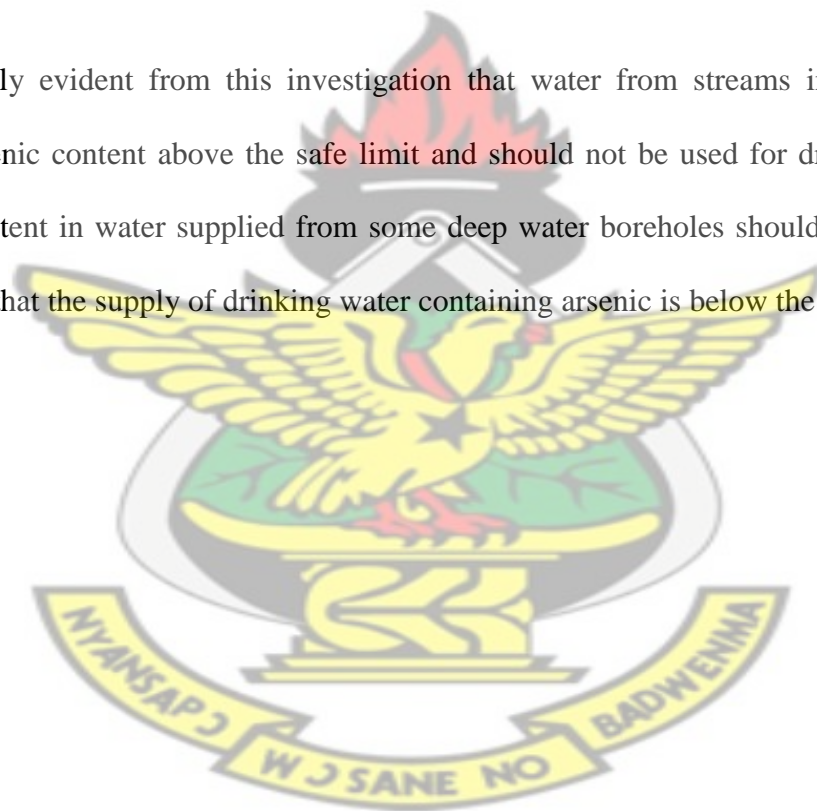
91 % of the water samples analysed showed the content of heavy metals (Zn, Pb, Cd and Hg) below detection limit. The 9 % of the heavy metals that was detected were lower than the WHO acceptable values for drinking water quality. The low concentration measured was probably the result of the reduced conditions (i.e. $\text{pH} < 7$) of the water samples, since concentration of most dissolved metals in water decreases with increasing alkalinity. On the contrary, the high concentration of iron recorded was high. This might be due to the dissolution of the arsenopyrite (FeAsS) which is present in the study area.

5.2 Conclusion

Selective reduction at different acid media allowed the speciation study of arsenic in natural waters. The procedure proved to be accurate, precise and little time consuming as just a very simple sample treatment is required.

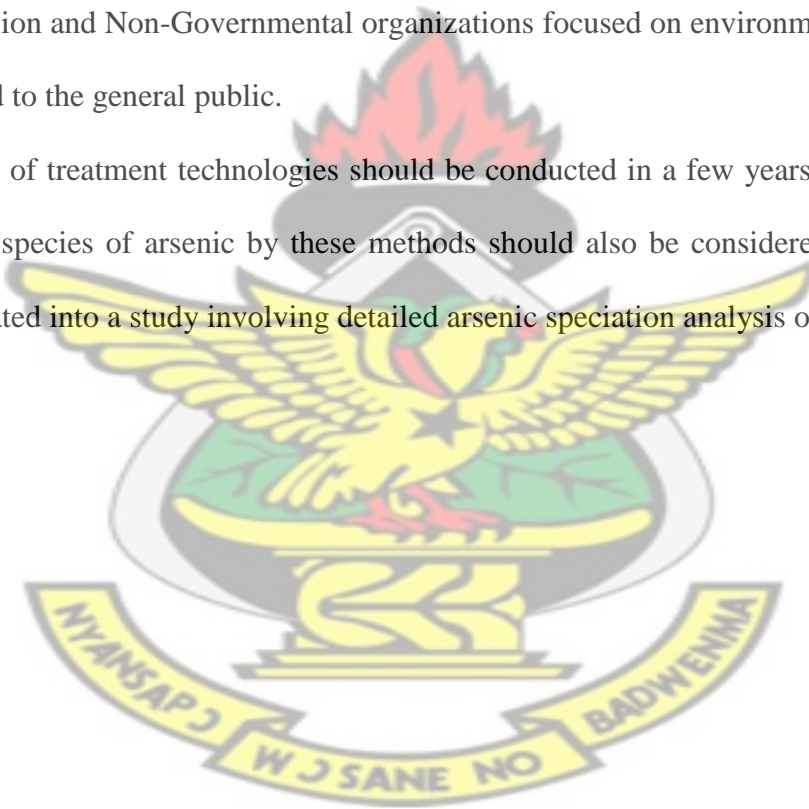
Results of water chemistry show differentials in concentration of elements in both ground and surface water. The levels of trace elements such as iron, cadmium, arsenic, mercury and lead were found to exceed WHO and GSB/GWC guidelines for drinking water.

It is conclusively evident from this investigation that water from streams in Amansie West district had arsenic content above the safe limit and should not be used for drinking purposes. The arsenic content in water supplied from some deep water boreholes should be monitored in order to ensure that the supply of drinking water containing arsenic is below the safe limits.



5.3 Recommendation

1. More boreholes, wells and streams should be speciation tested to explore undiscovered correlations and trends.
2. Speciation test method used in this study should be checked with an alternative methods (e.g. ICP-MS, NAA, on site test kits) in order to confirm the validity of the results.
3. Findings of this research should be made available to the Environmental Protection Agency, Food and Drugs Board, Community water and sanitation, Ghana Water Commission and Non-Governmental organizations focused on environmental issues to be translated to the general public.
4. A review of treatment technologies should be conducted in a few years. The removal of different species of arsenic by these methods should also be considered. This could be incorporated into a study involving detailed arsenic speciation analysis of groundwater.



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APPENDICES

Appendix A: Water sample locations in Amansie West

BW = Borehole, HW = Hand-dug well, SW = stream

Sample location	Type of water source
Akwasiso	BW1
Akwasiso	BW2
Assamang	BW3
Ayiribikrom	BW4
Bonsaso	BW5
Dadieso	BW6
Dataano	BW7
Dome	BW8
Koninase	BW9
Kumpese	BW10
Nkensere	BW11
Nkonten	BW12
Nyankomase	BW13
Tontokrom	BW14
Yawkrom	BW15
Dataano	HW1
Kumpese	HW2
Nyankomase	HW3
Bonsaso	SW1
Kumpese	SW2
Nkensere	SW3
Tontokrom	SW4
Yawkrom	SW5

Appendix B - Physical Properties of Arsenic Compounds

Molecular Formula & Substance Name	CAS Registry Number	Synonyms	Molecular Weight	Boiling Point °C	Melting Point °C	Density	Water Solubility
As ₂ O ₅ arsenic pentoxide	1303-28-2	arsenic oxide; arsenic anhydride; arsenic acid	229.84	---	800	4.32	1.5 Kg (16 °C)
H ₃ AsO ₄ ·1/2H ₂ O arsenic acid (hemihydrate)	7774-41-6	orthoarsenic acid, hemihydrate	150.96	160	35.5	2.0 - 2.5	170g (20 °C)
Ca ₃ (AsO ₄) ₂ calcium arsenate	7778-44-1	tricalcium arsenate; pencal; calcium orthoarsenate	398	---	---	---	0.13g (25 °C)
PbHAsO ₄ lead arsenate	7784-40-9	Schultenite	347.12	decomposes at 720	---	---	v. sl soluble
As ₂ O ₃ arsenic trioxide	1327-53-3	crude arsenic; arsenous acid; arsenious oxide	395.68	460	278	---	21g (25 °C)
NaAsO ₂ sodium arsenite	7784-46-5	sodium metaarsenite	---	---	---	---	very soluble
As ₂ S ₃ arsenic sulfide	1303-33-9	arsenious sulphide; arsenic trisulfide	246.04	707	312	3.43	insoluble in water
AsH ₃ arsine	7784-42-1	arsenic hydride; hydrogen arsenide	77.95	-55	-116	2.695	200 ml (20 °C)
CH ₃ AsO ₃ HNa monosodium methylarsonate	2163-80-6	bueno; ansar 170; weed hoe; MSMA	161.96	---	155 - 119	---	570g (25 °C)
(CH ₃) ₂ AsO ₂ H cacodylic acid	75-60-5	hydroxydimethyl arsine oxide; dimethylarsinic acid	138.01	---	192	---	830g (22 °C)

Appendix B. Standard calibration for heavy metal analyses

Iron	
Conc. (ppm)	Absorbance
1	0.007
2	0.015
5	0.023
10	0.030

Cadmium	
Conc. (ppm)	Absorbance
0.25	0.036
0.50	0.055
1.00	0.101
1.50	0.144

Zinc	
Conc. (ppm)	Absorbance
0.20	0.063
0.50	0.112
0.75	0.153
1.00	0.202

Lead	
Conc. (ppm)	Absorbance
1	0.040
2	0.078
5	0.112
10	0.146

Mercury	
Conc. (ppm)	Absorbance
0.02	0.04
0.04	0.078
0.06	0.112